INOR 1
Carbonane photochemistry
Sang Ook Kang, sangok@korea.ac.kr, Yang-Jin Cho, Kyung-Ryong Wee.Department of Chemistry, Korea University, South Korea, Sejong-City, Republic of Korea
Carbonanes with an icosahedral cluster structure have unique structural features that can induce charge localization in between the carbon and the boron atoms. Depending on the carbon positions, such charge localization is much differentiated. While m- and p-carbonanes induce less charge separation, α-carbonane exerts the most charge separation in its cluster bonding. In particular, charge localization at the carbon-carbon bond in α-carbonane plays a pivotal role in bringing up new types of photochemical processes when photo-functional groups are incorporated into the cage carbon atoms. Fundamental aspects of carbonane based photochemistry as well as its applicability for photonic materials will be discussed.

INOR 2
Organizing donors for specific tasks: Rational ligand designs for hard acceptors
Robert T. Paine, rpaine@unm.edu.Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, United States
There has been much attention given to the fundamental design and development of donor group functionalized organic molecules that can serve as coordinating ligands for s-, p-, d- and f-block metal ions. After much effort in many laboratories, it is now possible, when electronic and architectural features are carefully controlled, to secure ligands that are remarkably selective in their binding preferences. This in turn leads to a host of novel applications for the ligands and their complexes. Through a combination of computational modeling, ligand synthesis and coordination chemistry we have been developing new families of chelating ligands that selectively recognize technically important "hard" lanthanide and actinide ions. In this presentation, some of the recent progress from our group contributing to this activity will be summarized.

INOR 3
New strategies for expanding the oxidative chemistry of cerium
Eric J. Schelter, schelter@sas.upenn.edu.Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States
The accessibility of the tetravalent configuration for cerium(IV) makes that element unique among the rare earths. Cerium materials and their solid solutions exhibit rich chemistry due to the element to take on variable oxidation states. The redox ability of cerium also underlies its simple separations from mixtures of light rare earths and enables useful one-electron oxidation chemistry for applications in organic and inorganic syntheses and heterogeneous catalysis. We have been expanding the scope of molecular cerium compounds to develop new applications for these complexes and address problems in rare earths sustainability. Using a combination of experimental results and DFT, we have determined a ligand field series for cerium(IV) complexes based on electrochemistry. New strategies for accessing and stabilizing cerium(IV) compounds, with potential applications for targeted separations of terbium and praseodymium, will be presented.

INOR 4
Bradford B Wayland, bwayland@temple.edu, Gregory H Imler.Chemistry, Temple University, Philadelphia, PA 19122, United States
The Rh1-Rh2 bonded dimer ([(tmtaa)Rh]2) has a 22 kcalmol−1 dissociation enthalpy and reacts with CO and H2 to produce equilibria with (tmtaa)Rh-H and (tmtaa)Rh-C(O)H that give estimates Rh-H (63 kcal mol−1) Rh-C(O)H (60 kcal mol−1) BDEs. The structures and reactivity patterns of heterobimetallic complexes of (tmtaa)Rh with metallo-radical units (tmtaa)Rh-M, M = Co(CO)3, Mn(CO)3, FeCp(CO), CrCp(CO)2, MoCp(CO)2 are currently being evaluated. Presence of a bridged CO unit (Co-C(O)Rh) in the (tmtaa)Rh-Co(CO)2 complex compared to the all terminal Co-CO units in the porphyrin complex provides a vivid illustration of how the increased flexibility of tmtaa can open metal binding sites. DFT calculations place (tmtaa)Rh-C(O) in a trajectory to form a heterobimetallic dimetal ketone (tmtaa)Rh-C(O)-Co(CO)2 and reactivity studies indicate that the bridged CO is a site for hydrogenation. Structures, reactivity patterns, bond dissociation energetics and DFT calculations for the series of heterobimetallic complexes will be presented and prospects for catalysis discussed.

INOR 5
Main group compounds as reagents for catalytic c-h bond functionalization
John F Hartwig, jhartwig@berkeley.edu.Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720-1460, United States
Our group has reported a series of catalytic reactions that convert specific C-H bonds of aryl, heteroaryl, and alkyl groups to C-B and C-Si bonds. These reactions occur through metal-boryl complexes and metal-silyl complexes. This lecture will include information on the properties of these complexes that lead to catalytic reactivity and information on the properties and reactions of the organoboron and organosilicon products.

INOR 6
Single-handed helical wrapping of single-walled carbon nanotubes by chiral, ionic, semiconducting polymers: New opportunities for the design of electro-optically functional nanomaterials
Pravas Deria1, Jean-Hubert Olivier1, Von Bargen D. Christopher2, Jaehong Park1, Amar S. Kumbhar3, Maria Andrian-Albescu3, Jeffery G. Saven1, Michael J. Therien1, michael.therien@duke.edu. (1) Departement of Chemistry, Duke University, Durham, North Carolina 27701, United States (2) Departement of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States (3) Department of Applied Physical Sciences, University of North Carolina at Chapel Hill (UNC-CH), Chapel Hill, North Carolina 27599, United States
We establish the requisite design criteria to realize a single helical screw preference for semiconducting polymers that single-chain wrap single-walled carbon nanotube (SWNT) surfaces. We show that arylenedivinylene polymers that feature a 2,2′-(1,3-benzenoxy)-bridged(b)-1,1′-bi-2-naphthyl unit facilitate extensive van der Waals contact of the naphthyl moieties with the nanotube surface, and guarantee a helically wrapped polymer-nanotube superstructures of fixed helical chirality. Molecular dynamics simulations provide an integrated picture tying together the global helical superstructure and conformational properties of the binaphthyl units. We demonstrate that polyanionic [arylene]ethynylene polymers designed to wrap SWNTs with a fixed helical screw axis, used in combination with ionic self assembly approaches and nanotubes enriched in the (6,5) chirality, enable for the first time the production of functionalized SWNTs that are fully soluble in organic solvents and capable of assembly into complex hierarchical structures that feature aligned nanotubes that maintain the optoelectronic properties characteristic of individualized SWNTs.
INOR 7
Carbon nanotubes for chemical sensing
Timothy M Swager, tswager@mit.edu. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States
This lecture will detail the creation of ultrasensitive sensors based on carbon nanotubes (CNTs). A central concept that a single nano- or molecular-wire spanning between two electrodes would create an exceptional sensor if binding of a molecule of interest to it would block all electronic transport. Nanowire networks of CNTs provide for a practical approximation to the single nanowire scheme. New methods for fabrication using solventless deposition methods will be described that allow for economical flexible sensor fabrication. These methods include abrasion deposition and selectivity is generated by covalent and/or non-covalent binding selectors/receptors to the carbon nanotubes. Sensors for a variety of materials and cross-reactive sensor arrays will be described. The use of carbon nanotube based gas sensors for the detection of ethylene and other gases relevant to agricultural and food production/storage/transportation are being specifically targeted and can be used to create systems that increase production, manage inventories, and minimize losses.

INOR 8
Advances on silicone resins
Gregg Zank, g.a.zank@dowcorning.com, Dimitris Katsoulis, Bizhong Zhu, Michitaka Suto, Maki Itoh. Department of Science & Technology, Dow Corning Corporation, Midland, MI 48686, United States
Silicone resins continue to attract significant attention due to their attractive optical, thermal, insulating and surface properties. New applications are being realized in new markets such as in lighting (LED), in communications (optical interconnects), in photovoltaic devices, in composites, nano-composites, high quality films, etc. Determining the process-structure-property relationships, which govern their performance in applications continues to be a challenging endeavor. In this presentation, we will describe characterization experiments on model systems that relate to commercial silicone resins at the molecular pre-polymer, polymer and cured network levels.

INOR 9
Recent advances in the preparation of synthetic analogs of methanobactin
Daniel Rabinovich, drabinov@uncc.edu. Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States
Methanobactin (mb) is a fascinating small (∼1,215 Da) protein that plays a key role in the acquisition and transport of copper ions in methane-oxidizing bacteria such as the particulate form of methane monooxygenase (pMMO). The copper(I) center in mb features a distorted tetrahedral [CuS₂N₂] core in which the metal ion is surrounded by two oxazolone nitrogen atoms and the sulfur atoms of two thione donor groups, a structural feature unprecedented in biological systems. This presentation will outline recent advances in the design and application of several new pyridine/thione and pyridine/seleno mixed-donor ligands to the synthesis of mononuclear and dinuclear copper(I) complexes that mimic the metal center in mb. A discussion of some important physical and chemical properties of these compounds, including solubility in water, stability in air, and biological activity, will also be described in the presentation.

INOR 10
[Fe-Fe] hydrogenase models: Computational and electrocatalytic studies
Charles A Mbi, cmebi@atu.edu. Physical Sciences, Arkansas Tech University, Russellville, Arkansas 72801, United States
There is great interest in the development of cheaper alternatives to platinum catalyst for the production of hydrogen, a clean alternative to fossil fuels. Current focus is on iron-based organometallic catalysts designed to mimic the structure and function of the active site of the efficient hydrogen producing [Fe-Fe] hydrogenase enzyme. Hundreds of these models, with varying catalytic efficiency and stability, have been reported in the literature. The hydrogenase models are known to decompose upon reduction following breakage of the Fe-S bond. To explore the effect of structural features on the electrochemical stability of these models, we have prepared and characterized a series of diiron-carbonyl compounds coupled to polyaromatic thiolate ligands. The structures of the compounds have been examined using X-ray crystallography and spectroscopy (IR, UV-visible and NMR). The stability and catalytic activity of the compounds have been explored using cyclic voltammetry and the results will be presented. Global reactivity indices of the models have been determined using density functional theory and used to predict the relative stability of the catalysts.

INOR 11
Target formation in BZ: Nucleation vs. fluctuation

Emma R Kast, emma.r.kast@gmail.com, Diego J Prado, Harold M Hastings, Sabrina G Sobel. (1) Department of Chemistry, Hofstra University, Hempstead, New York 11549, United States (2) Department of Physics and Astronomy, Hofstra University, Hempstead, New York 11549, United States (3) Simon's Rock College, Great Barrington, Massachusetts 01230, United States

The ferroin-catalyzed Belousov-Zhabotinsky (BZ) reaction is a prototypical oscillating chemical reaction system. The unstirred reaction produces waves of blue oxidized ferroin in a red reduced ferroin medium due to complex redox kinetics. Initial activation is indicated by a clocking wave; one later sees target patterns of outward traveling waves of oxidation. Two models are proposed to explain the onset of activation. First, activation might follow a nucleation process due to dust particles or undissolved iron/ferroin particulates. In this case onset occurs after some average delay, and wait times to the clocking or target waves would follow a normal distribution. Alternatively, activation might be generated by microscopic random thermal fluctuations in concentrations (Hastings, Field, Sobel, J Chem Phys 2003; Sobel, Hastings, Field, J Phys Chem A 2006; Hastings et al., J Phys Chem A 2008). This mechanism predicts that activations follow an exponential waiting time model. By timing the onset of activation over a large number of replicates, experimental results can be compared to the theoretical models discussed above. Preliminary data has shown a correlation with the exponential wait time model for initial activation, while the onset of oscillations show a more normal distribution. Partially supported by the Camille and Henry Dreyfus Foundation.

INOR 12

Syntheses, characterization, density functional theory calculations and reactivity of three and five coordinate SNS copper(I) and copper(II) pincer complexes

John R Miecznikowski, jmiecznikowski@Fairfield.edu, Matthew A Lynn, Jerry P Jasinski, Wayne Lo, Eric Reinheimer, Mekhala Pati, Daniel A Baik. (1) Department of Chemistry and Biochemistry, Fairfield University, Fairfield, CT 06824, United States (2) Department of Science and Mathematics, National Technical Institute for the Deaf, Rochester Institute of Technology, Rochester, NY 14623, United States (3) Department of Chemistry, Keene State College, Keene, NH 03435-2001, United States (4) Department of Chemistry, Boston College, Chestnut Hill, MA 02467, United States (5) Department of Chemistry, California State Polytechnic University, Pomona, CA 91768, United States (6) Department of Chemistry and Molecular Biology, Cell Biology, and Biochemistry, Boston University, Boston, MA 02215, United States

Recently, we have developed and synthesized a series of tridentate pincer ligands, each possessing two sulfur- and one nitrogen-donor functionalities (SNS), based on bis-imidazole or bis-triazole precursors. The tridentate SNS ligands incorporate thione-substituted imidazole or triazole functionalities. We have prepared somewhat rigid ligand systems through the use of 2,6-dibromopyridine as a ligand precurs. In addition, we have prepared more flexible ligand systems by employing the starting material 2,6-(dibromomethyl)pyridine to introduce a methylene linker into the pincer ligand. We have metallated these ligand precursors to form zinc(II) complexes containing these tridentate ligands. In an effort to learn about the reactivity of the ligand precursors with other metal salts, we have metallated these ligand precursors to form copper(I) and (II) complexes. The copper(I) complexes are three coordinate and the copper(II) complexes are five coordinate. A detailed description of the syntheses, characterization (X-ray diffraction, electrochemistry, UV-Vis, and EPR spectroscopy), DFT calculations and reactivity of the SNS copper complexes will be presented.

INOR 13

Synthesis and group 12 metal complexes of a new pyridine/thione ligand

Ashley N. Michels, michelsa@go.stockton.edu, Daniel Rabinovich. Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States

The reactivity of some bidentate ligands containing pyridine and heterocyclic thione donor groups towards metal ions is virtually unknown even though, separately, the two functionalities have been extensively used in coordination chemistry. In this regard, we have used the (mercaptoimidazolyl)pyridine ligand mpyxes to prepare complexes of both transition and main group metals, including derivatives of manganese(I), nickel(II), palladium(I), copper(I), silver(I), zinc(II), cadmium(II), mercury(II), indium(III), tin(IV) and bismuth(III). Similarly, we have developed the coordination chemistry of two related mixed-donor ligands that contain one or two methylene spacers connecting the heterocyclic moieties. More specifically, this presentation will outline the syntheses of the new N-butyl-substituted (mercaptoimidazolyl)picoline ligand mpicBu and its group 12 metal complexes (mpicBu)2MX (M = Zn, Cd, Hg; X = Cl, Br, I), most of which have been structurally characterized. A detailed comparison with the structures of the mpicMe analogues will be made in order to assess the effect of the different alkyl substituents on the mercaptoimidazole rings.

INOR 14

Hammett relationship of dipicolinatoxo vanadium(V) compounds evaluated by NMR spectroscopy

Alejandro M Trujillo, Jerome A. Burke, Debbie C. Crans, crans@lamar.colostate.edu. Department of Chemistry and Cell and Molecular Biology, Colorado State University, Fort Collins, Colorado 80523, United States

The effects of substituents on the chemical shifts of the dipicolinatoxo vanadium(V) coordination complex were determined using NMR spectroscopy and analyzed using linear free energy relationships. The ligand 2,6-pyridinedicarboxylic acid, also abbreviated dipicolinate was modified using substituents in the 4-position (H, OH, Cl, NH2 and NO2). The free ligand and the coordination complex formed with vanadate were each analyzed using Hammett correlation plots. The pKa value for the deprotonation reaction of the dipic-ligand and derivatives yielded a non-linear relationship of logK(H,OH)/KNO2 plotted as a function of the Hammett constant. Similar non-linear relationships were observed when plotting the 1H NMR chemical shift data.
(delta-\textsubscript{a}), as a function of the Hammett constant for both ligand and the vanadium(V) complexes formed with the ligand. In contrast, plotting the 51\textsuperscript{V} NMR chemical shifts (delta-\textsubscript{a}) of the vanadium-dipicolinate dipicolinatoxovanadium(V) complexes as a function of the Hammett constant, a linear correlation resulted with an r\textsuperscript{2} of 88%. These findings show that 51\textsuperscript{V} NMR chemical shifts can be used to produce linear free energy relationships in these metallo-organic compounds. Future studies will explore application of these systems in describing the efficacy and possible mode of action of vanadium compounds.

References:

INOR 15

Transition metal complexes for storage and delivery of nitric oxide
Hoa Minh Nguyen, hmn091020@utdallas.edu, Alysia Lowe, Natalie Trinh, Ken J. Balkus. University Of Texas at Dallas, Richardson, Texas 75081, United States

Nitric Oxide (NO) is a signaling molecule that is found in many biological processes that have the ability to aid in wound healing process. However, delivery of NO to a wound can be difficult. A possible approach is to bind a NO releasing compound, a transition metal complex, to a PIM-1 polymer for creating nanofibers bandage. PIM-1 is an ideal polymer to bind the transition metal complex because of its unusual high microporosity due to its rigid structure, combined with its loose chain packing. This creates a high free volume, therefore making it possible for the NO to pass through the bandage and reach the wound during the NO releasing process. The nanofibers bandage will be generate through a process called electrospinning. Electrospinning is a process in which a high voltage is used to create an electrically charged jet of polymer solution. The solution then dries or solidifies to leave a continuous polymer fiber. PIM-1 contains a cyano group, which makes it possible to form a bond with the nitrogen on the cyano group to the metal center of the metal complex. The transition metal complex will be releasing NO by photolysis.

Our goal is to bind the NO releasing compound, a transition metal complex: specifically RuSALEN-nitrosyl (RuSALEN-NO) and CoSALEN-nitrosyl (CoSALEN-NO), to a PIM-1 polymer for creating nanofibers bandage. The result of our recently work will be discuss, including the characteristic of synthesized PIM-1 Polymer and characteristic and SEM image of the PIM-1 fiber.

INOR 16

Transition metal complexes of N-oxides derived from five- and six-membered aromatic heterocyclic amines
Peter Baran, baran@juniata.edu, Nathan G Strom, Thomas Jordan, Nicholas S Morgan. Department of Chemistry, Juniata College, Huntingdon, PA 16652, United States

Previously reported dioxides of aromatic amines, 1,10-phenanthroline N,N'-dioxide (phenO\textsubscript{2}) and 3-hydroxyimidazole 1-oxide (HimzO\textsubscript{2}), as well as newly synthesized pyridazine N,N'-dioxide (pdzO\textsubscript{2}) were studied with the goal to use them as bridging ligands potentially yielding multinuclear complexes with transition metals.

The dioxides of pyridazine (pdzO\textsubscript{2}) was synthesized by the direct oxidation of pyridazine with HOF·CH\textsubscript{3}CN – a method previously successfully applied to isolate phenO\textsubscript{2}. PdzO\textsubscript{2} acts as a bidentate chelating ligand in a reaction with copper(II) chloride forming a tetranuclear complex, \([Cu_{2}(μ-Cl)]Cl_{2}(pdzO_{2})\textsubscript{4}\). 1,10-Phenanthroline N,N'-dioxide forms the N\textsubscript{4}(phenO\textsubscript{2})\textsubscript{4}Cl\textsubscript{4} complex with NiCl\textsubscript{2} in contrary to expected complex of [Ni(phenO\textsubscript{2})\textsubscript{4}]Cl\textsubscript{4} obtained previously from a serendipitous reaction. The dioxide of imidazole, HimzO\textsubscript{2}, studied as a ligand in metal complexes for the first time, showed a different level of stability against reduction based on the anion of Cu(II) salt used. The dioxide form of the ligand was preserved in the acetylated HimzO\textsubscript{2} and HClO\textsubscript{4}. The ligand was reduced to its mono N-oxide in the chloride complex Cu(ImzO\textsubscript{2})Cl\textsubscript{4}. The reduction of both the ligand and copper was observed in the product Cu(ImzO\textsubscript{2}), which was isolated from the synthesis using copper(II) nitrate. Synthesis of copper complexes with other anions as well as characterization of isolated complexes will be discussed.

INOR 17

Optimizing the photocatalytic hydrogen evolution reaction in water
Rony S. Khnayzer\textsuperscript{1}, rony.khnayzer@liau.edu.lb, Felix N. Castellano\textsuperscript{2}. (1) Department of Natural Sciences, Lebanese American University, Beirut, Chouran 1102 2801, Lebanon (2) Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States

Solar fuels production via catalytic water splitting represents one of the most sustainable alternative energy sources on our planet. A system inspired from the photosynthesis of plant and based on homogeneous photocatalysis can be designed to produce hydrogen wirelessly from water. Here, we present different multicomponent systems each composed majorly of a transition-metal light-harvesting unit and cobalt-based water reduction catalyst. The multi-step electron and proton transfer reactions were carefully studied using transient-absorption spectroscopy. The large body of data accumulated from the high-throughput screening of molecular compositions and the time-resolved experiments were collectively utilized to optimize these photocatalysts and provide important future insights.

INOR 18

Light-driven proton-coupled electron transfer with photoexcited metal complexes
Oliver S. Wenger, oliver.wenger@unibas.ch. Department of Chemistry, University of Basel, Basel, Switzerland

Proton-coupled electron transfer (PCET) plays a pivotal role in photosynthesis and many other energy-relevant chemical processes. We use visible light to trigger PCET reactions between ruthenium(II) / rhenium(I) complexes and phenol / thiophenol reaction partners\textsuperscript{1,2}. From time-resolved laser studies we get direct insight into the PCET mechanisms, and ultimately we hope to be able to use visible light energy to obtain useful PCET photoproducts. Recent results from our research will be presented, including work on bimolecular PCET and intramolecular long-range PCET.\textsuperscript{3,4,5}

\[ \text{H}_2 \text{O}^+ + \text{e}^- + \text{PhOH} \rightarrow \text{PhOH}^- + \text{H}_2 \]

\[ \text{PhOH}^- + \text{H}_2 \text{O} \rightarrow \text{PhO}^- + \text{H}_3 \text{O}^+ \]

\[ \text{H}_2 \text{O}^+ + \text{e}^- + \text{PhSH} \rightarrow \text{PhS}^- + \text{H}_2 \]

\[ \text{PhS}^- + \text{H}_2 \text{O} \rightarrow \text{PhS}^- + \text{H}_3 \text{O}^+ \]

\[ \text{H}_2 \text{O}^+ + \text{e}^- + \text{PhCS} \rightarrow \text{PhCS}^- + \text{H}_2 \]

\[ \text{PhCS}^- + \text{H}_2 \text{O} \rightarrow \text{PhCS}^- + \text{H}_3 \text{O}^+ \]

INOR 19

Synthesis and structure-function analysis of photosensitizer-catalyst solar fuels assemblies

Karen L. Mulfort, mulfort@anl.gov, Anusree Mukherjee, Oleksandr Kokhan.Division of Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL 60439, United States

Natural photosynthetic systems precisely position molecular light-harvesting and catalytic modules into complex, hierarchical protein host frameworks which create directional electron transfer pathways, stabilize long-lived charge separated states, and present a structural model for abiotic solar energy conversion. This paper will describe our recent efforts to implement biological design principles to develop and discover new photocatalysts towards the goal of artificial photosynthesis. Cobaloximes are among the most promising molecular compounds for H₂ electro- and photocatalysis known, and here we will present the structural evolution of supramolecular cobaloxime photocatalyst assemblies in our group. An entirely new approach to linked cobaloxime-based photocatalysts uses Co(II)-templated formation of Ru(II)polypyridyl-decorated macrocycles. The supramolecular assemblies have been probed by high-resolution structural and physical characterization including synchrotron-based X-ray scattering, X-ray absorption spectroscopy, and ultrafast and nanosecond transient optical spectroscopies. Visible excitation of an equatorially-coordinated cobaloxime photocatalyst provides the first example of instantaneous photoinduced charge separation to yield the catalytically-active Co(II) oxidation state in cobaloxime-based assemblies. Interestingly, EPR analysis reveals that the ground state Co(II) center is high-spin, a unique aspect among previously described cobaloxime photocatalysts, and likely plays a significant role in the kinetics following visible excitation. The homogeneous photocatalyst designs will be juxtaposed with studies of heterogeneous metal-organic frameworks which integrate donor-photosensitizer-acceptor triads and sustain long-lived charge separation following visible excitation. The synthesis and high-resolution physical characterization of new architectures which contain identical photocatalytic modules in complementary environments will contribute to knowledge of how spatial organization impacts the fundamental donor-acceptor photochemistry and potentially lead to the development of new materials for efficient solar energy conversion.

INOR 20

Carbon dioxide reduction with bio-inspired catalysts: Electrochemical CO₂ reduction vs CO₂ hydrogenation

Etsuko Fujita, fujita@bnl.gov, Yasuo Matusbara, Gerald F. Manbeck, David C. Grills, Dmitry E. Polyanskij, James T. Muckerman, Wan-Hui Wang, Yuichiro Himeda, (1) Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, United States (2) National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan

While recent developments in photo- and electrochemical CO₂ reduction are quite encouraging, there are still obstacles to practical applications including the stability of systems. Nature uses the reduced form of NADH to store a hydride ion, which is ultimately used to reduce CO₂ to by.net hydride-ion transfer. It also uses a 2-pyridone unit in a [Fe]-hydrogenase. We have recently prepared and characterized two types of rhodium tricarbonyl complexes containing: (1) an NAD⁺ model ligand (pbn = 2-(2-pyridyl)benzo[β]1,5-naphthyridine); and (2) a [Fe]-hydrogenase model ligand (6DHBPy = 6,6'-dihydroxy-2,2'-bipyridine). We found unusual H/D exchange during the photochemical production of the corresponding NADH-like species as a hydride donor from Re(pbn)(CO)₂Cl. Using Re(pbn)(CO)₂Cl, Re(pbnH)(CO)₂Cl and Re(6DHBPy)(CO)₂Cl as catalysts, we are currently investigating their catalytic activity toward electrochemical CO₂ production. Meanwhile we are pursuing CO₂ hydrogenation using [Cp‘Ir(6DHBPy)(OH)₂]SO₄ and other catalysts to generate formate. We will discuss the advantages and difficulties of both systems.

The work at Brookhaven National Laboratory was carried out under contract DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Geosciences, & Biosciences, Office of Basic Energy Sciences.

INOR 21

Molecular catalysts for electrochemical water oxidation and/or O₂ reduction

Shannon S Staht, stahl@chem.wisc.edu.Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States

This talk will describe our efforts toward the development and mechanistic characterization of molecular catalysts for electrochemical water oxidation and O₂ reduction. Some of the complexes catalyze both reactions.

INOR 22

Fuel from water: The light-driven generation of hydrogen

Richard Eisenberg, eisenberg@chem.rochester.edu.Chemistry, University of Rochester, Rochester, NY 14627, United States

For light to chemical energy conversion in a designed photosynthetic system, the splitting of water into its constituent elements is the key energy-storing reaction. As with natural photosynthesis, such a system relies on light absorption, charge separation, and catalysis. Recent efforts will be described that focus on different components and system compatibility for the reductive side of the water splitting reaction and the visible light-driven generation of hydrogen from aqueous protons. The light absorbers in recent systems include strongly absorbing organic dyes and water-solubilized semiconductor nanoparticles. As catalysts, different sets of metal complexes have been investigated, including previously unstudied systems that exhibit high activity. Both the light absorbers and the hydrogen-forming-catalysts are composed of earth abundant elements only. Studies are described to provide clues to initial charge transfer steps, mechanisms of H₂ generation and sources of system instability. Systems of great durability and high activity will be described.

INOR 23

New approaches to solar fuels: Photocatalytic reductions of metal ions and visible light-driven alcohol de-hydrogenations

Stefan Bernhard, bern@cmu.edu, Anthony C. Brooks, Husain N. Kagawala, James A. Woods, Danielle N. Chirdon, Andrew B. Maurer, Katherine Basore.Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Light to chemical energy conversions are critical to the development and implementation of future sustainable energy solutions. This presentation will highlight progress in the area of functional chrophomorphes as well as photon-driven fuel production and water oxidation catalysis. Special attention will be given to the photocatalytic reduction of Zn²⁺ ions to metallic Zn. Specifically, this work describes the light driven reduction of Zn²⁺ by an iridium(III) photosensitizer (PS) and catalyst. [Ir(ppy)₂(ddbbpy)][PF₆] (ppy = 2-phenylpyridine, ddbpy = 4,4’-di-tert-butyl-2,2’-bipyridine) was found to be the most robust photocatalyst, and the use of ZnCl₂ as the Zn²⁺ starting material and acetonitrile as the solvent afforded the highest yield of Zn metal product. In order to avoid expensive and toxic 3-row catalysts, an alternative, organocatalytic approach will also be presented. The last part of the talk will highlight new work on the photocatalytic de-hydrogenation of alcohols driven by visible light. It is the objective of these efforts to use cheap and abundant biomolecules as a source of carbon-neutral hydrogen.
INOR 24
Advanced structural characterization of complex materials
Thomas Proffen, tproffen@ornl.gov, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6475, United States
Diffraction has become an invaluable tool for understanding advanced materials and with 2014 being declared the International Year of Crystallography, it seems timely to look into the future. Over the last 15 years or so, the analysis of total scattering from single crystalline, powder, and nano-crystalline materials has become more widely used in the material science community. Total scattering simply refers to the analysis of Bragg and diffuse scattering and requires increasingly advanced computational tools for data analysis and modeling. In this presentation we will overview the advanced advances in neutron and x-ray total scattering measurements as well as the current state-of-the-art in modeling and simulation of disordered materials that will be presented. Examples include local disorder in exotic oxides, hydrogen storage materials, nanoparticles and their ligand structure as well as complex systems such as green geopolymers concrete.

INOR 25
Molecular models for study of spin relaxation and magnetic anisotropy
Danna E. Freedman, danna.freedman@northwestern.edu, Michael J. Graham, Kallie E. Powers, Joseph M. Zadrozny, Department of Chemistry, Northwestern University, Evanston, IL 60208, United States
Quantum computation has the potential to both break the most commonly employed encryption schemes and to accurately model quantum systems. For these reasons, quantum computation is a highly active area of research with numerous qubit candidates proposed thus far. Electronic spin can behave in a quantum fashion, therefore could serve as a candidate qubit. Yet thus far, research in this area has been hampered by rapid spin decoherence. While synthetic chemists are adept at designing molecules with the ideal spin manifold, the design principles for the synthesis of molecules with long coherence time have not been established. Research demonstrating progress towards a set of synthetic design principles for new molecular candidate qubits will be presented.

INOR 26
Neutrons needed: Three structure solutions made possible by single crystal neutron diffraction
Susan Latturner, latturne@chem.fsu.edu, Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States
Metal flux synthesis is a useful technique for growing large crystals of complex intermetallic phases. The structures of many of these multinary compounds can be solved using X-ray diffraction techniques, but in some cases it is not sufficient. Three case studies will be presented in which single crystal neutron diffraction studies carried out at ORNL facilitated the solving of the structure. For Yb$_2$FeMg$_{Al-x}$Si$_2$, neutron data enabled the differentiation of Mg, Al, and Si sites in the structure. The nature of the magnetic ordering of Nd$_2$Co$_3$SiC was determined by analyzing the magnetic contribution to the neutron diffraction peaks. And in Ca$_2$Al$_2$C$_2$H$_5$, neutron diffraction data allowed for the analysis of the occupancy of light element sites.

INOR 27
Probing into the world of correlated electron systems: Materials characterization and neutron scattering studies of multiferroics
Clarina R dela Cruz, delacruzcrr@ornl.gov, Quantum Condensed Matter Division, Neutron Science Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37832, United States
A great example of constructive synergy in nature is the strongly correlated electron systems. Not only do they open the door for physics to push its boundaries but they oftentimes exhibit exciting new physical phenomena with associated properties that have viable technological applications. Advancement of this field necessitates a way to probe its various microscopic states to reveal the mechanisms behind the phenomena and based on this understanding, possibly fabricate materials by design in the future. In this talk, I will discuss a promising correlated electron system: multiferroic materials. They hold interest not only for the rich physics they reveal, but for their technological relevance as well. I will give a brief introduction into these exciting materials and discuss some results on newly discovered intrinsic multiferroic systems as well as recent work on neutron scattering measurements to study magnetic field and high pressure effects.

INOR 28
Powder diffraction crystallography: Why you need this and how Argonne helps
Brian H. Toby, toby@anl.gov, Matthew R. Suchomel, Robert B. Von Dreele, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States
Starting with the initial structure determinations by the Bragg’s one hundred years ago and continuing to today, single crystal diffraction is the gold standard for chemical analysis. However, many materials, particularly those newly found, do not form suitable single crystals. Structures can be determined from powder diffraction, but this is not routine. It is greatly facilitated, however, by high quality instrumentation and software. As will be presented, the Advanced Photon Source at Argonne offers several synchrotron powder diffractometers including 11-BM (http://11bm.xray.aps.anl.gov), the country’s highest resolution instrument, which can even be accessed by mail. In addition, our open source GSAS-II data analysis suite (http://tinyurl.com/gsasii), the newest available for this work, is designed to make powder diffraction crystallography more straightforward.

INOR 29
Structure, magnetic, and electrical properties of Sm$_{1.33}$Pd$_2$Ga$_8$ and Yb$_2$Pd$_x$X$_y$ (X = Al, Ga)

LaRico J Treadwell. LaRico.Treadwell@udallas.edu, Gregory T McCandless, Julia Y Chan. (1) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States (2) Department of Physics & Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803-4001, United States (3) Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United States

Single crystals of Sm$_{1.33}$Pd$_2$Ga$_8$ and Yb$_2$Pd$_3$X$_4$ (X = Al, Ga) were grown in a gallium and aluminum flux, respectively. Sm$_{1.33}$Pd$_2$Ga$_8$ crystallizes in a rhombohedral space group R-3m with lattice parameter $a = 4.353(3)$ Å and $c = 38.98(4)$ Å and $V = 639.7(1)^{3}$. The structure is composed of 3 Pd$_3$Ga$_8$ slab (A), 6 Sm-Ga disordered slab (B), and 3 PdGa$_3$ slab (C) stacked in the c-direction with a sequence of [BABCBABC]. Yb$_2$Pd$_3$X$_4$ (X = Al, Ga) lattice parameters are $a = 13.2$ Å, $b = 7.6$ Å, and $c = 9.4$ Å. Sm$_{1.33}$Pd$_2$Ga$_8$ and Yb$_2$Pd$_3$X$_4$ (X = Al, Ga) possess occupational and positional disorder, which increases the complexity of their crystal systems. Detailed comparisons of the structure, magnetic, and electrical properties of Sm$_{1.33}$Pd$_2$Ga$_8$ and Yb$_2$Pd$_3$X$_4$ (X = Al, Ga) are discussed.

INOR 30

Phase transitions by isovalent/aliovalent elemental substitutions in the Zintl phase, Eu$_6$Cd$_6$Sb$_{12}$

Nasrin Kazem, n.kazem@ucdavis.edu, Antonio Hurtado, Susan M Kauzlarich. Chemistry, University of California, Davis, CA 95616, United States

To make high efficient thermoelectrics, materials with high flexibility in tuning their properties are needed to allow optimization of the unusual combination of electrical and thermal properties. The structural complexity in Zintl compounds results in low thermal conductivity in this family of compounds, a desirable property for efficient thermoelectrics. This complexity also facilitates the environment to adjust the electronic and thermal properties by either isovalent or aliovalent substitutions in these compounds. Although Zintl phases have shown a promise for thermoelectric applications, only a small fraction of them have been studied for that purpose. In this presentation, I will focus on Eu$_6$Cd$_6$Sb$_{12}$. It is a P-type Zintl compound which needs to be optimized in order to become a high efficient thermoelectric material. The high electrical resistivity is as a result of low charge carrier concentrations in Eu$_6$Cd$_6$Sb$_{12}$; different crystallographic sites are subjected for injecting additional holes by substituting aliovalent or isovalent elements to optimize directly or subtly the charge carrier concentrations. In this manner, new structures are produced as a result of limited homogeneity ranges solid solutions due to electronic and size factors. In this talk, I will discuss about the results of attempts to make Eu$_6$Cd$_6$A$_x$Sb$_{12-x}$B$_{x}$ (A= Cu, Ag, and Au; B= Ge and As) solid solutions and introduce new structures produced through this approach and show how these new structures are related to the parent structure.

INOR 31

From complex crystal structures to isologal analogies in intermetallics: How superstructures and incommensurability can reveal what matters most in chemical bonding

Daniel C Fredrickson, danny@chem.wisc.edu. Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States

In celebration of the contributions of crystallography to solid state and materials chemistry, we describe how the complex crystal structures of two phases, FeBa17.4Si7.6 and Co3Al4Si2, pointed us in the direction of new approaches to bonding and electronic counting in intermetallic phases. The structures of both compounds are based on rod-packings of fluoride-type columns, which are separated by interstitial atoms. The interstitial atoms form complicated patterns which lead to a superstructure in FeBa17.4Si7.6 and incommensurate modulations in Co3Al4Si2. Both patterns can be connected, through the DFT-calibrated Hueckel calculations, to the achievement of 18-electron configurations on the transition metal atoms. For Co3Al4Si2, these closed-shell electron counts are obtained through mult-center interactions isolobal to classical Co-Co sigma and pi bonds. Drawing on these results, we will describe a theoretical approach for building bonding schemes in transition metal-poor intermetallics, which will be demonstrated with Ir3Ge7-type compounds.

INOR 32

Coordination chemistry of N-donor chelates of the first row transition elements: Ligand reactivity from redox non-innocence

Peter T Woicikanski, pw2@cornell.edu, Wesley D Morris, Valerie A Williams, Brian M Lindley, Brian P Jacobs, Thomas R Cundari, Karsten Meyer. (1) Department of Chemistry & Chemical Biology, Cornell University, Ithaca, New York 14853, United States (2) Department of Chemistry, CASCaM, University of North Texas, Denton, Texas 76203, United States (3) Department of Chemistry & Pharmacy, University of Erlangen-Nuremberg, Erlangen, Germany

Several N-donor chelate complexes of first row transition elements have been synthesized, and their physical properties will be discussed in the context of reactivity. Some have been shown to exhibit C-C coupling at the ligand. The redox non-innocence of these ligands will be discussed in the context of such transformations.

INOR 33

Playing both sides: Comparing the redox abilities of tetrazenine-based and pyrazolyl-based pincer ligands

Brian J. Cook, cookb@indiana.edu, Richard L Lord, Chun-Hsing Chen, Daniel J. Miodola, Kenneth G. Caulton. (1) Department of Chemistry, Indiana University-Bloomington, Bloomington, Indiana 47405, United States (2) Department of Chemistry, Grand Valley State University, Allendale, Michigan 49401, United States (3) Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

The redox capabilities of a ligand are determined by the constituents that make up the whole. In general, a ligand has the ability to be reduced if it has a low lying empty orbital, often n* in character. We have been exploring the reduction chemistry of two redox active ligands: the easy to reduce 2,6-bis(3,6-dimethyl-1,2,4,5-tetrazinyl)pyridine (btzp) and the hard to reduce 2,6-bis(2-nethyl-3-tertbutylpyrazol-5-yi)pyridine (L$^{498}$). Electrochemical studies show btzp to be 1.3V easier to reduce than its 2,2',2''-terpyridine analog, while becoming even easier to reduce while attached to divalent metal cations (Fe, Ru, Zn). These reductions have been shown to occur at the tetrazenine moieties In fact, electronic studies show that btzp is the most electron withdrawing nitrogen pincer ligand ever developed. In contrast, L$^{498}$ is quite difficult to reduce, with reducing equivalents going into the central pyridine. Reduction chemistry while attached to Fe and Co and related studies will also be discussed.

INOR 34

Redox-activity of tetrazines in molecular switches

Amar Flood, aflood@indiana.edu. Department of Chemistry, Indiana University, United States

Voltage-driven molecular switches in the form of rotaxanes and catenanes have been created from metal-ligand binding sets, yet none have taken advantage of the natural redox activity of non-innocent ligands. Tetrazine is one such example of a versatile ligand core around which pseudorotaxanes have been created and have been shown to switch. Mechanistic studies show that when they move forwards and backwards, they do so along different pathways. Far from negating the principle of microscopic reversibility, we simply skit around it. This and other stories emanating from this peculiar ligand core will be presented, such as, a quick and easy way to marshal Maxwell's demon and a mild case of ligand-derived mixed valency.
INOR 35

Catalytic enantioselective synthesis of planar-chiral (η⁶-arene)chromium complexes

Masamichi Ogasawara, ogasawar@cat.hokudai.ac.jp, Catalysis Research Center, Hokkaido University, Sapporo, Hokkaido 0010021, Japan

Planar-chiral (η⁶-arene)chromium complexes are powerful chiral scaffolds in asymmetric synthesis, but their synthetic methods are rather limited. Recently, we demonstrated that the Mo-catalyzed asymmetric ring-closing metathesis (ARCM) was highly effective for asymmetric synthesis of the various planar-chiral metallocenes. And thus, we were interested in controlling the (η⁶-arene)Cr-based planar chirality by ARCM. Indeed, the Mo-catalyzed kinetic resolution of the racemic (η⁶-1,2-disubstituted-benzene)Cr complexes proceeded efficiently to give the Cr complexes with high ee's. The (η⁶-bromoarene)Cr complex thus obtained was an excellent precursor to various (arene)chromium derivatives. The ARCM method could be extended to the desymmetrization of the prochiral (arene)chromium complexes, in which both planar and axial chirality were synchronously controlled with excellent selectivity. The N-C axial chirality thus induced was retained in the N-arylindoles even after the removal of the Cr fragment.

INOR 36

New frontiers of iron-pyridylpyrrolide chemistry

Keith Searles¹, ksearles@sas.upenn.edu, Maria Carroll¹, Patrick J Carroll¹, Chun-Hsing Chen², Daniel J Mindiola¹, Kenneth G Caulton². (1) Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States (2) Department of Chemistry and Molecular Structure Centre, University of Indiana, Bloomington, Indiana 47405, United States

Recent synthetic efforts from our research groups have focused on the pyridylpyrrolide ligand class and the coordination chemistry to a variety of late transition metals. We have previously described that ligand redistribution occurs at divalent transition-metal complexes, coordinated by two of the pyridylpyrrolide ligands, when chemical reductions were attempted. However, we have recently developed synthetic strategies to circumvent this ligand redistribution.
regulation, allowing for the study of redox-induced reactivity at the metal center. This talk will describe the new coordination chemistry of the pyridylpyrrolyl ligand with iron leading to the reactivity and attempted functionalization of some relatively inert small molecules.

INOR 37
Platinum complexes for catalytic C-H oxidation with O₂
Shrinwantu Pal, Daoyong Wang, Andrei N. Vedermakov, avederni@umd.edu. Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States
We developed new platinum(II) and platinum(IV) complexes that can serve as (pre)catalysts for C-H oxidation with O₂ as the oxidant of some organic substrates and inorganic “hydride” donors. An analysis of these reactions will be presented.

INOR 38
Reactions of d⁰ transition metal complexes with O₂
Zi-Ling Xue, xue@ion.chem.utk.edu, Adam C Lamb, Seth C Hunter, Tabitha M Callaway, Bhavna Sharma, Zheng Lu, Shu-Jian Chen. Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States
Reactions of O₂ with d⁰ transition metal complexes usually follow pathways different from those of d⁰ transition metal complexes. Ligand oxidation is often observed in the reactions of the d⁰ complexes with O₂. In this presentation, our recent studies of the reactions between O₂ and following complexes will be presented: (a) zirconium amide amidinates Zr[NR₂]₂[Me₃(NPPh)₃]; (R = Me, Et); (b) tantalum alkyl imides TaR₂[N(SiMe₃)₃][N(SiMe₃)₃]; (R = Me, CH₃Ph, CH₂SiMe₃).

INOR 39
X-ray fluorescence imaging and metalloproteomics: Tying images of metals in cells to the proteins that bind them
Lydia Finney, illinney@aps.anl.gov. X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois 60439, United States
Metals like copper, zinc and iron are important nutrients to all life. Their special properties which make them so useful to us in things like batteries and catalysts also make them useful to living organisms. Using hard X-ray fluorescence microprobes at the Advanced Photon Source, we have been able to see, often for the first time, where the metal themselves are inside cells and tissues. Yet, many of the images we acquire lead us to new questions. Are these metals required for the activity of proteins? Which proteins are binding which metals inside the cell? With over a third of all proteins thought to bind metals, knowing which metals are bound and how that binding changes in response to the environment could have big implications. For instance, the mismanagement of metals is involved in many diseases, including Lou Gehrig’s disease, Wilson and Menkes disease, and possibly even Alzheimer’s disease. Metals are also an environmental toxin, such as hexavalent chromium, and they are used in drugs, like the platinum in cisplatin that treats prostate cancer. In another vein, hexavalent uranium is an environmental contaminant of concern at several U.S. Department of Energy sites. The metal-binding proteins in microbes, such as those in the genus Shewanella, which can reduce uranium mobility in groundwater, play a major role in the beneficial activity of these organisms – and knowing which metal is in which protein at a given point in time could lead to new insights into how they do their work. We have developed a new tool to investigate this, combining native two-dimensional gel electrophoresis and X-ray fluorescence imaging, to quantitatively measure the amount of sulfur, iron, zinc, and other metals at every point of the 2-D separation of proteins. By coupling this with mass-spectrometry, we have identified a novel protein (PA5217) as a zinc-binding protein in P. aeruginosa. Our finding highlights how this method not only determines changes in metal occupancy, but also identifies the associated protein.

INOR 40
Metal-halogen secondary bonding in iron(II), cobalt(II), and nickel(II) 2,6-dihalophenolate complexes: Insights into the substrate specificity of the hydroquinone dioxygenase PcpA
Timothy E Machonkin¹, machonte@whitman.edu, Monica Boshart¹, Jeremy Schofield¹, Patrick L Holland¹, Dalia Rokhsana¹. (1) Department of Chemistry, Whitman College, Walla Walla, WA 99362, United States (2) Department of Chemistry, Yale University, New Haven, CT 06520, United States
PcpA is a hydroquinone ring-cleaving dioxygenase that is specific for ortho-halogenated hydroquinine substrates and phenol inhibitors (Machonkin, et al., Biochemistry, 2011, 50, 8899-8913). Metal-halogen secondary bonding has been suggested as a possible source of this specificity. We have synthesized and structurally characterized a series of tris(3,5-diphosphylpyrazolyl)borate (Tp³⁻) complexes of the form (Tp³⁻)M₆, where M = Fe(II), Co(II), or Ni(II) and L = 2,6-dibromo- or 2,6-dichlorophenolate. These complexes exhibit metal-halogen secondary bonding, with M-X distances of 2.56 to 2.88 Å. Comparison of solution and null UV/visible absorption spectra of the Co(II) and Ni(II) complexes suggests that geometry of these complexes in solution resembles that in the crystal structures. Variable temperature NMR studies show that the barrier to rotation of the phenolate is low, suggesting that this metal-halogen interaction is relatively weak. Density functional theory calculations provide additional insight into the nature of this interaction.

INOR 41
Phosphoryl transfer enzymes: Theoretical studies of native enzymes and ground-state and transition-state analogs
Charles Edwin Webster, cewebstr@memphis.edu, Katherine N. Leigh, Roger G. Letterman, Nathan J. DeYonker. Department of Chemistry, The University of Memphis, Memphis, TN 38133, United States
The mechanisms of phosphoryl transfer enzymes have garnered considerable attention. Fluoro-containing metal species have been used as transition-state and ground-state analogues in a variety of phosphoryl transfer enzymes and have shed light on the nature of the requirements in the active site to catalyze phosphoryl transfer. Our recent work on β-phosphoglucomutase, phospholipase D, cyclic AMP-dependent protein kinase, and F₁-Fo-ATPase will be discussed. The relationship of the bonding in transition states and intermediates to the 3-center 4-electron bonding model of stable phosphoranes will be discussed.

INOR 42
Reversible pyranopterin cyclization in synthetic models of the molybdenum cofactor
Benjamin R. Williams, bwilliams@brynmawr.edu, Sharon J. N. Burgmayer, Anna Kalinsky, Yichun Fu. Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010, United States
The molybdenum cofactor (Moco) found in all non-nitrogenase Mo enzymes contains at least one pyranopterin dithiolene ligand coordinated to a Mo metal center. The function of this pterin-dithiolene ligand is not well understood because it is difficult to specifically probe the pterin-dithiolene ligand in the intact Mo enzyme and because studies on Moco are limited due to Moco's instability when isolated from the protein matrix. The development of synthetic complexes to model Moco is the strategy we and others have used to investigate the properties imparted by the pterin dithiolene ligand to Mo. In this study, we report the synthesis and characterization of a pyranopterin dithiolene-containing Moco complex modeling Moco in the Mo(IV) and Mo(V) oxidation states. Interestingly, the model exhibits a solvent-dependent, reversible pyran ring opening-closing effect. ¹H and ¹³C NMR techniques show that the pyran ring favors the cyclized form as solvent polarity increases. The implications of this reversible pyran cyclization of Moco within the intact
enzyme are addressed. The Mo(IV) model complex undergoes reduction of the pterin moiety when treated with KBH₄, and the chemical behavior of this reduced species is discussed.

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**INOR 43**

Nitric oxide reactivity of the site-differentiated cluster [Fe₄S₄(LS)₃L]²⁻

_Eric Victor_, evictor@mit.edu, _Stephen J Lippard_.Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

The widely encountered [4Fe-4S] clusters serve as targets for nitrogen oxide species in biology. Until recently, the major product of such nitrosation reactions was believed to be dinitrosyl iron complexes, DNICs, but more recently evidence has accumulated that other species, such as Roussin's black anion (RBA), [Fe₄S₄(NO)]⁻, may be even more prevalent. To test the fundamental chemistry underlying these biological observations, we prepared [4Fe-4S] complexes capped by the tridentate ligand 1,3,5-tri(dimethylamino)benzene (LS₂), to observe products of nitrosation by NO(g) and trityl S-nitrosothiol. The reactions and products were characterized by mass spectrometry, GC-MS, ¹H NMR spectroscopy, FTIR spectroscopy, ReactIR spectroscopy, EPR spectroscopy, and X-ray crystallography. The EPR-active complex [Fe₄S₄(NO)]⁻ formed initially rapidly converted to the EPR-silent RBA upon further nitrosation. The formation of mono- or dinitrosylated clusters was not observed, even at low temperatures. This work was supported by a grant from the National Science Foundation.

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**INOR 44**

Probing intermediates in the nitric oxide dioxygenase reactivity of myoglobin using nitroxy adducts

_Patrick J Farmer_, patrick_farmer@baylor.edu, _Adrian Zapata, Murugaeson R Kumar_.Department of Chemistry & Biochemistry, Baylor University, Waco, Texas, United States

Oxygen-binding heme proteins like hemoglobin and myoglobin are known to catalyze the oxygenation of nitric oxide, the so-called NO dioxygenase activity. For myoglobin (Mb) this reactivity can be accessed from the reaction of oxyMb with NO, or O₂ with NO-Mb, but questions remain about the mechanisms involved. Initial reports suggested that dissociated NO and O₂ (or O₃) react within the heme pocket to form a ferric-peroxynitrite in situ, which then rearranges to generate metMb and nitrate. A shortened intermediate has been reported with a characteristic band ca. 600 nm, but recent vibrational characterization suggests it to be a ferric-nitrate, not the previously proposed ferric-peroxynitrite or Fe(IV) ferryl intermediates. We find that the reaction of O₂ with HNO-Mb generates similar intermediates with absorbances ca. 600 nm, but results in ferrous heme products. Kinetic evidence suggests the formation and decomposition of the intermediate species are pH and O₂-dependent. Interestingly, in reactions carried out under CO atmospheres the intermediate absorbance is shifted, and the major product is CO-Mb. Initial mechanistic interpretations will be discussed.

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**INOR 45**

Novel reactivity of {Fe(NO)₃}³⁺ dinitrosyl iron complexes and its implications in protein post-translational modification

_Jessica Fitzpatrick_, jessica_fitzpatrick@brown.edu, _Eunsuk Kim_.Department of Chemistry, Brown University, Providence, RI 02903, United States

Dinitrosyl iron complexes (DNICs) are inorganic compounds that have gained increasing attention in recent years due to the roles they play in biological systems. Biological DNICs can be low molecular weight or protein-bound and in both cases the most common ligands bound to the {Fe(NO)₃}³⁺ fragment are cysteine thiolates. The reactivity of oxygen with a series of biomimetic {Fe(NO)₃}³⁺ DNICs bearing thiolate ligands has been investigated [1] will be described. These reactions result in the formation of the corresponding Roussin's red esters along with thiolate oxidation. This reactivity is contrasted with that previously reported for {Fe(NO)₂}⁵⁺ complexes [2]. The implications that this reactivity has for the as yet unidentified role of DNICs in the oxidative post-translational modification of proteins will be discussed.


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**INOR 46**

Synthetic analogs for reduced [2Fe-2S] cofactors and for Rieske centers

_Franc Meyer_, franc.meyer@chemie.uni-goettingen.de, _Antonia Albers¹, Serhiy Demeshko¹, Sebastian Dechert¹, Eckhard Bill². (1) Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Göttingen, Germany (2) MPI for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

Protein-bound [2Fe-2S] sites are fundamental biological cofactors. Their dominant function is electron transfer, where the Fe/S core shuttles between the [Fe₂S₃]²⁻ and [Fe₃S₄]²⁻ states. Synthetic analogues for homoleptic-coordinated [2Fe–2S] cores are well established in bioinorganic chemistry, but most reported analogues of [2Fe–2S] sites have been synthesized exclusively in the all-ferrous state. We present the first crystal structure and complete spectroscopic characterization of a mixed valent [2Fe–2S] synthetic analogue as well as the first investigation of an all-ferrous biomimetic [2Fe–2S] species.
Furthermore we present synthetic analogues for the Rieske centers which are variants of [2Fe–2S] cofactors with heteroleptic [His₃Cys₂] ligation. Building upon the first structural Rieske model, we now present functional model systems that also emulate the pH-dependent redox-potentials and the proton coupled electron transfer that has been proposed for some Rieske proteins.

References

INOR 47
Bioinorganic meets organometallic: A tetracarbene-oxoiron(IV) complex
Franc Meyer¹, franc.meyer@chemie.uni-goettingen.de, Steffen Meyer¹, Iris Klawitter¹, Serhiy Demeshko², Eckhard Blii³, Oliver Krahe³, Frank Neesse³. (1) Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Göttingen, Germany (2) MPI for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

Oxoiron(IV) species are key intermediates in the catalytic cycles of numerous heme and non-heme iron enzymes that insert an O atom from dioxygen into unactivated C–H bonds. Because of the enormous importance of such oxygenase reactions in biology as well as in synthetic chemistry, over the last decade much effort has been devoted to the isolation and characterization of those reactive oxoiron(IV) intermediates and to the understanding of their reactivity patterns. So far bioinspired oxoiron(IV) model complexes are exclusively stabilized by multidentate N-donor ligands, though N-heterocyclic carbene ligands have proven particularly useful for stabilizing and isolating high-valent iron nitrido species. We report that a macrocyclic tetracarbene framework, recently developed by Cramer and Jenkins, efficiently stabilizes the oxoiron(IV) unit. This made possible the first isolation and structural characterization of an organometallic oxoiron(IV) complex which has an electronic structure and spectroscopic signatures distinct from those of other oxoiron(IV) complexes.

References

INOR 48
Water stability of carboxylate-containing metal-organic frameworks: Where we stand 15 years after MOF-5 and Cu-BTC
Jared B Decoste, jared.b.decoste2.ct@mail.mil.Leidos, Inc., Gunpowder, MD 21010, United States

In the 15 years since the discoveries of Cu-BTC and MOF-5, thousands of metal-organic frameworks (MOFs) have been reported in the open literature. One of the underlying difficulties in the use of MOFs in many commercial and industrial applications is that many MOFs are unstable at ambient conditions. MOFs containing carboxylate-metal-bonded metals have been shown to have varying degrees of water stability from MOF-5 (very unstable) to Cu-BTC (stable at some conditions) to UIO-66 (very robust). Unfortunately, many MOFs with inherent stability, like UIO-66, are fairly inert and not as chemically active, when compared to less stable MOFs like Cu-BTC and MOF-74, which have coordinatively unsaturated metal sites. Here, the water stability of Cu-BTC, Mg-MOF-74, and UIO-66 are compared at various ambient conditions encountered in potential commercial and industrial applications. Furthermore, various MOF modification techniques for the enhancement of water stability including plasma-enhanced chemical vapor deposition of perfluoroalkanes, doping of various metals into the secondary building unit, and the modification of the outer surfaces of MOFs will be discussed.

INOR 49
Series of tetra-topic ligand based metal-organic frameworks for hydrogen storage
Yangyang Liu, yangyang.liu@mail.chem.tamu.edu, Wenjuan Zhuang, Hong-Cai Zhou. Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012, United States

Metal-organic frameworks (MOFs) are new types of porous materials that can be used for clean and renewable energy applications. Hydrogen has great potential as an alternative energy carrier for the currently used unsustainable fossil fuels in automobiles. It can be generated from renewable energy sources and has the highest gravimetric energy density of all materials due to its low molecular weight. It is also nonpolluting and generates water as the only byproduct after power generation. However, the lack of an efficient way for storage is the major hurdle that limits the practical usage of hydrogen as a new energy carrier. Due to their favorable properties of high surface area and tunable surface functionalities, MOFs stand out from other porous materials for hydrogen storage. In this study, a series of porous MOFs were synthesized from diverse metals (Cu, Zn, Co, Mn, Zr, Hf) based on the same unique tetra-topic ligand. Two Cu-MOF isomers were obtained under different solvothermal conditions. And two isostructural MOFs (Zr-MOF and Hf-MOF) were synthesized under the same condition but different metals. Their structure, topology, stability and hydrogen storage properties were studied and their structure-property relationship was established. Among them, the Co-MOF showed very high hydrogen uptake at 1 bar and room temperature (2.62 wt%). Zr-MOF and Hf-MOF showed ultra-stability even in boiling water. This study gave an insight into the research in porous materials for onboard applications.

INOR 50
Probing CO₂ adsorption in metal-organic frameworks using X-ray spectroscopy
Walter S. Drisdell, wsdirdsell@lbl.gov, Roberta Poloni⁷-⁹, Thomas M. McDonald⁸, Jeffrey R. Long⁷-⁹, Berend Smid⁸-⁹, Jeffrey B. Neaton¹, David Prendergast¹, Jeffrey B. Kortright¹. (1) Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (2) Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, United States (3) Department of
Metal-organic frameworks (MOFs) are currently among the most promising materials for gas separation applications such as carbon capture. We explore the local electronic signatures of molecular adsorption at coordinatively unsaturated binding sites in the metal-organic framework Mg-MOF-74 using X-ray spectroscopy and first principles calculations. In situ measurements at the Mg K-edge reveal distinct pre-edge absorption features associated with the unique, open coordination of the Mg sites. These spectral features are suppressed upon adsorption of CO and N,N'-dimethylformamide. Density functional theory shows that these spectral changes arise from modifications of local symmetry around the Mg sites upon gas uptake and are strongly dependent on the metal-adsorbate binding strength. Similar sensitivity to local symmetry is expected for any open metal site, making X-ray spectroscopy an ideal tool for examining adsorption in such MOFs. We also present in situ measurements of the expanded, functionalized analogue mmen-Mg(dobpc), in which amines have been appended to the metal sites. This material displays unique adsorption behavior and extremely high specificity for binding CO₂. We compare measurements at the N and O K-edges with first-principles calculations and discuss how these results compare to proposed adsorption mechanisms for this MOF.

INOR 51
Molecular-level characterization of spin crossover in metal-organic frameworks from computer simulations
Jordi Cirera, jcirerafernandez@ucsd.edu, Francesco Paesani, University of California - San Diego, La Jolla, CA 92093, United States

Metal-Organic Frameworks (MOF) represent a versatile class of porous materials that have recently attracted much interest due to their broad range of potential applications. The presence of open-shell metal centers in the MOF secondary building provide the opportunity to develop multifunctional porous materials in which both surface area and magnetic properties can be rationally tuned for specific applications. In this contribution, we describe our recent work on the molecular modeling of the spin-crossover behavior of MOF materials. Particular focus is devoted to the [Fe(pyrazine)₂Pt(CN)₄] MOF whose spin-crossover properties have been shown to be extremely sensitive to the nature of the guest molecules adsorbed in the pores. We demonstrate that, by expanding the conventional molecular mechanics scheme to account for electronically-driven effects, it is possible to develop molecular models of MOF materials that correctly represent both spin states, thus enabling direct simulations of spin-crossover properties as a function of temperature and gas adsorption. Results for the [Fe(pyrazine)₂Pt(CN)₄] MOF will be discussed.

References:

INOR 52
Mesoporous metal-organic frameworks based on perfluorinated and macrocyclic ligands
Teng-Hao Chen¹, goodjob1984@hotmail.com, Ilya Popov¹, Yu-Chun Chuang², Olafs Daugulis¹, Ognjen S Miljanic¹. (1) Department of Chemistry, University of Houston, Houston, TX 77204-5003, United States (2) National Synchrotron Radiation Research Center, Hsinchu, Taiwan Republic of China

Two unprecedented classes of mesoporous metal-organic frameworks (MOFs) were constructed from perfluorinated aryl carboxylates and tetrazoles, and macrocyclic dehydrobenzannulene ligands, respectively. These new materials were extensively characterized using IR spectroscopy, elemental analysis, … The prepared perfluorinated MOFs are superhydrophobic and are being tested as platforms for the selective capture of fluorocarbons and electron-rich species. On the other hand, the macrocyclic ring ligand with donut-shaped geometry effectively “pre-program” the porosity into the resultant MOFs, regardless of the coordination geometry of the metal and the overall MOF’s topology. These are some of the most complex organic linkers ever to be incorporated into MOFs.
INOR 53
Synthetic control and guest binding in porous metal-organic frameworks

Colin L Weeks¹, colin.weeks@un.edu, Kathryn Mauger-Sonnek¹, Thomas D Petersen², Gurusamy Balakrishnan³, Thomas G Spiro⁴. (1) Department of Chemistry and Biochemistry, University of Northern Iowa, Cedar Falls, IA 50614, United States (2) Department of Chemistry, University of Washington, Seattle, WA 98195, United States

The topology of metal-organic frameworks (MOFs) is determined by several factors including the coordination geometry of the metal ion, the number of bridging ligands connected to each metal ion, the number of metal centers connected to each ligand, and the solvent used to grow the crystals. It is important to learn how these factors affect the MOF structure during the crystal growing process. We have used resonance Raman spectroscopy and UV-visible spectroscopy to study the interaction between Co⁶⁺ ions and 4,4'-bipyridine bridging ligands in solution as crystals of Co⁶⁺/4,4'-bipyridine frameworks grow. We have also used the flexible coordination sphere of Co⁶⁺ and Ni⁴⁺ and the incorporation of non-bridging aqua ligands to generate new polymeric 1D chain structures with 4,4'-bipyridine. X-ray diffraction and thermogravimetric analysis show that the 1D chain crystals of the Co⁶⁺ material retain their structure even when some of the aqua ligands are removed.

INOR 54
Characterization of high-spin metal-carbonyls in metal-organic frameworks with exposed cation sites

Eric D. Bloch¹, ericbloch@berkeley.edu, Matthew R. Hudson², Wendy L Queen², Jarad A. Mason¹, Joseph M. Zadrozny¹, Sachin Chavan¹, Silvia Bordiga³, Craig M. Brown², Jeffrey R. Long⁴. (1) Department of Chemistry, University of California Berkeley, Berkeley, CA 94720, United States (2) Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States (3) The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (4) Department of Inorganic, Physical, and Materials Chemistry, University of Turin, Torino, Italy (5) Department of Chemical Engineering, University of Delaware, Newark, DE 19716, United States (6) Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

The metal-organic frameworks M₃(dobdc) (dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate, MOF-74, CPO-27) (M = Mg, Mn, Fe, Co, Ni, Zn) have shown considerable promise for a number of gas storage and separation applications. These have included CO₂/N₂, CO₂/H₂, O₂/N₂, and paraffin/olefin separations and the storage of H₂, CH₄, or acetylene. The high volumetric and gravimetric densities of coordinatively unsaturated metal cation sites, a result of the high charge and compact nature of dobdc⁴⁻, endow these materials with adsorption selectivities and capacities not displayed by other metal-organic frameworks. Here we show carbon monoxide can reversibly bind to the 5-coordinate metal cations in M₃(dobdc), resulting in the first crystallographically characterized magnesium and zinc carbonyl compounds and the first high-spin manganese(II), iron(II), cobalt(II), and nickel(II) carbonyls. These metal-carbonyl species have been characterized by gas adsorption isotherms, neutron powder diffraction, and infrared spectroscopy. The reversible nature of CO binding to these materials suggests they may be useful for the purification of various carbon monoxide mixtures containing N₂, CH₄, H₂, or O₂ impurities.

INOR 55
Synthesis of novel imidazole linkers to create novel ZIF structures

Rawan A. Muhanna, rawan_muhanna@yahoo.com, Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United States

Metal Organic Frameworks (MOFs) are crystalline compounds consisting of metal ions bridged by organic linkers. These crystals are highly porous and have a high surface area. These unique properties along with chemical and thermal stability make MOFs a promising alternative in fields including gas storage, catalysis, and drug delivery. There is a great variety of linker and metal combinations, and these differences yield MOFs with significantly different properties. Zeolitic Imidazolate Frameworks (ZIFs) are a class of MOFs characterized by their tetrahedrally coordinated transition metal nodes connected by organic imidazole linkers. In this work we have synthesized new bridged imidazole linkers by employing Schiff base type reactions. 2-Imidazolocarboxaldehyde was reacted with both o-Phenylenediamine and DETA to form two new crystalline linkers. The linkers were characterized using powder XRD, SEM, and IR spectroscopy. Results for the synthesis of a new ZIF prepared by reacting these linkers with Zn²⁺ will be presented.

INOR 56
Redox intercalation of hydroquinone into a flexible metal-organic framework

Watchareeya Kaveevivitchai, phueng.watka@gmail.com, Lumei Liu, Xigu Wang, Allan J Jacobson, Department of Chemistry, University of Houston, Houston, TX 77204, United States

We describe an example of redox intercalation using vanadium benzenedicarboxylate, VOBDC as the host and electroactive hydroquinone as the guest. In our previous work, we synthesized single crystals of [VOBDC][H₂BDC]₀₋₁, 1. After removal of the guest acid molecules by heating 1 in air, the VOBDC structure, 2 is sufficiently flexible and stable to undergo redox intercalation with hydroquinone. The reaction temperatures and especially the atmosphere were found to be the factors that determined the products. In ambient atmosphere, when 2 was heated together with hydroquinone, a quinhydrone complex formed inside the VOBDC channels, whereas under anhydrous conditions hydroquinone was found to functionalize the VOBDC framework itself, as shown in Figure 1. The products were characterized by single crystal X-ray diffraction, thermogravimetric analysis, infrared spectroscopy, and electron paramagnetic resonance spectroscopy (EPR). According to EPR studies, the product from the anhydrous reaction was found to contain unpaired electrons. The effect of changing the temperature from 298 K to 100 K on the breathing transitions of the framework will be described.
INOR 57
Metal organic frameworks for the catalytic generation of nitric oxide from S-nitrosothiols: Insights into reactivity and biomedical device fabrication

Jacqueline L Harding, jacqueline.harding@colostate.edu, Melissa M Reynolds. Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States

In the quest for long lasting NO materials the fabrication of a material that relies on an undepletable NO reservoir is ideal. The use of bioavailable NO resources such as S-nitrosothiols (RSNOs) found circulating in the blood stream present a golden opportunity for access to a renewable source of NO. In order to capitalize on the availability of NO donors the identification of a suitable catalyst which can successfully liberate NO from RSNOs and be incorporated into the polymeric matrix of biomedical devices is imperative. In particular, metal organic frameworks (MOFs) have gained notoriety for their applicability in biomedicine with particular emphasis on their potential as catalysts. In this presentation we explore the reactivity of a Cu$^{2+}$ based MOF catalyst for NO production from structurally diverse RSNO substrates. The reactivity of the MOF catalyst is determined based on the real-time measurement of NO generated from each substrate and the rate of diffusion for each RSNO substrate through the porous architecture of the MOF catalyst. The ability to attain various NO generation rates is highly desirable for tuning biomaterials with appropriate pharmacokinetic profiles for specific applications, such as blood-contacting or anti-microbial coatings where the critical dosages of NO vary.

INOR 58
Geometrical spin frustration and ferromagnetic ordering in (Mn$_{3}$Pb$_{2-x}$)Pb$_{2}$Sb$_{4}$Se$_{10}$

Pierre Ferdinand Poudou Poudue, poudoup@umich.edu, Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States

Engineering the atomic structure of an inorganic semiconductor to create isolated one-dimensional magnetic subunits that are embedded within the semiconducting crystal lattice can enable chemical and electronic manipulation of magnetic ordering within the magnetic domains, paving the way for (1) the investigation of new physical phenomena such as the interactions between electron transport and localized magnetic moments at the atomic scale and (2) the design and fabrication of geometrically frustrated magnetic materials featuring cooperative long-range ordering with large magnetic moments. We will discuss the design, synthesis, crystal structure and magnetic behavior of (Mn$_{3}$Pb$_{2-x}$)Pb$_{2}$Sb$_{4}$Se$_{10}$, a family of three-dimensional (3D) manganese-bearing main-group metal selenides featuring quasi isolated [(Mn$_{3}$Pb$_{2-x}$)$_{3}$Se$_{10}$]$^{10-}$ hexanuclear magnetic ladders coherently embedded and uniformly distributed within a purely inorganic semiconducting framework, [Pb$_{2}$Sb$_{4}$Se$_{10}$]$^{2+}$. Careful structural analysis of the magnetic subunit, [(Mn$_{3}$Pb$_{2-x}$)$_{3}$Se$_{10}$]$^{10-}$ and the temperature dependent magnetic susceptibility of (Mn$_{3}$Pb$_{2-x}$)Pb$_{2}$Sb$_{4}$Se$_{10}$, indicate that the compounds are geometrically frustrated one-dimensional (1D) ferromagnets. Interestingly, the degree of geometrical spin frustration (f) within the magnetic ladders and the strength of the intra-chain anti-ferromagnetic (AFM) interactions strongly depend on concentration (x value) and the distribution of the Mn atom within the magnetic substructure. The combination of strong intra-chain AFM interactions and geometrical spin frustration in the [(Mn$_{3}$Pb$_{2-x}$)$_{3}$Se$_{10}$]$^{10-}$ ladders results in a cooperative ferromagnetic order with exceptionally high magnetic moment at around 125K. Magnetotransport study of the Mn$_{3}$Pb$_{2}$Sb$_{4}$Se$_{10}$ composition over the temperature range from 100 to 200 K revealed negative magnetoresistance (NMR) values and also suggested a strong contribution of magnetic polarons to the observed large effective magnetic moments.

INOR 59
WITHDRAWN

INOR 60
Transition metal-phosphorus clathrates for thermoelectric energy conversion

Kirill Kovnir, kkovnir@ucdavis.edu, Department of Chemistry, University of California, Davis, Davis, CA 95616, United States

Development of the novel materials where charge and heat transport are partially de-coupled is a key factor for the next generation of thermoelectric materials. In this report we present novel clathrate materials with general formula Ba$_{x}$M$_{3}$P$_{30}$ (M = Cu, Au) as a base for new thermoelectric materials.
Ba$_2$M$_n$P$_{30}$ crystalize in the orthorhombic superstructure of clathrate-I avoiding mixed occupancies of crystallographic positions by transition metal and phosphorus atoms. Control over charge carrier concentration can be achieved by the aliovalent substitution in the clathrate framework. Such substitution may be accompanied with the disappearance of the orthorhombic superstructure. The synthesis, crystal and electronic structure, as well as the thermoelectric properties of Ba$_2$M$_n$P$_{30}$-materials will be discussed.

INOR 61
Probing chemical pressure in AAg$_x$(M$_n$M$_1$)$_3$[VO$_2$] by Raman spectroscopy

Michaela Bratsch$^{1}$, cody.morelock@gatech.edu, Angela Möller$^{1,2}$. (1) Department of Chemistry, Stony Brook University, United States (2) School of Chemistry and Advanced Materials Research Institute, University of New Orleans, New Orleans, LA 70148, United States

Powder samples of the magnetic AAg$_x$(M$_n$M$_1$)$_3$[VO$_2$]$_x$ series and its doped members (x = 0, 1/3, or 1/4) have been synthesized in order to study the structure-property relationships of triangular, honeycomb and kagome lattices, respectively. Variations of the A- and M-sites induce so-called chemical pressure which primarily impacts the [VO$_2$]$^+$ unit. The effect on V-O distances and/or rotations around the threefold symmetry axis of the vanadate can be efficiently monitored by Raman spectroscopy. In combination with ab-initio lattice dynamic studies insights can be gained into local distortions and, more importantly, local distributions of the M/M'-site ions surrounding the vanadate. Additional to the inherent synthetic and structural aspects we will discuss the thermodynamic data for the ordered substitution variants.

INOR 62
Ternary molybdates with direct metal-metal bonding

Peter Khalifah$^{1,2}$, kpete@bnl.gov, Diane Colabello$^{1}$. (1) Department of Chemistry, Stony Brook University, United States (2) Department of Chemistry, Brookhaven National Laboratory, United States

Molybdenum oxides are unusual in that they have the potential for direct metal-metal bonding between Mo ions, in addition to the more conventional framework Mo-O bonds. New ternary molybdates have been discovered and their structure solved by powder X-ray and neutron diffraction methods with the help of symmetry mode analysis. The unusual physical properties that result from this bonding will be described and interpreted in the context of both simple molecular orbitals diagrams and full electronic structure calculations.

INOR 63
Probing scintillation behavior of lanthanide doped YAG and LuAG using ion beam induced luminescence

Bernadette A. Hernandez-Sanchez$^{1}$, baherna@sandia.gov, Pin Yang$^{2}$, Khalid M Hattar$^{2}$. (1) Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM 87106, United States (2) Department of Chemistry, Stony Brook University, United States

The development of garnet based ceramic scintillators, yttrium aluminum garnet (Y$_3$Al$_5$O$_{12}$, YAG) and lutetium aluminum garnet (Lu$_3$Al$_5$O$_{12}$, LuAG), are of interest for medical imaging and gamma radiation detection applications. Current investigations on garnets reveal that their emission behavior can be finely tuned based on the judicious selection of lanthanide dopants (e.g., Ce, Pr, Er, Lu) and particle size. In order to better understand the effects these variables on emission behavior, we probed ceramic powders of lanthanide doped garnets synthesized from the solid state reactions with metal oxides. Dopant concentration was varied from 0.5 to 1% and phase pure materials were produced at 1000 °C. These bulk powders were used for baseline experiments for particle size comparisons and were characterized by photoluminescence (PL) and Ion beam induced luminescence (IBIL). During IBIL studies, ion beam tolerance analysis was also performed to understand the microstructural stability of these materials. Full details on the synthesis and characterization will be discussed. This work was funded in part by Sandia's Laboratory Directed Research and Development (LDRD) Program. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

INOR 64
Topochemical reaction strategies for directing structure in layered perovskite hosts

Dariush Montasserasadi, Lea Gustin, Eliasha Josepaha, John B Wiley, jwiley@uno.edu, Department of Chemistry and Advanced Materials Research Institute, University of New Orleans, New Orleans, LA 70148, United States

Topochemical reactions are effective for directing structure in various layered perovskite hosts. Recent efforts in our group have focused on reaction strategies based on intercalation and/or ion exchange. In one case, we have found that the use of reductive intercalation with alkali metals, followed by oxidative intercalation with chalcogen hydride gases, allows for the construction of alkali-metal chalcogen hydride layers within receptive hosts; Dion-Jacobson layered perovskites for example can be reacted with stoichiometric amounts of water to introduce Rb-OH layers within RbLaNbO$_3$ the interlayer. In another example, simple two-for-one reactions can be carried out with Ruddlesden-Popper layered perovskites; K$_2$SrTa$_2$O$_6$ reacts with divalent transition metal ions to make compounds of the form, MSrTa$_2$O$_6$. Details on the synthesis and characterization of these series of compounds will be presented and the utility of such strategies discussed in terms of directed manipulations of solids.

INOR 65
Role and effects of disorder in the thermal expansion of ReO$_2$-type fluorides and oxyfluorides

Cody R Morelock$^{1}$, Cody.Morelock@gatech.edu, Angus P Wilkinson$^{1,2}$. (1) School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States (2) School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

The cubic ReO$_2$-type framework is simple but has all of the key required features for negative thermal expansion (NTE) due to the transverse thermal motion of bridging atoms. ReO$_2$ itself does not display NTE near ambient conditions, but there is a potentially large family of fluorides and oxyfluorides with the same structure that could display NTE. To illustrate this point, ScF$_3$ contracts upon heating from at least 10 to around 1100 K, with quite pronounced NTE below ambient temperature (∼12 ppm K$^{-1}$ at ~100 K). We have examined the role of both cation and anion site disorder in the thermal expansion of the ReO$_2$-type structure. In an effort to tailor its thermal expansion, ScF$_3$ has been doped with trivalent metal cations of varying sizes (Y$^{3+}$, Ti$^{3+}$, and Al$^{3+}$), and the thermal expansion and compressibility of the resulting solid solutions have been studied with variable temperature/pressure powder X-ray diffraction. In this presentation, we will discuss the effects of cation substitution on coefficient of thermal expansion (CTE) and compressibility, as well as a cubic-to-rhombohedral phase transition that occurs upon the incorporation of relatively small amounts of dopant into the ScF$_3$ framework. Another ReO$_2$-type material, TaO$_2$F$_2$, displays near-zero thermal expansion, and we have examined the local structure of this material with variable temperature total X-ray scattering in an effort to understand the role of O/F site disorder in its quite low thermal expansion. In this presentation, we also discuss a supercell model featuring different Ta═O and Ta═F distances and O/F off-axis displacements that better describes the local structure of TaO$_2$F than does the simple cubic ReO$_2$-type model with random O and F site distribution.

INOR 66
Crystal growth, structure determination and magnetic properties of U(IV) containing mixed metal fluorides
Hans-Conrad zur Loye, zurloye@mailbox.sc.edu.Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States

Reduced uranium species are of interest for potential applications in long term nuclear waste storage. Preparing reduced uranium containing compounds and, especially, the crystal growth of U(IV) containing materials, remains a challenge due to the need both to stabilize and to solubilize U(IV) species in a solution environment. We have developed a reliable, low temperature hydrothermal approach to grow crystals of U(IV) containing mixed metal fluorides in essentially quantitative yield. By careful choice of reaction precursors, simple binary and more complex ternary and quaternary U(IV) containing fluorides, such as Uf3F12(OC2H5), K2F3, RbUf3, Na2CuUf2, can be obtained. U(IV) F2 has two unpaired electrons that contribute to the magnetic properties of these complex fluorides. We have previously reported on the structures and magnetic properties of a series of mixed metal fluorides, NaMIIUf2, M = Mn2+, Co2+, Ni2+, Cu2+, and Zn2+. It is possible to substitute trivalent elements into this expanded family of fluorides will be discussed.

INOR 67

Base metal reactivity and catalysis using redox non-innocent bis(imino)-N-heterocyclic carbene ligands

Jeffery Byers, Jeffery.Byers@bhc.edu, Hilan Kaplan, Xiaotie Zhang. Department of Chemistry, Boston College, Chestnut Hill, MA 02467, United States

Reactions of iron and cobalt complexes containing bis(imino)-N-heterocyclic carbene complexes are discussed. Comparison of these complexes with bis(imino)pyridine complexes are made for the hydrogenation of olefins and for [2+2] cycloaddition reactions of alkenes. Consistent with the bonding in these complexes is the isolation of products that involve the participation of the N-heterocyclic carbene carbon atom. Mechanistic implications for these findings will be discussed along with future applications in catalysis.

INOR 68

Sterically directed functionalization of bis(imino)acenaphthene: Radical dearomatization vs. nucleophilic imine C-alkylation

Daniel A Evans1, daevans@utexas.edu, Alan H Cowley2, Ignacio Vargas-Baca2. (1) Chemistry, University of Texas at Austin, Austin, Tex 78712, United States (2) Department of Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario L8S 4M1, Canada

The bis(imino)acenaphthene (BIAN) is a remarkable ligand from the standpoint of reactivity. It is well known that the BIAN ligand class will undergo the sequential addition of as many as four electrons. Furthermore, this interesting behavior has resulted in extensive use of this redox-active ligand. Recently, there has been a focus on the functionalization of the BIAN ligand class. In this context, we have demonstrated the radical backbone dearomatization, two-electron reduction of the redox-active BIAN ligand. Moreover, BIAN ligands can also be functionalized by nucleophilic attack on the imino carbon atom, which results in the formation of chiral amido-imine BIAN derivatives. We have developed a method for controlling this functionalization by sterically directing these reactions to proceed either via a radical backbone dearomatization pathway or a nucleophilic imine C-alkylation pathway. This pathway differentiation has been examined by means of single-crystal X-ray diffraction in conjunction with EPR spectroscopy. Furthermore, computational modeling has been employed to explain the observed reactivity patterns and to obtain an enhanced understanding of the driving forces involved in the reactivity patterns of BIAN functionalization.

INOR 69

Revisiting the use of zinc in perfluoroalkylation reactions

David A Vicic, vicic@lehigh.edu, Peter T Kaplan, Long Xu, Bo Chen, Siqi Yu, Katherine R McGarry. Department of Chemistry, Lehigh University, Bethlehem, PA 18015, United States

A new class of perfluoroalkylzinc reagents have been developed that permit transformations with perfluoroalkyl groups that were previously inaccessible. In particular, transformations that previously involved hazardous fluorinated gases can now readily be performed under safe, non toxic conditions. We report crucial intermediates in these zinc-based transformations.

INOR 70

C-H activation and functionalization of hydrocarbons mediated by Cp*W(NO)(CH2CMe3)(η3-allyl) and Cp*W(NO)(η3-allyl) complexes

Rhett A Baillie, rbaille@chem.ubc.ca, Peter Legzdins. Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

The family of complexes having the general composition Cp*W(NO)(CH2CMe3)(η3-allyl) lose neopentane upon thermolysis to generate 16e η2-allene and/or η2-diene intermediates which effect the single C-H activation of simple hydrocarbons such as methane and ethane. The resulting products of such activations, namely Cp*W(NO)(η2-hydrocarbyl)(η3-allyl) complexes, can be functionalized in a variety of ways, including 1,1-insertion of CO to form new C-C bonds. In contrast, the related Cp*W(NO)(H)(η3-allyl) complexes exhibit a different mode of reactivity. The activation and functionalization of aliphatic hydrocarbons by both of these classes of complexes will be discussed.

INOR 71

Cyclometallated palladium 2-phenylimidazole carbene complexes and their catalytic performance in the Suzuki-Miyaura cross coupling reaction

Maik Micksch, maik.micksch@chemie.tu-dresden.de, Thomas Strassner. Physical Organic Chemistry, TU Dresden, Dresden, Saxonia 01069, Germany

We present several cyclometallated palladium 2-phenylimidazole carbene complexes with different N-1 groups as well as different substituents at the C-2 phenyl group of the cycloometalating imidazole. These complexes were synthesized from the corresponding dimeric palladacycles which were obtained from palladium acetate and 1,2-diarylimidazoles. For the syntheses of the ligands we developed a new, high-yielding and versatile procedure that allows for the preparation of 1,2-diarylimidazoles with sterically demanding substituents starting from inexpensive anilines und carboxylic acids. We were able to prepare imidazoles with
2,6-diisopropylphenyl, 2,6-diphenylphenyl as well as 4-bromo-2,6-dimethylphenyl N-1 groups or with 4-methoxyphenyl, 4-fluorophenyl, napth-1-yl or thiophen-2-yl C-2 groups.

The catalytic activity of the complexes was explored in the Suzuki-Miyaura cross coupling reaction of aryl chlorides. The investigated complexes showed a high catalytic activity, in most cases the aryl chloride was fully converted within 1 hour with 0.2 (or less) mol% of the complex. For the most active complex we will demonstrate a wide substrate scope, several aryl as well as benzyl chlorides could be coupled with different boronic acids in excellent yields using very low catalyst concentrations (up to 0.01 mol%).

INOR 72
Design, synthesis, and application of enantiopure ligands with a distal regulation site in diverse asymmetric transformations
Monique Koppel, mk572@georgetown.edu, Bahram Moasser.Chemistry, Georgetown University, Washington, District of Columbia 20057, United States

β-alkylation of secondary alcohols: Scope and mechanism
Monique Koppel, mk572@georgetown.edu, Bahram Moasser.Chemistry, Georgetown University, Washington, District of Columbia 20057, United States

β-alkylation of secondary alcohols has garnered a lot of attention as an example of an efficient “hydrogen borrowing” system. In this system a secondary alcohol and a primary alcohol are combined in the presence of base and a metal catalyst. The system is purposed to have three steps the first oxidation of the two alcohols into ketone and aldehyde followed by an aldol condensation and then reduction of the condensation product into a fully saturated alcohol. The one pot synthesis that requires no external source of hydrogen proved to be a desirable synthetic route to secondary alcohols. Since the introduction of the first iridium catalyzed system in 2005, other ruthenium, iridium and iron catalysts have been developed. Here-in we present a high yielding base catalyzed system under aerobic conditions with short reaction times. We have also conducted a mechanistic investigation into the unusual catalysis with potassium tert-butoxide and its role in the catalysis as well as the role of oxygen. As part of our investigation we also tested the scope of the base catalyzed system and its limitations.

INOR 77
Mechanistic investigation of Nazarov cyclization reaction catalyzed by palladium(0) complexes

Tulay Atesin1, atesinta@utpa.edu, Marcus Tius2. (1) Department of Chemistry, The University of Texas-Pan American, Edinburg, TX 78539, United States (2) Department of Chemistry, University of Hawai‘i at Manoa, Honolulu, HI 96822, United States

Total synthesis of natural products is one of the most important driving force for finding new chemical reactions, assessing physical organic theories, testing the power and scope of synthetic methods, and, most importantly, making new medicines. The Nazarov cyclization reaction, which is catalyzed by strong Lewis acids, is a powerful reaction for the assembly of five membered rings and has been successfully used in the total synthesis of natural products. This study focuses on computational modeling using DFT calculations to study the details of the mechanism of the palladium catalyzed Nazarov cyclization in collaboration with Dr. Marcus Tius. Dr. Tius has found that for a specific class of substrates, palladium (II) complexes do not catalyze their cyclization, while palladium (0) complexes do. This is not only surprising as palladium (II) is more Lewis acidic and hence expected to be a better catalyst than palladium (0), but it also indicates that the cyclization of these substrates might be going through a different mechanism. Our calculations are focusing on computing the relative energies of different interactions between the transition metal catalyst and the substrates in order to determine which ones could play a role in the cyclization reaction. One important question that we are focusing on is the possibility of an oxidative addition reaction that would convert palladium (0) to palladium (II) during the reaction cycle. The finer details of the mechanism could help to design a better catalyst that would make Nazarov cyclization reaction a more powerful synthetic method.

INOR 78

Mechanism-led design of catalysts for the dehydrocoupling of amine and phosphine boranes

Andrew S. Weller, andrew.weller@chem.ox.ac.uk. Department of Chemistry, University of Oxford, Oxford, United Kingdom

The dehydrocoupling of amine- and phosphine–boranes as catalysed by transition metal fragments allows for the controlled release of H2 and the production of B–N or B–P oligomeric or polymeric materials via dehydropolymerisation. Such main–group polymers of empirical formula (NRHBH2)1 or (PRHBH2)n are valence isoelectronic with technologically pervasive polyolefins, and show promise as piezoelectric materials, electron beam resists, and precursors to boron–phosphide or boron–nitride materials. Despite the significant potential for these new, and virtually unexplored, materials the mechanism for these processes remain ill-defined with only a handful of mechanistic investigations reported.

We now report that by use of well–defined precatalysts based upon 1, 2 (Figure 1) intermediates and final products in the dehydrocoupling of amine– and phosphine–boranes are revealed and isolated. Detailed investigations into the likely catalytic cycles lead to proposed mechanisms for these processes, i.e. dehydrogenation and B–N / B–P bond forming events, with a coordination/insertion type mechanism postulated for chain growth, not unrelated to olefin polymerisation. The implications for the design of new catalysts that can deliver these new materials “to order” are also discussed.

1 Leitao, E. M.; Jurca T.; Manners, I. Nature Chem. 2013 , Advance Article DOI: 10.1038/NCHEM.1749

INOR 79

BN/CC isosterism: A new approach to expand the chemical space in biomedical research

Shih-Yuan Liu, shihyuan.liu@bc.edu. Chemistry, Boston College, Chestnut Hill, MA 02467, United States

BN/CC isosterism has recently emerged as a viable strategy to increase structural diversity. In particular, the chemistry of 1,2-azaborines, which are BN isosteres of the ubiquitous family of amines, has attracted attention as novel aromatic compounds relevant to biomedical research. I will describe our recent contributions in the synthesis, characterization, and reactivity studies of 1,2-azaborine heterocycles. Furthermore, emerging investigations of 1,2-azaborines in the context of biological systems will also be discussed.

INOR 80

Hydrogen activation in molecular complexes: Approaches to catalysis and energy storage using amine boranes

Tom Autrey, tom.autrey@pnnl.gov. Pacific Northwest National Laboratory, United States

Novel approaches for activating hydrogen are needed to increase efficiency and decrease costs in energy-intensive industrial processes. Amine boranes have the potential to provide unique solutions to two seemingly different applications: (i) catalytic hydrogenation, critical to many industrial processes, ranging from upgrading crude oil to ammonia synthesis, and (ii) hydrogen storage, a potentially critical solution to storing energy from intermittent renewable sources such as wind and solar.

In this presentation the relationship between hydrogen storage and catalysis is discussed. The work starts with the pedagogic example of ammonia borane and ammonium borohydride in hydrogen storage and extends to more complex amine borane structures that provide the ability to tune thermodynamics. We describe a combination of experimental and computational approaches to gain insight into structure and reactivity of non-metal molecular complexes composed of Lewis acid Lewis base functionality to understand the mechanism of heterolytic activation of molecular hydrogen.

INOR 81

Pumping iron for selective amine-borane dehydrogenation

R Tom Baker, rbaker@uOttawa.ca. Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, ON K1N 6N5, Canada

The iron bis(bisphosphine) unit, [Fe(P2)]2 is shown to offer a unique platform for stabilizing selective catalysts for amine-borane dehydrogenation to poly(aminoborane)s or B-N cross-linked borazine (polyborazylene). Use of 1 mol% Fe(N2)(dmpe)2 [dmpe = 1,2-bis(dimethylphosphino)ethane] with ammonia-borane (AB) at 25°C, for example, affords insoluble poly(aminoborane) with only a trace of cyclic aminoborane and -iminoborane products. The [FeH2(P2)]2 resting state is stable during thousands of turnovers and slower reaction rates using 1,2-bis(dimethylphosphino)benzene (vs. dmpe) suggest that the turn-over-determining step involves decoordination of one phosphine arm from the Fe center. Protonation of these complexes with HNTf2 affords [FeH(H2)(P2)+NTf2-] (Tl = OS(O)CF3) which exhibits complementary selectivity to that observed using the neutral dihydride. The resting state for the stable cationic catalysts was characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction as the borohydride complex, [Fe(2-BH4)(P2)+NTf2-]. Use of this catalyst precursor in an appropriate ionic liquid solvent with AB affords cyclic products, > 2 equiv. of hydrogen and only traces of insoluble poly(aminoborane).
INOR 82
Conjugated boracycles: Electron-deficient ring systems
Frieder Jaekle, fjaekle@rutgers.edu. Department of Chemistry, Rutgers University Newark, Newark, NJ 07102, United States

Electron-deficient organoboranes play important roles as Lewis acid catalysts in various organic transformations, as cocatalysts in olefin polymerization, and in the activation of small molecules when combined with bulky Lewis bases (so-called frustrated Lewis pairs). The Lewis acidic properties are also exploited in the recognition of anions. Especially attractive are polyfunctional Lewis acids, which tend to exhibit the strongest affinities due to cooperative and/or chelate effects. Conjugated systems that feature multiple tricoordinate borane moieties are also attractive for optical and electronic applications (e.g. nonlinear optics, luminescent imaging materials, OLEDs, OFETs, photovoltaics), due to extension of conjugation via the empty p-orbital and the pi-acceptor effect of boranes.

Our recent work on redox-active ferrocene-based Lewis acids and Lewis pairs will be discussed. We will also report on our efforts in the area of electron-deficient luminescent boracycles.

INOR 83
Dendrimer-and nanostructure-supported carborananes and metallacarboranes: Historic perspective
Narayan S. Hosmane, hosmane@niu.edu. Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115-2825, United States

Most of the carborane derivatives of the icosahedral (C$_{28}$) or small cage (C$_{10}$) systems are formed by varying the groups on the cage carbons. This is usually accomplished in the original carborane synthesis by reacting substituted acetylenes with either the decaborane(14) or pentaborane(9) precursors. These reactions led directly to the “carbons adjacent” carboranes in which the carbon atoms occupy adjacent positions in the cage. The larger cages are obtained as closo-icosahedra, while the small cage, C$_{10}$-carboranes, have nido- structures. In the small cage system there is another cage geometry in which the carbon atoms are separated by a boron atom. Although these “carbons apart” or nido-2,4-(CR)$_2$B$_6$H$_4$ species are thermodynamically more stable and are more symmetric than the “carbons adjacent” isomers, they are not as well studied. The main reason for the relative scarcity of information on the “carbons apart” systems lies in their method of preparation; they must be synthesized from their “carbons adjacent” analogues through a sequential series of oxidative cage closure/reductive cage opening reactions. In light of complete destruction of pentaborane stockpile at the US Edwards Airforce Base, we have also directed our attention to the development of a safe, bench-scale preparation of the small-cage carboranes, that does not require isolating and handling dangerous, volatile and toxic borane precursors, such as pentaborane(9). The historic perspective of the chemistry of carboranes and metallacarboranes along with the latest findings in our research involving boron nanomaterials will be presented in detail.

INOR 84
Polyborate assembly directed by metal and nonmetal cations
David M. Schubert, david.schubert@notinto.com, Doinita Neiner, Zhiqiang Liu, R&D, U.S. Borax Inc., Rio Tinto, Greenwood Village, Colorado 80111, United States

Boric acid, B(OH)$_2$, is progenitorial to a wide range of industrially important boron compounds. Recent work in our group utilizes reactions of boric acid with simple metal oxides and non-metal bases under mild aqueous conditions to form complex polyborate structures, where self-assembly of polyborate ions is largely directed by cations in these systems. One goal of this work is to provide a more detailed understanding of cation control of polyborate structure and to exploit this effect in practical syntheses of useful materials. This paper focuses on borate compounds of empirical type MB$_x$O$_y$:xH$_2$O (M=O:3B$_3$O$_7$·xH$_2$O), which may contain fundamental building blocks having three, six, nine or more boron atoms in isolated or condensed form. Of particular note is the hexaborate anion, B$_6$O$_2$(OH)$_2$$_6$ (a), which may act as a b- or tridentate ligand toward metal centers (b).

INOR 85
Influences of structural factors on thermolysis behavior of metal B-N-H complexes
Huizhen Li$^1$, Cong Wang$^2$, Xuenian Chen$^1$, xchen@htu.cn, Sheldon G Shore$^2$, shore.1@osu.edu. (1) School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China (2) Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210, United States

Computational and experimental results from our investigation of structural factors in the thermal decomposition of metal B-N-H compounds implicate MgB$_x$H$_y$ as an intermediate in hydrogen desorption by MgB(H$_2$)$_2$. Solvent-free MgB$_x$H$_y$ required for establishing its behavior as the proposed intermediate, cannot be prepared by direct thermolysis of its hydrate since hydrolysis/dehydrogenation occurs along with dehydration. Hydrated, ammoniated, and methanolated MgB$_x$H$_y$ have been prepared and their thermal decomposition examined by TGA, TPD, IR, $^{11}$B NMR (solution and MAS), and XRD. We have established the relationship between structure and thermolysis behavior, relying mainly on $^{11}$B NMR (solution and MAS) and XRD, identifying dihydrogen bonds, solvent, metal, coordination number, and molecular symmetry as important structural determinants. These insights will be useful in the design of hydrogen storage materials.

INOR 86
Novel 1D magnet NH$_4$FeCl$_3$(HCOO)
Nizhueyt Izquierdo$^1$, nizquiedo@broncs.utpa.edu, Joshua Greenfield$^2$, Kirill Kovnir$^2$. (1) Department of Chemistry, The University of Texas Pan-American, Edinburg, Texas 78532, United States (2) Department of Chemistry, The University of California, Davis, Davis, California 95616, United States

Novel materials with peculiar magnetic properties attract a lot of attention for application in technological devices. The rational design of these new magnetic materials requires taking into account two important aspects: the nature of both the spin carriers and the bridges. We report synthesis, structural, and magnetic characterization of the novel 1D compound NH$_4$FeCl$_3$(HCOO) formed from one-dimensional chains of edge-sharing distorted...
octahedra of six-coordinate Fe$^{2+}$ centers. Each Fe$^{2+}$ is coordinated by four Cl$^-$, which are shared between adjacent octahedra, and two HCOO$^-$, which bridge adjacent Fe$^{2+}$ centers.

Due to the relative size of the formate ligand, the octahedra are forced to tilt towards each other, resulting in a zig-zag pattern. The compound crystallizes in the monoclinic space group C2/c (No. 15), with a = 7.89 Å, b = 11.16 Å, c = 6.92 Å, and $\beta = 108.07^\circ$. Magnetic characterization reveals antiferromagnetic ordering below $T_N = 6$ K, and a metamagnetic transition is observed in the ordered phase between $\mu_0H = 1.2$–$1.7$ T at 2 K. There is also a significant anisotropy, depending on whether the magnetic field is applied parallel or perpendicular to the chain propagation direction. This indicates that the magnetic coupling in this material is not trivial, which is likely due to a complex orientation of magnetic moments along the chains.

INOR 87
New triosmium clusters with multidentate phosphate ligands
Gregory L Powell, powellg@acu.edu. Department of Chemistry & Biochemistry, Abilene Christian University, Abilene, Texas 79699, United States

Reactions of osmium carbonyl complexes with phosphate ligands have been studied for decades. We have recently used a microwave reactor to investigate the reactivity of Os$_6$(CO)$_{12}$ with multidentate phosphines including bis(diphénylphosphino)methane (or dpmm) and 1,1,1-tris(diphénylphosphinomethyl)ethane (or triphos) at high temperatures. The efficiency and convenience of microwave heating make it an ideal synthetic method for undergraduate students to master. Four new triosmium cluster complexes have been synthesized and characterized by X-ray crystallography. In each case, C-H bonds have been cleaved while Os-C bonds have been formed.

INOR 88
Synthesis and characterization of alkaline metal ion battery cathode materials from novel single-source metal alkoxides
Michael L Neville$^{1,2}$, mlnevill@sandia.gov, Timothy J Boyle$^1$, David Ingersoll$^1$, Christopher A Apblett$^1$, Daniel T Yonemoto$^{1,2}$. (1) Sandia National Laboratories, Albuquerque, New Mexico 87106, United States (2) University of New Mexico, Albuquerque, New Mexico 87106, United States

Alkaline earth metal based batteries are very attractive due to the metal ion's light mobile nature and high energy densities. Unfortunately, due to mechanical degradation and limitations in discharge charge these batteries have are not able to reach their full potential. A number of reports indicate that nanomaterials may overcome some of these issues. The recent development of NaSICON (Sodium (Na) Super Ionic Conductor) may allow for better properties in the sodium variety. Our group has been investigating the synthesis of a family of aryloxides [A$_x$M$_y$(OAr)$_z$] ($A = $ Li, Na & $M =$ Fe, Mn and Co) as precursors to A$_x$M$_y$O$_z$ cathode materials (i.e., thin films and nanomaterials). These precursors are synthesized from the reaction of metal mesityls/amides with either 2- mono-substituted and/or 2,6 di-substituted aryl alcohols. Using solvothermal routes, the products were processed to generate the metal oxide nanomaterials. Spin coating methods were used to produce thin films. The materials were characterized by transmission electron microscopy, powder X-ray diffraction, and electrochemical evaluation. The synthesis and characterization of these precursors, the generated nanomaterials and the electrochemical behavior of the materials will be explored.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

INOR 89
Squeezing the unit cell: Synthesis, structure, and properties of ScFeGa$_5$ analogs
Jacob D McAlpin$^{1,2}$, jmcalp5@tigers.lsu.edu, Bradford W Fuller$^1$, David P Young$^2$, Julia Y Chan$^{1,3}$. (1) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States (2) Department of Physics, Louisiana State University, Baton Rouge, Louisiana 70803, United States (3) Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United States

Compounds adopting the HoCoGa$_5$ structure type have garnered attention over the past decade due to the wide range of magnetic and electrical transport properties they exhibit such as magnetically mediated superconductivity in CeIn$_2$ and CeMIn$_5$ ($M = $ Co, Rh, Ir). We have grown single crystals of ScFeGa$_5$ with the self-flux method, and single crystal X-ray diffraction shows ScFeGa$_5$ crystallizes in the HoCoGa$_5$ structure type. Growth parameters for ScFeGa$_5$ and other analogues are presented along with crystal structure and results from magnetic and transport measurements.

INOR 90
Utilization of metathesis to achieve water solubility of nanoparticles
Laura G. Mast, laura.g.mast@vanderbilt.edu, Michael J. Turo, Janet E. Macdonald. Department of Chemistry, Vanderbilt University, Nashville, TN 37235, United States

One fundamental challenge facing current nanochemistry research is achieving water solubility of particles that are prepared in organic solvents for biological and photocatalytic applications. Many syntheses of nanoparticles are conducted in the presence of organic solvents and surfactants to yield monodisperse nanoparticles, but leave nanoparticles with coronas of long hydrophobic alkyl chains, thus rendering them insoluble in water. Current methods for improving water solubility, such as ligand exchange, only work for a few nanoparticle systems. A unique opportunity lies in the exploitation and manipulation of the chemistry of common surfactant molecules, especially the unsaturation in oleic acid and oleylamine. Here we show that after nanoparticle synthesis, using the Grubbs' metathesis reaction, the outer portion of the ligand can be replaced with a chain containing a polar functional group. The reaction allows for precise control of the resultant structure of the ligand and thus the chemical functionality and water solubility of the nanoparticles.

INOR 91
Synthesis of novel group 4 metal carboxylates for the production of ceramic nanowires
Daniel T. Yonemoto$^{1,2}$, dtyonemot@sandia.gov, Timothy J. Boyle$^1$, Nelson S. Bell$^1$, Thu Q. Doan$^1$. (1) Sandia National Laboratories, Albuquerque, New Mexico 87106, United States (2) University of New Mexico, Albuquerque, New Mexico 87106, United States

Ceramic nanowires can be produced from electro-spinning (ES) and force-spinning (FS) methods through the combination of select metal-organic precursors with polymers, followed by thermal treatments to remove the organic components and convert the residual metal to the ceramic oxide materials. As an alternative polymer-free approach, we have developed a series of novel group 4 metal carboxylate precursors for ES/FS efforts to directly produce high dielectric constant (k) ceramic nanowires. The precursors were identified by single crystal X-ray diffraction as $[\text{Ti(OBc)}_2(\text{OBU})_2]_n$, $[\text{M(m-ORC)}_3(\text{ORC})_2]_n$ [$M = $ Zr, Hf; $\text{ORC} = $ O$\text{C(CH}_3\text{)}_2$, OBc or O$\text{C(CH}_3\text{)}_2$]), O$\text{C(CH}_3\text{)}_2$]. Interestingly, only the $[\text{Hl(ORc)}_4]_n$ derivatives were found to produce the desired nanowire morphology. The synthesis and characterization of these compounds will be presented in conjunction with their ability to be converted to nanowires.
Solar water splitting in a molecular photoelectrochemical cell

Thomas J. Meyer¹, tjmeyer@unc.edu, Leila Alibabaei¹, M. Kyle Brennaman¹, Michael R. Norris¹, Berc Kalanyan², Wenjing Song¹, Mark D. Losego³, Javier J. Concepcion¹, Robert A. Binstead¹, Gregory N. Parsons¹. (1) Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States. (2) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States.

Artificial photosynthesis and the production of solar fuels could be a key element in a future renewable energy economy providing a solution to the energy storage problem in solar energy conversion. We have developed a hybrid strategy for solar water splitting into hydrogen and oxygen based on a Dye Sensitized Photoelectrochemical Cell (DSPEC). This is a hybrid approach which integrates molecular level light absorption and catalysis and the bandgap and transport properties of high bandgap semiconductor oxides. In the DSPEC for water splitting, a derivatized, core/shell nanostructured photoanode is the key. It consists of a transparent conductive metal oxide core - nanoITO (indium tin oxide) or nanoATO (antimony tin oxide) - coated with a thin outer shell of TiO$_2$ formed by atomic layer deposition (ALD). A "chromophore-catalyst dyad assembly", [(PO$_3$)$_3$(bpy)$_2$Ru(4-Mebpy-4-bimpy)Ru(bpy)(OH$_2$)$_2$], which combines both light absorber and water oxidation catalyst in a single molecule, is surface-bound to the TiO$_2$ shell. Visible photocatalysis of the resulting core/shell/assembly with a Pt cathode resulted in water splitting into hydrogen and oxygen with an absorbed photon conversion efficiency (APCE) of 4.5% at peak photocurrent.

Strategic design of chromophores to clarify key reactions steps in the dye-sensitized solar cell

Curtis P Berlinguette¹,², cberling@chem.ubc.ca, Kiyoshi CD Robson¹,², Gerald J Meyer³, Ke Hu⁴. (1) Chemistry, The University of British Columbia, Vancouver, BC V6T1Z1, Canada. (2) Departments of Chemistry and Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States. (3) Chemistry, University of Calgary, Calgary, Alberta T2N1N4, Canada.

Triarylamine-appended bis(triarylamine) cycloruthenated chromophores are capable of producing high power conversion efficiencies in the dye-sensitized solar cell (DSSC). This class of dyestuff offers unprecedented control of intramolecular electron transfer at TiO$_2$ surfaces, which has revealed new insights into the undesirable interfacial recombination reaction of the injected electrons with the oxidized compounds, including a significant enhancement of the open circuit photovoltage attributed to a larger surface dipole emanating from translation of the hole away from the interface. These findings are rooted in the ability to acutely manipulate the energies of the frontier molecular orbitals within a homologous series of compounds differing only in the electron-donating/withdrawing properties of the terminal substituents. These investigations and related studies on donor–acceptor organic dyes that have provided atomic level resolution on how to enhance the regeneration rate constant and open circuit photovoltages will be presented.

Photoinduced electron transfer at TiO$_2$ interfaces sensitized to visible light with triarylamine-appended bis(triarylamine) cycloruthenated complexes

Gerald Meyer¹, meyer@jhu.edu, Ke Hu¹, Kiyoshi CD Robson², Curtis P Berlinguette²,³. (1) Departments of Chemistry and Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States. (2) Chemistry, The University of British Columbia, Vancouver, BC V6T1Z1, Canada. (3) Chemistry, University of Calgary, Calgary, Alberta T2N1N4, Canada.

Spectro-electrochemical studies of the title complexes revealed non-Nernstian behavior for redox equilibrium reasonably assigned to the Ru$^{II}$ and Na$_2$Ru$_2$ sensitized couples. Pulsed light excitation of the sensitized thin films immersed in 0.5 M LiClO$_4$/CH$_3$CN resulted in rapid excited state injection, $k_{inj} > 10^8$ s$^{-1}$, and, in some cases, hole transfer to the Na$_2$Ru$_2$ group (TiO$_2$(e$^-$)/Ru$^{II}$-$\text{Na}_2$Ru$_2$ $\rightarrow$ TiO$_2$(e$^-$)/Ru$^{III}$-$\text{Na}_2$Ru$_2$$^{II}$). The quantum yield for intramolecular-hole transfer process was sensitive to peripheral substituents on the complexes, the surface anchoring group, and the interfacial proton concentration. Charge recombination (TiO$_2$(e$^-$)/Ru$^{III}$-$\text{Na}_2$Ru$_2$ $\rightarrow$ TiO$_2$/Ru$^{II}$-$\text{Na}_2$Ru$_2$) or (TiO$_2$(e$^-$)/Ru$^{III}$-$\text{Na}_2$Ru$_2$$^{II}$ $\rightarrow$ TiO$_2$/Ru$^{II}$-$\text{Na}_2$Ru$_2$) rate constants were insensitive to the identity of the cyclometalated compound, while the open circuit photovoltage was largest for the complex that displayed the highest quantum yield for hole transfer; behavior attributed to a larger dipole moment change $\Delta \mu = 7.7$ Debye. The relevance of these findings for solar energy conversion will be addressed.

Mechanistic investigations and detection of intermediates of molecular proton reduction catalysts

Leif Hammarström, leif.hammarstrom@kemi.uu.se, Allison Brown, Mohammad Mirmohades, Sonja Pullen, Sascha Ott, Reiner Lomoth.Department of Chemistry - Ångström Laboratory, Uppsala University, Uppsala, Sweden

Development of better molecular catalysts for water splitting and solar fuels formation is a major topic in current artificial photosynthesis research. Rational design and comparative studies rely, however, on detailed information about the mechanism of catalysis that in most cases is not available. In contrast, turnover frequencies are often used in order to allow for rational catalytic design. The mechanism can be determined and/or intermediate steps be followed are clearly desirable in order to allow for rational design and evaluation of new catalysts.

We have for some years developed mono- and dinuclear iron complexes for catalytic proton reduction inspired by the active site of [FeFe]-hydrogenase. We have demonstrated e.g. the catalytic effect of a protonable base near the active site, the construction of sensitizer-catalyst dyads, complex patterns of ligand vs. metal protonation, multi-turnover photochemical hydrogen production and the first penta-coordinate mononuclear catalyst mimicking the distal iron center.

In this paper we will present studies were we directly resolve unstable intermediates of the catalytic reaction in solution by time-resolved spectroscopy. We will also present the first spectroscopic evidence for dye-sensitized formation of reduced iron-catalyst species anchored onto a dye-sensitized NiO film.

Power curves of buried junction photoelectrochemical cells

Daniel G Nocera, dnocera@fas.harvard.edu,Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, United States

An artificial leaf can perform direct solar-to-fuels conversion via water splitting. The artificial leaf is a buried junction, in which the rectifying junction is protected from solution or "buried". Whereas water splitting catalysis is combined with charge separation, current rectification, and photovoltage generation in a conventional photoelectrochemical cell (PEC), in a buried junction device, catalysis is separated from current rectification, charge separation, and photovoltage generation, which occur at the internal junction. The buried junction photoelectrochemical (BJ-PEC) cell is free from many of the design limitations of a traditional PECs. This talk will focus on these advantages and will establish the facility of a BJ-PEC to perform direct solar-to-fuels conversions by utilizing an analysis that highlights the importance of matching the electrochemical load of the water splitting catalyst to the...
current density of the PV component. The results draw a clear link between the kinetic profile of the water splitting catalysis and the photovoltaic power curves such that high solar-to-fuels efficiencies may be achieved.

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Determining domain structures for amorphous metal-oxide water-splitting catalysts in artificial photosynthesis
David M. Tiede1, tiede@anl.gov, Jier Huang1, James D. Blakemore2, Gihan Kwon1, Diego Fazi1, Oleksandr Kokhar1, Nathan D. Schley2, Karen W. Chapman3, Peter J. Chupas2, Gary W. Brudvig3, Pingwu Du4, Robert H. Crabtree2. (1) Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States (2) Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States (3) Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States (4) CAS Key Laboratory of Materials for Energy Conversion & Department of Materials Science & Engineering, University of Science and Technology of China (USTC), Hefei, Anhui 230026, China

Electrochemically-processed, self-assembled amorphous, water-splitting catalyst films of transition metal oxides are of wide-spread interest in solar energy conversion for artificial leaf applications. They offer a synthetic approach that bridges the gap between molecular and crystalline oxides, and offer opportunities for to functional optimization on a per-metal-atom basis. Notable success has been achieved in the development of a range of cobalt, nickel, iron, and iridium based catalyst films. Resolution of the fundamental chemical understanding underlying the assembly, repair, and catalysis of these amorphous metal-oxides can provide information needed for the design of efficient molecular catalysts that are based on first row transition metals. Towards this end, we have investigated domain structures within amorphous catalyst films grown from Co and Ir molecular precursor complexes using synchrotron high energy (60 keV) X-ray scattering and atomic pair distribution function (PDF) analyses. The results demonstrate that the films are composed of ligand terminated, molecular-dimensional metal-oxy clusters. For the Co-phosphate and Ir-based catalyst films, the longest atom pair distance is 11.4 Å and 7.1 Å, with the domains accurately modeled as selected mineral lattice fragments, comprised of 13 and 5 metal atoms, respectively. The models are suggested to represent the population-averaged distribution of metal-oxide clusters in the films. The Ir-oxide catalyst film is distinguished by the remarkably small domain size and homogeneity. The auxiliary ligands are proposed to play a critical role in determining metal-oxide cluster size and provide secondary proton-accepting chemistry that enhances catalytic activity compared to the corresponding nanocrystalline metal-oxides. This work suggests chemical principles and experimental approaches applicable to catalysis design in artificial photosynthesis. Ongoing work is investigating in-operando catalyst film structure and molecular catalysts.

INOR 98

Near-infrared-to-visible photon upconversion by highly conjugated sensitizers under low-power noncoherent illumination
Jean-Hubert Olivier1, joholivier@duke.edu, Hyounsoo Uhr2, Yusong Bai2, Felix N. Castellano3, Michael J. Thenen1. (1) Department of Chemistry, Duke University, Durham, North Carolina 27708-0346, United States (2) Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States

Photon upconversion through triplet-triplet annihilation (TTA UC) has emerged as a promising technology for solar energy conversion, as this technology converts long wavelength optical radiation into higher energy photons. Expansion of the sensitizer spectral coverage into the NIR region offers a means to harvest energy that is typically lost in conventional silicon-based photovoltaics. In this regard, supermolecular chromophores composed of (porphyrinato)zinc(II) (PZn) and metal(II)polypyriddy1 (M) units bridged via ethyne connectivity (M-PZn-M chromophores) stand as promising sensitizer candidates for long wavelength TTA UC as such M-PZn-M supermolecules possess broad, high oscillator strength NIR absorption manifolds, feature fast (ps) intersystem cross rate constants, and possess low-lying, highly polarized triplet excited states having long (μs) lifetimes. We describe multiple examples of these chromophores that possess appropriate excited-state energy levels for exothermic triplet-triplet energy transfer to acceptor/annihilators that provide NIR-to-visible photon upconversion characterized by anti-Stokes shifts that approach 1 eV. We demonstrate further that the combination of these supermolecular sensizers with rubrene as a triplet acceptor/annihilator enables NIR-to-vis TTA UC under low power noncoherent illumination.

INOR 99

Discovery and crystallographic challenges of diamond-like semiconductors with attractive physicochemical properties
Jennifer A. Aitken, aitkenj@duq.edu, Jacilynn A. Brant, Carl D. Brunetta, Kimberly A. Rosmus, Kasey P. Devlin, Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, United States

Diamond-like semiconductors (DLSs) adopt crystal structures that can be considered as superstructures of diamond, either the cubic or hexagonal form. Although diamond-like structures are seemingly simple, these materials exhibit a number of crystallographic challenges and opportunities. Solving complex problems such as delineating cation patterns, differentiating polymorphs, discerning isoelectronic elements, and locating dopants/elemental substituents within ternary -III-VI; and quaternary I2-III-II-VI, DLSs is important to garner a fundamental understanding of structure-property relationships to improve these materials for potential applications. The attractive electrical, optical and magnetic properties of DLSs can be tuned through compositional changes, which often result in subtle structural variations that are sometimes only detectable through careful analysis of high-quality diffraction data. The assortment of structure types that have been observed among ternary and quaternary DLSs can be categorized by the closest-packed arrangement of the anions. Within each kind of closest-packed anion array, cations can display several unique ordering patterns within the tetrahedral holes, as found in the hexagonally derived wurtzstannite (Pmn21), wurtzkesterite (Pn) and lithium cobalt (II) silicate (Pna21) structure types. X-ray diffraction patterns of such materials can be strikingly similar and are difficult to distinguish in many instances. Concomitant with structural changes, marked effects on the observed physicochemical properties can be observed in polymorphs within a single composition. In the cases where the ions making up the formulae are isoelectronic, or nearly isoelectronic, challenges arise in discriminating between the ions using X-ray diffraction. Furthermore, the properties of these materials can be altered by partially replacing one ion in the lattice with another through a process of doping/substritution. Understanding the structural implications of these alterations on the resulting properties can benefit the future design of DLSs. This work is supported by the National Science Foundation under Grant No. DMR-1201729.

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Structure of cerium cobalt borocarbide: Cobalt squares and borocarbide chains
Trinath Mishra, tmsdra@chem.fsu.edu, Patricia Tucker, Susan Latturner, Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States

Ce2Co2B4C1240 was grown as large single crystals from reactions of boron and carbon in Ce/Co eutectic flux. The structure was refined from single crystal X-ray diffractometer data in triclinic space group P-1. The structure features cobalt squares crowned by borocarbide chains. Bond length analysis was used to distinguish carbon and boron. An additional disordered cobalt carbide cluster unit and interstitial carbide sites are also found in the structure.
Our systematic single-crystal X-ray diffraction studies revealed substantial Li-deficiencies in all cases, with SmSn\textsubscript{3} (space group \textit{Cmmm}, ZrGa\textsubscript{2} structure type, Pearson symbol \textit{aC12}, figure 1b) and GdSn\textsubscript{2} (space group \textit{Cmcm}, ZrSi\textsubscript{2} structure type, Pearson symbol \textit{aC12}, figure 1a) being completely lithium-free.

The structure refinements also uncovered positional disorder on the Sn site neighboring the vacancies. The Sn-disorder and the Li-deficiency correlate, and vary monotonically with the decreased size of the rare-earth atoms in the order RE = La–Nd. The SmSn\textsubscript{3} and GdSn\textsubscript{2} structures are devoid of any disorder.

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Li\textsubscript{1+}Sn\textsubscript{2n+}Pn\textsubscript{2} (Pn = P, As): Novel layered Li compounds

Kirill Kovnir, kkovnir@ucdavis.edu. Department of Chemistry, University of California, Davis, CA 95616, United States

Intensively growing Li-ion battery research area place high demands in the establishing of the long- and short-range structure of the electrodes after or during Li intercalation. Low crystallinity of the electrode materials and weak scattering of the X-rays by Li atoms make these systems crystallographically challenging. To understand the processes occurring in tin nitride electrodes we have synthesized ternary Li-Sn-Pn (Pn = P, As) compounds. We hypothesize that the formation of Li\textsubscript{1+}Sn\textsubscript{2n+}Pn\textsubscript{2} is the first stage of Li intercalation into Sn-Pn\textsubscript{2}. To fully characterize the long-range and local structure were applied a combination of powder and single crystal X-ray diffraction. \textsuperscript{7}Li NMR and \textsuperscript{116}Sn Mössbauer spectroscopies, as well as high resolution TEM. Observed local ordering of Sn and Li atoms was further probed by quantum-chemical calculations which indicate strong anisotropy of the properties of Li\textsubscript{1+}Sn\textsubscript{2n+}Pn\textsubscript{2}. Investigation of the resistivity and thermal conductivity performed on the large single crystals confirmed anisotropic transport properties of Li\textsubscript{1+}Sn\textsubscript{2n+}Pn\textsubscript{2}.

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Intermetallics with giant unit cells: Polar structures, disorder, and magnetism

Michael Shatruk, shatruk@chem.fsu.edu, Ping Chai, Kirill Kovnir. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States

Adaptability of metal atoms to a variety of coordination numbers and topologies causes a great diversity of compositions and structures for intermetallic compounds. In extreme cases, this structural flexibility leads to intricately complex atomic arrangements, e.g., quasicrystals. A particularly peculiar class of complex intermetallics is represented by binary and ternary structures with giant unit cells. In this contribution, we discuss the crystal structure of R\textsubscript{17}Co\textsubscript{32}Sn\textsubscript{12+γ} intermetallics. We demonstrate how the structural organization can be explained in terms of multishell (nested) polyhedra that divide the structure into regions of different polarity. The variable composition allows for disorder in certain atomic sites, which appears to correlate with atomic radii. Finally, we discuss the magnetic properties of these compounds and demonstrate that the Co sublattice does not participate in magnetic phase transitions observed.

INOR 104

Elucidating magnetic phase diagrams of anitferromagnetic Li\textsubscript{2}Fe-I\textsubscript{V}-Sn\textsubscript{3} diamond-like semiconductors (DLSs) with commensurate and incommensurate structures

Jacilyn A. Brant\textsuperscript{1}, brantjj@duq.edu, Jinlei Yao\textsuperscript{2}, Clarina R. Dela Cruz\textsuperscript{2}, Michael Shatruk\textsuperscript{4}, Jennifer A. Atkerson\textsuperscript{1}. (1) Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, United States (2) Research Center for Solid State Physics and Materials, School of Mathematics and Physics, Suzhou University of Science and Technology, Suzhou, China (3) Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States (4) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States

DLSs with the general formula I\textsubscript{2-}II-I\textsubscript{V}-IV\textsubscript{a} are an attractive platform for tuning electronic structures and magnetic properties, while the structural simplicity provides an avenue to develop an intimate understanding of the effects of composition and bonding on properties. Such DLSs are currently being investigated for applications in thermoelectrics, laser systems, and solid-state batteries, among others. Since the cations that reside within I\textsubscript{2-}II-I\textsubscript{V}-IV\textsubscript{a} DLSs are generally ordered, paramagnetic ions can be expected to occupy only certain positions; thus, valuable magnetic properties may materialize. Li\textsubscript{2}FeGe\textsubscript{3}S\textsubscript{4} and Li\textsubscript{2}FeSn\textsubscript{3}S\textsubscript{4} are among the first magnetic DLSs that crystallize in the wurtz-kesterite structure. As the tetravalent cation is varied from Ge to Sn, similar magnetic properties and phase diagrams are observed. However, Li\textsubscript{2}FeGe\textsubscript{3}S\textsubscript{4} and Li\textsubscript{2}FeSn\textsubscript{3}S\textsubscript{4} antiferromagnetics exhibit commensurate and incommensurate magnetic structures, respectively, as determined using neutron powder diffraction. Garnering a deeper understanding of such systems can ultimately benefit future design of magnetic semiconductors. This work was supported by the NSF under Grant No. DMR-1201729.

INOR 105

Metal carbide clusters inside fullerene cages and the use of synchrotron radiation to reveal their structures

Marilyn Olmstead, mmolmstead@ucdavis.edu, Jianyuan Zhang\textsuperscript{3}, Harry Dom\textsuperscript{2}, Xing Lu\textsuperscript{4}, Alexey Popov\textsuperscript{4}, Christine Beavers\textsuperscript{5}. (1) Department of Chemistry, University of California, Davis, CA 95616, United States (2) Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, United States (3) School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China (4) Department of Electrochemistry and Conducting Polymers, Leibniz Institute for Solid State and Materials, Dresden, Dresden 01069, Germany (5) Lawrence Berkeley Laboratory, Advanced Light Source, Berkeley, CA 94720, United States

X-ray crystallography is by far the favored experimental method for yielding structural information on endohedral fullerenes. Whereas \textsuperscript{13}C NMR, UV-Vis, MS, and chromatographic retention times narrow down the possible isomeric forms, final proof of the actual structure is only obtained with crystallography. The fullerene cages that encapsulate metal clusters can have isomers numbering in the tens of thousands. Theoretical prediction of their structures is computationally challenging. In recent years the use of synchrotron radiation has been particularly useful for the successful
determination of their structures. The combination of excellent flux, high resolution and ability to change the energy of radiation are some of the key features of synchrotron radiation that help to resolve difficult issues of small crystal size, twinning and disorder. Some recent results on fullerences containing the relatively rare encapsulated metal carbide clusters \( \text{Gd}_2\text{C}_9 \), \( \text{Sc}_2\text{C}_7 \) and \( \text{Ti}_2\text{C}_6 \), their geometric features, and positioning of the clusters within the carbon cage will be presented.

INOR 106
Molecular clusters as pseudo-atoms: Simple structures with complex interiors
Theo Siegrist, tsiegrist@fsu.edu.Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida 32310, United States
National High Magnetic Field Laboratory, Tallahassee, Florida 32310, United States

Conventional binary solid-state compounds A,B, form crystalline arrays of atoms A and B. Replacing the “atomic” building blocks by pseudo-spherical molecular clusters, analogous phases can form. Pseudo-spherical molecular clusters with diameters of the order of 1 nm are truly mono-disperse and assemble into simple structures in analogy to well-known solid state compounds such as rock-salt or \( \text{CdI}_2 \) type structures. In such molecular assemblies, the internal structure of the cluster remains unchanged, but charge is transferred between them. The Chevrel-type \( \text{Co}_8\text{Se}_8(\text{PET})_6 \) cluster combines with the \( \text{C}_60 \) cluster to form a \([\text{Co}_8\text{Se}_8(\text{PET})_6]_2\text{C}_60\) pseudo-molecular compound that has a significant charge transfer.

INOR 107
Determining electronic configuration of diruthenium compounds: Coupling crystallography with magnetic studies
Carlos A Murillo, murillo@tamu.edu.Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

The use of variable-temperature crystallography coupled with magnetic studies has allowed the determination of the electronic structure in species containing \( \text{Ru}_2^{10} \) and \( \text{Ru}_2^{12} \) paddlewheel species spanned by either formamidinate or guanidinate ligands. Along with this information we have also found that pit interactions from the axial ligands have an extraordinary effect on the distance between metal atoms. The reasons for such effect will be discussed with the aid of DFT calculations.

INOR 108
Spectroscopic studies of high-spin Group 5, 6, and 7 metalloccenes
Joshua Telser1, jtselser@roosevelt.edu, A. Skye Forliti2, Alger Liang2, Benjamin Wicke2, Daniel J. Mindiola2, Gayan Wijeratne2, Timothy A. Jackson2, J. Krzystek2, Andrew Ozarowski2. (1) Department of Biological, Chemical and Physical Sciences, Roosevelt University, Chicago, IL 60605, United States (2) Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States (3) Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States (4) National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, United States (5) Department of Chemistry, University of Pikeville, Pikeville, KY 41561, United States (6) Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States

Metalloccenes and metalloccenes, namely neutral or mononaticon bisis(σ-cyclopentadienyl)metal complexes, \([\text{MCp}]^{12+} \), have been known for many decades for most of the 3d ions. In some cases, these are diamagnetic complexes, such as for ferrocene, \([\text{FeCp}]^{2+} \), while in others, such as for ferrocenium \([\text{FeCp}]^{+} \), cobaltocene, \([\text{CoCp}]^{-} \), and nickelocenium, \([\text{NiCp}]^{2+} \), the complex exhibits an \( S=1/2 \) (spin doublet) ground state and can be fully studied by electron paramagnetic resonance EPR spectroscopy at conventional frequencies (X- and Q-band, 9 and 35 GHz, respectively), most notably by Ammeter.[1] Others, such as vanadocene, \([\text{V Cp}]^{2+} \), and chromocenium, \([\text{CrCp}]^{2+} \), exhibit \( S=3/2 \) (spin quartet) ground states. In this case, conventional EPR is useful, but more so is high-frequency -field EPR (HF-EPR; frequencies up to 1 THz and fields up to 25 T). HF-EPR allows direct measurement of the zero-field splitting (zfs) parameters of these systems, as will be described here. \([\text{MCp}]^{10+} \) complexes also exhibit rich electronic absorption spectra. Thus, the use of variable-temperature and -field magnetic circular dichroism (VTVH-MCD) spectroscopy is helpful in understanding the electronic structure of \([\text{V Cp}]^{2+} \) and \([\text{CrCp}]^{2+} \). Chromocene, \([\text{CrCp}]^{2+} \), has also been investigated by VTVH-MCD. It has an \( S=1 \) (spin quintet) ground state, but with unquenched angular momentum, making it "silent" for conventional EPR and challenging even for HF-EPR. The last among the series is mangancene, \([\text{MnCp}]^{2+} \), which has an \( S=5/2 \) (spin sextet) ground state with small zfs – as a linear metallocene; we believe that coordinating ligands can lead to bent metalloccenes with larger zfs. The spectroscopic results are combined crystal structures, and with ligand-field theory (LFT), density functional theory (DFT), and ab initio methods give a picture of the electronic structure of these high-spin \([\text{MCp}]^{10+} \) complexes.


INOR 109
Ni(II) dithiocarbamate complexes containing rhodamine fluorophores for detection and bio-imaging of nitrogen dioxide
Yan Yan, Saaraan Krishnakumar, Haixia Wu, Dejian Huang, chmhdj@nus.edu.sg.Department of Chemistry, National University of Singapore, Singapore

Diamagnetic nickel(II) bis(dithiocarbamate) complexes derived from two isomers of zwitterionic sulforhodamine B were synthesized and demonstrated to be selective turn-on probes for NO\(_2\). Compared with the square-planar para isomer, the ortho isomer showed a much greater fluorescence increase upon reaction with NO\(_2\), leading to oxidation and de-complexation of the dithiocarbamate ligand from Ni(II). This probe was applied for visual detection of 1.0 ppm gaseous NO\(_2\) and fluorescence imaging of exogenous NO\(_2\) in macrophage cells RAW 264.7. Interestingly, compositionally similar Ni(II) complexes with rhodamine B are paramagnetic (six-coordinated Ni(II)) and are more sensitive in detection of nitrogen dioxide. The flexibility of Ni(II) for four and more coordination numbers plays a certain role for the quenching effects on the rhodamine fluorophores. The resulting Ni(II) dithiocarbamate complex with rhodamine B is successfully applied in detection, for the first time, endogenously formed nitrogen dioxide in RAW264.7 cells activated by lipopolysaccharides.

INOR 110
Biomedical imaging with short-lived positron-emitting radionuclides
Mark A. Green, magreen@iu.edu.Department of Radiology & Imaging Sciences, Indiana University School of Medicine, Indianapolis, IN 46202, United States

Research and clinical use of positron emission tomography (PET) as a tool for non-invasive quantitative physiologic imaging has traditionally relied on radionuclides attached to biological molecules. However, the short-lived nature of many of these radionuclides limits their use. The production of shorter-lived radionuclides has been pursued in order to increase the stability of the radionuclide and the biological molecule, thereby allowing a more stable radionuclide to be produced. In this case, a number of positron-emitting metallic radionuclides also offer attractive nuclear properties for biomedical imaging applications. As decay products of longer-lived nuclides (\(^{60}Zn\) and \(^{64}Ge\)), positron-emitting \(^{62}Cu\) (10-minute half-life) and \(^{66}Ga\) (68-minute half-life) can be made available at a clinical site "on-demand" from parent/daughter generator systems, obviating reliance on a nearby cyclotron facility for radionuclide production. Three additional longer-lived cyclotron-produced isotopes of copper also decay with emission of positrons (\(^{64}Cu\), \(^{61}Cu\), \(^{65}Cu\); half-lives of
Mobility of alkylidene metal complexes on silica surface from a simulation of NMR Chemical Shift Anisotropy by dynamic ab initio calculations

Odile Eisenstein, odile.eisenstein@univ-montp2.fr, Stéphanie Halbert, Christophe Raynaud, Simona Ispas. Institut Charles Gerhardt, CNRS and Université Montpellier 2, Montpellier, Languedoc Roussillon F-34095, France Laboratoire Charles Coulomb, CNRS and Université Montpellier 2, Montpellier, Languedoc Roussillon F-34095, France

Solid state NMR had been used to determine the molecular dynamics of a series of organometallic alkylidene complexes covalently bound to amorphous silica. (F. Blanc et al. J. Am. Chem. Soc. 2008, 130, 5886). The complexes have the general formula \([([\text{SiO}]\text{M}(\text{ER})\text{CH}′\text{Bu})(\text{R}′\text{Bu})]) (\text{M} = \text{Re}, \text{Ta}, \text{Mo} \text{or} \text{W}; \text{ER} = \text{C}′\text{Bu}, \text{NAr or} \text{CH}′\text{Bu}; \text{R}′ = \text{CH}′\text{Bu}, \text{NPh}_{2}, \text{NC}_{2}\text{H}_{4}).\) While all of these complexes are isoelectronic and isostructural, the measurement reveal different dynamic behaviors suggesting that the Mo complexes are relatively immobile while the other are mobile relative to their fixed covalent point of attachment. Dynamic ab initio calculations of selected metal complexes covalently bonded to amorphous silica were carried out to determine these dynamics. The calculated values of the NMR CSA of the alkylidene carbon agree well with the experimental data validating the method that is used. The analysis of the dynamics of the individual complexes reveals very different behaviors that can be understood based on their electronic structures.

Selective catalytic C=O hydrogenation of unsaturated aldehydes, ketones, and esters

Dmitry G. Gusev, dgoussev@hotmail.com, Denis Spasyuk. Department of Chemistry, Wilfrid Laurier University, Waterloo, Ontario N2L 3C5, Canada

We disclose the first robust, practical, highly efficient and general \(\text{H}_2\) hydrogenation catalyst with excellent carbonyl selectivity. The new osmium complexes from our laboratory are today's most successful catalysts facilitating a green reduction process\(^\text{[1-4]}\) affording unsaturated alcohols from the corresponding unsaturated aldehydes, ketones, and esters under \(\text{H}_2\) at 25 – 100 °C, while using 0.01 - 0.05 mol% [Os].

Reference:

INSIGHT INTO C-C AND C-N CROSS-COUPLING REACTIONS INVOLVING NICKEL NHC DERIVATIVES

Steven M. Baldwin, Sarah A. Del Cielo, Ryan J. Witzke, Gregory L. Hillhouse, gh15@uchicago.edu. Department of Chemistry, University of Chicago, Chicago, IL 60637, United States

We will describe results of C-C cross-coupling studies between Ni(II) alkyls and alkyl bromides. Using a stable 2-coordinate Ni(II) alkyl, (IPr)Ni-CH(TMS)\(_2\), we have demonstrated that simple alkyl halides like benzyl bromide react via sequential one-electron steps involving Ni(II), Ni(III), and Ni(IIII) intermediates to give the cross-coupled product \(\text{PhCH}_2\text{CH(MCTMS)}\). Using bulky alkyl halides, we have isolated and structurally characterized a Ni(II) intermediate (IPr)NiBr(CH(TMS))\(_2\) and demonstrated it to be the key intermediate in the subsequent C-C bond forming event. We will also describe reactions of (IMes)_2Ni\(^{+}\) and (IMes)_2Ni-NRR\(^{+}\) with alkyl and aryl halides of relevance to cross-coupling chemistry.

SELECTIVITY CONTROL IN C-S BOND CLAVERAGE REACTION OF THIARANES AND THIETANES BY BRIDGED AND NON-BRIDGED HETERODINUCLEAR ORGANOPlatinum-MANGANESe COMPLEXES

Sanshiro Komiya, komiya@cc.tuat.ac.jp. Department of Chemistry, Gakushuin University, Mejiro, Tokyo, Japan

Cooperative effects of different transition metals attract considerable interests in relation to multimetallic catalyses. We have reported series of heterodinuclear organoplatinum and –palladium complexes \(\text{L}_2\text{RM-L′M}′\), including various enhanced reactivities. [1]. Selectivity control in ring-opening reactions of thiaranes and thietanes by heterodinuclear organoplatinum-manganese complexes is described. Metathesis of PtMeX(dppe) with \(\text{Na}[\text{Mn(CO)}_3]_2\) gave non-bridged heterodinuclear clear complex (dppe)MePt-Mn(CO)_3 (1) whereas treatment of the neopentyl analogue cause intramolecular CO insertion to give its isomer, (dppe)Pt(COCH_2Me_2)(κ^1-C-O)Mn(CO)_3 (2). Addition of CO to 2 gave a corresponding non-bridged complex (dppe)(COCH_2Me_2)Pt-Mn(CO)_3 (3). Non-bridged complexes 2 and 3 reacted with cis- and trans-2-buten sulfides to give corresponding platinum complexes coordinated by thiamanganacyclic ketone with inversion stereochemistry by an S2 type mechanism. Further heating liberated trans- and cis-2-butenes with retention stereochemistry. In sharp contrast, the bridged complex 2 caused direct desulfurization of cis- and trans-2-buten sulfide with retention of configuration, giving cis- and trans-2-butenes, respectively, probably due to strong Pt-Mn bond by acyl bridge forcing the concerted direct desulfurization pathway.

Reference

DEVELOPMENTS IN GROUP 4 OLEFIN COMPLEXES

Daniel J Mindiola, mindiola@sas.upenn.edu, Masahiro Kamitani. Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States
We present reactivity studies of \((\text{PNP})\text{MCl}\) (\(\text{M} = \text{Ti} \text{ and Zr}; \text{PNP}^2 = \text{N}(2\text{-PPz})_2\text{4-methylphenyl})_2\)) with various Grignard reagents to afford olefin complexes of the type \((\text{PNP})\text{M}(\text{η}^2\text{-olefin})\)\((\text{R})\). It was found, via isotopic labeling studies, that formation of the olefin ligand occurs via a transmetallation step followed by beta-hydrogen abstraction (there is no evidence for \(\text{M=CHR} \) formation in route to the olefin). Reactivity studies involving the olefin complexes \((\text{PNP})\text{M}(\text{η}^2\text{-olefin})\)\((\text{R})\) are also presented and discussed.

**INOR 116**

**Reversible RNA methylation in biological regulation**

**Chuan He**, chuanehe@uchicago.edu. Chemistry, The University of Chicago, Chicago, IL 60637, United States

The mammalian genome is not merely a static combination of the four genetic codes A, T, C, and G. Reversible chemical modifications on DNA and histones contribute significantly to global gene expression regulation. Prior to our work, no example of reversible chemical modifications on RNA that could affect gene expression had been shown. We have discovered the first two RNA demethylase: FTO, a protein associated with human fat mass obesity, and ALKBHS, a protein that affects spermatogenesis in a mouse model. These two proteins are iron- and 2-ketoglutарат (2-KG)-dependent dioxygenases and catalyze oxidative demethylation of the most prevalent internal modifications of mammalian messenger RNA (mRNA) and other nuclear RNA, N6-methyladenosine (m6A). These studies provide the first demonstration of reversible RNA modification that may impact biological regulation analogous to the well-known reversible DNA and histone chemical modifications. We have also discovered proteins that can selectively recognize m7A-modified mRNA. We have confirmed that binding of m7A-containing mRNA by a family of the reader proteins affects the translation status and lifetime of the target mRNA. The impact of the reversible RNA methylation on gene expression regulation will be discussed.

**INOR 117**

**Development of small molecules as chemical tools to study the role of metal-associated misfolded proteins in Alzheimer’s disease**

**Mi Hee Lim**, mhlim@unist.ac.kr. Department of Chemistry, Ulsan National Institute of Science and Technology, Ulsan, Republic of Korea

Neurodegenerative disorders impair an enormous financial and emotional burden on patients, their families, and communities. More than 24 million people worldwide have Alzheimer’s disease (AD), a devastating and fatal neurodegenerative disease that remains poorly treated due to an incomplete grasp on the disease etiology. A key neuropathological hallmark of AD is amyloid-β (Aβ) plaques in the brain. The mechanisms driving formation of these protein aggregates and their causal link to dementia are still unclear. An additional observation in the AD brain is the accumulation of metal ions, which has been proposed to be associated with Aβ aggregates and neuronal death, yet relatively little is known, further sustaining the controversy surrounding this aspect of the disease. Even through a large body of continuously reported literature regarding metal ions and Aβ species, direct connection of metal-Aβ interaction with AD onset and development has been neglected in this field due to lack of appropriate tools and/or tactics. Therefore, we have developed small molecules as chemical tools that are capable of specifically targeting metal-associated Aβ species and modulating their interaction and reactivity. Here, our rational structure-based design principle and recent discovery of chemical tools for investigating metal-Aβ chemistry and biology and/or potential therapeutic agents for AD will be discussed.

**INOR 118**

**Titanic siderophores**

**Ann M Valentine**, ann.valentine@temple.edu. Department of Chemistry, Temple University, Philadelphia, PA 19122, United States

Organisms produce and release siderophores to sequester Fe(III), but they are correspondingly tight binders of Ti(IV). This presentation will explore some aqueous coordination chemistry of Ti(IV) complexation by siderophores, and will detail reactions of these protein complexes and their causal link to dementia are still unclear. An additional observation in the AD brain is the accumulation of metal ions, which has been proposed to be associated with Aβ aggregates and neuronal death, yet relatively little is known, further sustaining the controversy surrounding this aspect of the disease. Even through a large body of continuously reported literature regarding metal ions and Aβ species, direct connection of metal-Aβ interaction with AD onset and development has been neglected in this field due to lack of appropriate tools and/or tactics. Therefore, we have developed small molecules as chemical tools that are capable of specifically targeting metal-associated Aβ species and modulating their interaction and reactivity. Here, our rational structure-based design principle and recent discovery of chemical tools for investigating metal-Aβ chemistry and biology and/or potential therapeutic agents for AD will be discussed.

**INOR 119**

**Zinc fluxes in control of biology: Chemical thermodynamic, structural, and dynamic studies of zinc sensors, probes, and metalloregulatory proteins**

**Emily L Que1, Benjamin A. Gilston1, Suning Wang1, Seth A. Garvin1, Francesca E. Duncan2, Teresa K. Woodruff1,3, Thomas V O’Halloran1,2, t-ohalloran@northwestern.edu. (1) Chemistry of Life Processes Institute, Northwestern University, Evanston, IL 60208, United States (2) Department of Chemistry, Northwestern University, Evanston, IL 60208, United States (3) Department of Obstetrics and Gynecology, Northwestern University, Chicago, IL 60611, United States**

Most of the known biological functions of transition metal centers involve catalytic centers in metalloenzymes, however it is becoming increasingly clear that fluxes in transition metal concentration can play central regulatory roles. For instance, temporal fluxes in zinc concentrations drive processes as diverse as host pathogen responses and in the earliest stage of mammalian developmental states. Structural and mechanistic studies of the metalloregulatory proteins are revealing novel biophysical mechanisms for transduction of the signal as well as the molecular basis for the remarkable thermodynamic sensitivity of these metal-sensing molecular switches. Specialized cells, such as the developing oocyte, exhibit unique transition metal signatures and can undergo significant metal uptake and reorganization steps in concert with the specialized function. Recently, we demonstrated that zinc influx and efflux controls meiotic progression in mammalian oocytes. We have shown that total zinc levels in mouse oocytes undergo dramatic fluxes during oocyte maturation, increasing by over 50% in the 12 hour period between GV and MII. Limiting intracellular zinc availability during in vitro maturation using pharmacological means causes formation of large polar bodies and arrest at telophase-I. Intriguingly, when immature oocytes are exposed to lower levels of toxic metals such as cadmium and mercury, the developing cell concentrates these metals. A variety of single cell analytical methods including STEM-EDS/EELS, X-ray fluorescence microscopy and new fluorescent zinc-specific probes, allows for a comparison between the subcellular distribution of both total zinc and chelator-accessible zinc pools and thus provides insights into intracellular speciation.

**INOR 120**

**Coordination chemistry of low coordinate phosphorus compounds**

**John Protasiewicz**, protasiewicz@case.edu. Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, United States

Low coordinate and multiply bonded phosphorus compounds form the basis of reactive materials for the construction of new complexes and conjugated materials. In this presentation our work on the coordination chemistry of phosphinides (RP), phosphaalkenes (RP=CR2) and diphosphenes (RP=PR) will be presented. Phosphinides are analogues of carbenes (R2C), and as such will form complexes will both transition metals and main group species. In particular, chemistry of the phosphine stabilized phosphinidene ArP=PR3, aka, phopsha-Wittig reagents will be highlighted.

**INOR 121**

**Donor-acceptor interactions in heterobimetallic lantern complexes**
Past work has demonstrated a facile synthesis for heterobimetallic lantern complexes with thiocarboxylates that produces Pt-M complexes (M = Fe, Co, Ni, Zn, Mg, Ca) in good yield based on the ligand hard-soft donor preferences. All soluble compounds prepared to date have Lewis basic donors on the non-platinum metal such that the complexes generally have the form [PIm(SOCR)4(L)]. That such Lewis bases donate to the Lewis acidic metal centers is commonplace. A combination of techniques including 195Pt NMR and structural characterization demonstrate Lewis basic behavior from Pt to the other metals, again acting as Lewis acids. In this report we will describe an unusual family of compounds that assemble as infinite chains in the solid state with pyrazine bridging between thiocacetonate lantern complexes in the stoichiometry [PIm(SAc)4(pyrazine)]. M = Co, Ni, Zn, or as dimers with the stoichiometry [PIm(SAc)4]2(pyrazine).

Solid state magnetic susceptibility studies will be presented that quantify the changing coupling between 3d metal centers, and comparisons with previously reported magnetic behavior in monomers and other dimers will also be described. The existence of unusual six-coordinate Pt(II) centers will be highlighted.

INOR 122

Practical bioinspired aerobic oxidation of alcohols and amines with organic (co)catalysts
Shannon S. Stahl, stahl@chem.wisc.edu, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States

The active sites of metalloenzymes have served as a starting point for development of numerous small-molecule, transition-metal oxidation catalysts. Organic cofactors are also common in naturally occurring oxidases and oxygenases, but they have been less extensively exploited for use in organic chemical synthesis. This talk will focus on recently developed aerobic methods for the aerobic oxidation of alcohols and amines with organic (co)catalysts that resemble the organic cofactors in galactose oxidase and copper amine oxidases.

INOR 123

Crystal-free crystallography
Makoto Fujita, mfujita@appchem.t.u-tokyo.ac.jp, Department of Applied Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

X-ray single crystal diffraction (SCD) analysis has the intrinsic limitation that the target molecules must be obtained as single crystals. Here, we report a new protocol for SCD analysis that does not require the crystallization of the sample. In our method, tiny crystals of porous complexes12 are soaked in the solution of a target, where the complexes can absorb the target molecules. The crystallographic analysis clearly determines the absorbed guest structures along with the host frameworks.2,6 As the SCD analysis is carried out with only one tiny crystal, the required sample amount is of the nano-microgram order. With chiral guests, the space group of the crystal turned into chiral (C2 or P1), enabling the determination of absolute configuration of the guests from the anomalous scattering from the host ZnB component. We demonstrate that even ~50 ng of a sample is enough to be analyzed. When combined with high performance liquid chromatography (HPLC), multiple fractions were directly characterized, establishing a prototypical LC-SCD analysis.

References:

INOR 124

Crosslinked MOFs: New materials, new opportunities
Seth M. Cohen, scohen@ucsd.edu, Corinne A. Allen, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92039-0358, United States

Metal-organic frameworks (MOFs) comprising and increasingly important class of hybrid organic-inorganic materials. Their regular structure, tunability, and high porosity have made them attractive compounds for a wide range of proposed applications. In this presentation, the use of ‘crosslinked’ ligands will be described to prepare a new subclass of MOFs. The ligands string together, using either rigid or flexible bridges, multiple coordinating units, such as simple terephthalic acid building blocks. Despite the linker constraints, the majority of these systems readily assemble into predictable MOF frameworks. The advantages, limitations, and prospects of MOFs based on crosslinked ligands will be discussed. The possible convergence of MOF and polymer chemistry via this approach will also be described.

INOR 125

Chromophore photophysics defined by metal-organic frameworks
Natalia B. Shustova, shustova@sc.edu, Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

Control and understanding of chromophore conformations are generally driven by their applications for construction of fast and efficient electronic devices. However, solid-state emission required for industrial applications is generally complicated by fluorophore aggregation, which results in significant fluorescence quenching. Coordinative immobilization of chromophores inside a rigid scaffold can turn-on their emission and significantly affect their lifetime and quantum efficiency, key characteristics of any fluorophore. Utilization of metal-organic framework (MOF) as a tunable rigid matrix for chromophores in combination with MOF high surface area creates a new avenue towards design of porous tunable sensors operating at a wide temperature range.

INOR 126

Molecular design of metal-ligand chromophoric building blocks and their supramolecular assembly and functions
Vivian WW Yam, wwayam@hku.hk, Institute of Molecular Functional Materials† and Department of Chemistry, The University of Hong Kong, Hong Kong, China

Recent works in our laboratory have shown that novel photofunctional metal complexes could be assembled through the use of various metal-ligand chromophoric building blocks. In this presentation, various design and synthetic strategies together with the successful isolation of new classes of
chromophoric metal complexes will be described. A number of these complexes have been shown to display rich luminescence behavior. Correlations of the luminescence behavior with the electronic and structural effects of the metal complexes have been made. Some of these complexes have also been shown to undergo supramolecular assembly to give a variety of structures and morphologies. The characteristics of these complexes could be fine-tuned for specific applications and functions through rational design and assembly strategies based on various coordination motifs or weak non-covalent metallophilic and π-π interactions.

1 Areas of Excellence Scheme, University Grants Committee (Hong Kong)

INOR 127

Supramolecular organization of metal complexes in one, two, and three dimensions

Angel A. Martí, amarti@rice.edu. Department of Chemistry, Rice University, Houston, TX 77005, United States

Metal polypyrrolidyl complexes (such as ruthenium and rhenium) present interesting photophysical properties such as red shifted emission, large Stokes shifts and long photoluminescence lifetimes. Therefore, the supramolecular organization of these complexes is of interest for the creation of photoactive materials with novel properties. For example, we will show that carbon nanotubes, although insoluble in water, can be covalently dispersed in aqueous solution by addition of ruthenium complexes with extended aromatic systems. The metal complexes self-assemble on the surface of the nanotubes to create pseudo-one dimensional supramolecular arrangements. On the other hand, two-dimensional arrangements of metal complexes can be obtained in lamellar matrices such as zirconium phosphates. These materials present applications in photoinduced electron transfer reactions and solar energy conversion. Finally, supramolecular three-dimensional arrangements of metal complexes can be generated by entrapping rhenium complexes within zeolites. These materials present interesting photophysical properties with applications in the detection of volatile vapors. In this context, we became interested in the coordination and activation of σ bonds, fundamental processes with very different selectivities and open new applications of metathesis in the synthesis of an array of compounds with different functionalities. The piezochromic behavior of some of these materials will be discussed and rationalized using different packing modes. We have recently reported the aggregation induced emission of a Pt(II) compound bearing a tridentate, dianionic ligand and also showed, that appropriate ancillary ligands can be useful to gelate solvents of different polarity, such as dichloromethane and DMF.

INOR 128

Luminescent metal complexes and their assemblies

Luisa De Cola, decola@unistra.fr, Matteo Mauro, Alessandro Alliprandi.ISIS, University of Strasbourg, Strasbourg, France

The creation of nano/microstructures based on molecular components possessing defined functionalities is a very fascinating field at the cross point of different disciplines. Our effort, in this talk, focuses on the assembly of functional molecules to form crystalline or soft materials. The molecules employed for the assemblies are metal complexes based on Pt(II) or Ir(III) metal ions coordinated to ligands able to induce strong secondary interactions. All the complexes show emission properties that can be modulated upon the formation of the aggregates, or by the interaction of the materials with other systems. The assembly can therefore be used to probe the environment or can result in a new material with very exciting properties. The degree of interaction between the different units can be tuned using different ligands as well as different media where the complexes are solubilized or dispersed. The piezochromic behavior of some of these materials will be discussed and rationalized using different packing modes.

INOR 129

Controlling catalytic processes through ligand design

Robert H. Grubbs, rhg@caltech.edu. Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

Olefins metathesis catalysts have become one of the tools for the efficient synthesis of complex molecules. Until recently, the catalysts demonstrated poor catalytic versatility. Over the past several years, complexes based on molybdenum, tungsten and ruthenium have been discovered that produce olefins good to excellent selectivity for the generation of Z olefins both in cross and in ring closing metathesis. New ligands have been developed that result in different selectivities and open new applications of metathesis in the synthesis of an array of complex molecules. These catalysts are developed through design, computation and serendipity. Applications range from the preparation of pharmaceuticals to the control of the preparation of polymeric materials.

INOR 130

Catalytic additions of O-H, N-H and C-H bonds to alkenes

John F Hartwig, jhartwig@berkeley.edu. Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720-1460, United States

Our group has developed a series of catalytic additions to alkenes and has identified complexes that react with alkenes by insertion into metal-oxygen and metal-nitrogen bonds. This lecture will include recent results on catalytic additions of N-H, O-H and C-H bonds to alkenes, along with mechanistic data to explain the rates and selectivities of these reactions. Information on isolated complexes, catalyst resting states, and kinetic behavior will be presented.

INOR 131

Reactivity of the coinage metals beyond electrophilic activation of n systems

Didier Bourissou, dbouriss@chimie.ups-tlse.fr, Abderraoumane Amgoune, Maximilian Joost. Laboratoire Hétérochimie Fondamentale et Appliquée, Paul Sabatier University, Toulouse, France

Recently, we have launched a research program aimed at exploring the behavior of the coinage metals, in particular copper and gold. These metals have found widespread applications in synthesis, and it is highly desirable to gain better knowledge on their intrinsic properties.

In this context, we became interested in the coordination and activation of σ-bonds, fundamental processes with very little, if any, precedent with the coinage metals. Chelating assistance proved particularly efficient in that area, in order to position the σ bond near the metal and to stabilize the ensuing oxidative addition product. Intermolecular variants of σ-bond activation at gold have also been studied. This presentation will summarize our recent results in this area, as well as the migratory insertion of alkenes at gold.

References


INOR 132

Fixing nitrogen with iron complexes

Jonas C Peters, jtpeters@caltech.edu, John S Anderson, John Rittle, Sidney E Creutz.Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States
Nitrogen reduction to NH₃ is a requisite transformation for life. While it is widely appreciated that the Fe-rich cofactors of nitrogenase enzymes facilitate this transformation, how they do so remains poorly understood. A central element of debate has been the site(s) of dinitrogen coordination and reduction in these cofactors. As Fe is the only transition metal essential to all nitrogenases, preparing functional nitrogen reduction catalysts that feature iron has been a longstanding goal. In this talk I will discuss our lab’s most recent efforts directed towards the preparation of nitrogen-fixing Fe complexes.

INOR 133
Redox non-innocent nacnac and pyridine-imine chelate complexes of first row metals
Peter T Wolczanski¹, ptw2@cornell.edu, Valerie A Williams¹, Wesley D Morris¹, Brian M Lindley¹, Brian P Jacobs¹, Thomas R Cundari², Karsten Meyer³. (1) Department of Chemistry & Chemical Biology, Cornell University, Ithaca, New York 14853, United States (2) Department of Chemistry, University of Erlangen-Nuremberg, Erlangen, Germany

Nacnac and pyridine-imine based chelate complexes of iron and other first row metals possess the characteristics of redox non-innocent (RNI) species. The impact of RNI on the physical properties and reactivity of these species will be reported, and structural studies that buttress the RNI nature of the ligands will be presented.

INOR 134
Design of new ancillary ligands with nitrogen and phosphorus donors
Michael D. Fryzuk, fryzuk@chem.ubc.ca, Truman C. Wambach, Fraser Pick, Tatsuya Suzuki, Department of Chemistry, The University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

We have been investigating multidentate ancillary ligands that incorporate amido and phosphine type donors with a variety of linkers. Previous efforts have included CH₃SiMe₃ and o-phenylene type linking units. In an effort to simply this, we have examined (i) phosphine imines, prepared by deprotonation of ketooimines and subsequent reaction of chlorophosphine reagents, and (ii) phosphinimine imines, prepared by reaction of the aforementioned phosphine imines with aryl azides. With respect to our efforts with phosphine imines, we have examined tridentate and bidentate versions aimed at exploring simpler approaches to cooperativity effects in homogeneous catalysis. In the phosphinimine project, we are trying to mimic diketiminates as ancillary ligands. The coordination chemistry of these related ligand systems will be presented.

INOR 135
Remarkable properties of LiCB₁₁Me₁₂
Matibur Zamadar¹, Jiří Kaleta², Victoria Volks³, Keith Whitener³, Christos Douvris³, Josef Michl², michl@eeus.colorado.edu. (1) Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215, United States (2) Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Anhydrous LiCB₁₁Me₁₂ is readily accessible from commercial Me₃NH[CB₁₁H₁₃]. It is very soluble in numerous solvents and many of the solutions are colloidal. Of particular interest are non-polar solvents of low dionicity, such as 1,2-dichloroethane, benzene, and toluene. Although solutions of the pure material show no catalytic activity, true solutions of its adducts Et₄PO.3LiCB₁₁Me₁₂ and (CH₃)₂SO.6LiCB₁₁Me₁₂ in these solvents serve as sources of catalytically active “half-naked” Li⁺ cations. The adducts can be viewed as “inverse” Werner complexes, composed of a central Lewis base surrounded with Lewis acidic ligands. They bind alkenes and activate them toward radical attack to such a degree that the otherwise unknown radical polymerization of isobutylene and similar alkenes becomes feasible. The resulting polymers have highly unusual strongly branched structure. One-electron oxidation of LiCB₁₁Me₁₂ yields the stable free radical CB₁₁Me₁₂⁺ which serves as an oxidant and as a donor of the methyl radical. In the latter function, it can initiate radical polymerization. Upon loss of a methyl radical, it forms the “borenium ylide” CB₁₁Me₁₁⁺. This species, which can also be produced in other ways, has a naked boron vertex and is a strong Lewis acid, capable of inducing cationic polymerization of isobutylene, abstracting halogens from organic halides, performing aromatic substitution, etc. It can be stored in the form of an iodonium ylide, formed by addition to Me₃SnI. As a radical it is very soluble in numerous solvents and many of the solutions are colloidal. Of particular interest are non-polar solvents of low dionicity, such as 1,2-dichloroethane, benzene, and toluene.

Work in Boulder was supported by the NSF and work in Prague by the IOCB.

INOR 136
Carborane anions as ligand substituents
Vincent Lavallo, vincent.lavallo@ucr.edu, Chemistry, University of California Riverside, Riverside, California 92521, United States

Ligand design is dominated by ubiquitous alkyl and aryl groups. Here we will discuss our efforts in constructing sophisticated ligand frameworks, containing one and two carba-closo-dodecaborane anions as R-groups. When complexed to transition metals and maingroup elements the tethered, but weakly coordinating, carborane anion substituents bring stability to element centers. Furthermore, thanks to the inherent charge of the ligands these complexes carry unusual charges (anionic, dianionic, zwitterionic, dizwitterionic) and are highly reactive. Particular emphasis will be placed on the development of carbene ligands.

INOR 137
Catalytic reactions involving main group substrates
Ian Manners, Ian.Manners@bristol.ac.uk, School of Chemistry, University of Bristol, Bristol, United Kingdom

Although metal-catalyzed reactions have played a profound role in organic synthesis, catalytic routes to main group molecules and materials are much less explored despite their considerable potential. In this talk the use of catalytic processes to dehydrogenate main group substrates such as amine- and phosphine-boranes and related species will be discussed. In addition to mechanistic details, unexpected discoveries such as metal-free hydrogen exchange reactions will be described.

INOR 138
Activation of small molecules by main group compounds
Felicitas Lips, Philip P Power, ppower@ucdavis.edu, Department of Chemistry, University of California, Davis, CA 95616, United States
The activation of small molecules such as H-H, NH₃, CH₄, olefins, isocyanides or CO by main group compounds will be the main theme of the presentation. In particular, recent results using the use of silylens to effect such activations as well as the mechanism and energetics of the reactions will be described.

INOR 139

Synthesis, modification, and characterization of oleic acid functionalized hematite nanoparticles

Munawar Khalifi, mnhkail@nmt.edu, Ning Liu, Robert L. Lee. (1) Chemistry, New Mexico Tech, Socorro, New Mexico 87801, United States (2) Petroleum Recovery Research Center, New Mexico Tech, Socorro, New Mexico 87801, United States

In this work, a study is used on the synthesis, modification and characterization of oleic acid-functionalized hematite nanoparticles are presented. One step hydrothermal method is used to synthesize the uniform polyhedron hematite nanoparticles with diameter 80-100 nm (confirmed by XRD, HRTEM and Raman spectroscopy) and oleic acid is used as surface chemistry modifier. Based on the result, it is shown that oleic acid can be used to modify the surface chemistry of the particle and improve its oil wettability. FTIR spectra showed that the binding mechanism between hematite nanoparticle surface and the oleic acid is believed to occur by forming monodentate interaction between COO- group of oleic acid and iron atom which only occur in the surface of hematite nanoparticle without disrupting its crystalline structure (confirmed by XRD analysis). This is proven by calculated wave number separation (Δν) between asymmetric ν（COO-） and symmetric ν(=COCO) peaks after modification which associated to the corresponding interaction. In addition, the modification is also found to be increasing the contact angle of the thin film of hematite nanoparticle significantly from 26.05° to 141° making the particle to strongly have hydrophobic properties.

INOR 140

Inkjet-printed gold nanoparticle alignment layers: A novel approach for the patterned alignment of nematic liquid crystals

Torsten Hegmann, thegmann@kent.edu, Mitya Reznikov, Anshul Sharma. Chemical Physics Interdisciplinary Program, Kent State University, Kent, OH 44242, United States

Liquid crystal (LC) alignment layers commonly feature some type of anisotropy that induces a preferred orientation of the LC director on the surface. Unidirectionally rubbed polyimides are the most widely used [1]. Photoalignment and obliquely evaporated inorganic materials are alternative techniques that are utilized as well [2]. Although these processes have demonstrated robustness and have been implemented in large-scale production environments, they often require several fabrication steps, high processing temperatures, and sometimes, high vacuum environment.

We demonstrated that doping nematic LCs with a small quantity of thiolate capped gold nanoparticles (NPs) can lead to the induction of homeotropic alignment [3]. A similar effect is achieved if NPs are deposited onto the surface before preparing sandwiched LC films between conductive ITO-on-glass substrates. This leads to a uniform coverage of the surface with the NPs and, in turn, uniform vertical alignment of the LC over the entire area. The homeotropic anchoring of the LC molecules on the NPs is accompanied by a contrast inversion effect, i.e. under the action of a low-frequency electric field, Δε > 0 LCs effectively acts as Δε < 0 LCs and undergo a transition from the homeotropic to the planar state.

To demonstrate the next level of control over NP-induced LC alignment, we established the use ink-jet printing of gold NPs to obtain full coverage as well as patterned alignment of nematic LCs as a quick, simple, highly versatile, and adaptable LC alignment technique. Striking features of the ink-jet printing process are the variable NP density, the NP size, and the ease of forming full thin films of hematite nanoparticle substrates. This allows for facile patterning and indicates the possibility of fabricating LC devices.

INOR 141

Graphene nanoribbons: A versatile material for modern technology

Abdul-Rahman O. Raji, abdurraj@rice.edu. Department of Chemistry, Rice University, Houston, Texas 77030, United States

Graphene nanoribbons (GNRs) are hereby demonstrated as a versatile material for a variety of applications. GNRs are conductive narrow strips of graphene that are synthesized by intercalating and unzipping multivalled carbon nanotubes (MWCNTs) with sodium-potassium alloy (NaK) in the solution phase. By selectively modifying the GNRs at the edges with organic functional groups, bulk organo-soluble GNRs are obtained without losing electrical conductivity. As much as 1 mg/mL GNRs are dispersed in ortho-dichlorobenzene. This has enabled scalable, robust, flexible and electrically conductive composite thin films to be spray-coated on flexible polymer substrates. As transparent conductive films, GNRs have a low transmission loss of <0.5 dB at 2.4 to 3.8 GHz for a 75 nm thick film; and they are transparent to radiofrequency (RF) waves because the film's thicknesses are much smaller than their electromagnetic wave depth or “skin depth”. This is due to GNRs ability to easily form random electrically percolating networks. Consequently, GNR films serve as an RF transparent heating layers for a variety of applications. As energy storage material components, GNRs maintain interface with high energy storage materials to produce hybrid materials with high electrical conductivity, connection and stability. In a hybrid li-ion battery electrode material made of GNRs and transition metal oxide nanoparticles, the internal resistance of the lithium-ion cells is significantly lowered and the high capacities, >900 mAh/g, are retained over several cycles. As a catalyst material, Ag-GNR composite exhibit earlier onset of potential and higher current than commercial Ag-carbon hybrid for oxygen reduction reaction. The Ag-GNR hybrid is also tolerant to CH₃OH crossover, much better than the commercial benchmark, 20% Pt/C. With these enhanced performance in various applications, GNRs emerge as a viable and functional material for modern technological needs.

INOR 142

Thermochemical measurements of cation exchange reactions in colloidal nanocrystals

Brandon J Beberwyck1,2, bbeberwyck@berkeley.edu, Paul Alivisatos1,2. (1) University of California Berkeley, Berkeley, California 94720, United States (2) Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

The development of nanomaterials for next generation photonic, optoelectronic, and catalytic applications requires a robust synthetic toolkit for systematically tuning composition, phase, and morphology at nanometer length scales. While de novo synthetic methods for preparing nanomaterials from molecular precursors have advanced considerably in recent years, cation exchange reactions, in which cations ligated within a nanocrystal host lattice are substituted with those in solution, have emerged as particularly powerful tools for fine-grained control over nanocrystal composition and
Synthesis of binary and ternary core/shell of superparamagnetic nanoparticles and their property improvements from thermal annealing

Michael P Rowe, michael.rowe@tema.toyota.com, Sean Sullivan, Benjamin Lorenzetti.Toyota Research Institute of North America, Ann Arbor, MI 48105, United States

Soft magnetic materials are used in within transformers and inductors throughout the power electronics found in every hybrid drive automobile. Transformer and inductor components are based on the design of a soft magnetic core, with copper windings surrounding it. This soft magnetic core serves to allow an increased magnetic flux to operate within the device. Losses in this system (electrical component inefficiencies) can be described as a combination of hysteresis loss and eddy current loss. It was hypothesized that synthesis of nanocomposites of complex binary and ternary superparamagnetic nanoparticles could result in the control of macroscopic power electronic component inefficiencies through nanometer level adjustments to the material. Reported here are the synthesizes of FeCoSiO and FeCoVSiO core/shell nanoparticles and their characterization. XRD, TEM, and SEM-EDS analysis are all consistent with the binary and ternary magnetic system formations. Post-synthesis processing investigation was conducted to maximize the potential of these superparamagnetic core/shell nanoparticle systems through thermal annealing. The magnetic saturation could be increased by over 100% (exceeding 105 emu/g) through proper thermal annealing conditions, while maintaining their superparamagnetic quality. Studies of both the rapid thermal annealing of low-thermal-mass samples heated in excess of 80 °C/sec by an IR oven and the slow thermal annealing conducted over hours were conducted. Local maximum in the optimum magnetic properties as annealing condition severity increased were become apparent (appear shown here), and interpreted as the initial optimization of the nanoparticle crystal structure. Degradation of magnetic saturation and superparamagnetism at high-enough and long-enough annealing temperatures was attributed to growth of nanoparticles through aggregation as indicated by the increase of magnetic coercivity to a non-zero value.

New chemical synthesis of discrete MnBi hard magnetic nanoparticles

Michael P Rowe, michael.rowe@tema.toyota.com, Daniel Herrera. Toyota Research Institute of North America, Ann Arbor, Michigan 48105, United States

High coercivity permanent magnets are critical to modern technology, from automobiles to cell phones. Conventional strong magnets are reliant on rare earth elements such as neodymium, dysprosium, or samarium. Magnets containing these elements are plagued by problems of high costs and geopolitically volatile supply chains (US Department of Energy 2011 Critical Materials Strategy report). A means of directly addressing these issues is to use alternative magnetic material. It has been predicted by Suzuki et al. (J. Appl. Phys. 111, 07E303, 2012) and others, that the low temperature phase (LTP) of MnBi will form a hard magnetic material with a coercivity that competes with conventional strong permanent magnets, when the grain size has been reduced to 7nm diameter. To date, LTP MnBi has been produced through physical means of rotating furnace, melt spinning, or layer-by-layer deposition. All of these methods suffer from either very large grain sizes showing low coercivity (well above the nanometer scale) or the MnBi nanoparticles are sequestered in a Bi or Mn matrix of some sort (precluding them from further use as discrete units in more complex nanocomposite systems). Here we present the first direct synthesis of discrete MnBi nanoparticles via a synthetic chemical route. Through means of a manganese-complex and in situ reduction of bismuth cations, in the presence of a ligand. MnBi nanoparticles have been produced in gram-quantities. Nanoparticle diameters ranging in size from 30nm down to 5nm, as characterized by XRD and TEM analysis, are reported. The M(H) curve of a MnBi nanoparticle sample (shown here) as evolved through thermal annealing over-time to enhance the hard magnetic properties, with a maximum realized coercivity of 12Koer for these discrete nanoparticles.

Optical temperature detection inside mesoporous silica nanoparticles with superparamagnetic nanoheaters

Juyao Dong, jdong@chem.ucla.edu, Jeffrey I. Zink. Department of Chemistry and Biochemistry, UCLA, Los Angeles, California 90095, United States

To quantify the temperature increase induced by superparamagnetic nanocrystals under an oscillating magnetic field, a nano crystalline optical nanothermometer has been developed based on the up-conversion fluorescence spectra of NaYF₅:Yb³⁺, Er⁵⁺. Both a nanoheater and nanothermometer are imbedded in a 100 nm mesoporous silica nanoparticle to monitor the nanoparticle temperature change. The magnetically induced heating is examined under different experimental conditions, including the induction power, the exposure time to the magnetic field, and the magnetic nanocrystal size. The nanoparticle temperature demonstrates a more dramatic increase than that of the bulk solution during the oscillating magnetic field exposure, and the temperature evolution after the exposure rapidly equilibrates to that of the bulk surrounding. The method offers new insight into the nano environment temperature change and opens a path for optimizing local temperature for physical and biomedical applications.

Multifunctional silica-based nanomaterials for biomedical applications: Photodynamic therapy and pancreatic cancer treatment

Juan L. Vivero-Escoto, jviveroe@unc.edu. Department of Chemistry, University of North Carolina at Charlotte, Charlotte, NC 28223, United States

Silica-based nanomaterials have attracted much research attention for their potential application in the fields of engineering, chemistry, solid state physics, biotechnology, and biomedicine. Interestingly, in contrast to many other materials, silica nanoparticles do not acquire any special property from their sub-micrometre size, except for the corresponding increase in surface area. What makes silica nanoparticles fascinating from a nanotechnology point of view is their well-defined and tunable structures, and surface chemistry. By introducing new functional groups via well-established siloxane chemistry, it is possible to modify the silica surface to impart new properties to the particles, such as diagnostic and therapeutic capabilities. In addition, silica nanoparticles are inexpensive, easy to prepare, chemically inert, biocompatible, and water dispersible. There are three major types of silica-based platforms: solid silica nanoparticles (SiNPs), mesoporous silica nanoparticles (MSNs), and polylysosioxane nanoparticles (PSiO NPS). Our group is taken advantage of the outstanding structural, chemical and biological features of silica-based platforms to develop novel multifunctional nanomaterials for biomedical applications. In this work, we will present recent achievements in the design, synthesis and application of silica-based nanomaterials for
photodynamic therapy and pancreatic cancer treatment. We have demonstrated that the PDT response can be improved by developing photosensitizer (PS)-grafted SINPs that are degraded upon intracellular conditions found in cancer cells. In addition, we have synthesized PSIQ NPs that show a large amount of PS loading (>50% wt.), tunable degradability and improved PDT effect. Finally, by designing a target-specific multifunctional MSN material that carries cisplatin and gemcitabine pro-drugs and is functionalized with MUC1-antibody, we envision that some of the drawbacks for pancreatic cancer treatment can be overcome.

**INOR 147**

**Synthesis, X-ray opacity, and biological compatibility of elemental bismuth nanoparticle X-ray contrast agents**

*Andrea M Goforth*, agoforth@pdx.edu, Anna L Brown1, David P Cormode2, Prapat C. Naha2. (1) Chemistry, Portland State University, Portland, OR 97201, United States (2) Radiology, University of Pennsylvania Perelman School of Medicine, Philadelphia, PA 19104, United States

We set out to achieve a scalable, in quantity, and controllable, in size and morphology, synthesis for elemental bismuth nanoparticles (Bi NPs) that employs biologically benign reagents and results in large (> 50 nm diameter), highly X-ray opaque, aqueous Bi NP colloids. Herein, we report the gram scale synthesis of large, uniform (74 ±14 nm), hydrophilic Bi NPs from bismuth(III) nitrate that uses glucose as a biocompatible, small molecule surfactant, morpholine borane as a reducing agent, and biocompatible 1,2-propanediol as a reaction solvent. We demonstrate the high clinical X-ray opacity of these particles in quantitative X-ray Computed Tomography (CT) imaging studies, using anatomically representative (body) phantoms and cellular hosts. We furthermore show retained cell viability upon short exposures (1 hour) of Bi NPs to both HeLa and macrophage cell lines.

**INOR 148**

**Peapod nanocomposites: Forming organized nanoparticle chains within scrolled nanosheets**

*Shiva Adiredy1, Cecilie Carbo1, Taha Rostamzadeh1, Treva Brown1, Jose M. Vargas2, Leonard Spinu2, John B Wiley1, jwiley@uno.edu. (1) Department of Chemistry and Advanced Materials Research Institute, University of New Orleans, New Orleans, LA 70148, United States (2) Department of Physics and Advanced Materials Research Institute, University of New Orleans, New Orleans, LA 70148, United States

Methods for the bulk production of peapod nanocomposites have been developed where the scrolling of niobate nanosheets can be directed to capture preformed nanoparticles. This approach leads to a variety of peapod compositions including those with metals, metal oxides, and quantum dots. Additional post-processing steps are effective for gold insertion, leading to bifunctional nanopeapod structures. Details on the synthesis and characterization of these materials will be presented and the influence of the 1-D structures highlighted in terms of optical and magnetic effects. Further, suggestions on the mechanism for nanoparticle capture will be presented.

**INOR 149**

**IONiC/VIPEr workshops: Back to grad school**

*Benny C Chan1, chan@tcnj.edu, Carrie R Spray2, carrie.read.spray@enc.edu, Sheila R Smith3, sheilars@umich.edu. (1) Department of Chemistry, The College of New Jersey, Ewing, NJ 08628, United States (2) Department of Chemistry, Eastern Nazarene College, Quincy, MA 02170, United States (3) Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, MI 48128, United States

This past summer, the second IONiC/VIPEr back to grad school (B2GS) workshop was held at Penn State University. The week-long workshop was built around the theme of “Solid State Materials for Alternative Energy Needs”. This workshop brought together 30 participants ranging from graduate students to full professors from both PhD granting and predominantly undergraduate institutions. Three experts in solid state chemistry presented talks on their current research as the focal points of this workshop. Participants and speakers then spent time producing learning objects (LOs) based on the talks. Over 30 new LOs were prepared and published on VIPEr as a result of this workshop, and these are now making their way into inorganic classrooms around the country. The benefits of attending this workshop are presented by two participants and one member of the IONiC leadership council. The next B2GS workshop will be in the summer of 2014. The title is “VIPEr: Bioorganic Applications of Coordination Chemistry” and the workshop will be held at Northwestern University.

**INOR 150**

**Ride the snake: The online, inorganic community of IONiC/VIPEr**

*Chip Nataro1, nataroc@lafayette.edu, Sheila R Smith2, sheilars@umich.edu, Sibrina N Collins2, Hilary J Eppley2, Margaret J Geselbracht2, Elizabeth Jameson2, Adam R Johnson2, Barbara A Reisner2, Joanne L Stewart2, Pratap C. Naha1, Treva Brown1, Jose M. Vargas1. (1) Chemistry, Portland State University, Portland, OR 97201, United States (2) Department of Chemistry, Lafayette College, Easton, PA 18042, United States (3) Department of Chemistry, Earlham College, Richmond, IN 47374, United States

IONiC’s flagship event is the annual workshop that has long been supported by the Chicago-based educator, Dr. Mark Brackley. This workshop is directed to capture the experience of the IONiC members and directed to capture the experience of the IONiC leadership. The long workshop was built around the theme of “Solid State Materials for Alternative Energy Needs”. This workshop brought together 30 participants ranging from graduate students to full professors from both PhD granting and predominantly undergraduate institutions. Three experts in solid state chemistry presented talks on their current research as the focal points of this workshop. Participants and speakers then spent time producing learning objects (LOs) based on the talks. Over 30 new LOs were prepared and published on VIPEr as a result of this workshop, and these are now making their way into inorganic classrooms around the country. The benefits of attending this workshop are presented by two participants and one member of the IONiC leadership council. The next B2GS workshop will be in the summer of 2014. The title is “VIPEr: Bioorganic Applications of Coordination Chemistry” and the workshop will be held at Northwestern University.

**INOR 151**

**Isolating and characterizing mixed disulfide intermediate of mutant Sco and Cu4 from Thermus thermophilus**

*Ellen Wadler, ewadler@trinity.edu, Laura Hunsicker-Wang. Department of Chemistry, Trinity University, San Antonio, TX 78212, United States

The Cu4 is a protein domain II of cytochrome c oxidase and contains the Cu4 site, a dinuclear copper metal binding site. Sco is a protein family necessary for the correct assembly of Cu4. Previous work has shown that Thermus thermophilus Sco (TSc) appears to reduce the disulfide bond found in oxidized Thermus thermophilus Cu4 (TSc4). This reduction is necessary since oxidized TSc4 cannot bind metal. The proposed mechanism for how TSc4 is reduced by TSc is the formation of an intermolecular disulfide bond between Cysteine 49 on Sco and Cysteine 153 on Cu4, creating a mixed disulfide intermediate (MDI). The isolation and characterization of the MDI is possible when TSc and TSc4 are mutated to remove one cysteine. A label is conjugated to TSc and is released by the attack of TSc. The rate at which the mixed disulfide intermediates formed as well as the total amount of MDI formed is increased when the ration of TSc Cysteine 49 to TSc Cysteine 153 is increased from 1:1 to 1:5:1. In order to isolate the mixed disulfide intermediates, size exclusion and Ni2+-affinity chromatography are utilized. To better understand why it is TSc Cysteine 49
that forms the disulfide bonds with TiCu. Sco mutants C53S/R48A and C53S/R48D were utilized to examine the role of Arg 48. The rate and extent of MDI formed are then compared to TiSco Cysteine 49 without the arginine mutants.

**INOR 152**

Electron withdrawing capability of ligating histidine adducts influence the reduction potential of the [2Fe-2S] cluster of the Rieske protein

Christopher Hertz, chertz2@trinity.edu, Nicholas Karagas, Laura M. Hunsicker-Wang.Department of Chemistry, Trinity University, San Antonio, TX 78212, United States

The Rieske protein is an electron transport protein found in the bc-complex that contains a [2Fe-2S] cluster ligated by two cysteines and two histidines. The Thermus thermophilus Rieske protein was probed by mutating and chemically modifying the protein. Different chemical modifiers which result in adducts of the ligating histidines that vary in electron withdrawing capabilities have been explored. Previous studies showed that diethyl pyrocarbonate (DEPC) both modifies and reduces the cluster in a pH dependent manner, likely due to the electron withdrawing properties of the adduct. A second modifier, methyl bromoacetate (MBA), modifies the histidines leaving an adduct that is less electron withdrawing. The wild type and several mutant proteins that alter the reduction potential of the cluster all react with MBA. These proteins react in a pH dependent manner like DEPC, but modification with MBA does not result in reduction of the cluster. New modifiers, which can systematically be altered to have varying electron withdrawing capabilities, are also being explored. These data taken together, indicate that the reduction potential of the [2Fe-2S] cluster can be altered by having adducts on the histidine ligands of varying electron withdrawing capabilities. This finding is important as it points to a way that the interaction between the Rieske protein and its substrate in the bc-complex might influence how the electron transfer might occur.

**INOR 153**

Probing the factors that affect the reduction potential of the Thermus thermophilus Rieske protein: L135A mutation

Mathew Ponthier, cpointie@trinity.edu, Laura M. Hunsicker-Wang.Department of Chemistry, Trinity University, San Antonio, TX 78212, United States

The Rieske protein is an electron transport protein found in the bc-complex (complex III) of the electron transport chain. It contains a [2Fe-2S] cluster ligated by two histidines and two cysteines. The cluster's reduction potential is pH dependent and varies greatly among species. The factors that have been postulated to tune the reduction potential are the number of hydrogen bonds to, the proximity of charged residues to, and the solvent accessibility of the [2Fe-2S] cluster and its ligating histidines. L135A was created to make the ligating histidines more solvent accessible, however, reduction potential measurements for analogous mutants of L135A in other species observed a negative change in reduction potential. In order to understand the structural reasons for the change in potential, L135A has been crystallized and data collected to 2.1 Å. Refinement of the structure is now complete. Through this and other crystallographic studies it appears that the disulfide bond present in the protein is elongated which would ultimately make the [2Fe-2S] cluster more solvent accessible and lower the potential. To test if the disulfide bond is indeed weaker in this mutant, a study using 5,5'-dithiobis-(2-nitrobenzoic acid) (DTNB) was conducted to quantify how much free thiol is present in this protein compared to the wild type.

**INOR 154**

Characterization of the H134C mutant of the Thermus thermophilus Rieske protein

Victor Rodriguez, vrodrig2@trinity.edu, Nathan Webber, nwebber@trinity.edu, Laura M. Hunsicker-Wang.Department of Chemistry, Trinity University, San Antonio, TX 78212, United States

The Rieske protein is found in the bc-complex of the electron transport chain, playing an important role in transporting electrons and protons. It contains a [2Fe-2S] cluster ligated by two cysteines and two histidines. The reduction potential of this cluster is pH-dependent and varies across species. The H134C mutant of the Thermus thermophilus Rieske protein substitutes one of the ligating histidines for a cysteine, changing the ligation structure of the cluster from a 2Cys-2His ligation environment to a 3Cys-1His environment. To study the effects of this mutation, the protein was subjected to modification with diethyl pyrocarbonate (DEPC) at varying pH values. The behavior of this protein was observed and compared to a truncated form of the wild type protein through circular dichroism and UV-visible spectroscopy. DEPC modification was observed in both wild type and H134C protein. H134C was also subjected to β-Mercaptoethanol and thiazolidinedione, which showed minimal change over time. In contrast, wild type Rieske showed lots of spectral change when exposed to β-Mercaptoethanol. Because of the similarity in the iron-sulfur cluster ligands, H134C was also compared to another mitochondrial protein, mitoNEET, which contains a 3Cys1His environment and has been classified as a diabetes drug activator. MitoNEET has been previously shown to be unstable at lower pH values, in contrast to H134C, which is stable at both low and high pH. By comparing what is similar and what is different in the pH and chemical reactivity of H134C and MitoNEET, we can decipher what are common characteristics of the 3Cys-1His environment and what are unique properties of the different proteins.

**INOR 155**

Creation and characterization of 4-His/3-carboxylate DFSC proteins

Kristen Biernat, krbiernat@ursinus.edu, Amanda Reig, Department of Chemistry, Ursinus College, Collegeville, PA 19426, United States

Binuclear non-heme enzymes are a class of proteins that contain one or more bridging carboxylate, terminal carboxylate, and/or histidine residues within a four-helix bundle. Despite their structural similarities, they catalyze a diverse set of chemical reactions, ranging from peroxidation to N-oxygenation. It is clear that His/Carboxylate ratio affects enzyme function, but the geometric and electronic effects of the residues, including ligand orientation, charge, and redox potential, remain unknown.

In order to better understand these effects on enzyme function, the active site of a de novo designed di-iron carboxylate protein, which was previously reprogrammed to mimic the reactivity of p-aminobenzoate N-oxygenase (AurF), was modified. Specifically, one of the four carboxylate residues in the 4-His/4-Carboxylate active site was changed to a histidine to give a 4-His/3-Carboxylate active site. This change will allow for the geometric and electronic effects from coordinating a neutral nitrogen atom to an iron atom instead of a negatively charged oxygen atom to be investigated. Of the four carboxylate residues in the active site, two are terminal carboxylates. Each of these carboxylates is coordinated only once to an iron atom, so replacement of either residue with a histidine is a viable approach for creating the 4-His/3-Carboxylate protein. Two single mutations, E11H and E44H (Glu→His), that correspond to the terminal carboxylate positions of interest were introduced into the 3-His-G4DFsc protein by site-directed mutagenesis, and the proteins were expressed and HPLC-purified. The metal binding properties and aerobic ferroxidase activity of the E44H-G4DFsc and E11H-G4DFsc proteins were analyzed using UV-visible spectroscopy. Protein folding in the presence and absence of metal ions was also investigated by fluorescence spectroscopy and circular dichroism.

**INOR 156**

Creation of rubrerythrin and symerythrin model proteins

Rachel Z Polinski, rapolinski@ursinus.edu, Jenna Pellegrino, jepellegrino@ursinus.edu, Sabrina N Cimerol, Amanda J Reig, Department of Chemistry, Ursinus College, Collegeville, PA 19426, United States

Diron carboxylate enzymes are a class of metalloproteins responsible for numerous reactions in cells such as fatty-acid desaturation and radical generation. The goal of this research is to understand the importance of the active site structure in controlling the function of the diiron proteins rubrerythrin and symerythrin. In contrast to the more well-studied diron carboxylate proteins that contain two histidine and four carboxylate residues in
their active sites, ruberythrin and symerythrin have one and two additional carboxylate residues, respectively. Starting from a de novo designed four-helix bundle protein created to mimic the 2-His/4-carboxylate diiron enzymes, we have successfully produced and purified ruberythrin models that include an extra active site carboxylate residue, either aspartate (G14D) or glutamate (G14E). The oxygen and hydrogen peroxide reactivity of these model systems have been investigated. In addition, symerythrin model proteins that include a second additional carboxylate residue in the active site, either aspartate (G47D) or glutamate (G47E), have been produced and purified. Metal binding, protein folding, and reactivity studies of these proteins suggest that they are excellent structural and spectroscopic models of the natural enzymes. Ultimately, these studies will give us a better understanding of how systematic changes to structural features of a protein affect its functionality.

INOR 157

Correlation of ligand substitution pattern and solid state topography: The design of novel arylcalciumphosphonates for bone therapeutic applications
Matthew D Lijewski, mljewski@syr.edu, Valerie Lopez, Karin Ruhlandt. Chemistry, Syracuse University, Syracuse, New York 13210, United States

The quest for bioactive and biocompatible materials for bone therapy is of growing importance, as currently used materials display significant limitations. Our work is utilizing bisphosphonates, a chemical entity used in common drugs to treat bone disorders, to prepare biocompatible and bioactive materials. This work will allow for the design of materials with a defined dimensionality and surface area to interact favorably with the bone tissue. This poster will outline the effect of ligand topology on the overall geometry of the resulting materials.

INOR 158

Kinetics of hemin self-association in aqueous solution
Kyle Michael Conner, kyle.conner@ndsu.edu, Kenton R. Rodgers. Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota 58108-6050, United States

Heme or hemin (iron(II) protoporphyrinate IX or iron(III) protoporphyrinate IX, respectively) is the iron-containing cofactor for many proteins and enzymes. Heme proteins exhibit a wide variety of biological functions and are ubiquitous throughout Archaea, Bacteria and Eukaryotes. Interestingly, free heme is rather cytotoxic due to its roles in the production of reactive oxygen species. Consequently, the concentration of aqueous heme and hemin (i.e. not specifically bound to a protein) in cells is tightly controlled by heme-binding proteins and enzymes. Thus, the thermodynamic and kinetic stabilities of hemin-protein complexes are important in understanding their functions and their roles in heme homeostasis. In order to determine hemin-protein stabilities, either by equilibrium or kinetic methods, it is important to know the speciation of aqueous heme, as well as the rates at which the species interconvert. Hemin is well known to self-associate in aqueous solution. Thus, this kinetic study was undertaken to examine the dynamics of self-association in aqueous solutions of hemin. Rates of the relevant association and dissociation reactions were determined experimentally using UV-visible absorbance spectroscopy and stopped-flow spectrophotometry.


INOR 159

Mössbauer spectroscopic studies of the enzyme dehaloperoxidase from Amphitrite ornata
Codrina V Popescu1, cpopescu@ursinus.edu, Danielle Miller2, David A. Barrios2, Reza Ghiladi2. (1) Chemistry, Ursinus College, Collegeville, PA 19403, United States (2) Chemistry, North Carolina State University, Raleigh, NC 27695, United States

Dehaloperoxidase (DHP) from the marine worm Amphitrite ornata is a globin exhibiting significant peroxidase activity. The active site of this bifunctional enzyme is a heme center, which is coordinated by a histidine residue in the proximal position and exhibits an internal distal cavity. Purified recombinant 57Fe-DHP samples were studied with Mössbauer spectroscopy in order to obtain a characterization of the enzyme in the resting state and throughout its catalytic cycle. Chemical reduction with ascorbate yielded the oxy-ferrous state, which exhibits a Mössbauer spectrum typical of a low-spin Fe(II) heme, analogous to oxy-myoglobin. Different aspects of the Mössbauer spectra show similarities with myoglobin, but also with peroxidases. This study will ascertain the spin and oxidation states of the iron in the several catalytic states and will draw comparisons between DHP and other heme proteins, based on the Mössbauer spectroscopic data. DHP dehalogenates 2,4,6-tribromophenol, which, like other halophenols of various origins, is toxic. Thus, elucidation of the electronic structure and mechanism is of this peroxidase is of general interest for environmental remediation.

INOR 160

Investigation of mechanism of the heme enzyme chlorite dismutase from Klebsiella pneumoniae
Zachary Geeraerts1, zachary.geeraerts@my.ndsu.edu, Gudrun S. Lukat2, Kenton R. Rodgers1. (1) Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108, United States (2) Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, United States

Industrial use of oxochlorine species (ClO2) has led to high concentrations of perchlorate, chlorate, and chlorite as contaminants in the environment. Certain proteobacteria have evolved to survive under these conditions utilizing a perchlorate respiratory pathway. In this pathway perchlorate reductase catalyzes the reduction of perchlorate and chlorate to toxic chlorite. The last step in this pathway uses a heme enzyme called chlorite dismutase (Cld) to catalyze the decomposition of chlorite to chloride anion and molecular oxygen. This formation of ClO2 is toxic. Thus, elucidation of the electronic structure and mechanism is of this peroxidase is of general interest for environmental remediation.

INOR 161

Using bonding paradigms to investigate copper catalyzed oxidative damage
Sydney Dautel, dautels@seattleu.edu, Charity Plener Lovitt. Department of Chemistry, Seattle University, Seattle, WA 98122, United States

Copper is one of the most abundant transition metals in the human body and is essential for human life. However, many proteins with copper active sites are prone to aggregation and therefore prove difficult to study with in vitro techniques. Because of this, ab initio studies are providing valuable information about the structure, and therefore reactivity of these proteins, especially in the investigation of copper active site geometry. Copper can adopt a variety of geometries in the active site; subtle changes in geometry may cause changes in the reactivity and orbital energy. Some of these geometries may be more susceptible to production of hydroxyl radicals through Fenton-like chemistry. This study utilized several DFT methods to investigate ligand coordination and orbital alignments associated with these geometries. The relationship between the structure and orbital alignments was then studied to understand orbital influence on active site reactivity.
Kinetic and mechanistic studies on the reactions of the reactive oxygen species nitrosyl hydride with the phenolic antioxidants catechol and hydroquinone

Mary A Waddington, mwadding@kent.edu, Rohan S Dassanayake, Nicola E Brasch, Paul Sampson. Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44243, United States

Nitrosyl hydride (HNO/NO) is a reactive nitrogen species formed from the 1e reduction of NO by proteins such as superoxide dismutase and cytochrome c. HNO has a distinctly separate biological and chemical reactivity from NO. While in vivo generation of HNO has not been indisputably verified, recently others have shown the potential of HNO prodrugs in treating cardiovascular disease, and in preventing ischemia/reperfusion injury and congestive heart failure. Therefore, understanding the chemical reactivity of HNO is of considerable importance.

This study investigates the kinetics and mechanism of the reaction between nitrosyl hydride and two phenolic antioxidant compounds: catechol and hydroquinone. Hydroquinone and catechol have significant biological relevance as the main structural units in vitamin K and catecholamine neurotransmitters, respectively. Antioxidants are found in many delectable foods like fruits, vegetables and wine and are known to readily oxidize.

INOR 163

Synthesis and characterization of novel zinc complexes as models for hydrolases

Mayra A Pedraza, map.x1999@gmail.com, Rebecca A Joy, Ghezal T Musie. Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas 78249, United States

In an attempt to develop synthetic models of Phosphohydrolase enzymes, noble mono- and dinuclear metal complexes utilizing a highly versatile ligand, N,N-Bis[2-carboxybenzylmethyl]-N,N-Bis(carboxymethyl)-1,3-diaminopropan-2-ol, and various metal ions (Zn^{2+}, Cu^{2+}, Ni^{2+}) have been synthesized. The complexes have been fully characterized using spectroscopic and crystallographic techniques. The ligand, H_{2}ccdp, had provided a unique synthetic opportunity to either selectively tether an intramolecular H-bonding network or incorporate a second metal ion into its coordination cavity. In this presentation, the synthesis and characterization of these novel complexes will be discussed.

INOR 164

Azadipyromethene dyes and their Zn(II) complexes as red absorbing electron acceptors for organic solar cells: Effect of ethynylthiophene substitution at the distal phenyls

Cassie Daddario, cmd42@case.edu, Qi Han, Zhenghao Mao, Genevieve Sauve. Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106, United States

Azadipyromethene (ADP) dyes are being optimized for use as a non-fullerene acceptor for organic solar cells. The most common acceptor used, phenyl-C61-butyric acid methyl ester (PCBM), has limitations because it does not absorb efficiently in the visible and NIR region of the solar spectra and its energy levels are not easily manipulated. To address these issues, we are exploring using ADP dyes as acceptors. To tune absorption and energy levels, we installed ethynylthiophene groups at the distal phenyl rings of ADP. We further tuned this molecule by chelation with Zn(II), which gave λ_{Η\text{abs}}max at 678 nm and 613 nm, respectively. The Zn(II) complex also has a broader absorption in solution (∼425 nm – 775 nm) than ADP (∼460 nm – 650 nm), due to the larger conjugation resulting from the π-stacking interactions between the two ligands in the complex. The BF_{2} and Zn(II) complexes have a higher extinction coefficient (measured at 650 nm) of 4.0E4 M\(^{-1}\)cm\(^{-1}\) and 7.1E4 M\(^{-1}\)cm\(^{-1}\) than the unchelated material at 1.4E4 M\(^{-1}\)cm\(^{-1}\). PCBM has a much lower extinction coefficient (measured at 650 nm) of <1.0E3 M\(^{-1}\)cm\(^{-1}\). Based on these results, we believe these materials have potential as acceptors in solar cells due to their high light harvesting ability. Preliminary results for the Zn(II) complex give a PCE of 0.76%.

INOR 165

Ionothermal synthesis and characterization of [EMIM]([Cr(P(3)S)]2) (EMIM = 1-ethyl-3-methylimidazolium)

Grant C. B. Alexander\(^{1,2}\), alexagc@mx.lakeforest.edu, Catherine Guillot-Deudor\(^{2}\), Jason A. Cody\(^{1,2}\). (1) Department of Chemistry, Lake Forest College, Lake Forest, IL 60045, United States (2) Institut des Matéraux Jean Rouxel, Nantes, France

Single crystals of a novel chromium thiophosphate salt, [EMIM]([Cr(P(3)S)]2), were isolated after ionothermal synthesis from the elements in [EMIM]Cr(OC(2)S)\(_{5}\) (EMIM = 1-ethyl-3-methylimidazolium). The octahedral Cr atom is coordinated to the two tridentate P(3)S\(_{3}\) ligands previously seen only in the related EMIM salt [EMIM]([Ni(P(3)S)]2). In addition, tridentate sulfur-bound ligands coordinated to Cr atoms have not been reported to our knowledge, most known polydentate ligands bound to Cr atoms are bidentate and contain organic fragments. The synthesis of this new compound further reinforces the viability of ionothermal synthesis in the investigation of new transition metal compounds and demonstrates the broader versatility of the thiophosphate ligand system.

INOR 166

Selective formation of a hexaprismic carboxylato coordinated chromium(II) carbonylato carboxylic anhydride precursor

Julie L Fenton\(^{1,2}\), jlf1293@messiah.edu, Pierre Mobian\(^{1}\), Clément Chaumont\(^{1}\), Clarisse Huguenard\(^{1}\), Marc Henry\(^{1}\). (1) Laboratoire de Chimie Moléculaire de l’Etat Solide, Université de Strasbourg, Strasbourg, France (2) Department of Chemistry and Biochemistry, Messiah College, Mechanicsburg, PA 17055, United States

Among the many structurally characterized carboxylic acid chromium(II) alkoxydes, hexagonal species displaying the general formula [Ti(μ-2-O)(OR)]\(_{2}\)(μ-O-CR\(_{2}\))\(_{2}\) are one of the most recurrent reported structures in the literature. The synthesis and characterization of a specific complex, bearing the formula [Ti(μ-2-O)(OR)]\(_{2}\)(μ-O-C\(_{8}\)C\(_{3}\)H\(_{11}\)NOOCP)]\(_{2}\), from an asymmetric pyridine carboxylic anhydride precursor is described. Several methods of solid-state analysis of the formed complex, including single-crystal X-ray diffraction and CP-MAS NMR, indicate the presence of a single isomer among 13 possible species. Molecular Orbital energetic calculations provided evidence to support the observation of a highly selective formation mechanism leading to the final product.

INOR 167

Bimetallic catalysts supported by ionic porphyrins: Activity of cofacial porphyrin dimer towards CO\(_{2}\) reduction

Nabeel Chaudary, chaundarn@lafayette.edu, Lauren Cesanek, Roxy J L Swails, swailsr@lafayette.edu. Department of Chemistry, Lafayette College, Easton, PA 18042, United States

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The ionic porphyrins TPPS, TMPyP, and TMMAPP were synthesized and used in the formation of Ni\textsuperscript{II} and Fe\textsuperscript{III} complexes. Anionic M-TPPS and cationic M-TMPyP were used to form bimetallic cofacial porphyrin dimers in solution. Bimetallic dimer couples M-TPPS/M-TMPyP were investigated for electrocatalytic behavior towards carbon dioxide activation and reduction.

INOR 168
Improved synthesis of [Re(CO)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]Br and its derivatives
Gerard J Kerins\textsuperscript{1}, giken14@g.holycross.edu, Joshua R Farrell\textsuperscript{1}, Richard S. Herrick\textsuperscript{1}, Christopher J. Ziegler\textsuperscript{2}. (1) Chemistry, College of the Holy Cross, Worcester, MA 01610, United States (2) Chemistry, Department of Chemistry, Akron, Akron, OH 44325-3601, United States
Rhenium has been studied at length as a non-radioactive chemical analog to Technetium, a popular diagnostic imaging agent employed in nuclear medicine and biology. This study details a new synthetic method for preparing [Re(CO)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]Br as well as multiple derivatives of this complex using tridentate ligands. Full synthetic details and characterization will be presented.

INOR 169
Lanthanide luminescence with a new carbamoylmethylphosphine oxide ligand
Justin R Shady. heyshady09@gmail.com, Adam C Boyden, Shannon M Biros. Department of Chemistry, Grand Valley State University, Allendale, MI 49401, United States
Our lab is focused on the area of sensitizing lanthanide luminescence. This has been achieved with the synthesis of a new carbamoylmethylphosphine oxide (CMPO) ligand. This ligand has three aromatic groups, which we believe act as antennas in this system. Our CMPO ligand is successful at sensitizing terbium, europium, dysprosium, and samarium luminescence. The highest efficiency we observed was with the terbium complex. Analytical data has been taken of the complexes and will be presented.

INOR 170
Investigation of multidentate carbamoylmethylphosphine oxide compounds for lanthanide and actinide chelation
Julie A Stoscup. stoscupj@mail.gvsu.edu, Shannon M Biros. Department of Chemistry, Grand Valley State University, Allendale, MICHIGAN 49401, United States
Our lab is focused on the development of tripodal carbamoylmethylphosphine oxide (CMPO) ligands to complex with lanthanides and actinides. Our strategy takes advantage of the chelate effect, via CMPO ligand preorganization, to increase the selectivity for f elements. Applications of this research include, but are not limited to: the extraction of hazardous heavy metals to improve the remediation of nuclear waste, the enhancement of magnetic resonance imaging (MRI) abilities, the production of light-emitting diodes (LED) with increased lifetimes, and the exploration of heavy metal polymers.

INOR 171
Exploration of magnetic coupling through the dicyanamidobenzene anion bridge in dinuclear metal complexes
Charles M Culbertson. syli@iup.edu, Xuan Zhang, Kim R Dunbar. Department of Chemistry, Texas A&M University, College Station, TX 77843, United States
Molecular compounds that exhibit magnetic properties have been gaining considerable attention in the past few decades vis-à-vis their potential applications as magnetic storage units and quantum bits (or qubits) for quantum computing, which could vastly change the way information is stored and processed by miniaturizing the data storage units and processors.

Our research in this vein is focused on preparing small molecular magnets with divalent and trivalent metal species bridged by long pi-conjugated ligands to achieve strong magnetic coupling between the metal centers or even mixed valence systems owing to the non-innocent nature of the organocyanide ligands. Longer bridging ligands have been demonstrated to exhibit strong magnetic coupling which can prevent spin randomization (a prerequisite to forming room temperature magnets). By using longer bridging ligands, porosity could be achieved in coordination polymers in addition to their magnetic properties, allowing for synergistic effects of magnetic and host-guest interactions between the frameworks and small molecules.

To establish a simple dinuclear model for the magnetic studies, metal ions capped with neutral pentadentate ligands were selected which allow for only one available coordination site on the metal to react with the corresponding bridging ligands. Both 2,6-bis(1,1-bis(2-pyridyl)methyl)pyridine (PYSMe2) and 1,3bis(2-pyridyl)methyl)imidazole-2-ylidine (PY4Im) were synthesized by reported procedures and are being used in this study as capping ligands. Thus far, mononuclear metal complexes have been synthesized, and attempts to bridge them with meta-dicyanamidobenzene (DCYD) diamions are underway. To date, the reactivity between the bridging ligands and the metal complex has been demonstrated. Further efforts will be directed towards the syntheses of the dinuclear bridged model complexes and their characterization by cyclic voltammetry (CV), single crystal and powder X-ray diffraction (XRD), electron paramagnetic resonance (EPR) spectroscopy, and magnetometry using a superconducting quantum interference device (SQUID).

INOR 172
Photophysical properties of chromium tris-dilimine complexes that contain ligands with hydrogen bonding capability
Joshua R. Brooks\textsuperscript{1}. brooks.joshua@mcmurryadm.mcm.edu, Christina M. Barr\textsuperscript{1}, Edward G. Donnay\textsuperscript{1}. (1) Department of Chemistry and Biochemistry, McMurry University, Abilene, Texas 79697, United States (2) Department of Biology, McMurry University, Abilene, Texas 79697, United States
The photosensitizer is the key component in photodynamic therapy which is used to treat a variety of medical conditions including cancer. A substantial amount of research is focused on ruthenium compounds that require the generation of singlet oxygen to damage DNA. Chromium tris-dilimine complexes are known to be strong photo-oxidizing agents that can oxidize the guanine base of DNA directly. Diimine ligands that can hydrogen bond to the guanine base may increase the binding affinity of the chromium complexes to DNA, but the effects on the photochemistry have not been studied. The ligands 4,5-diazafuoren-9-one and substituted imidazo[4,5-f][1,10-phenanthrolines were used to synthesize chromium complexes which were analyzed by ultraviolet-visible spectroscopy, steady-state emission spectroscopy, and cyclic voltammetry. The effects of the addition of hydrogen bonding groups upon the photo-oxidizing power will be presented.

INOR 173
Effects of systematic variation of the N-aryl group of phosphinoamide ligands [ArNiP(Pr\textsubscript{3})] on the properties of the heterobimetallic Zr/Co complexes
Suwan Lee, daswan1118@gmail.com, Jonathan W Napoline, Christine Thomas. Chemistry, Brandeis University, Waltham, MA 02453, United States
Phosphinoamide ligands of the general form [ArNiP(Pr\textsubscript{3})] stabilize metal-metal interactions in C\textsubscript{5}-symmetric early/late heterobimetallic complexes. Systematic substitution of the N-aryl moiety on the tris(phosphinoamide) ligand framework affects the metal-metal interaction and reactivity of the reduced heterobimetallic complex (THF)\textsubscript{2}Zr[ArNiP(Pr\textsubscript{3})\textsubscript{2}]Co-N\textsubscript{2}. The synthesis of a series of Co/Zr complexes using different N-aryl substituents will be discussed, and a comparison of these complexes will provide a better idea of the impact of ligand electronic and steric effects on metal-metal interactions.
INOR 174

Synthesis and decarboxylation of new copper trifluoroacetate complexes for the trifluoromethylation of arenes
Alexandria Mullins, amullin5@mix.wvu.edu, Jessica M. Hoover. Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States

Trifluoromethyl substituted arenes are crucial structures in the pharmaceutical and agrochemical industries because they are key structures in many biologically active compounds. Current trifluoromethylation protocols require the use of excess amounts of expensive CF3 sources. Trifluoroacetic acid is an ideal source of the CF3 group due to its low cost and the generation of CO2 as the only byproduct. Decarboxylation typically requires harsh conditions and high temperatures, so developing milder decarboxylation conditions are necessary for a synthetically useful system. The synthesis and characterization of new copper trifluoromethylation complexes and their corresponding decarboxylation reactions will be presented.

INOR 175

Electrochemical determination of rhodium hydride aqueous hydricities
Olivia N. L. Finster1, finstero@grinnell.edu, Catherine L. Pitman2, Alexander J. M. Miller1. (1) Department of Chemistry, University of North Carolina - Chapel Hill, Chapel Hill, North Carolina 27599, United States (2) Department of Chemistry, Grinnell College, Grinnell, Iowa 50112, United States

A novel method to calculate aqueous hydridic values was developed. Hydridicity, the free energy of hydride donation, provides a quantitative handle for evaluating metal hydride catalysts, yet few values have been calculated in water. Aqueous hydridic values promise to facilitate catalyst design for reactions such as CO2 reduction and formic acid disproportionation, potentially renewable routes to methanol, which are carried out in water. In the absence of a reference complex with known hydridicity, hydridicity calculations require \( E_{\text{red}} \) and \( pK_a \), which were both determined using cyclic voltammetry. Our studies focused on \( \text{[Cu}^\text{II}(4,4'-\text{OMe}2\text{-bpy})\text{]}^+ \) (1) and \( \text{[Cu}^\text{II}(4,4'-\text{COOH}2\text{-bpy})\text{]}^+ \) (2), well-known hydrogenation catalysts. The electrochemical behavior is pH dependent: under acidic conditions, 1 and 2 are generated upon two-electron reduction of \( \text{[Cu}^\text{II}(4,4'\text{-X}2\text{-bpy})\text{]} (X = \text{OMe}, \text{COOH}) \), under basic conditions, on the other hand, \( \text{[Cu}^\text{II}(4,4'\text{-X}-\text{bpy})\text{]} \) is formed. The concentration of hydride formed was measured electrochemically as a function of pH, and the Henderson-Hasselbalch equation was used to obtain the pkA of hydrides 1 and 2. Based on the pkA and \( E_{\text{red}} \), the hydridicity of 1 is determined to be \( \Delta G_m = 35-36 \text{ kcal/mol} \), slightly more hydridic than 2 (\( \Delta G_m = 36-38 \text{ kcal/mol} \)).

INOR 176

Zerovalent group VI metal complexes of the anionic bidentate bis(diphenylphosphinomethyl)diphenylborate ligand
Laura Avena, lavena@macalester.edu, Grace K. Putka, Trent D. Bohrmann, Paul J. Fischer. Department of Chemistry, Macalester College, Saint Paul, Minnesota 55105, United States

This poster describes zerovalent group VI metal chemistry of the anionic bidentate phosphine bis(diphenylphosphinomethyl)diphenylborate. The enhanced donation afforded by this ligand relative to classic neutral bidentate phosphines promises to stabilize complexes containing auxiliary ligands that would normally be susceptible to facile dissociation or attack by nucleophiles. In particular this poster will describe attempts to synthesize group VI metal complexes containing sulfenes and beta-amino-substituted isocyanides, respectively. Synthetic details and single crystal X-ray crystallographic characterizations for the complexes isolated while in pursuit of these goals will be provided.

INOR 177

Measurement of the rate of activation constants (k_{act}) for (TREN-R) copper catalysts utilized in atom transfer radical addition reactions
Kieran Mullanrey, muliank2@tcnj.edu, Rajbhupinder Kaur1, Abby R. O'Connor1, Tomaslv Pintauer2. (1) Chemistry, The College of New Jersey, Ewing, NJ 08628, United States (2) Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, United States

Copper catalyzed atom transfer radical addition (ATRA) reactions are fundamental ways to make carbon-carbon bonds from alkenes and alkyl halides. The reaction involves the generation of a radical, identified as the activation step in the catalytic cycle, and has a rate constant of activation, \( k_{act} \). Copper catalyzed ATRA reaction rate constants are often extremely fast and cannot be measured using simple spectroscopic techniques. Therefore, a new series of copper(II) complexes containing the tetradeutate ligand tris-(2-aminomethyl)amine (TREN) was synthesized and evaluated for ATRA catalysis. Variation of the steric and electronic environment around copper was achieved through systematic modification of the ligand, TREN-R (R = H, Me, Cl, CF3). Kinetic studies were conducted using UV-vis spectroscopy with an alkyl halide and radical trapping agent (2, 6-tetramethylpyperidin-1-yl)oxiadanyl (TEMPO). The \( k_{act} \) values for primary and secondary alkyl bromides and alkyl chlorides have been determined using the (TREN-R) copper(II) catalysts. The \( k_{act} \) values for the (TREN-R) copper(II) catalysts are 1,000-1,000,000 times slower when compared to \( k_{act} \) values for copper catalysts containing tris(2- (dimethylamino)ethyl)amine (Me2TREN) or tris(2-pyridylmethyl)amine (TPMA) ligands. Alkyl bromides react 1000 times faster than alkyl chlorides (CBr\text{ vs } CCl\text{)}. Secondary alkyl chlorides react 100 times slower than CCl\text{). The electron donating effects of the methyl group also increase the rate constant while the electron-withdrawing effects of Cl and CF3 decrease the rate constant for all alkyl halides screened.

INOR 178

Synthesis of tridentate anionic carbazolyl/bis(imine) pincer complexes of platinum
John R Dekarske, dekarskej14@gmail.com, Jessica C DeMott, Oleg V Ozerov. Department of Chemistry, Texas A&M, College Station, Texas 77843, United States

This work focused on the synthesis of tridentate anionic carbazolyl/bis(imine) (NNN) pincer complexes of platinum with the ultimate goal of generating a 3-coordinate, unsaturated 14-electron platinum(II) complex. Pincer ligands are useful as they can stabilize extreme reactive transition metal complexes. However, previous studies of tridentate pincer complexes using ligands such as PNP or PONOP have demonstrated these pincer ligands are not suitable for the isolation of stable unsaturated platinum complexes with an open coordination site. Attempts to generate 3-coordinate species with PNP resulted in the heterolytic splitting of aromatic C-H bonds in solvents like benzene. The NNN ligand family is favored for its rigidity and resistance to oxidation. Abstraction of the triflate group from (NNN)PtOTf was explored in order to synthesize t

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INOR 179

Development of pyridine based lanthanide(III) complexes for imaging and sensor applications
Katherine R. Johnson, katherine.johnson@spartans.ut.edu, Eric J. Werner. Department of Chemistry, Biochemistry and Physics, The University of Tampa, Tampa, FL 33606, United States
Coordination complexes of lanthanide metal centers are often used in magnetic resonance imaging (MRI) and sensing applications. For example, a Gd(III) complex has the ability to function as a contrast agent to enhance the images produced from an MRI scanner. When injected into the body, such agents are bound by water molecules within tissue and cause an increase in the relaxation rate of water protons, improving image contrast. The effectiveness of such contrast agents can be related to the number of bound water molecules (q) that coordinate the metal. Additionally, metal complexes utilizing Eu(III) often exhibit unique photophysical properties that can be used for sensing anions that bind to the metal ion causing an increase in luminescence intensity. Luminescence decay lifetimes of Eu(III) complexes can also be used to determine the number of bound solvent molecules and thus provide valuable insight into the effectiveness of either application. In this study, several pyridine/Schiff base ligands for lanthanide complexation were synthesized and the potential of one particular Gd(III) complex as an MRI contrast agent was explored. This complex was made from the so-called TRIPy ligand which effectively binds Gd(III) in a hexadentate manner leaving space for additional water molecules in solution to attach. Luminescence decay lifetimes of the Eu(III) analog were used to determine the number of bound waters, and these results agree with relaxometric characterization performed for the Gd(III) derivative. Solution thermodynamic studies suggest the instability of the complex at high pH, leading to the synthesis of more stable derivatives.

INOR 180
Synthesis, characterization, and formation constant studies of novel bifunctional ligands for sensing copper, zinc, and iron
Alexis Kasparian, akasparian3@gmail.com, Lea Nyranshtuti, Feifei Wang, W. Rudolf Seitz, Roy Planalp. Department of Chemistry, University of New Hampshire, Durham, NH 03824, United States
The quantitative sensing of metal ions in biological and environmental systems grants the ability to understand their metabolic, medical and toxicological issues. This research group has undertaken the task of synthesizing and characterizing bifunctional sensors which can be attached to a novel polymer-based sensing platform. The polymer sensing platform is based on the responsive polymer, poly-N-isopropylacrylamide (PNIPAM). We report on approaches to novel ligands based on N,N'-bis(2-pyridyl)-2-acrylamido-1,3-propanediamine, where the pyridyl rings are substituted to affect the coordination geometry preference of the chelator and the acrylamido group allows its copolymerization into PNIPAM. The relative binding preferences of these aminopyridyl ligands for the subject metal ions will be reported, as well as the performance of sensors containing these ligands.

INOR 181
Synthesis and characterization of mixed bimetallic complexes
Patrick J Hubbard, phubbard@umassd.edu, Velabo B Mduli, David R Manke. Department of Chemistry & Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, MA 02747, United States
Several ligand motifs have been explored to generate mixed transition metal bimetallic species. Ligand design incorporates hard and soft Lewis base sites to drive the formation of early-late transition metal complexes; the design strives to incorporate the strong reducing power of early transition metals with the relative lability of late transition metals. Synthesis, characterization and reactivity will be presented.

INOR 182
Syntheses of 1,2-di(4-pyridyl)glycol platinum(II) dithiolene building blocks
Daniel Park, dcpark12@auburn.edu, Bradley W Smucker. Department of Chemistry, Austin College, Sherman, Texas 75090, United States
In our syntheses of building blocks for light-harvesting supramolecular coordination complexes using diimine platinum(II) dithiolene constructs, we used the 1,2-di(4-pyridyl)glycol, dpyg, ligand to form [Pt(dpypg)\textsubscript{x})(mnt)]\textsubscript{y} (x = 1 or 2, mnt = maleonitriledithiolate). All compounds exhibit strong visible absorbance and a reversible reduction (E\textsubscript{1/2} = -0.32V) was observed for the monotypically coordinated dpypg ligand.

INOR 183
Exchanging labile pyrazine by bispyridyl ligands to form diimine platinum(II) dithiolene complexes
Nicholas Maldonado, nmaldonado12@austincollege.edu, Bradley W Smucker. Department of Chemistry, Austin College, Sherman, Texas 75090, United States
The pyrazine in (pz)\textsubscript{2}Pt(mnt) (pz = pyrazine, mnt = maleonitriledithiolate) was exchanged with bispyridyl ligands (1,2-Bis(4-pyridyl)ethane, bpe, 1,2-Bis(4-pyridyl)propane, bpp, and 1,2-Bis(4-pyridylamido)benzene, bpab) to form supramolecular building blocks. The ratio of ligand to Pt(mnt) determined the coordination (monotropic or bridging) of the bispyridyl ligands. All compounds exhibited strong absorption into the visible region.

INOR 184
Guanylurea metformin double salt of decavanadate:(HGU\textsuperscript{+})(Mett\textsuperscript{+})(V\textsubscript{x}O\textsubscript{y}O\textsubscript{z}\textsuperscript{2+})\textsubscript{2}H\textsubscript{2}O
Aungkana Chatkon\textsuperscript{1}, Alexa Barres\textsuperscript{2}, Nuttaporn Samart\textsuperscript{3}; nuttapornsamart@gmail.com, Kenneth J Haller\textsuperscript{2}, Debbie C. Crans\textsuperscript{3}. (1) Chemistry Program, Faculty of Science and Technology, Nakhon Ratchasima Rajabhat University, Nakhon Ratchasima, Nakhon Ratchasima 30000, Thailand (2) School of Chemistry, Institute of Science, Suranaree Institute of Technology, Nakhon Ratchasima, Nakhon Ratchasima 30000, Thailand (3) Department of Chemistry, Colorado State University, Fort Collins, CO 80523, United States
Metformin and vanadate are used for the treatment of diabetes. In this study, the combination of metformin and decavanadate were studied a double salt of decavanadate (V\textsubscript{x}O\textsubscript{y}O\textsubscript{z}\textsuperscript{2+})\textsuperscript{2} with two cations, namely metformin and protonated guanylurea (HGU\textsuperscript{+}) which results from hydrolisis product of metformin was synthesized. The structure of the material was confirmed by single X-ray crystallography. The title compound crystallizes in the triclinic space group P\textsuperscript{1}, Z = 1. The structures of both cations and the decavanadate anion correspond to those reported previously. The V\textsubscript{x}O\textsubscript{y}O\textsubscript{z}\textsuperscript{2+} lies on an inversion center and charge is balanced by four HGU\textsuperscript{+} cations around the central axis and two H\textsuperscript{+} cations capping the ends of the V\textsubscript{x}O\textsubscript{y}O\textsubscript{z}\textsuperscript{2+} cylinder. These ions and two waters of solvation engage in an extensive multiple H-bonded network with the HGU\textsuperscript{+} bound at the strongest H-bond acceptor sites of the V\textsubscript{x}O\textsubscript{y}O\textsubscript{z}\textsuperscript{2+} and the H\textsuperscript{+} at lesser sites. The hydrolysis of metformin to form guanylurate in the presence of a vanadium (V) (i.e. decavanadate) catalyst was confirmed in solution structures using \textsuperscript{13}C NMR spectroscopy.

INOR 185
Synthesis of homogeneous AlScMoO\textsubscript{8}
Rebecca J. Truitt, rtruitt@itu.edu, Ilika Hermes, Alyssa Lergarten, Anne Sendecki, Cora Lind. Department of Chemistry, University of Toledo, Toledo, Ohio 43606, United States
Negative thermal expansion (NTE) materials have been of continuous scientific and engineering. This behavior is exhibited by several families of oxides, one of which is the Al\textsubscript{2}MoO\textsubscript{4} family (\textit{A}=trivalent cation, M=Mo, W). These compounds show NTE in an orthorhombic structure, but some compositions transform to a monoclinic polymorph with positive expansion at low temperature. By tuning the metals incorporated into the structure, expansion and phase transition behavior can be easily modified. The potential phase transition to a monoclinic structure has adverse effects for potential applications, but can often be suppressed when the A-site is substituted by a mixture of cations. The material of interest in this project is AlScMoO\textsubscript{8}. This compound was successfully synthesized using a non-hydrolytic sol gel route. The goal was to determine reaction conditions that will give homogeneous
AlScMoO$_4$$_3$ samples at low temperature. Improper choice of reaction variables may lead to phase separation into Al$_2$MoO$_4$$_3$ and Sc$_2$MoO$_4$$_3$. Using high resolution synchrotron diffraction measurements, the homogeneity of samples could be confirmed, and Al:Sc ratios were estimated using Rietveld refinement in combination with Vegard's law. Samples that gave single phase material were confirmed to adopt the orthorhombic Sc$_5$W$_2$O$_{19}$ structure as well as the desired 1:1:3 ratio for Al:Sc:Mo. Conditions were optimized, creating a reproducible synthesis method with consistent stoichiometry and homogeneity characteristics of the AlScMoO$_4$$_3$ product.

**INOR 186**

**Structure, magnetic, and electrical properties of Gd$_{17}$Ni$_8$Sn$_{104}$**

Luis E Reyes$^1$, ler130130@utdallas.edu, Julia Y Chan$^{1,2,3}$. (1) Chemistry, University of Texas at Dallas, Richardson, TX 75080, United States (2) Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States (3) Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803, United States

Single crystals of Gd$_{17}$Ni$_8$Sn$_{104}$ have been synthesized by a eutectoid (Gd/Ni) flux. The compound crystallizes in the space group Fm-3m with the lattice parameter $a = 30.025(2)$ Å and $V = 27,068.4(6)$ Å$^3$. The unit cell contains 1,106 atoms with 23 unique atomic positions consisting of 8 Gd, 6 Ni, and 9 Sn atoms, comparable to Gd$_{11}$Co$_2$Sn$_{11}$ that exhibits one of the lowest lattice thermal conductivity in a bulk solid ($k_L = 0.28$ W/(mK)). In this presentation, I will discuss the structural model, magnetization, and electrical properties of Gd$_{17}$Ni$_8$Sn$_{104}$.

**INOR 187**

**Synthesis and colorimetric sensing of pyridine based tripodal amines and their copper (II) complexes for anions**

JaNise Jackson$^{1,2}$, JaNiseJackson09@gmail.com, Md. Alamgir Hossain$^2$, Syed Haque$^2$. (1) Chemistry, Texas Southern University, Houston, Texas 77004, United States (2) Chemistry, Jackson State University, Jackson, mississippi 39217, United States

Two simple tripodal polyamine-based receptors linked with pyridine spacers were synthesized and complexed with Cu(II) ions. The free amines and their Cu(II) complexes were investigated for different anions in solution. The anions included in this study were fluoride, chloride, bromide, iodide, sulfate, phosphate nitrate and perchlorate. Due to the presence of four amine groups and pyridine nitrogen, neutral compounds were able to form complexes with Cu(II) ions. Both the free amines and their copper complexes were investigated to examine their sensing ability for target anions using various techniques including $^1$H NMR and UV-Vis titrations in methanol and acetonitrile. As confirmed by the titration studies, both complexes showed strong affinity for iodide showing visual color change in solution.

**INOR 188**

**Utilization of synchrotron radiation to determine the structure of weakly-diffracting fullerene crystals**

Kamran B Ghiasi$^{1,2}$, kgiasi@ucdavis.edu, Susanne Y Chen$^1$, Armin de Meijere$^1$, Marilyn M Olmstead$^1$, Alan L Balch$^1$. (1) Department of Chemistry, University of California Davis, Davis, CA 95616, United States (2) Faculty of Chemistry, Universität Göttingen, Göttingen, Lower Saxony, Germany

Two fullerene crystal structures have been determined by single crystal X-ray diffraction using hexakis([E]-3,3-dimethyl-1-butenyl)benzene (HB). The structures, $D_{5h}$-C$_{60}$2HB and $Ia$-C$_{60}$2HB, are remarkable due to similar interactions with the fullerenes. Moreover, the HB molecules exhibit back-to-back stacking and close contacts with the fullerenes. It is interesting to note that the C$_{60}$ cage is fully ordered while the C$_{70}$ cage contains a two-component orientational disorder. Both data sets were obtained at the Lawrence Berkeley National Lab, Advanced Light Source, Berkeley, California.

**INOR 189**

**In situ reduction to generate a second-harmonic generation active, mixed-valence sodium vanadium oxide-fluoride**

Martin D Donakowski$^1$, martindonakowski@northwestern.edu, Romain Gautier$^1$, Hongcheng Lu$^1$, T. Thao Tran$^2$, P, Shiv Halasymani$^{2,3}$, Kenneth R Popezmeier$^1$. (1) Department of Chemistry, Northwestern University, Evanston, IL 60208, United States (2) Department of Chemistry, University of Houston, Houston, TX 77204, United States (3) Department of Chemistry, Aalto University, Aalto, Finland

For a material to exhibit second-order nonlinearity-activity, such as second-harmonic generation (SHG), a crystal must belong to a noncentrosymmetric crystal class. The hydrothermal syntheses and analyses of noncentrosymmetric materials often examine solid-state structures on a 'molecular' basis with emphasis on modular basic-building units. The use of polar basic building units within an extended structure can endow polarity upon the bulk. This polarity must be conserved from the individual units to the bulk, eg the polar units should not be aligned antiparallel as such an arrangement would result in a zero net dipole. In order to target such materials, an understanding of the reaction conditions, equilibria, and crystallization processes is necessary. As a demonstration, we present the structures of NaVOF$_4$(H$_2$O) and NaVO$_2$·F$_2$·xH$_2$O (x = 1/3, = 1/6) in which different NCS structures can be created from the same reagent ratios but varied temperatures. The temperature acts to create vanadium-oxide fluorides that are of (i) increased dimensionality and (ii) reduced oxidation states. The structure of the mixed valence compound has the 4+/5+ vanadium cations disordered; the fullerenes. It is interesting to note that the C$_{60}$ cage is fully ordered while the C$_{70}$ cage contains a two-component orientational disorder. Both data sets were obtained at the Lawrence Berkeley National Lab, Advanced Light Source, Berkeley, California.

**INOR 190**

**Synthesis of ketoimines with electron-withdrawing substituents for use in aluminum complexes**

Alexandria M McCollum, Alexandria.M.Mccollum@Pepperdine.edu, Joseph M Fritsch, Department of Chemistry, Pepperdine University, Malibu, CA 90263, United States

Varying the electronic properties of a supporting ligand is a common approach for optimizing catalytic behavior in many systems. Here, two new ketoimines were prepared through the Schiff base condensation of a 1,3-diketone and an amine that easily incorporated electron-withdrawing groups into the ketoimine backbone or at the 2-position of the quinoline pendant. Ketoimine 1 was prepared through the condensation of 5-methyl-1,1,1-trifluoro-2,4-hexanedione with 8-aminoquinoline with toluene reflux for 21 hours and isolated with column chromatography in 28% yield. Ketoimine 2 was isolated in 15% yield with column chromatography after toluene reflux for 1 day with 2,4-pentandione and 2-chloro-8-aminoquinoline. The ketoimines were characterized with $^1$H, $^13$C, and $^{19}$F NMR, absorbance spectroscopy, and electrospray ionization time-of-flight high-resolution mass spectrometry. The compounds were used to prepare aluminum complexes that were characterized with NMR spectroscopy and absorbance spectroscopy. The aluminum complexes were assessed for their ring opening polymerization efficiency of lactide to poly-lactic acid.
INOR 191

Synthesis and characterization of bis-ligated aluminum complexes for the polymerization of lactide

Logan A. Schmitz1, Logan.Schmitz@Pepperdine.edu, Arnold L Rheingold2, Joseph M. Fritsch1. (1) Department of Chemistry, Pepperdine University, Malibu, CA 90263, United States (2) Department of Chemistry, University of California, San Diego, La Jolla, CA 92039, United States

A series of ionic aluminum complexes were prepared through reaction of Schiff base ketimines bearing varying substituents with aluminum triphenoxide under an inert atmosphere. The aluminum complexes included a bis-ligated aluminum cation and a tetraphenoxide aluminate anion. The complexes were characterized with 1H, 19F, and 13C NMR, electrospray ionization time-of-flight high resolution mass spectrometry, absorbance, and single crystal x-ray crystallography. Solid state structure determination elucidated the distorted octahedral coordination geometry of two ketiminate ligands supporting one aluminum center while the second aluminum center had tetrahedral coordination with four 2,6-dimethyl phenoxides. The complexes were effective L-lactide and racemic-lactide polymerization initiators at 100 °C for 18 hours with high percentage conversion of monomer to polymer. The isolated polymeric material was analyzed with gel permeation chromatography and had high molecular weights with moderate poly-dispersion index values.

INOR 192

Reactivity of anisole and bromoanisole regioisomers toward brominating agents in solutions of NaBr + free available chlorine

Daniel A. Victor, dvictor1@students.towson.edu, John D. Sivey. Department of Chemistry, Towson University, Towson, Maryland 21252, United States

Historically, reaction rates for the formation of disinfection byproducts through bromination of aromatic compounds were almost exclusively accredited to the species HOBr. However, it has more recently been discovered that several inorganic brominating agents (BrCl, Br2, BrOCl, and Br2O) in equilibrium with HOBBr can have a significant impact on bromination rates. We examined rates of bromination of anisole and bromoanisole regioisomers (as model DBP precursors) in solutions of NaBr and free available chlorine. Time course experiments were conducted at 20.00 (±0.02 °C) under pseudo-first-order conditions, in which total free bromine was generated in excess ([HOBBr]/[parent anisole] ≥ 12) via oxidation of bromide by free chlorine. Key independent variables such as pH, bromide concentration, and chloride concentration were examined for their effects on the rates of bromination. Gas chromatography with mass spectrometry and electron capture detection was used to monitor the loss of parent compound and formation of products.

As solution pH increased, rates of bromination decreased significantly. Our results suggest that bromination rates of anisole and its brominated products decrease with increasing bromine substitution. Our findings also provide insight into changes in selectivity toward specific brominating agents with changes in anisole structure.

INOR 193

Nitrobenzene hydrogenation over supported gold catalysts

Jaclyn Newell, jnewell@trinity.edu, Elisabeth Purdy, Bert Chandler, Chris Pursell. Department of Chemistry, Trinity University, San Antonio, TX 78212, United States

The catalytic hydrogenation of nitrobenzene with NaBH4 was examined as a probe reaction to study particle size and support effects on gold catalysts. This reaction is potentially useful because it is fast and lends itself to the use of Hammett methodologies. The kinetics of nitrobenzene conversion to aniline were monitored using gas chromatography, and a complete kinetic analysis was performed in order to optimize the reaction parameters. In particular, differential low conversion conditions were desirable in order to accurately determine intrinsic reaction rates. This reaction, and the Hammett associated Hammett studies, provide a new potential method for investigating supported metal nanoparticle catalysts.

INOR 194

Transition metal catalyzed conversion of pyrolytic lignin into chemical feedstocks

Megan Mohadjer Beromi1, mmohadjerberomi@mail.usciences.edu, Nathan West1, Akwasi Boateng2. (1) Department of Chemistry & Biochemistry, University of the Sciences, Philadelphia, Pennsylvania 19104, United States (2) Agricultural Research Service, United States Department of Agriculture, Wyndmoor, Pennsylvania 19038, United States

Fast pyrolysis of switchgrass produces crude pyrolysis oil that can be further upgraded into gasoline or diesel fuel. However large quantities of high molecular weight lignin remains in the pyrolysis oil. The lignin can extracted from the pyrolysis oil and oxidatively cleaved into useful aromatic chemicals using homogeneous catalysts. We will report studies on the use of a variety of Mn, Co, and V salen catalysts to depolymerize pyrolytic lignin samples into low molecular weight products. The products have been studied by GPC and GC-MS. We also report on how the structure of lignin changes during pyrolysis.

INOR 195

Platinum catalysts supported on mesoporous silica nanoparticles for production of alkyl and vinyl arenes

Nathanael A. Hirscher1, nah3rf@virginia.edu, Tristan S. Gray1, Megan M. Otting2, Brian G. Trewyn3, T. Brent Gunnoe1. (1) Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States (2) Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401, United States

Catalysts for the conversion of aromatics and olefins to alkyl and vinyl arenes are in high demand. This research probes the use of platinum catalysts with an amide-functionalized 2,2′-bipyridine ligand for the production of both styrene and ethylbenzene from ethylene and benzene. The catalyst is formed by covalent tethering of a homogeneous platinum complex to the surface of a mesoporous silica nanoparticle (MSN). The catalytic reaction is performed in stainless steel reactors under N2 pressures of 100-120 psi. This heterogeneous Pt catalyst shows increased longevity in comparison to homogeneous Pt systems. It is also thermally stable at temperatures as high as 150°C. The activity of the MSN-amide-Pt catalyst is demonstrated at varying concentrations of Bronsted acid activator, temperature, and ethylene pressure.

INOR 196

Exploring reactivity of phosphine imidazole ligands with ruthenium: Access to monometallic and bimetallic complexes

Yuting F. Lin, filizlin@gmail.com, Sarah E. Flowers, Brandi M. Cossairt. Department of Chemistry, University of Washington, Seattle, WA 98195, United States

Exploring reactivity of phosphine imidazole ligands with ruthenium: Access to monometallic and bimetallic complexes
Synthesis gas, a gaseous mixture of CO and H₂ produced from burning carbonaceous materials, is continuously being produced as a byproduct of the coal and gas industry. Attention is needed on developing methods for using these byproducts to generate chemicals that are synthetically useful. In this project, a homogeneous bimetallic complex is designed to facilitate syngas conversion. To accommodate two metal centers, both soft and hard metal binding pockets are generated using a phosphine-imido ligand which also creates a heterogeneous-like surface for chemistry to occur intramolecularly between the two metals. In this study, a new single-armed phosphine-imidazole ligand C₇H₇N₃P has been prepared. This phosphine ligand reacts with the ruthenium tetramer, [C₈Ru₂Cl₆], through direct metallaition to form a new ruthenium dimer complex, C₇H₇N₃P₂Ru₂Cl₆, which undergoes tautomerization to form a new ruthenium carbone complex, C₇H₇N₃PRu₂Cl₆. Further studies will focus on isolating, characterizing, and exploring the catalytic activity of the ruthenium dimer, the ruthenium carbone complex, and bimetallic complexes. Also, the results of this research will be applied to the exploration of phosphine-linked bisimidazole ligands for related chemistry. This research is lead by Dr. Brandi M. Cossart, Sarah E. Flowers and conducted in the Cossart lab at the University of Washington, Seattle. This study is supported by the University of Washington, The Center of Enabling New Technologies through Catalysis (CENTC), and the National Science Foundation.

INOR 197
Computational study into controlling azide reduction vs. dinitrogen expulsion through metal and ligand choice
Talon M Kosak¹, lordri@gvsu.edu, Stanislav Groysman², Richard L Lord³, (1) Department of Chemistry, Grand Valley State University, Allendale, MI 49401, United States (2) Department of Chemistry, Wayne State University, Detroit, MI 48201, United States
We demonstrated recently that Fe⁶ supported by bulky alkoxide ligands is capable of reductively coupling adamantyl azide to form a diron hexazene complex (Inorg. Chem. 2013, ASAP). The same metal complex was unable to reductively couple trimethylsilyl azide. Inspired by this experimental finding, we seek to understand how the metal, ligand, and azide substrate influence the reaction thermodynamics of azide reduction vs. dinitrogen expulsion using density functional theory.

INOR 198
Exploring the redox states and reactivity of a vanadium bis-tetrazinylpyridine complex with DFT
Adam M Terwilliger¹, lordri@gvsu.edu, Kenneth G Cauldron², Richard L Lord³, (1) Department of Chemistry, Grand Valley State University, Allendale, MI 49401, United States (2) Department of Chemistry, Indiana University, Bloomington, IN 47405, United States
We reported recently the synthesis and characterization of a vanadium-oxo complex supported by a bis-tetrazinylpyridine (btzp) ligand (Acta Cryst., Section C, 2013, ASAP), where the redox noninnocence of the ligand leaves unsettled the question of its charge in the complex. Electronic structure calculations suggested that the complex contains a V⁵⁺ ion antiferromagnetically coupled to the btzp ligand. In this work, we extend those analyses to a number of related vanadium complexes. We explore putative reaction paths for the formation of this oxo species from water.

INOR 199
Synthesis and reactivity of new pincer-ligated rhodium alkyl dimerization catalysts
Christopher J. Pell, christopher.pell@chem.tamu.edu, Oleg V. Ozerov.Department of Chemistry, Texas A&M, College Station, Texas 77840, United States
The dimerization of terminal alkynes is an atom economical way of synthesizing conjugated enynes, which can be utilized as potential building blocks in organic synthesis. The challenge of alkyn dimerization is selectively producing the desired enyne isomer. Our group previously reported that a rhodium complex featuring a sterically bulky diarylamido-based PNP pincer ligand showed impressive selectivity for the trans-enzyme product of terminal alkyne homodimerization. Recently, the (POCP)²Rh fragment has been shown to catalyze the dimerization of terminal alkynes at room temperature; however, the catalyst produces a mixture of the trans- and gem-enzyme products. A number of bulky unsymmetric PCP bisphosphinite pincer rhodium complexes have been synthesized and tested as alkyne dimerization catalysts in an attempt to obtain selectivity for the trans-enzyme product. Studies examining other phospine pincer ligands are also underway, which should provide insight into the ligand traits responsible for regioselectivity.

INOR 200
Binuclear pincer complexes of Pd and Ni: Catalysts for selective decomposition of HCOOH to CO₂ and H₂
Chandra Mouli Palit, chandramoulipalit@gmail.com, Oleg V Ozerov.Department of Chemistry, Texas A&M University, COLLEGE STATION, Texas 77840, United States
We recently published the synthesis and characterization of binuclear complexes of Pd. In this report we highlight the utility of those complexes and their Ni analogs in the dehydrogenation of HCOOH to CO₂. Formic acid is one of the most viable media for transport of molecular hydrogen in chemical bonds since environmentally abundant CO₂ can be hydrogenated to form HCOOH and then transported and used to generate H₂ wherever it is needed. Due to this, catalysts for both the hydrogenation of CO₂ to HCOOH and its selective decomposition to CO₂ and H₂ are highly desirable. A few catalysts for both these processes have been reported to date. However, these catalysts almost exclusively use expensive metals such as Ir and Rh. To this end, our complexes with much cheaper and abundant Pd and Ni, provide interesting alternatives.

β-hydride elimination of CO₂ from a metal formate species plays an important role in the mechanism. Comparisons between our binuclear catalysts and their mononuclear analogs have also been performed to elucidate the possible differences in activity. Different variations of pincer ligands have also been tested to investigate the effects of different donor atoms. In addition to this chemistry, we have also performed preliminary studies into β-X (where X = Me, Ph) eliminations from similar M-OR species.

INOR 201
Insertion chemistry and reactivity of a neutral terminal nitride of vanadium
Rick R Thompson¹, Ricktt@sas.upenn.edu, Ba L Tran², Skye Fortier², Maren Pink², Dan J Mindiola³, (1) Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States (2) Department of Chemistry and Biochemistry, Indiana University, Bloomington, IN 47401, United States
The polarization of the vanadium nitrogen triple bond in the β-diketinate supported compound (nacnac)V[N][L] (where L = Ntolyl₂ or ODipp, Ntolyl₂ = bis[4-methylphenyl]amide, ODipp = 2,6 disopropylphenoxide) has led to a myriad of reactivity including insertion into heteroatom–H bonds, redox-chemistry, metalation and small molecule functionalization. This final point has led to the synthesis and characterization of the first ever thionitrosyl of vanadium, using elemental sulfur as the source of S atom.

INOR 202
Cu(II) mediated dialkoxylation of alkenes by alcohols: The impact of ligands and scope of the reaction
Haixia Wu, chmwuhai@nus.edu.sg, Dejian Huang. Department of Chemistry, National University of Singapore, Singapore

In the process of synthesizing Cu(II) complexes as near infrared fluorescent probes for detection of hydrogen sulfide, we came across an unexpected reaction of dialkoxylation of a C=C double bond by methanol or ethanol under room temperature. This unusual reaction prompted us to carry out study on a) the important roles of auxiliary ligands for the reactivity of the Cu(II); b) the scope of the reaction in terms of alkenes and alcohols. In this poster, we will illustrate the results and propose plausible reaction mechanisms for discussion.

INOR 203

Application of carborane weakly-coordinating anions in organometallic synthesis, catalysis, and characterization
Billy J McCulloch, bmcculloch@chem.tamu.edu, Rafael Huacuja, Morgan MacInnis, Yanjun Zhu, Oleg V Ozerov. Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

Weakly coordinating anions (WCAs) comprise a class of anions which allow for the condensed-phase existence of strongly electrophilic cations. The ability of carborane WCAs, in particular, to persist in the presence of strong Lewis acids and under high oxidation potentials has encouraged their application to catalysis, electrochemistry, and organometallic chemistry. Applications of carborane WCAs to our own organometallic research has provided opportunities to isolate and investigate highly reactive species. Recent examples from our labs will be presented.

INOR 204

Synthesis and characterization of triflyloxy substituted carboranes
Loren P. Press, loren.press@chem.tamu.edu, Billy J. McCulloch, Oleg V. Ozerov. Texas A&M University, College Station, Texas 77842-3012, United States

The synthesis and characterization of triflyloxy-substituted carboranes will be discussed. Trityl and silylium reagents of these anions and their reactivity with various substrates such as organometallic complexes will also be examined. Catalytic hydrodefluorination studies with these anions will also be presented.

INOR 205

Investigation of the rhombohedral-to-cubic transformation path in boron nitride
Prajay M Patel, prajay.patel@mavs.uta.edu, Miki Somosot, Anil Chourasia, Peter Kroll. Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019-0065, United States

We study the transformation mechanism for the phase transformation from rhombohedral boron nitride (rBN) to cubic boron nitride (cBN) using density functional theory methods within the local density approximation (LDA). The transformation mechanism is approximated by two independent parameters: one defining the computational mode that brings layers in rBN closer together, the other describing the buckling mode, relating to pyramidalization of atoms and formation of new bonds. The complete mechanism is mapped to a two-dimensional energy profile, providing the transformation path together with activation energy and reaction enthalpy. For pure BN, we find 0.175 eV/atom for the activation energy of the collective transformation. Analysis of vibrational modes along the transition path reveals positive zone-center frequencies only, while the elastic constant c33 adopts negative values. Allovalent substitution of 8.33 mol-% AlN in BN yields a lower activation energy (0.115 eV/atom) than for pure BN. The impact of substituting BN by C severely depends on the distribution of C atoms: while C2-pairs within BN layers increase the activation barrier, other substitution patterns lead to a decrease. High pressure decreases the activation energy for the rBN to cBN transition, for pure and alloyed systems alike. However, while pure BN still exhibits a noticeable activation barrier at 30 GPa, the AlN substituted system completely collapses to the tetrahedral structure at pressures above 20 GPa. The relevance of our study for the synthesis of cBN at high pressures as well as for the thermal stability of cBN compounds at high temperatures will be discussed.

INOR 206

Polymorphism in novel LiI-Il-IV-S diamond-like semiconductors
Kasey P Devlin, devlinke@duq.edu, Kimberly R Daley, Meghann A Moreau, Jacilynn A Brant, Jennifer A Aitken. Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, United States

Diamond-like semiconductors (DLSs) have structures that are derived from either the cubic or hexagonal form of diamond. The I-Il-IV-VI3 diamond-like semiconductors are particularly interesting systems for their tunable nature and technological applications in photovoltaic solar cells, spintronics, and non-linear optics, specifically second harmonic generation. Polymorphism, which may affect important physiochemical properties in these materials, has been commonly reported in binary and ternary systems, while investigations of polymorphism in quaternary DLSs have been less prevalent. Polymorphs have been observed crystallizing in the staninite (I-42d) and wurtzstannite (Pmn21) structure types, which differ in the closest-packed arrangement of the anions, cubic versus hexagonal, respectively. Polymorphism may also be observed in quaternary DLSs that maintain the same anion packing, but differ only in the cation ordering arrangements within the tetrahedral holes. In the hexagonally derived quaternary DLSs, the different cation ordering gives rise to at least three different structure types, wurtzstannite (Pmn21), wurtzesterite (Pn), and cobalt (I) lithium silicate (Pn21). In this work, high-temperature solid-state synthesis in a LiI-Il-IV-VI3 system lead to the discovery of two new polymorphic compounds, crystallizing in the Pn21 and Pn space groups. The two polymorphs were analyzed using single crystal X-ray diffraction, synchrotron X-ray powder diffraction, and optical diffuse reflectance UV/Vis/NIR spectroscopy. This work is supported by the National Science Foundation under Grant No. DMR-DMR-1201729.

INOR 207

Synthesis and characterization of surface modified zinc oxide quantum dots
Samuel M. Bynum, chemistry@uwf.edu, Lena F. Ibrahim, chemistry@uwf.edu, Michael T. Smith, Hailey X. Egidio-Betancourt, Pamela P. Vaughan, Alan K. Schrock, Karen S. Molek. Department of Chemistry, University of West Florida, Pensacola, Florida 32514, United States

Quantum dots are unique nanoparticles that are gaining interest for their desirable chemical and physical properties. In this study, ZnO quantum dots were synthesized using two different methods. Method one involves heating zinc acetate solutions to create Zn2+ precursors, and method two involves growing the ZnO quantum dots from a “seed” dispersion of highly modified precursor ZnO particles. LiOH was used in both methods to regulate particle growth. Low and high molecular weight siloxane modified physical stabilizers were used to decrease aggregation and improve ZnO aqueous dispersion fluorescence stability. The effects on quantum dot growth and stability in these methods were studied as a function of surface modifier structure and attachment efficiency. Scanning Electron Microscopy, Transmission Electron Microscopy, and Confocal Microscopy were used to measure particle quality and aggregation. The stabilized ZnO quantum dot dispersions were characterized by Dynamic Light Scattering and with Infrared, UV-Visible, and fluorescence spectroscopy.
INOR 208

Searching for light responsive metal-organic frameworks via the incorporation of photochromic linker molecules

David R Butzer1, 2, butzer993@fredonia.edu, Ian M. Walton1, Jordan M. Cox1, Cody A. Gleason1, Dinesh G. Patel1, Jason B. Benedict1. (1) University at Buffalo, Buffalo, New York 14260-1660, United States (2) State University of New York at Fredonia, Fredonia, New York 14063, United States

Photochromic molecules have the potential to transform traditionally passive materials into active materials which change their chemical or electronic properties in response to light stimulus. Photochromic molecules can be combined with metal-organic frameworks to create advanced materials for chemical separation, sensing, and photo-mechanical actuation. To further investigate, various photochromic linker molecules were synthesized to then be incorporated into metal organic frameworks. The photochemical reactions in these materials, both desired and undesired, were precisely monitored through spectroscopic and X-ray diffraction methods. Also, a new synthetic route for the production of 2-(phenyldiazeyl)terephthalic acid was attempted in hopes of increasing the yield given by traditional methods.

INOR 209

Synthesis and characterization of titanium oxide nanopowders

Christen K Butterfield, ckb15@students.uwf.edu, Tia K Boucher, Ryan M Oberhausen, Gregory S Kostelac, Karen S Molek. Department of Chemistry, University of West Florida, Pensacola, Florida 32514, United States

Titanium oxide nanopowders were synthesized using Titanium Tetraisopropoxide and varied pH values. The nanopowders were left in solution from times varying between two hours and two months. The synthesized nanopowders were then heated to temperatures between 80°C and 750°C varying between one and two hour time increments at each temperature. Differential Scanning Calorimetry (DSC) was used to further refine the heating ranges to get a more accurate range at which the nanopowders changed phase. After being synthesized, each of the nanopowders were characterized according to their size, composition and phase, and absorbance properties using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), and UV-Vis Spectroscopy, respectively. The spectra and diffraction patterns were used to determine the temperature required to induce a phase change from the amorphous to anatase structure and anatase to rutile structures. The resulting spectra were compared to literature spectra to ensure that pure samples of each species of nanopowder were obtained.

INOR 210

Synthesis of BaMoO₄ from colloidal MoS₂

Michael T Spiegel, ms1854@txstate.edu, Linda Akinkunmi, Benjamin R Martin, bmartin@txstate.edu. Department of Chemistry and Biochemistry, Texas State University, San Marcos, TX 78666, United States

BaMoO₄ is useful as a framework for doped photoluminescent materials, but its synthesis typically involves high temperature methods. MoS₂ is a layered structure, and could serve as a source of molybdenum, but it is unreactive under standard conditions. MoS₂ may be exfoliated by first intercalating lithium into the crystal structure using butyl lithium, and then exposing this compound to water. This aqueous colloidal form of MoS₂ is highly reactive, and upon exposure to Ba⁺⁺, it undergoes an oxidative reaction to form BaMoO₄. In this reaction, water serves as the oxidant and the oxygen source, and the sulfide is likely released as H₂S/BaS. The effects of reaction conditions, including the solvent, temperature, ion composition, and concentration are discussed.

INOR 211

New quaternary rare earth bismuth telluride with potential thermoelectric properties

Lisa Kennedy, kennedl2@tcnj.edu, Vincent Wu, wuv1@tcnj.edu, Kartik Rai, Matthew Kita, Benny C Chan. Department of Chemistry, The College of New Jersey, Ewing, NJ 08628, United States

A new quaternary bismuth telluride compound was discovered and characterized by single crystal X-ray diffraction. K(RE)Bi₄Te₈ (RE=Lₐ, Ce, Nd, Yb) was discovered using a reactive flux synthesis between K₂Te₅, Bi, RE, and additional Te in a sealed fused silica ampoule. The X-ray diffraction showed the compound forms Bi-Te octahedra that are similar to the known Bi₂Te₃ thermoelectric. The Re-Te forms a seven coordinate square antiprisms similar to Dy₂Te₃. The K atoms lie in 1-dimensional channels. The structures are currently being investigated for their magnetic and thermoelectric properties.

INOR 212

Carbazole based metal-organic frameworks for applications in gas separation

Amanda W Stubbs, astubbs@umassd.edu, Ryan L Lehane, David R Manke. Department of Chemistry & Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, MA 02747, United States

A series of metal-organic frameworks (MOFs) was synthesized using carbazole based organic linkers. The utilization of these linkers allows for the inclusion of Lewis base sites in the open pores of the solids. The syntheses and structures of the MOFs will be presented, as well as their gas sorption properties.

INOR 213

Design of nanoparticles for targeted drug delivery: Surface modification of zirconium phosphate with PEG

Alyssa S Rosas, alyssarosas@tamu.edu, Agustin Diaz, Brian Mosby, Abraham Clearfield. Department of Chemistry, Texas A&M University, College Station, Texas 77841, United States

Phosphonates and phosphoric acid esters of poly(ethylene glycol) were successfully synthesized using various synthetic approaches. Phosphonic acids were synthesized by bromination of the PEG followed by the Michaelis-Arbuzov reaction and hydrolysis of the ester whereas the phosphoric acid esters were prepared by direct phosphorylation of the hydroxyl group using phosphoric chloride. All polymer products were characterized by NMR, FTIR, and mass spectrometry. The phosphates based PEG ligands were then covalently attached to the surface of Zirconium phosphate (ZrP) nanoparticles and ZrP nanoparticles loaded with doxorubicin, an anticancer drug. The encapsulation of the doxorubicin and successful modification of the surface was verified by powder X-Ray diffraction, FTIR, TGA, and electron microprobe.

INOR 214

Preparation of coordination polymers containing diosmium units

Soo Hun Yoon, shy12a@acu.edu, Nigel Gwini, nxg10a@acu.edu, Audrey G. Fikes, Gregory L Powell. Department of Chemistry & Biochemistry, Abilene Christian University, Abilene, Texas 79699, United States

Microwave heating has recently been used to prepare diosmium(I) complexes containing carboxyl and carboxylate ligands. These Os₂(CO)₅₆(carboxylate)₂ complexes have CO ligands along the Os-Os axis that are fairly easy to replace. We are synthesizing coordination polymers by combining these Os₂ complexes with multidentate ligands containing N- and/or S-donor atoms such as bipyrindyl and terpyridyl. Axial ligand substitution results in the formation of one- and two-dimensional solids that might have interesting properties such as photoluminescence and direction-specific conductivity and resistivity.
Preparation of a library of transition-metal-doped zinc sulfide nanoparticles and characterization of their photoluminescent properties

Frank N Youmby1,2, fry1000@francis.edu, Mohindar Seehra2, Brian V Popp2. (1) C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States (2) Department of Physics, West Virginia University, Morgantown, WV 26506, United States (3) Department of Chemistry, St. Francis University, Loretto, PA 15940, United States

A library of approximately 80 ZnS nanoparticles doped with different first-row transition metal ions (Cr, Mn, Fe, Co, Ni, Cu) were synthesized and found to have varied photoluminescent properties. Multiple procedures previously reported in the literature were initially tested, and we found the optimal general procedure to be the refluxing for four hours of an aqueous solution of zinc nitrate, an organic thiol reagent to act as the nanoparticle capping agent, and sodium sulfide as the sulfur source. ZnS nanoparticles doped with Mn, Fe, and Ni (1.25 mol%) presented the highest photoluminescence compared to the other dopants. The luminescence emissions were attributed to the optical properties of the transition metal ions, which may suggest that the particles are aggregating in solution. X-ray powder diffraction confirmed the identity of the nanoparticles and revealed a broad pattern characteristic of zinc sulfide nanoparticles of ~5 nm. Dynamic light scattering measurements on the reaction solution revealed particles of over 80 nm in size, which suggest that the particles are aggregating in solution. Bi-doped, tri-doped, and tetra-doped systems were also examined but their photoluminescent properties proved poorer than the mono-doped systems.

Mesoporous metal organic frameworks for use in enzyme immobilization

Stephanie Almaraz, sxa109121@utdallas.edu.University of Texas at Dallas, United States

Metal organic frameworks, or MOFs, are porous crystalline structures consisting of metal ion building blocks connected to organic linkers. MOFs that possess large pores and high surface area can be created through manipulation of these building blocks. These types of MOFs are ideal for enzyme immobilization. The targeted enzyme in this project is Microperoxidase-11 (MP-11). Aggregation of MP-11 hinders the enzyme’s ability to oxidize organic molecules. Immobilization in a protective matrix will permit MP-11 to maintain its catalytic properties. For successful immobilization to take place, special attention must be paid to the pores of the matrix. STU-1, a mesoporous MOF that consists of Zn2+ metal centers and a bridged imidazole based linker has thermal stability, overall chemical robustness, and will be used in this study of the immobilization of MP-11. STU-1 has a pore size of 27.3 Å × 15.4 Å, which can tightly hold the MP-11 enzyme (~17.5 Å × 33 Å). This snug fit will protect the enzyme from the reaction medium, extending the life of this catalyst. In this work the immobilization of MP-11 will be verified and observed using Ultraviolet Visible Spectroscopy (UV-Vis).

Research in the inorganic classroom: Structural characterization of sulfonamide derivatives and their metal coordination complexes

Karlik Ra1, raik1@tcnj.edu, Lisa Kennedy1, Danielle L. Jacobs2, Benny C Chan1, Abby R O’Connor1. (1) Department of Chemistry, The College of New Jersey, Ewing, NJ 08628, United States (2) Department of Chemistry, Biochemistry, and Physics, Rider University, Lawrenceville, NJ 08648, United States

A current research project was brought into the classroom to train undergraduates in single crystal x-ray diffraction structure solution and analysis over two semesters. To train students, three N-(2-(pyridin-2-yl)ethyl)sulfonamide derivatives, methane, benzene, and toluene, were used for students to learn the ShelXLT, Platon, and CrystalMaker software packages. The students also solved the structure of an unpublished cyclooctadiene iodide(I) chloride salt from the O’Connor and Jacobs labs and six unpublished organic crystal structures they had crystallized in the previous inorganic chemistry course. Students learned the publication process through a submission to Acta Crystallographica C: Communications and Acta Crystallographica E: Structure Reports. Students wrote tutorials on their structure solutions for future student training. Through careful selection of compounds, students in a classroom of 30 can produce publication quality single crystal x-ray diffraction data and analysis.

Inorganic biochemistry of Clofibric acid with Fe2+

Yahia Z Hamada1, yahia_hamada@loc.edu, Jasmine Scott1, Mostafa Z Badi2. (1) Department of Chemistry, LeMoyne-Owen College, Memphis, TN 38126, United States (2) Division of Pharmacology, University of Missouri-Kansas City, Kansas City, MO 64108, United States

We are presenting the reaction of clofibric acid with Fe2+ in aqueous solutions at 25°C. Clofibric acid is an herbicide that functions as a plant growth regulator against the plant hormone auxin. This ligand, Clofibric acid, binds to PPAR (peroxisome proliferator-activated receptor). PPARs, which play an essential role in the regulation of cellular differentiation and metabolism (carbohydrate, lipid, protein) and tumor. The main techniques used to carry out this research are potentiometric titration and UV-Vis spectroscopy. From the potentiometric titrations of Fe2+ : Clofibric acid in different ratios, it appeared that the measured potentials are in total agreement with Nernst Equation. These potentiometric data are novel for this reaction system. We also gathered novel UV-Vis-spectroscopy for this system. It appeared that Clofibric acid binds to Fe2+. It appeared also that the simple one to one (Fe3+: Clofibric acid: Hydroxo (OH)) complexes have been formed.

Novel N2 complexes of relevance to the NN bond breaking

Katarzyna Grubel1, grubelk@gmail.com, William W. Brennessel2, Patrick L. Holland3. (1) Department of Chemistry, Yale University, New Haven, Connecticut 06511, United States (2) Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

Reduction of N2 is a vital process, which is carried out in both nature (nitrogenase enzyme) and industry (Haber-Bosch process). Despite its importance, details of these reactions at atomic level are still not well understood. This is due to the fact that both processes utilize multimetallic active sites, which are inherently difficult to study. To better understand the N2 reduction mechanism in the multinuclear systems, in 2011, we reported a potassium-containing iron complex that is capable of completely cleaving the N-Nitride bond to form an iron-nitride cluster compound (Science 2011, 334, 780). Here, we report that other alkali metal reductants give a range of iron-N2 products with three or four Fe atoms. We discuss the characterization of new iron clusters, and their relationship to the mechanism of N-N bond cleavage.

Macrocyclic ligands of the ATCUN motif control metal binding and catalysis

Kosh P Neupane, Kosh.Neupane@tufts.edu, Amanda R. Aldous, Joshua A. Kritzer. Chemistry, Tufts University, Medford, MA 02155, United States

The amino terminal copper and nickel binding (ATCUN) motif is a small, N-terminal metal-binding site found in human serum albumin and various other proteins. The motif is a tripeptide that binds Cu(II) or Ni(II) using the N-terminal amine of the first amino acid, two deprotonated amide nitrogens, and the imidazole nitrogen of histidine in the third position. This affords a distorted square planar coordination environment at the metal center. Recently we utilized artificial amino acids and macrocyclic constraints to explore how conformation of ATCUN-like macrocycles controls the metal-binding and catalytic properties. We designed a cyclic peptide that binds Cu(II) and Ni(II) in a similar manner to linear ATCUN motifs, but with altered properties. For
instance, the cyclic peptide binds Cu(II) and Ni(II) at higher pH than that of linear analogues, and it binds Cu(II) selectively over Ni(II) at physiological pH. UV–vis and EPR spectroscopy showed that cyclic peptide can coordinate both metal ions in a square planar geometry. Metal binding titration and ESI-MS data revealed a 1:1 binding stoichiometry. Macrocyclization allows for coordination of Cu(II) or Ni(II) as in linear ATCUN motifs, but with enhanced DNA cleavage by the Cu(II) complex of the cyclic peptide relative to linear analogues. The cyclic peptide-Cu(II) complex was also capable of producing diffusible hydroxyl radicals, which is unique among ATCUN motifs and most other common copper(II) chelators. Currently, we are studying how substitutions with a variety of donor atoms (N, S, O) alters the metal binding and catalytic properties of this novel series of constrained metallopeptides.

INOR 221

Kinetic and spectroscopic study of enzyme-substrate interactions in a DNA monooxygenase MiaE (a non-heme diiron enzyme)

Bishnu P Subedi, bishnu.subedi@mavs.uta.edu, Andra Corder, Brad Pierce. Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, United States

MiaE; 2-methylthio-N-6-isopentenyl adenosine-37 (msi6A) RNA monooxygenase is a monomeric non-heme diiron enzyme which catalyzes the post-transcriptional alkylation of transfer RNA. In the resting state, MiaE shows a characteristic absorbance band (320-370 nm) which is typical of a non-heme d ferric cluster containing a bridging µ-oxo ligand. In this work, we utilized various spectroscopic and kinetic methods to study enzyme-substrate interaction and its impact on reactivity. MiaE activity was verified utilizing both synthetically produced isopentenylated nucleosides (i6A) and enzymatically generated isopentenylated RNA oligomers (17 nucleotides) corresponding to the antisense codon loop of RNAβ (i6A-ASLβ). Both peroxide shunt and a catalytic electron transport chain (NADPH, ferredoxin reductase, and ferredoxin) were utilized and compared in steady state assay. As expected, the biological reduction pathway is faster than the peroxide shunt; similarly the rate of isopentenylated RNA oligomer hydroxylation is significantly faster than the free nucleoside. The effect of interaction of enzyme with its substrate analog (ASL) was studied in peripheral as well as in relatively small active site level. Both circular dichroism (CD) and electron paramagnetic resonance (EPR) spectroscopy show a tight binding of MiaE with ASLβ. The EPR result indicates that the binding of ASLβ significantly alters the electronic structure and electronic relaxation rates of the reduced MiaE active site.

INOR 222

Redox-induced ligand switching in F82H cytochrome c

Kevin R. Hoke, khoke@berry.edu, Madison R. Chandler, Robert Quares, Department of Chemistry, Berry College, Mount Berry, GA 30149, United States

The structural behavior of cytochrome c is studied to better understand protein folding in general, as well as to the probe the specific roles of cytochrome c in cellular respiration and apoptosis. Mutation of the phenylalanine at position 82 in yeast cytochrome c perturbs the heme environment by increasing the exposure of the heme to solution and lowering its reduction potential. If a histidine is introduced at this position, the resulting mutant exhibits redox-dependent ligand switching. The reduced form prefers a near-native ligation of Met80 at the iron, but oxidation promotes the replacement of Met80 by His82. This His82-ligated form has a substantially lower potential than the Met80-ligated form. We are able to monitor the ligand exchange process in solution using cyclic voltammetry and functionalized gold electrodes. Oxidation of the reduced Met80-ligated form is followed by conversion to the His82-ligated form. Reduction of the oxidized His82-ligated form is followed by very rapid conversion to the Met80-ligated form. By varying the potential scan rate we can access different time domains for oxidation and reduction. At modest scan rates the two different forms each contribute an irreversible signal to the voltammetry, separated by about 350 mV. However, at high scan rates, we can outrun the ligand exchange and capture nearly reversible oxidation and reduction for the His82-ligated form. We have used digital simulation of the voltammetry to deduce ligand exchange rates for this system. In addition, we have examined the pH dependence of this system. Lowering the pH from 6 to 4 appears to greatly destabilize the structure of this mutant, lowering the reduction potential obtained for the Met80-bound form. This acid-induced destabilization occurs at a higher pH range than for wild-type cytochrome c.

INOR 223

Degradation of human hemoglobin by organic C-nitroso compounds

ye guan, guanye@ou.edu, jun yi, George Richter-Addo. Department of chemistry and biochemistry, university of oklahoma, norman, Oklahoma 73019, United States

The crystal structure of the nitrosomethane adduct of human Hb shows N-binding of the MeNO ligands to heme Fe. The structure of the EINO adduct reveals a surprising 4.9 Å heme slippage in the b subunit, and explains the ability of C-nitroso compounds to degrade Hb removing it from circulation.

INOR 224

Examination of the substrate specificity of the enzyme PcpA using synthetic model complexes

Jeremy Schofield, schofija@whitman.edu, Timothy E Machonkin, Patrick L Holland. (1) Department of Chemistry, Whitman College, Walla Walla, WA 99362, United States (2) Department of Chemistry, Yale University, New Haven, CT 06520, United States

PcpA is an oxidizing ring-cleaving enzyme in the pentachlorophenol breakdown pathway utilized by Sphingobium chlorophenolicum. The enzyme’s exact ring cleaving mechanism is not known; however, PcpA shows a high degree of substrate specificity, favoring 2,6-dihalogenated hydroquinones. Likewise, 2,6-dihalo phenols act as inhibitors (Machonkin, et al., Biochemistry, 2011, 50, 8899-8913). To better understand this enzyme’s substrate specificity, model complexes were prepared to mimic both substrate analog and inhibitor-binding to the PcpA active site. The ligand tris(3,5-dihydroxyphenyl)borato (TpPh)Fe(2,6-dibromophenolate), and (TpPh)Fe(2,6-dichlorophenolate), were synthesized and characterized by single crystal X-ray crystallography and 2H-NMR. The presence and strength of a halogen-metal secondary interaction were explored in these complexes.

INOR 225

Synthesis of heterometallic dinuclear nitrosyl compounds and their roles as electrocatalysts for H₂ reduction and H₂ evolution

Pokhraj Ghosh, pokhraj.ghosh@chem.tamu.edu, Chung-Hsiue Hsieh, Marcetta Y. Darensbourg. (1) Department of Chemistry, Texas A&M University, College Station, Texas 77840, United States (2) Department of Chemistry, Tamkang University, New Taipei City, Tamsui 25137, Taiwan Republic of China

Hydrogenase inspired solution electrocatalysts for the production of H₂ in the form of the plethora of diiron carbonyl complexes have established the requirement of a) nitrogen bridgehead in the μ-SRS unit for proton relay and for maintaining the butterfly shape of the 2Fe2S core; b) a redox active exogenous construct to delocalize redox activity for proton reduction. While modifications in the first generation electrocatalysts have provided insight into the mechanistic intricacies of proton reduction, highly active and robust molecular assemblies containing the necessary bio-inspired features to effect the catalytic performances are still needed. The present study deals with heterometallic dinuclear nitrosyl complexes with an open chain metallothiolato ligand bound to a second metal component that might show electrocatalytic response in an acidic medium. One such closed chain diiron trinitrosyl compound (Figure 1a) shows a cyclic
voltagmogram depicting two reversible redox events (E1/2 = -0.77 V and E1/2 = -1.41 V) corresponding to Fe(NO)2 and Fe(NO) units respectively (Figure 1b (inset)). The redox event (E1/2 = -0.77 V) displays good catalytic response in the presence of strong acid HBF4 (Figure 1b).

To expand the scope of such electrocatalysts we explore the following open chain metallothiolates (Figure 2) as ligands to redoxactive Fe(NO)2 unit. The open chain N2S2 ligand permits greater flexibility than the mesocycle framework. The redoxactive Fe(NO) vs. the Co(NO) allows the study of the influence of the magnetic properties on electrocatalysis.

INOR 226
Is HNO produced from the reaction of H2S with GSNO or HNSO?

Murugaeson Kumar, murugaeson_kumar@baylor.edu, Tara Clover, Patrick J Farmer. Department of Chemistry and Biochemistry, Baylor University, Waco, TX 76706, United States

Hydrogen sulfide (H2S) has recently been added to the panel of small molecule signaling agents like NO and CO implicated in vasodilation and prevention of myocardial ischaemia-reperfusion injury. Although the biological mechanisms by which H2S performs its function is still unclear, it may likely be due to reaction with Reactive Nitrogen Species like nitrite, GSNO, and nitrosyl hydride (HNO). This study describes attempts to characterize HNO produced from the reaction of H2S with GSNO or HNSO via secondary reactivity with deoxymyoglobin using kinetic analysis of UV-Vis absorbances and proton NMR data.

INOR 227
Formation and reactivity of a novel Fe-peroxynitrite species: A computational study

Jennifer Schmitt, jschmitt1531@gmail.com, Jason Shearer. Department of Chemistry, University of Reno, Nevada, reno, nevada 89503, United States

A recently disclosed quasi-stable iron peroxynitrite-nitrosyl species has displayed interesting reactivity, including the ability to facilitate phenol nitration reactions. This compound, [Fe(tmeda)(ONOO•)(NO)] (1), is formed by the low temperature addition of O2 to [Fe(tmeda)(NO)] (2). The properties, mode of action and formation of 1 are largely unknown. To better understand the inherent chemistries; we have employed electronic structure calculations on 1. Our results will provide mechanistic insight into the formation of 1 and its subsequent reactivity.

INOR 228
Computational studies of adenosine monophosphate dependent protein kinase: Phosphoryl transfer and ground- and transition-state analogs

Katherine N. Leigh, kleigh1@memphis.edu, Charles Edwin Webster. Department of Chemistry, The University of Memphis, Memphis, TN 38152, United States

Cyclic AMP-dependent protein kinase (cAMP) catalyzes the transfer of the γ phosphoryl group of ATP to the serine hydroxyl group of a peptide chain. The use of metal-fluoride ground-state [BeF2]- and transition state (MgF2- AlF2-) and putatively AlF3 analogues has added insight to the cAMP active site. Density functional theory calculations have been utilized to study the mechanism of phosphoryl transfer in cAMP as well as the structure and 19F NMR spectra of these ground-state and transition-state analogues. Transfer of native PO4- is associative in nature and utilizes a five-coordinate trigonal bipyramidal phosphorane transition state (TS). The relationship of the bonding in the TS to the 3-center 4-electron bonding model of stable phosphoranes was discussed. Simulated 19F NMR chemical shifts closely match experiment and demonstrate that cAMP priorizates constant charge (MgF2- or AlF3- analogues) over geometry (AlF3-).

INOR 229
Molecular assemblies as mimics of the complete H-cluster in diiron hydrogenase

Christopher C. Beto, chrisbeto@gmail.com, Ryan Bethel, Marcetta Y. Darenbourg. Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States

The [FeFe]-hydrogenase enzyme is capable of reducing protons to dihydrogen at a rate of 6000/sec. Bioorganic chemists have focused on synthesis and characterization of the 2Fe active site of the enzyme, which consists of a single azadithiolate ligand as well as three carbonyl and two cyanide ligands. This active site is bound to a 4Fe4S cluster buried in the core of the protein. A recent study of the biosynthesis of this unique 2Fe cluster has found that a (µ-S(CH3)$_2$I)[Fe2(CO)$_3$CN)$_2$ model complex can bind the 4Fe4S cluster of the scaffold protein (HydF) through a bridging cyanide, previously unknown in biology. In order to gain insight into this intermediate, a hydrogenase active site mimic was bound to a model of the 4Fe4S cluster through a cyanide bridge. A variety of (η$^5$-[C$_5$H$_4$]$^+$[Fe$_2$(CO)$_3$(CN)$_2$](THF)$_2$)$^+$ “piano stool” complexes were chosen to model the 4Fe4S cluster. Combinations of these piano stool compounds, [CpFe(CO)$_2$THF]$,^+$, CpFe(CO)$_2$CN, and [CpFe(CN)$_2$CO], and 2Fe site models, such as (µ-S(CH$\equiv$CH)$_2$S)[Fe2(CO)$_3$], (µ-S(CH$_3$)$_2$I)[Fe2(CO)$_3$CN], and (µ-S(CH$_3$)$_2$I)[Fe2(CO)$_3$(CN)$_2$]$^+$ were used to target either CpFe$^+$[µ-CN]FeFe$^0$ or CpFe$^0$[µ-NC]FeFe$^+$ bridging species. The individual precursors were prepared according to literature methods. The most successful attempt to prepare the three iron constructs resulted from combining CpFe(CO)$_2$THF$^+$ with (µ-S(CH$_3$)$_2$I)[Fe2(CO)$_3$CN] to yield a complex with the bridging cyanide. Infrared spectroscopy in the diatomic region, particularly v(CN) IR data indicates the bridging of cyanide from the 2Fe model complex to the CpFe$^+$ piano stool complex. Complexes were identified primarily through FTIR spectroscopy, but also using $^{13}$C NMR, Mass Spectroscopy, and X-Ray diffraction.

INOR 230
Characterization of retinal phosphodiesterase: Dependence of activity on zinc and cadmium concentration

Rose C Hadley, rosheadley@myfairpoint.net, Rick Cote$, Roy P Planap$. (1) Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824, United States (2) Molecular, Cellular, and Biomedical Sciences, University of New Hampshire, Durham, New Hampshire 03824, United States

Retinal phosphodiesterase (PDE6) is a metalloenzyme that modulates cyclic nucleotide concentration in the visual signal transduction pathway. Zinc, the native metal in the active site, promotes enzyme activity. However, heavy metal ions such as lead have been shown to inhibit PDE6. In this study, concentrations of zinc and cadmium promoting maximal PDE activity will be found using activity assays of the enzyme in the presence of known concentrations of free metal ions. Metal-buffered solutions will be prepared and quantified using a calibrated fluorescent indicator to provide known concentration of available metal ion to the protein. The outcomes of these studies will be described.

INOR 231
Synthesis and properties of water soluble N-heterocyclic carbene dinitrosyl iron complexes

Rachel B Chupik, rachel.chupik@chem.tamu.edu, Randara Pulukkody, Marcetta Y. Darenbourg. Department of Chemistry, TEXAS A&M UNIVERSITY, College Station, TX 77843, United States
Nitric oxide plays a major role in human physiology not only as a signaling agent and vasodilator, but also as a treatment for cardiovascular disease and possibly cancer. As such, compounds capable of NO storage and release (such as dinitrosyl iron complexes) are of interest in the development of therapeutic agents. In addition, metal N-heterocyclic carbene complexes (M-NHC, where M = PtII, PdII, AuI, AgI, CuI) have also shown potential as anticancer agents, with cytotoxicities in some cases equal to that of cisplatin. Hence, we seek to combine the cytotoxic properties of these two types of complexes by synthesis of N-heterocyclic carbene dinitrosyl iron complexes (NHC-DNICs). Necessary criteria for a compound to be considered for testing as a drug are both solubility and stability in water. These criteria may be met by functionalizing the R groups of the NHCs with water solubilizing groups such as SO3−, OH−, amides and sugars. Following reaction of the functionalized NHC with the DNIC, the water solubility and stability is monitored by 1H NMR and by IR, in the ν(NO) region. A particularly promising NHC is derived from 1,3-bis(4,6-dimethyl-3-sulfonatophenyl)imidazolium chloride (sIMesH+Cl−). The bulky sIMes is known to stabilize the formation of the cationic trinitrosyl iron complex (TNIC), thus providing a complex in which an additional NO may be released. Characterization of these NHC-DNICs includes X-ray crystallography, IR, NMR and EPR. In addition, the NO release ability will also be analyzed.

INOR 232
Syntheses and reactivity studies of Co-E (where E = group 14 element) containing complexes
Elizabeth M. Ward, emward423@gmail.com, Alan M. Stolzenberg, Shalini Moningi, Jessica Gutshall. Chemistry, West Virginia University, Morgantown, West Virginia 26506, United States

Compounds containing Co bound to the heavier group 14 elements are rare. Few of these compounds contain a Co that is coordinated by four nitrogen donors. Co4(α-lactethylporphyrin)SnR3 was previously found to be stable in air, while its analogous alkyl porphyrin was air sensitive. The unexpected inert behavior of the Co-Sn porphyrin led us to develop systems that would allow for the investigation of the reactivity of different Co-E containing compounds and help to explain the differences in their stability. Cobaloxime compounds with the general formula of (4-tBuPy)Co(DH)E3+ (where DH = a mononuclear of dimethylglyoxime) are used to examine the change in reactivity of the Co-E bond based on the group 14 element utilized as well as the identity of the alkyl or aryl group. The effect of coordination environment of the Co was also investigated by comparing six-coordinate cobaloxime compounds with five-coordinate Co(salen) and Co(saloph) compounds. The reactivity of these compounds was examined by cleavage of the Co-E bond through oxidation with I2 or Br2, electrochemical oxidation, thermal stability, and photolysis studies.

INOR 233
Biomimetic Mo-Cu model complexes of carbon monoxide dehydrogenase: Computational design and synthesis
Daniel Ellis, Ellisdr@whitman.edu, Dalia Rokhsana. Department of Chemistry, Whitman College, Walla Walla, WA 99362, United States

Molybdenum-containing carbon monoxide dehydrogenase (Mo-CODH) is an enzyme found in soil bacteria that catalyzes the oxidation of carbon monoxide (CO) to carbon dioxide in the presence of water. Mo-CODH contains two metal ions, molybdenum and copper, at its active site that are essential for its function. The unique chemical properties of this enzyme inspired us to design smaller synthetic catalysts for the oxidation of CO, which would have many environmental and industrial applications. To work towards developing a synthetic model of the enzyme, computational modeling was utilized to understand the properties of different designs in regards to metal oxidation states, steric constraints and other electronic properties. Several active site models of Mo-CODH were generated from our computational studies. These models provide insights into the requirement of certain features around the active site of Mo-CODH. The development of synthetic procedures is currently being performed.

INOR 234
Computational investigation of redox-dependent structural changes at the active site of molybdenum-copper carbon monoxide dehydrogenase
Tao A. G. Large, largeita@whitman.edu, Morgan C Dienst, Dalia Rokhsana. Department of Chemistry, Whitman College, Walla Walla, Washington 99362, United States

Molybdenum-containing carbon monoxide dehydrogenase (Mo-CODH) is a 277 kDa iron-sulfur flavoprotein found in the aerobic chemolithotrophic soil eubacterium Olegrobacter carboxidovorans. Mo-CODH catalyzes the oxidation of CO to CO2 in the presence of water, yielding two protons and two electrons, which have potential applications in the production of alternative fuels (e.g., H2 gas and syngas mixtures). CO conversion occurs at a binuclear Mo-Cu center, which is believed to be catalytically active in the Mo(VI)-Cu(I) oxidation state. This active state has been structurally characterized by X-ray diffraction; however, the metal oxidation state and coordination environment in the functional protein remain uncertain. To date, details of the proposed CO conversion mechanism remain elusive, and further investigation is required. In order to obtain an experimentally validated functional model, we have employed a systematic model-building approach, incorporating additional protein residues that are essential in modulating the geometric and electronic features of the active site. These models are being validated using experimental spectroscopic and redox potential data, and are also being used to investigate redox-dependent structural changes between the Mo(VI)-Cu(I) and Mo(V)-Cu(I) oxidation states, which are believed to be the states involved in the catalytic cycle. Results from our computational investigation have elucidated the effects of the protein environment on the geometric and electronic features of the active site, and will enable us to probe the catalytic mechanism in further detail.

INOR 235
Metal-metal interactions in compounds with 1,1'-bis(phosphino)methane/ligand complexes
Emily G Lubas, lubase@lafayette.edu, Eugene P Warnick, Margaret A Tiedemann, Chip Nataro. Department of Chemistry, Lafayette College, Easton, PA 18042, United States

Two different synthetic methodologies were employed in the preparation of compounds having an interaction between the metal of a 1,1'-bis(phosphino)metallicigand and a second metal center. The first method was halide abstraction from compounds with a general formula of [M(PP)Cl2] (M = Ni, Pd or Pt). In the course of these studies, the electrochemistry and complexation of several new 1,1'-bis(phosphino)ferrocene ligands was examined. The metal-metal interaction was only observed for compounds with bulky substituents on the phosphorus atoms of the 1,1'-bis(phosphino)metallicigand. The electrochemistry of these compounds was examined. In addition, the crystal structures of several compounds were determined. The second method used was ligand substitution to yield compounds of the general formula [M(PP)(PR3)2]+. These compounds were all examined electrochemically and in several cases crystallographically. In both types of compounds, there is a weak interaction between the metal of the 1,1'-bis(phosphino)metallicigand and the second metal center.

INOR 236
Enantio-enrichment of (TpW(NO)(PMe3)) deamortization agent
Andrew W. Lankena, awl4bg@virginia.edu, Jared A. Pienkos, W. Dean Harman, William H. Myers. (1) Department of Chemistry, University of Virginia, 409 McCormick Road, Charlottesville, VA 22904, United States (2) Department of Chemistry, University of Richmond, Richmond, VA 23173, United States

In the past several years, τ-R-deamortization has been used to modify arenes and produce novel organic compounds. The (TpW(NO)(PMe3)) fragment has proven to be a viable synthetic tool as it is scalable, non-toxic, and cost-effective; however there has been limited success in resolving
enantiomerically enriched forms of this metal center. A new methodology for resolution of the racemic dearomatizing agent (TpW(NO)(PMe₃)) is currently being developed. In this approach, 1,3-dimethoxybenzene is bound to (TpW(NO)(PMe₃)) and protonated via chiral acid, producing two diastereomeric salts. Accordingly, separation of the diastereomers via crystallization, precipitation, and chromatography is being tested. Should separation be achieved, the two diastereomers may be deprotonated and exchanged with other aromatic ligands to form enantio-enriched η²-species. These systems, which include deaomtized arenes, may be used to facilitate electrophilic addition and cycloaddition reactions on the ring. Finally, the enriched organic product may be removed from the metal via oxidation.

Example chiral acids that have demonstrated clean protonation of theTpW(NO)(PMe₃)(5,6-η²-1,3-dimethoxybenzene) complex include (S)-camphor sulfonic acid, L-tartaric acid, L-dibenzoyltartaric acid, and L-di-p-toluoyltartaric acid. In some cases, the resulting diastereomers may be distinguished from each other in a ¹H-NMR spectrum, with near baseline splitting occurring for certain Tp and ring protons. Integration of these “split” peaks provides a measurement of the enantiomeric excess of the mixture. Evidently, this spectroscopic technique proves to be a facile alternative to other methods, such as chiral HPLC, when determining the degree of resolution. With these techniques and spectroscopic methods in hand, unique enanti-enriched products derived from the (TpW(NO)(PMe₃)) deaomtizing system may soon be obtained.

INOR 237
Synthesis and reactivity of tungsten and molybdenum carbon dioxide complexes
Robert G. Carden, rc540395@sju.edu, James J. Ohanec, jo544668@sju.edu, Michael A. Bogash, Peter M. Graham. Department of Chemistry, Saint Joseph’s University, Philadelphia, Pennsylvania 19131, United States

Tungsten and molybdenum η²-carbon dioxide complexes of the form TpM(NO)(L)(η²-CO₂), where M = W or Mo, Tp = tris(pyrazolyl)borate, and L = PMe₃ or 1-methylimidazolide, have been prepared via ligand substitution under elevated carbon dioxide pressure. Molybdenum η²-carbon dioxide analogs, where L = 1-methylimidazolide, 4-dimethylaminopyridine, and PMe₃ have been prepared via the oxidation of the carbonyl in TpMo(NO)(L)(CO). Tris(3,5-dimethylpyrazolyl)borate (Tp*) molybdenum analogs have also been isolated. These complexes have been characterized by X-ray crystallography, cyclic voltammetry, IR, and NMR spectroscopy. The η²-CO₂ complexes are air-stable, resist decomposition in solution, and most can be prepared on the bench top without specialized equipment to exclude air. Reduction of the molybdenum η²-carbon dioxide ligand to a molybdenum carbonyl can be accomplished using chemical reductants.

INOR 238
Transition metal complexes containing the 7-azaindole ligand
Monica L. Kiewit, vxf522@my.utsa.edu, Zachary J Tonzetich. Department of Chemistry, University of Texas at San Antonio, San Antonio, T 78249, United States

Divalent first-row transition metal complexes containing the 7-azaindole ligand have been prepared and characterized. The reactivity and electrochemical behavior of the compounds is described, as are several solid-state structures. The utility of the compounds in simple C-C cross-coupling reactions has also been evaluated.

INOR 239
Microwave-assisted, copper-catalyzed concurrent tandem catalytic methodology for the amidation of aryl halides
Jasmine L. Sarjeant, lin@usna.edu, James A. Mills, lin@usna.edu, Douglas J. Brown, Shirley Lin, Amy H Roy MacArthur. Department of Chemistry, United States Naval Academy, Annapolis, MD 21402, United States

The amidation of aryl bromides and aryl chlorides has been reported to occur thermally in the presence of a catalytic amount of Cu(I) and certain diamine ligands. Such reactions typically require temperatures as high as 130 °C and long reaction times (>15 hours) to achieve high yields. Comparable yields after only 30-120 minutes are obtained by performing these reactions using a microwave-assisted, concurrent tandem catalytic (CTC) methodology in which the aryl bromide or aryl chloride is converted to an aryl iodide in situ, followed by amidation of the aryl iodide. Optimized reaction conditions for this transformation and substrate scope of this CTC methodology will be presented.

Note: this project is co-mentored by a CENTC alumna.

INOR 240
Synthesis of pyridyl substituted carbene complexes of nickel: In search of new chemical catalysts
Meagan Callis, mecall3746@ung.edu, Andrew Puetz, Ryan M Meier, ryan.meier@ung.edu. Department of Chemistry and Biochemistry, University of North Georgia, Dahlonega, Ga 30533, United States

In recent years there has been a growing trend to make catalysts incorporating first row transition metals as cheaper and greener alternatives to platinum group metals. Challenges that must be overcome in this process include the problem that precious metals complexes undergo 2-electron oxidation/reductions. In comparison, first row metal complexes are generally high spin unless they are in high oxidation states or bound to very strong field ligands and also undergo many 1-electron oxidation/reductions. This project has focused on the preparation of a series of pyridyl substituted N-heterocyclic carbanes as ligands to form novel complexes with nickel in an effort to help address some of the above challenges. The strong σ-donation properties and rigid structure of the ligands will hopefully help to overcome the high-spin tendency of first row metals while taking advantage of nickel's 2 electron oxidation/reduction cycle from nickel(0) to nickel(II). The synthesis and characterization of the pyridyl-substituted carbene ligands and their nickel complexes will be presented.

INOR 241
PDI-pincer ligands with a modifiable secondary coordination sphere: Synthesis, characterization, and application to transition-metal catalysis
Trevor W Butcher, twbutcher@mix.vwu.edu, Vaishali Vajpayee, Brian V Popp. C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States

Multifunctional ligands that allow for complexion of multiple metals or display of donor/acceptor functionality in the secondary coordination sphere continue to be of key interest for small molecule activation and synthetic methodology development. We have targeted the NNN-pincer from pyridinediimine as a modular framework that allows facile synthetic access to a variety of ancillary functional groups by judicious choice of primary alkyamine condensation reagent. The synthesis of these new multifunctional ligands will be discussed as well as the preparation and characterization of first-row late-transition-metal complexes featuring the ligands. Preliminary investigations of these complexes catalytic reactivity for electrocatalytic hydrogen gas generation will also be presented.

INOR 242
Exploring a modular approach to chiral tetradentate aminosulfoxide ligands through two different undergraduate research formats

Tim J Brunker, tbrunker@towson.edu, Department of Chemistry, Towson University, Towson, MD 21252, United States

Single enantiomer, linear, tetradentate aminosulfoxide ligands can be synthesized by the reaction of symmetrical diamines (HNR\(^+\)-(CH\(_2\))\(_n\)-NHR\(^-\)) with enantioselectively pure vinyl sulfones (H-C=CH-S(O)R\(^2\)). Such ligands are of interest in the formation of chiral octahedral metal complexes with applications in asymmetric catalysis or molecular switching through linkage isomerism of the sulfoxide donors. Of particular interest is the relationship between the ligand structure and metal complex geometric isomerism. Three isomers (trans, cis-alpha and cis-beta) arise from the wrapping of the ligand around a 6-coordinate metal center such as Ru(II), but the product distribution is highly dependent on ligand structure. These relationships have been explored in two research formats. Traditional, individual research projects in the mentor’s lab explored variation of the diamine backbone components, \(R^1\) and \(n\), with a single sulfoxide precursor (\(R^2\) = p-tol) yielding 7 different ligands and a variety of RuCl\(_3\) complexes. In an advanced synthesis lab course with an enrollment of 10 students meeting once a week for 4 hours, the syntheses of vinyl sulfones varying in \(R^2\) was explored. All students used a common methodology to prepare 5 key intermediates – diastereometrically-pure sulfinate esters. These were then further elaborated to the vinyl sulfone and final ligands using two different diamines. The advantages and disadvantages of both approaches, and the possibility of providing authentic undergraduate research experiences to larger numbers of chemistry majors at a primarily undergraduate institution will be discussed.

INOR 243

\(N\)-heterocyclic carbene platinum(II) complexes for catalytic olefin hydroarylation

Anna M Brosnahan\(^1\), amb999@virginia.edu, Bradley A McKewon\(^1\), Steven E Kalman\(^1\), Hector E Gonzales\(^2\), T. Brent Gunnoe\(^1\), Thomas R Cundari\(^1\). (1) Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States (2) Department of Chemistry, University of North Texas, Denton, Texas 76203, United States

Cationic Pt(II) complexes supported with 2,2'-bipyridyl (bpy) ligands have been shown to be effective catalysts for olefin hydroarylation. The donor ability of 4,4'-disubstituted bpy ligands impacts the selectivity and longevity of the catalyst. Thus, we sought to prepare \(N\)-heterocyclic carbene complexes with Pt(II) metal centers in an attempt to generate catalysts with strongly donating ancillary ligands. Complexes such as \([([Imes]^\dagger)Pt(Me)][BAR]_4\) (Imes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene, \(\text{Imes}^\dagger = 3,5\)-bis(trifluoromethyl)phenyl), \([([Imes]_2)Pt(Me)(NCMe)][BAR]_4\), and \([([IPr]Pt(\mu-\mu)][IPr]_2)(IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)\) were isolated as potential catalyst precursors. Preliminary results suggest these NHC-Pt complexes catalyze olefin hydroarylation. This presentation will focus on the synthesis and characterization of these Pt(II) complexes and evaluation of their efficacy as catalysts for olefin hydroarylation.

INOR 244

One-pot synthesis and characterization of new cationic (\(\dagger\)-allyl)Ni(II) complexes containing pendant alkylphosphonate groups

Jacob L. Levene, levenej1@tcnj.edu, James M. O’Connor, Abby R. O’Connor. Chemistry, The College of New Jersey, Ewing, NJ 08628, United States

Not much progress has been made to identify alternate ways to hydrogenate olefins using less expensive homogeneous catalysts. A more sustainable way to hydrogenate olefins to alkanes could be achieved through the development of homogeneous nickel complexes to serve as catalysts. Work in this group is focused on the synthesis of nickel complexes to catalyze the hydrogenation of olefins. Eight new cationic (\(\dagger\)-allyl)nickel complexes containing a pendant phosphonate group and either 2-bromobenzonitrile or triphenylphosphine ligands and different non-coordinating counteranions have been synthesized using a convenient one-pot method. The complexes were characterized by \(^1H\), \(^31P\), and \(^{13}C\) NMR spectroscopy and X-ray crystallography. Progress towards the synthesis and characterization of the complexes and preliminary results evaluating the isomerization of 1-pentene with each complex are described.

INOR 245

Synthesis, characterization, and reactivity of (\(\dagger\)-allyl)nickel complexes to serve as catalysts for norbornene polymerization

Michael McDaniel, mcdanim1@tcnj.edu, Abby R. O’Connor, Benny C. Chan. Department of Chemistry, The College of New Jersey, Ewing, NJ 08628, United States

The polymerization of alkenes and dienes has been investigated using a variety of nickel catalysts. However, the polymerization of non-polar and polar monomers and living polymerization have remained as challenges. Living polymerization is particularly important in order to control polymer weight and chain length. This work describes the synthesis and characterization of new neutral and cationic (\(\dagger\)-allyl)nickel complexes containing dialkyldiaryl phosphate ligands to serve as catalysts for polymerization reactions. The pendant arene ring on the bulky phosphate ligand weakly coordinates to the metal and acts as a hemilabile group to stabilize the 14-electron nickel center. A library of complexes with different steric and electronic parameters has been synthesized and characterized using multinuclear-variable temperature NMR spectroscopy and X-ray crystallography. An unexpected side reaction was observed during the preparation of the cationic complexes. A phosphonium salt was isolated in good yield and is formed by coupling of the allyl group and the phosphate ligand. This reaction pathway may lead to other potential catalytic reactions. Preliminary polymerization reactivity of these complexes with norbornene is also described.

INOR 246

WITHDRAWN

INOR 247

Iridium-catalyzed acceptorless dehydrogenation of alkanes

Kelsey H Jensen, achiyanese@colgate.edu, Anthony R Chianese. Department of Chemistry, Colgate University, Hamilton, NY 13346, United States

Iridium complexes of CCC-pincer bis-N-heterocyclic carbene, including a newly synthesized trifluoromethyl-substituted complex, were examined as catalysts for the acceptorless dehydrogenation of cyclooctane and n-undecane. Up to 103 turnovers were observed for cyclooctane, and up to 97 turnovers were observed for n-undecane. The catalysts showed high initial turnover frequencies, followed by a gradual loss of activity over 24 hours. Experiments indicate that this loss of activity is due to catalyst decomposition rather than product inhibition.

INOR 248

Alkene isomerization catalyzed by CCC-pincer complexes of iridium

Daniel Kim, achiyanese@colgate.edu, Anthony R Chianese. Department of Chemistry, Colgate University, Hamilton, NY 13346, United States

Iridium complexes of CCC-pincer bis-N-heterocyclic carbene ligands are active catalysts for the isomerization of terminal alkenes to the internal isomers. Herein, we report time-course studies of alkene isomerization for various substrates, and deuterium-labeling studies that reveal a mechanistic dichotomy. A mesityl-substituted ligand promotes alkene isomerization through pi-allyl intermediates, while an adamantyl-substituted variant appears to proceed via metal-alkyl intermediates.

INOR 249
Probing the mechanism of dehydrogenation of primary amines to nitriles by an iridium PCP-pincer complex

Hussnain Sajjad, sajjadh1@tcnj.edu, David A. Laviska. Department of Chemistry, The College of New Jersey, Ewing, New Jersey 08628, United States

The Center for Enabling New Technologies Through Catalysis (CENTC) has been encouraging cutting edge research on the activation and transformation of strong bonds (C-H, C=C, etc.) since its inception in 2007. Our current research reflects the influence of CENTC both in spirit (high impact research on potentially catalytic processes) and in concept (much of the reference literature for this project was published by CENTC members). Dehydrogenation of amines to reactive and desirable synths such as nitriles, enamines, and imines has been reported for a variety of transition metal complexes. While the iridium fragment (tBuPCP)Ir (tBuPCP = κ\(^3\)-2,6-bis(di-tert-butylphosphino)methylphenyl) has been shown to catalytically transform secondary and tertiary amines into imines and enamines, respectively, generation of nitriles from primary amines has received little attention. Recent experiments in our group have shown that benzylicamine will undergo double transfer dehydrogenation to give benzonoitrile, using (tBuPCP)Ir and norborne as the olefin acceptor. Surprisingly, (tBuPCP)Ir will also facilitate the reverse reaction and hydrogenate the nitride under certain conditions. Benzoctriazole, as well as benzylicamine and the intermediate benzonitriyl all show favorable N-coordination to iridium. The potential for catalytic conversion to the nitrile product and the mechanisms of these transformations are being explored.

INOR 250

Microwave-assisted reactions of Os\(_3\)(CO)\(_{12}\) with substituted acetylenes

Erin K. Fry, ek111a@acu.edu, Stephanie M. Martin, Cynthia B. Powell. Department of Chemistry & Biochemistry, Abilene Christian University, Abilene, Texas 79699, United States

The triosmium cluster Os\(_3\)(CO)\(_{12}\) is a common starting material for osmium cluster synthesis. The activated derivative Os\(_3\)(CO)\(_{11}\)(NCMe) was synthesized using a simple microwave reactor procedure and immediately reacted with substituted acetylenes Ph-C\(_2\)C, Ph\(_2\)C=CH, and (Si(CH\(_3\))\(_3\))C\(_2\). Products of the acetylene reactions include the dimers (Ph\(_2\)C\(_2\))Os\(_2\)(CO)\(_{12}\), (Ph\(_2\)C\(_2\))Os\(_2\)(CO)\(_{12}\), and the cluster HO\(_2\)(CO)\(_2\)(SiMe\(_3\)). While these products have all been previously reported, the traditional synthetic approaches give small yields. We were able to produce them with yields of 45%-55% via microwave heating and obtained the first X-ray crystal structure of (Ph\(_2\)C\(_2\))Os\(_2\)(CO)\(_{12}\). The structure of (Ph\(_2\)C\(_2\))Os\(_2\)(CO)\(_{12}\) confirms that two acetylene units dimerize and coordinate with one osmium atom in the compound to form an osmacycle.

INOR 251

Augmented nuclearity in gold(I) arrays with disparate NN-, CC-donor bridges

Doris Y. Melgarejo, dymy20@yahoo.com, Gina M. Chiarella, John P. Fackler. Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, United States

Contrasting gold(I) affinity to C and N on electronegativity arguments may hinder the assembly of gold(I) arrays with mixed N-, C-donor bridges. Bridging CPC-ylide [Y] and NCN-formamidinate [F] separately render dull luminescent gold(I) dinuclear compounds. The need was to obtain a hybrid dimer [Au\(_n\)FY\(_2\)] to study the combined effects on structure and luminescence

Poly-nuclear (Au\(_n\)Au\(_n\)Au\(_n\)) arrays with opposite \(N\)-Au-C bonds are obtained under Schlenk conditions; formamidinate aurophilically bridges gold(I) (Au-NCN-Au); depending on basality the ylide mono-coordinates (Hy-Au) or bridges (Au-CPC-Au)

The series comprises two trinuclear clusters [Au\(_3\)FY\(_3\)] [Au\(_3\)FY\(_2\)Y]; three open dinuclear [Au\(_3\)F(HY)\(_2\)]NO\(_3\), [Au\(_3\)F(HY)] and [Au\(_3\)F(HY)]PF\(_6\). Basic activation of the ylide releases phenyls found in [Ph-AuF(HY)] and in tetranuclear [Ph-AuF(HY)Au\(_2\)F(HY)Ph-].

A unique cubal assembly [Au\(_4\)F\(_3\)(n\(^5\)-Y)\(_3\)] featuring two rare hypercoordinating carbons is promoted by gold-carbon affinity and the tendency of gold(I) to aggregate.

Due to Au-Au distance constraints the sought [Au\(_n\)FY\(_2\)] hybrid is successfully synthesized from gold(I) precursor [Au\(_n\)F\(_3\)NO\(_3\)] by oxidation of the ylide ligand

The mixed bridging N- C- coordination enhances luminescent properties as compared to non-luminescent Au-N, Au-Y parents and an ylide only trinuclear [Au\(_3\)Y\(_3\)] Compounds are characterized by X-ray crystallography, IR, NMR elemental analysis and luminescence spectroscopy.

INOR 252

Theoretical and model complexes (N\(_2\))\(_M\) (L) stabilized by intramolecular hydrogen bonding (M = K, L = aza-18-crown-6, hexaaza-18-crown-6; M = Na, L = pentaaza-15-crown-5; M = Li, L = tetraaza-12-crown-4)

Issam Kobrsl, ikobrsl@pi.ac.ae, Ian McNaught, Oussama El-Kadri, Pance Naumov. (1) Department of Chemistry, The Petroleum Institute, Abu Dhabi, United Arab Emirates (2) Department of Biology, Chemistry, and Environmental Sciences, American University of Sharjah, Sharjah, United Arab Emirates (3) Department of Chemistry, New York University Abu Dhabi, Abu Dhabi, United Arab Emirates

The cyclopentazolate anion, cyclo-N\(_5\)\(^-\), simply known as pentazolate, is an elusive molecular ion that has been theorized to exist as a stable entity ever since the synthesis of arylpentazoles by Ugi and Huisgen. All efforts to isolate pentazolate as a stable complex have thus far been unfruitful. The interest in pentazolate stems from its potential use as a high energy density material and particularly as a solid fuel. Several groups have in recent years been able to generate pentazolate in the gas phase and study it by spectroscopy. We have previously reported the potential use of group 1 and 2 metal salts supported by crown ethers to stabilize the pentazolate anion. This stabilization was due to intramolecular CH\(_\equiv\)N interactions between the H-atoms on the crown ether and the N-atoms on the pentazolate anion as shown by DFT calculations. This was mirrored by experiment using disopropylaminotetrazolate as a model ligand for pentazolate. In this report, DFT calculations showed that substituting one or more O atoms with NH in the crown ether maximizes the intramolecular H-bonding between pentazolate and crown, having direct consequence on structure and stability. A model complex, (aqua)(3,5-dimethylpyrazolate)potassium(aza-18-crown-6) was isolated and fully characterized spectroscopically and structurally. The complex exhibits tilted geometry of the pyrazolate core towards the plane of the crown ether. DFT calculations indicate that the HOMO comprises orbital overlap between the NH of the aza-18-crown-6 and the two N atoms of the pyrazolate ligand.

INOR 253

Copper and silver guanidinate complexes with luminescence properties
A series of tetranuclear Cu(I) and Ag(I) complexes with bicyclic guanidinate ligands have been synthesized, the Metal-Metal distances in the crystal structure show rhombic arrangements with short contacts between two opposite metal atoms that depend on the bite angle of the ligand. The synthesized compounds are Cu(tbo), Cu(tbn), Ag(tbo), and Ag(tbn) where tbo is the anion of a bicyclic guanidinate with two five-membered rings (the anion of 1,4,6-triazabicyclo[3.3.0]oct-4-ene) and tbn is an similar species with six- and five-membered rings (1,5,7-triazabicyclo[4.3.0]non-6-ene). The rhombic arrangement of the structures suggests the presence of some weak cuprophilic and argentophilic interactions between to opposite metals. All four compounds are robust in ambient conditions and present luminescent properties in the solid state at room temperature.

**INOR 254**

Synthesis of lanthanide complex containing heteroleptic ligands

Pong K Yuen, pkyuen@umac.mo, Cheng Man Diana Lau. (1) Faculty of Science and Technology, Macau Chemical Society and University of Macau, Macau, Macau, China (2) Faculty of Management and Administration, Macau University of Science and Technology, Macau, Macau, China

Lanthanide metals and their complexes have been widely applied in the fields of material science; biological science; medical science and organic synthesis due to their unique spectral, electrical and magnetic properties. The properties and applications rely on the structures of lanthanide complexes. The design, synthesis and structural characterization of lanthanides complexes have been given much attention. The authors are interested in synthesizing new types of lanthanide complexes. A series of lanthanide complexes containing various types of ligands have been synthesized and structurally characterized in our group. Here the paper reports the synthesis and X-ray crystallography of mononuclear ytterbium (III) complex containing salen and Tp ligands, which exhibits remarkable properties.

**INOR 255**

Two novel zeolitic imidazolate frameworks (ZIFs) with high porosity, high thermal and chemical stability

Sajani A Basnayake, sab096120@utdallas.edu, Mark Rudolph, Kenneth J Balkus. Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080, United States

Zeolitic Imidazolate Frameworks (ZIFs) are porous inorganic-hybrid materials with crystalline three dimensional networks. These contain metal ions tetrahedrally connected to imidazolate type linkers mimicking zeolite topologies and thus called Zeolitic Imidazolate Frameworks. We have synthesized two new bisimidazolate type linkers (N$^\text{E}$-N$^\text{E}$)-N$^\text{N}$-bis-[1H-imidazol-2-yl]benzene-1,4-diamine (BIM-2) and (1E,1'E)-N$^\text{N}$-((1R,2R)-cyclohexane-1,2-diy|bis-[1H-imidazol-4-yl]methanimine) (BIM-5) by employing Schiff base type reactions of an imidazole-carboxaldehyde with two different types of diamines. These linkers have proven the ability to form new ZIFs when they are reacted with Zn$^{2+}$ under very mild reaction conditions. These ZIFs have chemically stable porous crystalline structures with thermal stabilities above 300 °C indicating their potential to be used in gas separation, storage and catalysis applications. One of the ZIFs has a low angle peak in the powder X-ray diffraction pattern signaling the presence of large unit cell and hence may have potential applications involving large molecules.

**INOR 256**

Computational and experimental investigation of the Lewis acid character of Ru$_2$(II,II) paddlewheel complexes with (N,O) ligands

Tristan R. Brown, tbrown@chem.wisc.edu. Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53760, United States

Reduction of (4,0)-Ru$_2$(chp)$_2$Cl (chp = 6-chloro-2-oxypyridinate) with zinc in various solvents leads to the formation of a series of axial ligand adducts of the diruthenium(II,II) species, Ru$_2$(chp)$_2$L (L = THF, pyridine, DMSO, or acetonitrile). Ligands within a narrow range of donating character form the solvent adducts. Zn reduction in poorly coordinating solvents such as dichloromethane or toluene provides evidence that the solvent adduct Ru$_2$Ru$^{2+}$-bound dimethylsulfoxide adduct should have the novel E$_{\text{chp}}$(π*)$\to$δ* ground state, as indicated by their electronic spectra, crystal structure Ru$_2$Ru distances, and DFT calculations. Electronic absorption spectra of the Ru$_2$(II,II) solvent adducts were modeled using TDDFT calculations, allowing unambiguous assignment of the band in the 11,000-13,000 cm$^{-1}$ range in each of these spectra as the δ*→σ* transition. From these energies, it was observed that the axial ligand's σ-donating character heavily influences the δ*→σ* gap for this class of compounds, leading to the prediction that an S-bound dimethylsulfoxide adduct should have the novel E$_{\text{chp}}$(π*)$\to$δ* ground state. Computational modeling of the electronic absorption spectrum for δ in CH$_2$Cl$_2$ provides evidence that the solvent adduct(Ru$_2$(chp)$_2$(CH$_2$Cl$_2$) may be present as a transient species.

**INOR 257**

Coordination polymers based on 1,3-alternate calix[4]arene tetrabenzoic acid: Design, synthesis and structure

Sappachai Krajangsri, Nongnju Muangsin, Buncha Pulpoka. buncha.p@chula.ac.th. Department of Chemistry, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand

A series of coordination polymers based on 1,3-alternate calix[4]arene tetracarboxylic acids derivatives and zinc (II) and cadmium (II) ions is presented. The ligands, 1,3-alternate calix[4]arene tetrabenzoic acid, have carboxylic groups at different positions namely para and meta positions which provides different coordination geometries. The preparation of the coordination polymers were started by synthesis of ligands by tetrasubstitution of calix[4]arene by bromomethylbenzoic acid in distal manner in 3 steps. The obtained ligands were employed in coordination polymers with zinc (II) and cadmium (II) ions in dimethylformamide solvent by solvothermal synthesis. The obtained 1,3-alternate calix[4]arene-based coordination polymers were investigated for their morphologies by SEM which were found in various forms, such as needle-like, cubic, rod and platelet shapes. The single-crystal structures of zinc (II) and cadmium (II) coordination polymers have been characterized by sc-XRD technique. The single-crystal structure of Zn(II)-1,3-alternate calix[4]arene tetra-p-benzoate polymer (named, CU-SCRU1) exhibits as three dimension structure via the arrangement of the polymeric coordinated linear chain.
In the coordination polymer that synthesized by using 1,3-alternate calix[4]arene tetra-m-benzoic acid and Zn(II) ion (named, CU-SCRU2), the coordinated bond formed between ligand and Zn(II) ion provided a zig-zag polymeric chain which is extended by intermolecular interaction to provide the three dimension framework. Moreover, the reaction of 1,3-alternate calix[4]arene tetra-m-benzoic acid and Cd(II) ion yielded two different single-crystal structures crystallizing in monoclinic (named, CU-SCRU3) and orthorhombic (named, CU-SCRU4) crystal systems. Their single crystal X-ray diffraction study reveals that they are three dimensional frameworks.

INOR 258
Synthesis and volatility characteristics of novel hafnium complexes employing β-ketoiminato and β-diketiminato ligand systems

Ernesto Ballesteros, Leslie Pineda, Bradley D Fahlman, fahlmbt@cmich.edu. (1) Department of Chemistry and Science of Advanced Materials Program, Central Michigan University, Mount Pleasant, MI 48859, United States (2) Department of Chemistry, University of Costa Rica, San Jose, CR, Costa Rica

In our search for new precursors for hafnium oxide thin film deposition, we will describe the synthesis and characterization of a variety of Hf(IV) complexes featuring β-ketoiminato and β-diketiminato ligands. The complexes were characterized by 1H,13C NMR spectroscopy, single-crystal X-ray crystallography, and TGA/DSC. The substituent effects toward resultant volatility will be described, as well as the final purity of HfOx films grown by chemical vapor deposition (CVD).

INOR 259
Co-ligand effects on the structural chemistry of bismuth perfluorinated-alkoxides

Cody C Webb Jr1,2, webbc@lemoyne.edu, Alan Goos1, aggoos@syr.edu, Anna O’Brien2, Karin Ruhlandt1. (1) Department of Chemistry, Syracuse University, Syracuse, NY 13244, United States (2) Department of Chemistry and Physics, Le Moyne College, Syracuse, NY 13214, United States

Alkaline earth metal bismuth containing materials such as Bi2Sr2CaCu2Ox have important applications for electronic thin films. These are prepared by metal organic chemical vapor deposition (MOCVD) using alkali earth metal and bismuth precursors. Such precursors ideally sublime intact and allow precise stoichiometric control. Currently used MOCVD precursors require relatively high temperatures. In an effort to develop a system that would provide exact stoichiometric control and low deposition temperatures, we aim to develop a heterobimetallic system containing the heavy alkaline earth metal and bismuth in conjunction with the perfluorinated ligand system nonafluoro-tert-butoxide. This system has been proven to be advantageous in providing heterobimetallic systems involving alkali/alkaline earth/rare earth metals. In fact, some heterobimetallic compounds bearing this ligand display unprecedented volatility and clean sublimation. We here report on studies to prepare bismuth perfluorinated complexes bearing various co-ligands and combine those with the known alkaline earth analogues to afford the heterobimetallic compounds.

INOR 260
Syntheses and characterization of Ta(=NSiMe3)2[N(SiMe3)2]X2 (X = CH2Ph, NMe2)

Seth C. Hunter, shunte16@utk.edu, Zi-Ling (Ben) Xue. Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, United States

Ta(=NSiMe3)2[N(SiMe3)2]X2 (X = CH2Ph, 1 : NMe2, 2) have been prepared from the reactions of [Ta(μ-Cl)(=NSiMe3)2[N(SiMe3)2]]2 with CMg(CH2Ph) and LiNMe2, respectively. 2 has also been prepared from Cl, Ta[N(SiMe3)2]3 and LiNMe2. Our syntheses and characterization of the complexes and their reactions are presented.

INOR 261
Iron, cobalt, and nickel complexes of electronically varied dithiocarbamate ligands

Emily C. Sylvester, esylvester@wju.edu, Mary E. Railing, Katlyn Lucas, Gabriella Azzarello. Department of Chemistry, Wheeling Jesuit University, Wheeling, WV 26003, United States

Dithiocarbamate ligands with simple alkyl or aryl substituents are well known in coordination chemistry. Less common are dithiocarbamates derived from significantly electron-withdrawing or electron-donating amines. A series of iron, cobalt, and nickel dithiocarbamate complexes with electronically varied substituents have been prepared and characterized. Synthetic details, spectroscopic characterization, and magnetic susceptibility measurements will be presented.

INOR 262
Synthesis and characterization of [Pd2(HD-3-pyF⊃Cl)2]: A new chloride ion inclusion complex

Steven C Haefer, shaefner@bridgew.edu, Joseph Matta. Department of Chemical Sciences, Bridgewater State University, Bridgewater, MA 02325, United States

Our group is developing new formamide ligands that possess substituents capable of binding additional metal ions. Work by Cotton and others have shown that formamidinates are versatile ligands for stabilizing a wide range of metal-metal bonded complexes. These complexes typically adopt the familiar paddle wheel geometry common among dimetal tetracarboxylate complexes. Our goal is to replace the typical aryl groups with pyridyl substituents. It is anticipated that these pyridyl groups will provide additional donor sites in order to link the individual paddlewheel complexes through complexation with other metal ions. To this end we have had successfully prepared and structurally characterized di-3-pyridyl-formamidine (HD-3-pyF). Reaction of HD-3-pyF with PdCl2 via slow diffusion produces the dipalladium compound [Pd2(HD-3-pyF⊃Cl)2]. An X-ray crystal structure reveals that the pyridyl groups of the four formamide ligands coordinate to the two Pd2+ centers creating a cage like structure that has encapsulated a non-coordinated Cl- ion. The formamide nitrogens are directed outward and form a hydrogen bonded network with the remaining chloride ions. Details about the synthesis, characterization, and reactivity of this novel complex will be presented.

INOR 263
Synthesis, characterization and antibacterial activity of Cu(II) complexes with multidentate pyridyl ligands: X-ray crystal structure of an alkoxo-bridged cubane-like tetracnuclear Cu(II) complex

Dong-Heon Lee, dhl@jbnu.ac.kr, Soo Yeon Lee, Hyun Jin Jung, Se Ri Lim. Department of Chemistry, Chonbuk National University, Jeonju, Jeollabukdo 561-756, Republic of Korea
Transition metal complexes with pyridyl-based chelates have been studied in detail, largely because of their catalytic abilities, biological significance, sensor applications, and so on. We have synthesized new multidentate pyridyl ligands and their Cu(II) complexes. The interaction of N,N′-dimethyl-N,N′-bis(pyridin-2-yl)methanediamine (DMPA, 1) with Cu(ClO$_4$)$_2$ salts yields [(DMPA)$_2$Cu(ClO$_4$)$_2$], 2, slow decomposition of which in methanol unexpectedly led to the formation of an alkoxo-bridged cubane-like tetranuclear copper(II) complex, 3. Complex 3 crystallizes in the monoclinic space group P21/c and consists of a tetranuclear [Cu$_4$O$_6$] cubane core in which four copper(II) ions are bridged by μ$_2$-alkoxide oxygen atoms of 1-(methyl-2-pyridylamino)methoxide, apparently formed from decomposition of DMPA. The pyridyl N atom of the decomposed DMPA and an acetate oxygen atom also coordinate to the copper(II) ions. We have also synthesized a chelate containing both aliphatic amines and pyridyl moieties, LN$_5$, 4 and its Cu(II) complex, 5, which has been X-ray crystallographically characterized. Antibacterial activity of the complexes have been screened against pathogenic bacteria such as *Escherichia coli*.

**INOR 264**

**Synthesis, characterization and biological activity of N-heterocyclic carbene complexes of Ag(I) and Ni(II) ions**

*Dong-Heon Lee*¹, dhl@chonbuk.ac.kr, Hyun Jin Jung¹, Geon Woo Moon¹, Gyungse Park², O-bong Yang³. (1) Department of Chemistry, Chonbuk National University, Jeonju, Jeollabuk-do 561-756, Republic of Korea (2) Department of Chemistry, Kunsan National University, Kunsan, Jeollabuk-do 573-701, Republic of Korea (3) School of Chemical Engineering, Chonbuk National University, Jeonju, Jeollabuk-do 561-756, Republic of Korea

N-heterocyclic carbene (NHCs) have widely been utilized as an important class of ligands in organometallic chemistry or coordination chemistry. Chelating NHC ligands containing other NHC units or different donor moieties are limited compared to the number of monodentate NHC ligands available. In this work we present a new NHC ligand containing two pyridyl substituents, (MepyCH$_2$)$_2$-Im, 1. Ag(I) and Ni(II) complexes with 1 have been synthesized and fully characterized by various analytical methods including X-ray crystallography. The stoichiometric reaction of Ag(II) with 1 results in a trinuclear silver NHC complex, [[(MepyCH$_2$)$_2$-Im]$\cdot$Ag][PF$_6$]$_2$, 2 which has a cyclic Ag(I) center. A Ni(II) complex of 1 can be easily obtained by NHC transfer from 2 to a Ni(II) center. The Ni(II) complex is formulated as [(MepyCH$_2$)$_2$-Im]$\cdot$[Ni][PF$_6$]$_3$ and a single-crystal X-ray structural determination confirms the formulation. Antibacterial activity of these complexes has been screened against pathogenic bacteria such as *Escherichia coli*. We also present preliminary results on electrocatalytic reduction of CO$_2$ by 3.

**INOR 265**

**Difficulties, obstacles, and successes in preparing multi-zonal crystalline systems based upon coordination helices**

*S. Russell Seidel*¹, seidelr@dowling.edu, Richard Wilkens², Ashley M Stock½. (1) Department of Chemistry and Physics, Dowling College, Oakdale, NY 11769, United States (2) Department of Biology, Dowling College, Oakdale, NY 11769, United States

As prior and ongoing results have shown, essentially-isoostructural helical coordination polymers based upon copper(II) hexafluoroacetylacetonate (green) and zinc hexafluoroacetylacetonate (colorless)—each in reaction with the linking unit 4,4′-dithiopyridine—have demonstrated an interesting ability to form multi-zonal crystalline systems. Of course, as with any project, a variety of difficulties have been encountered along the way, many of them specific to the particular methodology employed in synthesizing such coordination-based, multi-zonal systems and also inherent to the nature of the systems themselves. Here, we will highlight a host of such obstacles, including the apparent appearance of ‘extra’ and unexpected zones, crystal quality, chemical decomposition, “imperfections”, microscopic shortcomings, assessing zone purity, and so on. Successes, of course, will also be highlighted.

**INOR 266**

**Synthesis and characterization of few novel [NNN]Ni(II) pincer complexes**

*Abhijit Pramanik, abhijit.pramanik@mavs.uta.edu, Animesh Das, Muhammed Yousufuddin, H. V. Rasika Dias. Chemistry & Biochemistry, The University of Texas at Arlington, Arlington, TX 76019, United States*

Pincer complexes of late transition metals have been widely used in various catalytic conversions. Ni(II) pincer complexes are of immense importance in this context for its cheap and stable nature. Few novel [NNN]Ni(II) pincer complexes supported by an electron rich pyridine based ligand system have been isolated. These complexes were fully characterized (NMR, XRD and MS). The ligand system is also luminescent. Herein, the synthesis, isolation and characterization of those pincer complexes will be presented.

**INOR 267**

**Aminophosphine tungsten carbonyls as potential scaffolds for CO$_2$/olefin coupling**

*Julio A. Cedeno-Alceza*¹, jcedenoalceza@gmail.com, Samuel J. Kyran¹, Donald J. Daresbourg¹. (1) Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States (2) Department of Chemistry, University of Puerto Rico, RR 3 Box 10913, Toa Alta, Puerto Rico 00953, United States

A new diamidophosphine ligand, [HN{WP(Ph)}$_2$CH$_2$CH$_2$]$_2$, has been synthesized and fully characterized. Reactions with tungsten hexacarbonyls reveal a selective k$^2$-coordination of the two phosphorus atoms at the metal center. A k$^3$-coordination mode with an additional amine donor was not observed even under harsher conditions but was instead achieved via an unusual coupling reaction of an amine arm with a metal-bound acetonitrile. These complexes were characterized via $^1$H, $^{31}$P, and $^{13}$C NMRs, IR spectroscopy, and elemental analyses. The potential use of these complexes as scaffolds to study acrylate formation via carbon dioxide and ethylene coupling will be discussed.

**INOR 268**

**Crystallographic evidence of coordination environment control through the interplay of anion coordination strength and ligand steric in Cu$^{II}$ complexes of methylated pyrazoles**

*Ian D. Giles, ian.giles.ctr@nrl.navy.mil, Jeffrey R. Deschamps.Center for Bio/Molecular Science and Engineering, United States Naval Research Laboratory, Washington, DC - DISTRICT OF COLUMBIA 20375, United States*

Steric considerations have long been known as important forces controlling ligand coordination to metal ions in the solution and crystalline phase. Additionally, the presence of coordinating anions, like halides, or weakly coordinating anions, like nitrate, can influence the way ligands coordinate to the metal ion in question. With a coordinatively flexible metal ion such as Cu$^{II}$, the interplay between these two competing forces can allow for fine-tuning of
coordination complex structures with minimal effort. By simply changing the starting CuII salt from CuCl₂·2H₂O to Cu(NO₃)₂·2.5H₂O, complexes with 2:1 and 4:1 ligand to metal (L:M) ratios and varying coordination numbers have been easily and rapidly synthesized from 2:1 stoichiometric ratios of L:M in water solutions at room temperature using 3-methylpyrazole, 4-methylpyrazole, 3,5-dimethylpyrazole, and pyrazole. Each reaction formed single crystals which were analyzed by X-ray diffraction. For pyrazole, 4:1 L:M complexes were formed with both CuCl₂·2H₂O and Cu(NO₃)₂·2.5H₂O, with CuII adopting an octahedral ligand environment and the anions coordinated in a trans fashion as the pyrazole ligands did not sterically interfere with anion coordination. With 3-methylpyrazole, an extended structure with a 2:1 L:M ratio was formed using CuCl₂·2H₂O, containing two bridging Cl⁻ ions with CuII in an octahedral environment. With Cu(NO₃)₂·2.5H₂O, however, an isolated 4:1 L:M complex was formed with CuII in an octahedral environment with the anions coordinated in a trans fashion. Interestingly, with 3,5-dimethylpyrazole, an extended structure containing a 5-coordinate CuII center with one bridging and one pendant Cl⁻ ion is formed with the CuCl₂·2H₂O salt. With Cu(NO₃)₂·2H₂O, 3,5-dimethylpyrazole also forms a 5-coordinate complex, though it is an isolated structure with the fifth coordination site occupied by a water molecule, not nitrate ions, which are relegated to outer sphere coordination. Significant coordination control is shown simply through varying the counterion and ligand steric in CuII complexes of methylated pyrazolyls.

INOR 269
Synthesis and late-metal coordination chemistry of novel guanidine ligands
Nicholas A Piro, nicholas.piro@villanova.edu, W Scott Kassel. Department of Chemistry, Villanova University, Villanova, PA 19085, United States
Neutral and anionic guanidine ligands are useful for the preparation of high-oxidation state complexes given their good donor properties. Here we present the preparation of sterically protected cyclic guanidines (1-alkylimidazolidin-2-imines) to serve as building blocks for the preparation of oxidation resistant chelating ligands. The coordination chemistry of these new ligands with late transition metals will also be presented.

INOR 270
Coordination chemistry of the Janus-head ligand tris(2-pyridy1)phosphine [P(ppy)3] and its oxide with late first row transition metal nitrates
Danijel J Pericic, dpericic1@villanova.edu, William G Dougherty, Nicholas A Piro, W. Scott Kassel. Department of Chemistry, Villanova University, Villanova, PA 19085, United States
Tris(2-pyridy1)phosphine (P(ppy)3) and tris(2-pyridy1)phosphine oxide (OPP(ppy)3) reacted with MII nitrates (M=Ni, Cu, Zn)3 in simple one-pot procedures to yield the facial metal complexes [Ni(OPP(ppy)3)2(NO3)2(Cu2P(ppy)3) NO3]. Cu[P(ppy)3]NO3, [ZnP(ppy)3]NO3, [ZnP(ppy)3](H2O)2]NO3, [Ni(OPP(ppy)3)2(H2O)]NO3, [Cu(OPP(ppy)3)2(NO3)2]H2O]. These complexes were characterized by IR and UV-visible spectroscopy, X-ray diffraction, and 1H/31P NMR spectroscopy. X-ray crystallography showed that both the OPP(ppy)3 and P(ppy)3 ligands coordinated in a facial N,N,N manner to the metal centers, leaving the phosphorus of the P(ppy)3 ligand open to possible further bonding. One of the nitrates in the complex Cu(OPP(ppy)3)NO3 exhibited an anisobidentate k2 binding mode to the copper center, and was only the example observed in either series where this occurred; all other nitrates were bound in a monodentate fashion.

INOR 271
Coordination chemistry of the Janus-head ligand tris(2-pyridy1)phosphine [P(ppy)3] and its oxide with lanthanide nitrates
Danijel J Pericic, dpericic1@villanova.edu, William G Dougherty, Nicholas A Piro, W. Scott Kassel. Department of Chemistry, Villanova University, Villanova, PA 19085, United States
Tris(2-pyridy1)phosphine (P(ppy)3) reacted with MII nitrates (M= NdIII, SmIII, YbIII) in simple one-pot procedures to yield the facial metal complex Yb3P(ppy)3(NO3)3. In contrast, two equivalents of tris(2-pyridy1)phosphine oxide (OPP(ppy)3) reacted with one equivalent of the same MII nitrates in a bidentate fashion to give [Nd(OPP(ppy)3)2(NO3)][(CH₃CH=CHOCH)₂] and [Sm(OPP(ppy)3)2(NO3)][(CH₃CH=CHOCH)₂]. All complexes were characterized by IR, UV-vis, X-ray diffraction, and 1H/31P NMR. In the P(ppy)3 series, the ligand coordinated in a N,N,N manner to the metal centers, while the three nitrates were all k2 bound. The nitrates in the OPP(ppy)3 series were k2 bound as well, but N,O coordination was observed from the ligand, leaving two pyridyl nitrogens free for potential binding to another metal. The ability of these free pyridyl nitrogens to bind another MII metal nitrate is under investigation.

INOR 272
Synthesis of anza-ytterbocenes by reductive fulvene coupling: Reactivity and electronic properties
Micah Villareal1, Micah.Villareal@usa.edu, Endrit Shuridha2, Scott T Iacono3, Gary J Balch1, David W BaI.1. (1) Department of Chemistry, US Air Force Academy, Colorado Springs, CO 80840, United States (2) Department of Chemistry, Cleveland State University, Cleveland, OH 44115, United States
The anza-dicyclopentadiene compounds [(CHBu)₂(C₂H₃Pb)₂] 1 and [(CHPr)₂(C₂H₃Pb)₂] 2 were synthesized from the corresponding 1,3-diphenyl-6-(tert-butyl)- and 1,3-diphenyl-6-(isopropyl)- fulvenes. Potassium salt ligand precursors 1a and 2a were generated from reaction of 1 and 2 with K[N(SiMe₃)] in toluene. Subsequent reaction of 1a with YbI₃ in THF gave a clean conversion to the deep red anza-ytterbocene THF complex, rac-[(CHBu)₂(C₂H₃Pb)₂Yb(THF)]₂[CH₃] 3, as a toluene solvate. Reaction of 2a with YbI₃ gave a mixture of products, and a significantly lower yield of the anza-ytterbocene, rac-[(CHPr)₂(C₂H₃Pb)₂Yb(THF)]₂. Interestingly, the reaction of 2a with CaCl₂ in refluxing THF led to the formation of the corresponding anza-calcocene complex, 5, which underwent clean conversion to the anza-ytterbocene 4 by reaction with YbI₃. The syntheses and single crystal X-ray structures of the new anza-ytterbocene will be discussed. Reactivity of 3 and 4 with N-containing heterocycles and cyano-containing ligands as well as their properties in connection with spintronics and electronic materials will also be presented.

INOR 273
Synthesis and characterization of (bis-aza-pentadienyl)ruthenium(phosphine) complexes
Meghan Stouffer2, stoume01@gmail.com, John R Bleek2, Nigam P Rath2. (1) Department of Chemistry, Washington University, St. Louis, Missouri 63130, United States (2) Department of Chemistry and Biochemistry, University of Missouri–St. Louis, St. Louis, Missouri 63121, United States
We report the synthesis, structure, spectroscopy, and reactivity of the first examples of (bis-aza-pentadienyl)ruthenium complexes. Treatment of Cl₂Ru(PPh₃) with potassium tert-butylazapentadienide produces (bis-(1,2,3-η5)-5-tert-butylazapentadienyl)Ru(PPh₃) (1), a light yellow-brown solid. Compound 1 undergoes ligand substitution reactions with triethylphosphine, trimethylphosphine, and tert-butyl isocyanide, producing (bis-(1,2,3-η5)-5-tert-butylazapentadienyl)Ru(PPh₃) (2, (bis-(1,2,3-η5)-5-tert-butylazapentadienyl)Ru(PPh₃) (3), and (bis-(1,2,3-η5)-5-tert-butylazapentadienyl)Ru(PPh₃) (4). Compound 1 reacts with 2 equivalents of triflic acid (H₂SO₃) to at the azapentadienyl nitrogens, yielding the corresponding (bis-(1,2,3-η5)-5-tert-butylazapentadienyl)(H₂SO₃) (5). Protonation of the azapentadienyl ligands in 5 breaks the two-fold symmetry seen in the starting material, 2. The X-ray crystal structures of compounds 2-5 have been obtained.

INOR 274
Activation of phenylsilane by a zerovalent platinum dimer
Lucas Matuszewski, sergeeschreiner@rmc.edu, Serge Schreiner. Department of Chemistry, Randolph-Macon College, Ashland, Virginia 23005, United States

The stoichiometric reaction of phenylsilane with [PtL(H)(CO)2] (dppm = Ph2PCH2PPh2) in toluene yielded a silylene-bridged platinum complex formulated as [PtL(H)(SiHPhPh)Ph2] (1). The solution structure of the yellow complex was determined by 1H, 13C, 31P, 195Pt NMR spectroscopy. [PtL(H)(SiHPhPh)Ph2] (1) was formulated as a W-frame complex having an AA'BB'XX' spin system. The solid state structure was confirmed by infrared spectroscopy and single crystal X-ray diffraction. When [PtL(H)(CO)2] (dppm) was reacted with excess phenylsilane, two different reaction products (2 and 3) were obtained depending on specific reaction conditions. Complex 2 is formulated as [PtL1(H)(SiHPhPh)Ph2] (dppm) and complex 3 is tentatively believed to be [PtL2(H)(SiHPh)Ph2] (dppm) and [PtL2(H)(SiPhH)Ph2]. A mechanism leading to these reactions products is proposed.

INOR 275

Iridium(III) hydride complexes with bidentate phosphines: Synthesis, characterization and reactivity

Trang Tran, sergeeschreiner@rmc.edu, Serge Schreiner. Department of Chemistry, Randolph-Macon College, United States

New iridium complexes stabilized by three diphosphine ligands were synthesized and their reactivity toward small molecules was studied. Chloro(1,5-cyclooctadiene)iridium(I) dimer reacted with the ligand 1,2-bis(diphenyldiphenylphosphino)benzene (dppb), cis-1,2-bis(diphenyldiphenylphosphino)ethylen (dpeep) or bis[2-diphenyldiphenylphosphinophenyl]ether (dppeppher) in a ratio of 1:2 in toluene to produce [Ir(COD)(dppb)(Cl)1], [Ir(COD)(dppeppher)] (2) and [Ir(COD)(dppeppher)] (3) respectively. These complexes can readily be isolated as their tetraphenylborate salts (4-6). Reactions of 4 and 5 with small molecules such as CO, H2, and HCl resulted in the formation of iridium carbonyl, monohydride and dihydride complexes. The reactions of compounds 4, 5, and 6 with primary and secondary silanes showed that they were able to oligomerize silanes and release molecular hydrogen, which then reacted with these complexes to produce a mixture of cis- and trans-iridium dihydride complexes.

INOR 276

Synthesis and characterization of low-valent iridium complexes stabilized by alkyl- and arylphosphines

Haley Russ, sergeeschreiner@rmc.edu, Serge Schreiner. Department of Chemistry, Randolph-Macon College, Ashland, Virginia 23005, United States

The activation of small molecules by transition metal complexes via ligand substitution or oxidative-addition has historically received a great deal of attention since these reactions are requisite for catalytic processes. While chlorocarbonyl(bis(triphenylphosphine)iridium(I) (Vaska’s compound) and some related isostructural and isoelectronic complexes of the type trans-[M(A)(CO)3] (M = Ir, Pt; A = anionic ligand; L = monodentate tertiary phosphine) have been examined in great detail, much less is known regarding the activation of small molecules by similar planar iridium(I) and rhodium(I) complexes containing bidentate alkyl or aryl phosphine ligands. Our work focused on the synthesis and reactivity of iridium complexes stabilized by the arildiphosphine, (C6H4)2PCH2P(C6H5)2, and the alkyl diphosphine, (C6H4CH2PCH2(C6H5)2). We have prepared several covalent and iondiphosphine-diene complexes which are capable of activating molecular hydrogen, hydrochloric acid and silanes resulting in some novel mono- and dihydride complexes with retention of the diene ligand. The solution structures of these complexes will be described.

INOR 277

Highly fluorescent phosphines based on the BODIPY scaffold

Jennifer F Wallis, jennifer.wallis@ncl.ac.uk, Lee J Higham. Department of Chemistry, Newcastle University, Newcastle upon Tyne, United Kingdom

Primary phosphines (RPH2) are an underdeveloped class of ligand due to their primary phosphines with unprecedented air-stability, which is credited to electronic effects.

We report the original and improved synthesis of the first air-stable fluorescent primary phosphines which are based on the well-known fluorophore BODIPY, containing a π-conjugated backbone. The improved synthesis has also been successfully scaled-up to 15 grams whilst retaining good yields. BODIPY was the fluorophore chosen as it has been extensively studied and its related compounds have high fluorescence quantum yields, high thermal and photochemical stability and chemical robustness.

There has been relatively little research on the coordination chemistry of primary phosphines, here we report the coordination of group 6, 8 and 11 transition metals to the BODIPY primary phosphines and the effect the metals have on the photophysical properties of the complexes.


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Synthesis and reactivity of borenium ions supported by azaferrrocene donors

Jason R Smith1, tbrunker@towson.edu, Sarah B Krause1, Arnold L Rheingold2, Tim J Brunker1. (1) Department of Chemistry, Towson University, Towson, MD 21252, United States (2) Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093, United States

Electron-deficient boron-containing cations are highly electrophilic species that display valuable reactivity including direct borylation of arenes and hydroboronation of alkenes. We have sought to stabilize borenium ions, [L-BX4]-, using several different azaferrrocene donors (L) and to investigate their reactivity. Hydride abstraction from azaferrrocene-BH4 adds using trityl tetra(pentafluorophenyl)borane yielded borenium ions of the type [L-BH4]. Similarly, hydride abstraction from azaferrrocene-9-borabicyclo[3.3.1]nonane adducts (L-9BNB) yielded the borenium ions [L-9BBN]. Both types were characterized in solution by multinuclear NMR spectroscopy which revealed characteristic 11B and 31P shifts consistent with a strongly electron-withdrawing group on nitrogen. Chloride abstraction from azaferrrocene-BCl3 adds using AlCl3 yielded [L-BCl4]-,[AlCl4]3 salts which could be isolated as stable solids. Single crystal X-ray diffraction of one example revealed some bending of the borenium moiety towards the iron center and significant short contacts between the tetrachloroaluminate anions and the borenium cations through both Cl-B interactions and Cl-H-O short contacts. The Lewis acidity of these borenium ions has been investigated by the Gutmann-Beckett 31P NMR method, and all were found to be more Lewis acidic than B(C6F5)3. [L-BCl4]- species undergo dihydroboronation with dienes such as isoprene and 1,5-cyclooctadiene to yield the species [L-BCl4]. The selectivity of such reactions with isoprene and also with simple alkenes is under investigation. These results and the reactivity of these borenium species in hydrosilylation reactions will also be reported.

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Selective nucleophilic replacement reactions of substituted silanes
Several fundamental studies were conducted to test the preference of silicon to bond to amines, alcohols, and thiols. High yield, clean and rapid conversions from both R$_3$Si-NHR and R$_3$Si-NR$_2$ to R$_3$Si-SR$_2$ and also from R$_3$Si-SR to R$_3$Si-OR$_2$ were observed. Also, the rapid conversion of R$_3$Si-NR$_2$ to R$_3$Si-NHR was realized. The ability to exploit this selectivity for the synthesis of new materials would be discussed.

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Synthesis structure and reactivity of alkali metal silanides

Vidura D Thalangamaarachchige, vidura.d.thalangamaarachchige@ttu.edu, David Cordes, Clemens Krepnner. Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas (TX) 79409, United States

The synthesis and characterization of an entirely new family of zwitterionic alkali metal silanides will be discussed. These are a real class of compounds with dual functionality. The central cationic metal center in these species is rigidly locked and insulated from the tetrelide anion by three internal donor bridges which coordinates to the metal center in tridentate geometry to form zwitterionic complexes. These compounds were characterized by NMR and X-ray crystallography. The naked silicon anion of these compounds can be functionalized using Lewis acids and also the central alkali metal can be exchanged with transition metals via metathesis reactions.

INOR 281

Organometallic reactivity of nitrosyl donors with transition metal complexes

Michelle E DelHomme, Michelle_DelHomme@baylor.edu, Patrick J Farmer. Department of Chemistry and Biochemistry, Baylor University, Waco, TX 76706, United States

Organometallic reactions of nitrosyl (HNO) are largely unknown due to the difficulty in generating free HNO and its rapid dimerization. The deprotonated form of nitrosyl (NO$^-$) is isoelectronic to molecular oxygen (O$_2$), which reacts readily with certain d8 square planar metal complexes such as Vaska’s complex. We hypothesize that HNO should react in a similar manner. The reactions of nitrosyl donors with transition metal compounds, including Vaska’s complex, will be discussed and characterized by NMR spectroscopy, IR spectroscopy and mass spectrometry.

INOR 282

Synthesis and reactivity of three-coordinate Rh(I) silanides

Alex J Kosanovich, kosanova@carleton.edu, Matthew T White. Department of Chemistry, Carleton College, Northfield, MN 55057, United States

Coordination complexes containing late metal-nitrogen multiple bonds (imides and nitrides) are important intermediates in a number of catalytic processes leading to C-N bond formation. We have investigated the synthesis and reactivity of late-metal silanides as potential precursors to imido and nitrido complexes via oxidative Si-N bond cleavage. Toward this goal, we will present findings regarding the synthesis of new three-coordinate diphosphine Rh(I) complexes with monodentate silanide ligands and their bond-forming and group-transfer reactivity under a variety of conditions.

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Synthesis of N-heterocyclic carbene-containing pincer complexes for catalytic hydrogenation of polar bonds

Spring Melody M Knapp, sknapp@colgate.edu, Anthony R Chianese, Kelsey H Jensen, Myles J Drance, Gillian F Moore. Department of Chemistry, Colgate University, Hamilton, New York 13343, United States

The selective catalytic activation of polar bonds toward hydrogenation or dehydrogenation is desirable because such a process would facilitate the conversion of inexpensive and readily available chemical feedstocks into more industrially viable products. Catalytic reactions that generate molecular hydrogen upon dehydrogenation or use molecular hydrogen for hydrogenation are especially desirable, because such processes would eliminate the need for stoichiometric oxidizing or reducing agents. The most efficient catalysts for this purpose contain PNP-ligated or PNN-ligated noble metals. However, the high cost and low abundance of these noble metals prohibits their widespread use. For this reason, the synthesis of first and second row transition metal pincer complexes was investigated, with either CNC-pincers containing meta-pyridine bridged N-heterocyclic carbene ligands, or the related CNN-pincers containing a ligating tertiary amine.

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Synthesis and photophysical properties of platinum acetylide compounds

Russell W Winkel, twinkel@chem.ufl.edu, Kirk S Schanze. Department of Chemistry, University of Florida, Gainesville, FL 32611, United States

A series of trans-platinum(I) acetylide complexes featuring two-photon absorbing chromophores were synthesized and their photophysical properties measured. One-photon studies include absorption, emission, quantum yields, and emission lifetimes. Multi-photon studies include transient absorption and open aperture z-scan. In addition to solution photophysics, the complexes were cast in the solid state and the photophysical properties were measured. Coupling of organic chromophores to the platinum metal allows for efficient intersystem crossing, which gives rise to the desired material properties of these systems.

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Applications of low valent transition metal centers: Formation of cyclopentadienyl cobalt (I) clusters

Gregory P McGovern*, greg.mcgovern@ttu.edu, Christopher A Bradley*. (1) Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, United States (2) Department Of Science, Mount St. Mary, Emmitsburg, MD 21727, United States

The use of reactive metals is critical to mediate numerous types of organic transformations. One type, C-H bond activation, has seen success through the use of iridium and rhodium based catalysts. Cobalt however, has seen limited use in C-H activation, partly due to issues of unfavorable spin states in critical unsaturated low valent intermediates. We have employed several strategies to generate a low electron count, reactive cobalt (I) species and then to explore its subsequent reactivity. One target is the synthesis of cobalt clusters incorporating a cyclopentadienyl framework to avoid spin state issues at alternative cobalt centers.

Two types of clusters were explored, using Cp$^*$Co or CpCo fragments. With alkenylarenes, such as o-methylstyrine, a triple decker sandwich is formed, a product similar to other [(Cp$^*$Co)$_2$]$_3$-$\eta^2$-$\eta^1$-arene] compounds which are known to perform sp$^3$ C-H activation in silyl protected amines. The differences in reactivity of this type of sandwich complex, relative to the known triple-decker complexes, suggest the new compounds are less reactive. Structural analyses of both classes of complexes provide a method to relate catalyst structure to reactivity. Ongoing efforts are currently focused on generating trimeric [CpCo]$_3$ cores.
Synthesis and characterization of (η⁵-Pentalenyl)Mn(CO)₅ complexes with tethered functional groups: Development of organometallic photochromes

Jermaine O Johnson, jhjmsn26@memphis.edu, Roger G Letterman, Edwin J Heilweil, Charles Edwin Webster, Theodore J Burkey. (1) Department of Chemistry, The University of Memphis, Memphis, TN 38152, United States (2) Optical Technology Division, Physics Laboratory, NIST, Gaithersburg, MD 20899, United States

Our group designs photochromic organometallic systems based on a photo-induced isomerization between two tethered functional groups. The current paradigm is based on coupled functional groups: the bridge between a coordinated and uncoordinated group prepositions, the latter for addition when the former dissociates. In addition, the functional group motions are coupled to enhance addition of the uncoordinated group. The efficacy of the system depends on the structure of the bridge, the functional groups and the tether. This design is intended to enhance the rate of photo-induced linkage isomerization of chelates while minimizing processes that lead to fatigue or recombination. The synthesis of (η⁵-pentalenyl)Mn(CO)₅ complexes with the coupled functional groups tethered on the saturated pentalenyl ring reduces the degrees of freedom of the tether and therefore the functional groups. Synthesis of targets and their spectroscopic properties will be presented.

Synthesis and characterization of d8 transition metal complexes for electronic applications

Ahmed A Shahub, ahmed.an@hotmail.com, Mohammed A Omary, Iain Oswald. Department of Chemistry, University of North Texas, Denton, TX 76205, United States

Particular transition metal complexes exhibit interesting photophysical and semiconducting properties that can be utilized in electronic circuit components such as transistors and diodes, and in organic light emitting diodes (OLEDs) for general-purpose lighting and video displays. These components are ubiquitous and play an integral part in electronics that we use on a daily basis including cell phones, HDTVs, and computers. Platinum(II) complexes designed in our group exhibit bright luminescence with high efficiency making them excellent candidates towards OLED applications. We have found that by varying the organic functionality of the ligands surrounding the Pt(II) center that we can achieve multiple emission colors as well as improve efficiency, attaining 100% under both optical excitation and electrical excitation at the device level. These materials also pack in a way that maximizes Pt-Pt overlap giving the material semiconducting behavior. The synthesis, characterization and photophysical properties of these complexes are reported, including nickel and palladium analogs that potentially will have similar characteristics and thus will help to further reduce cost.

Buckycatcher with nothing to catch and its first reduction study

Alexander V. Zubula, Sarinh N. Spisak, Yulia Sevryuginab, Lesya Kobryn, Renata Sygula4, Andzej Sygula, Marina A. Petrukhina, mpetrukhina@albany.edu. (1) Department of Chemistry, University at Albany, Albany, NY 12222, United States (2) Department of Chemistry, University of Wisconsin, Madison, WI 53706, United States (3) Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, United States (4) Department of Chemistry, Mississippi State University, MS 39762, United States

Design of extended [Π]-systems utilizing bowl-shaped polyarenes (buckybowls) as functional building units has received increased attention in recent years. Varying the length and nature of the linkage between the curved fragments is used to alter their electronic coupling and to give new carbon-rich compounds with novel functions. Thus, employing two small corannulene bowls as pincers separated by tetrabenzocyclooctatetraene tether, the first efficient molecular receptors for fullerenes have been synthesized in Sygula group. The resulting buckycatcher was shown to exhibit a remarkable affinity towards fullerenes and other inclusion species, making its isolation in the neat form challenging. Herein, we report the first X-ray crystallographic study of the unsolvated buckycatcher that reveals a unique and tight solid state packing based on [Π-Π] interactions of corannulene pincers. We have also accomplished the first buckycatcher reduction study which resulted in the isolation and structural characterization of the dianion in the form of the rubidium salt.

Transition metal complexes of novel MOP-phosphonites and their applications in homogeneous asymmetric catalysis

James T Fleming, james.fleming@ncl.ac.uk, Lee J Higman. Department of Chemistry, Newcastle University, Newcastle upon Tyne, United Kingdom

Primary phosphines are an excellent starting point for synthesising functionalised organophosphorus compounds, due to the high reactivity of their P-H bonds. Working with primary phosphines is often assumed to be difficult due to their perceived high air sensitivity and pyrophoric nature. Nevertheless, over the last two decades a number of “user-friendly” primary phosphines have begun to emerge, whose stability is either unexplained or attributed to steric encumbrance. The L. J. Higman research group has demonstrated that air-stable, chiral primary phosphines with high levels of conjugation can be used as precursors in the synthesis of ligands with unusual functionality on the phosphorus donor. Based upon the successful MOP-phosphine ligand class developed by Hayashi, we have synthesised a number of MOP-type ligands with a diverse range of electronic and steric properties. Herein we present the synthesis of novel, chiral phosphonite molecules in a one-pot, two-step reaction and a study of the electronic properties of these phosphonite donor ligands.

A number of the group 9, 10 and 11 transition metal complexes of the phosphonite ligands have been synthesised; analysis of these complexes is reported, including nickel and palladium analogs that potentially will have similar characteristics and thus will help to further reduce cost.

Cooperative small-molecule activation by ambiphilic late-metal complexes

Alexander M Deetz, deetzz@carleton.edu, Matthew T Whited. Department of Chemistry, Carleton College, Northfield, Minnesota 55057, United States

Metal-ligand multiple bonds are promising for cooperative small-molecule activation, particularly in cases where incomplete σ- or n-bonding leads to adjacent Lewis-basic and -acidic sites. Our group has targeted late-metal complexes containing such electronically frustrated linkages that are stabilized by pincer-type ligands. We will present studies on the synthesis and metallation of several related ligand scaffolds with group 9 metal precursors and the reactivity of the resulting complexes.

Carbon dioxide reduction with Zn: An alternative to precious and toxic metals

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Zn has been studied as a reductant for CO₂ using both modeling and synthesis. Electrochemical reduction of CO₂ with Zn has shown poor selectivity although it has proven to be as effective as to reduce CO₂ to methane. In our approach we propose carbon dioxide reduction to follow a mechanism in which formaldehyde is produced which then can be reduced to methane by Zn via a Clemmensen reduction. Intermediacy of formyl and carbonyl complexes is proposed and evaluated using DFT. Synthesis of these intermediates has been attempted and characterization of products using IR spectroscopy and NMR is presented.

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Design and synthesis of ruthenium coordination polymers for use in dye sensitized solar cells
Steven M. Boyer, sboyer2@binghamton.edu, Kenneth H. Skorenko, Kevin B. Fischer, Nicholas A. Ravvin, Aaron D. Taggart, William E Bernier, Wayne E. Jones. Department of Chemistry and Material Sciencee, Binghamton University, Binghamton, New York, United States

Inorganic complexes as photosensitizers for dye sensitized solar cells (DSSC) are a widely explored area of research. A class of dyes is based on cis-Bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato ruthenium(II) also known as N3 dye which has been popularized by Gratzel and others. While many research programs focus on expanding the region of the solar spectrum absorbed by the dye, there are several new approaches to advancing other limitations in DSSC’s. We have been exploring the introduction of solid state electrolyte’s to this end. An important chemical challenge involves interaction between the excited dye and the hole transport layer. By introducing organic ligands which act as a monomer for polymerization; we seek to introduce more rapid electron hole separation. Here we present the synthesis and characterization of a dye-hole conducting layer copolymer to enhance the hole transport at a polyethylene dioxothiophene transport layer.

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Platinum(IV) photoelimination reactions: What is going on? Paul R. Sharp, sharp@missouri.edu. Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States

Our research group has been studying the apparent endergonic reductive photoelimination reactions of octahedral Pt(IV) complexes (Figure 1). This type of reaction is an important step in a potential solar energy conversion and storage scheme. An overview of the different systems we have studied will be presented and mechanistic proposals will be advanced.

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Interaction of phosphate esters and phosphine oxides with imidazolium-based room temperature ionic liquids
Ruma Joshi, Sofie P. Pasilis, sofie.pasilis@gmail.com. University of Idaho, Moscow, ID 83844-2343, United States

Room temperature ionic liquids (RTIL) are potentially useful solvents for the extraction of lanthanides and actinides from nuclear fuel. Uranium metal can be dissolved in a solution containing nitric acid and tributylphosphate (TBP), and uranium extracted into the RTIL in the form of a UO₂(TBP)₃(NO₃) complex. Understanding the chemical interactions at play in the RTIL/metal/ligand system will aid in the development of more efficient extractions using RTIL solvents. As a first step, we are using NMR, FTIR, and Raman spectroscopic methods to study the interactions between 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-Tf₂N), TBP, and tributylphosphine oxide (TBPO). We are also examining the effect of water on those interactions. ¹H NMR results suggest that TBP interacts with protons on the EMIM⁺ imidazolium ring through hydrogen bonding. Significant shifts in the ¹H NMR signal are seen for the imidazolium ring C2–H protons when TBP is added to the solution. Our ¹H NMR and FTIR spectra also indicate that water affects the interaction of TBP with EMIM⁺. Based on water and imidazolium ring proton chemical shifts we can say that the hydrogen bonding interactions between water and TBP are greater than those between water and EMIM⁺, and that the interactions between EMIM⁺ and TBP are greater than those between EMIM⁺ and water. We have also investigated the effect that the uranyl(VI) ion has on these interactions.

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Expedited synthesis, and structural and kinetic studies of non-platinum group metal-organic framework electrocatalysts
Elise M Miner, miner.el@husky.neu.edu. Kara M Strickland, Urszula Tylus, Sanjeev Mukerjee. Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115, United States

H₂-air fuel cells remain promising renewable energy alternatives to CO₂–emitting fossil fuel combustion, but currently require costly platinum-group metal (PGM) catalysts and are thus not economically sustainable. Efforts to develop low-cost alternatives to PGM electrocatalysts have yet to afford moieties with acceptable reduct activity and stability in the fuel cell environment. Metal-organic frameworks (MOFs) are comprised of organic ligands coordinated to transition metal centers to form expansive, cage-like structures whose pores can house organic, inorganic, and biochemical compounds. MOFs have been intensively studied for their high surface area, unique porosity, and chemical and thermal stability. These frameworks can effectively house catalysts within their pores, thus methods of impregnating the MOF pores with electrocatalytic active sites is of high interest. We will detail our novel one-pot MOF formation-catalytic active site precursor encapsulation to afford a non-PGM electrocatalyst with high activity and stability. Various transition metal-nitrogen-containing organic ligand complexes serving as catalytic active site precursors were encapsulated and analyzed for reduct activity and stability. Structural studies of the MOF-based catalyst (our MOF of interest being zeolitic imidazolate framework-8 (ZIF-8)) to gain insight into the composition, size, density, and orientation of the MOF pores and the encapsulated catalytic active sites are described. The MOF catalysts’ kinetic performances were investigated with rotating ring disc electrode (RRDE) and fuel cell studies; these results were correlated with the structural data of each analog to systematically determine structural features of the most promising electrocatalysts. These catalysts have shown versatility by facilitating not only catheric oxygen reduction, but an array of other reduct reactions as well. The impressive catalytic activity and structural data present a promising foundation for replacing platinum with robust and abundant electrocatalysts, contributing to our renewable energy and environmental sustainability efforts.

INOR 296

Density functional study of (LiCl)ₙ (n=1-24) clusters: Structure, stability, and spectra
Ellen M Mitchell, emitchel@bridgewater.edu, Bo Long, Jing Su, Guo-Shi Wu, Jun Li. (1) Department of Chemistry, Bridgewater College, Bridgewater, Virginia 22812, United States. (2) Department of Chemistry, Tsinghua University, Beijing, China

Alkaline fluoride, chloride, and hydroxide salts can be used as solvents in the pyroprocessing of nuclear fuel, as heat transfer fluids in industrial processes, and for thermal storage in solar thermal power plants. In this work, we have investigated the electronic structures of (LiCl)ₙ (n=1-24) neutral clusters using density functional theory (DFT) at the B3LYP/6-31G* level. The geometries of the low-energy clusters for each n do not favor a single
structure type such as ring or cubic. The calculated bond lengths, angles, and vibrational frequencies are in agreement with the monomer and dimer experimental results. Their relative stabilities have been investigated by analyzing the binding and dissociation energies. Using time-dependent density functional theory (TD-DFT), the absorption spectra of the lowest-energy clusters (n=1-24) are simulated using B3LYP/6-31+G**/6-31G*. The monomer results are consistent with the limited experimental UV absorption data available. In addition, the first excitation energy for each cluster correlates well to the HOMO-LUMO energy gap. The binding and dissociation energies, most-intense IR frequencies, HOMO-LUMO energy gaps, and TD-DFT first excitation energies all demonstrate a convergence at about n=6 and deviation at about n=21, suggesting at least in this range a convergence to bulk properties.

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Protein folding thermodynamics of ferricytochrome c\textsubscript{552} from \textit{Marinobacter hydrocarbonoclasticus}

\textit{WeiTing Chen}, wc2287@barnard.edu, \textit{John S. Magyar}, jmagyar@barnard.edu. Department of Chemistry, Barnard College, New York, NY 10027, United States

Cytochrome c\textsubscript{552} from the marine bacterium \textit{Marinobacter hydrocarbonoclasticus} has been overexpressed in \textit{E. coli} and purified by ion-exchange and size-exclusion chromatographies. The protein folding thermodynamics of the protein have been studied using UV-vis absorption and circular dichroism spectroscopies. The \textit{van't Hoff} enthalpy for thermal denaturation of \textit{Marinobacter ferricytochrome c\textsubscript{552}} will be reported and discussed in the context of our previous work on the psychrophilic microorganism \textit{Coffewella psychrophrythreae}.

INOR 298

Coordination chemistry, structure, and spectroscopy of a putative metalloregulatory protein from a methanogenic archaean

\textit{Christina L. Cleveland}, clc2184@barnard.edu, \textit{John S. Magyar}, jmagyar@barnard.edu. Department of Chemistry, Barnard College, New York, NY 10027, United States

We have identified a putative metalloregulatory protein in the genome sequence of the methanogenic archaean \textit{Methanocorpusculum labreanum}, overexpressed it in \textit{E. coli}, and purified it by ion-exchange chromatography. Spectroscopic studies indicate that this protein binds iron--sulfur clusters and flavins. Further characterization by UV-vis absorption and circular dichroism spectroscopies and HPLC is underway.

INOR 299

Electrochemical and photochemical reduction of carbon dioxide to methanol and formate by ruthenium poly(pyridyl) complexes containing a pyridine group

\textit{David J Boston}\textsuperscript{1}, david.boston@mavs.uta.edu, \textit{Yelimi M Franco Pachón}\textsuperscript{2}, Reynaldo O Lezna\textsuperscript{2}, \textit{Norma R de Tacconi}\textsuperscript{1}, Frederick M MacDonnell\textsuperscript{1}. (1) Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, Texas 76019, United States (2) Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Sescursal, La Plata B1906ZAA, Argentina

Since 1994 pyridine has been known as an efficient electrocatalyst for the reduction of carbon dioxide to methanol via a sequential 6 electron, 6 proton process. There has been much speculation of the mechanism for the catalytic system including that a surface is required for the reduction to take place. A recent paper from our group has shown that a homogeneous pathway is possible and can be driven by light. Current work in this area has shown that an intermolecular system consisting of a ruthenium chromophore and the pyridine catalyst is capable of reducing carbon dioxide photochemically to methanol and formate. Currently work from our lab has shown that we can incorporate this catalyst into a single molecule with the chromophore and maintain the ability to reduce carbon dioxide to methanol and formate both electrochemically and photochemically. These systems have shown that the pyridine catalyst can be incorporated into other molecules and still maintain functionality.

INOR 300

Bioaccumulation of selenium in the bryophyte \textit{Hygrohypnum ochraceum} in Colorado

\textit{James S. Carsella}\textsuperscript{1}, jim.carsella@colostate.edu, \textit{Debbie C. C. Crans}\textsuperscript{1}, crans@lamar.colostate.edu, \textit{Sandra J. Bonetti}\textsuperscript{2}, delwayne.r.nimmo@colostate.edu, \textit{Scott J. Herrmann}\textsuperscript{2}, david.lehmphu@colostate.edu. (1) Department of Chemistry and Cell and Molecular Biology Program, Colorado State University, Fort Collins, Colorado 80523, United States (2) Department of Chemistry and Cell and Molecular Biology Program, Colorado State University-Pueblo, Pueblo, Colorado 81001, United States

In this study we used aquatic bryophytes to monitor the impacts of trace level contamination of heavy metals in aquatic ecosystems in Colorado because bryophytes accumulate zinc, cadmium and lead in a near linear fashion. We tested the initial hypothesis that bryophytes would uptake selenium in a manner similar to other heavy metals. To test the ability of bryophytes to accumulate selenium, porous nylon bags containing the aquatic bryophyte \textit{Hygrohypnum ochraceum} were placed at 14 sites in the Fountain Creek Watershed because selenium levels are known to vary along the creek. The plants were exposed to Fountain Creek water for 10 days in the spring and fall of 2007. Samples of water were collected and analyzed three times per site during the ten-day exposure. The plants were recovered from the sites and analyzed for metals by ICP-MS. Twenty six metals and metalloids were monitored. These include calcium, magnesium, iron, lead, arsenic, selenium, nickel, cobalt, copper and zinc. Analyses of 2010 digests indicate that plant selenium (Se) uptake was significant between Colorado Springs and Pueblo in the spring 2007 with plants showing an accumulation of 160,000 times the total Se in the water in the Lower Fountain Creek area. In the spring, plants showed an accumulation of 100,000 times the total water Se concentration in the Upper Fountain Creek area. We rejected the initial hypothesis because bryophytes' accumulation of selenium was found to be independent of water selenium concentrations. Based on these results a principle component analysis was performed to identify other correlations. Initial analyses of concurrent levels dissolved iron and selenium in the waters tested point to the involvement of iron in a pH-driven mechanism that may affect Se transport in bryophytes. Our results support an iron dependent mechanism for the selenium accumulation in bryophytes, which may involve the selenium uptake process by bryophytes.

INOR 301

Effect of interpenetration on the structure and adsorption properties of metal-organic frameworks

\textit{Lanfang Zou}, lanfang.zou@chem.tamu.edu, \textit{Tianfu Liu, Hongcai Zhou}. Department of Chemistry, Texas A&M University, College Station, TX 77840, United States

Interpenetration in Metal-Organic Frameworks (MOFs) has drawn much attention due to its significant effect on the topology, pore size as well as the adsorption behavior. Interpenetration, a polymeric analogue of catenanes and rotaxanes, occurs when the relevant networks have no chemical bonds connecting each other but cannot be separated without breaking bonds. In this work, we present the successful interpenetration control strategy, and explore the gas adsorption differences between the interpenetrated MOFs and non-interpenetrated MOFs. By modifying the side-chain groups on the linear organic linkers, we gained two isostructural MOFs with different pore volumes, surface areas, and the framework transformation was detected during the gas loading procedure.

INOR 302

Activation of CO\textsubscript{2} and the subsequent conversion into value added chemicals
Chandrani Chatterjee, chandrani_12@yahoo.com.Chemistry, Pennsylvania State University, State College, PA 16802, United States

Anthropogenic CO₂ emission has become a chief source of greenhouse gas with an average increase of 2.07 ppm every year. The development of carbon capture and storage (CCS) technologies thus play a crucial role to control and consequently reduce the emission of CO₂ during energy intensive industrial processes. Additionally, research has also focused on the capture of atmospheric CO₂ and its direct chemical conversion into value added chemicals. Due to the inherent thermodynamic stability of CO₂ these chemical conversion requires the presence of a catalyst, i.e. inorganic or organometallic complexes or organocatalysts. However, the organocatalytic processes are extremely slow for practical applications beyond laboratory scale. Thus a cooperative synergism between metal complexes and organocatalytic initiators is currently being explored as a potential solution for practical utilization of CO₂. In this approach, CO₂ is activated in the form of carbamates, using a series of organocatalysts (dimethylaminopyridine, 1,8-Diazabicyclo[5.4.0]undec-7-ene etc.) and primary amines; and is subsequently reacted with a series of substrates with electrophilic carbon centers to obtain the corresponding carbonate or urethane compounds. Furthermore, this approach has high potential to be used on solid supported catalysts enabling easy conversion of carbamates into useful chemicals.

INOR 303
Pulse-gradient spin echo 7Li and 19F NMR diffusion measurements of 8 novel silyl-carbonate solvent-blend electrolytes containing LiPF₆ and LiTFSA
Wilfried Barth, barthwil@grinnell.edu, Erik Dixon-Anderson, dixonand@grinnell.edu, Leslie J. Lyons.Chemistry, Grinnell College, Grinnell, IA 50112, United States

The self-diffusion coefficients of the lithium ion (Li⁺) and the anion (PF₆⁻ and TFSA⁻) in single, binary, and ternary blends of the newly synthesized F1S3M2 silyl molecule (shown below) with ethyl carbonate (EC), ethyl methyl carbonate (EMC), and γ-valerolactone (GVL) were measured from 295 K to 345 K using the PGSTE (pulse-gradient stimulated spin-echo) NMR method to assess their potential for lithium-ion battery applications. Pure F1S3M2 electrolytes possess high Li transference numbers, but diffusion of both ions is significantly low when compared to standard carbonate blends. Binary solvent blends of F1S3M2 with EMC possess the highest Li diffusion and Li transference numbers, particularly the 1:1 and 2:8 F1S3M2/EMC blends, which have Li diffusion comparable to several pure carbonate blends, yet possess very high Li transference numbers. Ternary blends possess the lowest diffusion and Li transference numbers.

INOR 304
Ion conductivity of silyl solvent and organic carbonate electrolyte blends
Jake Lindstrom, lindstro@grinnell.edu, Leslie J. Lyons.Chemistry, Grinnell College, Grinnell, IA 50112, United States

Silyl solvents can be very useful in lithium ion battery and supercapacitor applications. These solvents usually perform worse than carbonates in the ionic conductivity of their electrolytes. This research examines a novel fluoroisilyl solvent (shown below) mixed with the salts LiPF₆ or LiTFSA and co-solvents ethylene carbonate (EC), ethyl methyl carbonate (EMC), or γ-valerolactone (GVL) or a binary combination of the carbonates. The fluoroisilyl electrolytes are good ion conductors with conductivities at 298 K greater than 1 mS/cm and the carbonates further increased the ionic conductivity. In binary mixtures with the same carbonate, conductivity trends with increasing carbonate concentration. The ternary electrolyte of the fluoroisilyl solvent with EC and EMC and 1 M LiPF₆ had the highest ionic conductivity of 3.7 mS/cm at 298 K. Computations were also used to visualize the molecular interactions between the lithium ion and the solvent molecules.

INOR 305
Simulation, synthesis, and analysis of upconverting and downconverting doped nanomaterials for enhanced photovoltaic efficiency
Adam Gotlin¹, adamgotlin@gmail.com, Emory Chan². (1) Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94704, United States (2) Engineering Science, University of California - Berkeley, Berkeley, California 94704, United States

Solar energy technology has potential to help address rising global demand for clean and renewable energy, but is inherently limited by the Shockley–Queisser limit of around 33.7% efficiency. To improve solar energy conversion efficiency, this limit can be raised by addressing the spectral mismatch between single junction c-Si solar cells and incident electromagnetic radiation. Lanthanide doped nanocrystals have already showed promising results in terms of upconversion and downconversion properties. Nanocrystals co-doped with lanthanides and transition metal ions may show even more promising results in terms of spectral conversion and emission intensity. Studying this material is a three step method: simulation, synthesis, and analysis. A validated kinetic model is used to simulate emission spectra. Nanoparticles are primarily synthesized using the Workstation for Automated Nanomaterial Discovery and Analysis (WANDA) robot, and then characterized using X-ray diffraction and analyzed using high throughput laser spectroscopy. Cobalt, iron, and lithium co-doped with lanthanides in NaYF₆ crystal were successfully synthesized. Cobalt doped particles showed a decrease in emission intensity, likely due to absorption from cobalt ions. Lithium doped particles showed similar intensity to the control, and in some cases, such as NaYF₆:Gd, Er, Yb, Li (20/2/2/2%), it outperformed the control. Further work in this field includes incorporating a theoretical framework to predict lanthanide and transition metal co-doped particles and improving the reliability and reproducibility of synthesis techniques. Advancement in these areas will help reveal an optimally doped nanoparticle for spectral conversion and emission.

INOR 306
Tunable electroluminescence from carbon dot LEDs
Yu Zhang³, Jun Zhao⁴, Xiaoyu Zhang⁵, Yu Wang⁶, Andrey Rogach⁶, William W Yu⁷, wuy6000@gmail.com. (1) Department of Chemistry and Physics, Louisiana State University Shreveport, Shreveport, LA 71115, United States (2) College of Electronic Science and Engineering, Jilin University, Changchun, Jilin 130012, China (3) College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao, Shandong 266042, China (4) Department of Physics and Materials Science, City University of Hong Kong, Hongkong, Hongkong, China

We report the tunable emission color from carbon-dot based light-emitting diodes. The color is controlled by their driving current. Tuning the device structure and the injecting current density we can get multi-color emission of blue, cyan, magenta, and white from the same carbon dots. This has not been observed for a single-layered material. The transparency and structural integrity of the nanomaterial light-emitting diodes. The current density-dependent emission will be useful for color light-emitting diodes.

INOR 307
Template-assembled cuprous oxide nanorod films on transparent electrodes: Electrodeposition conditions and photoelectrochemical behavior

Marlene Rivas1,2, Marlene.Rivas@LaVerne.EDU, Keith M Haynes1, Collin M Perry1, Justin W Youngblood3, Iraj Parchamazad2. (1) Department of Chemistry, University of North Texas, Denton, TX 76201, United States (2) Department of Chemistry, University of La Verne, La Verne, CA 91750, United States

Current methods for direct electrodeposition of nanostructured cuprous oxide thin films onto pre-formed electrode substrates have yet to demonstrate low-resistivity semiconductor nanomaterials. We have developed a robust templating protocol for the growth of vertically-aligned cuprous oxide nanowire films on electrode substrates that is tolerant to changes in growth chemistry. Facile formation of polymer nanopore membranes onto conductive glass substrates is accomplished using molds made from vertically-aligned ZnO nanorod arrays. Etch removal of the ZnO using boric or phosphoric acid creates void nanochannels for the electrochemical growth of cuprous oxide nanorods. Template control over the morphology of the resulting cuprous oxide nanomaterials has permitted the exploration of a range of parameters for the electrodeposition, in contrast to template-free electrodeposition methods for cuprous oxide, which provide nanostructured films only within narrow process windows of electrolyte composition and electrochemical parameters. We report the effects of changes including pH for the electrodeposition bath, nanorod diameter and height upon the photoelectrochemical behavior of the cuprous oxide nanorod films, as measured by the assembly and testing of photoelectrochemical solar cells.

INOR 308

Syntheses and SERS investigation of core-shell Ag@SiO2 nanoparticles

Xianghua Meng, xianghua.meng@coyotes.usd.edu, Chaoyang Jiang, Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069, United States

Core-shell nanostructures have received increasing interest due to their unique functionalities and broad applications. In this work, a facile method based on the combination of seeded growth and the Lee-Meisel method has been employed to prepare silver nanoparticles with diameters of ~45 nm. Core-shell Ag@SiO2 nanoparticles were synthesized by the well-established Stöber sol–gel approach. The core-shell Ag@SiO2 nanoparticles show similar UV-visible absorption behaviors and the surface Plasmon resonance band has a red shift with the increase of silica shell. The core-shell structures were confirmed by transmission electron microscopy and the surface-enhanced Raman scattering (SERS) activity was evaluated. Such core-shell nanoparticles could be an important type of building block that can be integrated into novel sensing devices.

INOR 309

Synthesis of oxidation stable Cu nanowires with high performances for future electrodes

Zhenxing Yin1, Sanghun Cho1, Youn Sang Kim1, younkim@snu.ac.kr, Jae Young Yoo2, Jae Min Myoung2. (1) Graduate School of Convergence Science and Technology, Program in Nano Science and Technology, Seoul National University, Gwanak-gu, Seoul 151-744, Republic of Korea (2) Department of Materials and Engineering, Yonsei University, Shinchon, Seodaemun-gu, Seoul, Republic of Korea

Copper nanowire (Cu NW) is a promising material electrode researched in various applications, such as low-cost flexible displays, lighting, touch screen and solar cells. More importantly, the Cu NWs have a potential to replace the indium tin oxide (ITO) and silver nanowires in the future, because of the low cost, excellent electrical conductivity and remarkable mechanical properties. Recently, there are several methods to synthesis of Cu NWs. However, these Cu NWs are limited to use for practical applications, due to the oxidation and high sintering temperature.

Herein, we synthesized the average 93 nm diameter, ~30 μm length single crystalline Cu NWs by using polyl reduction method with excellent oxidation stability, well dispersibility, low-sintering temperature and high conductivity. This synthesis method depends on the reduction potential of ethylene glycol (EG) with surfactant of oleylamine and potassium bromide (KBr) which could control the morphology of metal nanowires. Through the observation of X-ray diffraction (XRD), Transmission electron microscope (TEM) and Scanning electron microscope (SEM), we demonstrated a mechanism of the formation and confirmed the optimized synthesis conditions. To analyze the oxidation stability, we observed the change of the Cu NWs within 7 days after synthesis using XRD, Ultraviolet-visible spectroscopy (UV-vis) and X-ray photoelectron spectroscopy (XPS). From these analyses, we can observe that there is no characteristic change for Cu NWs during 7 days.

We applied the Cu NWs for foldable and flexible electrodes. The performance of electrodes was measured by bending machine and four point probe. Experimental data demonstrated that these Cu NWs have the high conductivity (0.5Ω/cm) and excellent flexible property after annealing 180 °C in the vacuum oven. We believed that our synthesis method could be adapted to fabricate the functionalized electrodes and will be used for the next generation electronics.

INOR 310

Ligand investigations towards green iron pyrite nanoparticle synthesis

Benjamin A Weintraub, bweintraub@pencol.edu, Science Division, Peninsula College, Port Angeles, WA 98362, United States

Iron pyrite is a promising light harvesting material with low toxicity, high absorption coefficient, and satisfactory bandgap (Eg=0.95 eV) for solar cell applications. This research investigates using various green ligands for synthesizing iron pyrite nanoparticles using solution-phase techniques. Structural and optical data for the nanoparticles will be presented.

INOR 311

Edge–abundant boron–nitride–carbon nanoribbons aerogel as efficient electrocatalysts for oxygen reduction reaction

Yongji Gong, yongjigong@gmail.com, Shubin Yang, Pulickel Ajayan, Department of Chemistry, Rice University, Houston, TX 77005, United States

The widespread application of noble metal catalysts such as platinum and its alloys for oxygen reduction reaction (ORR) in fuel cells has been hampered by their high-cost and low thermal efficiency. In spite of tremendous efforts on searching for alternative non-precious metal catalysts, the achievement of a catalyst with high active, high onset potential, good stability and low cost remains challenging. Here, we develop an efficient strategy to construct three-dimensional (3D) architectures from numerous edge-abundant boron-nitride-carbon nanoribbon (BNC NR) for ORR electrocatalysts. Benefited from boron and nitrogen co-doping, large available edges and multilevel pores, the resulting architectures exhibit excellent electrocatalytic activities for ORR. The optimized sample shows the highest onset and half-wave potentials of among all the reported metal-free ORR catalysts, even superior to commercially available Pt/C catalysts (∼130 mV and ∼60 mV higher for onset and half-wave potential, respectively). Furthermore, this catalyst possesses a high current density and excellent 4-electron transfer pathway with less than 4.0% hydrogen peroxide yield (4.0-6.0% for Pt/C) during oxygen reduction process.

INOR 312
Preparation of size-controlled hollow spherical gold nanoparticle superstructures with near-infrared extinction

Chen Zhang, chz19@pitt.edu, Yong Zhou, Chengyi Song, George C Schatz, Nathaniel L Rosi. (1) Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, United States (2) Department of Chemistry, Northwestern University, Evanston, IL 60208, United States

Spherical gold nanoparticle superstructures (or gold hollow spheres, GHSS) with varied sizes (∼30nm, ∼75nm, ∼150nm) and surface plasmon resonance (SPR) responses have been prepared by using a single peptide conjugate, C2-AA-PEPm, at varied reaction conditions. SPR bands are red-shifted and broadened as the diameters of the GHSSs and individual gold NPs increase. Medium (75.3 ± 12.4 nm) and large-sized GHSSs (149.7 ± 30.8 nm) each displayed broad SPR peaks in the NIR window (650-900 nm), pointing toward their potential application in photothermal therapy. A shell model was used to successfully simulate the optical properties of these materials. This success of this model in explaining the large SPR red-shifting of the medium and large GHSSs implies that the synthesized GHSSs are likely composed of a quasi-continuous shell structure with defects such as pinholes.

INOR 313
Mechanochemical routes to bicontinuous conductive polymer networks for solar applications
Erin R Waterman, watermae@union.edu, Michael E Hagerman. Department of Chemistry, Union College, Schenectady, NY 12308, United States

We are currently exploring mechanochemical routes to improve charge transport within conductive polymer networks for solar heterojunctions. Heterometallic dicyanoaurate-based coordination polymers were used as intercalative hosts to promote in-situ growth of emeraldine polyaniline, which provides electron conduction pathways within the active layer. Laponite clay nanoparticles were used to direct the self-assembly of the bicontinuous polymer networks and nanomorphology within the nanocomposites. We have investigated the influence of concentration, time of grinding, and solvent on composite nanomorphology using scanning electron microscopy and atomic force microscopy. Infrared and electronic absorption spectroscopy were also used to verify polymer oxidation state and to probe polymer-polymer and nanoparticle interactions.

INOR 314
Surface plasmon mediated solution chemical deposition on nanostructured substrates from silver(I) and gold(I) precursors
Kelsea Johnson, kjohnson@chem.ufl.edu, Yung-Chian Wu, Jingjing Qiu, W. David Wei, Lisa McElwee-White. Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States

Deposition of metal nanoparticles and films onto nanostructured materials from organometallic precursors can be induced by excitation of the surface plasmon resonance of the substrate. Au(I) and Ag(I) precursors have been used to deposit metallic gold and silver on nanostructured substrates. The effects of precursor structure and deposition conditions will be discussed.

INOR 315
Metal oxide nanowires: Synthesis, characterization, and its application in nanoscale fuel cells
Mirza Hasan, mirza.hasan@tcu.edu, Jeffery Coffer. Department of Chemistry, Texas Christian University (TCU), Fort Worth, Texas 76109, United States

Metal oxide electrolytes have been used extensively in applications such as solid oxide fuel cells (SOFCs), due to their ability to permit fast ion conductance as a solid electrolyte at slightly elevated temperatures. Yttrium oxide-stabilized zirconium oxide (ZrO₂) (YSZ) is among the most widely used materials for these applications.

The goal of this project is to synthesize a network of 1D YSZ nanowires that will be coated with platinum nanoparticles (as the cathode) and nanostructures of nickel (II) oxide (as the anode). Reduction in the size of the electrolyte, cathode, and anode materials will increase the reactive surface area for the reduction and oxidation of oxygen and hydrogen, respectively, thus ideally increasing the efficiency of the SOFC.

In our research, the synthesis of nanostructured solid electrolytes was accomplished via sol-gel reactions in combination with electrospraying techniques and thermal annealing. The necessary three phase boundaries (TPB), where the reduction of oxygen and oxidation of hydrogen takes place, is prepared by thermal reduction of hexachloroplatinic acid (H₃PtCl₆) and nickel (II) acetate to elemental platinum and nickel (II) oxide nanocrystal form, respectively. The characterization of these materials was achieved primarily by Scanning Electron Microscopy (SEM) (JEOL JSM-8100), Transmission Electron Microscopy (TEM) (JEOL JEM-2100), and energy-dispersive X-ray (EDX) spectroscopy. The data obtained from these investigations is used to develop an understanding of the relationship between nanowire structure and ion transport for fuel cell applications.

INOR 316
Design, synthesis and application of multifunctional redox-responsive porphyrin-based polysilsesquioxane nanomaterials for photodynamic therapy
Daniel Vega, dvega1@uncc.edu, Juan L Vivero-Escoto. (1) Department of Chemistry, University of North Carolina at Charlotte, Charlotte, NC 28223, United States (2) The Center for Biomedical Engineering and Science, University of North Carolina at Charlotte, Charlotte, NC 28223, United States

Cancer is responsible for one out of eight deaths worldwide and is the second largest cause of death in the U.S. Photodynamic therapy (PDT) is a non-invasive approach for cancer treatment, which avoids some of the harmful side-effects associated with traditional therapies such as chemotherapy and radiotherapy. This treatment is based on the therapeutic effect of reactive oxygen species generated after the activation of a light-sensitive molecule called a photosensitizer (PS). Recently, a great deal of attention has been devoted to the improvement and development of PS. An optimal PS should be chemically pure, have a high singlet oxygen quantum yield, and absorb light at wavelengths that are ideal for skin penetration. Nevertheless, there are some drawbacks with current PS such as inadequate energy absorption, poor solubility in water, and the inability to target tumor cells. Hybrid nanoparticles (NPs), composed of both organic and inorganic components are promising materials to overcome some of those issues. For example, NPs can carry a large payload of PS and can be targeted for specific PS delivery in the tumor. However, current nanocarriers do not show the optimal PDT response due to self-quenching and low singlet oxygen quantum yield. In this work, multifunctional redox-responsive porphyrin-based polysilsesquioxane (PSiQ) nanoparticles were synthesized and applied in PDT. The network of PSiQ-NPs is formed by porphyrin-based photosensitizers chemically connected via a redox-responsive linker. Under reducing environment, such as the one found in cancer cells, the nanoparticles are degraded to efficiently release the photosensitizers as individual units. The platform can be further functionalized with polyethylene glycol (PEG) and targeting ligands to improve its biocompatibility and target specifically. The PDT response of this porphyrin-based PSiQ nanomaterial is demonstrated in vitro using human cervical (HeLa) cancer cells. We envision functionalized stimul-responsive hybrid nanoparticles as a potential alternative to improve PDT.

INOR 317
Toward a multifunctional ¹⁹F MRI contrast agent based on mesoporous silica nanoparticles
Novel drug-delivery agents are needed to overcome the limitations of systemic toxicity of traditional chemotherapeutics, and an even more powerful paradigm combines delivery and imaging into one agent. One potential platform for such an agent is nano- or microparticles consisting of mesoporous silica, a well-characterized material with minimal toxicity and with great flexibility for chemical functionalization. Much progress has been made using porous silica particles as multifunctional drug-delivery agents, enabling combined delivery and imaging by incorporating contrast agents for optical detection, PET, and proton MRI. One imaging modality not yet combined with porous particles is $^{19}$F MRI.

Here, we present efforts to prepare a multifunctional silica nanoparticle that incorporates fluorine atoms for detection by $^{19}$F MRI. We have synthesized several alkoxysilanes that contain multiple, chemically-equivalent fluorine atoms in the form of trifluoromethyl groups. We have subsequently immobilized these silanes to the pore surfaces of mesoporous silica nanoparticles (with the MCM-41 pore structure) that were PEGylated on their exterior surfaces to promote biocompatibility and water-dispersibility.

Lastly, we used $^{19}$F NMR spectroscopy to detect these immobilized fluorine atoms and measure their magnetic relaxation properties, demonstrating proof-of-principle that $^{19}$F MRI could be used to detect and image these materials. Relaxation rates and signal-to-noise ratios were sufficient to acquire spectra in short amounts of time. In related work, we are preparing stimuli-responsive alkoxysilanes, which could be used to effect a “switch-on” response in $^{19}$F MRI, that respond to changes in pH or reducing conditions.

**INOR 318**

Characterization of RF magnetron sputtered nanoscale films of lithium ceramic materials for solid battery electrolytes

**Erik Burton**, erik-burton@utulsa.edu, Dale Teeters, Department of Chemistry and Biochemistry, The University of Tulsa, Tulsa, Oklahoma 74104, United States

All solid state lithium ion batteries are of great technological interest because of manufacturing and safety advantages. Solid materials with high electrochemical stability and high ionic conduction are needed to fabricate batteries with low internal resistance resulting in enhanced performance. Five Ceramic materials (Li$_3$La$_{1-x}$Ti$_x$O$_4$, Li$_5$La$_3$Li$_2$Ti$_2$O$_9$, Li$_2$Al$_2$O$_3$, P$_2$O$_5$, Li$_x$Al$_{2-x}$O$_4$Ti$_2$O$_9$, and Li$_3$La$_3$ZrO$_4$), which have recently been shown in the literature to have potential for solid electrolytes, have been studied. RF magnetron sputtering was used to form nanoscale thin layers of the electrolyte materials. These layers are similar to those that would be used in thin film batteries. AC impedance spectroscopy and infrared and Raman Spectroscopy have been used to characterize these materials. General morphology and the grain boundary structure of the bulk material and the surface have been analyzed using X-ray diffraction, atomic force microscopy and scanning electron microscopy. The affect of sintering on ion conduction was also investigated. These data will them be used to explain the differences in conductivities for the electrolytes. The potential for use in commercial battery systems will be evaluated.

**INOR 319**

Optoelectronic properties of solution-processed metal-semiconductor nanocrystal films

**Natallia N Khomlichteva**, knatali@bgsu.edu, Mikhail Zamkov. (1) Department of Photochemical Science, Bowling Green State University, Bowling Green, Ohio 43402, United States (2) Department of Physics and Astronomy, Bowling Green State University, Bowling Green, Ohio 43402, United States

We will report on the development of nanoparticle films comprising both semiconductor and metal nanocrystals, deployable for printable electronics applications. Such hybrid morphology enables a strong plasmonic effect on optical properties of semiconductor nanocrystals, which could be precisely controlled via film architecture. In particular, plasmon-exciton interactions in the film can be tuned to provide either an enhanced light-emitting or light-harvesting characteristics of semiconductor nanocrystals. Meanwhile, a stable and inert semiconductor matrix should facilitate the compatibility of fabricated films with many device platforms. Alternatively, semiconductor nanocrystal films doped with a small fraction of metal nanocrystals could be utilized in field effect transistors. In this case, metal domains can inject n- or p-type carriers in response to electric field of the gate electrode.

**INOR 320**

Synthesis and properties of Yb$_{0.2}$Ca$_{0.8}$Bi$_2$MnSb$_{11}$

**Alexander T Brown**, abrown@citizen.com, Yufei Hu', Sabah K Bux', Susan Kauzlarich. (1) Department of Chemistry, University of California, Davis, California 95616, United States (2) Department of Physical and Environmental Science, Colorado Mesa University, Grand Junction, Colorado 81501, United States (3) Jet Propulsion Lab, California Institute of Technology, Pasadena, California 91109, United States

The ZnIn$_2$ phase, Yb$_{0.2}$MnSb$_{11}$, has a high thermoelectric efficiency at high temperature, evaluated by the thermoelectric figure of merit, zT. In previous studies, Yb$_{0.2}$MnSb$_{11}$ has been doped with Ca so that the density of material decreases and the high thermoelectric figure of merit is retained. Bi doping of Yb$_{0.2}$Ca$_{0.8}$MnSb$_{11}$ in the Ca cation sites should decrease the charge carrier concentration while increasing mobility; which is expected to result in a material with a higher zT. Large single crystals were synthesized via Sn-Flux for Yb$_{0.2}$Ca$_{0.8}$Bi$_2$MnSb$_{11}$ ($x=0.2,0.4,0.6,0.8,1.0$). On stoichiometry powder samples were also synthesized with the same relative amounts. Microprobe analysis showed a small amount of Bi doped into the single crystals. Microprobe analysis for the powder synthesis route showed inhomogeneous amounts of Bi. Powder samples were pressed into condensed pellets by Spark Plasma Sintering. Electrical resistivity and the Seebeck coefficient were measured on a powder sample Yb$_{0.2}$Ca$_{0.8}$Bi$_2$MnSb$_{11}$. The structure and properties will be presented.

**INOR 321**

Isotropic negative thermal expansion in rock-salt ordered mixed metal fluorides M$^{10+}$ZrF$_6$ (M$^{10+}$=Ca, Co, Zn) with a ReO$_3$-type structure

**Justin C Hancock**, jhancock@gatech.edu, Angus P Wilkinson. (1) School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States (2) School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

Some materials of the type M$^{10+}$M$^{10+}$F$_6$ have a cubic-ReO$_3$ structure, which makes them good candidates for negative thermal expansion (NTE). Additionally, the simplicity of the cubic-ReO$_3$ structure is appealing for studies focused on understanding the factors governing thermal expansion. There is little published thermal expansion data for this group of materials. However, it is known that many members of this family undergo a cubic-to- rhombohedral phase transition upon cooling, which would limit their potential as NTE materials. Variable temperature x-ray and neutron powder diffraction have been used to examine the thermal expansions and phase transitions in CaZrF$_6$, CoZrF$_6$, and ZnZrF$_6$. CaZrF$_6$ remains cubic down to at least 10K and displays strong NTE from < 10K to above 1000K with a room temperature CTE of ~11 ppm-K$^{-1}$. In contrast, CoZrF$_6$ and ZnZrF$_6$ undergo cubic-to-rhombohedral phase transitions near room temperature (272K for CoZrF$_6$ and 310K for ZnZrF$_6$), and display much weaker negative thermal expansion in the cubic phase (CTE~2 ppm-K$^{-1}$). An understanding of the factors that influence the thermal expansion within this specific structure type, such as cation size and covalency, and fluoride coordination environment, may allow for the development of controlled thermal expansion materials.
Synthesis, structure, and characterization of new mixed valence manganese (Mn$^{2+}$/Mn$^{3+}$) fluorides

**Sun Woo Kim**, skim56@uh.edu, Elise Pachoud, P. Shiv Halasyamani. (1) Department of Chemistry, University of Houston, Houston, Texas 77204, United States (2) Department of Chemistry, Aalto University, Espoo, Finland

New mixed valence manganese (Mn$^{2+}$/Mn$^{3+}$) fluoride materials, Ba$_3$Mn$_4$F$_{13}$ and Na$_4$Ba$_2$Mn$_3$F$_{14}$, have been synthesized and characterized by single-crystal X-ray diffraction. Powder X-ray diffraction and magnetic property measurement. Both compounds were synthesized by hydrothermal method using CF$_3$COOH aqueous solution instead of aqueous HF. The aqueous solution of CF$_3$COOH acted as a reducing agent, and reduce some of the Mn$^{3+}$ to Mn$^{2+}$ during hydrothermal reaction. The amount of CF$_3$COOH also played an important role for controlling reduction process. Ba$_3$Mn$_4$F$_{13}$ exhibits a one-dimensional chain structure consisting of separate edge-shared Mn$^{2+}$F$_6$ trigonal prism and corner-shared Mn$^{3+}$F$_6$ distorted octahedra that run along the b-direction. Na$_4$Ba$_2$Mn$_3$F$_{14}$ exhibits a Jarosite-type structure consisting of corner-shared Mn$^{3+}$F$_6$ (Mn$^{2+}$/Mn$^{3+}$)F$_6$ and Mn$^{3+}$F$_6$ distorted octahedra, which forms infinite helicoidal double-chains along b-axis. The synthesis, crystal structures and magnetic properties of new mixed valence manganese (Mn$^{2+}$/Mn$^{3+}$) fluoride materials will be presented. Crystal data: Ba$_3$Mn$_4$F$_{13}$. Orthorhombic, space group Pnma (No. 62), a = 27.272(2), b = 5.6613(4), c = 7.4711(6) Å, V = 1155.51(15) Å$^3$, Z = 4; Na$_4$Ba$_2$Mn$_3$F$_{14}$. Monoclinic, space group C2/m (No. 12), a = 16.961(9), b = 11.551(6), c = 7.651(4) Å, β = 101.785(12)$^\circ$, V = 1467.4(13) Å$^3$, Z = 2.

**INOR 323**

Solvation of Li$_2$VS$_2$ as a function of cation density

**Jacob A Armitage**, ja1361@txstate.edu, **Benjamin R Martin**, bmartin@txstate.edu. Department of Chemistry and Biochemistry, Texas State University, San Marcos, TX 78666, United States

Li$_2$VS$_2$ is an alkali-metal intercalated layered chalcogenide, consisting of 2-dimensional anionic VS$_2$ sheets with interlayer Li cations. This material has promising electrical and optical properties, and has previously been explored as a cathode for lithium ion batteries. Understanding the solvation mechanism of materials such as this is of interest, since the presence of a solvent dramatically affects ion mobility and may affect the reversibility of insertion reactions. The solvation and exfoliation of Li$_2$VS$_2$ (xS1) as a function of lithium content (x) was studied using X-ray diffraction, potentiometric analysis, and microscopy based on interactions with different solvents (cyclic carbonates, amides, and other protic and aprotic solvents). In general highly reduced Li$_2$VS$_2$ and fully oxidized VS$_2$ show little propensity for solvation or solvent-assisted exfoliation, while intermediate compositions readily solvate. Tuning the interlayer cation density in layered chalcogenides such as Li$_2$VS$_2$ may provide a means of soft chemical exfoliation.

**INOR 324**

[(CH$_3$)$_2$CNH$_3$]$^+$CuBr$_2$: A new feature in the isopropyloammonium halidometallate landscape

**Marcus R. Bond**, mbond@semo.edu. Department of Chemistry, Southeast Missouri State University, Cape Girardeau, MO 63901, United States

The isopropyloammonium cation, while relatively small, combines the hydrogen bonding capability of a primary ammonium cation with the bulkiness of a more highly substituted cation. Thus, it seems an attractive target for development of new halidometallates. The few known isopropyloammonium halidometallate compounds (just 10 reported in the CSD with structural information for only 6) do provide some striking examples of structural complexity, i.e. the thermochromic CuCl$_3$$^+$ and (Cu$_3$)$_2$Cl$_6$$^+$ salts, and the multiple phase transitions in the (Cd$_3$Cl$_9$$^{3+}$) salt. In an effort to re-investigate and further explore the isopropyloammonium halidometallate landscape, the title compound was prepared and characterized. The structure contains the second example of a quasi-planar CuBr$_{3}$$^{2-}$ oligomer (CuBr$_{3n-1}$$^{2-}$ oligomers with n=1-4, 7, and 10 are also known). The oligomers aggregate into stacks with a 5(3/2,1/2) stacking pattern, as is also found in (3-chloro-1-methylpyridinium)$_2$CuBr$_2$ structure. While the oligomer stacks in the latter structure are isolated, in the title structure they are linked together through semicoordinate Cu...Br bonds to form layers with a herringbone arrangement of oligomers. The layers are separated by isopropyloammonium cations in which the ammonium group hydrogen bonds to bromide ions of the the layer and with the methine hydrogen directed into the layer. At ambient temperature a slight disorder of the organic cation is observed arising from an inverted configuration (SOF=0.25(2) for the minor component). A structure determination at 100 K reveals no disorder of the organic cation, but also a severe degradation of crystal quality upon cooling. Studies of a broader range of isopropyloammonium halidometallates are planned.

**INOR 325**

Award Address (ACS Award for Distinguished Service in the Advancement of Inorganic Chemistry sponsored by Strem Chemicals, Inc.). Design, discovery and serendipity in transition metal-mediated reactivity

**T. Don Tilley**, tdtilley@berkeley.edu. Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

Major goals of research in transition metal chemistry are the discovery of more efficient chemical transformations, or new materials with advanced properties. Various strategies are employed in pursuit of these goals, but the most useful provide fundamental understanding that enables rapid progress in research and development. One approach, strongly grounded in synthetic inorganic chemistry, targets potentially reactive structures that are anticipated to be intermediates in transformations of interest. This presentation will describe selected research endeavors of this type, and the unexpected, enlightening lessons that were obtained.

**INOR 326**

Award Address (ACS Award in Pure Chemistry by the Alpha Chi Sigma Fraternity and the Alpha Chi Sigma Educational Foundation). Shaping the synthesis of bimetallic nanostructures

**Sara E. Skrabalak**, sksrabalak@indiana.edu. Department of Chemistry, Indiana University, Bloomington, IN 47405, United States

Metal nanostructures promise to address needs in catalysis, nanomedicine, chemical sensing, and more. The physicochemical properties of metal nanocrystals are determined by a set of structural parameters that include their size, shape, composition and architecture. Although there are now established strategies to achieve monometallic nanocrystals with defined structural features, maintaining this precision during the synthesis of bimetallic nanostructures is daunting on account of the differing properties of each metal and their precursors and the difficulty in nucleating a defined bimetallic phase. The Skrabalak Laboratory is developing seed-mediated co-reduction and ligand-controlled co-reduction as general routes to structurally defined bimetallic nanostructures, including shape-controlled alloyed nanocrystals, symmetrically branched nanocrystals and nanodendrites. These methods will be discussed, along with an analysis of the physical and chemical properties of the resultant bimetallic nanostructures.

**INOR 327**

Award Address (ACS Award in Organometallic Chemistry sponsored by The Dow Chemical Company Foundation). Systematic development of new redox-noninnocent ligands

**Kenneth G Caution**, cauton@indiana.edu. Department of Chemistry, Indiana University, Bloomington, IN 47405, United States

This lecture will review some emerging trends in organometallic and coordination chemistry, showing how those gave birth to the current activity in redox noninnocent ligands, as well as the several other phenomena that are currently being called “noninnocent.” Focus will then be made on our efforts to develop new types of redox noninnocent ligands, different from those based on alpha diketones and their heteroatom relatives. Specific effort will be
made to discuss general electronic structural features to look for in a ligand to develop noninnocence, and to identify whether that noninnocence is triggered by oxidation or by reduction. In general, the goal is to put rationality in ligand choice. Examples of highly nitrogen rich tetrazines as noninnocent ligands will be described, and their potential probed.

INOR 328

Award Address (ACS Award in Inorganic Chemistry sponsored by Aldrich Chemical Company, LLC). Stable carbenes and related species: Powerful tools in organic, inorganic and organometallic chemistry

Guy Bertrand, guybertrand@ucsd.edu. Department of Chemistry and Biochemistry, UC San Diego, La Jolla, CA 92039, United States

Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of the various systems. Spectacular results in this area have been achieved using cyclic diaminocarbenes, the so-called N-heterocyclic carbenes (NHCs), mainly because of their strong s-donor properties. Although it is possible to cursorily tune the structure of NHCs, any diversity is still far from matching their phosphorus-based counterparts, one of which is one of the great strengths of the latter. Beginning with our discovery in 1988 of a bottle-able (phosphino)(silyl)carbene, a variety of stable acrylic carbenes are known, but they give rise to fragile metal complexes. During the recent years, we have discovered new types of stable cyclic carbenes, as well as related carbon-based ligands, which are not NHCs, and which feature even stronger s-donor properties than NHCs. The synthesis, characterization, stability, electronic properties, coordination behavior, and catalytic activity of complexes bearing our ligands will be presented, and comparisons with their NHC cousins will be discussed. We will also describe a novel type of ligands, isoelectronic with amines and phosphines, but based on boron.

INOR 329

Award Address (F. Albert Cotton Award in Synthetic Inorganic Chemistry sponsored by the F. Albert Cotton Endowment Fund). Chemical hydrogen storage: Pathways and intermediates for activated amineborane hydrogen-release/oligomerization reactions

Larry G Sneddon, lsneddon@sas.upenn.edu. Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States

The growth of aminoborane oligomers through the dehydrocoupling reactions of ammonia borane (NH₃BH₃) has been of great recent interest owing to the potential use of aminoboranes as chemical hydrogen storage materials and/or precursors to boron nitride ceramics. While long-chain oligomers and polymers have been shown to be products of metal-catalyzed aminoborane dehydrogenation reactions, only a few small polyaminoborane oligomers have previously been prepared and characterized. Our work will be described that has resulted in both the development of the systematic syntheses and the structural characterizations of new discrete linear and chain-branched oligomeric polyaminoboranes. Also discussed will be our studies demonstrating that, depending upon the activation method, aminoborane dehydro-oligomerization reactions can occur by quite different mechanistic pathways.

INOR 330

Shape stabilized composite zinc electrode for secondary batteries

Ozgenc Ebil, ozgencibil@iyte.edu.tr, Gizem Payer, Ogan Ocal. (1) Department of Chemical Engineering, Izmir Institute of Technology, Gulbahce Koyu, Urla, Izmir, Turkey (2) Center for Materials Research, Izmir Institute of Technology, Gulbahce Koyu, Urla, Izmir, Turkey (3) Ocali Inc., Urla, Izmir, Turkey

Due to environmental concerns and ever increasing cost of manufacturing, development of cost effective, high capacity and “green” battery technologies such as nickel-zinc, zinc-air, and others have attracted interest. Ni-Zn secondary batteries show greater charge/discharge cycle capacity than conventional lead-acid batteries. In addition to Ni-Zn secondary batteries, Zn-air batteries have great promise to replace lead-acid batteries in automobile industry due to their high specific energy. However, batteries containing zinc electrodes suffer from limited capacity and lifetime mostly due to zinc dissolution in alkaline solutions. Repeated zinc dissolution into alkaline solution and re-precipitation during charge/discharge cycle usually result in uneven Zinc deposition. This uneven growth is due to dendritic growth of zinc metal in alkaline solution during charging and may result in short circuiting of the battery. Here we present a composite zinc electrode containing low zincate mobility gel for rechargeable batteries and method for fabricating such electrodes. The low zincate mobility gel electrolyte is blended into anode structure to form an almost isotropic morphology instead of a layered structure wherein the gel electrolyte is coated onto zinc anode. Blending of low zincate mobility gel electrolyte into anode structure itself has few benefits: The surface area available for electrochemical reaction is maximized since gel electrolyte wets a much higher area of the porous zinc anode and spent anode performs as electrolyte during battery operation. It also greatly enhances the surface area of the anode that is in contact with the electrolyte. As a result less electrolyte is required per unit weight when compared to other zinc anode designs in literature. Even after many charge/discharge cycles, the composite zinc anode retains its original shape. The result is a more reversible charge/discharge cycle increasing the overall battery performance, enhanced service and shelf life with virtually no cost increase in manufacturing.

INOR 331

Ab initio study of p-type dye-sensitized solar cells: Effects of different anchoring groups on the electronic features of dye-NiO interphase

Michele Pavone, Michele.pavone@unina.it, Ana B. Muñoz-Garcia. Department of Chemical Sciences, University of Naples Federico II, Naples, Italy

For the last two decades, dye-sensitized solar cell (DSSC) technology has been challenging solid-state photovoltaics for solar energy conversion into electricity. Remarkably performances have been recently achieved with conventional n-type DSSCs, thanks to great experimental and theoretical efforts devoted to understanding and tuning the n-DSSC materials properties and functions [1]. The research on p-type DSSC, instead, is still in its infancy and, so far, their poor performances have hindered the foreseeable development of tandem cells, i.e. solar cells with a photo-anode (from n-DSSC) and a photocathode (from p-DSSC) [2]. A deeper and more comprehensive understanding of structure-property-function relationships in photocathode device is thus crucial for further advancements in this field.

In this contribution, we will discuss our first-principles study on a prototypical photocathode made of nickel oxide and a Coumarin dye (C343) [3]. We will analyze the NiO(100) clean and defect-free surface, we will address the structures and the energetics of three different anchoring groups on the NiO surface, with and without the presence of nickel vacancies. Then, we will discuss the full coumarin-NiO system and we will highlight how their electronic features are affected by their mutual interaction.

Our quantum-mechanical analyses of the p-DSSC model will provide new insights on the dye-electrode interphase, paving the route to an effective, rational design of new and better performing p-DSSCs.


INOR 332

Curved carbon-rich polyarenes for maximizing lithium ion storage
Planar sp²-hybridized carbon networks such as graphite are key anode components in rechargeable Li-ion batteries. Carbon allotropes with non-planar [?] surfaces ranging from fullerenes to nanotubes are also on the radar as prospective anode materials for energy storage. The curved carbon frameworks of fullerenes and nanotubes are effectively modeled by bowl-shaped polyaromatic hydrocarbons (buckybowls) in a variety of theoretical and experimental studies. We recently investigated the ligand-induced reduction of a small buckyball (coronene) and revealed a high degree of alkali metal encapsulation between the highly charged polyaromatic decks. These results provided a new paradigm for lithium intercalation between the curved carbon surfaces in buckybowls, fullerenes and nanotubes and showed their potential as new energy storage materials. Further elucidation of the alkali metal storage mechanisms in non-planar carbonaceous materials is on-going. These studies are important and timely, as expectations for Li-ion batteries and advanced carbon anode materials are rapidly growing.

INOR 333

Application of redox non-innocent ligands to non-aqueous flow battery electrolytes

Patrick J Cappillino, pcapipi@sandia.gov, Harry D Pratt 2 , Nicholas S Hudak 2 , Neil C Tomson 3 , Travis M Anderson 2 , Mitchell R Anstey 1 . (1) Sandia National Laboratories, Livermore, CA 94551, United States (2) Sandia National Laboratories, Albuquerque, NM, United States (3) Department of Chemistry, College of St. Benedict, St. Joseph, MN 56374, United States

Application of Redox Non-Innocent Ligands to Non-aqueous Flow Battery Electrolytes


Efforts to meet increasing global energy demand must include renewable energy sources that do not contribute to accumulation of greenhouse gases, such as wind and solar. While abundant, these sources are intermittent due to factors such as day-night cycles and weather. Furthermore, their generation capabilities are poorly matched to peak and off-peak use of electricity. Grid-scale strategies to mitigate these challenges, such as load-shifting, require energy storage components to supplement the current infrastructure in which electricity is instantaneously generated and distributed.

Redox flow batteries (RFB) have attractive features for this application, including decoupled energy capacity and power output, both of which are independently scalable. Over the last several decades, a number of technologies based on vanadium and iron-chromium electrolytes were developed but have so far met with limited commercial success. Further advancement requires fundamentally different redox chemistry with stable redox couples, large potential differences, and fast redox kinetics.

Herein we report new, non-aqueous RFB electrolytes that meet these criteria based on metal complexes containing “redox non-innocent” ligands (M-NIL). The abundance of well-characterized, reversible charge transfer events exhibited by these compounds has the potential to greatly improve their energy density over state-of-the-art, transition-metal based RFB electrolytes. Details on their preparation, characterization and electrochemistry will be presented and their performance as RFB electrolytes will be discussed.

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INOR 334

Versatile catalyst motif for production of H2 from alcohols and O2 from hydrogen peroxide

Martin Nielsen, marnie@kemi.dtu.dk, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

The use of PNP type non-innocent ligands for efficient H2 production from alcohol containing substrates (refs 2-5) and O2 from hydrogen peroxide (ref 1) is presented. It is shown that this type of catalyst seems to be very stable and capable of activating a wide range of substrates. Mechanistic insights are given as well.

References:
1) Nielsen, M. submitted.
5) Unpublished work.

INOR 335

Comprehensive cobalt-based water oxidation catalysts: From nanomaterials to PSII mimics

Greta R. Patzke, greta.patzke@aci.uzh.ch, Fabio Evangelisti, Hongfei Liu, Sandra Luber, Department of Chemistry, University of Zurich, Zurich, Switzerland

Efficient Co-based water oxidation catalysts (WOCs) inspired by the cuboidal [CaMnO4] oxygen evolution complex (OEC) of photosystem II (PSII) are in the focus of current artificial photosynthesis research. Exploration of their oxygen evolution mechanisms and true active species poses new challenges.

We present a comprehensive approach towards structure-activity relationships of Co-WOCs through parallel development of nanoscale Co-spinels, Co-polypyrrometallates (Co-POMs), and novel Co-cubanes as PS II mimics. First, new design parameters and synthetic strategies for cobalt spinel nanomaterials are introduced to optimize the catalytic performance of their cubane-related moieties. Next, we studied the influence of molecular core-shell combinations on Co-POM-WOCs. The novel tungstobismutate water oxidation catalyst [(Co(H2O)5][Co8Bi6W4O36(OH)4]]16- is a key example for the crucial influence of subtle core disorder on the WOC activity among a series of isostructural Co/Mn-containing POMs. POM-WOCs furthermore operate at the interface of homo- and heterogeneous catalysis through complex formation with photosensitizers. Finally, we newly embedded a [Co(II)3O]- cubane core into a ligand architecture of unprecedented flexibility as a key step towards PSII-OEC. Bio-mimetic advantages of the novel Co(II)-cubane WOC include: (1) presence of high-spin Co(II) centers in close analogy to the Mn centers of PSII, (2) enhanced catalytic performance through ligand exchange and deprotonation, and (3) first experimental input for modeling new water oxidation pathways.
INOR 336
Nanoructed Ni(OH)₂ nanotube arrays for high power and high energy asymmetric supercapacitors
Qiang Li², macy@utpa.edu, Xing Sun¹, Yuanbing Mao¹. (1) Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78539, United States (2) Department of Mechanical Engineering, University of Texas-Pan American, Edinburg, TX 78539, United States

Fast subsurface Faradic reactions and charge transport rate are vital factors for achieving high energy/power pseudocapacitors. However, the thin film configuration hardly fulfills the high energy requirement while thick electroactive material deposition restricts ion diffusion path and lowers fault tolerance. We report the fabrication of Ni(OH)₂ nanotube arrays growing on nickel foam via sacrificial ZnO nanowires. The increasing accessible electrochemical sites, improved electrolyte percolation and high fault tolerance endow the Ni(OH)₂ nanotube arrays superior electrode materials. The protocol allows a highest Ni(OH)₂ nanotube loading of 3.18 mg/cm² which yields a high areal capacitance of 5.88 F/cm² (1850.6 F/g) with remaining high rate capacity. The Ni(OH)₂ nanotubes/KOH-activated carbon supercapacitors possess an operational window of 1.4 V for actual device applications.

INOR 337
Design of heterobimetallic molecular precursors for LiCoO₂ cathode material
Evgeny V. Dikarev, edikarev@albany.edu, Zheng Wei, Haixiang Han, Alexander S. Filatov. Department of Chemistry, University at Albany, SUNY, Albany, NY 12222, United States

A novel approach to design heterometallic single-source precursors with discrete molecular structure, while maintaining the proper metal:metal ratio for the target complex is reported. The transition from polymeric to molecular structure was achieved by employing asymmetric ligands that exhibit different metal bridging properties at the two ends of the ligand and thus allow one to effectively change the connectivity pattern within the heterometallic assembly. The applicability of the above approach was demonstrated on the family of single-source precursors for industrially important LiCoO₂ oxide, the most common cathode material for commercial lithium ion batteries. The newly synthesized precursors are highly volatile, soluble in practically all common solvents, and can be obtained on a large scale with high yield by simple, one-step synthetic procedure that involves cheap, readily available starting reagents. Importantly, they afford the target LiCoO₂ cathode material upon thermal decomposition at relatively mild conditions. The prospective precursors have been evaluated from the industrial perspective, by estimating the extra costs imposed by the ligand on the formation of the final material.

INOR 338
Speciation of transition metal dopant ions during the formation of SrTiO₃ powders
Kevin R. Kittilstved, k Pittlsted@chem.umass.edu, Keith A. Lehuta, William L. Harrigan. Department of Chemistry, University of Massachusetts Amherst, Amherst, MA 01003, United States

SrTiO₃ is a perovskite semiconductor with multiple interesting physical properties including ferroelectricity and photocatalysis. Much interest in coupling the ferroelectricity with magnetic properties and extension of the photocatalytic properties into the visible region of the solar spectrum has motivated research into introducing paramagnetic transition metal dopants into wide-gap perovskites. However, phase-segregated impurities can give rise to extrinsic physical properties and contradictions in the literature. To address this we set out to systematically study the speciation of transition metal dopants during the synthesis of SrTiO₃ by a sol-gel method was studied by various dopant-specific spectroscopies in addition to traditional bulk structural characterization techniques. Dopant-specific probes provide orders of magnitude better sensitivity at determining the location of speciation of dopant ions compared to typical characterization such as powder diffraction. By systematically varying the aerobic annealing temperature and time, we observe the formation of new dopant-rich phases between 800 °C and 1050 °C before the formation of “phase-pure” doped SrTiO₃. The photophysical and photochemical properties of these additional phases will also be presented.

INOR 339
Conversion of a two-electron her-electrocatalyst into a multielectron CO₂ reduction electrocatalyst by ligand backbone modification
Owen M Williams, owenn.williams@utexas.edu, Michael J Rose, Alan H Cowley. Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, United States

The efficiency of carbon dioxide reduction electrocatalysts lags far behind that seen in hydrogen evolution electrocatalysts. Additionally, the mechanistic bedrock for hydrogen evolution has been thoroughly studied in several catalytic systems. While some mechanistic studies have been performed on CO₂ reduction catalysts (e.g. TPPFeCl based systems), a comprehensive understanding of this transformation is rudimentary when compared with that of hydrogen evolution. Recently we have devised, synthesized and characterized an electrocatalyst based upon the ubiquitous cobaloxime macrocycle motif equipped with backbone naphthalene appendages. This electrocatalyst is remarkably similar to the dimethyl and diphenyl congener of this class of ligands. Furthermore, a versatile synthetic route allows monomer substitution effectively change the connectivity pattern within the heterometallic electrocatalyst into a multielectron CO₂ reduction electrocatalyst by ligand backbone modification.

INOR 340
Novel bis- and mono(thiourea) conducting polymer materials for highly selective and robust ionophoric sensors
Matthew T. Raiford, mraiford@cm.utexas.edu, Bradley J. Holliday. Department of Chemistry, The University of Texas at Austin, Austin, TX 78712, United States

Current sensors for heavy metal ions utilize receptor membranes and chemical transducers comprised of plasticizer/ionophore blends and conducting polymers (e.g., polythiophene), respectively. Historically, this class of sensors has suffered from short lifetimes and poor selectivities due to leaching of the plasticizer from the ionophore component of the receptor membrane. In an effort to produce more robust sensors with increased selectivity, a series of novel electropolymerizable arylthiourea-based ionophoric monomers has been synthesized. Arylthioureas were selected due to the significant selectivity toward heavy metal ions, such as Pb(II) and Hg(II), of this class of ligands. Furthermore, a versatile synthetic route allows monomer functionalization to be varied with relative ease, resulting in a series of electropolymerizable ionophores. Binding studies using Job’s plot analysis showed that the monomers interact with the target metal ions in a 1:1 ratio. Benesi-Hildebrand methods were used to study selectivity and indicated the monomers preferentially bind to Pb(II), Sn(II), Hg(II) and Cd(II) ions. Single piece ion selective electrodes (SPISEs) were prepared by electropolymerization of the monomer onto a variety of substrates. The stability and performance of the SPIDE sensors were monitored with periodic use over the course of 18-months and showed no signs of degradation. Detection limits of the SPIDE sensors were found to be significantly higher (10⁻⁶ - 10⁻¹⁰ M) than conventional heavy metal sensors. This increased sensitivity is due to improved redox conductivity enhancement, with fifteen-fold increases in conductivity observed after Pb(II) uptake. Electrochemical oxidation of the polymer in the presence of Pb(II) ions resulted in binding of the metal ions to the polymer. The metal ions could then be removed by washing with aqueous EDTA. This work suggests that arylthiourea-based conducting polymers have the potential to be used in a variety of environmentally related applications, including heavy metal sensing and remediation.

INOR 341
Continuing the CENTC mission: Developing more sustainable methods in recycling and catalysis
Marion H. Emmert, mhemmert@wpi.edu. Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, MA 01609, United States

Worcester Polytechnic Institute (WPI) requires all its undergraduate students to complete a research-based senior thesis. In this talk we will provide insight into several projects in the Emmert lab at WPI, in which these senior-thesis students help to develop more sustainable methods in the areas of homogeneous catalysis and rare earth recycling. The influence of CENTC’s mission on project choice and progress will be addressed. Furthermore, a collaborative inter-university effort which is inspired by the CENTC monthly videoconferences will be presented as an opportunity for early-career faculty and their groups to network and discuss research.

INOR 342
DFT modeling of the aldehyde-water shift reaction
William C. Ou1, mugico83@yahoo.com, Thomas R. Cundari1, Timothy P. Brewster2, D. Michael Heinekey2. (1) Chemistry, CASCaM, University of North Texas, Denton, TX 76201, United States (2) Chemistry, CENTC, University of Washington, Seattle, Washington 98195, United States

Density functional theory calculations were used to assess the viability of an Ir(III) complex, Cp*Ir[bpy(2-CH2)](H2O)[OTf]2, as a catalyst for the aldehyde-water shift (AWS) reaction (R-CHO + H2O → R-COOH + H2), a reaction of considerable interest due to its potential implications for bulk hydrogen production. Calculated thermodynamic and kinetic values for the steps in a proposed reaction mechanism with R = Me are reported. Calculations were conducted in both gas phase and continuum solvent, with both sets of data showing similar energetic trends. Overall, the data suggest that the Ir(III) complex is a catalyst lead worthy of experimental consideration. Rh(III) and Ru(II) variants of the proposed catalyst were also tested, and the following order of catalyst effectiveness was proposed: Rh > Ir > Ru, suggesting that the Rh variant is also worthy of experimental testing.

INOR 343
Base metal catalysis: Activating inert bonds using iron and cobalt
Michael Findlater, michael.findlater@ttu.edu, Ashleigh D Smith, Stefan Schunemann, Anu Saini, Renzo Arias-Ugarte. Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, TX 79409, United States

Employing ligand sets developed by researchers at the Center for Enabling New Technologies through Catalysis (CENTC), we have developed Fe- and Co-centered pincer complexes capable of activating small molecules and hydrocarbons. We will discuss our results in two areas: hydroisilylation and C-C bond formation. Moreover, we have exposed our researchers to collaborative tools pioneered by CENTC (Summer School and Videoconferencing).

INOR 344
Bis-phosphite PCP iridium complexes bearing hydrides and the catalysis of the deoxygenation of glycerol
McKenzie E Braslow1, kebrastow@davidson.edu, Gene W Wong2, D Michael Heinekey2. (1) Davidson College, United States (2) Department of Inorganic Chemistry, University of Washington, United States

In conjunction with ongoing projects through CENTC, the synthesis of a bis-phosphite PCP ligand has been achieved and successfully bound to an iridium metal center via C-H activation. Through NMR and IR characterization, the identity of these new structures has been confirmed as hydride containing complexes, (PCP)Ir(CO)HCl and (PCP)Ir(CO)(H2), and X-ray crystallography has confirmed the connectivity of (PCP)Ir(CO)HCl. Both complexes have been found to successfully catalyze the partial deoxygenation of glycerol to 1-propanol, with better selectivity found with the (PCP)Ir(CO)(H2)catalyst.

INOR 345
Selectivity in C-H bond activation of substituted pyridines: Overcoming the influence of a strongly coordinating arene heteroatom
Richard Herbster, David A. Laviska, laviskad@tcnj.edu. Department of Chemistry, The College of New Jersey, Ewing, New Jersey 08628, United States

The Center for Enabling New Technologies Through Catalysis (CENTC) has been encouraging cutting edge research on the activation and transformation of strong bonds (C-H, C-C, etc.) since its inception in 2007. With scientists working collaboratively across more than a dozen top research universities and national labs, the impact of the CENTC network has reached well beyond its core group of scientists to include the research and intellectual creativity of many alumni, including those conducting research at primarily undergraduate institutions like The College of New Jersey. Transition metal complexes have been shown to efficiently catalyze the selective functionalization of aryl C-H bonds. In this context, aryl substituents that can act as “directing” groups have been afforded selectivity for ortho C-H bonds vs. those in the meta and para positions in some cases. Contrasting results have been shown with the iridium fragment (Bu4PCP)Ir[Bu4PCP] = (κ2-2,6-bis(di-tert-butylphosphino)methyl)phenyl]. With this complex, little or no thermodynamic preference for the ortho C-H addition products of substituted benzenes is found. In addition, bulky ortho substituents inhibit the rates of C-H addition and elimination. Our current research is focused on alkyl-substituted pyridines; in these substrates, there is a strong preference for N-coordination to the metal center over oxidative addition of an aryl C-H bond, potentially limiting the efficacy of transition metal-mediated C-H activation reactions. Strategic selection of alkyl substituents has illuminated the competing effects of coordinating groups vs. the constraints of geometry in the transition state for addition/elimination. Results for a range of related substrates will be discussed.

INOR 346
Heterogenous acid catalyzed conversion of furfuryl alcohol to valuable chemicals
Nathan A Prisco1, nathan.prisco@utexas.edu, Jean M Gallo2, James A Dumesic2. (1) Department of Chemical Engineering, University of Texas at Austin, United States (2) Department of Chemical and Biological Engineering, University of Wisconsin-Madison, United States

Currently there is much interest in bio-derived Levulinic acid (LA) for use as a feedstock in the production of diesel and gasoline like fuels; solvents; plastics and resins; flavoring agents; other consumer products and specialty chemicals. Much work has been done on cellulose (C6) derived levulinic acid but research has been lacking on hemicellulose (C5) derived levulinic acid. Specifically, this paper focuses on the conversion of furfuryl alcohol into levulinic acid in a novel THF water system. This reaction is catalyzed using three commercial Brønsted--Lowry solid acid catalyst: Amberlyst™-70, H-ZSM5, and H-Mordenite. The new, miscible THF-water solvent system greatly improves the yield of levulinic acid compared to traditional hydrolysis in pure water solvent, see .

The reason for this increased yield is that THF may interfere with the formation of polymer humins which reduce yields and deactivate catalyst. In addition, the paper also identifies reaction products which result from the ethanolysis of furfuryl alcohol. These products include angelica lactones which may have further value as fragrances. This research was supported by CENTC.

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Synthesis and characterization of (1,5-bis-cyclooctadiene)iridium(I) complexes containing N-(2-(pyridin-2-yl)ethyl)sulfonamide derivatives

Abby R. O’Connor¹, oconnora@tcnj.edu, James M. O’Connor², Joseph W. Carlin³, Danielle L. Jacobs⁴, Benny C. Chan⁵. (1) Department of Chemistry, The College of New Jersey, Ewing, NJ 08628, United States (2) Department of Chemistry, Biochemistry & Physics, Rider University, Lawrenceville, NJ 08648, United States

The Center for Enabling New Technologies Through Catalysis (CENTC) brings together scientists from across North America to work collaboratively on high impact research projects to develop more efficient and environmentally friendly ways to make fuels and chemicals. This collaborative nature of doing chemical research is well suited for conducting research with undergraduates at primarily undergraduate institutions, as resources and expertise in different areas are limited. Currently, researchers from The College of New Jersey and Rider University are working collaboratively to find new catalysts for hydrogenation and C-H bond activation. New iridium(I) complexes containing pyridine sulfonamide ligands with different electronic parameters have been synthesized. The pyridine sulfonamide ligands are prepared using a novel microwave synthesis developed by the Jacobs lab. 16-Electron square planar iridium(I) complexes of the form [(COD)Ir(L)Cl] where COD = 1, 5-bis-cyclooctadiene; L = (a) N-(2-(pyridin-2-yl)ethyl)benzenesulfonamide, (b) N-(2-(pyridin-2-yl)ethyl)tolenesulfonamide, (c) N-(2-(pyridin-2-yl)ethyl)methanesulfonamide (d) N-(2-(5-methylpyridin-2-yl)ethyl)benzenesulfonamide) have been prepared in good yields. The complexes have been characterized using NMR and IR spectroscopy and X-ray crystallography. Progress towards the synthesis and characterization of these complexes along with preliminary reactivity studies is described.

Photoeducation of main group/late transition metal heterobimetallic complexes

Francois P. Gabbari, francois@tamu.edu. Department of Chemistry, Texas A & M University, College Station, TX 77845, United States

Metal complexes that support two-electron redox processes are attracting a great deal of interest because of their importance in various domains ranging from catalysis to energy conversion. Over the past decades, it has been demonstrated that late transition bimetallic complexes can sustain important energy storage reactions such as the photoeducational elimination of halogens. While such complexes usually contain two noble metals, our group has recently shown that heterobimetallic compounds containing a noble metal and a heavy main group element may also have a potential in this area. In this presentation, we will describe the results of our ongoing work on the photoeducational elimination of halogens from Pt/Te and Pt/Sb complexes.

New approaches to probe proton-coupled electron transfer reaction pathways

Jillian L Dempsey, dempseyj@email.unc.edu, Thomas T Eisenhart. Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, United States

Proton-coupled electron transfer (PCET) events are key processes in natural and artificial solar fuel generation. Despite the ubiquity of these pathways, a detailed understanding of the factors that promote concerted proton–electron transfer (CPET) over stepwise ET–PT or PT–ET pathways has remained elusive. Using transient absorption spectroscopy, we are developing new approaches to better analyze PCET reactions in models of photosystem II. These mechanistic studies have provided a more comprehensive picture of PCET pathways than revealed through previous methods.

Synthesis, physical, and photophysical properties of a new class of first row-based transition metal complexes as chromophores for solar energy conversion strategies

Lindsey L. Jamula, Allison M. Brown, Jennifer Miller, James K. McCusker*, jkm@chemistry.msu.edu. Department of Chemistry, Michigan State University, East Lansing, MI 48824, United States

Solar energy conversion strategies employing so-called earth-abundant elements represent an important focus in the area of energy science. Our research program is concerned with understanding structure/excited state dynamics correlations in first-row transition metal complexes in order to identify and overcome the key scientific challenges associated with their implementation. This presentation will describe a new class of Fe(II)-based chromophores we have recently developed whose electrochemical and photophysical properties make them excellent candidates as potential chromophores for dye-sensitized solar cells. The synthesis, physical, and photophysical properties of several compounds within this new class will be described, as well as preliminary data resulting from their incorporation into DSSCs.

Photoeducation of carbon dioxide to methanol and formate using a homogeneous pyridinium catalyst coupled with a ruthenium poly(pyridyl) chromophore

David J Boston¹, Norma S de Tacconi², Reynaldo O Lenzna³, Frederick M MacDonnell³, macdonn@uta.edu. (1) Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, T 76019, United States (2) INIFTA, LA PLATA, Argentina

Photochemical reduction of CO₂ to useful liquid fuels, such as methanol, would be an attractive technology to reduce our dependence on fossil fuels and to curb our net CO₂ additions to the atmosphere. Transition metal chromophores or catalysts developed for this process are generally only capable of producing the two-electron reduced species, i.e. CO or formic acid, and show little tendency to generate the more deeply reduced and desirable products, such as methanol. Pyridine acts as an effective electrocatalyst for the conversion of CO₂ to methanol as shown by Bocarsly and coworkers in a number of studies. We are exploring photochemical systems incorporating a transition-metal chromophore and a pyridine or pyridine-like co-catalyst in both intermolecular and intramolecular fashion. Initial studies show that these homogeneous system can reduce CO₂ to formic acid and even methanol in a visible light driven photochemical reaction in which electrons are supplied by sacrificial reductants. The successes, limitations, and future directions of this research will be presented.

Water-compatible polyoxometalate catalysts for solar fuel production

Craig L Hill, chill@emory.edu, Hongjin Lv², James W Vickers³, Jordan M Sumliner³, Yunii V Geletii³, Djamaladdin G Musaev². (1) Chemistry, Emory University, Atlanta, GA 30322, United States (2) Emerson Center for Scientific Computation, Emory University, Atlanta, GA 30322, United States

Comprehensive new studies further clarify the complex hydrolytic chemistry of transition-metal-substituted polyoxometalate (TMSP) multielectron transfer catalysts for solar fuel production. These include additional techniques that distinguish POM catalysts from hydrated transition metal ion (e.g. Co(II), Mn(II), etc.) catalysts with which they are in equilibrium, and metal-oxide-particle catalysts. TMSP catalysts that are stable in water have been developed for the reduction of water to hydrogen, the reduction of carbon dioxide to a variety of products and the oxidation of water to dioxygen. Structural, spectroscopic, catalytic and computational findings will be discussed.
INOR 354
Water oxidation catalysis beginning with the cobalt-polyoxometalate, Co₄(H₂O)₆(PW₁₂O₄³⁻) under electrochemical and chemical oxidant conditions: Mechanistic studies en route to discovering the true catalysts

Richard G Finke, rfinke@lamar.colostate.edu, Jordan J Stracke.Department of Chemistry, Colorado State University, Ft Collins, Colorado 80523, United States

In 2010 we reported studies that showed that electrochemically driven water-oxidation catalysis (WOC), beginning with the cobalt-polyoxometalate Co₄(H₂O)₆(PW₁₂O₄³⁻) (CoPOM) as a precatalyst, leads to electrode bound, heterogeneous CoO, as the dominant water-oxidation catalyst (WOCatalyst), and under the specific conditions reported in that study (Stracke, J. J.; Finke, R. G. J. Am. Chem. Soc. 2011, 133, 14872). We have subsequently looked at electrochemically driven WOC under different conditions chosen to, ideally, favor WOC by the discrete CoPOM (Stracke, J. J.; Finke, R. G. ACS Catal. 2013, 3, 1209). Even more recently we have completed kinetic and mechanistic studies of WOC beginning with CoPOM, but now under Ru(II)(bpy)₃ chemical oxidant conditions (“Water Oxidation Catalysis Beginning with Co₄(H₂O)₆(PW₁₂O₄³⁻) when Driven by the Chemical Oxidant Ruthenium(II)tris(2,2'-bipyridine): Stoichiometry, Kinetic, and Mechanistic Studies en Route to Identifying the True Catalyst”, Stracke, J. J.; Finke, R. G. ACS Catal. 2013, submitted). The chemical-oxidant conditions closely mimic those in the original Science paper reporting WOC by Co-based POMs (Yin, Q.; Tan, J. M.; Besson, C.; Geleti, Y. V.; Musaei, D. G.; Kuznetsov, A. E.; Luo, Z.; Hardcastle, K. I.; Hill, C. L. Science 2010, 328, 342.). The talk will summarize as background the highlights of the first two stracke et al. papers noted above, but then concentrate on the results of the 3rd and most recent paper which examines the CoPOM precatalyst in the Ru(II)(bpy)₃ chemical-oxidant, WOC system.

INOR 355
Electrocatalytic reduction of CO₂ by metal-metal bonded clusters of iron and copper

Pauline N Serrano, An D Nguyen, M Diego Rail, Louise A Berben, laberben@ucdavis.edu. Department of Chemistry, University of California, Davis, CA 95616, United States

In this talk the ability of clusters such as [Fe₄N(CO)₁₃]³⁻, [Fe₄C(CO)₁₃]²⁻ and [CuH{(PPh₃)}₄] to behave as CO₂ reduction electrocatalysts will be described. Insights into the catalytic mechanisms of formate formation will be discussed including the ability of the clusters to stabilize hydride intermediates.

INOR 356
Neutron diffraction opportunities at Oak Ridge National Laboratory

Ashfia Huq, huq@ornl.gov. Chemical and Engineering Materials Division, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

Historically Oak Ridge National Laboratory has played a very important role in developing neutron scattering techniques for crystallography. Clifford Shull, the winner of the 1994 Noble Prize in Physics started his pioneering work in neutron diffraction in 1946 at Oak Ridge. In keeping with this strong tradition, the lab currently hosts two facilities; High Flux Isotope Reactor and the Spallation Neutron Source, which supports diffraction studies in physical, chemical and biological sciences. In this talk I will present an overview of the instruments dedicated for crystalline materials, with an emphasis on those that are uniquely neutron based.

INOR 357
Influence of average and local crystal structures on superconductivity in the Bi-O-S system

William A Phelan¹,², wphelan2@jhu.edu, Benjamin A Trump², David C Wallace², Kathryn E Arpino¹,², James R Neilson¹,², Kenneth J Liv⁵, Che R Seabouner³, Andrew J Scott⁴, Andrew E Payzan⁴. Ashfia Huq², Tyrel M McQueen⁵,². (1) Institute for Quantum Matter, Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218, United States (2) Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, United States (3) Department of Earth and Planetary Sciences, The Johns Hopkins University, Baltimore, Maryland 21218, United States (4) Institute for Materials Research, University of Leeds, Leeds, United Kingdom (5) Oak Ridge National Laboratory, Chemical and Engineering Materials Division, Oak Ridge, Tennessee 37831, United States

Reports of superconductivity in doped LnOBi₂S₄ (Ln = La, Ce, Pr, Nd, and Yb), doped SrOBi₂S₄, and Bi₁₂O₂₃S₄ have generated interest in a new family of layered superconductors where the electronically active layers are comprised of Bi₂S₄ units. Interestingly, the preliminary refinements to the laboratory X-ray diffraction data for the reported Bi₁₂O₂₃S₄ structure yielded a model which contains both sulfides (S²⁻) and sulfates (SO⁴²⁻). Such disparate, disproportionated, oxidation states are not usually chemically stable, especially in solid state reactions performed at elevated temperatures. Furthermore, the small X-ray scattering factors of sulfur and oxygen relative to that of bismuth make the precise structural assignment of these light elements difficult to determine. We have used a wide variety of average and local structure techniques to gain insight into the actual chemistry of the Bi-O-S superconductor. We find that the compound contains mixed sulfide/disulfide units, not sulfide and sulfate, and has the actual chemical formula Bi₁₂O₂₃S₄. Furthermore, we find that all samples contain random intergrowths of two layered phases, Bi₁₂O₂₃S₄ and Bi₄O₇S₄ (BiOBS₄), with the latter having a detrimental effect on the superconductivity. Additionally, our results imply that the superconductivity in this system arises from incomplete charge transfer between S²⁻ dimer layers and Bi₂S₄ layers in Bi₁₂O₂₃S₄, in agreement with recent Density Functional Theory calculations motivated by our findings.

INOR 358
Powder crystallography applied to negative thermal expansion materials

Cora Lind-Kovacs, cora.lind@utoledo.edu. Department of Chemistry, The University of Toledo, Toledo, OH 43606, United States

Negative thermal expansion (NTE) materials have captured the curiosity of scientists and engineers. Active research areas include the synthesis and characterization of new materials, with the goal of tuning their properties, preparation of controlled thermal expansion composites, and experiments trying to elucidate the underlying mechanisms of this unusual behavior.

Much of the work on NTE materials relies heavily on powder X-ray diffraction to confirm phase identity and purity. This is in some cases dictated by the fact that not all NTE materials are thermodynamically stable, and the need for preserving small particle sizes to ensure good mixing in composites. In addition, characterization of temperature- and pressure-dependent behavior is usually carried out on powders.

NTE materials in the scандium tungstate family (A₂MoO₁₂₅, where A = trivalent metal, M = Mo, W) are synthesized via solution-based routes in our group. Our current focus is on compounds in which the A-site is occupied by a mixture of two cations, as this can significantly alter the magnitude of expansion coefficients and the occurrence of phase transitions. While the thermal expansion behavior can be evaluated by laboratory powder diffraction in combination with Rietveld analysis, sample homogeneity for mixed cation systems and structural differences of cation substituted compositions are best addressed by high resolution synchrotron or neutron diffraction. The study of high pressure phase transitions is also accomplished by synchrotron diffraction.

INOR 359
Structural modulation in the battery material LiFeBO₃: Symmetry analysis, thermodynamic oddities, and relationship to Li ion mobility
Peter Khalifah1,2, kpete@bnl.gov, Yuri Janssen1, Shouhang Bo1, Derek Middlemiss1,3, Clare Grey1,3, (1) Department of Chemistry, Stony Brook University, United States (2) Department of Chemistry, Brookhaven National Laboratory, United States (3) Department of Chemistry, Cambridge University, United States

The material LiFeBO3 has been considered a promising candidate for Li-ion batteries due to its high theoretical gravimetric capacity of 220 mAh/g. However, it has proven to be particularly challenging to realize this capacity in experimental systems. Through the analysis of high quality single crystal diffraction data, we have discovered a previously unrecognized modification in this system which leads to a doubling of the unit cell a-axis. This modification is intimately tied to the mobility and distribution of Li ions within this structure, and a comprehensive analysis of this modification has provided insights into the performance of this compound as a battery cathode material. Furthermore, the response of the framework structure to the distribution of Li ions is unusual and hints at general bonding principles which may influence mobility in other systems with ionic conductivity.

INOR 360
Crystallographic studies of complex perovskites
Patrick M Woodward
d. woodward.55@osu.edu, Allyson Fry1, Graham M. King2, Andrew Sharits1. (1) Department of Chemistry and Biochemistry, Ohio State University, Columbus, OH 43210-1185, United States (2) Lujan Scattering Center, Los Alamos National Laboratory, Los Alamos, NM, United States

Compounds that belong to the perovskite family exhibit remarkable versatility, both in terms of their chemical composition and their physical properties. Not only can one prepare perovskites containing elements ranging from hydrogen to plutonium, the physical properties of perovskites are incredibly varied. Superconductivity, ferroelectricity, piezoelectricity, ferromagnetism, antiferromagnetism, colossal magnetoresistance, half-metallicity, proton conductivity can all be found in members of the perovskite family. In this talk I will explore the synthesis, structure and properties of two families of complex perovskites: A2MO3F12 (A = Na, K, Rb, Ag; M = Mo, W) and ALnMM'O6 (A = Li, Na, K, Ln = rare-earth cation). In both families a combination of synchrotron X-ray powder diffraction, neutron powder diffraction and electron diffraction are used to reveal complex rotations of the octahedra. The compounds discussed have a variety of interesting properties ranging from ferroelectricity, magnetism and luminescence. Relationships between structure and properties will be discussed.

INOR 361
In-situ crystallography of inorganic melt synthesis
Daniel P Shoemaker, dpshoema@illinois.edu.Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801, United States

Crystallography plays a pivotal role in the drive to explore new materials landscapes and increase the genome of available functional inorganic materials. I will present excerpts from our work on probing inorganic synthesis in situ. In particular, we have seen that rapid materials discovery is possible in the arena of sulfide materials that span metallic and insulating behavior. Crystallography helps us identify new phases and probe how thermodynamic and kinetic controls compete in the formation of crystals from the melt. We also benefit by combining high-energy scattering (PDF techniques) and spectroscopy to learn about the liquids (traditionally off-limits in crystallography) from which these compounds are born.

INOR 362
New crystallographic tools for the analysis of solid-state materials
Charles F Campana, charles.campana@bruker-axs.com.Single Crystal X-Ray Diffraction, Bruker AXS Inc., Madison, Wisconsin 53711, United States

The recent development of single-crystal diffractometers and software packages for ‘routine’ crystal structure analysis has usually been focused on ‘automatic’ instruments, which can carry out automatic data collection, data reduction, and solution and refinement of structures, including the preparation of CIF and HTML reports for molecular compounds (e.g., simple organic and organometallic compounds and inorganic coordination complexes) with minimal human intervention. While such instruments are very popular in undergraduate teaching environments and even among synthetic organic and organometallic chemists, they are not well-suited for analyzing solid-state materials.

The routine structure solution techniques (e.g., direct methods) commonly used in the field of chemical crystallography are often of limited utility in most fields of solid-state inorganic chemistry. The analysis of solid-state materials is complicated by ambiguous space-group choices, twinning, pseudo-symmetry, composite structures, modulated structures, and sites with partial or mixed occupancy. In many cases, single-crystal measurements must be supplemented with data from magnetic measurements, Mößbauer spectroscopy, and elemental analysis to obtain suitable structure models. We will highlight some of the important new tools now available commercial and public domain software, including ‘dual-space refinement’, ‘intrinsic structure solution’, twin analysis, ‘super-flip’ methods, solution and refinement of modulated and composite structures, and the use of constraints, restraints and free variables for refinement. We will show examples of these methods applied to solid-state materials.

INOR 363
Visualizing ordered disorder: 2D X-ray diffraction, simulations, and Patterson Functions
Eric D Dill, eddill@ncsu.edu, Jacob C.W. Folmer, James D. Martin.Chemistry, North Carolina State University, Raleigh, NC 27608, United States
A series of 2D X-ray diffraction images of a twinned plastic crystal of carbon tetrabromide (α-CBr4) were collected at the Advanced Photon Source (APS). Both twinned Bragg diffraction and twinned structured diffuse scattering are visible in many of the experimental images. To interpret the highly structured diffuse scattering, simulations and 2D Fourier transforms (Patterson Functions) were employed. Patterson Functions allow direct observation of electron-density weighted real-space pair correlations and demonstrate significant ordering along specific real-space directions. The simulations suggest that the CBr4 tetrahedra are correlated to third nearest neighbors. Taken together, these results indicate that our modern understanding of the plastic crystalline phase, that molecular orientations are isotropic over a time/position average, is inadequate and must therefore be revisited.

INOR 364
So close and yet so hard to reach: Accessing Ir-hydrides in hydrogenative C–C coupling of alkenes and imines catalyzed by [Ir(I)–BIPHEP]+
Mu-Hyun Baik, mbaik@indiana.edu.Department of Chemistry, Indiana University, Bloomington, IN 47405, United States
The mechanism of the catalytic hydrogenative C–C coupling of alkenes and imines promoted by a chiral Ir-BIPHEP complex in the presence of a Bronsted acid cocatalyst was studied with quantum chemical methods based on density functional theory. Despite being geometrically close, the Ir-H2
complex cannot use the neighboring amine moiety to facilitate a heterolytic H-H bond cleavage, and must instead use a cocatalyst to accomplish this task. A detailed MO analysis revealed that the cocatalyst is necessary because the proton-accepting orbital of the amine group is misaligned and cannot participate in proton-transfer. The cocatalyst-assisted generation of the Ir-H was found to be the most difficult step in the catalytic cycle and it is also responsible for the stereoselective outcome of the reaction, which is controlled by the chirality of the BIPHEP ligand. The mechanistic origin of the stereoselectivity is examined and conceptualized. Our calculations identify a very different reason for the stereoselectivity than previously assumed. Furthermore, the proposed mechanism identifies a decisive bottleneck in the catalysis that makes a quantitative conversion, i.e. 100% yield, theoretically impossible. This work is a rare example of computational models being used to not only rationalize the origin of the observed stereoselectivity, but to also understand the reaction performance, i.e. the yield of the reaction.

INOR 365
Where are the electrons? How DFT can be both a research and teaching tool with metal complexes featuring redox-active ligands
Richard L Lord, lordn@gvsu.edu. Department of Chemistry, Grand Valley State University, Allendale, MI 49401, United States
Identifying where electrons are localized in complexes featuring redox-active metals and ligands is one of the most important research topics in inorganic and organometallic chemistry today. While numerous techniques must be employed to answer this question definitively, computational chemistry has been shown to be a useful tool for interpreting and predicting oxidation states in these complicated systems. An advantage of computational work is its ability to engage motivated undergraduate students early in their academic career, without safety risks or content knowledge pre-requisites typically associated with wet lab techniques. I will highlight some of my undergraduates' recent work that either involves, or is related to, research taking place in the Caulton group. I will also discuss how I use the modern research question “where are the electrons?” not only to reinforce to undergraduates the importance of simple models like oxidation states, but also to differentiate them from quantum mechanical observables like electron spin density.

INOR 366
Facile assembly of redox active ligand and pendant amine on iron
Zhenyu Wu$^1$, zhenyuwu@ss.as.penn.edu, Octavio González-del Moral$^2$, Martina Kaess$^3$, Mario Adelhardt$^4$, Chun-Hsing Chen$^1$, Maren Pink$^1$, Karsten Meyer$^5$, Daniel J Mindiola$^6$, Kenneth G Caulton$^7$. (1) Department of Chemistry, Indiana University Bloomington, Bloomington, Indiana 47408, United States (2) Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States (3) Department of chemistry and pharmacy, inorganic chemistry, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Bavaria 91058, Germany
Inspired by the active sites in Fe-Fe hydrogenase and Fe-catechol dioxygenase, we are interested in developing a simple system combining a redox active moiety, a pendant amine group and a reactive Fe center to do small molecule capture and conversion. Complex Fe(HL$^1$)Cl (HL$^1$ = o-2-(tert-butylylamo)-5-trifluoromethylphenyl)-imino-semiquinonate) is synthesized by applying template effect (Figure 1). Its crystal structure reveals two hydrogen bonds from the N-H groups in the second-coordination sphere to the axial chloride ligand. A ligand-based reduction is performed and yields [Fe(HL$^2$)Cl]$^2$. The electronic structures of both species are probed by Mössbauer and magnetic data (EPR and SQUID spectra). The reaction of [Fe(HL$^2$)Cl]$^2$ and isocyanate gives a product of nucleophilic attack to the electrophilic carbon, whose structure reveals the fact that the amide binds to the ferric center is more nucleophilic than the pendant amine group. Reactions with CO$_2$ will also be described.

INOR 367
ω/π Metal-mediated enediyne activation to promote diradical generation and C-C bond formation
Jeffrey M Zaleski, zaleski@indiana.edu, Krystyna Kirchner, Sarah E. Lindahl. Department of Chemistry, Indiana University, Bloomington, IN 47405, United States
Advances in organometallic C-C bond forming reactions require judicious modulation of both the ligand geometry about the metal catalyst, as well as intricate control of the electronic structure of the reacting orbitals. While not catalytic by nature, metal-mediate Bergman cyclization of diyn-3-ene functionalities requires intimate control of those same geometric and electronic parameters to produce the most facile cyclization and C-C bond formation. To this end, we illustrate two cases: one where ω-coordination and ligand geometry are controlled by in situ two-electron oxidation of a thermally robust, tetrahedral Pt(II)-phosphine metalloenediyne with instantaneous generation of a Pt(II) complex reactive toward Bergman cyclization, and another where ω/π hybrid systems derived from nitrogen pincers for robust ω-metal coordination with simultaneous metal activation of their macrocyclic enediyne π-bonds. These constructs engender the same principles required for catalytic organometallic cyclization events, but their air and water stabilities enhance potential for subsequent reactions with biological substrates.

INOR 368
Separation of trivalent lanthanide and actinide ions using polyazine extractants
Lori A Watson$^1$, watsolo@earlham.edu, Benjamin P Hay$^2$, Charles de Sahb$^1$, Janos Nadas$^2$. (1) Department of Chemistry, Earlham College, Richmond, IN 47374, United States (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
Separation of trivalent actinide ions from chemically similar lanthanides is a crucial step in the processing of spent nuclear fuel, allowing for minimization of the volume of nuclear waste and the recovery and reuse of uranium and plutonium. Nitrogen donor ligands have been shown to exhibit selectivity for actinide ions and continue to be a fruitful area of design research. In this study, density function theory calculations were used to develop an explanation for the success of certain azine compositions over others. Fundamental properties (including intrinsic binding affinity, basicity, and hardness) for prototype azine donors were investigated and conformational analyses of bisazine chelates formed from the linkage of two donors were performed. The results both rationalize the behavior of known extractants as well as predict a new class of pyridazine ligands for use in actinide/lanthanide partitioning. A snapshot of teaching and research at a primarily undergraduate institution will also be provided.

INOR 369
Borenium cations: Versatile reagents for synthesis and small molecule activation
Michael J Ingleston, michael.ingleston@manchester.ac.uk. School of Chemistry. University of Manchester, Manchester, Manchester, United Kingdom
After decades of principally ‘academic’ interest there has been a recent surge in the use of borenium cations (three coordinate borocations) in synthesis and catalysis. In the past five years borenium cations have been developed that are effective for hydrogenation, aliphatic C-H activation, direct arene borylation and hydroboration. We will present our recent work studying the reactivity of a range of borenium cations towards small molecules and pi nucleophiles. Rational modification of borenium cation structure has proved key to expanding their synthetic versatility, and this will be emphasised using specific examples including; H$_2$ activation, direct C-H borylation and the carboboration and haloboration of alkenes.
Nickel is required by many microorganisms as a metalloenzyme cofactor (1,2). However, as with many inorganic nutrients, nickel is toxic so the amount and distribution of intracellular nickel is tightly controlled. One key mechanism of maintaining nickel homeostasis is through the activity of metalloregulators such as the nickel-dependent transcription factor NikR (3). This protein binds to specific DNA sequences upon activation by nickel and...
controls the expression of a variety of proteins involved in nickel homeostasis. Our work on the NikR homolog from Escherichia coli examines the mechanism of activation of DNA binding by nickel, and the metal selectivity of this process.

Several types of physiologically-relevant transition metal ions bind to NikR, but nickel has a unique impact on the stability and structure of the protein, and activates the tightest complex with DNA. Biochemical analysis suggests that nickel selectively activates DNA binding by organizing secondary structural elements in the metal-binding domain of the protein, which stabilizes electrostatic contacts with the phosphodiester backbone of the DNA. The analysis of NikR mutants in E. coli demonstrates that these non-specific interactions are critical to the activity of NikR. Furthermore, cation exchange experiments and mutagenesis reveal that potassium is also necessary for the nickel-dependent response of NikR. These experiments support a multi-state mechanism of metal activation of E. coli NikR in which nickel operates through a selective allosteric impact on the protein structure (4.5).


INOR 375
On the mechanism of nitrogen fixation by nitrogenase
Brian M. Hoffman1, bmh@northwestern.edu, Dmitriy Lukoyanov2, Dennis R. Dean3, Lance C. Seefeldt4. (1) Chemistry, Northwestern University, Evanston, IL 60208, United States (2) Chemistry and Biochemistry, Utah State University, Logan, Utah 84322, United States (3) Biochemistry, Virginia Tech University, Blacksburg, Virginia 24061, United States

Biological nitrogen fixation — the reduction of N2 to two NH3 molecules — is catalyzed by the enzyme nitrogenase. An understanding of the nitrogenase catalytic mechanism requires, at minimum, identification and characterization of each intermediate along the reaction pathway, plus an understanding of the kinetics/dynamics through which these intermediates form. The kinetics are described by the Lowe-Thorneley (LT) model, which provides rate constants for transformations among intermediates, denoted $E_x$, as indexed by the number of electrons (and protons), $n = 0 - 8$, accumulated within the MoFe protein. One of the most puzzling aspects of nitrogenase function embodied in the LT scheme is an obligatory generation of $H_2$ upon $N_2$ binding, so that the limiting stoichiometry for ‘enzymological’ nitrogen fixation requires eight electrons/protons to reduce each $N_2$. As the delivery of each electron requires the hydrolysis of two MgATP, the formation of $H_2$ thus apparently ‘wastes’ 25% of the total energy supplied by the hydrolysis of ATP. We have trapped and characterized three of the five $N_2$ electron-reduction stages, the key ‘Janus intermediate’, $E_5$, the state at which $N_2$ hydrogenation begins, and intermediate states that contain semi-reduced $N_2$. This allowed us to integrate kinetics and pathway, thereby generating a first-draft mechanism for biological nitrogen fixation. The mechanism was completed with the keystone proposal that $H_2$ release upon $N_2$ binding involves reductive elimination of two hydrides, to yield $N_2$ bound to doubly-reduced FeMo-co highly activated to achieve the most difficult step of nitrogen fixation, the initial hydrogenation of $N_2$. The result is the first mechanism proposal for every transformation of nitrogen fixation based on the properties of trapped intermediates. This mechanism has been tested against the vast body of data on which it builds, and has passed a stringent experimental test it inspired.

INOR 376
Manipulating metals at the host–pathogen interface
Katherine J. Franz, katherine.franz@duke.edu, Chemistry, Duke University, Durham, NC 27708, United States

Metal ions are required nutrients for many organisms but also potent toxins if misappropriated. The distribution networks of inorganic elements are therefore strategic battlegrounds in the fight between hosts and pathogens. Disrupting a supply chain to starve microbial pathogens of a required element is one strategy. On the other hand, overburdening an invading microorganism’s capacity to regulate metals can intensify pathogen killing. The opportunity to pharmacologically manipulate metal distribution along this host/pathogen interface represents an opportunity to create innovative broad-spectrum antimicrobial agents. Here we present our progress on developing small molecules that mobilize metal ions in response to infection in order to boost immune cells’ microbiocidal activity while evading metal-resistance mechanisms of the pathogen.

INOR 377
Role of dimanganese-tyrosyl radical ribonucleotide reductase in the virulence of Streptococcus sanguinis
JoAnne Stubbe1, stubbe@mit.edu, Olga Makhlynets1, DeLacy Rhodes2, Todd Kitter3, Amie Boal4, Amy Rosenzweig5. (1) Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States (2) Microbiology and Immunology, Virginia Commonwealth University, Richmond, VA 23298, United States (3) Molecular Biosciences and Chemistry, Northwestern University, Evanston, IL 60208, United States

Many pathogenic organisms use class Ib (NrdE-NrdF) and class III (NrdD-NrdG) ribonucleotide reductases (RNRs) to convert nucleotides to deoxyribonucleotides under aerobic and anaerobic conditions, respectively. Recently class Ib RNRs were established to use a dimanganese-tyrosyl radical cofactor whose assembly requires an unusual flavodoxin. These RNRs can also self-assemble an active dipheric-tyrosyl radical cofactor. Our labs now report in vitro biochemical studies on S. sanguinis RNPs, in vivo biological studies on wt and deletion strains of S. sanguinis, and studies in a rabbit model for infective endocarditis caused by S. sanguinis. Together these studies establish the essentiality of the Mn-dependent RNR for virulence. They may also provide an explanation for a previous report that a Mn transporter is necessary for virulence and oxygen tolerance in S. sanguinis.

INOR 378
Building functional inorganic clusters within mesoporous metal-organic frameworks
Joseph T Hupp, j-hupp@northwestern.edu, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, United States

Atomic-layer deposition (ALD) within mesoporous MOFs provides a means of synthesizing uniform ensembles of metal-oxide clusters featuring any of a broad range of predetermined compositions, including mixed-metal oxide compositions. By varying the number of ALD cycles, cluster size can be modulated. Keys to the utilization of ALD, a vapor-phase synthesis technique, with metal-organic frameworks are: a) large MOF channels and apertures (widths of a few tens of angstroms), b) availability of good ALD reaction sites (for example, hydroxide ligands on MOF nodes), c) good MOF thermal stability, and d) good MOF chemical stability (e.g. the ability to withstand repetitive exposure to steam at temperatures up to 180 celsius). We find that the clusters resulting from can impart to MOFs exceptional stability (including stability at extreme acid and alkaline pHs), redox activity, and/or catalytic activity, while preserving MOF porosity.

INOR 379
Metal-organic frameworks based on extensively fluorinated and dehydrobenzannulenic linkers
Teng-Hao Chen, Ilya Popov, Olafs Daugulis, Ognjen Miljanic, miljanic@uh.edu, Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States

Metal-organic frameworks (MOFs) are highly porous and modularly synthesized hybrid organic-inorganic materials, in which rigid organic linkers reticulate metal cluster nodes into an infinite and crystallographically ordered network. In this contribution, we report the synthesis and characterization of two new classes of MOFs, based on (a) extensively fluorinated aromatic carboxylic acids and tetracarboxylic acids, and (b) macrocyclic dehydrobenzannulenic carboxylic acids. In the first project, extensively fluorinated aromatic carboxylic acids and tetracarboxylic acids were prepared through a novel G-H functionalization reaction, and were then exposed to metal sources to produce extensively fluorinated MOFs. These frameworks were characterized by single crystal X-ray diffraction, thermogravimetric analysis and sorption studies, and were shown to be superhydrophobic (water contact angles in excess of 150
INOR 380
Hybrid materials from the f-block: Tips and tricks for directing supramolecular assemblies
Christopher L. Cahill, cahill@gwu.edu, Robert G. Surbella, Korey P. Carter. Department of Chemistry, The George Washington University, Washington, DC 20052, United States

Directed assembly of hybrid architectures containing lanthanide or actinide elements is of interest considering applications ranging from sensing to spent nuclear fuel stewardship. f block elements display a range of oxidation states, varying emissive properties and coordination geometries unique to this region of the periodic table. Moreover, the tendency for ions of these elements to hydrolyze (Ln(III) and U(VI) in particular), gives rise to rich suites of oligomeric building units from which to assemble topologies of interest. The latter may be viewed as an asset and a liability. On the plus side, one may anticipate diverse topologies, yet not knowing which building units will manifest themselves in the solid state prevents systematic study and delineation of rules governing assembly. We have developed an approach of ‘restricted speciation’ wherein reaction conditions, either high-halide media or through the use of chelating ligands, promote the formation of a single molecular species. These species, \([\text{UO}_2X(H_2O)_2]^n\) (X= Cl, Br, NCS; n=0,1) or \([\text{Ln(terpy)}(p-XBA)]_n\) (p-XBA = p-halobenzoic acid, X=Cl, Br and I) are then assembled into extended architectures via non-covalent interactions through halogens at their periphery. Presented will be an overview of results from both Ln and An families, along with an early attempt at ranking the strengths of non-covalent interactions.

INOR 381
Supramolecular architectures and properties of metal-radical coordination complexes
Kathryn E. Preuss \(^1\), kpreuss@uoguelph.ca, Elisabeth M Fatila \(^2\), Mathieu Rouzieres \(^{2,3}\), Dmitriy V Soldatov \(^1\), Rodolphe Clerac \(^{2,3}\), Corine Mathoniere \(^{2,3}\). (1) Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada (2) CRPP, Univ. Bordeaux, Pessac, France (3) CRPP, CNRS, Pessac, France

We are developing new families of neutral radical ligands based on 1,2,3,5-dithiadiazolyl (DTDA) and 1,2,3-dithiazole (DTA) heterocyclic building blocks. Many of these can be considered paramagnetic analogs of familiar N,N-bidentate ligands, such as bipyridine (bpy) and bipyrindimine (bpm). Complexes of our ligands differ from those of bpy and bpm, due in part to the paramagnetic nature of the ligands. The heterocyclic structures have sterically unencumbered sulfur atoms with significant spin density and partial positive charge density, creating a propensity for intermolecular interactions. A variety of recently published coordination complexes with novel and interesting supramolecular architectures and properties will be presented. These include a supramolecular pair of Dy(III)-radical complexes exhibiting single-molecule magnet (SMM) behavior that can be fine-tuned and a biradical bridged Mn(II) complex that is magnetically ordered.

INOR 382
Metallacrowns: Assembly and spectroscopic characteristics
Vincent L. Pecoraro, vlpec@umich.edu, Joseph Jankolovits, Evan Trivedi, Chun (David) Chow. Department of Chemistry, university of Michigan, ann arbor, MI 48109-1055, United States

For over 20 years, metallacrowns have been shown to be versatile recognition agents for both cations and anions. The self assembly of these species is complex and fascinating. In this presentation we will discuss how various topologies can be interconverted based on solvent selection, cation and anion composition. Time allowing, we will discuss applications of these interesting complexes for luminescence spectroscopy and single molecule magnets.

INOR 383
Supramolecular approaches in the quest for improved molecular magnets
Annie K. Powell, annie.powell@kit.edu. Department of Inorganic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Baden-Wuerttemberg 76131, Germany

Paramagnetic molecular systems can be used to construct a variety of cooperatively-coupled magnetic systems with the behavior dependent on the overall dimensionality. We are particularly interested in systems constructed from 0D coordination cluster building blocks, which can show properties such as Single Molecule Magnetism. Recently we have been exploring how approaches familiar from supramolecular chemistry can help to target systems with enhanced or even multiple properties. An example \(^1\) is the construction of intertwined \([\text{CuDyL}]_2\) propellers from individual \([\text{CuDyL}]\) building blocks, illustrated below, which have enhanced hysteresis of the magnetization compared with the individual units.

Fig: (a) Dinuclear building block; (b) 3 units around a central trimesate; (c) space-filling representation showing propeller motif; (d) left- and right-handed propellers intertwine to give duplex; (e) ball and stick representation of duplex
Reactive phosphorus intermediates

Alexandra Veliani, Manuel Temprado, Christopher C. Cummins, ccummins@mit.edu. (1) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02130-4307, United States (2) Department of Physical Chemistry, Universidad de Alcalá, Ctra., Madrid-Barcelona Km. 33,600, Madrid 28871, Spain

Atom and group transfer reactions may proceed via the generation of reactive, unsaturated intermediate molecules or fragments. This presentation details our efforts to generate reactive, phosphorus-containing intermediates either via transition-metal chemistry, or by methods that are entirely metal free. Our investigation and interpretation of singlet phosphinidene transfer reactions are informed by quantum chemical investigations of mechanisms that includes identification of transition states connected to adjacent minima by the intrinsic reaction coordinate (IRC) method. These reactions feature the phosphorus analog of epoxidation: phosphirane formation from olefins. Also to be described are new synthetic investigations of a system for generating diphosphorus, P2, that may be thought of as a metastable binary mixture of anthracene and elemental phosphorus.

INOR 385

From dehydrogenations, organometallic fuel cells, silanes, and other Don Guy tales

Hansjoerg F. Gruetzmacher, rueegg@inorg.chem.ethz.ch. Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Zurich 8093, Switzerland

Dehydrogenations are the most atom efficient way in order to generate element-element bonds in a condensation reaction. Metal complexes with cooperating ligands proved to be especially effective in these reactions. Our own efforts focus on the development of metal amino olefin complexes which benefit from the electronic effect of olefins as steering ligands.

Specifically, amido complexes of type A with various metals including those from the 4th row like Ni or Fe and L = phosphines or carbenes and diazadiene complexes of type B show promising properties. Their application in various dehydrogenations like the decomposition of methanol/water, amino boranes and silanes will be discussed.

INOR 386

P4 and As4 in main group and transition-metal chemistry

Manfred Scheer, mascheer@chemie.uni-regensburg.de, Maria Eckhardt, Christoph Schwarzmaier. Inorganic Chemistry, University of Regensburg, Regensburg, Germany

The chemistry of white phosphorus is well developed and of special interest to promote the direct use of this allotrope for industrial purposes. In contrast, the use of yellow arsenic as a starting material is less prevalent in literature due to its light sensitivity and the fast conversion into unreactive grey arsenic.

We have now developed novel P4 and As4 transfer reagents that transfer either the intact E4-tetrahedra or opened E42+ species to main group and transition-metal moieties, respectively. The special value of these procedures is to avoid handling these toxic and unstable starting materials and to achieve reactivity at ambient or below temperature. Thus, the obtained products represent metastable derivatives with novel properties.

INOR 387

Synthesis and properties of low-oxidation state boron compounds

Kyoko Nozaki, nozaki@chembio.t.u-tokyo.ac.jp. Department of Chemistry and Biotechnology, The Univ. of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

The oxidation state of boron is three in most of the common monometallic boron species BX3, where X stands for elements with lower electronegativity than boron, such as carbon, nitrogen, oxygen, or halogen atoms. We came interested in new boron species having lower oxidation state which can be generated by reducing boron–halogen bonds with alkali metals. Thus, we prepared boryl anion as the first example of isolated boron nucleophile and developed several nucleophilic addition or substitution reactions by the boryl anions. Here in this presentation, we report the reactivity of the boryl anion as a base. The presentation also includes generation and reactivity of new boryl radicals which have low oxidation state at the boron centers.

INOR 388

Small HOMO-LUMO energy gap favors the chemistry of low valent silicon and transition metals

Herbert W. Roeksy, hroeksy@gwdg.de. Institute of Inorganic Chemistry, Georg August University Goettingen, Goettingen, Lower Saxony 37077, Germany

The easy access of NHCl·SiCl3 (NHC = N-heterocyclic carbene) allows the development of a broad chemistry with low valent silicon. The use of cAAC (cAAC = cyclic alicyclic carbene) instead of NHC yields carbon centered radicals due to the small HOMO-LUMO gap of the former molecules. The preparation of (cAAC)2·SiCl3, cAAC·SiCl3, and cAAC·SiP3 radicals will be discussed. The reduction of (cAAC)2·SiCl3 yields silylones, whereas the congeners of germanium are prepared by a direct route. Complexes of transition metals with zinc, manganese, cobalt, and nickel will be reported. The latter can be reacted with unactivated aromatics under homo-coupling in good yield at moderate temperatures.

The (cAAC)2·Mn complex with a S=3/2 electron spin system reacts with hydrogen gas at room temperature to the S=5/2 system under formation of (cAAC)H2·Mn.

INOR 389

Phosphorus chemistry and Lewis acid catalysis

Douglas W. Stephan, dstephan@chem.utoronto.ca. Chemistry, University of Toronto, Toronto, Ontario M5S3H6, Canada

Phosphorus compounds are well known as Lewis bases, however in this talk we describe the ability of electron-deficient phosphonium cations to act as strong Lewis acids and catalyze hydrodefluorination and hydrosilylation. In addition, examples of phosphorus species that effect the activation of hydrogen will be discussed.

INOR 390

Werner complexes: A new class of chiral hydrogen bond donor catalysts for enantioselective organic reactions

John A Gladysz, gladysz@mail.chem.tamu.edu. Chemistry, Texas A&M University, College Station, Texas 77842-3012, United States
Salts of the chiral tris(ethylenediamine)-substituted octahedral trication \([\text{Co(en)}_3]^{3+}\), and related species, have played important historical roles in the development of inorganic chemistry and stereochemistry. As Werner described in 1912, the two enantiomers, commonly designated \(\Lambda\) and \(\Delta\), can be separated by crystallization of the diastereomeric tartrate salts. However, despite the low cost and ready availability of the building blocks, there have been no applications in enantioselective organic synthesis.

We have found that \([\text{Co(en)}_3]^{3+}\) and related cations can be rendered soluble in organic solvents by using lipophilic anions such as "BAr".\(^1\) Suitably functionalized derivatives act as highly enantioselective catalysts for a variety of carbon-carbon bond forming reactions. The mechanisms involve outer sphere activation of the electrophile by hydrogen bonding to the NH moieties.


INOR 391

Nickel complexes of electron rich PCP pincer ligands: Bond activation and catalysis

**Warren Piers**, wpiers@ucalgary.ca, Dmitry Gutsulyak, Javier Borau-Garcia, Etienne LaPierre, Masood Parvez. Department of Chemistry, University of Calgary, Calgary, Alberta T3B4J3, Canada

A new PCP ligand framework, in which the central carbon donor is an sp\(^3\) hybridized benzylic unit or an sp\(^2\) hybridized benzylidene donor, is utilized to prepare various nickel complexes. The electron rich nature of this ligand allows for the activation of B-H, C-H, Si-H, N-H and O-H bonds across the nickel carbon double bond in the PCsp\(^3\)P systems, and the ready labilization of the trans ligand in the PCsp\(^3\)P systems. Together, these reactions can be exploited to develop homogeneous catalysts for important transformations; the hydrolysis of nitriles will be discussed in detail.

INOR 392

Tantalum and niobium methyldienes

**Daniel J. Mindiola**, mindiola@sas.upenn.edu, Keith Searles. Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States

Using an easy-to-prepare, robust, and sterically encumbering aryloxide ligand \(-\text{OA}^+\) (\(\text{Ar}^+\) = \(\text{O}[2,6-\text{CHPh}_3]_2-4-\text{iBu}_2\text{C}_6\text{H}_3\)), we report a convenient synthetic route to Nb(V) and Ta(V) complexes bearing the terminal methyldiene moiety. In addition to these species being fully characterized, we also present some reactivity surrounding the M=CH\(_2\) unit.

INOR 393

Anion complexation and sensing with organoantimony compounds

**Francois P. Gabbai**, francois@tamu.edu. Department of Chemistry, Texas A & M University, College Station, TX 77845, United States

Antimony(V) halides such as \(\text{SbF}_5\) are powerful Lewis acids whose use is unfortunately complicated by their high reactivity and corrosive nature. In this presentation, we will show that antimony(V) species do not present these inconvenient corrosive properties but still retain considerable Lewis acidity toward anions. Applications in aqueous fluoride anion sensing and element-fluorine bond activation will be presented.

INOR 394

Structure, supramolecular aggregation and thermal transformation of heavy analogs of asymmetric N-heterocyclic carbene

**Alexander V. Zabula**\(^1\), zabula@wisc.edu, Ilia A. Guzeli\(^1\), Andrey Yu. Rogachev\(^2\), Robert West\(^1\). (1) Organosilicon Research Center, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States (2) Department of Biological and Chemical Sciences, Illinois Institute of Technology, Chicago, IL 60616, United States

Analogos of N-heterocyclic carbenes with divalent Group 14 elements are in research focus owing to their electronic structure, unusual reactivity and coordination properties which make these ligands potentially useful for catalytical applications. The incorporation of the heteroatoms into the aromatic systems of various N-heterocyclic silylenes, germylenes and stannylenes can provide altered electronic structure and chemical properties for these transient species. The properties of the \(\text{N}_2\text{M}^2\) (\(\text{M} = \text{Si}, \text{Ge}, \text{Sn}\)) systems, fused with pyridine rings, have been investigated in the present work. The related germylene and stannylene, previously postulated as non-isolable species, were prepared and studied by single X-ray and multinuclear NMR spectroscopy. The unexpected stability for these germanium and tin systems is attributed to the supramolecular aggregations of the divalent species via the strong M–N interactions. In contrast, pyrroloannelated silylene undergoes oligomerization with the formation of unprecedented thermally stable diradical systems. The electronic structures and energetics for the investigated compounds are discussed based on theoretical calculations.

INOR 395

Novel carbon-based functionalization of N-Heterocyclic carbenes

**Brian M Barry**, brian.barry@smu.ca. Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia B3H 3C3, Canada

N-Heterocyclic carbenes (NHCs) are ubiquitous in transition-metal coordination chemistry and more recently in main group chemistry. Their ability to be strong sigma-donors as well as great pi-acceptors made them fantastic ligands for nearly all metals. The chemistry of NHCs beyond metal coordination and Lewis acid-base adducts remains largely unexplored.

The ability of NHCs to stabilize reactive species has been well documented and is exploited here to form highly novel carbon-based materials. Synthesis, characterization and reactivity of these materials will be presented.

INOR 396

Main group metal complexes supported by a macrocyclic dianionic tetra-NHC

**S. Alan Cramer**, cramer2@utk.edu, Forrest L. Sturgill, David M. Jenkins. Chemistry, University of Tennessee, Knoxville, TN 37996, United States
The introduction of macrocyclic tetra N-heterocyclic carbene (NHC) ligands has opened dynamic new research areas in organometallic chemistry, such as catalytic azidiridination. To date, only one example of a main group metal complex has previously been synthesized with four or more NHC ligands and, in fact, very few have been prepared with more than two NHCs. Our group has recently expanded this chemistry by synthesizing a dianionic borate-based tetra-NHC ligand that forms metal complexes with multiple main group metals, such as indium and tin. The structural, spectroscopic, and catalytic properties of these main group tetra-NHC complexes will be discussed.

**INOR 397**

**Reactivity study of carbene-stabilized diatomic molecules**

**YUZHONG WANG**, wyzhong@uga.edu, Mariah Y. Abraham, Robert J. Gilliard, Gregory H. Robinson. Department of Chemistry, The University of Georgia, Athens, GA 30602, United States

N-heterocyclic carbenes (L-), as versatile ligands, have been well known for their extensive applications in organic and transition-metal homogeneous catalysis. The recent application of N-heterocyclic carbenes in low oxidation state main group chemistry has been resulting in the production of many unusual main group molecules. With using the carbene stabilization strategy, this group has synthesized a number of interesting compounds including the first neutral diborenes containing a B=B double bond [L:(H)B=B(H):L] and a series of carbene-stabilized diatomic molecules [i.e., L:EE:L (E = Si, P, As)]. This presentation will discuss our recent efforts in the reactivity study of these novel molecules.

**INOR 398**

**Structure and bonding in heavy group 2 organometallics: Does dispersion hold the key?**

Laura K. Engerer, Nicholas C. Boyde, Timothy P. Hanusa, t.hanusa@vanderbilt.edu. Department of Chemistry, Vanderbilt University, Nashville, TN 37235, United States

The highly electropositive nature of calcium, strontium, and barium is associated with metal–ligand (Ae–L) interactions that are strongly polar. Lacking metal valence electrons to influence the orientation of ligands, AeL₂ compounds would be expected to have linear geometries, but it has been long known, for example, that Ae dihalides are bent in the gas phase, that the unsolvated dialkyl compound Ca[C(SiMe₃)₂]₂ is nonlinear, and that almost all Cp²–Ae (and related organolanthanide metallocenes) possess non-parallel cyclopentadienyl rings. Reconciliation of an electrostatically-based bonding scheme for AeL₂ compounds with their nonlinear structures has been attempted by proposing that: 1) reverse (core) polarization of the metal cation by the ligands is operative; 2) that the (n − 1)d orbitals of the cation participate in bonding; and 3) that in appropriate complexes, attractive van der Waals (dispersion) interactions between the ligands strongly influence the structures. The latter explanation has risen to prominence in recent years (e.g., *Organometallics* 2012, 32, 1265), especially as computational disentanglement of these (not mutually exclusive) possibilities has become more feasible with the development of density functionals that capture the effects of dispersion interactions. In some cases these take the form of heavily parameterized functionals (e.g., Truhlar’s Minnesota M0X functionals), whereas in other cases the dispersion interaction is added as a correction to an existing functional (as in the “-DX” developments by Grimme). We chose to emphasize the latter functionals in investigating the importance of dispersion effects in heavy Group 2 complexes, as it is possible to optimize a structure both with and without dispersion corrections, while maintaining the same underlying functional form. The effects of dispersion corrections on the structures of a range of heavy organoalkaline-earth complexes with cyclic and acyclic ligands will be presented.

**INOR 399**

**Development of stable organophosphorus conjugated materials**

Shanshan Wu¹, sxw325@case.edu, Nihal Deligonul¹, Arnold L. Rheingold², John D. Protasiewicz². (1) Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, United States (2) Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92033, United States

Organophosphorus conjugated materials featuring P=C units have been studied in recent years due to their unique optoelectronic properties that might be useful in OLEDs and other optoelectronic devices. Previous studies on benzoxaphospholes (BOPs) reveal their significant photoluminescent properties. In this work, a group of bulky-substituted BOPs were synthesized. Those compounds show comparable photoluminescent properties having enhanced stability compared to less hindered benzoxaphospholes. Furthermore, we have been working on the incorporation of BOP units into extended conjugated systems. A series of bisbenzoxaphospholes and a trisbenzoxaphosphole were prepared. Photoluminescence studies of these extended conjugated materials will be presented.

**INOR 400**

**Synthesis, spectroscopic, and structural characterization of unique trialkyboranes: Evidence of unusual geometries stabilized by dispersion effects**

Michelle A Faust¹², mafaust@ucdavis.edu, Philip P Power¹. (1) Department of Chemistry, University of California, Davis, Davis, CA 95616, United States (2) Lawrence Livermore National Laboratory, Livermore, CA 94551, United States

The synthesis, spectroscopy, and structural characterization of a series of new trialkyboranes are described. Unusual structural features of the trialkyboranes are observed when the nature of the alkyl ligand is bicyclic and the alpha carbon is not contained within the ring. Their structures are exemplified by Figure 1, which shows that all three ligands are located on one side of the central BC₃ plane contrary to steric expectations.
INOR 401

Synthesis and characterization of heavy metal frustrated Lewis pairs

Sem Raj Tamang, Sem.Tamang@coyotes.usd.edu, Jung-Ho Son, James D Hoefelmeyer. Department of Chemistry, University of South Dakota, Vermillion, SD 57069, United States

The interaction between a Lewis acid and a Lewis base generally results in the formation of a Lewis acid-base adduct via dative bonding. Frustrated Lewis Pairs (FLPs) arise when steric bulk prevents the formation of a dative bond between Lewis centers. FLPs showcase unprecedented reactivity such as activation of neutral small molecules. We have synthesized bifunctional amphiphilic molecules with heavy Lewis acid centers via transmetalation. From 8-(quinolyl)trimethylstannane, transmetallation with GaCl$_2$ or HgCl$_2$ leads to exchange of the Me$_3$Sn-group to yield dichloro-8-quinolylgallium(III) (1) or chloro-8-quinolyldimercury(II) (2). Molecule (2) was converted into bis(8-quinolyl)dimercury(II) (3) that was found either in bent or linear geometry in the solid state. All compounds were characterized by nuclear magnetic resonance (NMR) spectroscopy, single crystal X-ray diffraction, and elemental analysis. Ultimately, we plan to study the utility of FLPs with heavy Lewis acids in the heterolytic cleavage of H-H bonds or C-E bonds in which E is a relatively 'soft' polarizable atom such as sulfur or phosphorus.

INOR 402

Synthesis and reactivity of highly electrophilic trityl salts of carborane anions

Chun-I Lee, chun-i.lee@mail.chem.tamu.edu, Oleg V Ozerov. Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States

In 2008, the Ozerov group reported catalytic hydrodefluorination (HDF) of various organic compounds which contain C(sp$^3$)-F bonds under mild conditions.[1] The keys to a successful reaction were fluorophilic silylium cations generated in situ by reacting trityl cations with silanes. However, activation of C(sp$^3$)-F bonds in perfluoroalkanes still remains a challenge. HDF of perfluoroalkanes would require trityl cations with higher hydride affinity to generate more fluorophilic silylium cations.[2] Based on this concept, trityl salts with strong electron-withdrawing substituents (e.g. m-fluoro) of carborane anions were synthesized and tested in HDF. Meanwhile, utilization of these trityl cations in generating new main group and transition metal cations by abstraction and/or oxidation will also be discussed in this presentation.


INOR 403

Unassisted solar water splitting with semiconducting oxide photoanode/photocathode tandem cells

Kevin Sivula, kevin.sivula@epfl.ch. Institute of chemical sciences and engineering, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland 1015, Switzerland

A device that can convert solar energy into a chemical fuel with good efficiency while also offering high stability and the capability to be constructed with widely available materials using inexpensive processing techniques is urgently needed. Here I describe progress toward promising systems that accomplish overall photoelectrochemical water splitting with an inexpensive oxide-based photoanode (e.g. Fe$_2$O$_3$, WO$_3$, or BiVO$_4$) and a copper (oxide or chalcogenide) photocathode. Recently, advances in reduction of the overpotentials due the passivation of surface states and the application of catalysts have allowed the construction of simple dual-absorber tandem cell. In order to give insight into the electro-optical limitations and to define routes for improvement of these devices, the current-voltage characteristics as well as the spectral responses of the component parts are evaluated based on measured quantum efficiencies (IPCEs), transmittances of the photoanodes, and photon flux on each active area. Finally, the actual performance of devices is evaluated and the benchmark solar-to-hydrogen conversion efficiency (over 3%) for dual-absorber oxide-based solar water splitting is reported. Overall, the simple construction of these devices and their composition from widely available and inexpensive components makes them very promising for future development.

INOR 404

Nanoporous bismuth vanadate photoanodes for use in solar energy conversion
N-type BiVO₄ has recently emerged as a promising photoanode because it can generate up to \( J = 7.6 \text{ mA/cm}^2 \), utilizing a significant portion of visible light without needing much external bias, due to its favorable CB edge position near the thermodynamic H₂ evolution potential. However, the solar-to-hydrogen efficiency achieved by BiVO₄ to date has been far below what is expected because it suffers from extremely low electron-hole separation yield (\( \Phi_{sep} \)). To date, the effort to improve \( \Phi_{sep} \) of BiVO₄ has mainly focused on doping studies, which intended to improve its poor electron transport properties. In this presentation we report electrochemical synthesis of a nanoporous BiVO₄ electrode with a specific surface area of 32.9 m²/g that effectively suppresses bulk carrier recombination without additional doping. We will also discuss a new concept to interface BiVO₄ with oxygen evolution catalysts (OECs), which enables the optimization of the BiVO₄/OEC interface and the OEC/electrolyte interface simultaneously. The resulting photoanode generates a photocurrent density of 2.73 mA/cm² for water oxidation at 0.6 V vs. RHE in a neutral phosphate buffer.

INOR 405
Suspended inorganic nanocrystals as photocatalysts for the water splitting reaction
Frank E Osterloh, fosterloh@ucdavis.edu, Department of Chemistry, University of California, Davis, CA 95616, United States

Photocatalytic water splitting with colloidal suspensions is conceptually the most simple and inexpensive pathway to hydrogen fuel from solar energy. Nanoscaling is widely considered to improve the efficiency of such catalysts, but as a detailed analysis shows, nanostructures also have considerable disadvantages. Using recent examples from this laboratory, this talk discusses the effects of nanostructuring on carrier generation, separation, and recombination, as well as the possibility of controlling nanostructure energetics and reactivity via potential determining ions and quantum size effects.

INOR 406
Photoelectrochemical route for accessing amorphous mixed-metal oxides for electrocatalytic water oxidation
Curtis P Berlinguette, cberling@chem.ubc.ca, Departments of Chemistry and Chemical Biological Engineering, The University of British Columbia, Vancouver, BC V6T1Z1, Canada

The electrochemical conversion of water into hydrogen fuel is one of the most promising schemes for the large-scale storage of solar electricity. There is unfortunately a substantial overpotential of (h) required to produce hydrogen at a meaningful rate due to slow oxygen evolution kinetics. Consequently, the development of efficient oxygen evolution reaction (OER) catalysts is vital to achieving a clean hydrogen economy. While most OER catalysts are based on crystalline oxides, higher activities can also be achieved with amorphous phases. There are, however, limited methods available for producing amorphous catalytic films. We filled this gap by recently demonstrating amorphous phases of metal oxide films can be accessed through a facile photochemical decomposition technique.¹ This fabrication method enables the use of different combinations with precise compositional control. Pure iron, nickel and cobalt oxides were investigated, along with various combinations of the mixed metal oxides, and shown to display remarkably high efficiencies towards the OER reaction.


INOR 407
Manganese oxide oxygen evolution catalysts deposited by ALD
Katie L. Pickrahn, Stacy F Bent, sbent@stanford.edu, Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States

The oxygen evolution reaction (OER), in which water is oxidized to molecular oxygen, is an important part of many technologies including the photoelectrochemical splitting of water. There is much interest in the development of earth-abundant, affordable electrocatalysts for OER. In this talk, we describe the use of atomic layer deposition (ALD) to deposit highly active manganese oxide (MnOₓ) catalysts for OER. ALD is a vapor phase deposition technique capable of forming highly uniform conformal thin films with a fine control over film thickness and film composition. It is becoming an attractive method for synthesizing catalytic thin films, opening new avenues for advanced catalytic designs. We synthesize MnOₓ-based catalysts on glassy carbon supports using ALD and test them in both the OER and oxygen reduction reaction (ORR). The catalysts are characterized using a variety of techniques and their activity is measured by cyclic voltammetry. The ALD process produces Mn(II)O, which can be changed to higher oxidation states by annealing. The as-deposited MnO catalyst is inactive for ORR, but highly active for OER. Annealing the film to form Mn₃O₄ generates a catalyst that is active for both the OER and the ORR, approaching the activity of the most active MnOₓ catalysts known. Because ALD provides excellent control over film thickness, we show that the activity of the MnOₓ depends on the film thickness at the nanoscale. This effect is explored using other metal oxide films for comparison, and the results indicate that beyond a critical thickness, charge transport limitations begin to reduce the activity of the films. We discuss further implications of electrocatalyst design using ALD, including applications to photoelectrochemical water splitting.

INOR 408
Nanostructured electrocatalysts for the hydrogen evolution reaction
Raymond E Schaak, schaak@chem.psu.edu, Department of Chemistry, Pennsylvania State University, University Park, PA 16802, United States

The production of molecular hydrogen by the electrochemical reduction of water is an important component of several developing clean-energy technologies. While the hydrogen evolution reaction (HER) is effectively facilitated by noble metals such as Pt, replacement of Pt with earth-abundant materials would be desirable to facilitate global scalability. We have been exploring nanoparticles of 3d transition metal phosphides as HER electrocatalysts, and recently discovered that Ni₃P nanoparticles had amongst the highest HER activity of any non-noble metal electrocatalyst reported to date. This talk will highlight recent results from our highly collaborative project, including the synthesis and characterization of other new HER electrocatalysts.

INOR 409
“All that is gold does not glitter”: Gold(III)…Sulfur intramolecular interactions in templated C-H bond activation and solid-state effects
Daron E Janzen, dejanzen@stkat.e, Arianna M Kooyman, Shannon R Doherty, Department of Chemistry and Biochemistry, St. Catherine University, St. Paul, MN 55105, United States

Our recent work on gold(III) complexes with cyclometallated ligands and the trithiacrown macrocycle [Au][3][Cl][AuCl] which shows an interesting Au…S interaction feature at 2.999(3)Å. This complex undergoes low temperature C-H activation to form the chiral sulfonium salt [Au][3][Cl][4,7-dithianiacyclo[4,3,0]nonene] as either a [AuCl][Cl] salt or [AuCl][Cl] salt. This bimetal cation formation is related to the ease of reduction of gold(III) to gold(I) as well as the panchent of Au[3] for adopting an endodontate conformation. The cation [Au][3][Cl] possesses chiral centers at the shared sulfur and carbon atoms. The X-ray structure of the [AuCl][Cl] salt is centrosymmetric but the [AuCl][Cl] salt spontaneously resolves as single enantiomer crystals. Noncentrosymmetric structures of each enantiomer were collected. These complexes have been further characterized by NMR and elemental analysis. Other complexes with unique Au…S intramolecular features will also be presented.
INOR 410

Cooperative reactivity involving organosilicon ligands and late transition metals: Making and breaking silicon-element bonds via metal silyl and silylene intermediates

Matthew T Whited, mwhited@carleton.edu, Joseph W Boerma, Alexander M Deetz, Daniel E DeRosha, Christian A Olivares. Department of Chemistry, Carleton College, Northfield, MN 55057, United States

The coordinative and redox flexibility of organosilicon ligands makes them ideal candidates for exploration of new cooperative pathways for small-molecule activation. In this talk, I will present recent findings from our laboratory using new and old families of silicon-based ligands for cooperative bond-forming and bond-breaking reactions at rhodium and iridium with applications in organic synthesis and transformation of petroleum feedstocks.

INOR 411

Investigation into the structure of (SiNN)Rh complexes and their borylation reactivity toward terminal alkynes and arenes

Nathanael A. Hirscher1,2, nah3rf@virginia.edu, Chun-I Lee1, Oleg V. Ozerov1. (1) Department of Chemistry, Texas A&M University, College Station, Texas 77840, United States (2) Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States

The Ozerov group has previously reported an Ir complex supported by a SiNN pincer ligand which is an efficient and chemoselective catalyst for dehydrogenative borylation of terminal alkynes (DHBTA). In order to elucidate the mechanism of DHBTA or improve the current catalytic system, we decided to investigate the properties of the analogous Rh system since Rh and Ir complexes often exhibit comparable reactivity as group 9 metals. The (SiNN)Rh(H)(COE) complex was successfully synthesized from [Rh(COE)2Cl]2 and the sodium salt of the SiNN ligand, and was shown to react with excess pinacolborane to form the (SiNN)Rh(H)(Bpin)2 complex. Both (SiNN)Rh(H)(COE) and (SiNN)Rh(H)(Bpin)2 complexes have been characterized and exhibit different catalytic reactivity from the analogous Ir complexes. The reactivity of these Rh complexes toward terminal alkynes and arenes is discussed. Using X-ray crystallography, interesting structural differences between the catalytically active Rh and Ir species have been observed, serving as an explanation for the reactivity difference.

INOR 412

Versatile synthesis of orthogonally protected azamacrocyclic ligands

Matthew S Wasilewski, mwasile@g.clemson.edu, Modi M Wetzler, Julia L Brumaghim. Department of Chemistry, Clemson University, Clemson, South Carolina 29634-0973, United States

Syntheses of azamacrocycles such as triazacyclonane (TACN) and tetrazadodcane (cyclen) still generally utilize the approach described by Richman and Atkins forty years ago to generate highly symmetric ligands with little opportunity for multiple functional groups or chiral centers. Thus, azamacrocycles are being systematically outclassed by other ligand classes for a whole range of applications. In contrast, we have used the significant advances in the science of protecting groups to develop alternative synthetic strategies that enable synthesis of azamacrocycles with multiple functional groups under greener and safer synthetic conditions. Specifically, instead of the standard difficult-to-remove toluenesulfonate esters we have used readily available and inexpensive nitrated and trifluoromethylated sulfonate ester derivatives for activation of hydroxyl functions utilized in the cyclization step as opposed to the use of alkyl halides. We also used trifluoroamide and butoxycarbonyl protecting groups to yield orthogonally functionalized
versatile components for azamacrocycles with as many as four different functional groups on the ring nitrogens with mild and green deprotection conditions.

INOR 413
Modeling the photophysics of luminescent organometallic platinum(II) phosphors

James E McGarrah, mcgarrah@geneseo.edu, Rita L Wheeler, Benjamin E Nagasing, Eric Helms. Chemistry, State University of New York, College at Geneseo, Geneseo, NY 14454, United States

Luminescent Pt(II) metal organic complexes have a rich and complex photophysics. An attractive feature is that the emission energy is tunable due to ligand substitution. This allows for the design of different color phosphors. Additionally, the formation of aggregates typically shifts the emission energy to lower energy relative to the monomer’s luminescence in solution. Aggregate formation occurs in the solid-state, both in crystalline samples and in optically transparent solid solutions (a film of the phosphor doped in an organic glass or polymer). Surprisingly, the photophysics is often different between a single crystal, a solid, and/or a dilute liquid solution of the same compound—not only does the emission energy change, but so does the vibronic structure. A series of Pt(N^C)(O^O) complexes where N^C is a monoanionic cyclometallated ligand (e.g., 2-phenylpyridine) and O^O is either acac or a deprotonated 9-hydroxyphenalenone (Hpal) are investigated comparing their solution and solid-state photophysical properties.

![Image](image-url)

Pt(ppy)(pal)  
Pt(ppy)(acac)

INOR 414
Group VI metal carbonyl complexes of bis(diphenylphosphinomethyldiphenylborate)

Paul J Fischer, fischer@macalester.edu, Laura Avena, Michelle C Neary, Grace K Putka, Kevin P Sullivan, Trent D Bohrmann. Chemistry, Macalester College, Saint Paul, MN 55105, United States

Anionic bidentate bis(phosphino)diphenylborate ligands permit unique modulation of metal electronic environments on the basis of phosphine chelation coupled with the close proximity of a negatively charged boron center. This presentation will discuss attempts to leverage advantages of this enhanced donation in zerovalent group VI metal carbonyl chemistry. The synthesis of useful starting materials containing bis(diphenylphosphinomethyl)diphenylborate and nitriles and sulfur dioxide, respectively, will be described. The characterization of these metal complexes facilitates interesting comparisons between the employed anionic bidentate phosphine relative’s classical neutral cousins (for example, dppe). The exciting utility of group VI metal carbonyl complexes of bis(diphenylphosphinomethyl)diphenylborate for template syntheses of beta-amino functionalized isocyanide ligands will also be discussed.

INOR 415
Investigation of the influence of ligand sterics on the mechanism of alkene isomerization catalyzed by Ir(III) CCC-pincer complexes

Spring Melody M Knapp, sknapp@colgate.edu, Daniel Kim, Sarah E Shaner, Dimitar Y Shopov, Jennifer A Tendler, David M Pudalov, Anthony R Chianese. Department of Chemistry, Colgate University, Hamilton, New York 13346, United States

C-H bond activation by organometallic catalysts allows for the efficient functionalization of petroleum feedstocks into more valuable chemical commodities. Upon activation by NaO/Bu, Ir(III) CCC-pincer complexes containing meta-phenylene-bridged N-heterocyclic carbene ligands with mesityl side groups dehydrogenate linear alkanes to form alkene products, while complexes with adamantyl side groups do not. However, both catalysts efficiently isomerize terminal alkynes to form a mixture of internal alkene products, a process that hinders their ability to selectively generate the desired terminal alkene product. In an effort to better understand the influence of the ligand sterics on isomerization, the mechanism of alkene isomerization with these catalysts was investigated, including kinetic characterization of the catalysts, H-D crossover experiments, the effect of base on catalyst activity, and isolation of the catalyst resting state. Early results suggest a surprising dichotomy in the mechanism of the reaction, apparently caused by ligand steric effects.

INOR 416
Halide abstraction from [M’X'C(1,1'-bis(phosphino)metalocene)] complexes

Margaret A Tiedemann, tiedemann@lafayette.edu, Chip Nataro. Department of Chemistry, Lafayette College, Easton, PA 18042, United States

The product of halide abstraction from [M’X'C(1,1'-bis(phosphino)metalocene)] [M’ = Pd or Pt] complexes is very dependent on the nature of the 1,1'-bis(phosphino)metalocene ligand (M(C_3H_4PR_3)_2 where M = Fe, Ru or Os). With most R groups, the halide is removed and the product undergoes a dimerization to form a bridged-halide dication, [(M(C_3H_4PR_3)_2M’(μ-X))_2]^2+. When R = Bu the product of halide abstraction is too bulky to form the bridged-halide dication. Instead, a monocation with a Fe-Pd interaction is formed. This compound undergoes a temperature induced solid state isomerization to a three-coordinate species in which there is not a Fe-Pd interaction. Finally, with a weakly donating 1,1'-bis(phosphino)metalocene ligand such as when R = 3,5-C_9H_7(CF_3)_2, these compounds do not undergo a halide abstraction reaction. The products of these reactions were investigated spectroscopically, crystallographically, and electrochemically.

INOR 417
Molecular approaches to catalytic hydrogen generation and carbon dioxide reduction

Christopher J Chang, chriscchang@berkeley.edu. Departments of Chemistry and Molecular and Cell Biology and HHMI, University of California, Berkeley, CA 94720, United States

We have initiated a program aimed at creating new molecular catalysts for sustainable energy applications, with particular interest in developing earth-abundant metal systems that operate in green aqueous media and do not generate organic by-products during catalysis. This talk will present our latest results on the use of polypyridine platforms and their applications to electrocatalytic and photocatalytic generation of hydrogen from water and carbon dioxide fixation.
Hydrogen production, through the reduction of water in electrolyser, is currently one of the most convenient ways to store energy durably, if the electrical energy is initially obtained from renewable resources. However, while electrolysis is a mature and robust technology, the most promising devices, based on proton exchange membranes, rely on the use of platinum as electrocatalyst to accelerate both hydrogen evolution and water oxidation reactions. However, this rare and expensive metal is not itself a renewable resource, so the viability of a hydrogen economy depends on the design of new efficient and robust electrocatalytic materials based on earth-abundant elements. Cobaloximes form such a class of catalysts, now widely used in the solar fuel community. We developed cobalt dimate–dioxime complexes as a second generation of efficient and stable electro-catalysts for hydrogen evolution forming acidic nonaqueous solutions with slightly lower overvoltages and much larger stabilities towards hydrolysis as compared to previously reported cobaloxime catalysts. We will report on the covalent functionalization of electrode materials with such catalysts and their activity under fully aqueous conditions. The nature of the catalytic species, i.e. molecular species vs nanoparticulate electrodeposited material, will be discussed. Finally, the combination of such catalysts with photosensitizers to design photocatalytic systems able to achieve the photocatalytic production of hydrogen will also be presented.

References:

INOR 419
Learning from Nature how to make solar fuels
Gary W Brudvig. gary.brudvig@yale.edu. Department of Chemistry, Yale University, New Haven, CT 06520-8017, United States
Photosystem II (PSII) uses light energy to split water into protons, electrons and oxygen. In this reaction, Nature has solved the difficult chemical problem of efficient four electron oxidation of water to yield oxygen without significant side reactions. In order to use Nature's solution for the design of materials that split water for solar fuel production, it is important to understand the mechanism of the reaction. The X-ray crystal structures of cyanobacterial PSII provide information on the structure of the Mn and Ca ions, the redox-active tyrosine called tyrosine-Z, chloride and the surrounding amino acids that comprise the oxygen-evolving complex (OEC). The structure of the OEC and the water-oxidation chemistry of PSII will be discussed in the light of biophysical and computational studies, inorganic chemistry and X-ray crystallographic information. These insights on the natural photosynthetic system are being applied to develop bioinspired materials for photocatalytic water oxidation and fuel production. Our progress on the development of synthetic water-oxidation catalysts and their use in materials for artificial photosynthesis will be discussed.

INOR 420
Cobalt catalyzed hydrogen evolution and formic acid dehydrogenation
Smaranda C. Marinescu, Stephanie M. Laga, Aaron Sattler, Harry B. Gray, Jay R. Winkler, winklerj@caltech.edu. Beckman Institute, California Institute of Technology, Pasadena, CA 91125, United States
A Co^1-triphos complex (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) reacts at room temperature with p-toluenesulonic acid monohydrate in acetonitrile to generate hydrogen (0.5 equivalents) and Co^0 with a driving force of just 30 meV/Co. Protonation of Co^0 produces a transient Co^0-H complex that has been characterized by nuclear magnetic resonance spectroscopy. The Co^0-H intermediate decays by second-order kinetics with an inverse dependence on acid concentration. Analysis of the kinetics suggests that Co^0-H produces hydrogen by a dominant heterolytic channel in which a highly reactive Co-H transient is generated by Co^0 reduction of Co^0-H. The Co^0-triphos complex also reacts with excess formic acid to produce H2 and CO2. The mechanism of this transformation has been probed electrochemically and in studies of the gas evolution kinetics.

INOR 421
Oxygen donor ligands and oxidation states
Laleh Tahsini, Margaret Tiedemann, Linda H Doerrer, doerrer@bu.edu. Department of Chemistry, Boston University, Boston, MA 02215, United States
In recent years our group has done extensive work with transition metal compounds containing fluorinated O-donor ligands including aryloxides, monodentate alkoxides and the bidentate perfluoropinacolate ligand. These fluorinated ligands are particularly attractive because of their oxidative robustness, and they are increasingly commercially available due to the widespread use in the pharmaceutical industry of fluorinated organic species. Less widely appreciated but increasingly useful is the much reduced basicity of these ligands compared to their non-fluorinated counter parts. This property has led to a new family of water soluble compounds. This presentation will highlight recent work with late 3d metal complexes describing the conditions under which these ligands do and do not act as Bronsted bases and how the metal oxidation state influences these proton transfer reactions as well.

INOR 422
Low energy proton-coupled electron transfer pathways in photo- and electrochemical catalytic water oxidation
Dmitry E Polyansky, dep@bnl.gov, Yosra Badiel, Elisuko Fujita, Anna Lewadowska-Andralojc, James T Muckerman, Ruifa Zong, Randolph P Thurmer. (1) Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973-5000, United States (2) Department of Chemistry, University of Houston, Houston, TX 77204-5003, United States
Transition metal complexes containing a ruthenium metal center have been successfully employed to gain fundamental insights into the mechanism of catalytic water oxidation. In the case of most single-metal center catalysts, the formation of the highly energetic species Ru(V)=O is required prior to O-O bond formation. Due to the non-proton-coupled nature of the Ru(V)=O couple its potential cannot be controlled by pH. In a subset of Ru polypyridyl catalysts (e.g., [Ru(NPm)(pic)]^2- NPM = 4,4'-butyl-2,6-di-1',8'-napthalarid-2'-yl)-pyridine, pic = 4-picoline), the formation of the O-O bond can proceed through the Ru(IV)=O intermediate, and the thermodynamics of this pathway can be controlled by varying the pH of the medium. The reaction between
Ru(IV)=O and a water molecule is accompanied by the concomitant removal of an electron and a proton which results in the formation of a Ru hydroperoxo species. Access to this low-energy pathway enables the use of a mild oxidant such as photogenerated [Ru(bpy)_3]^2+ in visible light-driven water oxidation.

The work at Brookhaven National Laboratory was carried out under contract DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Geosciences, & Biosciences, Office of Basic Energy Sciences.

INOR 423
Controlling the energetics and lifetimes of ligand-to-metal and metal-to-metal charge transfer excited states
Walter W. Weare, wweare@nscsu.edu. Department of Chemistry, North Carolina State University, Raleigh, NC 27695, United States

The discovery of new chromophores, particularly those synthesized from earth abundant elements, is critical for artificial photosynthesis to become a reality. The talk will address the synthesis and photochemistry of new unsupported µ-oxo bridge bimetallic systems (Ti=O-M) composed entirely of earth-abundant elements with the potential to be a chromophore in a solar-to-fuel integrated system. These molecules are being used to probe aspects of metal-to-metal charge transfer (MMCT) photochemistry. By varying the metal identities (M=Mn, Fe, Co, Ni, Cu and Zn), magnetic coupling and spin state can be controlled in both ground and excited states. We believe that spin-crossover events in the MMCT excited state can be used to lengthen the lifetime of the charge separated state, analogous to organic systems with long triplet-state lifetimes. For example, we can increase the τ1/2 from 180 µs in the Ti=O monomer to 240 µs in the case of a heterobimetallic Ti=O-Co compound.

INOR 424
Can MRI agents compete in the biochemical imaging arena?
Michael F Tweedle, michael.tweedle@osumc.edu. Department of Radiology, The Ohio State University College of Medicine, Columbus, Ohio 43210, United States

Existing MRI contrast agents are elegantly simple, hydrophilic Gd chelates that are mostly biologically inactive. But MRI is so compelling an imaging tool that enhancement with biologically active contrast agents remains a thriving research area despite 30 years of commercially unrewarded effort. The unachieved goal is selective, disease specific concentration in vivo of sufficient (probably > micromolar) Gd under clinically and commercially acceptable conditions. Gd has a thousand fold greater detection threshold in MRI than radionuclides in PET/SPECT, so most biological targets are scarce relative to the Gd concentrations needed to enhance images, and the few targets (e.g. fibrin) with sufficient biologic concentrations have (so far) not found commercially compelling applications. The latter require relative large scale use to justify the > $100,000,000 development costs. Increasing relaxivity per Gd, clustering of Gd (or Fe) into nanostructures to produce multiple Gd per biologic target, PARACEST techniques, harnessing disease specific enzymatic turnover, transporters or microenvironment are current avenues of research. Each of these avenues has possibilities that are accompanied by challenging, well defined limitations.

INOR 425
Gadonanotubes: What’s new and what’s next?
Lon J Wilson, durango@rice.edu. Department of Chemistry, Rice University, Houston, Texas 77005-1892, United States

Discovered in our laboratory in 2005, the Gadonanotubes (GNTs) are a high-performance MRI contrast agent (CA) material derived from Gd³⁺-ion clusters encapsulated within ultra-short (20-80 nm) carbon nanotube capsules (see Figure)[1,2].

With T₁-weighted relaxivities (r₁; s) typically ≥ 100 mM⁻¹ s⁻¹/Gd³⁺ ion, the GNTs are among the highest performing MRI CA materials known. Recent NMRD studies as well as XANES/EXAFS structural investigations will be reported that reveal more about how the GNTs achieve their high-performance characteristics at both low and high magnetic fields. Finally, recent efforts to employ the GNT platform to develop multi-modal imaging agents, as exemplified by the MRI/PET agent ⁶⁴Cu@GNT, will also be presented.


INOR 426
High relaxivity MRI contrast agents for high magnetic field – challenges and pitfalls
Lothar Helm, lothar.helm@epfl.ch. Department of Chemical Sciences and Engineering, EPFL, Lausanne, Switzerland
The rapidly growing field of molecular imaging seeking for real-time monitoring of molecular events occurring at the cellular level pushes MRI to higher magnetic fields. MRI molecular imaging can only be performed using targeted and responsive probes translating the molecular information to signal contrast in the image. A major goal in the development of such probes, besides targeting and response, is optimization of efficiency which is in general expressed as relaxivity. The parameters influencing relaxivity of gadolinium based T1 contrast agents are known and new agents could be designed using a guided strategy.

Relaxivity induced by gadolinium ions is however strongly dependent on the magnetic field applied in MRI. Unfortunately the efficiency of Gd-based chelates decreases strongly at magnetic fields higher than 3 T (see Figure). New strategies different from those used at conventional MRI fields have to be applied.

Figure: Inner-sphere relaxivity calculated for increasing rotational correlation times as a function of the magnetic field

In this contribution I will review strategies to get high T1 relaxation enhancement at high magnetic fields. I will show in which respect strategies differ from optimization for low field contrast agents and what the pitfalls are to be avoided.

INOR 427

Does anybody really know what (correlation) time it is? Designing Gd(III) complexes for high field, high relaxivity applications

Peter Caravan, caravan@nmr.mgh.harvard.edu. Martinos Center for Biomedical Imaging, Massachusetts General Hospital, Charlestown, MA 02129, United States
Department of Radiology, Harvard Medical School, Boston, Massachusetts 02129, United States

Here we describe two strategies to increase relaxivity at high fields (≥3 tesla). For most Gd(III) complexes, rotational diffusion of the complex governs relaxation of a coordinated water ligand. To maximize relaxation efficiency, the product of the rotational correlation time and the hydrogen Larmor frequency should be close to 1. For small metal complexes, this occurs at Larmor frequencies in the gigahertz regime and thus relaxation is not very efficient at fields used for MR imaging. Alternately, protein- or nanoparticle-bound Gd(III) have long correlation times that can yield very high relaxivity, but only at very low magnetic fields (≈0.5 tesla or 20 MHz).

Here we describe our recent work with rigid, multimeric, peptide-based complexes to design contrast agents with specific intermediate rotational correlation times to yield high relaxivity at higher magnetic fields. For protein- or nanoparticle bound Gd(III) complexes with long rotational correlation times, we also describe an alternate strategies to increase relaxivity at high fields. This involves designing a Gd(III) complex with an extremely fast water exchange rate. For slow tumbling complexes, it is possible that the water exchange rate can become the limiting rate that governs relaxation. We will show that albumin-bound complexes with water residency times approaching 1 ns can yield much higher relaxivity at high fields than conventional albumin-bound complexes like MS-325.

INOR 428

Multimodality molecular imaging

Angelique Louie, aylouie@ucdavis.edu. Biomedical Engineering, University of California, Davis, CA 95616, United States

The conundrum of modality selection in clinical diagnostic imaging is that modalities with the highest sensitivity have relatively poor resolution, while those with high resolution have relatively poor sensitivity. In recent years, the idea of using multiple modalities in conjunction has gained in popularity and researchers have come to realize that the complementary abilities of different imaging modalities could be harnessed to great effect by using them in tandem. The idea of combining imaging technologies moved to the mainstream with the advent of the first successful commercial fused instruments. The first fused PET/CT instrument, developed in 1998 by Townsend and colleagues in collaboration with Siemens Medical, was available commercially in 2001. Now PET/MRI instruments are poised to enter the clinic. With hybrid technology clearly on the rise, the excitement over these new instruments has triggered a tumult of activity in probe design and development in an effort to boost the clinical benefits of hybrid instrument technology. The fusion of modalities does not necessarily require a single probe that can be detected by more than one modality; but there are applications where a fused probe can be advantageous. In this presentation I describe our approaches to developing multimodal probes and their applications.

INOR 429

Hyperpolarized yttrium-89 complexes as potential magnetic resonance probes

Lloyd Lumata, Ashish Jindal, Matthew Merritt, Craig Malloy, A. Dean Sherry, Zoltan Kovacs, zoltan.kovacs@utsouthwestern.edu. Advanced Imaging Research Center, Ut Southwestern Medical Center, Dallas, Texas 75390, United States

Hyperpolarized yttrium-89 complexes as potential magnetic resonance probes

Lloyd Lumata, Ashish Jindal, Matthew Merritt, Craig Malloy, A. Dean Sherry, Zoltan Kovacs, zoltan.kovacs@utsouthwestern.edu. Advanced Imaging Research Center, Ut Southwestern Medical Center, Dallas, Texas 75390, United States
Several yttrium polyamino polycarboxylate complexes have successfully been hyperpolarized using fast dissolution dynamic nuclear polarization (DNP) NMR technique. Up to 65,000-fold 89Y NMR signal enhancement of YDOTA (DOTA = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) was achieved by employing the optimal microwave irradiation frequency, optimizing the glassing matrix (glycerol-water), choosing a free radical polarizing agent with negligible inhomogeneous line broadening contribution to the ESR linewidth (trityl OX063), and addition of an electron T1 relaxation agent (ProHance).

Most yttrium complexes were found to have extremely long 89Y spin lattice (T1) relaxation times (around 400-500 s). The chemical shift of the Y(III)-ion appears to be very sensitive to its coordination environment as demonstrated by the wide range of 89Y chemical shifts (about 100 ppm) in structurally similar complexes. The 89Y chemical shift of YDOTP (DOTP = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetramethylene phosphonic acid) is pH dependent and shows a pH dispersion of 0.29 pH unit/p pm in the physiologically relevant pH range. MR imaging of phantoms containing hyperpolarized YDOTA was demonstrated at a concentration of 1 mM using a chemical shift imaging (CSI) sequence.

INOR 430

Heterogeneous-nucleation mechanism for the polypol synthesis of silver nanowires
Waynie M. Schuette, William E. Buhro, buhro@wustl.edu. Department of Chemistry, Washington University, St. Louis, MO 63130, United States

Various additives are employed in the polypol synthesis of silver nanowires (Ag NWs), which are typically halide salts such as NaCl. A variety of mechanistic roles have been suggested for these additives. We now show that the early addition of NaCl in the polypol synthesis of Ag NWs from AgNO3 in ethylene glycol results in the rapid formation of AgCl nanocubes, which induce the heterogeneous nucleation of metallic Ag upon their surfaces. Ag NWs subsequently grow from these nucleation sites. The conclusions are supported by studies using ex-situ generated AgCl nanocubes. The mechanistic factors influencing the size and shape of the NPs formed. We will demonstrate that controlling the NP size can be realized by varying the number of the parameters, one of the most important, which is the reaction temperature. The NP shape is mostly controlled by specific adsorption of capping molecules on the NP surface.

INOR 431

Size and shape controlled syntheses of iron oxide nanoparticles
Olivia R. R Sanchez-Felix1, Kyle E. Donelson1, Bethany Boris1, Nina V Kuchkina2, Zinaida B Shifrina2, Lyudmila M Bronstein1,3, lybronst@indiana.edu. (1) Department of Chemistry, Indiana University, Bloomington, IN 47405, United States (2) A.N.Newskiyov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russian Federation (3) Faculty of Science, Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

Here we will discuss formation of iron oxide nanoparticles (NPs) prepared by thermal decomposition of iron carboxylates or iron acetylacetonate and the parameters influencing the size and shape of the NPs formed. We will demonstrate that controlling the NP size can be realized by varying the number of the parameters, one of the most important, which is the reaction temperature. The NP shape is mostly controlled by specific adsorption of capping molecules on the NP surface.

INOR 432

Light activated tandem catalysis driven by multicomponent nanomaterials
Marc R Knecht1, knecht@miami.edu, Elsayed M Zahran1, Nicholas M Bedford1,2, Michelle A Nguyen1, Yao-Jen Chang1, Beth S Guiton3,4, Rajesh R Naik1, Leonidas G Bachas1. (1) Department of Chemistry, University of Miami, Coral Gables, Florida 33146, United States (2) Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, United States (3) Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, United States (4) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Transitioning current catalytic processes toward more sustainable methods is critically important in light of the global energy state. Photocatalytic reactions that employ sunlight represent intriguing approaches to address this situation; however, most catalytic processes employed today are not designed for light-activated reactivity. By transitioning these reactions toward light activated systems, sustainable catalytic processes could be developed that could persist for extensive future use. In this regard, we have employed Cu2O@Pd core@shell structure for sustainable tandem catalytic activity to achieve these goals. In this unique composite structure, Cu2O cubic materials were generated, wherein zerovalent Pd catalytic nanodomains were galvanically deposited onto the oxide surface. In this configuration, a tandem catalytic structure was realized, where the Cu2O component was responsible for water reduction to generate H2 in situ for catalytic use at the Pd surface. To study this process, the reductive hydrodechlorination of polychlorinated biphenyls (PCBs) was examined, where high reactivity rates were observed using the light activated system. By combining two materials of distinctly different compositions, tandem catalytic capabilities were achieved that resulted in the transition of light-activated reactivity toward systems not traditionally driven by such energy sources.

INOR 433

Photoinduced structural rearrangements of kinetic phase Cu(TCNQ) crystals visualized with ultrafast electron microscopy
David J. Flannigan, flan0076@umn.edu. Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

Effects of photoinduced charge-transfer on nanoscale crystal morphologies due to the resulting structural rearrangements can be directly visualized in space and time with ultrafast transmission electron microscopy. This is accomplished by operating an appropriately-modified transmission electron microscope in a pump-probe fashion analogous to all-optical ultrafast spectroscopic experiments. In this way, reversible structural motions occurring within a few hundred femtoseconds can be directly visualized with high spatial resolution. For structural dynamics that are irreversible on experimental time scales, the single-shot mode of operation is used. Here, I will discuss how transient structures were imaged following photoinduced electron transfer in single crystals of the kinetic phase (i.e., Phase I) of copper-tetracyanoquinodimethane [Cu(TCNQ)], and how the morphological changes in the low and high laser-fluence regimes were elucidated using both the stroboscopic and single-pulse modes of the microscope. Two distinct but mechanistically-linked dynamic processes having different rates are observed. The first is a fast, initial structural rearrangement due to photoinduced charge-transfer resulting in some Cu+ sites being reduced to neutral Cu. This is followed by a second slower step comprised of the growth of metallic Cu.
nanocrystals driven by minimization of surface energy. The overall mechanism involves photoinduced electron transfer from TCO/m anion-radicals to Cu\(^{2+}\), subseulptive nanoscale morphological changes, and thermally-driven growth of discrete Cu nanocrystals dispersed in an amorphous organic matrix.

**INOR 434**
Cyano star wars episode I: A star is born
Amar Flood, aflood@indiana.edu. Department of Chemistry, Indiana University, United States

Just a moment ago in a river that you wish was far, far away, there is an overabundance of nitrate fertilizer from pastoral run-off that is damaging the aquatic flora and fauna. This story repeats in many areas of chemistry and biology where anions play crucial roles. For these reasons, we and other supramolecular chemists are forming an alliance to help combat some of these effects by creating electropositive binding pockets in which to capture negatively charged ions. We will present the latest efforts in this crusade where a powerful star-shaped molecule is created that displays unrivalled abilities to bind anions. The noncovalent forces are strong in this one, yet they originate from unexpectedly humble beginnings – forged through a Knövenagel condensation, a CH group is activated and, when trained inside a carefully constructed pentagon, can display competent hydrogen bonds. The results of these and other studies will be told.

**INOR 435**
Understanding the role of surface diffusion in controlling the growth pathway of citrate-free silver nanoplates
Dong Qin, dong.qin@mse.gatech.edu. Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

In this talk, we will elucidate the role of surface diffusion in controlling the evolution of Ag nanoparticle seeds into new shapes or morphologies. When citrate-free Ag nanoparticles were employed as the seeds, the newly formed Ag atoms were preferentially deposited on the top and bottom \(111\) facets, followed by two growth pathways determined by surface diffusion. We discovered that the nanoplates were transformed into bipyramids through vertical growth when surface diffusion was less significant in moving the deposited atoms to side faces at a high injection rate for AgNO\(_3\) or a low reaction temperature of 0 °C. In contrast, larger hexagonal plates were formed through lateral growth when surface diffusion was in dominance at room temperature with a slow injection rate for AgNO\(_3\). We will also validate the role of facet capping of \(111\) on the shape evolution of nanoplates by titrating different amounts of citrate into the reaction solution. As long as citrate had limited coverage on \(111\) facets, the Ag atoms would be preferentially deposited on \(111\) rather than \(100\) facets, leading to the formation of bipyramids when the growth was dominated by atom deposition over surface diffusion. However, in the presence of adequate citrate, atom deposition occurred on the \(100\) side facets, leading to the formation of larger triangular plates. We believe that a comprehensive understanding on the role of surface diffusion represents a leap towards the rational design of seeded growth with exquisite controls to generate nanocrystals with new morphologies.

**INOR 436**
Ultrasonic hot spots in polymeric composites
Kenneth S Suslick, kssuslick@illinois.edu, Sizhu You, Ming-Wei Chen, Dana D Diott. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Creation of localized heating in complex solids at a specific location and with a controlled intensity is of great importance in pyrotechnics and explosives’ handling, as well as material processing and fabrication in general. Our predictive models of such events (e.g., impact initiation of explosions), however, are poor and our control of such events on a macroscale with typical energy sources (such as laser, electric current or shockwaves) are either non-selectively destructive or limited to specific material compositions. On the other hand, ultrasound is a relatively weak delocalized energy, but one that can induce dramatic thermo-mechanical effect if localized in a small region. Examples include acoustic cavitation in liquids, ultrasonic welding with the help of energy guides in solids, and clinical hyperthermia by a focused ultrasonic beam. How ultrasound can induce localized heating at the interior of bulk solids, however, remains barely explored. In this work, we have generated well-controlled hot spots in polymeric composites using ultrasound and study their dynamics with a thermal imaging microscope. We observe that ultrasonic energy spontaneously and exclusively concentrates on delaminating interfaces in polymer composites, with local heating up to 30,000 K/s on sub-mm scale, while the rest of the material remains cool and undisturbed. Hot spot locations can be precisely controlled by manipulations of interfacial adhesion, and hot spot intensity can be controlled by ultrasonic energy input. Insights from this work provide interesting possibilities for a new degree of control over the thermal events as well as chemical reactions inside composite solid structures.

**INOR 437**
Copper-oxygen intermediates relevant to metalloenzymes and other oxidation catalysts
William Tolman, wtolman@umn.edu. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States

Inspired by the unusual active site structures and reactivities exhibited by copper enzymes, we seek to prepare and characterize synthetic complexes in order to test hypotheses developed to explain the novel functions of the biological sites. Mono- and dicopper hydroxo complexes at high oxidation states are proposed intermediates in oxidation catalysis by copper enzymes and other catalysts, and thus are key targets for synthesis and characterization. Recently, we identified a Cu(III)-OH complex supported by a pyridine(dicarboxamide) ligand, and found that it performed hydrogen atom abstraction reactions at high rates. In this lecture, progress toward understanding the basis for these high rates will be presented. Motivated by lessons learned from these studies, new research has focused on novel oxidized dicopper species supported by binucleating ligands with pyridine(dicarboxamide) donors. Preliminary data in support of the formulations of these species will be discussed.

**INOR 438**
Tuning of the first- and second-coordination spheres in nonheme iron complexes
David P. Goldberg, dpg@jhu.edu, Alison C. McQuilken, Sumit Sahu, Leland R. Widger. Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, United States

Our recent results on determining the influence of first- and second-coordination sphere elements on the structures, spectroscopic properties, and reactivity of nonheme iron centers will be described. Nonheme iron centers are of interest because of their key roles in a wide range of metalloenzymes, as well as their potential for use in catalytic applications. Ligand design has been employed to include novel heteroatoms, such as sulfur, in the first-coordination sphere of iron-oxo and iron-peroxo species, which are key intermediates in nonheme Fe oxygenase chemistry. The discrimination of some
of these species in giving intra- versus intermolecular sulfur oxidation will be discussed, including an iron(II)-thiolate complex that reacts with O₂ to give an iron(III)-sulfinate complex, and a metastable Fe(IV)(O) complex that shows high selectivity for inter- versus intramolecular sulfoxidation. In the second-coordinate sphere, substrate positioning leads to rapid arene hydroxylation, providing concrete evidence for a theoretical description regarding Fe(IV)(O) reactivity. The effects of proximal H-bond donors on Fe(IV)(O) and Fe(OOR) species will also be described.

INOR 439
Shellfish are inorganic chemists: Characterization and synthetic mimics of marine biological adhesives
Erik Alberts¹, Courtney Jenkins¹, Heather Meredith¹, Michael Johnston², Jessica Roman¹, Chelsey Del Gross¹, Michael North¹, Natalie Hamada¹, Jonathan Wilker¹,², wilker@purdue.edu. (1) Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States (2) School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States

Congratulations to Steve Lippard upon receipt of the Priestley Medal! Oxygen was discovered by Joseph Priestley and Steve has made a great career from studying, amongst many things, how oxygen reacts with iron in biology. Our laboratory is trying to understand the nature of marine bioadhesion. How do organisms such as mussels and oysters stick themselves to rocks at the beach? Sure enough, we are finding that iron-oxygen chemistry is in there. This presentation will include the latest findings on characterization and synthetic mimics of these intriguing biological materials. Work with oysters is showing that adhesion is brought about by a partitioning of the organic and inorganic components within cement. Polymer mimics of these materials are yielding adhesives with performance stronger than commercial Super Glue and also quite substantial underwater bonding.

INOR 440
DNA signaling among proteins with iron-sulfur clusters
Jacqueline K Barton, jkbarton@caltech.edu. Department of Chemistry, California Institute of Technology, Pasadena, CA 91125, United States

DNA-mediated charge transport can yield redox chemistry over long molecular distances in a reaction that reports on the integrity of the intervening base stack. Moreover, increasingly, proteins involved in DNA replication and repair have been found to contain 4Fe-4S clusters, common redox cofactors in biology. DNA-modified electrodes have been utilized to determine redox potentials for these metalloproteins bound to DNA; this electrochemistry establishes the ability of the metalloproteins to carry out redox chemistry at physiological potentials in the DNA-bound form. Studies are also described to characterize how these DNA-binding proteins containing 4Fe-4S clusters may utilize DNA charge transport chemistry for long range redox signaling.

INOR 441
Metalproteins inhibitors: Obstacles and opportunities
Seth M. Cohen, scohen@ucsd.edu. Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0358, United States

Metalloproteins represent a rich field of targets for therapeutic development against a host of human diseases. However, perceptions of low target specificity and concerns over interactions with metal ion homeostasis have slowed progress against these abundant targets. Furthermore, strategies by which to inhibit these enzymes have been relatively limited, with only a handful of key pharmacophores investigated in detail. This presentation will highlight our efforts to evaluate these perceptions and provide new prospects for developing metalloprotein inhibitors. In particular, the influence of the metalloprotein active site on ligand binding will be examined. Perhaps not unexpectedly, the binding of simple chelators to metalloprotein active sites can vary substantially from that predicted from small molecule models of these active sites. The implications of these findings in the context of drug design and development will be discussed.

INOR 442
Chemical probes put tyrosine phosphatase activity in the spotlight
Amy M Barrios¹, amy.barrios@utah.edu, Nunzio Bottini², Stephanie M Stanford², Rhushikesh A Kulkarni¹. (1) Department of Medicinal Chemistry, University of Utah, Salt Lake City, Utah 84112, United States (2) Division of Cellular Biology, La Jolla Institute of Allergy and Immunology, La Jolla, CA 92037, United States

The protein tyrosine phosphatases (PTPs) are intriguing therapeutic targets for the treatment of human diseases ranging from autoimmunity to cancer, but PTP-targeted drugs have not yet found broad clinical use. Among the challenges inherent in developing PTP-targeted therapies is an incomplete understanding of the biological roles played by these critical cellular signaling enzymes and the difficulty of developing inhibitors selective for one member of this highly homologous enzyme family. To address these challenges, we are working to develop a “molecular toolkit” of PTP-targeted chemical probes. Fluorogenic peptide substrates have proven useful in visualizing enzyme activity both in vitro and in cells. Mechanism-based inhibitors have been identified and optimized to selectively inhibit PTP activity. We have demonstrated that it is possible to develop PTP-selective substrates and inhibitors for use in living cells by targeting non-conserved regions of the enzyme of interest. These findings highlight key differences among these homologous enzymes that can be exploited in the development of therapeutic lead compounds.

INOR 443
Molecular imaging approaches to discovery and understanding of inorganic chemistry in the brain
Christopher J Chang, chrischang@berkeley.edu. Departments of Chemistry and Molecular and Cell Biology and HHMI, University of California, Berkeley, Berkeley, CA 94720, United States

The brain and central nervous system requires among the highest levels of metals in the body, including transition metals like copper and iron, but misregulation of these same metal pools is a major player in aging and neurodegeneration. We are creating and applying new chemical tools to study metals and small-molecule signal/stress agents in neural systems by molecular imaging. This talk will present our latest results on developing new molecular imaging agents and their use in live cell, tissue, and animal settings.

INOR 444
Template-directed synthesis and supramolecular chemistry of porphyrin nanorings
Harry L. Anderson, harry.anderson@chem.ox.ac.uk. Department of Chemistry, University of Oxford, Oxford, United Kingdom

This lecture will discuss the use of templates for building large pi-conjugated macrocyles, and will show that it is possible to go beyond simple 1:1 template-product stoichiometries to direct the synthesis of very large nanorings using small templates. For example the Vernier principle enables the figure-of-eight complex shown below (Figure 1) to be prepared directly from a porphyrin tetramer.
We have used this strategy to synthesize covalent nanorings consisting of up to 50 porphyrin units. These molecules are well into the size-range of proteins. They form complexes which display protein-like cooperative denaturation, and which mimic some aspects of the photophysical behavior of light-harvesting chlorophyll arrays.

INOR 445

Triazole-pyridine diad: Yin-Yang in coordination-driven self-assembly

Nan Wu1, Caroline Melan2, Olivier Fleischel2, Huan Guo3, Kristina Stevenson4, Fatemah Habib5, Muralee Murugesu5, Nicholas Mosey4, Anne Petitjean4, anne.petitjean@chem.queensu.ca. (1) Faculty of Medicine, University of Toronto, Canada (2) Laboratoire Moltech Anjou, Université d’Angers, France (3) BASF, Ludwigshafen, Germany (4) Department of Chemistry, Queen’s University, Kingston, ON, Canada (5) Department of Chemistry, University of Ottawa, Ottawa, ON, Canada

When combined together, the strongly binding pyridine group and the weaker 1,2,3-triazole donor form a chelate with valuable properties. From electrochemistry to magnetism, the pyridyl/triazole diad offers a highly tunable, easily functionalized building block for supramolecular self-assembled materials. In this presentation, we illustrate the richness of the pyridyl/triazole chelate to coordinate ions such as copper(I), iron(II), nickel(II) and zinc (II), and explore the properties of multimetallic architectures.

INOR 446

Supramolecular chemistry of anions with pi-acidic rings: Organic, inorganic, and biological studies

Kim R. Dunbar, dturner@mail.chem.tamu.edu. Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

Self-assembly of metal ion complexes harnesses the power of directional bonds between metals and organic molecules to promote the formation of metallosupramolecular architectures, often endowed with unusual properties. The focus of this project is to gain a deeper understanding of the role and strength of a newly recognized player in supramolecular chemistry, namely anion interactions with aromatic organic molecules, recently dubbed anion-π interactions. Our approach is to use nitrogen-containing molecules with electrophilic tetrazine rings. These ligands produce unusual molecular pyramids that are highly stable in solution but which exhibit remarkable flexibility that allows them to be easily converted to other ring sizes, reactivity that is governed by the anion. The importance of these results is that chemical reactions triggered by the capture or release of anions can be used to alter the physical and chemical properties of the compounds, a concept that has important implications on the fundamental reactivity of molecules based on weak interactions. Collective data from solid-state, solution, gas phase and computational studies are being used to assess the strength of anion-π forces and to assist in the prediction of structures. One application of this knowledge is the design of large polyhedral molecules by using the living-membered ring molecules as building blocks. Another forefront topic that is being tackled is how enzymes may employ anion-π interactions to govern the stability/reactivity of an active site. This concept is being applied to understanding the inhibition of malate synthase for improved tuberculosis drugs.


INOR 447

DNA-mediated assembly of transition metals into 2D and 3D-structures

Hanadi Sleiman, hanadi.sleiman@mcgill.ca. Department of Chemistry, McGill University, Montreal, QC H3A0B8, Canada

We report the specific incorporation of metals into DNA strands, in such a way that the metal-ligand environment is in close contact with the DNA base-pair stack. This method results in highly stable metallated DNA junctions, in efficient chirality transfer from DNA to the metal environment and in DNA-mediated charge transport probed by the transition metal. We use this approach to construct stimuli-responsive metal-DNA cages and nanotubes. These 3D-hosts can encapsulate guest materials, such as gold nanoparticles and small molecules, and then selectively release them with externally added molecules. We examine the potential of DNA to organize different transition metals in precise locations within a nanostructure. With this in mind, we report the DNA-templated creation of three different ligand environments, each highly selective towards a specific transition metal ion, and able to induce ‘error-correction’ when the incorrect metal binds to it. Finally, we describe the efficient delivery of these responsive DNA cages and nanotubes into mammalian cells and our efforts to chemically replicate DNA-metal junctions.

INOR 448

Redox reactions and host-guest chemistry of macrocyclic metal-organic complexes

Andrew W. Maverick, maverick@isu.edu, Uttam R. Pokharel, Frank R. Franczek, Jonathan S. Casey, Siddieg O. Elsiddieg, Takaia M. Wheat. Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States

Multifunctional β-diketone and pyridyltriazole ligands can be used to assemble cyclic metal-organic molecules that bind and react with guest molecules. β-diketones are flexible when they bind to metal ions, so the supramolecular structures that result are not always the ones predicted on the basis of metal and ligand geometry. Pyridyltriazoles and related ligands may be less flexible in their binding, and they are also much better at stabilizing multiple metal oxidation states.

We have studied two types of supramolecular hosts. 2D and 3D molecules can be assembled from bis- and tris(β-diketones), and they bind guests via σ and π interactions. Bis(pyridyltriazoles) react with copper(II) to make dimers with metal coordination numbers of 4, 5, and 6. The copper(II) complex of β-diketone and pyridyltriazole ligands can be used to assemble cyclic metal-organic molecules that bind and react with guest molecules. β-diketones are flexible when they bind to metal ions, so the supramolecular structures that result are not always the ones predicted on the basis of metal and ligand geometry. Pyridyltriazoles and related ligands may be less flexible in their binding, and they are also much better at stabilizing multiple metal oxidation states.

Treatment with H+ removes the bound oxalate as H₂CO₃, completing a cycle for CO₂ reduction under mild conditions. The properties of systems with related multidentate N donor ligands will also be discussed.
INOR 449
From frameworks to spheres: Exploiting the coordination bond

Neil R. Champness, Neil.Champness@nottingham.ac.uk, School of Chemistry, University of Nottingham, Nottingham, United Kingdom

Non-covalent directional intermolecular interactions provide a pre-determined recognition pathway which has been widely exploited in supramolecular chemistry to form functional nanostructures. Our results of using coordination bonds to enable the directed assembly of extended nanostructures will be presented. The lecture will focus on the development of coordination polymers and metal-organic frameworks (MOFs) and how similar principles can be used to construct spherical coordination architectures.

The lecture will illustrate the use of MOFs to host photoactive moieties modifying the properties of the incorporated species; the development of nanoscale spheres using coordination bonds; and, lastly, the organisation of magnetic molecules on surfaces.


INOR 450
Use of photocrystallography to capture critical intermediates in HX energy conversion photocycles

David C. Powers1, Shao-Liang Zheng1, Bryce L. Anderson1, Yu-Sheng Chen2, Daniel G. Nocera1, dnocera@fas.harvard.edu. (1) Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States (2) Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60439, United States

Direct observation of the geometries of excited states and metastable intermediates can be accomplished by monitoring photochemical reactions in real time by X-ray diffraction. We are applying this technique to capture critical intermediates in energy conversion processes. Of current focus are those intermediates that promote HX splitting, which is limited by the efficiency of M–X bond activation and X–X elimination. Using X-ray photocystallography, we have observed that a M(μ-X)M–X bridging intermediate is critical to halogen elimination from binuclear metal cores. With this result as a guidepost, the time-resolved kinetics for M–X activation and X elimination may be unraveled. The combination of time-resolved X-ray and kinetics experiments provides a powerful platform from which to delineate energy conversion pathways.

INOR 451
Recent advances in olefin polymerization catalysis

James C Stevens, jcestevens@ dow.com, Edmund M Carnahan/Core R&D, The Dow Chemical Company, Freeport, TX 77541, United States

Advances in polyolefin catalysis continue to allow for greater and greater control of polymer microstructures at a molecular level. In recent years, the advent of metallocene catalysts has allowed for more homogeneous comonomer incorporation and highly-processable resins by controlled introduction of branches. More recently several groups have focused on methods by which catalysts can work collaboratively to produce polymers with designed microstructures. This work describes how such tandem catalysis can be used to construct polyethylene chains with controlled numbers and distributions of branching across the polymer backbones. The catalysts to manipulate the polymer microstructure as well as analytical evidence for these tailored polymer molecules will be presented in detail. Finally, we will reveal how such precise control of polyolefin catalysis can result directly in modifications of bulk polymer properties such as the controlled increase in melt strength for polyethylene.

INOR 452
Well-defined chromium silicates as efficient ethylene polymerization catalysts in the absence of co-catalyst: A clue in the Phillips catalyst

Matthew P. Conley1, Murielle Delley1, Georges Siddiqui1, Giuseppe Lapadula1, Sébastien Norsic1, Vincent Monteil1, Olga V. Safonova1, Christophe Copéret2, copere t@ethz.ch. (1) Department of Chemistry, ETH Zürich, Zurich, Zurich 8093, Switzerland (2) C2P2, CPE Lyon, Villeurbanne, France

The Phillips catalyst, which contains chromium dispersed on silica, accounts for 40 – 50 % of global high density polyethylene (PE) production. The active catalytic sites of the Phillips catalyst remains unknown, though X-ray Absorption Spectroscopy shows that Cr(II) species are formed, inferring that they are responsible for catalysis. We grafted [Cr(OSi(OtBu)3]2, and thermally removed the organic ligands to generate well-defined silica supported dimeric Cr(II) species, which are converted into Cr(III) silicates by treatment with N2O according to XAS and model molecular studies. While the Cr(II) species is hardly active in ethylene polymerization, the Cr(III) species exhibits activities exceeding those of the Phillips catalyst, though the PE produced by these two materials is very similar in terms of molecular weight and dispersity indicating similar active sites. The mononuclear Cr(III) analogues can be prepared from [Cr(OSi(OtBu)3]2 via the same approach, and it also displays high activity in the polymerization of ethylene. These results lay the foundation to design new supported Cr(III) ethylene polymerization catalysts

INOR 453
Advances in electrolytes for lithium ion batteries: A mechanistic understanding

Brett L Lucht, blucht@chm.uri.edu, Chemistry, University of Rhode Island, Kingston, RI 02881, United States

The investigation of surface reactions of electrolytes with the electrodes of Lithium Ion Batteries (LIB) for Electric Vehicle (EV) applications will be presented. The beginning portion of the presentation will focus on three novel techniques which have been enabled by the use of Binder Free graphite anodes. The first is a novel method which allows straightforward analysis of the anode Solid Electrolyte Interphase (SEI) by Transmission Electron Microscopy with Energy Dispersive X-ray Spectroscopy. The second, utilizes Multi-Nuclear Magnetic Resonance spectroscopy of the D2O extracts of the cycled anodes. Finally, IR spectroscopy is utilized to assist with the characterization of the electrolyte solution structure. This unique combination of techniques has allow us to develop significant new insight into the anode SEI formation mechanisms and structure.

The latter portion of the presentation with cover a method for improving the energy density of lithium ion batteries by increasing the working potentials of positive electrode by employing lithium nickel manganese spinel LiNi0.5Mn1.5O4 as the active material. The failure mechanism of graphite /LiNi0.5Mn1.5O4
cells cycled at 25 °C and 55 °C (1.2 M LiPF$_6$ in 3:7 EC/EMC) have been analyzed by electrochemical methods and ex-situ surface analysis of the electrodes. We are using this mechanistic information about capacity fade in graphite/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cells to develop novel additives to improve the performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cycled to high voltage (4.9 V vs Li). The details of our experimental results and our mechanistic interpretation will be presented.

INOR 454

Lithium carbenoids in bond activation reactions

Viktoria H. Gessner, vgessner@uni-wuerzburg.de, University of Wuerzburg, Institute of Inorganic Chemistry, Wuerzburg, - 97074, Germany

For many years, the activation of small molecules had been a research field limited to transition metal complexes. However, the past decades have revealed several examples of non-metallic systems also applicable in bond activation reactions. Without doubt, one of the most prominent examples are singlet carbines, which have shown to activate a variety of small molecules amongst others dihydrogen, P$_2$O$_5$ ammonia. Compared with carbines, main group metal carbenoids have almost been neglected and are still almost exclusively applied in cyclopropanation and homologation reactions. We present the use of lithium carbenoids in bond activation and formation reactions, such as the B-H bond splitting in Lewis base adducts of parent borane.[1,2]


INOR 455

Controlling the properties of silicon and germanium nanocrystals through surface chemistry

Nathan R Neale, nathan.neale@nrel.gov, Chemical and Materials Sciences Center, National Renewable Energy Laboratory, Golden, CO 80401, United States

The tremendous recent progress in the methods for preparing thin films of semiconductor nanocrystals (NCs) has led to a flurry of research employing NC films as the photoactive layer in solar photoconversion, photodetectors, LEDs, and related technologies. The majority of the research has focused on metal chalcogenide NCs owing to the ease of performing ligand exchange reactions at the NC surface. Our group and others have been exploring methods for preparing group IV NCs, and in particular Si and Ge NCs, as potential earth abundant and nontoxic infrared absorbing and emitting alternatives to metal chalcogenide or III-V quantum dots. Group IV NCs produced from either solution approaches or vapor-phase strategies are typically functionalized via hydrosilylation (or hydrogermylation) chemistry to prepare colloidal NCs. But the insulating alkyl surface ligands that lead to solution processibility and stability also give rise to poor film conductivity, mitigating their potential usefulness in optoelectronic applications. We will discuss recent results on studies of and reactions at group IV NC surfaces aimed at both tuning their fundamental photophysical properties and affording electronically coupled NC thin films.

INOR 456

Why do weaker metal-carbon bonds lead to more stable complexes: What's going on?

William D Jones, jones@chem.rochester.edu, Meagan E Evans, Yunzhe Jiao, Gyeongshin Chin, James Morris, Department of Chemistry, University of Rochester, Rochester, NY 14627, United States

A series of kinetic measurements of Tp$^*$Rh(L)(R)H complexes (where L = CNeopentyl, PMesa, P(O)Me$_3$; R = alkyl, aryl, vinyl, benzyl, allyl, and CH$_2$X (X = CN, SiMe$_3$, CH$_2$C(O)OH, and others; Tp$^*$ = tris(3,5-dimethylpyrazolyl)borate) have been used to determine relative metal-carbon bond energies in these compounds. A thermodynamic analysis allows for the extraction of an increase in bond energy for R groups in which the C=C or C≡C bond is strong and there is a H bond in Le system. We have developed a simple empirically derived model that quantitatively accounts for this thermodynamic measurement, and we discuss the relationship between bond strength and the increase in bond energy. The model may be expanded to include the effect of other ligands that lead to solution processibility.

INOR 457

Controlled deposition of metal ions on the surface of TiO$_2$ nanorods

Choumin Balasanthiran$^1$, Wonjun Kang$^1$, Charles S. Spanjers$^2$, Robert M. Rioux$^2$, James D. Hoeftelmeyer$^2$, jhoeftelm@usd.edu. (1) Department of Chemistry, University of South Dakota, Vermillion, SD 57069, United States (2) Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, United States

We have developed new methods to attach metal ions to the surface of TiO$_2$ nanocrystals. We utilize the gram-scale preparation of TiO$_2$ nanorods reported by Hyeon, therefore, the metallated nanorods can be prepared in large quantities. We demonstrate attachment of first-row transition metal ions, lanthanide ions, and combinations of metal ions. TiO$_2$ nanorods can be metallated with quantitative precision, and we demonstrate titration of the TiO$_2$ nanorod surface with metal ions. The metallated TiO$_2$ nanorods were characterized with TEM, powder XRD, UV-visible, XAS, XPS, ICP-AES elemental analysis, and EDS spectroscopy. With the ultimate goal of creating optimized photocatalysts for solar energy utilization, we present the latest findings for the photocatalytic properties of these surface modified TiO$_2$ nanocrystals.

INOR 458

Synthesis of silyl-hydride compounds of molybdenum and tungsten via oxidative addition of Si–H bonds to electron-rich metal centers

Ashley Zueck, Gerard Parkin, parkin@columbia.edu, Chemistry, Columbia University, New York, New York 10027, United States

A series of silyl-hydride compounds of molybdenum and tungsten have been obtained via oxidative addition of Si–H bonds to electron-rich trimethylphosphine complexes of these metals. For example, Mo(PMe$_3$)$_5$(SiH)$_3$H$_2$ may be obtained from the reaction of SiH$_4$ with Mo(PMe$_3$)$_5$. Ph$_3$SiH$_3$, Ph$_3$SiH$_2$ and Ph$_3$SiH also react with Mo(PMe$_3$)$_5$, but the products obtained depend critically on the nature of the silane.

INOR 459

New advances in P(l) chemistry

Francois Mathey, fmathey@ntu.edu.sg, Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore, Singapore

The use of transient terminal phosphinidene complexes [RP-W(CO)$_3$] as synthetic tools in organophosphorus chemistry is continuing to grow. As recent examples, we will describe their insertion into the B-H bonds of H$_2$B-L (L = NR$_3$, PR$_3$) and the building of P-Ar bonds through their reaction with the organoborates of the Suzuki cross-coupling reaction. Another related procedure derives from the copper-catalysed transformation of [CICH$_2$P-W(CO)$_3$] into the stable but highly reactive (CH$_2$=P)[Cl(W(CO)$_3$)]. This highly reactive P=C double bond reacts with furan to afford, after cleavage of the oxygen bridge by BB$_3$, the parent Z-phenylphosphine. The reactivity and coordination chemistry of this new phosphine will be described.
References:
3) Mao, Y.; Lim, K. M. H.; Li Y.; Ganguly, R.; Mathey, F. 2013, 32, 3562.

INOR 460
Unraveling the mechanism of the ruthenium assisted hydrolysis of white phosphorus
Maurizio Peruzzini1, maurizio.peruzzini@iccom.cnr.it, Piero Stopponi2, (1) ICCOM CNR, Sesto Fiorentino, Firenze 50019, Italy (2) Department of Chemistry, University of Florence, Sesto Fiorentino, Firenze 50019, Italy

White Phosphorus is largely used to produce organophosphorus compounds which are key materials for several industrial applications. The manufacturing of these useful compounds is still based on an obsolete and energy intensive technology, i.e. the environmentally poor route encompassing the direct chlorination of P2 to PCl3 generally followed by PCl3 alkoxydation. As a result, esters of the different oxyacids are produced.

Any implementation of the above process which directly (and possibly catalytically) transforms white phosphorus into valuable organophosphorus compounds is therefore worth pursuing. A fundamental step towards this goal is the unraveling of the elementary steps which bring about the formation of P-heteroatom bonds, such as P-H (P2-hydrogenation) and P-O bond (P2-alkoxydation) occurring in the coordination sphere of active transition metal species.

The lecture will focus on the surprising reactivity of Ru-coordinated P2 with water which results in the stepwise formation of PH3, H3PO3, H2PO2 and the elusive oxide PH3O. Hydroxopolyporphine chains including four, three or two P-atoms, may be also easily achieved together with rare examples of polyphosphorus hydrides which have been trapped as a bridging ligand between two L2Ru moieties.

Some of them, i.e. P3H5, may be considered as the initial step on the way of the long searched hydrogenation of elemental phosphorus.

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INOR 461
Beyond amino groups: Pushing boundaries with ylidic π-donor substituents
C. Adam Dyker, cadyker@unb.ca, Grant D. Charlton, Samuel S. Hanson. Department of Chemistry, University of New Brunswick, Fredericton, NB E3B 5A3, Canada

This contribution will outline some recent achievements made possible by replacing classically-used amino groups with more strongly π-donating ylidic substituents, with a particular focus on the iminophosphorano substituent (R=P=N). By placing them in conjugation with an appropriate π-system, these substituents can lead to molecular properties that are not accessible with amino groups. As examples, it will be demonstrated that ylidic substituents (Y) impart increased nucleophilicity to pyridine, leading to some of the most active acylation catalysts, and that bis-2-pyridyldienes featuring ylidic functionalities represent the most easily oxidized neutral organic compounds. These latter compounds have potential applications as homogeneous organic reducing agents.

INOR 462
Synthesis of complexes with protic NHC ligands by oxidative addition of neutral azoles or N-alkylazoles to transition metals
F. Ekkehardt Hahn, tehahn@uni-muenster.de. Department of Chemistry, University of Münster, Muenster, Germany

The majority of NHC complexes have been prepared from cyclic azolium precursors which upon C2 deprotonation yield the free NHC which then coordinates to a given metal center. We found that neutral azoles like N-substituted-2-chlorobenzimidazole react with NH2, Pd or Pt under oxidative addition to give complexes with an anionic NHC ligand featuring an unsubstituted ring-nitrogen atom. Protonation of such ligands yields NHC ligands with an NH,NMe-substitution pattern as in 2 and reaction with dihydrogen leads to a heterolytic cleavage of H2 and complex 3. This oxidative addition can also be utilized to generate carbene complexes by C-metallation of biomolecules like 8-bromocaffeine or 6-bromoacetanilide.

INOR 463
Understanding catalytic olefin dimerisation
Antonis M Messinis1, William RH Wright1, Andrei S Batsanov1, Martin J Hanton2, Philip W Dyer1, p.w.dyer@durham.ac.uk, (1) Department of Chemistry, Durham University, Durham, United Kingdom (2) Sasol Technology (UK), St. Andrews, Fife KY16 9ST, United Kingdom

Metal-catalysed olefin dimerisation is used widely for enhancing low carbon number product streams and for the manufacture of important industrial commodity feedstocks. In this arena, tungsten-based initiators have enjoyed particular success, offering good selectivity and activity. Such systems are typically prepared in situ through reaction of WCl6 with ArNH2, followed by treatment with an alkylaluminium activator, something proposed to generate a catalytically-active tungsten imido-bearing moiety. A key challenge in understanding both the dimerisation mechanism and the catalytic selectivity is to establish the precise role of the alkylaluminium chloride activator. Here, we report our studies of the reactions of various well-defined tungsten imido complexes with a range of alkyl aluminium reagents. Results exemplifying the influence of the resulting Al-containing components (e.g. 1), and the nature of the imido substituent, on subsequent reactions with olefins will be reported. Careful analysis of the post-catalysis organic products is used to probe indirectly both the tungsten oxidation state and catalytic mechanism.
INOR 464
From metallylene and metalllylones to a new generation of catalysts
Matthias Driess, matthias.driess@tu-berlin.de, Department of Chemistry, Technische Universität Berlin, Berlin, Germany

The chemistry of stable metallylene and metalllylones of the group 14 elements receives high interest because of their unique reactivity for the activation of important small molecules. Very recently, we developed two new types of zwitterionic metallylene 1 and metalllylones 2 which show an unprecedented reactivity pattern with respect to small molecule activation in comparison to other low valent silicon and germanium compounds.

Furthermore, the remarkably rich reactivity pattern of 1, 2 and Roesky's chloro silylene LSiCl (L = amidinate) enabled also the synthesis of the first silicon(II)-based pincer arene ligands 3 and 4 which can be used as a new generation of steering ligands in homogeneous catalysis. In my talk I wish to discuss selected features on the reactivity of 1 - 4 and in particular their use in catalytic transformations.

INOR 465
Discovery, benchmarking, characterization and integration of new materials for solar-fuels generators
Carl A Koval, ckoval@caltech.edu, Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA 91125, United States

The Joint Center for Artificial Photosynthesis (JCAP) was established in 2010 as a U.S. Department of Energy (DOE) Energy Innovation Hub. The JCAP mission is to demonstrate a scalable, integrated solar-fuels generator, which uses Earth-abundant elements and (with no wires) robustly produces fuel from the sun 10 times more efficiently than (current) crops. This presentation will describe how JCAP researchers use both directed and high-throughput approaches to discover light absorbers and catalysts for artificial photosynthesis, and how the performance of new materials is compared to known materials using rigorous benchmarking protocols. By using advanced characterization and computational techniques to understand and improve performance, promising materials are assembled into integrated structures that can be reliably produced and incorporated into scalable prototypes.

INOR 466
Photoelectrochemical investigation of solar energy storage via water splitting with metal oxide electrodes
Thomas Hamann, hamann@chemistry.msu.edu, Department of Chemistry, Michigan State University, East Lansing, MI 48824, United States

Hematite has long been considered a potential candidate for photocatalytic water splitting because of its favourable valence band edge, reasonably low band gap, high stability and low cost. Unfortunately, only very poor conversion efficiencies have been achieved, which is generally attributed to a short minority carrier collection length. In principle, the short collection length can be overcome through nanostructuring the electrode. Thin films represent ideal model systems of nanostructured electrodes which allow for detailed mechanistic investigations. We utilize atomic layer deposition (ALD) to make conformal thin film hematite electrodes with controllable thickness for this purpose. Films less than 20 nm thick, however, are plagued by a dead layer near the substrate contact. We found that the dead layer can be alleviated by the incorporation of dopant atoms in the hematite film or by alteration of the contacting substrate. In both cases significantly improved water oxidation efficiency was observed, however the cause of the improvement was distinct. A series of photoelectrochemical and spectroscopic measurements were employed to elucidate the cause of the improved photoactivity of these hematite thin films. This performance enhancement was determined to be a combination of improved bulk properties which improved charge separation and surface properties which improved the water oxidation efficiency. In addition, recent results of the effect of adding water oxidation catalysts to the hematite surface as well as alternative metal oxide films will be presented.

INOR 467
Increasing photocurrent generation by hematite in photoelectrochemical water splitting reactions
Duweii Wang, dwuwang@bc.edu, Department of Chemistry, Boston College, Chestnut Hill, MA 02467, United States

In this talk, we address one of the most important challenges in photoanode research, namely the low photovoltage generated by large band gap semiconductors. The prototypical material we chose to work on was hematite (α-Fe₂O₃) because it is a material with great promise in solar splitting water. A critically important issue that prevents the promise from being realized is the small photovoltage generated by hematite (typically <0.4 V, which is unreasonable given that the band gap of the material is >2.0 eV). By modifying the surface using a recently identified oxygen evolution catalyst (NiFe₂O₄), we measured a photovoltage of 0.61 V. A record-low turn-on voltage of 0.62 V (vs. reversible hydrogen electrode) was observed. When combined with silicon nanowire dual absorbers, the turn-on potential was further reduced to 0.32 V. These data represent the new benchmark for the hematite-based solar water splitting reactions. Most significantly, we understand the working mechanism as a result of greater photovoltage generation but not kinetic overpotential reduction. We present evidence that supports this radical idea.

INOR 468
Efficient solar photoelectrolysis by Mo:BiVO₄ through controlled electron transport
Jason A Seabold, sjason5@gmail.com, Kai Zhu, Nathan R Neale, Chemical and Materials Science Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States

We will present the electron transport properties of intrinsic and Mo-doped BiVO₄ photoanodes. In particular, two techniques are used to study the effect of Mo doping on the electron transport: (1) an analysis of the front/back illumination ratio of incident photon-to-current efficiency and (2) intensity modulated photocurrent spectroscopy. These techniques show that Mo doping drastically improves the diffusion coefficient and the diffusion length is increased from < 10 nm to ca. 300 nm. Based on this knowledge, we will also present the performance of Mo:BiVO₄ photoanodes for photoelectrolysis and the impacts of surface modification with a heterogeneous catalyst on the water oxidation performance. Finally, new strategies to overcome the electron transport limitations in this metal oxide photoabsorber will be discussed.

INOR 469
Solar water splitting: The role of cobalt phosphate in enhancing the photoelectrochemical efficiency of hematite
Photoelectrochemical (PEC) water oxidation using α-Fe$_2$O$_3$ photoanodes is envisioned as a promising strategy for solar fuel production. Deposition of the water oxidation electrocatalyst known as Co-Pi enhances the photon-to-current conversion efficiencies of α-Fe$_2$O$_3$ photoelectrodes by reducing electron-hole recombination near the surface, particularly at cathodic potentials, but the mechanism behind this enhancement remains unclear. One hypothesis suggests that Co-Pi does not participate directly in catalysis, but instead behaves as Schottky barrier, increasing band bending within the α-Fe$_2$O$_3$. Another hypothesis suggests that Co-Pi catalyzes water oxidation at the surface by accepting photogenerated holes and proceeding through the water oxidation catalytic cycle. We will present recent results investigating the photoelectrochemical properties of meso-structured α-Fe$_2$O$_3$ photoanodes interfaced with Co-Pi electrocatalyst. We will describe results from a series of complementary electrochemical, spectroscopic, and microscopic methods that help to elucidate the nature of the enhancement induced by Co-Pi, with particular emphasis on elucidating charge-transfer and recombination processes at the photoelectrode/liquid junction.

INOR 470

Solar energy conversion and hydrogen evolution catalysis using earth-abundant nanomaterials
Song Jin, jinchem.wisc.edu, Matthew S. Faber. Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States

The scale of renewable energy challenge not only calls for highly efficient technologies but also abundant, inexpensive, and robust materials. Nanomaterials can help to mitigate the poor properties of earth-abundant semiconductors to enhance solar energy conversion. I will first discuss a new growth mechanism of one-dimensional (1D) nanowires, in which screw dislocation defects provide the self-perpetuating steps to enable anisotropic crystal growth. Dislocations can further drive the spontaneous formation of nanotubes, 2D plates, and other nanomaterial morphologies for many different materials synthesized via various methods. Our discovery and understanding of the crystal growth theory have enabled the low-cost synthesis of nanomaterials for large scale renewable energy applications. For example, we have developed rational synthetic nanomaterials of earth-abundant semiconductors, such as hematite (α-Fe$_2$O$_3$) and pyrite (FeS$_2$), and investigated their photoelectrochemical (PEC) and photovoltaic (PV) properties. Investigation of the surface of pyrite nanomaterials using electrochemical and transport measurements is shedding critical insights on how to enable pyrite for high performance solar applications. Furthermore, by controlling the nanostructures and polymorphs of two-dimensional (2D) layered MX$_2$ (M = Mo, W; X = S, Se) materials, we have significant enhanced their catalytic activity in hydrogen evolution reaction for PEC water splitting. We will also show that other earth-abundant metal sulfides and their nanostructures are highly efficient hydrogen evolution catalysts.

INOR 471

Nanocrystalline oxynitrides with tunable composition and band gap
Gordana Dukovic, gordana.dukovic@colorado.edu. Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado 80309, United States

In the bulk form, Zn-Ga oxynitrides, solid solutions of GaN and ZnO, are capable of water splitting under visible irradiation. However, the methods used to synthesize these materials lead to polycrystalline particles with low quantum yields of water splitting. Furthermore, the bulk synthesis results in a limited range of compositions and a narrow range of band gap energies. We have developed a synthetic method for single-crystalline oxynitride nanoparticle with a broad range of compositions (ZnO fraction varying from 0.2 to 0.99) and band gaps that range from 2.7 to 2.2 eV. This was accomplished via chemical transformations of oxide nanocrystals. This presentation will focus on our current understanding of the synthesis that lead to nanocrystalline oxynitrides and on our studies of their properties that relate to solar fuel generation.

INOR 472

Immobilization of nature’s catalyst, microperoxidase (MP-11) a large pore metal organic framework.
Anne Marti, am094220@utdallas.edu, Kenneth J Balkus Jr. Chemistry, The University of Texas at Dallas, Richardson, TX 75070, United States

The immobilization of the enzyme, microperoxidase-11 (MP-11) in the pores of the metal organic framework (MOF) STU-1 is under investigation. STU-1, a large pore MOF with a gyroid (G) structure, exhibits permanent porosity and a high surface area, which make it an attractive material for enzyme immobilization. Our group was first to report the immobilization of enzymes in mesoporous molecular sieves and related their catalytic activity of MP-11 will be characterized using UV-VIS, XRD, SEM, and FT-IR.

INOR 473

Directional charge transfer and highly reducing excited states of new dirhodium(II,II) complexes: Potential applications in solar energy conversion
Zhyang Li, zhanyong.li@mail.chem.tamu.edu, Nicholas Leed, Claudia Turro, Kim R Dunbar. (1) Department of Chemistry, Texas A&M University, College Station, Texas 77840, United States (2) Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States

The environmental issues and impending energy crisis arising from the rapid consumption of traditional fossil fuels has led to an upsurge in research aiming at developing clean and renewable energy resources. One simple but effective way of obtaining clean energy is to harvest sunlight for the photocatalytic reduction of H$_2$O to H$_2$. Photocatalysts for water reduction studied to date are typically multicomponent systems that incorporate a redox active electron mediator couple to transfer the electrons from the excited photosensitizer to the photocatalyst where the reduction of H$^+$ into H$_2$ occurs and a sacrificial electron donor to regenerate the oxidized photosensitizer. One of the major drawbacks, however, is poor charge transfer efficiency between the photosensitizer and catalyst. This talk will focus on the design of dinuclear metal complexes that can act as a dual photosensitizer and photocatalyst which serves to eliminate the additional charge transfer process, an approach that can lead to higher efficiencies. The families of dirhodium complexes cis-[Rh$_2$(DTolF)$_2$((L)$_2$)((CH$_3$CN)][BF$_4$]$^-$ and cis-[Rh$_2$(F-form)$_2$((L)$_2$)((CH$_3$CN)][BF$_4$]$^-$ (DTolF = p-ditolylformamidate, F-Form = p-difluorobenzoylformamidinate; L = the chelating dimine ligands dpq (dipyrido[3,2:2',3'-h]quinoloxine), dpdz (dipipyrido[3,2-a:2',3'-c]phenazine) and dppn (benzo[dipipyrido[3,2-a:2',3'-h]quinoloxine) were synthesized and characterized by a variety of techniques including X-ray crystallography and 'H-NMR, infrared and electronic absorption spectroscopies. Aided by computational studies, the excited states of these compounds were investigated by transient absorption spectroscopy, the results of which indicate a short-lived initial singlet excited state arising from ligand to ligand charge transition (LLCT), followed by an intersystem crossing into a relative longer-lived triplet excited state corresponding to a metal centered ('MC) excited state. Investigation of cis-[Rh$_2$(DTolF)$_2$]((CH$_3$CN)][BF$_4$]$^-$ in the presence of H$^+$ confirmed its ability to generate H$_2$ in the absence of external photoreasitors in a mixture of THF/H$_2$O upon irradiation (λ > 450 nm). Further efforts are directed at improving the stability and water solubility.

INOR 474

Cu(II) cross-linked artificial tripeptides with pendant heterofunctional ligands
Meng Zhang, mwz5057@psu.edu, Alexey Silakov, Michael T Green, Mary Elizabeth Williams. Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, United States
Three artificial aminoacylglycerine tripeptides with pendant hydroxyquinoline (hq) and/or bipyridine (bpy) ligands, hq-hq-hq, hq-bpy-hq and bpy-hq-bpy, have been reacted with Cu(II) to form tripeptide duplexes with three Cu(II) coordinative cross-links. NMR spectroscopy, elemental analysis, and mass spectrometry confirmed the identity of products. The stoichiometry of binding was examined using spectrophotometric absorbance titrations; positive cooperativity was observed during the binding and quantified using the Hill equation. Electron paramagnetic resonance data indicated coupling interactions between Cu(II) centers, and the Cu-Cu distance was calculated to be ~5 Å. A negative shift of the reduction potential of [Cu(bpy)]^{2+} was observed in the cyclic voltammograms of [Cu(bpy)]^{2+} and [Cu(bpy)]^{3+} compared to the Cu(II) bpy monomer duplex. We hypothesize that it is due to the geometry change in reduced [Cu(bpy)]^{2+} in the duplex, the close packing of Cu-ligand layers flatten the tetrahedral geometry of Cu(bpy)_{2}^{'}, increasing the energy level of the SOMO of the Cu(II). This hypothesis was supported by spectroelectrochemical experiments and DFT calculations.

INOR 475

New class of PN3-pincer ligands for metal-ligand cooperative catalysis

Kuo-Wei Huang, hkw@kaust.edu.sa KAUST Catalysis Center and Division of Physical Science and Technology, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

A new class of pincer ligands that have a unique disubstituted phosphinoaminophosphine (NH-PR2) arm are introduced. Upon complexation to transition metals, a series of ruthenium, rhodium, nickel, iron, chromium, and cobalt complexes have been proven to be efficient catalysts for dehydrogenative coupling, hydrogenation, and olefin polymerization reactions. Selective examples of ethanol dehydrogenation to ethyl acetate and carbon dioxide reduction will be highlighted.

INOR 476

Single source precursors for heterometallic fluoride nanomaterials

Shashank Mishra1, shashank.mishra@ircelyon.univ-lyon1.fr, Erwan Jeanneau2, Gilles Ledoux2, Stephane Daniel1. (1) IRCELYON, 2 Avenue A. Einstein, University of Lyon1, Villeurbanne, France (2) Centre de Difractométrie, 5 rue de La Doua, University of Lyon1, Villeurbanne, France

The nanstructured and functionalized inorganic fluoride nanomaterials, ranging from nanoparticles or glass ceramics to thin layers and coatings, find many applications. However, due to scarcity of suitable metallic precursors, the chemical routes to heterometallic fluoride remain almost un-explored. We report new Na-Ln trifluorurate complexes with glyme ligands as excellent single source precursors for lanthanide-doped NaY(Gd)F4, upconverting (UC) nanocrystals, which efficiently convert infra-red radiation to shorter wavelength UV-visible region. These heterometallic precursors have multiple advantages over the extensively used homometallic Ln(TFA)3(H2O), for above UC nanomaterials. These include their being anhydrous (presence of water molecules is detrimental for the UC properties), having comparatively low decomposition temperature and containing glyme ligand, which acts as a capping reagent during decomposition to provide controlled size and stable dispersion of nanoparticles in organic solvents. A comparative study on the decomposition behaviour of the Na-Y and Na-Gd precursors shows that the hexagonal phase of the NaY(Gd)F4 matrix, which is many fold more efficient for the UC process, is easily obtained at much lower temperature for the latter. Catalytic applications of these nanomaterials, either as support for gold catalysts in the oxidation reactions or their nanocomposites with titania for NIR-driven photocatalysis will be presented.

INOR 477

One-pot synthesis, spectroscopic characterization, crystal structure, and biological activity of supramolecular Fe(III), Cu(II) and Zn(II) compounds obtained from pyridine-dicarboxylic acid and 3,5-diamino-1,2,4-triazole

Atim Sunday Johnson1,2, atimjohnson@gmail.com, Sammer Youssuf1, Arif Syed Kazmi2, Offiong Etangh Offiong2, Wan Sin Loht3, Fun Hoong Kun4,5. (1) Heusen Ebraham Jamal (H.E.J.) Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi, Karachi 75270, Pakistan (2) Department of Chemistry, University of Uyo, Uyo, Akwa Ibom State 520001, Nigeria (3) Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State O87, Nigeria (4) X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, Penang, Penang 11800, Malaysia (5) Department of Pharmaceutical Chemistry, King Saud University, Riyadh, Riyadh 11451, Saudi Arabia

Abstract

Three new supramolecular carbazole complexes, [HdtzH][Fe(dipic)2]·6H2O (1) [HdtzH][Cu(dipic)(dipic)3]·3H2O(2) and (HdtzH2)[Zn(dipic)]·4H2O (3) (HdtzH= 3,5-diamino-1,2,4-triazolium ion, dipic = pyridine-2,6-dicarboxylic acid) were synthesized and characterized by elemental analyses, spectroscopic methods (IR, UV, 1H NMR and Mass spectroscopy), and single crystal X-ray diffraction technique. The room temperature magnetic susceptibility measurements show magnetic moments of 5.92, 1.67 and 0 B.M at 298K for compounds (1), (2) and (3), respectively indicating that (1) and (2) are paramagnetic while (3) is diamagnetic. The asymmetric unit of (1) consists of Fe(dpic)3 and HdtzH+ and six molecules of water layer, compound (2) contains two tridentate dipicolinate ligands, one triazolium ion and three water molecules while the asymmetric unit of (3) contains two tridentate dipicolinate ligands, two triazolium ion, and four water molecules. The coordination environment around the metal ions is such that the two dipicolinate ligands are assembled perpendicularly to each other with two axially oriented N atoms and four O atoms on the equatorial positions revealing distorted octahedral geometries for compounds 1-3. The hydrogen bonding, that is O···H···O, O···H···N and N···H···O between carbazole, (HdtzH)+ and water play significant roles in stabilizing the crystal structures. Compound (2) shows a significant free radical scavenging ability while (1) and (3) show good antimicrobial activities.

Keywords: Metal complexes, hydrogen bonding, pyridine-2,6-dicarboxylic acid, antioxidant and antimicrobial activities.

INOR 478

Activation of small molecules by polar heterobimetallic complexes

Upul Jayarathe, upul@uic.edu, Sharareh Bagherzadeh, Neal P Manikad Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States

The activation of small molecules such as CO2 and N2O is of great interest not only because both are major contributors to the greenhouse effect but also because converting the former into liquid fuels is highly desirable. The polarity and cooperative reactivity of heterobimetallic complexes provide a basic platform for activating such molecules. Combination of N-Heterocyclic carbene (NHC) Cu fragments, with FeL(CO)3 anions resulted in complexes of the type (NHC)Cu-FeL(CO)3 (L=Cp, Cp*) which have been crystallographically characterized. An interesting and diverse reactivity of these complexes towards heterocumulene substrates such as CS2, N2O, isocyanates and carbodiimides has been observed. The reactivity of modified systems such as (NHC)Cu-FeL(CNR)3a (n= n, 1; R= Bu, Ph) will also be discussed. The presence of a polar metal-metal bond is thought to be key towards enabling all of these small molecule activation processes.

INOR 479

Coordination of first-row transition metals in biologically relevant oligopyrrolic fragments

Elisa Tomat, tomat@email.arizona.edu, Sanhita Sinharay, Tsuhen M. Chang, Sarah G. Poplin Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United States
Oligopyrrolic compounds are essential to all forms of life and play a critical role in the chemistry of transition metals in living systems. The coordination chemistry of tetrapyrrolic porphyrin and chlorin macrocycles is essential to the understanding of their numerous biological roles and to their application in a multitude of settings from catalysis to materials science to pharmaceuticals.

When macrocyclic tetrapyrroles are metabolized in living systems, linear oligopyrrolic fragments (containing four, three or two pyrrolic units) are generated. Furthermore, tripyrrolic and dipyrrolic natural products are biosynthesized by certain bacterial strains. In spite of their occurrence in multiple biological settings, the chemistry of several dipyrrolic and tripyrrolic scaffolds remains largely unexplored.

With the goal of providing insights into their emerging toxicological profiles, we report our study of the coordination and redox chemistry of pyrroldipyrinin scaffolds found in bacterial pigments known as prodigiosins. Furthermore, we examine the metal binding properties of dipyrrolic fragments deriving from the decomposition of heme in human metabolism.

Presenting an electron-rich scaffold and an array of pyrrolic nitrogen donors, these linear fragments are well poised for metal coordination. Because they lack the macrocyclic structure of porphyrin and other pyrrole-based pigments, these chelators enable the formation of complexes in which the metal center is more accessible for substrate coordination in catalytic applications. In addition, these fully or partially conjugated ligands maintain a high tunability of donor capacity and redox potential. The effect and biological relevance of metal coordination on the reactivity of several dipyrrolic and tripyrrolic fragments is investigated.

INOR 480
Synthesis, coordination chemistry, and applications of sulfur donor ligands
Perumalreddy Chandrasekaran, chandru@lamar.edu, Lakshmi Nishanth Kakarla, Sandeep Kallapu, Jagadish Kumar Mopartii, Nashwa Alahmar, Kvl Thanusha.Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710, United States

Coordination chemistry of sulfur donating ligands to metal centers are not prolific, compared to nitrogen, phosphorus, and carbon donating ligands. Thiolates (RS) and sulfide (S2−) dominates the coordination chemistry of sulfur ligands, whereas coordination chemistry of thioethers, and ketones are overlooked, due to both poor sigma-donating and pi-accepting ability of thiogroups, and ketones. To shed light on coordination chemistry of neutral sulfur ligands, we prepared set of thioethers and thioketones. The coordination chemistry of these thioether, thioketones with group 11 metals, and their potential applications, will be discussed.

INOR 481
Siamese twin porphyrin and its bimetallic complexes: Story of a non-innocent chiral twist
Franc Meyer1, franc.meyer@chemie.uni-goettingen.de, Lina K. Blusch1, Serhiy Demeshko2, Sebastian Dechert1, Christian Brückner2, Kathryn E. Craigo3, Ashley B. McQuarters1, Nicolai Lehner1, Eckhard Büt1, Vlad-Martin-Diaconescu1, Serena DeBeer4. 1) Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Göttingen, Germany. 2) Department of Chemistry, University of Connecticut, Storrs, Connecticut CT 06269-3060, United States 3) Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, United States 4) MPI for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

The Siamese twin porphyrin is a novel type of expanded porphyrin that consists of four pyrrole and two pyrazole units.[1] It can be viewed as the fusion of two (N4) porphyrin-like coordination sites, and hence it can bind two metals in close proximity within the highly preorganized scaffold. The Siamese twin porphyrin and its dinuclear metal complexes feature various interesting properties that will be presented, including:

- (i) a complex protonation sequence of the two (N4) porphyrin-like sites[2]
- (ii) persistent helical chirality that arises from the severe twisting of the pyrazole-expanded core[2]
- (iii) unusual ferromagnetic coupling between the metal ions in the binuclear complexes[3]
- (iv) hidden non-innocence of the ligand scaffold that gives rise to a complex sequence of redox events, both metal- and ligand-centered.[3]

References

INOR 482
Versatile coordination chemistry modes for monovalent coinage metal molecular and supramolecular complexes
Mohammad A. Omary, omary@unt.edu.Chemistry, University of North Texas, Denton, Texas 76203, United States

This presentation will overview recent and ongoing efforts by our group and several collaborators regarding versatile coordination modes for monovalent coinage metal complexes, including Au(I), Ag(I), and/or Cu(I) with a broad spectrum of N-rich or electron-poor core, respectively.

INOR 483
Correlation between magnetism and luminescence in redox active single molecule magnets
Lahcene Ouahab, ouahab@univ-rennes1.fr, Fabrice Pointillart, Stephane Golhen, Olivier Cadot.Institute of Chemistry, UMR 6226 CNRS-University of Rennes 1, Rennes, France

Lanthanide ions are well-known to exhibit large magnetic moments and strong magnetic anisotropy and therefore they are considered as good candidates for the elaboration of Single Molecule Magnets (SMMs). Complexation of these particular metal ions by redox active ligands derived from TTFs led to electroactive SMM with antennae effect of the ligands as well as very good correlation between magnetism and luminescence at the molecular scale. We report in this lecture several compounds exemplifying these features.

Among them, dinuclear complexes of lanthanides associating both 4,5-Bis(thiomethyl)-4'-carboxyltetraethylfulvalene and 4,5-Bis(thiomethyl)-4'-ortho- pyridyl-N-oxide -carbamoyltetraethylfulvalene ligands have been elaborated. Dc magnetic susceptibility measurements highlight ferromagnetic interactions between the metallic centres. The two Dy(III) and Yb(III)-based analogues display SMM behaviour. Experimental and theoretical magnetic and photo-physical investigations have confirmed that a multi-electroactive luminescent SMM is obtained in the case of the Yb(III) analogue[4]
INOR 484

Fluoro-acetate and -alkoxy lanthanide precursors for lanthanide fluoride-based ion sensors

Timothy J. Boyle1, tboyle@Sandia.gov, Ryan F. Hess1, Daniel T. Yomemoto1, Michael L. Neville1, Gregory A. K. Stillman1,2, Samuel P. Bingham1. (1) Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM 87106, United States  (2) EERE: Geothermal Technologies Office, Department of Energy, Washington, DC 20585, United States

The characterization of reservoir fracture networks is important in the development of geothermal power. Ion-based tracers studies can be used to elucidate the extent and connectivity of these fracture networks. Collecting real-time down-hole track data requires the development of novel ion detecting sensors. These detectors must survive the high brine levels, high temperature, high pressure, and other caustic environmental conditions encountered in these deep-hole wells. Several detectors are being pursued for this application, with our efforts have focused on developing fluorine ion selective electrodes. One proposed material for this is LaF3. While this compound is commercially available, we have developed several novel precursors in order to allow production of LaF3 nanomaterials, which are of interest due to their high surface area. The synthesis and characterization of a series of lanthanide trifluoracetates and hexafluoro iso-propoxide derivatives as well as their conversion to the subsequent nanomaterials will be presented.

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INOR 485

Synthesis and photophysical properties of emissive Ln(III)-capped carbon dots

Travis D Cournoyer, tcournoyer@unr.edu, Ana de Bettencourt-Dias. Department of Chemistry, University of Nevada, Reno, Reno, NV 89557, United States

New emitting nanoparticles were prepared by decorating the surface of carbon dots (CDs) with the lanthanide (Ln(III)) ions Eu(III) and Tb(III) in an aqueous environment. The Ln(III)-capped CDs were prepared by thermal decomposition of acetic acid using phosphorus pentoxide in water with subsequent addition of the Ln(III) nitrate and triflate salts. After addition of the ancillary EDTA ligand the aqueous solutions emit in the characteristic Ln(III) colors, as quenching from solvent is avoided. The synthesis and photophysical characterization of these new Ln(III)-capped CDs will be presented.

INOR 486

Sensitizing lanthanide luminescence with CMPOs

Shannon M Biros, biross@gvsu.edu, Justin Shady, Adam C Boyden. Department of Chemistry, Grand Valley State University, Allendale, MI 49401, United States

We report here investigations into the sensitization of lanthanide luminescence with a phenyl substituted carbamoylmethylphosphine oxide (CMPO) ligand. This new ligand sensitizes the luminescence of all four lanthanides that emit in the visible region (Sm3+, Eu3+, Tb3+, Dy3+). The most intense emission is seen from the Tb3+ complex. The resulting metal-ligand complexes have been studied in both the solution and solid state (including x-ray crystallography).

INOR 487

Emissive Eu(III)-containing polymers with pyridine-bis(oxazoline) on a poly(vinylbenzyl) backbone

Jeffrey S Rossini, jrossini@gmail.com, Ana de Bettencourt-Dias. Department of Chemistry, University of Nevada, Reno, Nevada 89557, United States

Luminescent lanthanide-containing polymers can be used in electronic displays and optical fiber amplifiers. We appended a pyridine-bis(oxazoline) sensitizer onto the polymer chain of poly(vinylbenzyl chloride). Upon complexation of Eu(III), the metal ion-centered emission was observed. We will describe the photophysical properties of the polymer and of its related monomers.

INOR 488

Quinoxolinol modified ligands for spectrophotometric molecular recognition

Michael A DeVore II, mzd0007@auburn.edu, Anne Gorden, Spencer Kerms. Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, United States

A spill of nuclear waste is of an utmost concern for people living near nuclear power plants and potential underground storage caverns. While there a number of techniques that are sensitive enough for the detection of actinides in the environment, they are not portable or cost effective. An UV-Vis spectrometer can be low-cost and portable. Chromophores have been made that will bind actinides selectively resulting in a unique signal; however other metals such as copper can interfere.

Previously, our group has synthesized a quinoxaline salen ligand that shows a difference in the UV-Vis spectra. Now modifications are being made to increase the detection limit and the changes in the UV-Vis spectra. TDDFT will be used to determine the single electron transitions with NTOs to determine ligand to ligand, ligand to metal, and metal to ligand transitions.

INOR 489

Highly conjugated electropolymerizable antenna ligands for the sensitization of near-IR and visible Ln(III) emission

Matthew T. Raiford, mraiford@cm.utexas.edu, Bradley J. Holliday. Department of Chemistry, The University of Texas at Austin, Austin, TX 78712, United States

A new class of lanthanide complexes exhibiting metal-based visible and near-IR photoluminescence has been designed, synthesized and characterized. A pair of highly conjugated electropolymerizable ligands were produced via condensation reactions between 3,4-ethylenedioxythiophene and dipyriddophenazine (EDOT-dppz) or dipyriddoquinaxoline (EDOT-dpq). Luminescent analysis indicated that the structural differences of (EDOT-dppz) and (EDOT-dpq) have little effect on the triplet excited state energy levels of the ligands. Two triplet excited state energy levels were observed for each ligand at approximately 320 and 500 nm, both of which were investigated for possible lanthanide sensitization. A series of (β-diketonate)3Ln(III) (EDOT-dpq/EDOT-dppz) complexes was produced in order to probe the potential of the ligands to sensitize visible and near-IR Ln(III) emission. Excitation of the higher energy triplet excited state level at ~320 nm lead to lanthanide-based emission from Tb(III), Dy(III), and Eu(III) complexes. Above average emission (QY ~ 2-8%) and long lifetimes (24-29 μs) were observed from the Dy(III) complexes. Terbium complexes displayed quantum yields between 21-36% and lifetimes from 636-888 μs. Electropolymerization of the Tb(III) monomers resulted in conducting metallocopolymers with metal-based emission ranging from quantum yields of 0.01–0.03%. Excitation of the lower energy triplet excited state level at ~500 nm lead to effective
sensitization of near-IR emitting Yb(III) complexes. Yb(III) emission in the complexes was observed with quantum yields of up to 5.3% and lifetimes as long as 29.4 μs. The metal-containing monomers were electropolymerized and Yb(III)-based emission was observed from the metallopolymer with quantum yields of ~0.3% and lifetimes of ~14.6 μs. This work indicates that (EDOT-dpz) and (EDOT-dpq) ligands are effective sensitizers of visible and near-IR emission in both lanthanide-containing monomers and conducting metallopolymers.

INOR 490
Reactivity of low-valent f elements supported by siloxide ligands
Marinella Mazzanti1, marinella.mazzanti@cea.fr, Clement Camp2, Victor Mougel1, Jacques Pécaut1, Laurent Maron2. (1) CEA, Grenoble, France 38950, France (2) Laboratoire de Physique et Chimie des Nano-objets, Universite Paul Sabatier, Toulouse, France, France
Siloxides can be used to isolate stable complexes of low-valent uranium and lanthanides which can promote the transformation of small molecules such as CO2, CS2, and azides. Siloxide ligands provide a versatile tool to modulate the sterical and electronic environment of low-valent uranium which allows the tuning of the metal reactivity leading to complexes with original structure. Recent redox chemistry of siloxide complexes carried out in our laboratory will be presented.

INOR 491
Spectroscopy and cell studies of water-soluble lanthanide ion complexes with –NH₂-bearing ligands
Ana de Bettencourt-Dias1, abdi@unr.edu, Jorge H.S.K. Monteiro2, Fernando A. Sigoil3, Luciana M. de Holland3, Daisy Machado3, Marcelo Lancellotti2. (1) Department of Chemistry, University of Nevada, Reno, Reno, Nevada 89557, United States (2) Department of Chemistry, University of Campinas, Campinas, Sao Paulo 13083-970, Brazil (3) Department of Biology, University of Campinas, Campinas, Sao Paulo 13083-970, Brazil
Lanthanide ion luminescence is long lived and the emission bands are sharp. These properties make the ions interesting for bioimaging applications. We synthesized two ligands bearing -NH₂ functional groups, which form water-soluble complexes with the lanthanide ions, and which sensitize their emission in water. We will discuss the properties of the resulting complexes, their emission efficiency, as well as their ability to penetrate the cell membrane and be used in bioimaging applications.

INOR 492
Paramagnetic fluorine-based responsive MRI contrast agents
Valerie C. Pierre, pierre@umn.edu. Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, United States
Despite the increasing number of such agents reported, gadolinium and particulate-based responsive contrast agents for MRI have found limited practical use in biomedical and clinical research due to their limited response, the interference of physiological anions, and most importantly, due to their inability to distinguish a change in signal intensity due to the presence of the targeted analyte from those resulting from variations in local concentration of the contrast agent. Herein we present a new class of responsive MRI contrast agents based on the Lanthanide Induced Shift (LIS) and Paramagnetic Relaxation Enhancement (PRE) of two 19F-fluorine signals of a same complex modulated by binding or reaction with a targeted analyte. The advantages and limitations of 19–F-LIS responsive contrast agents over their Gd and MION analogues will be highlighted in a case study focusing on imaging copper, a metal involved in the neurodegenerative Alzheimer's disease.

INOR 493
Intramolecular hydrogen-bonded phenol U-SHY CEST MRI probes
Xing Yang1, Xiaolei Song1, Nithbay Yadav1,2, Hannah Edelman2, Peter C.M. van Zijl1,2, Sangeeta Ray Banerjee2, Martin G. Pomper1, Michael T. McMahon2,3, mtmcmaho@gmail.com. (1) F.M. Kirby Research Center for Functional Brain Imaging, Kennedy Krieger Institute, Baltimore, MD 21205, United States (2) Department of Radiology, Johns Hopkins University School of Medicine, Baltimore, MD 21205, United States (3) Center for Nanomedicine, Johns Hopkins University School of Medicine, Baltimore, MD 21205, United States (4) Oncology, Johns Hopkins School of Medicine, Baltimore, MD 21205, United States
Chemical exchange saturation transfer (CEST) contrast agents gain more and more attention after their first introduced in 2000 as a new alternative to the traditional water relaxivity-based contrast agents. Since the mechanism involves selective irradiation of fast water exchangeable protons to amplify the signal, CEST has its advantage in quantification of environmental parameters, including: pH and cation concentrations, however wide application of CEST agents is still limited by sensitivity, due to both signal amplification and signal contamination from the background. In order to improve this, we have developed Uncommonly Shifted HYdrogen-bonded (U-SHY) exchangeable proton diaCEST probes based around the phenol scaffold. Saliycic acid is the simplest example of this class of probes, with the addition of the carboxylic acid proximal to the OH reducing the exchange rate of these protons, which can be viewed as making these "shy" protons. A series of water soluble phenols were investigated, including 3-, 4-, 5-, and 6- substituted 2-hydroxybenzoic acids. We found that 4- and 5- substituted 2-hydroxybenzoic acids, including hydroxyl-, amino-, chloro-, carboxyl-, sulfonyl- and nitro-groups with the electronic effect on the U-SHY phenol protons were clearly reflected on the chemical shift of the peak CEST signal. 2,5-dihydroxybenzoic acid and 5-aminosalicylic acid with electron donating groups para to the U-SHY protons showed peak signal at 8.5 ppm, compared with the 9.5 ppm in salicylic acid. We also found that substitution at the 6- position is quite tricky, any bulky modification could result in dramatic changes in the hydrogen bonding between the carboxylate and U-SHY proton. In particular 2-hydroxy-1-naphtholic acid and 6-methoxysalicylic acid still gave U-SHY contrast at 9.5 ppm and 9.0 ppm, the exchange rates were around 6-8 times faster compared with salicylic acid, making them less useful for low power MR applications. Finally, we have incorporated these probes into liposomes and have monitored these lipoCEST nanocarriers after tail vein administration into mice bearing tumors. The results of these studies will be discussed.

INOR 494
Metallprotein contrast agents for molecular MRI
Alan Jasanoff, jasanoff@mit.edu. Department of Biological Engineering, MIT, Cambridge, MA 02139, United States
Protein imaging agents have pride of place as reagents for optical studies of cell biology, but ongoing research aims to find analogs that can be detected in deep tissue in conjunction with noninvasive imaging techniques. Here I describe protein engineering strategies used in my lab to generate metalloprotein-based molecular MRI probes for neuroimaging. I focus particularly on contrast agents designed to detect neurotransmitters and on genetically encodable sensors for detecting intracellular signaling by MRI. In our neurotransmitter imaging research, we applied a protein engineering approach called directed evolution to search for molecules that bind neurotransmitters and exhibit the so-called reactivity changes which in our case provide the basis for analyte sensing in MRI. Using this strategy, protein sensors for dopamine and serotonin have been identified. We combined the dopamine sensor with brain stimulation techniques to map neurotransmitter signalling in the ventral striatum of rats, and are comparing results with conventional functional MRI. Using the serotonin sensor, we are mapping neurotransmitter reuptake processes and studying their modulation by pharmacological agents. Current work aims at producing analogous neurotransmitter sensors with greater target sensitivity. Our work on genetically encodable sensors revolves largely around the protein ferritin, which we have modified to produce reactivity changes in response to kinase activity or...
From paraCEST to lipo- and cellCEST: Routes to multiplex MRI detection

Silvio Aime, silvio.aime@unito.it, Giuseppe Ferrauto, Enza Di Gregorio, Daniela Delli Castelli, Enzo Terreno. Department of Molecular Biotechnology and Health Sciences & Molecular Imaging Center, University of Torino, Torino, Italy

In the field of Molecular Imaging, MRI stands out among the other modalities for the superb anatomical resolution, the high in-depth penetration and the possibility to exploit different mechanisms to generate contrast. The MRI contrast agents of common use (CAs) perturb the relaxation times of water protons and therefore do not allow displaying more than one event/molecule in the image because their effect on the water signal is not specific. It has been shown that multilabeling can be pursued by using frequency encoding CAs that include: 1) Chemical Exchange Saturation Transfer (CEST) agents; 2) hyperpolarized molecules; 3) heteronuclei-containing probes (e.g. 19F). CEST agents offer the considerable advantage of being able to be utilized in traditional 1H-MR experiments. The contrast is generated at will by simply applying a suitable RF pulse to selectively irradiate the NMR resonances of the exchangeable protons of the CA to be visualized. This unique property allows new applications such as the detection of more than one agent in the same MR image as well as the set-up of ratiometric methods for the quantitative evaluation of the physico-chemical and biological parameters that characterize the micro-environment in which the CAs are distributed. Different type of CEST CAs have been developed starting from paraCEST agents to arrive to lipoCEST and cellCEST probes. In particular, the macroyclic complex YbHPDO3A can be used as pH reporter, providing high resolution maps of pH distribution inside tumors. In addition, DyHPDO3A-loaded erythrocytes act as reporters of the microvasculature. Finally, the analysis of the distribution of both these probes can be used to gain insights into the vascular permeability. These data allow us to obtain multiparametric maps of tumor, a tool of considerable importance for the characterization of the cancer microenvironment.

NICEST, CoCEST and ferroCEST MRI contrast agents

Janet R Morrow, jmorrow@buffalo.edu, Pavel B Tshitovich, Abiola O Olatunde, Sarina J Dorazio. Department of Chemistry, University at Buffalo, State University of New York, Amherst, New York 14260, United States

Fe(II), Ni(II) and Co(II) complexes are under development as paraCEST MRI contrast agents (paraCEST = paramagnetic chemical exchange saturation transfer). Our approach uses aza or mixed oxa-aza macrocycles with pendent groups that contain exchangeable OH or NH protons. NICEST (Ni(II)), CoCEST (Co(II)) and ferroCEST (Fe(II)) agents that contain amide pendent groups are stabilized in the divalent state. CEST peaks are shifted up to 112 ppm with an optimal effect at close to neutral pH. Heterocyclic pendent groups including aminopyridines, benzimidazoles and pyrazoles give rigid macrocyclic complexes with sharp and highly shifted proton resonances along with more variable metal ion redox potentials. One CoCEST agent with pendent pyrazole groups has a redox potential of -107 mV versus NHE. This produces an MRI active Co(II) state which is switched on with cysteine and off with oxygen. Progress towards magnetic resonance imaging studies with these agents in biological media will be discussed.

Moving the goal posts: PARASHIFT contrast agents for magnetic resonance

David Parker, david.parker@dur.ac.uk. Department of Chemistry, Durham University, Durham, United Kingdom

Paramagnetic probes for chemical shift imaging are described, in which a reporting tert-butyl resonance is integrated and placed about 6 to 6.5 Å from a lanthanide ion. At this distance, the resonance is shifted to a region of the 1H NMR spectral window far away from the usual range, permitting selective observation. Furthermore, judicious selection of the lanthanide ion, according to the applied magnetic field strength, leads to relaxation rate enhancements of the order of 100–200, permitting more rapid data acquisition per unit time in both spectroscopy and imaging experiments. The enhanced sensitivity allows the detection of these complexes in mice within a few minutes using shift imaging, following tail vein injection of doses of the order of 0.1 mmol kg⁻¹. Similar strategies have been developed for various 19F paramagnetic probes using complexes labelled with trifluoromethyl groups. In complexes with large ligand fields (>>kT), the breakdown of Bleaney’s theory of magnetic anisotropy becomes more apparent and the validity of literature values of magnetic susceptibility for the later lanthanide ions (Tb to Yb) has been brought into question.


New type of responsive MRI contrast agent that modulate T2ex relaxation: Detection of nitric oxide

Iman Daryaei, imandaryaei@email.arizona.edu, Marty Pagei,ii,iii. (1) Chemistry and Biochemistry, University of Arizona, Tucson, Arizona 85719, United States (2) Biomedical Engineering, University of Arizona, Tucson, Arizona 85719, United States (3) University of Arizona Cancer Center, University of Arizona, Tucson, Arizona 85719, United States

PARACEST MRI contrast agents with a proton that has a large chemical shift and a fast chemical exchange rate can generate T2 exchange relaxation, which negatively impacts the sensitivity of CEST detection. We sought to use this disadvantage as an advantage to create a new class of molecular imaging agents, known as responsive T2ex MRI contrast agents. Specifically, Yb(III)-(1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid)-orthoaminoanilide (Yb-DODA-oAA) has been shown to be responsive to nitric oxide, but in vivo CEST detection of this agent is difficult due in part to T2ex relaxation caused by the agent. We designed a similar agent, Tm-DODA-oAA, which has a larger chemical shift and therefore should have a stronger T2ex relaxation effect. A chemical reaction with nitric oxide should modify the chemical exchange rate of the agent and therefore cause T2ex to be responsive to nitric oxide. Our results demonstrate that Tm-DODA-oAA (as the first example of a responsive T2ex agent) can detect nitric oxide via T2-weighted MRI. Importantly, the T1 relaxivity does not change after treatment with nitric oxide, and the ratio of T2 and T1 relaxivities is independent of concentration, so that this ratio can detect nitric oxide in a concentration-independent manner. This ratio of T2 and T1 relaxivities is only mildly dependent on temperature, which improves the specificity of the nitric oxide detection. These results demonstrate that a new class of responsive MRI contrast agents can be developed based on changing the chemical exchange rate of an agent and obtaining T2-weighted and T1-weighted MR images.

INOR 498

Novel formulation of isopropyl amine: An additional, non-enzymatic method of detecting low levels of nitric oxide

Valeria Rihal, valeria.rihal@email.arizona.edu, Thomas P. Grant, Robert L. Langer, Jenifer Chan. (1) Center for Molecular Imaging Research, Massachusetts Institute of Technology, Cambridge, MA 02139, United States (2) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

In this paper, we describe the synthesis and characterization of new nanoformulations of an enzyme-free, isopropyl amine (IPA) sensor for nitric oxide (NO). Low levels of NO were detected using the new formulation, with a detection limit of 10 nmol/L, which is more sensitive than commercially available NO sensors. The new formulation can be stabilized with sucrose, which results in an increase in the shelf life of the sensor. This new formulation can be used to detect NO in a variety of biological samples, such as blood or cerebrospinal fluid. In addition, the new formulation can be used to detect NO in living organisms, such as mice, using an in vivo micro-CT imaging technique. The results of this study demonstrate that the new formulation is a useful tool for detecting NO in low concentrations, which is important for understanding the role of NO in disease processes.

INOR 499

The potential of multifrequency and cosemic bioorthogonal probes for detection of nitric oxide

Jing Li, jing.li@email.arizona.edu, Janice R. Morrow, Michael J. Pajvani, Liqing Zhang. (1) Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260, United States (2) Chemical and Biological Engineering, University at Buffalo, State University of New York, Buffalo, New York 14260, United States

In this paper, we describe the development of multifrequency and cosemic bioorthogonal probes for detection of nitric oxide (NO). The probes are based on the use of bioorthogonal clickable groups and the use of multifrequency magnetic resonance imaging (MRI), which allows for the detection of NO at multiple frequencies. The probes were designed to be sensitive to NO concentrations as low as 10 nmol/L, and the detection limit was determined to be 10 pmol/L. The results of this study demonstrate that the probes are useful for detecting NO in low concentrations, which is important for understanding the role of NO in disease processes.

INOR 500

The potential of multifrequency and cosemic bioorthogonal probes for detection of nitric oxide

Jing Li, jing.li@email.arizona.edu, Janice R. Morrow, Michael J. Pajvani, Liqing Zhang. (1) Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260, United States (2) Chemical and Biological Engineering, University at Buffalo, State University of New York, Buffalo, New York 14260, United States

In this paper, we describe the development of multifrequency and cosemic bioorthogonal probes for detection of nitric oxide (NO). The probes are based on the use of bioorthogonal clickable groups and the use of multifrequency magnetic resonance imaging (MRI), which allows for the detection of NO at multiple frequencies. The probes were designed to be sensitive to NO concentrations as low as 10 nmol/L, and the detection limit was determined to be 10 pmol/L. The results of this study demonstrate that the probes are useful for detecting NO in low concentrations, which is important for understanding the role of NO in disease processes.
synthetic protocols are applied to previously underexplored materials systems. This talk will highlight our recent advances in the synthesis of colloidal nanocrystals across diverse materials systems, including metal chalcogenides, metal oxides, metal nitrides, and intermetallic alloys. Emphasis will be placed on the chemistry that leads to their formation, as well as insights into their structures and morphologies.

INOR 500
Highly-ordered, chemically stable and thermally robust organic interfaces at metal surfaces
Steven L. Tait, tait@indiana.edu, Daniel Skomski.Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

The use of small organic molecules to control surface structure as well as electronic and chemical functionality is a critical field for the development of inexpensive and highly functional organic technologies in energy conversion, sensors, electronics, and other applications. We have studied the self-assembly of highly-ordered organic nanostructures at surfaces to develop well-controlled, functional organic layers. Characterization is made by high-resolution scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy. Here, we report on interfacial organic layers that allow thiophene and other functional species to form highly ordered layers without any of the chemical decomposition usually observed at metal interfaces. We also report on strategies developed in our group to enable self-assembly of highly robust nano-architectures consisting of a 2D ionic crystal. The latter form by reaction of carboxylic acid functional groups with NaCl on a Cu(100) surface, show uniform ordering with annealing, and have high thermal stability, as determined by molecular resolution STM at high temperatures.

INOR 501
Recent progress in controlling the synthesis of colloidal noble-metal nanocrystals
Younan Xia, younan.xia@bme.gatech.edu, Department of Biomedical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

Significant progress has been made in recent years with regards to the synthesis of noble-metal nanocrystals with controlled sizes, shapes, and structures. With the introduction of uniform and well-controlled seeds into a synthesis, it has become possible to separate growth from nucleation and further investigate the explicit roles played by thermodynamics and kinetics in controlling the shape evolution of colloidal noble-metal nanocrystals. Using single-crystal seeds enclosed by a mix of low-index (100), (111), and (110) facets as an example, we have been able to deterministically access many different types of shapes that are only allowed under a specific condition set by either thermodynamics or kinetics. The insights we have learnt from these studies can also be applied to explain the shapes previously observed in the conventional one-pot synthesis. In this talk, I will focus on these most recent developments.

INOR 502
Virus particles as templates for mineral nanoparticle synthesis
Trevor Douglas1,2, tdouglass.illinois.edu, Masaki Uchida1,2, Peter E Prevelige3, Courtney Reichhardt3. (1) Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, United States (2) Department of Chemistry, Indiana University, Bloomington, IN 47405, United States (3) Microbiology, University of Alabama, Birmingham, Alabama 35294, United States

Biomimetic chemistry offers new approaches to materials synthesis and assembly. We have demonstrated that an assembled viral protein cage, comprising an organic core–shell structure, can be used as a template for the size constrained synthesis of inorganic nanoparticles such as Fe3O4. We have expanded the use of noninfectious viral capsids from the bacteriophage P22 to initiate particle nucleation, directed by specific genetic modifications to the inner scaffold protein layer. The size of the inorganic nanoparticles are determined by the volume of the protein cage. P22 assemblies from 420 identical copies of a coat protein with the assistance of a variable number of a 303 residue scaffold protein (100 to 300 copies per capsid) resulting in a cage-like structure of 60 nm in diameter with a 50 nm diameter interior cavity. The C-terminal region of the scaffold protein is required for the templated assembly of the capsid and the N-terminal region of the scaffold protein can be significantly modified without loss of assembly. Our aim was to mimic the mineral sequestering abilities of the iron storage protein ferritin in a system with a much larger interior volume by genetically fusing a polyamionic peptide to the scaffolding protein, localized to the interior of the viral cavity, which would nucleate the iron oxide. The Fe3O4 particles were 41±5 nm in diameter, suggesting that particle growth was constrained by the P22 protein shell. Alternatively, by fusing the entire ferritin protein subunit to the scaffold protein we can enforce the assembly and encapsulation of 10-20 copies of the fully assembled, 25 subunit, ferritin cage within the P22 capsid. The encapsulated ferritin can act as a size-constrained platform for iron oxide mineralization. The resultant architectures are the molecular equivalents of ‘Russian nested doll’ structures and are complex and hierarchically structured composite nanomaterials.

INOR 503
Colloidal nanoparticle alloys
Jill E. Millstone, jem210@pitt.edu, Christopher M. Andolina, Lauren E. Marbella, Patrick J. Straney, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, United States

Discrete gold nanoparticles with diameters between 2 and 3 nanometers (nm) show remarkable properties including enhanced catalytic behavior and photoluminescence. However, tunability of these properties is limited by the tight size range within which they are observed. Here, we report the synthesis of discrete bimetallic nanoparticle alloys (diameter $\pm$ 2-3 nm) where gold is mixed in combination with a wide range of transition metals. Interestingly, although both theory and experiment indicate the particles are metallic, they display bright photoluminescent properties that can be tuned by changing the alloy composition. Electron microscopy, X-ray photoelectron spectroscopy, inductively coupled plasma mass spectrometry, and pulsed field gradient stimulated echo $^1$H NMR measurements show that the nanoparticles are homogeneous, discrete, and crystalline. The impact of surface chemistry on the formation and physical properties of these materials will be discussed as well as their utility in NIR imaging and reaction-tracking applications.

INOR 504
Searching for algorithms of reaction anisotropy
Catherine J. Murphy, murphyjc@illinois.edu, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

The growth of anisotropic metallic nanocrystals is governed, in the lab, by a combination of art and science. In this talk I will describe our more recent results of growing anisotropic crystals in aqueous solution, and how we have been inspired by the award winner.

INOR 505
Catalytic production of carbonyl sulfide (S=C=O) and isothiocyanates (S=C=NR) under near ambient conditions via facile sulfur-atom transfer
Wesley S Farrell, wfarrell@umd.edu, Peter Y Zavallj, Lawrence R Sita, Department of Chemistry and Biochemistry, University of Maryland-College Park, College Park, Maryland 20742, United States

This talk will present the first reported case for direct, catalytic synthesis of carbonyl sulfide (COS), a possible condensing agent in the formation of peptides under primordial conditions, from its most basic components, namely, carbon
monoxide (CO) and elemental sulfur (S\textsubscript{8}). The photolytic reaction proceeds at room temperature and is catalyzed by a molybdenum complex supported by the pentamethylcyclopentadienyl (C\textsubscript{5}Me\textsubscript{5}) amidinate \([\text{N}(\text{Pr})\text{C}(\text{Ph})\text{N}(\text{Pr})]\) \((\text{CpAm})\) ligand environment. All reaction intermediates have been identified and structurally characterized, and it was found that addition of acetonitrile (NCCH\textsubscript{3}) to the reaction mixture lead to increased reaction rates by preventing the formation of the thermodynamically stable dithiocarbonate molybdenum IV complex (C\textsubscript{5}Me\textsubscript{5}Mo(κ-S, κ-Sʻ-S\textsubscript{8}-CO))[N(Pr)C(Ph)N(Pr)]. Furthermore, the same methodology has been employed for the room temperature, catalytic synthesis of isothiocyanates from S\textsubscript{8} and the corresponding isonitriles. This process is not sensitive to the presence of other small organic molecules, such as amines, thus providing a potentially 'greener' on-demand generation of hazardous isothiocyanates that are reactive intermediates for industrial production of pesticides and pharmaceuticals.

INOR 506

**Activation of small molecules by Pt-Sn heterobimetallic complexes**

Anjanyulu Koppaka, a.koppaka@umiami.edu, Veeranna Yemptally, Lei Zhu, Burjor Captain, George C Fortman, Carl D Hoff. Department of Chemistry, University of Miami, Coral Gables, FL 33143-0431, United States

The reaction of \(\text{Pt(COD)}_2\) bis(1,5-cyclooctadiene)platinum) and Bu\textsubscript{3}SnH (tri-\text{t}-butyl tin hydride) in a 1:1 ratio yielded Pt(H)(COD)(Bu\textsubscript{3}Sn), 1. Compound 1 reacts with one equivalent each of Bu\textsubscript{3}SnH and BuNC (\text{tert}-\text{t}-butyl isocyanide) to give the di-hydro Pt-Sn compound Pt(H)\textsubscript{2}(Bu\textsubscript{3}Sn)\textsubscript{2}(BuNC), 2. Compound 2 contains an 18 electron platinum atom in a distorted octahedral geometry. Compound 2 loses its hydride ligands in solution and in the solid state to give the complex Pt(\text{Bu}\textsubscript{3}Sn)\textsubscript{2}(BuNC), 3. The Pt atom in 3 has a 16 electron configuration with a formal oxidation state of +2. Addition of an equimolar mixture of H\textsubscript{2} and D\textsubscript{2} to a solution of 2 results in rapid formation of HD gas. When CO gas is purged through a hexane solution of 2, at room temperature it forms Pt(CO)(Bu\textsubscript{3}Sn)\textsubscript{2}(BuNC), 4. Compounds 3 and 4 in the presence of H\textsubscript{2} gas regenerate 2. Compound 1, upon reaction with another equivalent of Bu\textsubscript{3}SnH and subsequent CO gas purge affords Pt(SnBu\textsubscript{3})\textsubscript{2}(CO), 5. Compound 5 reacts with two equivalents of BuNC and loses a CO molecule to form product 4. Compound 1 reacts with one equivalent of NHC carbene, BF\textsubscript{3}(N, N-di-\text{t}-butylimidazol-2-ylidene) to give the dimer [Pt(SnBu\textsubscript{3})(BF\textsubscript{3})(H)]\textsubscript{2}, 6. Compound 6 activates H\textsubscript{2}, CO and C\textsubscript{2}H\textsubscript{4} at room temperature and forms [Pt(SnBu\textsubscript{3})(BF\textsubscript{3})(H)]\textsubscript{2}, 7, [Pt(SnBu\textsubscript{3})(BF\textsubscript{3})(CO)(H)]\textsubscript{2}, 8 and [Pt(SnBu\textsubscript{3})(BF\textsubscript{3})(C\textsubscript{2}H\textsubscript{4})(H)]\textsubscript{2}, 9 respectively.

INOR 507

**Unusual ligand effects and unexpected C-H amination side reactions in palladium-catalyzed amination reactions en route to new monodentate binaphthyl-based ligands**

LeGrande M. Slaughter\textsuperscript{a}, legrande@unt.edu, Sachin Handa\textsuperscript{b}, Aaron A. Ruch\textsuperscript{c}. (1) Department of Chemistry, University of North Texas, Denton, TX 76203, United States (2) Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United States (3) Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States (4) Center for Nanostructured Materials, The University of Texas at Arlington, Arlington, Texas 76019, United States

Palladium-catalyzed amination reactions provide a powerful means of creating carbon-nitrogen bonds from readily available aryl halides or triflates. These reactions are known to be highly sensitive to the structures of both substrate and ancillary ligand, but little information is available regarding potential deactivation pathways or side reactions. Binaphthyl 2-triflates bearing various aryl or alkyl 2'-substituents represent a challenging substrate class for amination given the significant steric bulk adjacent to the substitution site. Yields in palladium-catalyzed Buchwald-Hartwig aminations of these chiral synths were found to depend strongly on the bite angle of the diphosphine ligand as well as the metal:ligand ratio. Under some conditions, a C-H amination side process occurred, giving rise to chiral [5]helicene derivatives. Reaction conditions were tuned to provide either amination or C-H amination products for a range of substrates. The former are precursors for a new family of monodentate chiral carbene ligands, while the latter have potential materials applications.

INOR 508

**Platinum catalyzed ethane C-H functionalization: Unexpected products, reactivity, and mechanism**

Brian G Hashiguchi\textsuperscript{a}, bhashigui@scripps.edu, Michael M Konnick\textsuperscript{b}, Steven M Bischof\textsuperscript{c}, Muhammed Yousufuddin\textsuperscript{d}, Daniel H Ess\textsuperscript{e}, Roy A Periana\textsuperscript{f}. (1) Department of Chemistry, The Scripps Research Institute, Scripps Florida, Jupiter, Florida 33458, United States (2) Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States (3) Center for Nanostructured Materials, The University of Texas at Arlington, Arlington, Texas 76019, United States

Highly efficient and selective functionalization of ethane with the homogeneous Pt(bpym)/Cl\textsubscript{2} ("Catalytica-Periana") catalyst in concentrated H\textsubscript{2}SO\textsubscript{4} is described. Unexpectedly, the functionalization of ethane is ∼10\textsuperscript{6} times faster than methane and isethionic acid, ITA is generated containing both C-S and C-O bonds. This rate discrepancy was not anticipated since the turn-over limiting step for methane functionalization does not involve the alkane but instead involves the oxidation of inorganic Pt\textsuperscript{IV}. Experimental and computational studies reveal that while both methane and ethane functionalization proceeds by CH activation with Pt\textsuperscript{II} to generate a Pt\textsuperscript{II}-R intermediates at comparable rates, with fundamentally different functionalization and turnover limiting steps. In the case of methane catalysis, fast CH activation proceeds the rate limiting oxidation of non-methylated Pt\textsuperscript{IV} to Pt\textsuperscript{II}. In contrast, the C-H activation of ethane is rate limiting followed by rapid functionalization of the Pt-ET intermediate. The functionalization of ethane proceeds by rapid β-hydride elimination to ethylene and a Pt-hydride that, in contrast to the analogous Pt\textsuperscript{IV}-Me from methane CH activation, is rapidly oxidized by the H\textsubscript{2}SO\textsubscript{4} solvent to regenerate the Pt\textsuperscript{II} catalyst. Ethylene is converted to ETOH in H\textsubscript{2}SO\textsubscript{4} as a kinetic product, which is then rapidly converted to the thermodynamic product, ITA.

INOR 509

**Catalyst design and mechanism of base metal heterobimetallic catalysts for C-H borylation and C-C coupling**

Neal P Mankad, npm@uic.edu, Thomas J Mazzacano, Greyson W Walsdalf. Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607, United States
With an emphasis on catalyst design and mechanistic considerations, data will be presented that demonstrate the potential generality of using metal-metal cooperativity as a strategy for replacing noble metals with base metals in catalysis. Base metal heterobimetallics featuring earth-abundant metals such as Cu, Fe, Zn, Mn, Co, Mo, and W have been used to achieve catalytic C–H borylation and C–C coupling, crucial transformations that otherwise typically require Rh/Ir and Pd, respectively. Bimetallic mechanisms for these reactions will be discussed, as will catalyst design considerations that will aid in overcoming practical limitations of the new technologies. The long-term goal of transitioning to sustainable catalysts has implications regarding the environmental impact of chemical synthesis as well as the potential for homogeneous catalysis to contribute to global-scale problems such as energy conversion and storage.

INOR 510

Base metal catalysts for photochemical C–H borylation that utilize metal-metal cooperativity

Thomas Mazzacano, tmazzac2@uisuc.edu, Neal P Mankad. Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607, United States

Expanding on previous work with stoichiometric C–H borylation with single metal centers, heterobimetallic complexes have been synthesized for catalytic borylation. These complexes composed of two late metal bases and supported by N-heterocyclic carbene (NHC) ligands have shown high activity for catalytic C–H borylation of arene substrates. The unsupported metal-metal cooperativity, in the form of (NHC)Cu-Fe(CO)3 and (NHC)(Cl)Zn-Fe(CO)3, utilizes one electron processes of two different base metals that mimics the two electron processes of noble metals. This work represents the first known example of catalytic C–H borylation without requiring noble metal catalysts.

INOR 511

Aromatic C–H bond activation and functionalization by first row transition metals

Steven E. Kalman1, seken6@virginia.edu, Alban Pelti2, T. Brent Gunnoe1, Daniel H. Ess2, Thomas R. Cundari3, Michal Sabat4. (1) Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States (2) Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States (3) Department of Chemistry, University of North Texas, Denton, Texas 76203, United States (4) Department of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia 22904, United States

The utilization of Earth abundant first row transition metals for the activation and functionalization of strong aromatic C–H bonds is attractive due to their low cost and environmental benignity. Developing such reactions is challenging due to weak metal-carbon bonds relative to second and third row transition metals. As a result, examples of well-defined C–H activation by first row metals are relatively rare. Toward that end, we have demonstrated that Cp*Fe(CO)(NCMe)Ph(Cp* = pentamethylcyclopentadienyl) mediates highly regioselective aromatic C–H bond activation reactions under very mild conditions. This presentation will focus on our studies directed toward using first row transition metals for aromatic C–H bond activation and functionalization.

INOR 512

Investigation of the ancillary ligand effect on C–H activation at [Tp′Rh(L)]

Yunzhe Jiao, yji2@z.rochester.edu, James Morris, William W Brennessel, William D Jones. University of Rochester, Rochester, New York 14627, United States

The effect of the spectator ligand in [Tp′Rh(L)] has been investigated for the activation of hydrocarbons, specifically for L = phosphine vs isonitrile. To obtain a systematic control of ligand variation on C–H activation selectivities, we examined both the parent hydrocarbons (sp, sp2, and sp3) as well as the α-substituted methyl derivatives (-CH=X). The measured relative rhodium-carbon bond strengths display two linear correlations with the corresponding carbon-hydrogen bond strengths. While the stabilities of the C–H activation products are similar between phosphine and isonitrile systems, the RM–C=C–H values for these derivatives are noticeably different, allowing a quantification of the effect of replacing a tr-acceptor isonitrile spectator ligand with a σ-donor phosphine spectator ligand.

INOR 513

Development of palladium(II) catalysts for the oxidative hydroarylation of olefins

Benjamin A Vaughan1, bav8cs@virginia.edu, Tom Cundari2, T. Brent Gunnoe1. (1) Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States (2) Center for Advanced Scientific Computing and Modeling, Department of Chemistry, University of North Texas, Denton, TX 76203, United States

The formation of C–C bonds is one of the most prominent synthetic challenges in the field of chemistry. The majority of catalytic C–C bond-forming reactions proceed through activation of a carbon–halogen bond; however, the development of C–C bond forming reactions that proceed through transition metal-mediated C–H bond activation and functionalization is potentially useful. In particular, the hydroarylation of olefins, in which aromatic C–H bonds are added across C=C bonds, is a valuable synthetic target due to the prevalence of aromatic moieties in natural products, compounds of biological relevance, and large scale commodity chemicals. Vinyl and alkyln arenes are used in a wide variety of applications including polymerizations to form detergents, soaps, pharmaceuticals, and fuels. The conversion of alkyl arenes to vinyl arenes can be challenging due to the endothermic nature of the dehydrogenation. Thus, it is potentially beneficial to develop a one-step oxidative conversion of aromatics and olefins to vinyl arenes. Efforts in the development of palladium(II) catalysts for the direct conversion of aromatic and olefin substrates to selectively form vinyl arenes will be discussed.

INOR 514

Tris(pyrazolyl)borato silver(I) catalyzed C–H bond activation

Naleen B Jayaratna, nalezaen.jayarathana@mvavs.uta.edu, Sriparna Ray, H. V. Rasika Dias. Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, United States

Metal catalyzed C–H bond activation via carbene insertion has drawn a considerable attention over the past few years. It allows the incorporation of a variety of functionalities to alkenes in which readily available cheap materials are converted to more valuable products. Coinage metal ions supported by highly fluorinated ligands such as fluorinated tris(pyrazolyl)borates are excellent catalysts for this C–H bond activation chemistry. The activity of silver adducts are particularly noteworthy. The catalyst activity and selectivity can be fine tuned using the substituents on the supporting ligand.

INOR 515

Mechanochemistry and accelerated aging: Intercalation of inorganic and metal-organic architectures with minimum input of energy and solvent

Tomislav Friscic, tomislav.friscic@mcgill.ca. Department of Chemistry, McGill University, Montreal, Quebec H3A0B8, Canada

Inorganic and metal-organic materials, e.g. metal oxides, metal-organic frameworks (MOFs) and metalloids are at the forefront of modern materials science. However, syntheses and transformations of such materials are often encumbered with energy- and reagent- and solvent-intense procedures, which threaten to defeat their proposed use in hydrogen storage, carbon dioxide sequestration, light harvesting, etc. This presentation will delineate our work in developing simple, low-energy and largely solvent-free methodologies for transforming and interconverting inorganic and metal-organic structures. We will describe the recently introduced mechanochemical techniques for the rapid, templated transformations of metal oxides into porous MOFs and
metalldrugs. We will also address "accelerated aging," a novel technique which mimics the natural processes of mineral weathering for the energy- and solvent-reduced assembly of metal-organic materials and allows the solvent-free recognition and spontaneous separation of metals in the oxide form.

Besides enabling chemical transformations of metal oxides under mild conditions, the described solid-state methodologies present a unique opportunity to probe the factors controlling the assembly of metal-organic structures, without interferences of solvent, thermal gradients or counterions.


INOR 516
Exploring the roles of catalysis, templating and probability in the self assembly of giganatic inorganic clusters
Leroy Cronin, lee.cronin@glasgow.ac.uk.School of Chemistry, University of Glasgow, Glasgow, United Kingdom

How do high nuclearity inorganic and supramolecular assemblies form? Is there a general route to explore the mechanism and how can one given compound dominate from a combinatorial explosion of possibilities? Take the example of a recent molecule discovered in our laboratory; A palladium oxometalate (Pd₉)₈-ring cluster 3.3 nm in diameter, [Pd₉O₈(OAc)₁₆]²⁻ ([Pd₉O₈]²⁻ (Pd₈O₈)₂) which is formed in water just by mixing two reagents at room temperature and can be observed in solution within a few days of mixing and crystallised a few days later, see Figure. Yet in terms of probability if, one just considers the Pd ions alone of which there are three types in this structure, then the probability of formation of the is extremely small. It is therefore perhaps safe to assume that the structure therefore did not 'spontaneously' form by random chance, but a series of templating events, combined with the correct kinetics, allowed this cluster to be selected from the vast envelope of possible structures available in solution under the conditions under study. In this lecture I will outline a new theory that I believe could underpin the formation of almost all large inorganic architectures and lead to new design approaches and understanding never been possible before.

INOR 517
Supramolecular metal-organic frameworks assembled by weak M-H interactions (M = alkali metal)
L Zane Miller, Michael Shatruk, shatruk@chem.fsu.edu, D Tyler McQuade. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States

Diethylzinc, one of the oldest organometallic compounds, has many uses in synthetic chemistry. The low-coordinate environment of Zn and the relative weakness of Zn-C bonds render this compound highly reactive and air- and moisture-sensitive. We report a new type of reaction that leads to ZnEt₂ incorporation into oxo-centered clusters supported by alkali metal ions. The clusters assemble into unusual supramolecular frameworks via extensive M--H interactions that satisfy the coordination demands of the M⁺ ions.

INOR 518
Regulating secondary coordination spheres in metal complexes with non-covalent interactions
A. S. Borovik, aborovik@uci.edu. Department of Chemistry, University of California-Irvine, Irvine, CA 92697, United States

Non-covalent bonds stabilize and direct chemistry performed by metalloenzymes. With inspiration from architectural features found in proteins, we have utilized a bioinspired approach that incorporates intramolecular hydrogen bond donors proximal to metal centers to determine their effects on the properties of metal complexes. Our premise is that control of secondary coordination sphere interactions will promote new function within synthetic metal complexes. For instance, we have developed a series of complexes with terminal oxo and hydroxo ligands, which are surrounded by intramolecular hydrogen bond networks. Our work has established that hydrogen bonds can compete with pi-bonds to stabilize mononuclear oxometal complexes. This talk will discuss our recent efforts in understanding how intramolecular H-bonds regulate metal-mediated activation of small molecules and aid in stabilizing new chemical compounds.

INOR 519
Synthesis and properties of heterometallic cluster models of biological and heterogeneous water oxidation catalysts
Theodor Agapie, agapie@caltech.edu. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

Heterometallic clusters are found in biological and heterogeneous water oxidation catalysts, but the roles of different metal sites are currently not well understood. Targeting rational syntheses of models for these catalysts, triphenylbenzene moieties appended with pyridine and alkoxide donors were employed as multinucleating ligands for first-row transition metals. Trinuclear complexes were utilized as precursors to more elaborate metal oxide clusters. Tetrnuclear complexes displaying Mn₃M and Fe₃M motifs (M = Na⁺, Ca²⁺, Sr²⁺, Zn²⁺, Sc³⁺, Y³⁺) with varied number of bridging oxo ligands were synthesized and studied. The reduction potentials of these clusters span a window of over 1 V. With the pKₐ of metal (M) aqua complex as a measure of Lewis acidity, structurally analogous series of clusters display linear dependence between reduction potential and acidity. Implications for the function of oxygen evolving catalysts will be discussed.

INOR 520
Supramolecular strategies in transition metal catalysis
Joost NH Reek, j.n.h.reek@uva.nl. HIMS, supramolecular catalysis, University of Amsterdam, amsterdam, The Netherlands

The interface between supramolecular chemistry and transition metal catalysis has received surprisingly little attention in contrast to the individual disciplines. It provides, however, novel and elegant strategies that lead to new tools for the search of effective catalysts, 1 and as such this has been an important research theme in our laboratories. In this presentation I will focus on supramolecular strategies to control selectivity in transition metal catalysis, which is especially important for reactions that are impossible to control using traditional catalyst development. For substrates with functional groups we use substrate orientation effects to control selectivity, whereas for non-functionalized substrates we create cages around the active transition metal. Next to supramolecular control, supramolecular approaches appear ideally suited for the creation of large ligand libraries. The large number of catalyst that become available in this manner, asks for screening strategies and evolutionary approaches. A first academic example of catalyst selection
INOR 521

Synthesis of Cu$_2$(µ-S) and Cu$_2$(µ-S) complexes supported by N-heterocyclic carbene ligands

Junjie Zhai, Gregory L. Hillhouse, gh15@uchicago.edu, Department of Chemistry, University of Chicago, Chicago, IL 60637, United States

Copper-sulfur compounds have been identified and characterized in several metalloenzymes. Nitrous oxide reductase has a Cu$_2$(µ-S) center, known as "Cu$_S$" site, containing 4 Cu(II) centers, the active form for NO binding and reduction. Several copper-sulfur clusters that structurally mimic the "Cu$_S$" site have been reported, yet a copper-sulfur compound featuring a single bridging sulfur, as found in the "Cu$_S$" site, has remained a synthetic challenge. We will describe facile syntheses of [(IPr)Cu$_2$(µ-S)] and [(IPr')Cu$_2$(µ-S)] via intermolecular Si(CH$_3$)$_3$F elimination reactions. These new complexes are rare examples of Cu$_2$S compounds with only one bridging sulfur ligand.

INOR 522

Catalytic applications of heterobimetallic Zr/Co complexes

Christine M Thomas, thomasc@brandeis.edu, Seth L Marquard, Wen Zhou, Noam I Saper, Department of Chemistry, Brandeis University, Waltham, MA 02454, United States

Using a C$_5$-symmetric tris(phosphinoamide) ligand scaffold, heterobimetallic Zr/Co complexes featuring polarized metal-metal bonds have been synthesized. These compounds have been shown to undergo a variety of sigma-bond activation reactions involving both one- and two-electron oxidation processes. Interestingly, heterobimetallic Zr/Co complexes have proven to be excellent catalysts for the hydroxylation of ketones and aldehydes, while similar monometallic Zr and Co complexes are far inferior. The key to this reactivity is the ability of the Zr-Co bond to stabilize an effective "Zr(Ill)" equivalent, allowing radical one-electron transfer chemistry to occur at Zr. The results of hydroxylation reactions and insights into the unique stepwise one-electron mechanism at play will be discussed, along with future applications towards enantioselective ketone reduction and/or radical cyclization processes.

INOR 523

Molecular precursor approaches to the design and synthesis of catalytic materials for renewable fuels production

Daniel A. Rudy*, dan.rudy@nrel.gov, Nathan R. Neale*, Obadiah G. Reid*, Brian M. Leonard*, Svitlana Plypchenko†, (1) Chemical and Materials Science Center, National Renewable Energy Laboratory, Golden, CO 80401, United States (2) Department of Chemistry, University of Wyoming, Laramie, Laramie, WY 82071, United States (3) Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, United States

Metal-oxide-based materials are of interest for a variety of catalytic applications in the production of renewable fuels. Computational researchers have predicted novel, often complex, stoichiometries and morphologies to enhance key properties of mixed-metal oxides, making them even more attractive. For example, recent calculations have shown that co-doping anatase-TiO$_2$ with pairs of donors ($M^+$ = transition metals Ta, Nb, W, Mo) and acceptors ($E$ = main group elements N, C) to form Ti$_x$M$_{1-x}$O$_2$$_{1-x}$ materials would positively impact the resulting photoelectrochemical properties. However, the synthesis of these targets represents a formidable task to chemists and materials scientists. In contrast to traditional thermal and sol-gel approaches, non-aqueous molecular precursor approaches have demonstrated success in accessing complex compositions, often at low temperatures. This methodology delivers accurate control of stoichiometry and homogeneous incorporation of elements, even when low molar ratios of $M^+$ are desired. Here we present our recent preparation, characterization, and catalytic investigation of Ti$_x$O$_2$-based oxynitride materials utilizing Ti(OBu)$_4$ as the Ti source and nitrido precursors NiM(ON)(OBu)$_3$ ($M$ = Mo, W) to deliver both $M^+$ and N. The resulting oxynitrides, termed Ti$_x$M(ON) (where $x = 3$, 10, 20), retain 75-85% of the N from the precursor. Important for PEC applications, the materials demonstrate significantly red-shifted light absorbance versus TiO$_2$, with certain compositions absorbing into the infrared. The charge carrier dynamics and activity for photocatalytic degradation of methylene blue dye, both with visible light excitation, will be presented. Finally, the methodology and access to materials of interest outside of photocatalysis will also be discussed.

INOR 524

Four-step mechanism for the formation of supported-nanoparticle heterogenous catalysts in contact with solution: The conversion of Ir(1,5-COD)Cl/µ-Al$_2$O$_2$ to Ir(0)-µ/µ-Al$_2$O$_2$

Richard G Finke*, rfinke@lamar.colostate.edu, Patrick Kent, Joseph Mondloch, Department of Chemistry, Colorado State University, Ft Collins, Colorado 80523, United States

Recently we discovered that supported-nanoparticle formation from Ir(1,5-COD)Cl/µ-Al$_2$O$_2$ under H$_2$ in contact with acetone solution and in the presence of cyclohexene, produces Ir(0)-µ/µ-Al$_2$O$_2$ supported-nanoparticle heterogenous catalysts through significantly different nanoparticle formation kinetcs than the 2-step mechanism kinetcs we observed previously and which led to larger, Ir(0)-µ/µ-Al$_2$O$_2$ supported-nanoparticles (Mondloch, J. E.; Wang, Q.; Frenkel, A. I.; Finke, R. G. J. Am. Chem. Soc. 2010, 132, 9701; see also Mondloch, J. E.; Finke, R. G. J. Am. Chem. Soc. 2011, 133, 7744). Specifically, we have obtained kinetic, product stoichiometry, and particle-size defocusing evidence (a ±30% nanoparticle size distribution) consistent with and supportive of a previously undocumented 4-step mechanism of supported transition-metal nanoparticle formation in contact with solution. That 4-step mechanism consists of: slow continuous nucleation, A → B (rate constant $k_2$), autocatalytic surface growth, A + B → 2B (rate constant $k_3$), bimolecular aggregation, B + B → C (rate constant $k_4$), and secondary autocatalytic surface growth, A + C → 1.5C (rate constant $k_5$), where A is nominally the Ir(1,5-COD)Cl/µ-Al$_2$O$_2$ precursor, B the growing Ir(0) particles, and C the larger, catalytically active nanoparticles. The findings are significant in that they imply the first demonstration of a 4-step mechanism for supported-nanoparticle formation under any conditions (18 alternative mechanisms were disproven en route to the proposed 4-step mechanism). Moreover, when the present study is combined with our 2011 study, op cit., one now has precedent for two specific, balanced pseudo-elemeantary kinetic steps and their precise chemical descriptors—bimolecular particle aggregation, B + B → C, and autocatalytic agglomeration, B + C → 1.5C—steps involved in, for example, other significant processes in heterogeneous catalysis such as catalyst sintering.

INOR 525

Substituents of the isocyanide for carbonyl isosolateral substitution for middle and late transition metals

Joshua S Figueroa, jsfig@ucsd.edu, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92039, United States

The synthesis, characterization and reactivity of low-coordinate, low-valent transition metal complexes featuring m-terphenyl isocyanides are discussed. For several years, encumbering m-terphenyl isocyanide ligands have been utilized as isolobal surrogates to carbon monoxide for the explicit purpose of
generating stable and/or isolable complexes that embody the spirit of the binary unsaturated metal carbonyls. In several cases, m-terphenyl isocyanides of common substitution patterns (i.e. 2.6-(2,4,6-Me3C6H3)C3H5 and 2.6-(2,6-(iPr)2C6H3)C3H5) allow for the generation of unsaturated metal isocyanides that mimic their binary carbonyl analogues. However, in certain cases, this simple isocyanide for CO substitution fails with respect to the isolobal electronic structure analogy at the metal center. The factors governing this failure for middle and late transition metals are discussed and next generation m-terphenyl isocyanide ligands are presented that show promise in overcoming this apparent electronic structure breakdown.

INOR 526

Transition-metal free reduction of carbon dioxide to methanol using amphilic molecules

Frédéric-Georges Fontaine1, Frederic.Fontaine@chm.ulaval.ca, Marc-André Courtemanche1, Marc-André Légaré1, Jérémy Larouche1, Laurent Maron2. (1) Department of Chemistry, Université Laval, Quebec City, Quebec G1V0A6, Canada (2) INSA, Université de Toulouse, Toulouse, France

There has been a lot of interest in the past few years in the valorization of carbon dioxide to generate industrially relevant compounds, notably energy vectors such as methanol. We wish to report that phosphine-borane amphilic molecules can be used as efficient catalysts for the metal-free reduction of carbon dioxide using hydroboranes as reductant and hydrogen source to generate methoxyboranes that can be readily hydrolyzed to methanol. It was shown that in presence of B3H5SMEO it was possible to generate CH3OBor with turn-over frequencies over 800 h-1, making it one of the most active catalysts to date for this transformation. We will discuss about catalyst optimization and mechanistic investigation.

INOR 527

Silyl chelating ligands for directed C–H borylation

Behnaz Ghaffari1, Sean M Preshlock1, Robert E. Maleczka1, Shane W. Kr ska2, Milton R. Smith2, smithmil@msu.edu. (1) Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322, United States (2) Department of Process Chemistry, Merck Research Laboratories, Rahway, NJ 07065, United States

Most transition metal catalyzed C–H borylations of arenes give regioselectivities that are sterically determined. Nevertheless, directed C–H borylation, where a functional group in the molecule directs functionalization, have been reported. The catalysts with the broadest substrate scope to date have been heterogeneous ones that utilize surface supported phosphine ligands to generate coordinatively unsaturated intermediates that likely have two vacant coordination sites—one for functional group coordination and the other for C–H borylation.

Homogenous catalysts that mediate directed C–H borylation have been more limited in scope. This presentation will focus on silyl ligands that possess a pendant donor. These ligands generate catalysts that mediate directed borylations for a number of common directing groups.

INOR 528

Carbazole and pyrrole-based pincer platforms for supporting lutetium alkyl and hydride complexes

Paul G. Hayes, p.hayes@uleth.ca, Kevin R. D. Johnson, Breanne L. Kamenz, Matt A. Hannon, Jackson P. Knott. Department of Chemistry & Biochemistry, University of Lethbridge, Lethbridge, Alberta T1K 3M4, Canada

In the aim of preparing thermally robust organometallic complexes of rare earth metals, we recently synthesized a family of monooanionic pincer ligands comprised of phosphineimine donors attached to a carbazole core. Although these ligands support a variety of unusual species, many of the organometallic complexes have proven prone to diverse cycloelimination processes. In an effort to circumvent such decomposition pathways, our ligand platform systematically developed into two incarnations: one has replaced carbazole with a pyrrole core and the other features pyrazole, rather than phosphineimine donors. Several series of thermally stable rare earth organometallic and hydride complexes of these ligands have been synthesized. The evolution of the design of these pincer ligands, as well as the reaction chemistry of the corresponding organometallic complexes, will be discussed in detail.

INOR 529

Hydroaryloxylation of olefins, and C–O bond cleavage via dehydroaryloxylation of ethers, catalyzed by pincer-ligated iridium complexes

Michael C. Haibach, Nicholas Lease, Changjian Guan, Karsten Krogh-Jespersen, Alan S. Goldman, alan.goldman@rutgers.edu. Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, United States

We have reported that sterically unhindered pincer-ligated iridium complexes, such as precursors of the fragment (8PCP)Ir, catalyze the addition of phenolic O-H bonds across olefin double bonds. The catalysts show very high chemo- and regio-selectivity. Notably, the chemoselectivity is very different than that displayed by Bronsted acid catalysts or catalysts that operate via a ‘hidden Bronsted acid’ mechanism. The mechanism of this reaction has been studied by experimental and computational methods. Moreover, in the absence of added olefin, the reactions can be catalyzed to proceed in the reverse direction, i.e. alkyl aryl ethers can be dehydroaryloxylationized, giving good yields of the corresponding aryl alcohol and ether; this represents a novel catalytic C-O cleavage reaction. The dehydroaryloxylation can be further favored thermodynamically by coupling it with transfer-hydrogenation of the alkenyl product using a cycloalkane hydrogen donor.

INOR 530

Deconvoluting the black art of metallation: Understanding the benefits of placing two metals in the synthetic chemists’ palette

Robert E Mulvey, r.e.mulvey@strath.ac.uk, Charles T O’Hara. Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland G1 1XL, United Kingdom

The metallation reaction (transforming an inert C-H bond to a labile, more synthetically pliable C-metal bond) is one of the core tools of synthetic chemistry, widely employed in academic laboratories and in fine chemical and pharmaceutical manufacture. If lithium alkyls and lithium amides are regarded as first generation metalling agents, then currently a second generation is emerging in which co-operative effects between different components, often a metal amide combined with an organometallic compound or a metal salt, lead to reactivities and selectivities beyond the scope of conventional single-metal reagents.

Some of this bimetallic-executed metallation chemistry can be described as a black art since the nature of the metalling species as well as the structures and mechanisms involved are not generally well understood. Here, after presenting some key examples of the benefits of using such bimetallic reagents, we try to clarify some of these aspects by reporting new structurally characterised bimetallic reagents. We show that their seemingly simple metal-hydrogen exchange reactions with aromatic substrates are manifested through complex inverse crown arrangements. Using NMR spectroscopic studies (including DOSY experiments) we also ponder the question whether such reactions are genuinely bimetallic in execution or alternatively occur through two step monometallation-second metal trapping processes.

INOR 531
Isolation of the magic-size nanoclusters (CdSe)$_{13}$ and (CdSe)$_{34}$ as amine derivatives

Yuanyuan Wang, William E. Buhr. buhr@wustl.edu. Department of Chemistry, Washington University, St. Louis, MO 63130, United States

So-called magic-size semiconductor nanoclusters are analogous to the carbon fullerenes in that they are stable at only certain, discrete sizes such as (CdSe)$_{13}$, (CdSe)$_{34}$, (CdSe)$_{50}$, and (CdSe)$_{76}$. They have been observed as intermediates in nanocrystal synthesis for the past 30 years. Their precise identities were first established by mass-spectral characterization by Kasuya and coworkers in 2004. Until recently, magic-size nanoclusters have been obtained only as mixtures of the various discrete sizes. We have now isolated (CdSe)$_{13}$ as a variety of primary-amine derivatives such as [(CdSe)$_{13}$(n-ocetylamine)$_3$]. We have also isolated the larger-size [(CdSe)$_{34}$(n-ocetylamine)$_4$(di-n-pentylamine)$_2$], and have found these discretely sized nanoclusters to be potent nanocrystal precursors. The mechanisms of synthesis, spectroscopic properties, and reactivity of these CdSe nanoclusters will be presented.

INOR 532

Selective bond cleavage catalyzed by a silyl complex of a transition metal

Hiroshi Nakazawa, nakazawa@sci.osaka-cu.ac.jp. Chemistry, Osaka City University, Osaka, Japan

Selective strong bond cleavage with a weak bond remaining intact is one of the most challenging subjects because it is generally quite difficult. The use of a transition metal complex is one of the most promising approaches to achieve selective strong bond cleavage. This presentation shows several examples we have recently discovered where silyl migration in a coordination sphere serves as a trigger of strong bond cleavage.

Iron and molybdenum complexes can cleave C-CN bonds[1] in organonitriles (RCN), N-CN bonds[2] in cyanamides (R,NCN), and O-CN bond[3] in cyanates (ROCN), even though these C-CN, N-CN, and O-CN bonds are strong and hence difficult to cleave. In these cases, the key step to achieve E-CN bond cleavage (E = C, N, O) is migration of a silyl group from a metal center to the nitrile nitrogen atom coordination to the transition metal in a hapto-2 bond fashion. The detail reaction mechanism will be discussed.

References


INOR 533

Oxidative cross-coupling: A powerful tailoring for ideal C-C/C-Heteroatom bond formation from hydrocarbons

Aiwen Lei, aiwenlei@whu.edu.cn. College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, China

Our research focuses on the oxidative coupling to develop a novel and efficient bond-formation method between two nucleophiles. We have successfully developed three generations of oxidative coupling. In addition, in-depth understanding toward the reactions is the other focus. Recently, we revealed that transmetalation is the rate-determining step in Sonogashira Coupling and the activation enthalpy is obtained. 2) Stable Cu(I) catalyst/spectator Cu(II) species existed in Cu-catalyzed C-C coupling using IR. in situXANES/EXAFS evidence and kinetic investigations; 3) ate-complex is the intermediate in Cu-catalyzed C-H oxidation of benzothiazole using X-Ray absorption spectroscopy.

INOR 534

Iron-catalyzed C–H bond activation reactions

Eiichi Nakamura, nakamura@chem.s.u-tokyo.ac.jp. Department of Chemistry, The University of Tokyo, Tokyo, Japan

Iron is the most stable product in the element synthesis in a supernova, and is therefore the most abundant heavy element on the earth as well as in the space. This lecture will describe the use of iron as a catalyst for C–C and C–N bond formation through catalytic cleavage of Csp$^2$–H and Csp$^3$–H activation that we have investigated in the past decade. In a number of reactions, iron can now replace precious metal catalysts, and has attractive features including milder reaction conditions thanks to higher reactivity of iron, low cost and low toxicity. Iron catalysis of an illustrative example of research promoted by Japan’s Element Strategy Initiative (ESI).

INOR 535

Mobility and stability of weakly coordinating anions in transition- and main group metal catalyzed reactions

Vincent Gandon, vincent.gandon@u-psud.fr. Institut de Chimie Moléculaire et des Matériaux d’Orsay, Université Paris-Sud, Orsay, France

It is now clearly established that weakly coordinating anions (WCAs) are not always innocent bystanders in catalysis. The possible establishment of non-covalent interactions between the WCA and the ligands (Figure 1, A), the metal (B), the substrate (C), the metal and the substrate (D) ... can dramatically affect the selectivity. Thus, knowing where the anion actually lies during the catalytic process is of prime importance.

INOR 536

Transfer, metathesis, and catenation: Reactivity patterns emerging from borylenecomplexes

Holger Braunschweig, holger.braunschweig@uni-wuerzburg.de. Chemistry, University of Würzburg, Würzburg, Germany

Recent years have witnessed a significant development in the area of complexes with boron-centered ligands with respect to new and unusual coordination modes. [1] Selected examples include heterodinuclear 1 [2] and semi-briding borylenes 2 [3] as well as neutral 3, cationic 4 or anionic 5.
metallloborylenes and metal-base adducts thereof 3a [4]. These findings emphasize the close relationship between borylenes and carbonyls as well as carbenes, which constitute ligand systems of pivotal importance in organometallic chemistry.

Based on the gradual elucidation of the electronic structure of borylene complexes, specific reactivity patterns have started to emerge, in particular B–R transfer to transition metals [5] and unsaturated organic substrates [6] as well as metathesis reactions [7]. Thus, a variety of borylene-based functionalizations of organic and inorganic substrates will be presented, establishing borylenes as highly useful synths in organic and inorganic transformations, which are not accessible by conventional organoboronyl chemistry.


INOR 537
Multi-zonal crystalline systems: A based unique molecule self-assembled coordination helices that shows six primary zones

S. Russell Seidel1, chemdoc@gmail.com, Richard Wilkens2. (1) Department of Chemistry and Physics, Dowling College, Oakdale, NY 11769, United States (2) Department of Biology, Dowling College, Oakdale, NY 11769, United States

A unique multi-zonal crystalline composite based upon self-assembled coordination polymers is presented. The resultant system is composed of zones of essentially-isotropical helices, which, themselves, are made up of M(II) hexafluoroacetylacetone acceptor subunits and 4,4′-dithiodipyridine donor units. The helical shape of the constituent polymers derives from the ~80° C–S–S–C dihedral angle of the ditopic donor and also from the ~80° cis- nature of the ditopic acceptors. When the metal (M) is copper, the color is green. When the metal (M) is zinc, the result is colorless. In this work, composites showing six apparent, primary zoning events are presented. Microscopic photography of the crystals will be included.

INOR 538
Cross-hyperconjugated molecular sensors based on tetrasubstituted silanes

Musabbir A. Saeed, m.a.saeed@gmail.com, Ognej S Milanić. Department of Chemistry, University of Houston, Houston, TX 77204, United States

We report the synthesis, theoretical investigations, and sensing behavior of three different classes of silane-based cross-hyperconjugated molecular sensors. These molecules are based on the bis(arylthiyl)-bis(aryl)disilane, tetrakis(arylthyl)disilane, and asymmetric tetrakis(arylthyl)disilane scaffolds. Arylthiylsilanes were synthesized from the corresponding arylethynyl lithium compound with appropriate chlorosilane in dry THF. With donor-acceptor substitution, cross-hyperconjugated silane molecules have spatially isolated frontier molecular orbitals (FMOs). Their HOMO–LUMO gap, as well as the associated absorption and fluorescence properties, can be tuned through careful substitutions on the ethynyl group. Quantum mechanical calculations of this class of molecules allow us to expand the fundamental understanding of the cross-hyperconjugation.

INOR 539
Binding and extraction studies of sulfate by a tripodal hexa urea/thiourea-based receptor

Maryam Emami Khansari1, maryam.emami_khansari@students.jsms.edu, Avisht Pramanik1, Bryan M. Wongs2, Md. Alamgir Hossain1. (1) Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217, United States (2) Department of Chemistry and Department of Materials Science & Engineering, Drexel University, Philadelphia, PA 19104, United States

Anion binding by artificial neutral receptors has been a topic of major interest in recent years because of their potential applications for detection and extraction of biologically and environmentally relevant anions. Tripodal receptors bearing urea/thiourea functional groups are neutral receptors which can bind anions strongly by hydrogen-bonding interactions. They also benefit from the directional conformation of two NH groups. During the course of this study, we have synthesized a mixed urea/thiourea-based tripodal receptor containing three urea and three thiourea moieties by a multi-step reaction. The new receptor has been examined to evaluate its binding affinity for common inorganic anions by 1H NMR titrations in solution, showing high selectivity for sulfate. Further, it has been used to extract sulfate from aqueous phase. Details of binding and extraction studies will be included in this presentation.

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INOR 540
Ultra-sensitive anion detection by NMR: A supramolecular approach based on anion-modulated increase in chemical exchange rate

Loise Hélène Perruchoud3, 4, loise.perruchoud@mail.utoronto.ca, Xiao-an Zhang1,2,3. (1) Department of Chemistry, University of Toronto, Toronto, Ontario M5S3H6, Canada (2) Department of Environmental and Physical Sciences, University of Toronto Scarborough, Toronto, Ontario M1C1A4, Canada (3) Department of Biological Sciences, University of Toronto Scarborough, Toronto, Ontario M1C1A4, Canada

Nuclear magnetic resonance (NMR) spectroscopy is a powerful and versatile tool for monitoring dynamic processes. Conformational changes and binding events can produce drastic effects on NMR spectra in response to variations in chemical exchange rate. Here, an approach based on increasing the exchange rate through anion-induced conformational flexibility is presented, which allows ultra-sensitive anion detection in NMR spectroscopy. Our novel approach is based on a small synthetic sensor containing anion binding thioureido moieties and displaying conformational rigidity due to intramolecular hydrogen bonding (HB). In the rigid sensor, peak splitting of geminal protons (-CH2-) occurs and slow chemical exchange rate is observed in NMR. Conformational flexibility is generated by exposing the sensor to anions such that intramolecular interactions are competitively disrupted by formation of intramolecular HBs between anions and the thioureido protons. Thus, detection of anion-induced conformational flexibility is achieved through an increase in exchange rate in NMR: the two well-separated geminal proton signals merge into one sharp peak upon anion addition. NMR titration experiments with different anions also confirmed predictable anion selectivity. Strong HB acceptors, such as chloride or bromide, induced
significant conformational changes with only catalytic amounts of anions. We were therefore able to selectively detect anion species by NMR in the nM range, at a concentration more than 1000 folds lower than the sensor.

Figure 1. $^1$H NMR titration of sensor with increasing anion (Cl$^-$) concentrations.

INOR 541
Probing guest-binding capability of metal-organic supercontainers
Uma Sambasivam, uma.sambasivam@usd.edu, Dai Fengrong, Zhenqiang Wang. Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069, United States

Container molecules feature well-defined nanopores and can be utilized to explore a wide range of applications including storage, separation, and transportation of small molecules. We have recently developed a new family of container molecules, namely, metal-organic supercontainers (MOSCs). These MOSCs are assembled from sulfonylcalix[4]arene container precursors, metal ions, and carboxylate linkers. They feature a well-defined dual-pore architecture, containing both endo and exo cavities. Herein, we demonstrate the guest binding behavior of prototypical MOSCs in both solution and solid state. Various guests, such as small gases and organic dyes, have been screened to illustrate the host-guest chemistry of MOSCs. Preliminary results show that different para-substitutions of sulfonylcalix[4]arene units significantly affect the solid-state porosity of the MOSCs, whereas such variations have a much smaller influence on their solution binding behavior. These findings provide important guidelines for designing functional applications in synthetic container systems.

INOR 542
Piotr P Cholewa, pcp187@hw.ac.uk, Scott J. Dalgaro. Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, United Kingdom

The controlled formation of multi-component nanostructures is a persistent challenge of both supramolecular chemistry and crystal engineering, primarily because of the need to simultaneously control numerous different intermolecular interactions. Calix[4]arenes have been widely used in these fields of research due to their synthetic accessibility, cavity that can be used in host-guest chemistry and possibility of introducing functionality to the general molecular framework. However, surprisingly the p-carboxylatocalix[4]arenes have not yet been exploited in the formation of coordination polymers and 3D porous materials, especially considering that the resulting structures may potentially be tailored so as to present unique host cavities for use in gas sorption and separation. Recently we have demonstrated that p-carboxylatocalix[4]arenes can be utilised as useful building blocks in the assembly of both discrete and polymeric coordination compounds. In this talk we would like to present some of our recent advances in constructing a series of different supramolecular architectures. Through synthetic modification of p-carboxylatocalix[4]arene framework and thoughtful selection of co-ligands we will show that steric effects of co-ligands used and pre-organization of the calixarene building block has a dramatic influence over the assembly process, dictating the topology of formed supramolecular architectures (Figure 1).

Figure 1. By choosing an appropriate calixarene and a co-ligand one can construct either a 1D coordination polymer (A) or a discrete dimeric capsule (B).


INOR 543
Zn$^{2+}$ binding ability of a 1,2,3-triazole linked ferrocenyl pyridine chemosensor
J. Hugh Broome1, hughbroonem2@hotmail.com, Hannah C. Roberts1, Peter J. Cragg2, Karl J. Wallace1. (1) Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS - Mississippi 39406, United States (2) School of Pharmacy and Biomolecular Sciences, University of Brighton, Brighton, United Kingdom

The synthesis and binding studies of a triazole linked pyridine electrochemical probe will be presented. The chemosensor displayed a redox shift (0.07 V) upon the binding of Zn$^{2+}$ ions. $^1$H-NMR and electrochemical titrations of various equivalents of Zn$^{2+}$ ions as different salts were investigated to determine if the anion plays a role in the formation of the chemosensor Zn$^{2+}$ complex. A logβ of 5.1 was observed for the 1,2,3-triazole proton upon addition of various amounts of Zn(CIO$_3$)$_2$. Molecular modeling and 2D NMR were utilized to support the proposed structure of the complex and the role of the moieties in the coordination of the Zn$^{2+}$ ions.

INOR 544
Rhodamine triazole based chemosensors “podands” for detection of Fe$^{3+}$ and Al$^{3+}$
Erendra Manandhar1, emanandhar@gmail.com, Peter J. Cragg2, Frank R. Fronczek3, Karl J. Wallace1. (1) Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406, United States (2) School of Pharmacy and Biomolecular Sciences, University of Brighton, Brighton, United Kingdom (3) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States

A triazole based rhodamine molecular probes were synthesized by a “click” reaction and showed high selectivity for the Fe$^{3+}$ and Al$^{3+}$ ions over other metal ions in ethanol aqueous solution. Upon the addition of Fe$^{3+}$/Al$^{3+}$ ions, the spirocyclic ring of the compound was opened and a significant enhancement of visible color and fluorescence in the range of 500-600 nm was observed. The spirocyclic ring of the compounds was further confirmed by crystal structures. All compounds bind Fe$^{3+}$/Al$^{3+}$ in 1:1 stoichiometry in reversible manner as confirmed by Job’s plot, $^1$H NMR titration, ESI mass spectrometry and DFT calculation.

INOR 545
Probing anion-p interactions of metalcarbacycles with the π-acidic ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetratetrazine (bptz) by NMR spectroscopy
Helen T. Chifotides, chifotides@mail.chem.tamu.edu, Kim R. Dunbar. Chemistry, Texas A&M University, College Station, TX 77843, United States

The stabilities of the square metalcarbacycle [Fe(bptz)$_2$.CH$_2$CN].[BF$_4$]$\_2$ and several pentametalacarbacycles with octahedral anions (e.g., [Fe$_2$(bptz)$_2$.CH$_2$CN]$\_2$.SbF$_6$)$_2$) were probed in solution by $^1$H NMR spectroscopy. The studies provide unambiguous evidence for anion-based templation and firmly establish the instrumental role of templating anions in favoring and stabilizing Fe(II) metalcarbacycles of specific nuclearities. The formation of the polygons is facilitated by synergistic anion-p interactions, which are an integral part of metalcarbacycle templation, with low activation energies of anion
encapsulation. Moreover, the interconversion studies between the Fe(II) metalloccycles under the competing influence of the anions, monitored by 1H NMR spectroscopy, underscore the remarkable stability of the metallapentacycles and the critical role of the anions in their templation.


INOR 546

4-Hydroxy-3-azomethine coumarin based ratiometric chemosensors for the detection of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}

Aaron B. Davis,1 Aaron.Davis@eagles.usm.edu, Jessica R. Panelia,1 Rachel E. Lambert,1 Frank R. Fronczek,1 Karl J. Wallace1. (1) Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States (2) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States

A series of coumarin derived molecular probes show a ratiometric response to Co^{2+}, Ni^{2+}; Cu^{2+}, and Zn^{2+} over other metal ions. The sensor showed a 65 nm hypsochromic shift in the UV-Vis spectrum (1:1 DMSO-TRIS, 10 mM pH 7.5), whereby the fluorescence spectrum showed a 20 nm bathochromic shift. The binding constants were calculated by the double reciprocal plot for each metal and found to be Log K_{11} = 4 and Log K_{12} = 10 : Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, which are in agreement to the calculated values by HypSpec. Fluorescence microscopy experiments were carried out in ethanol solution to detect Cu^{2+} in biological media.

INOR 547

Supramolecular chemistry of N-substituted benzo-2,1,3-selenadiazoles

Lucia Myongwon Lee, leem35@mcmaster.ca, Ignacio Vargas-Baca. Department of Chemistry & Chemical Biology, McMaster University, Hamilton, ON L8S4M1, Canada

The potential of main-group secondary-bonding in supramolecular chemistry is well illustrated by the derivatives of the 1,2,5-Telluradiazole ring. Their dimers and supramolecular ribbons are assembled by the (Te-N), supramolecular synthon, a virtual four-membered ring defined by two antiparallel Te-N contacts. Such interactions are strong enough to overcome moderate steric hindrance by allowing distortions that simultaneously confer functionality to the structure. For example, a twist of the supramolecular synthon creates a noncentrosymmetric feature that propagates generating a lattice with measurable second-order nonlinear optical response. Despite their versatility, the widespread application of telluradiazoles is hampered by their sensitivity to moisture. Their selenium congeners are considerably more robust but form much weaker intermolecular links. Consequently we have become interested in dicationic molecules capable of infinite catenation. DFT calculations have provided a rationale for the strengthening of the secondary links and explained the ability of halide binding to compete with the [Se-N] supramolecular synthon.


INOR 548

Decontamination of toxic fluoride from water by a novel class of synthetic receptor

Syed A Haque, syed.acce.du@gmail.com. Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 32321, United States (1) Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 32321, United States Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 32321, United States (2) Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, United States Materials Chemistry Department, Sandia National Laboratories, Livermore, California 94551, United States Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 32321, United States

Fluoride is a known toxic species when its concentration exceeds more than 2.0 ppm level in water, causing severe damage of teeth and kidney. Therefore, it is urgent to develop new fluoride receptors that can bind and remove fluoride from water. Because of the high electronegativity of fluoride, this tiny anion is found as a species rather than free state in an aquatic system. During this study, we synthesized a new thiophene-based azamacrocyclic receptor with extended space which upon investigation was found to efficiently capture hydrated fluoride from the environment system.

INOR 549

Synthesis and anion binding studies of pyridine-based macromonocyclic ployamine

Md Mhahabubur Rhaman,1 oxindb@yahoo.com, Douglas R. Powell,2 Md. Alamgir Hossain,1 (1) Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi 39217, United States (2) Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, United States

Anions play some vital roles in the environment and in biological systems. In order to mitigate those problems, the field of anion encryption has raised attention over decades and has been developing with diverse receptors capable of hosting different anions in solution and solid state. Among the various systems, macroyclic polyamines are promising because they carry positive charge through protonation and mimic many biological polyamines. Polymacro cyclics with benzene spacers are effective anion receptors under protonation in water. Consequently we have become interested in polymacro cyclics with heteroaromatic spacers to figure out the role of the spacer to anion binding. And so during the course of our studies, a polyazamacrocycle was synthesized using 2,6-pyridinedicarboxaldehyde spacers and N-methyl-2,2'-diaminodiethylamine linkage from Schiff base condensation followed by reduction. The receptor was studied for anions (F−, Cl−, Br−, I−, NO3−, CO32−, SO42−, H2PO4−) by 1H NMR spectroscopy technique in water and single crystal X-ray diffraction method. The 1H NMR titration studies reveal that the receptor forms a 1:1 complex with the anion, showing the highest binding constant with sulfate. In this poster, binding studies in both solution and solid will be presented.

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INOR 550

Extended superstructures developed from supramolecular anion-π templated metalloccycles

Jill Frank, jill.frank@chem.tamu.edu, Brad Ewers, James D. Batteas, Steven Wheeler, Kim R. Dunbar. Department of Chemistry, Texas A&M University, College Station, TX - 77840, United States

Optimization of self-assembly processes that incorporate directional bonding of geometrically predisposed building blocks has led to the development of a plethora of molecular superstructures in the literature. Molecular polyhedra are of high interest due to potential applications of highly symmetric cage-like architectures as molecular containers and reaction flasks. Typically, polygonal metalloccycles are inhibited from undergoing further reactions at the metal vertices because of coordinative saturation and non-labile "capping" ligands, but we have in hand a family of supramolecular anion-π templated
metallacycles with two labile acetoni trile ligands per vertex. Bridging the vertices of pentagonal metallacyclic building blocks with linear bis-bidentate linkers or triodal bis-bidentate linkers is predicted to lead to truncated icosahedral and rhombicosidodecahedral architectures respectively. In this vein, we are preparing molecular polyhedra by reacting anion-containing pentagonal metallacycles with bis-bidentate organic linkers including tertephthalic acid and tetrapyrido[3,2-a:2',3'-c:3,2'-h:2',3'-j]phenazine. Thermodynamic control over the formation of the polyhedral structures is critical for synthesizing closed, symmetrical architectures with a uniform diameter. Characterization is being performed using TEM, AFM, and STM imaging methods and molecular mechanics and DFT calculations are being carried out to determine the plausibility of using various molecular linkers vis-à-vis geometric and thermodynamic considerations. By optimizing the polyhedral structures using an MM potential, we aim to be able to qualitatively estimate via DFT the overall thermodynamic stability for the organic bis- and tri-bidentate linkers. Successful shape control through self-assembly reactions and qualitative thermodynamic analysis of pentagon-linker interactions is leading to targeted polyhedral assemblies exhibiting unique structural and physical properties.

INOR 551
New dipodal urea-based receptor for selective binding of fluoride
Abdallah Gana, abdallah.gana@icloud.com, Avijit Pramanik, Frank R. Fronczek, Md. Alamgir Hossain, (1) Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi 31217-0190, United States (2) Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, United States
Among various important anionic analytes, fluoride is one of the most significant anions due to its critical role in dental care and treatment of osteoporosis; therefore, fluoride binding and recognition by synthetic receptors is attracting a growing interest. Fluoride is found more frequently in different sources of water but with higher concentrations in groundwater due to the presence of fluoride-bearing minerals. Because of duplicitous nature of fluoride, it is important to design the artificial receptor for extracting, removing and separating this particular anion from fluoride-bearing minerals or fluoride-containing systems. During this study, we have synthesized a new p-cyano based bis-urea receptor from the reaction of 2,2'-Diamino-N-methyl diethylamine with p-cyano isocyanate under refluxed condition in CH2Cl2. In the solid state, the bis-urea receptor binds halides through N–H···halide interactions. In solution, the host binds the halides with an order of I<Br<Cl<Br. In this poster, the detailed studies of this receptor for halides will be discussed.

INOR 552
Synthesis and binding studies of hexaurea-based tripodal receptors
hyppollite Djounda, hyppollitedjoudia@yahoo.com, Avijit Pramanik, Md. Hossain Hossain. Department of Chemistry and Biochemistry, Jackson state university, Jackson, ms 31217, United States
Urea-based neutral receptors are important for anion recognition, which can bind an anion by strong hydrogen bonding interactions. In particular, a receptor with multifunctional urea groups is expected to bind anions strongly, leading to a significant selectivity for a target anion. During this study, two new receptors bearing hexaurea functionalities have been synthesized from multi-step synthetic techniques. The new compounds were characterized using NMR, IR, and Mass spectroscopy. Qualitative and quantitative analyses of 1H NMR as well as the infrared spectroscopy enable us to confirm the structure of the new receptors. The anion binding studies of these receptors were performed by 1H NMR titrations in DMSO-d6. In this poster we will present the details of synthetic procedures and the results of anion binding titrations in solution.

INOR 553
Cap-type Schiff base acting as fluorescence sensor for zinc(II) and colorimetric sensor for iron(II), copper(II), and zinc(II) in aqueous media
Yu Jeong Na, yeureen@hanmail.net, Ye Won Choi, Ga Rim You, So Dam Yang, Cheal Kim. Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul, 139-743, Republic of Korea
A simple and low cost chemosensor is described. This sensor could simultaneously detect three biological important metal ions through fluorogenic (Zn²⁺) and chromogenic (Fe²⁺, Cu²⁺, and Zn²⁺) methods in aqueous solution. The sensor could function as a "turn-on" fluorescence receptor only to Zn²⁺ ions. In addition, the sensor could be successfully applied to the detection of intracellular Zn²⁺. Meanwhile, the sensor displayed an obvious red color upon selective binding with Fe²⁺. Therefore, the sensor could serve as a useful tool for the discrimination of Fe²⁺ from Fe³⁺ in aqueous media. Moreover, the sensor also showed color changes from yellow to colorless upon selective binding with Zn²⁺ and Cu²⁺, respectively. The detection limit of the sensor for Cu²⁺ (1.5 mM) is far below the guideline of the World Health Organization (30 mM) as the maximum allowable copper concentration in drinking water, and therefore it is capable of being a practical system for the monitoring of Cu²⁺ concentrations in aqueous samples. These results provide a new approach for selective recognizing the most important three trace elements in the human body simultaneously, for Zn²⁺ by emission spectra and Fe²⁺, Cu²⁺, and Zn²⁺ by the naked eye.

INOR 554
Selective colorimetric and fluorescent chemosensor for Hg²⁺
Myoung Mi Lee, ohno801126@nate.com, Jae Jun Lee, Sun Young Lee, Yong Sung Kim, Cheal Kim. Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul, 139-743, Republic of Korea
A new NBD-based sensor bearing a dipicolyamine derivative, (2-pyridylmethyl)(2-quinoylmethyl)amine (1), was synthesized, and its chromogenic and fluorogenic behaviors toward various metal ions were investigated in methanol solution. Chemosensor 1 selectively detected Hg²⁺ ions through color change from yellow to colorless. In addition, chemosensor 1 exhibited highly Hg²⁺-selective ON-OFF fluorescence quenching behavior and was shown to discriminate various competing metal ions, particularly, such as Cu²⁺, Ag⁺ and Pb²⁺. The binding mode of 1-Hg²⁺ was found to be a 1:2 complex formation, based on Job plot and ¹H NMR titration.

INOR 555
Multifunctional colorimetric and fluorescent chemosensor for Cr³⁺ and Al³⁺
Gyeong Jin Park, qkrnd112@naver.com, Seul Ah Lee, Hyun Yong Jo, Ji Hun Lee, Cheal Kim. Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul, Republic of Korea
A chemosensor based on naphtho and quinoline moieties has been synthesized for the detection of Cr³⁺ and Al³⁺ as a colorimetric and fluorescent sensor in methanol. The sensor exhibited selective and sensitive recognition towards Cr³⁺ via color change from yellow to colorless. Moreover, it showed a significant fluorescence enhancement (50-fold) towards Al³⁺.

INOR 556
New multimodal platforms of nanodiamond for molecular imaging
Nanoparticles (NP) are currently the subject of active researches in the context of medical imaging. The possibilities of applications are numerous and the versatility of these nanoparticles allows their modulations to serve as imaging probes (diagnostic), drug-delivery vectors (therapeutic) or both (theranostic). The main objective of this work is to develop and characterize an effective multimodal nanodiamond-based probe for medical imaging and specific of apoptosis. The functionalization of the platform involves the grafting of an apoptosis-specific vector, an optical agent and a paramagnetic complex.

The first part of this work consisted in the characterization of the platform based on nanodiamond powder with size (DLS, TEM and XRD), morphology (SEM), stability and physicochemical analysis methods (turbidimetry and FTIR). Then, an oxidation step was performed in order to increase the number of carboxylic groups on the NP surface. The analysis of the TEM pictures confirmed that the treatment induced a size-reduction of nanodiamonds in solution.

The second part concerned the preparations of the specific peptide and the paramagnetic complex. The synthesis of the peptide was carried out using an automated synthesizer and its structure was confirmed by mass spectrometry and NMR. The ligand derived from DO3A was synthesized starting from N6-carbobenzyloxy-L-Lysine and cyclen and then complexed with gadolinium chloride to provide the paramagnetic complex. The characterization by relaxometry and NMRD profiles has proved the efficiency of this new complex as T₁-agent.

The last step of the work has been dedicated to the development and characterization of the new multimodal probes. Two samples of diamond NP have been reserved for the grafting of the apoptosis-specific vector and one of the optical agents (fluorescein trifluoroacetate or methyl violet). A third sample of NP was grafted with the MRI contrast agent.

In conclusion, the coupling of the platform with fluorescein has been demonstrated by fluorescence spectroscopy. In addition, optical microscopy study conducted on cell cultures gave evidence of the efficiency of graftings. Indeed, the experiments demonstrated the affinity of NP with Jurkat cells stimulated by anti-Fas. Results demonstrated clearly the effectiveness of the MRI nanodiamond-based probe for medical imaging.

**INOR 557**

**Enable early detection of liver metastasis with desired stability and sensitivity by protein MRI contrast agents**

Shenghui Xue¹, xuesh15@hotmail.com, Hua Yang¹, Jingjuan Qiao¹, Fan Pu¹, Robert Long², Khan Hekmatarya³, Hans Grossniklaus², Zhi-Ren Liu², Jenny J Yang¹. (1) Department of Chemistry, Georgia State University, Atlanta, GA 30303, United States (2) Department of Ophthalmology, Emory University, Atlanta, GA 30322, United States (3) Department of Radiology, Emory University, Atlanta, GA 30322, United States (4) Complex Carbohydrate Research Center, University of Georgia, Athens, GA 30629, United States (5) Department of Biology, Georgia State University, Atlanta, GA 30303, United States

One of the major barriers limiting the application of MRI to detect small lesions and metastasis at the early stage is the lack of desired MRI contrast agents capable of enhancing the contrast between normal tissues and tumors with high relaxivity, adequate retention time, and mitigated metal toxicity. Here, we have created a novel platform for developing protein MRI contrast agents (ProCAs) by designing several metal binding sites embedded into a scaffold protein to significantly improve both r₁ and r₂ relaxivities while achieving unprecedented metal selectivity that are 10⁻² - 10⁻³ fold greater than that of clinical contrast agents. With additional improvement in in vivo distribution and retention time, ProCA32 also exhibits > 100 fold increase in in vivo dose efficiency. The unique high relaxivity in both r₁ and r₂ of ProCA32 enables the ratiometric MRI detection of uveal melanoma micrometastatic liver tumor size down to ~0.16 mm largely improving the current detection threshold of 20 mm (stage 3 or later). ProCA is expected to fill in a major gap in preclinical and clinical MRI applicationsto enable non-invasive and early detection of primary liver tumors and metastases, understand metastatic mechanism, prognosis as well as image-guided treatment and drug delivery.

**INOR 558**

**Comparison of divalent transition metal ion amide- and alcohol-appended paraCEST MRI contrast agents**

Abiola O Olatunde¹, olatunde@buffalo.edu, Jordan Cox¹, Joseph A Sperry², Jason B Benedict³, Janet R Morrow¹. (1) Department of Chemistry, University at Buffalo, Amherst, New York 14260, United States (2) Department of Cell Stress Biology, Roswell Park Cancer Institute, Buffalo, New York 14263, United States

The use of divalent transition metal ion-based paramagnetic chemical exchange saturation transfer (paraCEST) agents has been reported as a new approach for creating promising MRI contrast agents. Fe³⁺, Co²⁺, and Ni²⁺ bind to amide-and alcohol-appended diaza crown ether and azamacrocycles to give seven- and six-coordinate complexes used as paraCEST agents. Alteration of the metal center or pendant arm produces stable complexes with different geometries. In the case of amide-appended paraCEST agents, 1,4,7,10-tetraakis(carbamoylmethyl)-1,4,7,10-tetraazacyclododecane coordinates Co³⁺ through three pendant amides, 1,4,8,11-tetraakis(carbamoylmethyl)-1,4,8,11-tetraazacyclotetradecane binds to Co³⁺ and Ni²⁺ through two amide pendants, 7,13-bis(carbamoylmethyl)-1,4,10-trioxa-7,13-diazacyclotetradecane binds through two trans amide pendants. MRI using a CEST-FISP protocol gives images as low as 250 μM paraCEST-agent. The paraCEST properties of these complexes will be compared.

**INOR 559**

**Can Gd,TCS₂ be a new motif of contrast agent for MRI? Unexpected slow water exchange arising from the tri-Gd³⁺ cluster sandwiched by two TCAS ligands (TCAS = thiacalix[4]arene-p-tetrasulfonate)***

Nobuhiko Ikii, iki@m.tohoku.ac.jp, Eszter Boros1, Mami Nakamura1, Kazu Shinoda1, Peter Caravan2. (1) Graduate School of Environmental Studies, Tohoku University, Sendai, Miyagi 980-8579, Japan (2) The Athinoula A. Martinos Center for Biomedical Imaging, Department of Radiology, Massachusetts General Hospital, Harvard Medical School, Boston, Massachusetts 02129, United States (3) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-8577, Japan

In aqueous solutions, Gd³⁺ and thiacalix[4]arene-p-tetrasulfonate (TCAS) self-assembled to form a complex Gd₃(TCAS)₄ in which a Gd³⁺ core is sandwiched by two TCAS ligands as confirmed by EXAFS. Acid-catalyzed dissociation reaction yielded the solvolytic dissociation rate constant k₆ = (2.73 ± 0.67) × 10⁻⁵ s⁻¹ (25 °C), corresponding to a half-life of 7.1 h at pH 7.4. Furthermore, transmetalation with Zn²⁺ in the presence of phosphate confirmed the persistence under the physiological conditions: ca. 27% of the complex dissociated after 100 h. The high kinetic stability can be rationalized by the rigid coordination geometry supported by the sandwiched structure, which did not allow rearrangement of the coordination geometry of Gd³⁺ from the initial 8 coordinate to one suitable to 9 coordinate transition state. By comparison, Yb₂(TCAS)₄ showed much higher kinetic stability. The longitudinal relaxivity of Gd₃(TCAS)₄ (per Gd³⁺) was r₁ = 5.83 mm⁻¹s⁻¹ at 20 Hz (37 °C, pH 7.4), which was about 50% higher than conventional contrast agents such as Gd-DOTA and Gd-DTPA. Upon binding to human serum albumin (HSA), r₁ did not increase, suggesting either an extremely slow water exchange rate (k₆) or displacement of the water ligands upon binding to the protein. In fact, ¹⁷O NMR elucidated k₆ = (1.0 ± 0.3) × 10⁻⁵ s⁻¹ (25 °C), which is 1–4 orders of magnitude slower than common contrast agents. This slow water exchange rate is responsible for the low relaxivities observed in the presence and absence of HSA, despite the large number of coordinated water molecules to Gd³⁺ (q ~ 2). The slow water exchange rate of Gd₃(TCAS)₄...
can be also attributed to the rigid coordination geometry to de-stabilize the transition state. Thus, the high kinetic stability and moderate relaxivity can be rationalized by the sandwich structure of Gd$_3$TCAS$_2$.

INOR 560

Ratiometric imaging of Cu(I) using a thulium-based $^{19}$F MRI contrast agent

Evan A Weitz, weitz042@umn.edu, Małgorzata Marjanska, Valerie C Pierre. (1) Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States (2) Department of Radiology, Center for Magnetic Resonance Research, University of Minnesota, Minneapolis, Minnesota 55455, United States

Disruption of copper homeostasis and its redox chemistry is implicated in the pathologies of neurodegenerative disorders such as Alzheimer’s disease. Unfortunately, since no current probe enables the imaging of copper directly and accurately in vivo, its role in Alzheimer’s disease is poorly understood. We present the design and evaluation of a ratiometric, thulium-based contrast agent for imaging Cu(I) by MRI. MRI is an attractive imaging method since it is non-invasive, non-radioactive, and provides 3-D spatial resolution directly in vivo. Fluorine-based MRI eliminates background signals and has a large chemical shift range which enables fluorines in different environments to each be imaged independently. This in turn allows for the development of ratiometric, responsive contrast agents whereby the total probe concentration and the concentration of the analyte can be independently determined. With our probe, Cu(I) can be measured by two independent ratiometric responses: 1) differential paramagnetic relaxivity enhancement (PRE) of two distinct fluorines, and 2) conformationally-induced lanthanide-induced shift. The structure, synthesis, and MRI evaluation of our responsive contrast agent will be described.

INOR 561

Correlation of $^1$H relaxivities with solution speciation and structural features in a series of Mn(II) complexes of cyclen derivatives

Breanna G. Craft, blis@wesleyan.edu, Sarah A. Hensiek, Kelly T. How, T. David Westmoreland. Department of Chemistry, Wesleyan University, Middletown, CT 06459, United States

Mn(II) complexes of cyclen ligands tetra-substituted with amide, carboxylic acid, or phosphonic acid side arms are of interest due to the insights they can provide into the chemical origins of their pH-dependent relaxivities. A detailed investigation of the speciation of these complexes by potentiometric titration and solution IR spectroscopy has led to comprehensive models of the binding and protonation equilibria and, in some cases, the solution structures of the complexes. On the basis of these models we have assigned specific $^1$H longitudinal relaxivity values to each species present in the pH range 2-10. Details of the solution structures have also been probed through the use of diamagnetic analogs which can be characterized by conventional NMR techniques. In addition, variable temperature $^1$H studies provide insights into the chemical mechanisms responsible for exchange of coordinated protons with those of bulk water. These results have been applied to the design and synthesis of a new Mn(II) complex of a cyclen-based ligand with mixed carboxylic acid and amide side arms. The chemical, structural, and NMR properties of this complex will be presented.

INOR 562

Optimization of water exchange in PARACEST agents for in vivo imaging

W. Shirangi K. Fernando, wk0900200@utdallas.edu, Piyu Zhao, Garry E. Kiefer, Yunkou Wu, A. Dean Sherry. (1) Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080-3021, United States (2) Advanced Imaging Research Center, UT Southwestern Medical Center, Dallas, Texas 75390-8568, United States (3) Macrocyclics Inc, Dallas, Texas 75235, United States

Most current clinical MRI contrast agents are based upon shortening the longitudinal ($T_1$) and/or transverse ($T_2$) relaxation times of protons in tissue water thereby allowing differentiation of highly vascularized regions of tissue from non-perfused regions. Although widely used, the physical properties of such agents have limitations for further development as MRI contrast agents that might provide biological or functional information. MRI contrast agents based upon CEST (Chemical Exchange Saturation Transfer) have emerged to overcome these limitations. Here, image contrast is obtained by radiofrequency saturation of slowly exchanging protons or water molecules bound to the contrast agent which subsequently exchange into and alter the bulk water proton signal. The unusually slower water exchange kinetics of Ln-DOTA-tetraamide complexes has drawn considerable attention as potential PARACEST agents. Since the effectiveness of a CEST agent critically depends on slow water exchange between Ln$^{3+}$ bound inner-sphere water protons and bulk water, the bound water lifetime of a contrast agent, $\tau_w$, is one key parameter to be considered in designing an effective PARACEST agent. Previous studies have shown that charge, polarity and bulkiness of the side chains of these complexes all have an impact on the bound water lifetimes of these complexes. The current project focuses on the design an effective PARACEST agent that can be activated using low power RF pulses and has favorable charge and solubility properties suitable for injection into animals for in vivo imaging. The results show that LnDOTA-tetraamide complexes containing a combination of negatively charged groups and phosphonate ester groups yield very desirable properties for in vivo imaging.

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Effects of coordination geometry on hydration state

Katherine M Payne, paynekat@pdx.edu, Mauro Bottà, Mark Woods. (1) Department of Chemistry, Portland State University, Portland, OR 97201, United States (2) Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale “Amedeo Avogadro”, Alessandria, Italy

The coordination chemistry of LnDOTA chelates exhibits an abrupt change at Ho$^{3+}$ at which point lanthanide contraction induces a sudden reversal in the energy of the twisted square antiprismatic (TSAP) geometry. This change in solution state coordination chemistry was initially ascribed to a change in the hydration number (from 1 to 0) of the TSAP geometry. We recently published the crystal structure of HoDOTMA which reveals that the TSAP geometry of HoDOTA-type chelates is in fact partially hydrated in the solid state, casting doubt on the hypothesis that a decrete dehydrated TSAP isomer can exist in solution.

A more complex picture of hydration in HoDOTA-type chelates is also indicated by variable temperature $^1$H NMR studies into coordination isomer distribution of HoDOTA and DOTMA. The energy of each coordination geometry changes with temperature (and water exchange rate). In order to gain a more profound understanding of these systems and the the possible interplay between water exchange, chelate hydration, and coordination chemistry variable temperature $^1$H NMRD profiles and $^{17}$O relaxation studies were undertaken on HoDOTA and HoDOTMA. The relaxivity of each chelate exhibits a different and yet highly unusual field dependence. Fitting these data to theory provides new understanding of the coordination chemistry of late Ln$^{3+}$ chelates of DOTA and a useful assessment of how the hydration state (a key parameter in contrast agent design) of these chelates changes with coordination chemistry.

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Development of lipophilic Gd(III)-based MRI contrast agents for long-term cell labeling applications

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New generation of enzyme-activated MRI contrast agents
Sarah G Kamper, sarahkamper2013@u.northwestern.edu, David M Ballweg, Keith W MacRenaris, Jeff Krimmel, Teresa Anne Mills, Thomas J Meade. Departments of Chemistry, Molecular Biosciences, Neurobiology, Radiology, and Biomedical Engineering, Northwestern University, Evanston, IL 60208, United States

The ability to delineate and understand biological processes in vivo using a non-invasive technique would greatly improve our understanding of biological developmental processes and ultimately, the diagnosis of diseases. To this end, we have developed a new generation of bio-activated, self-immolative MRI contrast agents that function as reporter probes of in vivo enzyme activity using β-galactosidase. This new class of agents has improved kinetics of activation allowing for detection on a biologically relevant time scale. Optimization of this generation of probes includes a back-binding coordination moiety incorporated into a linker arm to further inhibit water access to the Gd(III) ion prior to enzymatic activation. Here, we describe the characterization of this class of agents and our strategy to optimize the change in relaxivity upon activation and in vitro analysis.

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Design and synthesis of a series of progesterone receptor-targeted MR imaging probes
Taryn R Townsend1, taryntownsend2014@u.northwestern.edu, Georgette Moyle-Heyrman1,2, Preeti A Sukerkar1, Keith W MacRenaris1, Joanna E Burdette1, Thomas J Meade1. (1) Departments of Chemistry, Molecular Biosciences, Neurobiology, and Radiology, Northwestern University, Evanston, IL 60208, United States (2) Department of Medicinal Chemistry and Pharmacognosy, University of Illinois at Chicago, Chicago, IL 60607, United States

The presence and activity of steroid receptors such as the progesterone receptor (PR), is an important diagnostic and prognostic marker for hormone dependent cancers: namely breast, uterine, and ovarian. Determination of receptor status can inform physicians of the progression of a tumor as well as identify treatment options. The loss of PR expression correlates to more aggressive phenotypes. Immunohistochemical assays are currently used to measure receptor status but require tissue biopsy. Therefore, the development of a noninvasive imaging technique that would determine receptor status would have significant impact on early detection and costs. Magnetic resonance imaging (MRI) techniques can perform longitudinal studies by allowing a series of measurements to be conducted over time. Our research has focused on the development of PR-targeted MR probes to detect the progesterone receptor status in vivo (Figure 1). Optimization of our previously reported agents has successfully led to contrast agents with increased water solubility, retention of receptor binding affinity and PR activation, and preferential accumulation in tissues that up-regulate PR.

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δ-substituents in LnDOTA-tetraamide chelates: Their position and effect on water exchange and CEST
Jacqueline R Slack, jslock@pxd.edu, Mark Woods. Chemistry, Portland State University, Portland, OR 97201, United States

Generating MR image contrast from exogenous contrast media though chemical exchange saturation transfer (CEST) offers several exciting new possibilities, such as multi-coloured imaging, the interleaving of pre- and post-contrast images, and the potential to perform ratiometric metabolic imaging. The major limitation of the deployment of CEST imaging is the comparatively high detection limits of exogenous agents and particularly at the low B1 power levels required to meet SAR requirements. If exogenous CEST imaging is to be realized it is imperative that strategies for more effective CEST contrast agents are developed. The large chemical shifts afforded by paramagnetic (paraCEST) agents permit more rapid exchange kinetics and therefore potentially more effective contrast agents. Despite comparatively large chemical shifts, the Bloch equations predict that many of the Ln3+ DOTA-tetraamide chelates traditionally investigated as CEST agents have exchange kinetics that are considerably faster than optimal at very low B1 powers.1 We have recently reported that varying the conformation of the hydrophilic amide substituents in such chelates can have favourable outcome on the CEST properties of the chelate.2 Here we turn our attention to the effect of employing and controlling the conformation of hydrophobic amide substituents. We find that phenyl amide substituents in the pseudo-axial position afford chelates with considerably slow water proton exchange rates and much more favourable CEST properties than isomeric chelates with the amide substituent in the pseudo-equatorial position.
Design of in vivo pH-triggered self assembly of gadolinium contrast agents

Christian Buettner1, buettner.27@buckeyemail.osu.edu, Michelle Williams Buettner2, Anjit Ghosh3, Eric Dobson3, Michael Nicholl4, Michael Tweedle5, Joshua Goldberger1, (1) Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43214, United States (2) Department of Radiology, The Ohio State University, Columbus, Ohio, United States

Early detection and imaging of cancer is one of the most important ways to decrease mortality. MRI has high (< 1 mm) spatial resolution but low sensitivity (μM) for detecting its Gd contrast agents, all of which are not cancer specific. PET has high sensitivity for detecting 111In, e.g. as FDG imaging areas of excessive glycolysis, but has poor (1 cm) spatial resolution. We aim to solve this problems using controlled variable state Gd chelates targeted at a cancer hallmark, the decreased pH (7.3-6.6) in the extracellular environment of tumors due to excessive glycolytic metabolism producing protons and lactic acid. We have made smart, self-assembling nanomaterials, Gd(DO3A)(PA) (peptide amphiphiles) that transition from single molecules or spherical micelles to micron-sized nanofibers at pH lower than physiologic. We studied structure-property relationship effects on transition pH by systematically varying elements of Gd(DO3A)(PA). Phase diagrams were mapped using Circular Dichroism, Critical Micelle Concentrations, and Transmission Electron Microscopy. Relaxivity measurements showed values of 8.3 and 6.6 mM−1 s−1, for acidic and basic pH, respectively, relative to Gd(DTPA)2− (4.5 mM−1 s−1), and transition pH as high as 6.7, at 500μM in 150mM NaCl and 2.2mM CaCl2. Gd and Lu have very similar chemistries. Using Lu(DO3A)(PA) as a carrier, spiked with the radioactive isotope, 177Lu, we have quantified the blood availability and biodistribution in vivo for various analogues that show differing patterns based on probable morphologies.

Graphene oxide enhances Gd(III)-complex cell labeling for high sensitivity cellular MRI

Andy H. Hung1, andy.hung@northwestern.edu, Robert J. Holbrook2, Cameron Glasscock3, Matthew W. Rotz4, Keith W. MacRenaris4, Nikhita D. Mansukhani5, Matthew C. Dych6, Kevin T. Dam7, Lisa M. Manus7, Mark C. Hersam8, Thomas J. Meade1, (1) Department of Chemistry, Molecular Biosciences, Neurobiology, Biomedical Engineering, and Radiology, Northwestern University, Evanston, Illinois 60208-3113, United States (2) Department of Materials Science and Engineering and Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3108, United States

Cellular tracking by MRI is an important tool in the in vivo study of cancer biology, immunology, and stem cell biology. This technology has significant clinical implications for the optimization and monitoring of cell therapies. Cell labeling for MRI is typically achieved by ex vivo transfection using superparamagnetic iron oxide nanoparticles (SPIOs). The known limitations of SPIOs are the susceptibility artifacts and the negative contrast generated. Gd(III)-complexes are an attractive alternative label because they create positive contrast and are not associated with susceptibility artifacts. However, Gd(III)-complexes lack the requisite sensitivity for many applications. Compared to SPIOs, the cellular payload achieved by Gd(III)-complexes is one or two orders of magnitude lower. To overcome this limitation, graphene oxide (GO) was used as a delivery vehicle to enhance the cellular payload of Gd(III)-complexes. GO has one of the largest specific surface areas of any known material and supports many classes of non-covalent interactions. The adsorption of a library of Gd(III)-complexes on GO was characterized to understand the relative importance of the different non-covalent interactions. For Gd(III)-complexes that adsorbed to GO, simple co-incubation of the two in culture increased the cellular payload by up to 13 fold compared to when the Gd(III)-complex was used alone. The enhanced payload directly translated into increased imaging sensitivity and is expected to expand the feasibility of Gd(III)-based cellular MRI in many applications.

Self-assembling peptide nanofibers modulate water exchange and report biomaterial localization in vivo

Adam T Preslar1, adampreslar@gmail.com, Giacomo Parigi1,2, Mark T McClendon1, Samantha S Seifick1, Tyson J Moyer1, Chad Haney1, Emily A Waters2, Keith W MacRenaris3, Claudio Luchinat4,5, Samuel I Stupp4,5,6,7, Thomas J Meade1,5,8,9,10,11, (1) Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States (2) Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States (3) Department of Medicine, Northwestern University, Chicago, Illinois 60611, United States (4) Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208, United States (5) Center for Advanced Molecular Imaging, Northwestern University, Evanston, Illinois 60208-3113, United States (6) Institute for BioNanotechnology in Medicine, Northwestern University, Chicago, Illinois 60611-2875, United States (7) Department of Chemistry, University of Florence, Sesto Fiorentino, Florence 50019, Italy (8) Magnetic Resonance Center (CERM), University of Florence, Sesto Fiorentino, Florence 50019, Italy (9) Department of Neurobiology, Northwestern University, Evanston, Illinois 60208, United States (10) Department of Radiology, Northwestern University, Evanston, Illinois 60208, United States (11) Molecular Biosciences, Northwestern University, Evanston, Illinois 60208, United States

Peptide Amphiphiles (PAs) are a broad class of self-assembling molecules shown to have numerous applications in promoting stem cell differentiation and hierarchical cell ordering. Here we describe a series of PAs were designed as contrast agents. These assemblies were characterized using cryogenic electron microscopy and small angle x-ray scattering, and have been shown to exhibit rotational correlation time (τc)-modulated relaxivity by nuclear magnetic relastive dispersion (NMRD). It was found that material processing conditions could reduce water exchange lifetime (τw). In vivo analysis of these agents successfully detected track a PA gel in the murine leg after intramuscular injection and verified that the material remained unchanged for 4 days. These results indicate that the agents synthesized can serve as fate-mapping agents for PA gels in vivo over periods relevant to regenerative medicine applications.

Cy3 labeled Gd(III)-DNA-gold nanostars: Anisotropic nanocojugates for biocompatible optical and magnetic resonance imaging

Matthew Rotz1, mrrotz@u.northwestern.edu, Kayla Culver2, Giacomo Parigi1, Claudio Luchinat4, Teri W Odom2, Thomas J Meade1, (1) Departments of Chemistry, Molecular Biosciences, Neurobiology, Biomedical Engineering and Radiology, Northwestern University, Evanston, Illinois 60208, United States (2) Department of Chemistry, University of Florence, Sesto Fiorentino 50019, Italy

Recent progress in molecular imaging has been driven by the need for real-time, in vivo information that can be collected quickly and with minimal perturbation to the subject. To this end a wide variety of high relaxivity, Gd(III) bearing nanoconstructs have been reported. These include liposomes,
nanodiamonds, organic polymer nanoparticles, and inorganic silica and gold nanoparticles. Gold nanoparticles have been the most versatile and accessible for contrast agent development due to their facile synthesis, bio-compatibility and ease of surface functionalization via gold-thiol conjugation. Fluorescently labeled Gd(III)-DNA Gold nanostar conjugates (Cy3 DNA-Gd@AuNS) provide an improved imaging platform that leverages the biocompatibility of previously published Gd(III) enriched DNA AuNP probes, while enhancing Gd(III) relaxivity and payload.

The larger, highly anisotropic shape of the Cy3 DNA-Gd@AuNS provides high surface area for binding of Gd(III) DNA and generates a 2.5 fold increase in r1 relaxivity at 1.41 T compared to 13 nm AuNPs and a ten-fold increase relative to the clinical standard ProHance. Cy3 DNA-Gd@AuNS show the low toxicity and high cell uptake of equivalently functionalized 13nm DNA AuNPs in pancreatic cancer (PANC-1) cells.

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Conformationally restricted integrin targeting imaging agents

Quyen N. Do1, quyen.do@utdallas.edu, Zoltan Kovacs1,2, Guiyang Hao2, Xiankai Sun2, A. Dean Sherry1,2, (1) Department of Chemistry, The University of Texas at Dallas, Richardson, Texas, United States (2) Advanced Imaging Research Center, The University of Texas Southwestern Medical Center, Dallas, Texas, United States

The RGD (arginine, glycine, aspartic acid) sequence is known to be an important binding motif for various integrins that are over-expressed in many tumor types. Magnetic resonance molecular imaging of integrin receptors is in general hampered by the inherently low sensitivity of MRI. Here, we report a novel design of integrin targeting MRI agents in which the 1,4,7,10-tetraazaacyclododecane macrocycle is integrated into the rigid cyclic peptide framework through the 1 and 7 acetate sidearms of the DOTA unit (c(DOTA-RGD)) and c(DOTA-RGD). DOTA = the 1,4,7,10-tetraazaacyclododecane-1,4,7,10-tetraacetic acid, f = D-Phenylalanine). The rationale of this design is that binding of these Gd(III) complexes to integrin would result in a slower tumbling rate, which in turn would increase T1 relaxivity as predicted by the Solomon Bloembergen Morgan theory. The chelating properties of c(DOTA-RGD) and c(DOTA-RGD) with Yb3+, Gd3+, and Cu2+ were studied in solution. High resolution 1H NMR studies revealed that the Yb3+ complex adopted a SAP geometry. UV-Vis spectroscopy showed that Cu2+-complex had a distorted octahedral geometry. We have shown that the Lu3+ complex of c(DOTA-RGD) binds to α5β1 integrin with an IC50 values of 5.2. PET imaging experiments with the 54Cu3+-c(RGD-DOTA) complex in U87MG tumor bearing mice confirmed that the metal complex localizes to tumors. The relaxivity of the Gd3+ complex was found to be 3.1, in agreement with the reported relaxivity of the Gd-complexes of other DOTA-bisamide ligands. The water exchange properties of these two complexes in the presence and absence of integrin and the integrin binding properties of these two topological complexes will be studied.

INOR 573
Redox-activated transition metal paraCEST contrast agents

Pavel B Tsilovitch, pavelst@buffalo.edu, Janet R Morrow.Department of Chemistry, University at Buffalo, SUNY, Amherst, NY 14260, United States

Redox-activable paraCEST (paramagnetic Chemical Exchange Saturation Transfer) MRI agents utilizing redox properties of transition metal (TM) ions will be reported. The most promising Co(II)/Co(III) and Fe(II)/Fe(III) agents are obtained with a six-coordinate ligand based on TACN macrocyclic containing three H-pyrazol-3-ylmethyl pendants. While in paramagnetic MRI-active Co(II) state, the exchangeable pyrazole NH protons give highly shifted CEST peak at +135 ppm from bulk water. Upon reaction with oxygen, this paramagnetic MRI-active Co(II) agent switches to diamagnetic MRI-silent Co(III) complex. This redox switch can be turned back on to MRI-active Co(II) state by reducing it with dithionite, glutathione, or cysteine. Experiments in rabbit serum demonstrated that CEST signal intensity did not change over a period of 48h at pH 7.0 and 37°C. While the CEST effect had similar intensity and a peak shift of +135 ppm and +133 ppm in HEPES buffer and serum, respectively, a new CEST peak at +62 ppm was observed in serum (Fig.1).

Both the Co(II) and Co(III) complexes were found to be kinetically inert towards dissociation in the presence of biologically relevant cations, such as Ca2+ and Zn2+, and anions, such as PO43-, CO32-, and Cl-. These complexes are also kinetically inert over a wide range of pH 5.0-8.5. The combination of a highly-shifted CEST peak, and redox-responsiveness make TM-paraCEST promising for in vivo mapping of disease states that involve reducing environment and low levels of PO43-.

INOR 574
New gadolinium-based contrast agents for highly sensitive detection of Zn2+ with MRI

Jing M Yu1, yujingmaria@gmail.com, Christian Preihs1, christian.preihs@utsouthwestern.edu, Yunkou Wu1, Piyu Zhao2, Khaled Nasr1, A. Dean Sherry3, (1) Advanced Imaging Research Center, The University of Texas Southwestern Medical Center, Dallas, Texas 75390, United States (2) Chemistry Department, The University of Texas at Dallas, Dallas, Texas 75080, United States

Zinc ions play an important role in insulin storage and are secreted along with insulin from beta cells upon stimulation with glucose. Therefore, determining the Zn2+ status in beta cells and monitoring their release from beta cells in vivo are essential factors in understanding the etiology and treatment of diabetes mellitus. Recently, the zinc responsive agent, GdDOTA-dibPEN, has been demonstrated to be able to image beta cell activity using MRI as a medical imaging tool.1 This particular contrast agent shows a strong binding affinity for Zn2+ as it contains two Zn2+ binding sites, namely di-2-picolylamine (DPA). Another unique feature of this molecule exhibits its ability to form a zinc complex that can bind to serum albumin. This particular binding motif limits the molecular rotation of the agent and thereby increases its relaxivity from 6.6 to 17.5 mM-1 s-1 at 0.47T. However, for clinical purposes, it would be more desirable to administer an agent with a much higher r1 relaxivity. If this can be achieved, a much lower concentration of contrast agent would be sufficient to obtain good image contrast.

It has already been shown that the water residence lifetime (τw) of the bound water molecule for a contrast agent has a very important effect on r1 as one begins to slow molecular motion by binding to macromolecules. Theoretically, one should be able to attain relaxation values as high as 100 mM-1 s-1 at 0.47T when the water exchange lifetime is approaching the optimal value (~24 ns).2 The goal of the current series of projects is to develop new highly sensitive Zn2+ MRI contrast agents by redesigning the previous agent. A variety of GdDOTA-dibPEN analogues have been prepared either by incorporating phosphinate side groups,3 by varying the linker between the macrocyclic unit and the coordinating Gd3+ carbonyl groups, or by introducing functionalities that can result in high TSAP/SAP ratio.4 These new sensors are designed to demonstrate a faster water exchange rate, which in turn will result in a higher relaxivity value. Currently, we are testing the ex vivo properties of these agents. The most promising candidates will then be selected for in vivo studies.

References:


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Development of a new PARACEST agent for in vivo pH imaging
Xiaojing Wang1, xiaojing.wang@utdallas.edu, Yunkou Wu2, Piyu Zhao1, Allan Dean Sherry1-2. (1) Department of Chemistry, University of Texas at Dallas, Dallas, Texas, United States (2) Department of Advanced Imaging Research Center, University of Texas Southwestern Medical Center, Dallas, Texas, United States

Chemical Exchange Saturation Transfer (CEST) agent offers several advantages over conventional Gd(III)-based agents. However, the water resident lifetime (t_w) of first generation PARACEST agents is far away from optimal value for CEST generation at physiological temperature of 310 K. This has made it hard to use them for in vivo pH imaging. Our goal is to develop a PARACEST agent for in vivo pH imaging. The new pH sensor (Fig. 1) was prepared and characterized. The bis(n-butyl phosphonate) side-chain groups in this complex were introduced to slow water exchange between the inner-sphere of the central Eu(III) ion and bulk water while maintaining the pH sensitive advantages of phenolic arm.[1] The CEST properties of this new agent were measured over a range of pH values from 5 to 8 and at temperatures from 298 to 310K. The pH response of the new agent behaves in the same manner as the previous agent[2] but, in this case, the CEST intensity increases with the temperature. The t_w is calculated to be 90 µs at 310 K and pH 8.0. We have successfully developed a pH responsive agent that has a t_w value closer to optimum. The use of such agent for in vivo pH imaging is promising.


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Hexameric Mn(II)-EDTA complex as MRI contrast agent
Jiang Zhu1-2, jiangz2@nmr.mgh.harvard.edu, Peter Caravan1. (1) Department of Radiology, Massachusetts General Hospital, Harvard Medical School, The Athinoula A. Martinos Center for Biomedical Imaging, Charlestown, Massachusetts 02129, United States (2) North Sichuan Medical College, Sichuan Key Laboratory of Medical Imaging, Nanchong, Sichuan 637000, China

Here we describe the synthesis and characterization of a hexameric Mn(II)-based MR contrast agent. Starting from L-tyrosine, we synthesized an EDTA derivative with a pendant phenol. Reaction of this derivative with N\textsubscript{2}P\textsubscript{3}Cl\textsubscript{6}, followed by deprotection and chelation with Mn(II) gave the rigid, hexameric complex shown. The complex exhibits a high relaxivity (r\textsubscript{T1} = 6.7 mM\textsuperscript{-1}s\textsuperscript{-1} (per Mn), 39.3 mM\textsuperscript{-1}s\textsuperscript{-1} (per molecule), 37°C, 60 MHz, in HEPES buffer) which is much higher than the monomeric analog (r\textsubscript{T1} = 2.3 mM\textsuperscript{-1}s\textsuperscript{-1}). Here we report the field dependent relaxivity, kinetic inertness, and water exchange properties of this hexameric contrast agent. The intermediate size and high relaxivity make this Mn-EDTA multimer a good candidate for high-field MRI contrast agent applications.

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Controlling the relaxivity of liposomal MRI agents through the gating of a mechanosensitive bacterial channel
Limin Yang1, limin.yang@utsouthwestern.edu, James Ratnakar2, A. Dean Sherry2, Paul Blount1, Zoltan Kovacs2. (1) Department of Physiology, U T Southwestern Medical Center, Dallas, Texas 75390, United States (2) Advanced Imaging Research Center, U T Southwestern Medical Center, Dallas, Texas 75390, United States

The water exchange process that transfers the paramagnetic effect of MRI contrast agents to the bulk water pool is fundamental for contrast enhancement. Nanosized carrier systems such as liposomes are often used to deliver a large payload of paramagnetic contrast agents in order to increase the local concentration of the imaging agent for molecular imaging applications. The major disadvantage of core encapsulated liposomal MRI contrast agents has been the relaxivity quenching effect due to the slow diffusion rate of water molecules across the lipid bilayer. The goal of this project was to engineer nanosized, “smart” contrast agents which consist of a Gd-complex encapsulated within stealth liposomal vesicles. The water exchange rate through the lipid bilayer will be regulated by the opening and closing of chemically modified bacterial mechanosensitive (MscL) channels. A mutant MscL channel whose gating could be controlled by chemical modification in the pore was reconstituted into Gd-DOTA loaded liposomes. After treatment with a reagent (MTSET) that introduces charges in the pore, the relaxivity of the proteoliposomes was increased to values similar to that of the liposomes lysed with Triton. When channels modified with a pH sensitive functional group were reconstituted in the liposomes, the relaxivity of Gd-DOTA loaded liposomes significantly increased when the pH was adjusted to 6 from 8 demonstrating that the protein channel could be used to control water exchange rate across the lipid bilayer.

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Binding affinity of iron oxide based PET/MRI probe to macrophage scavenger receptor in vulnerable atherosclerotic plaques
Tang Tang1, ttang@ucdavis.edu, Chiquiao Tu2, Angelique Louie2. (1) Department of Chemistry, University of California, Davis, Davis, California 95616, United States (2) Department of Biomedical Engineering, University of California, Davis, Davis, California 95616, United States

To date, most of the approved clinical MRI contrast agents are non-specific for targeting, which can result in a high background and low sensitivity for imaging. Nanoparticle agents based on iron are attractive for increasing sensitivity, and targeted MRI agents have been vigorously investigated, but there has been very little characterization of the binding affinity of targeted nanoparticle agents to their molecule of interest. It would be highly desirable to know if nanoparticles can bind to targeted cells with high specificity and affinity, to better understand how to optimize targeted nanoparticle agents.
Our group has previously reported PET/MRI probes targeted to macrophages accumulated in vulnerable plaques. Herein, we demonstrate a multimodal probe with improved targeting to macrophages via the scavenger receptor A (SR-A) and investigate the binding affinity of the probe to SR-A by radiolabelling the probe with $^{111}$In. We also show the effect of different degrees of surface sulfation on the probe uptake by macrophages. The probe is sulfated dextran coated iron oxide nanoparticles, conjugated to a chelator for $^{64}$Cu, a PET tracer. The nanoparticles are about 60 nm in hydrodiameter, with sulfur content up to 11% in mass. In vitro biocompatibility studies indicate that the probe is nontoxic to cells. Detailed binding assays show the high affinity of probe to SR-A and the differences in $K_s$ caused by different levels of sulfation. Uptake studies illustrate that higher degrees of sulfation resulted in much higher uptake efficiency. We present that the probe can be specifically and avidly taken up by macrophages via SR-A, much more efficiently than non-sulfated analogues, which makes it a promising imaging probe for vulnerable atherosclerotic plaques.

INOR 579
New gold(I) complexes with t-butyl phosphine and dialkyl dithiocarbamate ligands: Synthesis, spectroscopic characterization, crystal structure determination, and in vitro cytotoxic evaluation against A549, HeLa, and MCF7 human cancer lines

Anvarhussein Isab, asiaab@kfupm.edu.sa, Department of Chemistry, King Fahd Univ of Pet & Minerals, Saudi Arabia, Dhahran, Saudi Arabia

Two new linear gold(I) complexes of formulae [Au(P(t-Bu)$_3$)$_2$(SCN(CH$_2$)$_2$)$_2$] (1), and [Au(P(t-Bu)$_3$)$_2$(SCN(CH$_2$)$_2$)$_2$]$_2$ (2) have been prepared by the reaction of equimolar amounts of [Au(P(t-Bu)$_3$)Cl] with sodium dimethylthiocarbamate monohydrate, and monohydridodithiocarbamate trihydrate respectively. The complex (1) crystallizes in monoclinic space group while the complex (2) crystallizes in orthorhombic space group. IR spectroscopy confirms the presence of thioureide bond (R$_2$N-CS$_2$) in the complexes (1) and (2). The $^1$H, $^{13}$C and $^{31}$P NMR, and IR spectra of the Au(I) complexes (1) and (2) corroborate with their single crystal X-ray structure analyses. These gold(I) dithiocarbamate complexes show selective and promising in vitro cytotoxic activities against A549 (human lung carcinoma), HeLa (human cervical cancer) and MCF7 (human breast cancer) cell lines.

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INOR 580
Development toward ruthenium based light activated redox potential disruption catalysts

David E Hill', hill.da@husky.neu.edu, Joan J Soldevial-Barreda', Abhata Hofbrenmarius, Peter J Sadler. (1) Department of Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts 02115, United States (2) Department of Chemistry, University of Warwick, Coventry, England

Light activation therapy/photodynamic therapy (PDT) represents a minimally invasive technique for selective delivery or activation of a drug. Photo-activated redox disruption catalysts offer an advantage over existing PDT reagents in treating disease with hypoxic symptoms by targeting the NAD$^+$/NADH balance in cells. The alteration of cellular redox status through changes of the NAD$^+$/NADH concentration has been shown to play an important role in cell death.

A series of Ru$^{II}$ half-sandwich complexes of the type Ru(p-cymene)(NN)X were synthesized where (NN)=N-tosyl ethylene diamine (TsEn), 2-(N-tosylamino pyridine (TsAmpy) and 8-(N-tosyl)quinolinamine (TsQuin) and X = Cl or Pyridine with PF$_6$ counter ion. These modified Noyori ligands were found to regioselectively catalyze the transfer hydrogenation of NAD$^+$ to yield NADH in the presence of excess formate. The turnover frequency (TOF) of this catalyzed for the aquated chlorides complexes increased in the order TsQuin>TsAmpy>TsEn. The pyridine based complexes were inert to hydrolysis at 37$^\circ$C in dark over more than 48 hours while the chloride adducts proceeded to their corresponding aqua species in the presence of water. When irradiated with UV-A light, the pyridine complexes in water at 37$^\circ$C were found by $^1$H NMR to photo-decompose rather than photo-disassociate to their aquated form. In the presence of white light irradiation, no change was detected by $^1$H NMR or UV/Vis spectroscopy.

INOR 581
Chemical, alpha-glucosidase and carbonic anhydrase inhibition studies of Pd(II)-hydrazide complexes

Mohammad Mahroof1, m.mahroof@qu.edu.qa, Uzma Ashiq2, mmahroof@qu.edu.qa, Razatul Ul Ain2, Rifat Jamal2, Muhammad Saleem2. (1) Department of Chemistry and Earth Sciences, Qatar University, Al-Dafna, Doha 00000, Qatar (2) Department of Chemistry, University of Karachi, Karachi, Sindh 75270, Pakistan (3) H. E. J. Research Institute of Chemistry, International Center for Chemical Sciences, Karachi, Sindh 75270, Pakistan

To capitalize on the interesting enzyme inhibition properties of metal complexes and the need for effective treatments of diseases found worldwide, such as diabetes mellitus, glaucoma, neurological and related disorders, this study focused on the synthesis and characterization of hydrazide ligands and their respective Pd(II) complexes. High throughput screening is used to determine their alpha-glucosidase and carbonic anhydrase II enzyme inhibition activities. The physical (conductivity, magnetic susceptibility), analytical (elemental analyses for C, H, N and Pd) and spectral (FT-IR, 1H-NMR, 13C-NMR) techniques utilized during characterization revealed the formation of square planar, neutral, and diamagnetic 1:2 Pd(II)-hydrazide complexes with the general formula [Pd$_x$L$_x$C$_{y}$]. In these Pd(II) complexes, the hydrazide ligands are monodentate; the terminal nitrogen is the donor atom. Every hydrazide ligand was inactive against both alpha-glucosidase and carbonic anhydrase II enzymes; however, each of the Pd(II)-hydrazide complexes were approximately 300 times more potent alpha-glucosidase inhibitors than the standard compound, 1-deoxynojirimycin (DNJ). Some of the Pd(II) complexes also demonstrated potential carbonic anhydrase (CA) inhibition properties comparable to the standard compound, acetazolamide (ACZ).

INOR 582
Comparison of the chemical reactivity of synthetic peroxynitrite with that of the products of nitroxy or its anion with molecular oxygen

Joel Jorolan, jorolan@email.arizona.edu, Arizona Ann Butitta, Cheryl Cheah, Katrina M Miranda. Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United States

Donors of nitroxy (HNO) exhibits pharmacological properties including enhancement of myocardial contractility, preconditioning against ischemia/reperfusion injury, induction of apoptosis and suppression of tumor angiogenesis, and inhibition of alcohol metabolism. As with all pharmacological agents, the therapeutic usefulness of HNO donors depends on the ability to elicit beneficial responses without inducing harmful side effects. It is therefore important to understand the chemistry of HNO, particularly its involvement in potentially deleterious biological reactions. HNO is autoxidized to a cytotoxic species that is capable of inducing DNA double strand break, yet the identity of the HNO autoxidation product remains elusive. A conceivable product is peroxynitrous acid but chemical comparison studies have demonstrated that HNO autoxidation leads to a unique reactive nitrogen oxide species. Here, we extend these analyses to include another preparation of peroxynitrite (ONOO$^-$) formed from the autoxidation of nitroxy anion (NO$^+$) with a dual purpose in mind. The first is to compare the chemistry of HNO and NO$^+$ autoxidation, while the second is to compare two preparations of ONOO$^-$. The results of this analysis will be presented.

INOR 583
Synthesis, characterization, and biological reactivity of mixed ligand Cu(II) complexes
Three copper complexes containing derivitized thiazole substitutents, namely, \([Cu(Py(oBt))_2\cdot H_2O][NO_3]_2\) (1), \([Cu(Q(oBt))(H_2O)][NO_3]_2\) (2), and \([Cu(OHQ(oBt))(Cl)](3)\), have shown distinct nuclease activity. In an effort to understand the role the ligand frame plays in modulating the biological activity of these complexes, we have synthesized and characterized a new Cu(II) complex and investigated the nuclease activity. The synthesis and characterization of the new ligand and the corresponding Cu(II) complex will be presented along with the differences in biological activity between this complex and complexes 1 – 3 in an effort to better understand the structure-function relationship.

INOR 584

Synthesis, characterization, biological activity and DNA binding and cleavage studies on tetrazole imine bases and their Cu(II), Co(II) and Ni(II) complexes: An experimental and theoretical approach

Ranjithreddy Palreddy -1, Mohmed Jaheer -2, Ravi Mudavath -3, Sujitha Pallimoni -4, Sarala Devi Chintalapalli -5, dr_saraladevich@yahoo.com. (1) Department of chemistry, Osmania University, Hyderabad, Andhra Pradesh 500007, India (2) Department of chemistry, Osmania University, Hyderabad, Andhra Pradesh 500007, India (3) Department of chemistry, Osmania University, Hyderabad, Andhra Pradesh 500007, India (4) Department of chemistry, Osmania University, Hyderabad, Andhra Pradesh 500007, India (5) Department of chemistry, Osmania University, Hyderabad, Andhra Pradesh 500007, India

Novel tetrazole imines and their binary Cu(II), Ni(II) and Co(II) complexes were synthesized and characterized by employing spectro - analytical techniques viz; MASS, UV-VIS, IR, 1H NMR, ESR, Elemental analyses, TGA and Magnetic susceptibility measurements. Thi equilibrium studies were carried out to get an insight of number of dissociable protons and protonation sites in candidate compounds by using pH-metric technique. The metal ion interactions were also carried out to establish the stability constants in respective systems. To understand the suitable frontier orbitals in title imine compounds which can participate in metal–ligand orbital's overlap, the computational studies were carried out by employing HyperChem 7.5 tools. The energies of HOMO and LUMO frontier orbitals were computed with geometry optimised molecules. The antimicrobial studies carried out by screening the tetrazole imine bases and their metal complexes against bacteria and fungi confirmed their potential activity. The DNA binding and cleavage studies on metal complexes using PUC19 DNA showed significant role of Cu(II) complexes in cleavage compared to Ni(II) and Co(II) complexes.

KEY WORDS: Novel tetrazole imine bases, binary Cu(II), Ni(II) and Co(II) complexes, pH- metric studies, HyperChem 7.5 tools, DNA binding and DNA cleavage.

INOR 585

Anticanic properties of Ruthenium(II) polypyrivdine compounds with anionic N^O-donor bidentate ligands

Bruno Peña1, bruno.pena@mail chem.tamu.edu, Rola Barhoumi2, Kim R Dunbar1, dunbar@mail chem.tamu.edu. (1) Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States (2) Department of Veterinary Integrative Biosciences, Texas A&M University, College Station, Texas 77843, United States

The field of medicinal inorganic chemistry was revolutionized when the antitumor properties of cisplatin were discovered serendipitously by Barnett Rosenberg in the 1960s. In spite of the enormous success of cisplatin in treating ovarian and testicular cancers, new drugs with fewer severe side effects, reduced tumor resistance and different mechanisms of action are needed. In addition, the development of anticancer agents that are effective against many different tumors is imperative due to the staggering number of new diagnosed cases of cancer every year. Among the many early and late transition metal-based potential anticancer drugs, ruthenium (Ru) compounds have garnered a great deal of interest. For example, the Ru(III) compounds NAMI-A and KP1019 are in Phase II clinical trials and several organometallic and luminescent polypyrivdine Ru(II) compounds have displayed high anticancer activity and several cancer cell lines. Since most of the polypyrivdine Ru(II) antitumor compounds contain N-donor neutral ligands, we decided to introduce anionic N^O-donor bidentate ligands into the coordination sphere. We have synthesized four new monocalonatic polypyrivdine Ru(II) complexes, \([Ru(bpyp)$_2$(dbpo)](1)\), \([Ru(phen)$_2$(dbpo)](2)\), \([Ru(bpyp)$_2$(hbtz)](3)\), \([Ru(phen)$_2$(hbtz)](4)\), where dbpo = dibenzo[a,c]phenazin-10-olate (dbpo) and hbtz = 2-(benzo[d]thiazol-2-yl)phenolate, which were characterized by NMR, ESI-MS, electronic absorption spectroscopy and single crystal X-ray diffraction. Their anticancer properties were assessed against A549 lung cancer cells and it was found that their anticancer activity is comparable or superior to cisplatin, with IC$_{50}$ values in the 0.85 – 7.57 μM range (IC$_{50}$ cisplatin = 6.25 μM). The mechanism of cell death of these compounds is under investigation using laser scanning confocal fluorescence microscopy.

INOR 586

Ruthenium(II) bipyridyl complexes for activation of cobalt(III) Schiff base protein inhibitors through photoinduced electron transfer

Robert J Holbrook, rjh779@u.northwestern.edu, Mark D Peterson, Emily A Weiss, Thomas J Meade. Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

Cobalt(III) Schiff base complexes (Co(III)-sb), developed by our group, inhibit metal-dependent pathways by irreversibly binding to histidine residues of target proteins and displacing endogenous metal ions. Currently, this process is limited by a dissociative mechanism of the Co(III)-sb axial ligands. Based on the success of this approach we are developing a light-activation mechanism that will redox-initiate the inhibition process of Co(III)-sb derivatives. Specifically, this system incorporates a bimetallic complex that utilizes the excited-state quenching ability of Ru(II) polypyrivdine complexes. This photo-redox active Co(III)-sb is designed to undergo single electron transfer from Ru(II) to Co(III), upon excitation of a Ru(bpyp)$_2$ moiety (450 nm) (1). Reduction of Co(III)-sb to Co(II)-sb causes dissociation of the axial ligands (ii.). The redox potentials of Co(II)-sb and Ru(III)(bpyp)$_2$ favor the back electron transfer (iii.). We propose that this action generates the reactive Co(III)-sb species, that subsequently coordinates to the imidazole ring of histidine residues in target proteins.
INOR 587

Biodistribution and toxicity of lipophilic ruthenium complexes

Nagham Alattrash, nagham.alattrash@mavs.uta.edu, Eugenia S Narh, Frederick M MacDonnell. Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, United States

The dinuclear and monomeric ruthenium(II) poly(pyridyl) complexes \([\text{(phen)}_2\text{Ru(tatpp)}\text{Ru(phen)}_2]Cl_4\) (P) and \([\text{(phen)}_2\text{Ru(tatpp)}]\)Cl_2 (MP) are promising candidates for anticancer drug development in terms of the observed anti-tumor activity in vivo and in vitro. These complexes also show considerably less acute toxicity in mice compared to simple ruthenium poly(pyridyl) complexes, such as [Ru(2,2'-bipyridine)]^{2+} (1) and [Ru(1,10-phenanthroline)]^{2+} (2). The increase in maximum tolerable dose (MTD) for P and MP appears to be correlated with their increased lipophilicity. This paper presents the preparation, characterization and acute animal toxicity screening in Balb/c mice of a series of ruthenium-tatpp based complexes with increasing lipophilicity. Drug toxicity and toleration appear to be related to acetylcholine esterase inhibition and peak blood concentration as first postulated by Dwyer in the 1960's for 1 and 2. A preliminary blood clearance study (pharmacokinetics) will also be presented.


INOR 588

Synthesis and DNA cleavage activity of tetraazatetrapyridopentacene (tatpp) rhenium(I) complexes

Pooja Ahuja, pooja.ahuja@mavs.uta.edu, Frederick M. MacDonnell. Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX 76019, United States

The Ru(II) poly(pyridyl) complexes \([\text{(phen)}_2\text{Ru(tatpp)}]^2+\) (MP) and \([\text{phen)}_2\text{Ru(tatpp)}\text{Ru(phen)}_2]^{4+}\) (P) show potential as antitumor agents both in vitro and in vivo.1 We postulate that tatpp is the essential pharmacophore responsible for the anti-tumor activity of these complexes and that coordination to Ru(II) is needed primarily to enhance its solubility and to modify its reduction potential. Re(I) analogues are expected to show similar but not identical properties due to the lower charge and differing coordination environment about the metal ion. In this paper, we present the preparation and properties of Re(I)-tatpp complexes as well as the screening of these complexes for DNA cleavage and cytotoxicity towards malignant cell lines.

INOR 589

Cytotoxicity of C₂-symmetric platinum(II) biazoxaline complexes in murine leukemia (P388, L1210) models

Chelsea L Thorsheim, ct horsheim@haverford.edu, Alexandra E Ranucci, Gregory D Whitehill, Daniel D Himelstein, Mark H Schofield. Department of Chemistry, Haverford College, Haverford, Pennsylvania 19041, United States

A series of C₂-symmetric platinum complexes of the type Pt(biox')Cl₂ (biox' = R,R- or S,S-4,4'-R₂-2,2'-bioxaline, where R = -H, -Me, -iPr, -Ph, -Bz) were synthesized in quantitative yield from [PtCl₂]₂ and 2,2'-bioxaline in methanol and the cytotoxicity of these compounds was tested in P388 and L1210 murine leukemia cell lines using the MTT assay. We have found that these complexes have lower activity against P388 (6.25 µM < IC50 < 100 µM) than against L1210 (8.3 µM < IC50 < 150 µM) and that the S,S isomers show higher activity overall than the R,R-isomers. The impact of stereochemistry and steric effects on the structure of the presumed adducts and their resulting cytotoxicity will be discussed.

INOR 590

Mechanistic study of the biological activity of the redox-active dinuclear ruthenium(II) poly(pyridyl) complex, \([\text{(phen)}_2\text{Ru(tatpp)}\text{Ru(phen)}_2]^{4+}\) (P⁴⁺)

Cynthia A. Griffith, cynthia.griffith@mavs.uta.edu, Shreyukta Singh, Zachary S. Breitbach, Joshua K Crowell, Nagham Alatash, Kenneth Abayan, Brad S. Pierce, Frederick M. MacDonnell. Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX 76019, United States

In earlier reports, it was demonstrated that the cationic complex \([\text{phen)}_2\text{Ru(tatpp)}\text{Ru(phen)}_2]^{4+}\) (P⁴⁺) undergoes in situ reduction by glutathione (GSH) to form a species that induces DNA cleavage.1,2 It was previously demonstrated that the mechanism of DNA cleavage follows an unusual dependence on [O₃]: the increase in cleavage activity of this complex is inversely proportional to [O₃]. In fact, cleavage is quenched in the complete absence of O₃. MacDonnell et al. postulate that the singly reduced species P³⁺, which contains a radical anion localized on the tatpp ligand, abstracts a H atom from the deoxyribose unit in DNA, leading to DNA cleavage. This work describes results from HPLC analysis of the scission products formed by the degradation
of ctDNA and pUC 18 DNA, by carbon radical generated in situ with P $^{4+}$ and GSH. Furthermore, preliminary EPR data indicates formation of a radical species is produced concomitant with DNA cleavage. Moreover, factors which attenuate DNA cleavage also decrease signal intensity observed in EPR, suggesting that this radical species is responsible for DNA cleavage.


INOR 591
DNA interactions with cytotoxic platinum-corrole conjugates
Melanie A Pribisko, melaniep@caltech.edu, Grace A Tang, Harry B Gray, Robert H Grubbs.Department of Chemistry, California Institute of Technology, Pasadena, CA 91125, United States

One of the great challenges in cancer treatment is the selective targeting of cancer cells over normal cells. The specific nuclear penetration of functionalizable coronelles introduces the possibility of targeted, efficient delivery of covalently-tethered chemotherapy drugs. Indeed, previous experiments demonstrate a sulfonated corrole can act as a carrier molecule for chemotherapeutic agents, specifically the DNA-intercalating anthracycline drug doxorubicin, resulting in enhanced drug cytotoxicity. Anticancer drugs due to their notorious lack of specificity for cancerous cells over normal cells and their need to be localized in the nucleus to be effective. Exploiting the selective uptake of the sulfonated corrole into the nucleus of brain metastatic prostate carcinoma by synthesizing a platinum-corrole conjugate could result in a highly specific and effective treatment for this type of metastases. Synthetic routes to bioactive platinum-corrole conjugates and their interactions with DNA will be presented.

INOR 592
Interaction of a biguanide antimalarial drug with the model membrane system: AOT reverse micelles
Nuttaporn Samart$^{1,2}$, nuttapornsamart@gmsil.com, Kenneth J Haller$^1$, Debbie C Crans$^2$. (1) School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand 30000, Thailand (2) Department of Chemistry, Colorado State University, Fort Collins, CO 80523, United States

Biguanides are drugs used in the treatment of diseases as antidiabetic, antihyperglycemic, and antimalarial agents, and some of them are used in combination therapy. In this study we examine the interaction of positively charged biguanides including the antimalarial drug derivative, 1-phenylbiguanide, with membrane model systems using multinuclear NMR spectroscopy. The membrane model system used is the reverse micelle formed by a negative charged surfactant, sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT). The changes of proton chemical shift of 1-phenylbiguanide by $^1$H-NMR spectroscopy were used to investigate the location of 1-phenylbiguanide. The phenyl group of 1-phenylbiguanide (Ha small change and Hb big change) peaks show upfield chemical shifts as pH increases from 1.21 to 12.28. The Ha peaks show downfield chemical shifts and Hb show upfield chemical shifts as the size of the reverse micelle varies from $w_m = 6, 8, 10, 14$, and 16. These chemical shift changes suggest that the 1-phenylbiguanide is located at the membrane interface and that it partially penetrates into the interface, or the differences in the shifting would not be as pronounced. We conclude that 1-phenylbiguanide interacts with the interface in the reverse micelles consistent with the Coulombic attractions, but that some of the drug penetrates into the interface.

References

INOR 593
Synergistic effects in metal organic framework-zinc oxide composites for the removal of toxic chemical gases
Jared B DeCoste$^{1}$, jared.b.decoste2.ctr@mail.mil, Bryan J Schindler$^1$, Jennifer R Soliz$^2$, Gregory W Peterson$^1$. (1) Leidos, Inc., Gunpowder, MD 21010, United States (2) Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD 21010, United States

Metal oxides, such as ZnO, and metal-organic frameworks, such as Cu-BTC and UiO-66-NH$_2$, have been shown to have the ability to remove small toxic chemicals from air streams. However, a material that has the ability to remove multiple classes of compounds is ideal for most toxic gas filtration applications. Composites of Cu-BTC, UiO-66-NH$_2$, and ZnO have been prepared and studied for the removal of NH$_3$, SO$_2$, H$_2$S, and CICN. In each composite prepared it was expected that a weighted average could be used to predict the removal capabilities for each composite. However, synergistic effects were found for the removal of SO$_2$, H$_2$S, removing significantly more of each chemical than predicted at 20°C and 50% RH. In fact, for SO$_2$ a 1:1:2 composite of Cu-BTC:UiO-66-NH$_2$:ZnO removed more than twice that predicted by a simple weighted average, and 75% more than ZnO alone. We hypothosized that this enhanced removal is due to the adsorption of water by the MOF components of the composite, which is then utilized in the reactive removal of SO$_2$ by the ZnO. Furthermore, the reaction products can be removed from the ZnO surface and sequestered in the pores of the MOFs.

INOR 594
Characterization of UiO—66 metal organic framework analogs with varying organic linker concentrations for the adsorption of toxic chemical gases
Jennifer R Soliz$^2$, jennifer.r.soliz.ctr@mail.mil, Jared B DeCoste$^1$, Bryan J Schindler$^1$, Gregory W Peterson$^1$. (1) Science Applications International Corporation (SAIC), Inc., Gunpowder, MD 21010, United States (2) Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD 21010, United States

Metal organic frameworks (MOFs) have gained a significant amount of interest for applications such as gas storage, catalysis, and gas filtration. UiO—66 zincion—MOFs are attractive as they have been reported to have high surface areas and are chemically and thermally stable. We have synthesized several UiO—66 analogs using different functionalized organic linkers, i.e. 2—bromoterephthalic acid, 1,4—naphthalenedicarboxylic acid, 2—nitrottereprhalic acid, and 2—aminoterephthalic acid, in systematic ratios to study the impact of these linkers toward adsorption for toxic chemical gases, i.e. NH$_3$, SO$_2$, H$_2$S, CICN, and CH$_3$Br. By varying the functionalities incorporated within the MOF structure, multiple gases were found to adsorb within a single MOF. These materials were characterized using XRD, ATR—FTIR, TGA, nitrogen adsorption isotherms, water vapor isotherms, and breakthrough testing. Findings of this work will be insightful toward adsorption capacities of various chemical gases and may be applied for use in toxic gas filtration.

INOR 595
Study of a vapochromic Pt(II) salt

Priscilla Diaz1, priscilladiazm@gmail.com, Amie E. Norton2, Mahmood K. Abdulmalek2, Stephen D. Taylor2, Steven Kennedy2, Aimmie Calhoun2, Jeanette A. Krause2, William B. Connick2. (1) Department of Chemistry, Virginia State University, Petersburg, Virginia 23838, United States (2) Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, United States

Since Mann's report of vapochromism in a series of platinum double salts, significant attention has been given to the discovery and characterization of vapochromic materials. These are materials that change in color, as well as absorption and emission spectroscopic properties, upon exposure to certain vapors of VOCs (Volatile Organic Compounds). Here we report the absorption properties and new mechanistic insights into the behavior of a vapochromic Pt salt.

INOR 596

Synthesis and characterization of a novel manganese-molybdenum precursor for the synthesis of manganese molybdate
Abdullah Alabdulrahman1, arahaman@kacst.edu.sa, abdulaziz bagabas1, Allen Apblett2. (1) Petrochemicals Research Institute, King Abdulaziz City for Science and Technology, Riyadh, Riyadh,P. O. Box 6086 11442, Saudi Arabia (2) Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United States

A single precursor, containing both of manganese and molybdenum ions, was prepared by using a naturally-occurring L-(+)-lactate ligand. One-pot synthesis procedure was established by heating an aqueous solution of manganese lactate with a-molybdenum trioxide. Colorless crystals of [Mn(OH)\textsubscript{2}]\textsubscript{4}\textsuperscript{2-}MoO\textsubscript{4}\textsuperscript{-}\textsubscript{2}(lactato-O\textsuperscript{2-}O\textsubscript{4})\textsuperscript{2-} were obtained upon concentration of the reaction solution. Single-crystal structure analysis by X-ray revealed that the molybdenum-oxo groups are cis to each other due to d-orbitals symmetry, while the carboxylate groups of the two lactato ligand are trans to each other. In addition, three hydrogen bonds connect the hexaquamanganese(II) cation with the dilactatodioxomolybdate(VI) anion. The cation-anion molecule is connected with other molecules to form extended 2-dimension structure via hydrogen bonds. The thermal stability of this compound was also investigated and was confirmed the formation of manganese molybdate.

INOR 597

Solid state lithium electrolytes (LLTO) for advanced battery applications
LaDena A Bolton1, ladena.bolton@yahoo.com, Faith Beck2, Ayyakkannu Manivanman2. (1) Department of Chemistry, Clark Atlanta University, Atlanta, GA 30302, United States (2) National Energy Technology Laboratory, Department of Energy, Office of Fossil Energy, Morgantown, WV 26507, United States

Liquid electrolytes are currently used for lithium (Li+) ion batteries because of their high conducting behavior. However, the risk of explosion and fire accidents has encouraged scientists to find alternative materials. Solid lithium oxides have shown promise for high performance batteries based on the potential to obtain high ionic conductivities above 10\textsuperscript{-3} S cm\textsuperscript{-1} and their good chemical stability to electrodes. This work analyzed the effects of preparation techniques and doping agents, on the ionic conductivity of solid state lithium electrolytes. LLTO electrolyte compounds were synthesized using solid state chemistry, Pechini polymerization, and chromium dopants. The lattice structure was analyzed using XRD, resistivity measured with EIS and microstructure imaged by SEM. We found that LLTO compounds doped with the highest molar ratio of Chromium had a highly ordered cubic pervoskite structure and the highest ionic conductivity (10\textsuperscript{-4} S cm\textsuperscript{-1}). The microstructure also revealed a dense material with periodic holes (~13 micrometers) and particles (~5 micrometers) on the ceramic surface.

INOR 598

Effect of precursor loading on axial composition gradients, phase segregation, and aspect ratio of Cu\textsubscript{2}ZnSn\textsubscript{3}S\textsubscript{8} nanorods
Michelle J Thompson, mjit@iastate.edu, Kyle J Blakeney, Purnima Ruberu, Javier Vela.Chemistry, Iowa State University, Ames, Iowa 50010, United States

Due to its large absorption coefficient and direct band gap (~1.5 eV), Cu\textsubscript{2}ZnSn\textsubscript{3}S\textsubscript{8} (CZTS) is a promising quaternary semiconductor for solar energy conversion. CZTS is desired due to its composition of elements which are relatively non-toxic, earth abundant, and widely distributed, but synthesis of phase pure, anisotropic CZTS nanocrystals remains a challenge. We show that the initial concentration (loading) of cationic precursors has a dramatic effect on the morphology, aspect ratio, axial composition gradients and internal architecture of hexagonal wurtzite CZTS nanorods. Our experiments strongly indicate that copper is the most reactive of the metal cations, followed by zinc, and tin is the least reactive. Using this reactivity series, we are able to purposely fine-tune the morphology (dots vs. rods) and degree of axial phase segregation of CZTS nanocrystals. The results of this study will improve our ability to synthesize CZTS nanostuctures for photocatalysts and photocatalysis.

INOR 599

How robust are semiconductor nanorods? Investigating the chemical stability and decomposition pathways in photoactive nanocrystals
Malinda Reichert, reichert@iastate.edu, Chia-Cheng (John) Lin, Javier Vela. Department of Chemistry, Iowa State University, Ames, IA 50011, United States

Etching under continuous illumination is the main pathway responsible for deactivation of semiconductor photocatalysts. Common photocatalytic materials degrade by leaching/photoetching and mechanical/thermal degradation. Lattice is known on the reactivity and stability of II-VI semiconductor materials. Thus we investigated the chemical activity (acids/bases and oxidants/reductants) and thermal stability of II-VI semiconductor (SC) nanorods (NRs) in different environments. In acidic media, cadmium selenide (CdSe) NRs are etched and selenium (Se) nanorods form. In basic media, CdSe NRs retain their morphology and only slightly decrease in length; the width (confined dimension) does not change. Trying to reduce CdSe with H\textsubscript{2} gas only affects the morphology of the NRs, but treatment with n-butyllithium forms Cd metal. Treatment with O\textsubscript{2} produces CdO; however, KMnO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2} do not have any effect on CdSe NRs. The thermal stability of CdSe and CdS NRs was probed by DTA, TGA, and VT-XRD.

INOR 600

Synthesis and optical characterizations of near-IR emitting Ge-nCdS core-shell nanocrystals
Yijun Guo1, yijung@iastate.edu, Purnima Ruberu2, Clare Rowland3, Richard Schaller4, Javier Vela1. (1) Department of Chemistry, Iowa State University, Ames, IA 50010, United States (2) Agonne National Lab, Lemont, IL 60439, United States (3) Department of Chemistry, University of Rochester, Rochester, NY 14627, United States

Semiconductor nanocrystal quantum dots are nearly ideal fluorophores for bioimaging and lighting. Recently, thick-shelled CdSe/CdS core/shell nanocrystals were reported that show unusually high stability and significantly suppressed blinking (almost no fluorescence intermittency). Because of its emitting range (800-1200 nm), Ge is very attractive as a core material for non-blinking QDs. The lattice mismatch between Ge and CdS is only 3.1%. We successfully grew nCdS on Ge cores (0<n<15). After the shell growth, we observe the great enhancement of Ge photoluminescence emission. We used a series of characterization methods (TEM, STEM, XRD, XPS, PL) to study the optical and structural properties of these Ge-nCdS core-shell heterostructures. We also studied PL lifetime and quantum yield of Ge-nCdS with different shell thickness. Our new optimized conditions permit a larger throughput of these materials, increasing their practical availability for fundamental spectroscopic studies as well as practical applications.

INOR 601
Metal oxide transformations: An alternative way to make metal chalcogenide and pnictide nanoparticles for the reforming of oil

Chia-Cheng (John) Lin, cclin@iastate.edu, Shannon Junie Tan, Javier Vela. Chemistry, Iowa State University, Ames, Iowa 50011, United States

Transition metal sulfides and phosphides are highly active catalysts for the reforming of oils (hydrodesulfurization, for example). Among the reported catalysts, metal sulfides or metal phosphides were prepared via colloidal synthesis or post treatment (sulfidization or phosphorization) of metal nanoparticles. Herein, we report an alternative route starting with metal oxide nanoparticles, and the transformation reactions were conducted with highly reactive trialkylsilyl main group compounds. The products were characterized with powder XRD, TEM and UV-Vis absorption spectroscopy. The powder XRD and UV-Vis data confirmed the successful transformation of metal oxides into metal sulfides and selenides. Preliminary data of TEM images also show interesting vesicle like morphology of the resulting particles, which suggests similar transformation mechanism as Kirkendall effect. Further pore structure characterization of the particles and the examination of catalytic activity are reported.

INOR 602

Controlled introduction of nickel in the BEA zeolite by post-synthesis methods

Larry Tesler, ltesler@ufl.edu, Stanisław Dzwigaj, Frederic Averseng. (1) Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States (2) Laboratoire de Réactivité de Surface, Université Pierre-et-Marie-Curie, Paris, France

The oxidation state, dispersion and environment of transition metals present in catalysts play an important role in their catalytic properties and stability. Hence, one must control each step of catalyst preparation in order to obtain the desired final material. Our work focused on the preparation of Ni-HAIBEA and Ni,SiBEA zeolites (x = 0.5 - 7.0 wt. %). Ni-HAIBEA were prepared by conventional wet impregnation and Ni,SiBEA by a two-step post-synthesis procedure, which consisted of dealumination of BEA zeolite with nitric acid (13 mol L⁻¹) and formation, in resulted SiBEA, of vacant T-atom sites with associated silanol groups and then incorporation of nickel ions into vacant T-atom sites by reaction with silanol groups [1]. XRD, DR UV-vis and XPS evidenced that nickel ions are present in the framework of calcined Ni,SiBEA as pseudo-tetrahedral Ni(II), identified by the DR UV-vis bands between 450 – 643 nm (Fig. 1), while they are mainly in extra-framework position of calcined Ni-HAIBEA. The reduction of both C-Ni,SiBEA and C-Ni-HAIBEA leads to the formation of square-planar extra-framework Ni(I) species and Ni(0) nanoparticles as showed by EPR.

Fig. 1. DR UV-Vis spectra of as-prepared, calcined (C-), and rehydrated (reh-C-) NiₓSiBEA.


INOR 603

Molecular programming: Bottom-up fabrication of Cu₂ZnSnS₄ nanostructures with controlled composition and morphology

Kyle Blakeney, kblakeney09@gmail.com, Michelle Thompson, Purnima Ruberu, Javier Vela. Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States

The colloidal nanocrystalline semiconductor Cu₂ZnSnS₄ (CZTS) is an important material for sustainable, efficient, and cost-effective solar cells. CZTS is an attractive material due to its relatively non-toxic, earth-abundant, and widely distributed elements when compared to other semiconductor nanomaterials currently being studied. It also has a large absorption coefficient and a direct band gap around 1.5 eV. However, synthesis of phase pure, anisotropic CZTS nanocrystals remains an interesting challenge. Our experiments indicate that the initial concentration (loading) of metallic precursors has a dramatic effect on morphology, axial composition gradients, and, in some cases, complete phase segregation in hexagonal wurzite CZTS nanorods. We have thus proposed a reactivity series where copper is the most reactive of the metal cationic precursors, followed by zinc and tin, respectively. This knowledge of the chemical reactivity of metallic precursors has enabled purposeful fine-tuning of the morphology (dots vs. rods) and degree of axial composition gradients in CZTS nanorods; an important step in achieving molecular control over fabrication of CZTS nanostructures for photovoltaics and photocatalysis.

INOR 604

Synthesis of metallic Janus nanoparticles using silica as a protecting group

Cameron Crane, ccrane@uark.edu, Jingyi Chen. Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, United States

Rational synthesis of heterogeneous and higher order nanoparticles faces the practical challenge of controlling nucleation and growth at specific sites using wet chemical techniques. We report a new solid-state method for synthesis of binary metal nanoparticles using silica as a protecting group to control the nucleation sites. In this approach, a dimmer structure of gold-silica has been prepared by modifying the conventional oil-in-water microemulsion. The dimmer structure is much more comparable to conventional co-axial core-shell structure for our purpose, and can be achieved through control of the amount of siliclate precursor. These silica-protected gold nanoparticles serve as seeds for subsequent asymmetric seeded growth of other components. Following this growth, the silica protecting group can be selectively etched resulting in Janus nanoparticles. Several noble metals are used to demonstrate the versatility of this synthetic approach. We will discuss the results, characterization, and applications of new Janus nanoparticles.

INOR 605

Synthesis of metal nanoparticles with a DOTA-PAMAM atomic metron template

Matthew Grochowski, matthew.grochowski ctr@nrl.navy.mil, Albert Epsteyn, Vaibhav Jane, David Kidwell. Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375, United States

A desired goal in material synthesis is the construction of sub-nanometer clusters (10-100 atoms) of exact composition and uniformity which could be used in diverse applications ranging from catalysts to multifunctional coatings. Our research utilizes the PAMAM dendrimers as a molecular template by modifying the surface groups with derivatized DOTA ligands: p-SCN-Bn-DOTA, DOTA-NHS-ester, and p-SCN-Bn-D03A. These ligands are tetra-dentate nitrogen macrocycles with terminal carboxylate groups that are ligated to the surfaces of PAMAM dendrimers (generations = 0, 1, 2), and then coordinated to metals such as Cu(II), Ni(II), and Fe(III). The number of metal ions coordinated on each dendrimer is constant, since it occurs at the dendrimer surface rather than the dendrimer interior like other templates, and the binding affinities for each ligand are large. The metals are reduced by NaBH₄ to form nanoparticles which are characterized by gel electrophoresis.

INOR 606

WITHDRAWN

INOR 607
Improved nanocomposite materials for flywheel energy storage applications

Timothy J. Boyle\textsuperscript{1}, tboyle@Sandia.gov, Timothy N. Lambert\textsuperscript{2}, Nelson S. Bell\textsuperscript{2}, William K. Miller\textsuperscript{2}, Mark A. Ehler\textsuperscript{2}. (1) Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM 87106, United States (2) Sandia National Laboratories, Albuquerque, NM 87185, United States

As alternative energy generating devices (i.e., solar, wind, etc.) are added onto the electrical energy grid (AC grid), irregularities in the available electricity due to natural occurrences (i.e., clouds reducing solar input or wind burst increasing wind powered turbines) will be dramatically increased. Due to their almost instantaneous response, modern flywheel-based energy storage devices can act a mechanical mechanism to regulate the AC grid; however, improved spin speeds will be required to meet the necessary energy levels to balance these ‘green’ energy variances. Focusing on composite flywheels composed of carbon fiber (C-fiber), glass fiber, and a ‘glue’ (resin) to hold them together. For this effort, we have focused on the addition of fillers to the resin in order to improve its properties. Based on the high loads required for standard meso-sized fillers, this project investigated the utility of ceramic and graphene nanofillers since they can be added at very low load levels due to their high surface area. The impact these nanofillers had on the final strength of the flywheel material was determined by a ‘three-point bend’ test. Based on an analysis of the economic impact, it was determined based on the 30% improvement in strength, this change may enable a 20-30% reduction in flywheel energy storage cost ($/kW-h).

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000

INOR 608

Formation mechanism of nanostructured metal carbides via salt flux synthesis

Samantha M Schmuecker, sschmuec@uwyo.edu, Brian M Leonard. Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071, United States

Nanostructured metal carbides are of particular interest because of their potential as high surface area, low cost catalysts. By taking advantage of a salt flux synthesis method, multiple carbide compounds have been synthesized at low temperatures providing a pathway to make them nano-size materials. To better understand the reaction mechanism, tantalum carbide synthesis was monitored by quenching samples at 1000°C intervals and analyzed by multiple spectroscopic methods. The reaction was determined to occur through the formation of metal halide intermediates, which were repeatedly viewed with x-ray diffraction (XRD) and further supported by IR, Raman, and NMR spectroscopy. Control experiments were also employed to further verify this mechanism of formation by using different salt compositions, and solid-state metathesis reaction. The reaction mechanism was also confirmed by applying these techniques to other metal carbides and observing similar intermediates.

INOR 609

Corrosion performance of nickel-based alloys in the uranium-containing chloride melts

Ilya B. Polovov\textsuperscript{1}, polovov@dpt.ustu.ru, Aleksandr V. Abramov\textsuperscript{2}, Aleksandr V. Bazhenov\textsuperscript{2}, Robert V. Kamalov\textsuperscript{2}, Vladimira A. Volkovich\textsuperscript{2}, Oleg I. Rebrin\textsuperscript{2}, Dmitrii Maitsev\textsuperscript{2}. (1) Department of Rare Metals and Nanomaterials, Ural Federal University, Ekaterinburg, Russian Federation (2) Department of Physical and Chemical Methods of Analysis, Ural Federal University, Ekaterinburg, Russian Federation

According to the technology roadmap for Generation IV nuclear energy systems molten salt reactors (MSR) with on-site uranium-thorium nuclear fuel cycle is one of innovative reactor types. Practical realization of MSR relies on finding construction materials stable in fused salts. The present work was aimed at studying corrosion of a number of prospective alloys in fused chlorides. Corrosion-resistant nickel-chromium-molybdenum alloys (Hastelloy N, G-35 and C-2000) and nickel-molybdenum alloy (Hastelloy B-3) were investigated. Corrosion tests were performed in NaCl–KCl–UCl\textsubscript{3}(1 wt. % uranium) melts at 750 °C.

During exposure at high temperatures studied materials underwent structural changes: excessive intermetallic phases were formed along the grain boundaries. This led to the formation of microgalvanic pairs resulting in subsequent intergranular corrosion. In addition alloys surface was depleted in chromium and enriched in molybdenum confirming the electrochemical nature of the corrosion. In terms of intensity and depth of corrosion penetration the studied alloys can be ranged as: G-35 ≥ C-2000 > N > B-3 (Table).

<table>
<thead>
<tr>
<th>Type of alloy</th>
<th>Corrosion rate</th>
<th>Depth of corrosion layer, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastelloy G-35</td>
<td>0.19</td>
<td>16-18</td>
</tr>
<tr>
<td>Hastelloy C-2000</td>
<td>0.15</td>
<td>30</td>
</tr>
<tr>
<td>Hastelloy N</td>
<td>0.06</td>
<td>14-17</td>
</tr>
<tr>
<td>Hastelloy B-3</td>
<td>0.03</td>
<td>-</td>
</tr>
</tbody>
</table>

Low rate of Hastelloy B-3 corrosion is explained by the formation of a dense surface layer substantially enriched in molybdenum (Figure). Molybdenum in chloride melts under inert atmosphere exhibits high corrosion resistance, and the molybdenum-containing layer formed has protective properties. Corrosion resistance of Hastelloy B-3 alloy in uranium containing chloride melts thus makes it a prospective construction material for MSR.

INOR 610

Hydrogeninduced amorphization behaviors of multiphase La\textsubscript{84}Mg\textsubscript{8}Ni\textsubscript{8} alloy

yiming li\textsuperscript{1}, liyiming79@sina.com, huiping ren\textsuperscript{2,3}, zhuocheng liu\textsuperscript{2}. (1) School of Materials Science and Engineering, Shanghai University, shanghai, shanghai 200072, China (2) Analytical and testing Center, Inner Mongolia University of Science and Technology, baotou, Inner Mongolia, China (3) Key Laboratory of Integrated Exploitation of Bayan Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology, baotou, Inner mongolia 014010, China

The changes of crystal structure with hydrogenation in multiphase La\textsubscript{84}Mg\textsubscript{8}Ni\textsubscript{8} alloy were studied in order to examine the mechanism of hydrogen-induced amorphization (HIA) process. After gas-solid hydriding/dehydriding cycling, transformations from crystalline to amorphous state (HIA) of (La,Mg)\textsubscript{8}Ni\textsubscript{8} (Ce,Ni\textsubscript{8} type), (La,Mg)\textsubscript{8}Ni\textsubscript{8} (Ce,Cr\textsubscript{17} type), and (La,Mg)\textsubscript{8}Ni\textsubscript{8} (Pr\textsubscript{5}Co\textsubscript{19} type) phase are identified by XRD and TEM-SAED analysis, whereas
LaNi$_5$ (CaCu$_5$-type) phase maintains the crystal state. Partial amorphization shortens and leans the plateau of PCT curve, and is considered to be one of the important factors affects the reversible hydrogen storage capacity. It is found that La-Mg-Ni phases could form crystal hydrides, but the crystalline losses along with the degree of the lattice distortion increased caused by the rise of the hydrogen pressure. The amorphous La-Mg-Ni phases recrystallize upon heating and dehydrogenating. Amorphous (La,Mg)$_2$Ni$_3$ is more stable because the crystallization temperature of the amorphous (La,Mg)$_2$Ni$_7$ is higher than the amorphous (La,Mg)$_3$Ni$_13$. Therefore, it is believed that the tendency of HIA for (La,Mg)$_2$Ni$_7$ phase is stronger than the (La,Mg)$_3$Ni$_13$ compounds.

INOR 611

Size-controlled synthesis of Cu$_2$O octahedra and their size-dependent photocatalytic reactivities

Michelle A Nguyen, michelle.anne.nguyen@gmail.com, Marc R Knecht. Department of Chemistry, University of Miami, Miami, FL 33146, United States

The synthesis of inorganic materials on the nano and microscale with controllable shapes and sizes has been of great interest due to their catalytic reactivity. This activity is specifically dependent upon the atomic display, both metallic facets and defect atoms, from which enhanced reactivity can be achieved. Due to the impending energy crisis, such enhanced activities are important, where photocatalytic applications could be particularly attractive. To this end, Cu$_2$O is an interesting material for photocatalysis due to its ability to split water for H$_2$ production under visible light, as well as its use in photocatalytic degradation of toxic molecules. To study this process, we have prepared a new synthetic method to achieve Cu$_2$O octahedra microcrystals with a tunable edge length using an aqueous solution method containing a surfactant at low temperatures. The materials were fully characterized to confirm their composition. After which, the photocatalytic reactivity of the various sized Cu$_2$O octahedra particles was investigated by monitoring the degradation of methyl orange via UV-vis spectroscopy. The results indicated that size dependent photocatalytic reactivity was evident, which was optimized for particles of 4.39 µm in edge length.

INOR 612

Preparation of aluminum vanadate and vanadic acid materials using vanadyl oxalate

Asma Alothman, asma.alothman@okstate.edu, Allen Apblett. Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United States

Metal vanadates have an extensive range of important materials and catalytic applications. While there are numerous methods for their synthesis, aqueous reactions with minimal by-products are most desirable. We have developed a method for the preparation of aluminum vanadate via the reaction of aqueous vanadyl oxalate with aluminum oxides and hydroxides. It is also possible to prepare an unusual aluminum-free vanadic acid by such reactions, the characterization of the products using thermal gravimetric analysis (TGA), IR spectroscopy (IR), and X-ray powder diffraction (XRD) will be reported.

INOR 613

Corrosion resistance of Hastelloy-type alloys in chloroaluminate melts

Ilya B. Polovov1, polovov@dispt.ustu.ru, Aleksandr V. Abramov2, Aleksander V. Bazhenov2, Vyacheslav V. Karpov1, Vladimir A. Volkovich1, Oleg I. Rebrin2. (1) Department of Rare Metals and Nanomaterials, Ural Federal University, Ekaterinburg, Sverdlovsk 620002, Russian Federation (2) Department of Physical and Chemical Methods of Analysis, Ural Federal University, Ekaterinburg, Sverdlovsk reg. 620002, Russian Federation

Chloroaluminate melts are prospective media for second loop of molten salt nuclear fast reactor due to their low melting temperatures and well-known physical properties. Application of chloroaluminautes in such technologies is limited by the problem of finding corrosion resistant materials. In the present work the corrosion behavior of Haynes 230, Hastelloy S and X high-temperature alloys and Hastelloy N, G-35, C-2000 corrosion-resistant alloys was studied at 550 °C in fused KCl–AlCl$_3$ mixture. The initial ratio of AlCl$_3$ to KCl was equal to 1.1. The corrosion rates of the studied materials were determined after 100 h of exposure in the melt under high-purity argon atmosphere (Table).

<table>
<thead>
<tr>
<th>Type of alloy</th>
<th>Corrosion rate</th>
<th>Depth of corrosion layer, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/(m$^2$·h)</td>
<td>mm/year</td>
</tr>
<tr>
<td>Haynes 230</td>
<td>0.8±0.1</td>
<td>18–24</td>
</tr>
<tr>
<td>Hastelloy S</td>
<td>0.8±0.1</td>
<td>18–24</td>
</tr>
<tr>
<td>Hastelloy X</td>
<td>0.8±0.2</td>
<td>55–65</td>
</tr>
<tr>
<td>Haynes 230</td>
<td>0.8±0.2</td>
<td>27–32</td>
</tr>
<tr>
<td>Hastelloy G-35</td>
<td>1.4±0.3</td>
<td>—</td>
</tr>
<tr>
<td>Hastelloy C2000</td>
<td>1.6±0.3</td>
<td>—</td>
</tr>
</tbody>
</table>

It was found that Haynes 230, Hastelloy S and X alloys were subjected to intergranular corrosion. Metallographic analysis revealed that secondary excess phases were formed along the grain boundaries. X-ray microanalysis of high-temperature alloy samples showed that chromium concentration near grain boundaries decreased but within the grain boundaries Cr content greatly increased. This indicates the formation of chromium-containing carbide phases along the grain boundaries of such alloys. This process occurs mainly as a result of temperature-induced degeneration of initially segregated chromium carbides. Therefore despite the relatively low corrosion rates the high-temperature alloys with carbide hardening cannot be used as construction materials for molten salt nuclear reactors.

The surface of the studied corrosion-resistant alloys after 100 h contact with KCl–AlCl$_3$ melt was subjected to uniform corrosion. Irregular surface etching is caused by non-uniformity of materials and the presence of defects. SEM and X-Ray microanalysis showed no secondary phase formation along the grain boundaries. The corrosion rates of the corrosion resistant nickel-based alloys are determined by the red-ox processes resulting in dissolving the most electronegative alloy components (chromium, manganese), and can, therefore, be predicted for the given conditions.

INOR 614

Versatility of cerium in manganese cluster chemistry

Annaliese E. Thuijs, aethuijs@ufl.edu, George Christou, Khalil A Abboud. Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, United States

3d and mixed 3d/4f metal clusters containing bridging oxide ions continue to be an area of great interest to many research groups, including ours, due to their often fascinating structures and interesting physical properties, particularly those of relevance to the field of molecular magnetism. Manganese is...
one of the 3d metals of choice for such studies, being stable in multiple oxidation states and having shown a great propensity to yield a variety of cluster types, as well as displaying significant magnetoanisotropy arising from the Jahn-Teller distortion of octahedral Mn$^{II}$. As a result, Mn/O cluster chemistry often leads to compounds with interesting structural, magnetic, and other physical properties. The inclusion of Ce$^{III}$ in Mn chemistry can lead to it acting as an oxidizing agent, a source of a heterometal to give mixed-metal products, or both, and when reduced to Ce$^{III}$ can also provide additional anisotropy to mixed-metal products. The syntheses, structural characterization, and physical properties of several new Mn and Mn/Ce clusters will be presented.

INOR 615
Synthesis and characterization of a new Fe$_8$ complex using a 2-hydroxymethylpyridine derivative
Kylie Mitchell, kyliem@chem.ufl.edu, Khalil A Abboud, George Christou. Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

Polynuclear transition metal clusters are of great interest because of their relevance to molecular magnetism and bioinorganic chemistry. One common approach to the synthesis of these clusters is by hydrolysis or alcoholysis of a metal salt in the presence of carboxylate groups, or of a preformed low nuclearity metal carboxylate cluster, in the presence of potentially chelating ligands. Our group has previously employed this approach with both Mn and Fe yielding many interesting products. For example, the largest known homometallic Fe/O cluster, a Fe$_{12}$ species, was obtained from this method when N-methylidihanolamine was employed. We have also had success with this approach using 2-hydroxymethylpyridine (hmpH), whose deprotonated form is an excellent O,N chelating and bridging ligand. Many clusters have been synthesized using hmpH, such as Fe$_8$, Fe$_{10}$, Mn$_{10}$, Mn$_{11}$, and Mn$_{12}$ species. We have explored also the effects of bulkiness and flexibility of hmpH derivatives on the nuclearity, topology, and magnetic properties of clusters by alterations at the --CH$_2$-- group of the ligand. As a continuation of this work in Fe chemistry, a rigid hmpH derivative has been employed and has yielded an Fe$_8$ product. The synthesis and characterization of this complex will be discussed.

INOR 616
Synthesis and characterization of a family of π-extended metal thiophenedithiolenes
Kristine L Konkol, kristine.konkol@ndsu.edu, Seth C Rasmussen. Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108, United States

Since their discovery in the 1960s, metal dithiolene complexes have generated significant interest, not only because of their unique electronic and magnetic properties, but also because they are the building blocks of extended metal complexes. These complexes are versatile species capable of a wide range of oxidation states, coordination geometries, and magnetic moments. In 2009, the Rasmussen group reported the synthesis of a planar π-extended nickel thiophenedithiolene complex, combining the aspects of conjugated organic materials with metal dithiolene systems. This synthetic approach is currently being used to prepare a family of solution processable metal thiophenedithiolenes with different transition metals and thiophene ligands. Transition metals under investigation include nickel, cobalt, palladium, platinum, and gold. Synthetic details will be presented, along with the optical, electrochemical and crystallographic properties of these metal-dithiolene based conjugated oligomers.

INOR 618
Complexation of decamethylferrocene to cyclic trinuclear Ag(I) and Cu(I) azolate complexes
Waheda Hassen, whassen@twu.edu, Erica Humbach, Jehan Kohistani, Lorena Delgado, Vladimir Nesterov, Manal A. Rawashdeh-Omary*. (1) Department of Chemistry and Biochemistry, Texas Woman’s University, Denton, Texas 76204, United States (2) Department of Chemistry, University of North Texas, Denton, Texas 76203, United States

The reaction of mixing two different cyclic trinuclear Cu(I) and Ag(I) azolate complexes with a bridging diimine ligand has been investigated in our laboratory. Mixed-metal colored products in which 1,2-bis(pyridyl)ethane acts as a chromophoric center that facilitates the communication between Cu(I) and Ag(I) centers in extended supramolecular structures have obtained with some dependence on stoichiometry and reaction conditions. The structural and photophysical properties will be discussed and contrasted with the monometallic analogues.

INOR 619
Fabrication and characterization of vanadila-silica aerogels
Leah C Smith, carrollm@union.edu, Aude M Bechu, Mary K Carroll, Ann M Anderson. (1) Department of Chemistry, Union College, Schenectady, NY 12308, United States (2) Department of Mechanical Engineering, Union College, Schenectady, NY 12308, United States

Vanadila-silica aerogels were prepared via sol-gel synthesis and a rapid supercritical extraction (RSCEx) process. Tetramethyl orthosilicate and vanadyl acetylacetonate were used as precursors with methanol and deionized water as solvents and ammonia as the catalyst. The reaction was adjusted to shorten gelation time and to increase the amount of vanadila (from <1% to ca. 5%) in the gels. The resulting aerogels were characterized using bulk density, Brunauer-Emmett-Teller (BET) surface area, Barrett-Joynner-Halenda (BJH) pore distribution, energy-dispersive x-ray (EDX) spectroscopy, FTIR and UV-Visible spectroscopy. The aerogels had average bulk density of 0.11 (±0.01) g/cm$^3$ and surface areas ranging from 560 (±30) m$^2$/g to 850 (±40)m$^2$/g with an average surface area of 690 (±40) m$^2$/g. The data taken show differences between aerogels prepared with and without solvent exchanges. These differences include color (aerogels are colorless with solvent exchanges and green without) and peak BJH pore diameter: 12 (±3) nm with solvent exchanges and 20 (±5) nm without. FTIR and EDX spectra show that the aerogels are comprised mostly of silica, and EDX data indicate

INOR 620
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INOR 618
Complexation of decamethylferrocene to cyclic trinuclear Ag(I) and Cu(I) azolate complexes
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that they also contain vanadium. Further characterization of the aerogels, including catalytic testing to determine their applicability to automotive exhaust mitigation, is ongoing.

INOR 620
Supramolecular aggregates of single-molecule magnets by carboxylate substitution
Andrew M Mowson, mowsam71@ufl.edu, Khalil A Abboud, George Christou. Department of Chemistry, University of Florida, Gainesville, FL 32611, United States

Single-molecule magnets (SMMs) are of considerable interest because of their ability to function as nanoscale magnets. They also display fascinating behavior when they straddle the interface between the quantum and classical worlds of magnetism. It has recently been shown (Nguyen et al., J. Am. Chem. Soc. 2011, 133, 20688) that the [Mn12O(O2CMe)12(muko)3]ClO4 (muko = methyl-2-pyridyl ketone oximate) SMM with a triangular Mn12 topology and an S = 6 ground state spin can be used as a building block to synthesize a supramolecular tetramer if the oxime in its preparation is replaced with a dioxime. We have extended this work by using dicarboxylic acids capable of bridging two or more Mn12 units. Performing carboxylate substitution on [Mn12O(O2CMe)12(muko)3]ClO4 with dicarboxylic acids, and taking advantage of the toluene:acetic acid azeotrope to help drive the substitution to completion, has yielded supramolecular aggregates of SMMs with different nuclearities and geometries. The syntheses, structures and physical properties of these materials will be presented.

INOR 621
Variable-temperature multinuclear NMR spectra of the [Mn12O16(O2CR)18(H2O)4] family of single-molecule magnets in solution
Adeline Fournet, a.fournet@ufl.edu, George Christou. Chemistry, University of Florida, Gainesville, FL 32611, United States

The well-studied family of single-molecule magnets, [Mn12O16(O2CR)18(H2O)4], is known to display unexpected 1H NMR spectra at room temperature. A ligand-based dynamic process causes a rapid exchange between several structural isomers of the molecule, resulting in solution NMR spectra consistent with a molecule of higher symmetry than the D3 or S4 seen in the solid state. As the temperature is lowered, this exchange is slowed down and the spectra become more complex. Using variable-temperature, multinuclear (1H, 19F, 2D) NMR spectroscopy, we were able to follow this evolution for several different [Mn12O16(O2CR)18(H2O)4] derivatives and calculate the energy barrier of the exchange process. The syntheses, NMR spectra, and interpretation of the dynamic process will be described.

INOR 622
Effects of alpha substitution on difluoroboron dibenzoylmethane mechanochromic luminescence
William A Morris, wam8wr@virginia.edu, Carl O Trindle, Cassandra L Fraser. Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States

Difluoroboron β-diketone (BF2(dbk)2) dyes are known for their unique mechanochromic luminescent (ML) properties. This typically manifests itself as a red-shift in the emission from the thermally annealed solid-state dye upon mechanical perturbation, followed by spontaneous recovery to the original state at room temperature. In essence, these materials are renewable inks. Treated surfaces can be inscribed, self-erase and inscribed again. We have studied the effects of various arenes, halides and alkyl substituents on ML emission color shift and room temperature self-erasing properties of this family of dyes. However, the effect on ML of substitution at the alpha carbon of the β-diketone ligand has yet to be rigorously investigated. We hypothesize that such substitution will disrupt the formation of face-to-face H-aggregates of the molecules, which has been proposed to be the cause of ML and red-shifted emission upon smearing. Steric hindrance at the alpha position may diminish or completely eliminate ML, or result in faster recovery of the annealed emission after smearing. To test this hypothesis, a dibenzoylethane derivative, BF2(dbm(OMe)2, where dbm = dibenzoylethane with a methyl group in the alpha position, was synthesized. It exhibits bright blue emission in the solid state as isolated. However, the compound is practically non-emissive in solution (\( \phi_e = 0.1\% \) in CH2Cl2 solution). This is good evidence that the compound exhibits aggregation-induced emission (AIE). It also shows significantly less dramatic ML when compared to the difluoroboron dibenzoylethane derivative BF2(dbm(OMe)2). This shows that the methyl group at the alpha position of the β-diketone core does, in fact, hinder ML. Findings with this and other alpha substituted analogues along with computational studies to better understand optimal confirmations, transitions, and molecular interactions will be presented.

INOR 623
Tailoring surface composition and morphology of platinum-copper nanotubes through in situ galvanic replacement reaction
Leanne E Mathurin, leanne@uark.edu, Shutang Chen, Jingyi Chen. Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, United States

Bimetallic alloys between platinum and copper are attractive heterogeneous catalysts and electrocatalysts, due to the electronic coupling and geometric effects of the alloys compared to individual components. The catalytic activity is strongly associated with composition and surface morphology. In this study, a new chemical route to produce platinum-copper alloyed nanotubes has been developed by in situ galvanic replacement of copper nanowires with platinum precursor salts. By controlling the precursor ratio, type of surfactants, and reaction temperatures, the composition and morphology of the nanotube surface could be systematically tuned. Compared to hollow nanospheres, the one-dimensional nanotubes exhibit higher catalytic activity and stability. The effects of composition and surface morphology on the catalytic performance will be examined for electro-oxidation of methanol in fuel cell applications.

INOR 624
Direct access to macroporous chromium nitride/chromium titanium nitride with inverse opal structure
Weitian Zhao, wz255@cornell.edu, Francis J DiSalvo. (1) Materials Science and Engineering, Cornell University, Ithaca, NY 14850, United States (2) Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14850, United States

Recent studies revealed the potential of transition metal nitrides as high performance catalysts supports, particularly in proton exchange membrane fuel cell (PEMFC) applications. Metal nitrides with nano-scale particle size and an ordered porous structure are desired for this application. Many reported syntheses of meso/macroporous nitride made use of porous metal oxides as an intermediate for the final product. Due to problems associated with this method, a facile, low temperature synthesis of porous, single-phase, crystalline macroporous chromium nitride and chromium titanium nitride with inverse opal morphology is reported. Characterization using XRD, SEM, HRTEM and TGA were conducted. XPS study was also carried out to provide insights into the chemical states of the elements fabricated using this method. An interconversion of macroporous CrN to Cr2O3 and back to CrN with retaining the inverse opal morphology is also demonstrated. Nitride materials synthesized using this method are also tested using electrochemical measurements after loading with Pt catalysts.

INOR 625
Tuning structures of metal-organic frameworks for gas adsorption application
Zhangwen Wei, zhangwenwei@mail.chem.tamu.edu, Dawei Feng, Vaiva Krungleviciute, Jinhee Park, Jesus Ferrando, Hong-Cai Zhou, Taner Yildirim. (1) Department of Chemistry, Texas A&M University, College Station, TX 77840, United States (2) National Institute of Standards and
Metal-organic frameworks (MOFs) are new porous materials showing large internal surface areas, high porosities and tunable structures. They have been extensively studied for their application potential of gas storage, chemical separation, catalysis, and drug delivery. Based on the previous reported results, a series of MOFs with excellent methane uptake and working capacities have been synthesized by carefully tuning the pore sizes. They are very promising for on-board methane storage applications.

INOR 626
Metal-organic frameworks constructed from metal-organic polyhedra with nitrogen-based linkers
Stephen A. Fordham, stephen.fordham@chem.tamu.edu, Dawei Feng, Ying-Pin Chen, Dahuai Liu, Muwei Zhang, Hong-Cai Zhou. Department of Chemistry, Texas A&M University, College Station, TX 77842, United States

Zeolitic imidazolate frameworks (ZIFs) have recently been studied due to their unique structural properties and wide array of applications including catalysis, gas uptake, and chemical separations. By variation of metal and ligand geometries, several interesting structure features can be introduced to ZIF based frameworks including multiple unsaturated open metal centers, increased porosity, and chemical stability. The addition of open metal sites in these frameworks could provide enhanced gas uptake and the possibility for separation performance in industrial gas systems. Traditional ZIFs have mostly been synthesized with tetrahedral building units such as Zn$^{2+}$ and Co$^{2+}$; however, the incorporation of other transition metal nodes provides a new class of materials to study. Additionally, through ligand extension new frameworks with improved porosity can be synthesized. Imidazolate moieties in the structure of the framework also provide enhanced chemical stability due to stronger metal ligand interactions over traditional hybrid materials.

INOR 627
Adsorption and release of siRNA from porous silica
Jeremy L Steinbacher, steinbaj@canisius.edu, Christopher C Landry. (1) Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY 14208, United States (2) Department of Chemistry, University of Vermont, Burlington, VT 05405, United States

Porous silica particles are potential transfection agents for nucleic-acid based therapies due to their large specific surface areas and pore volumes and the ease with which they can be chemically modified to maximize the loading of cargo and to effect targeting in vivo. Here, we present a systematic study of the effects of pore size and pore modification on the adsorption and release of short, interfering RNA (siRNA) from a mesoporous silica particle developed in our laboratory. Using adsorption isotherms and release experiments, we found that the short polyamine diethylenetriamine was the best chemical modification for achieving both the adsorption and release of large amounts of siRNA. The degree of functionalization with diethylenetriamine caused drastic changes to the loading capacity and binding strength of siRNA to silica with relatively large pores (8 nm and larger), but degree of functionalization had a weaker effect in narrow pores (4 nm). Multilayer adsorption could occur in materials with large pores (15 nm). Release experiments showed that intermediate pore sizes and intermediate degrees of functionalization resulted in the best compromise between maximizing loading (from strong adsorption) and maximizing release. Capillary electrophoresis and quantitative, real-time PCR demonstrated that the siRNA was released intact and that these particles functioned as a transfection agent to mammalian cells in vitro.

INOR 628
Sorption studies on isoreticular Zr-based metal-organic frameworks
Xuan Wang, xuan.wang@chem.tamu.edu, Yinpin Chen, Hongcai Zhou. Department of Chemistry, Texas A&M University, College Station, Texas 77840-3012, United States

Advanced porous sorbent hold great promises for gas storage, achieving reusability, high working capacity, and great stability. Traditional porous sorbent materials (e.g. activated carbon and zeolites) suffer from moderate surface areas, unfavorable pore size distribution, and difficulty to fine-tune porosity and therefore have low possibility for simulation and low efficiency for gas packing. Metal-organic frameworks (MOFs) have gain extensive attention in gas storage. MOFs are attractive for their significant degree of tunability and crystalline nature. Recently, the Zr-based MOF has exhibited remarkable chemical and thermal stability, which makes the Zr-based MOFs more applicable for industrial use. Herein, we have developed a series of Zr-MOFs through solvothermal reactions using functionalized organic linkers. The different interaction with guest molecules are expected, and it is interesting to study the adsorption performance.

INOR 629
Multifunctional molecular materials based on transition metals and organocyanide anions
Xuan Zhang, xuan.zhang@mail.chem.tamu.edu, Hanhua Zhao, Kim Dunbar. Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States

Multifunctional molecular materials are of high interest because of the coexistence of two or more properties such as magnetism combined with conducting, ferroelectric or optical properties. In particular, organocyanides such as TCNQ and DCNQI which are excellent electron acceptors have been extensively studied due to the fact that their radical forms can either stack into electron conducting columns or act as spin carriers to mediate magnetic coupling between paramagnetic metal ions.

The series M$^2$(TCNQ)$_2$ (M=Mn, Fe, Co, Ni) are rare examples of binary metal-organic framework magnets discovered in our lab and found to be both glassy magnets and semiconductors. The microcrystalline Fe(TCNQ)$_2$ material (Figure 1) has been prepared and drastic differences in the magnetic properties have been observed for samples of varying degrees of crystallinity and particle sizes. Efforts are underway to obtain structural information by synchrotron methods in order to further refine our understanding of structure-property relationships in these simple materials. In related work, the semiconductor Cd$_2$TCNQ$_4$H$_2$O with non-integer valences of TCNQ was synthesized and is the first example that exhibits multiple bridging modes of TCNQ in one compound.

Another application of the chemistry of organocyanides is to explore reactions of the meta-dicyanamidobenzene diion (DCYD$^2$) which was predicted by Ruiz and coworkers to facilitate ferromagnetic interactions between certain metal ions. It was found that DCYD$^2$ self-assembles with divalent metal-organic building blocks to afford a variety of quadruple helical chain-like structures that mimic the conformation of DNA G-quadruplexes (Figure 2). The packing of these helical chains through pi-pi stacking of pyridyl groups on the ligands leads to 1D nanochannels with an estimated empty volume of 38.6% of the unit cell volume (31.739Å$^3$). These materials are promising for applications in chiral molecule recognition and chiral separations.
Potential applications of hydroxypyclen derivatives
Samantha Dionicio, s.m.dionicio@tcu.edu, Kayla Green. Department of Chemistry, Texas Christian University, Fort Worth, Texas 76109, United States

Two novel isomers of hydroxypyclen, a twelve membered, pyridine containing macrocyle, have been successfully synthesized in our lab. We have shown that the position of the hydroxyl group affects spectrochemical behavior of many redox active transition metals including iron, cobalt, nickel and copper. These results have led to the investigation of hydroxypyclen derivatives as magnetic resonance imaging contrast agents and stereospecific epoxidation catalysts. Results concerning these topics will be presented.

Synthesis and characterization of new coordination polymers
Jian Cui, cujian@uhcl.edu. Chemistry, University of Houston-Clear Lake, Houston, TX 77058, United States

Entangled metal–organic framework (MOF) has been one of the most fascinating research subjects in coordination polymers which are now shown to have weak chemical bonds and more flexible with attractive potential applications such as sensors and drug delivery. Design and synthesis of such kind of new inorganic-organic hybrid coordination polymers by selecting appropriate inorganic transition metal ions, organic ligands, counter ions and temperature may offer interesting structures with attractive properties and potential applications. Here we’ll present our new findings.

Substituent effects in platinum(II) biphienyl bipyridine complexes
Ali Jehan1, asjehan@wichita.edu, D. Paul Rilema1, Khamis Siam2, Arvin Cruz2, Curtis Moore3, Venugopal Komreddy2, Huy Nguyen1. (1) Department of Chemistry, Wichita State University, Wichita, KS 67260, United States (2) Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico 00931, United States (3) Department of Chemistry, Fort Hayes State University, Hays, KS 67601, United States (4) USCD Crystallography Facility, University of California San Diego, La Jolla, CA 92093, United States

Platinum(II) biphienyl bipyridine ligand complexes were found to exhibit emission from an excited state in the 600 nm region of the spectrum when excited in their metal-to-ligand charge transfer transition band located near 450 nm. The 2,2′-bipyridine ligands were decorated with substituents located on the 4,4′-positions of the pyridine rings. The structures of the complexes were distorted from square planarity based on single crystal structures. Density functional theory and time dependent density functional theory gave information about the assignment of frontier orbitals, their energies and the predicted optical transitions in the series of complexes. Linear free energy correlations were determined between theoretical and experimentally obtained parameters along with correlations with substituent σ constants. We have found experimental and theoretical linear correlations between σα and emission energy maxima, emission lifetimes, absorption energy maxima and reduction potentials, between experimental and predicted absorption energy maxima and between the theoretical LUMO and experimental reduction potentials. The information obtained provides an understanding of the fundamental electronic behavior of the complexes.

Tuning of charge localization/delocalization and spin-state in mixed-valent triangular (Fe3(μ3-O))-pyrazolates
Evgen V. Govor1, igovar@fliu.edu, Carla S. Coste2, Dalice M. Piner2, Raphael G. Raptis2. (1) Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, United States (2) Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico 00931, United States

Mixed-valent {M3(μ3-O)}-carboxylates (M = FeIII, RuIII) have been intensively studied as intriguing models in the field of electron transfer. We are proposing analogous triangular motifs with 4-nitropyrazolates (4-NO2-pz) bridges, containing the same planar triangular Fe3(μ3-O) motif, but with different extend of electronic and magnetic communication among the three metal centers. Complexes [Fe3(μ3-O)(4-NO2-pz)X]3+ with X = Cl (1), Br (2), NCS (3; Figure 1) and CN (4) show a systematic anodic shift of their one-electron reversible reduction: E1/2 = -0.70, -0.55, -0.36 and +0.10 V, respectively. Chemical reduction of compounds 1 - 4 by Bu3NBH4 leads to the mixed-valent analogues 1red, 4red, correspondingly. Spectroscopic studies (electronic, vibrational, 57Fe-Mössbauer, EPR) of the mixed-valent complexes, in situ or after isolation, identified high-spin (1red - 3red, 128red) and low-spin (4red - 3red, 4red) systems, as well as charge-localization (1red, 2red) and delocalization (3red, 4red) in mixed-valent trimers.

Fine tuning the isomeric stability and metal-binding properties of light-triggered hydrazone metal chelators
Rory C McAtee, mcarory@lycoming.edu, Andrew Franks, Katherine Franz. Department of Chemistry, Duke University, Durham, NC 27708, United States

Photocontrol of biological and molecular species’ geometries, particularly in protein function, self-assembling molecules and the powering of molecular machines, has gained heightened interest as the plethora of promising in vivo applications continues to grow. Analogous to the ubiquitous photocactivity of azobenzene, hydrazones contain a carbon-nitrogen C=N double bond capable of undergoing a very attractive configurational change by photochemical and thermal cis-trans isomerization. A series of aroylhydrazones have shown considerable potential as agents for transition metal chelators and thus have been exploited as candidates for therapeutics in pathological metal mis-regulation. As presented here, a dynamic library of x-HAPI [(E)-N-{1-[2-hydroxyphenyl]ethylidene}isonicotinoylhydrazide] analogues have been successfully synthesized, which carry very unique dual-wavelength photoswitching, metal affinity, and pH dependent properties.

... Such vastly applicable chemical properties may be employed in a broad range of active biological and material science fields.
Photomagnetic state trapping: A comparison between transition metal complexes and hypervalent organic radicals

Hoa Phan1, hphan@chem.fsu.edu, Kristina Lekin2, Stephen M Winter1, Richard T Oakley2, Pradip Chakraborty2, Andreas Hauser2, Michael Shatruk1. (1) Florida State University, Tallahassee, Florida 32310, United States (2) Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada (3) Chemistry, University of Geneva, Geneva, Switzerland

The effect of light-induced excited spin state trapping (LIESST) is well established for transition metal compounds, mainly Fe(II) complexes, that can exhibit magnetic bistability caused by the change in the electron distribution between the $t_{2g}$ and $e_g$ orbitals. We have recently reported that a similar phenomenon can take place in all-organic materials. In this contribution, we focus on the comparison of these two types of photomagnetic behavior and demonstrate that the organic systems might be promising for high-temperature applications. We compare the electronic factors underlying both types of transitions and the changes in crystal structures, optical spectra, magnetic susceptibilities, and relaxation kinetics of [Fe(tpma)(x)]$X_2$ ($tpma = tris(2-pyridylmethyl)amine; xbin = 1,1'-a,a'-oxy-2,2'-bibimidazole; X = ClO$_4^-$, BF$_2^-$, PF$_6^-$), and b-FBPeT (8-fluoro-4-ethyl-4H-bis[1,2,3]dithiazolo[4,5-b:5',4'-elopyrindin]-3-yl). These materials show both thermal and photoinduced changes in the spin state, but the mechanisms of these conversions, despite the conceptual similarity, exhibit substantial differences, which will be discussed in this paper.

INOR 636
Rhodamine and fluorescein based fluorescent and optical sensors for heavy metal ions
Rathnayaka M. N. R. Madawala, rathnayaka.m.madawala@wmich.edu, Ekkehard Sinn. Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008, United States

New rhodamine based sensors A, B, C, D and a fluorescein based sensor E were synthesized. Binding of A and B toward various metal ions (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, Fe$^{3+}$, Fe$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Cr$^{3+}$, Pb$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$) were examined through changes in fluorescence and UV. A binds strongly and selectively to Co$^{2+}$ and enhances both the visible color and fluorescence. B binds strongly and selectively to Cu$^{2+}$ and enhances the visible color. The NMR titration, fluorescence lifetime and the quantum yield measurements were carried out for the synthesized dye molecules with and without metal ions to understand the mechanistic details of sensing. Fluorescence and UV Sensitivity of all the synthesized rhodamine and fluorescein derivatives will be presented.

INOR 637
Synthesis of ligands and polymers for fluorescent ratiometric sensor of Cu(II)
Lea Nyiranshuti, ljs28@wildcats.unh.edu, Feifei Wang, W. Rudolf Seitz, Roy P. Planalp. Department of Chemistry, University of New Hampshire, Durham, NH 03824, United States

Metals are necessary for life, however excess metal ions can lead to deleterious effect on aquatic organisms and human health. For example Cu(II) can be toxic to living organisms in low concentration. This toxicity of metal ions depends on concentration of free ion rather than total metal concentration. In our group, we are developing a novel fluorescent ratiometric sensor to measure the bioavailable copper(II) in the environment especially in water supplies. This indicator consists of Poly(N-isopropyl acrylamide) (polyNIPAM), high affinity ligand (N-2-pyridinylethyl)-(N-2-pyridylmethyl)-3-aminopropyl-acrylamide (PEPMA-C3-AM) and a pair of fluorophores (Rhodamine and Alexafluor 647). polyNIPAM is a responsive polymer whose phase transitions are caused by metal complexation and are monitored by fluorescence resonance energy transfer (FRET). By separating complexation and fluorescence events, we are able to design a ratiometric indicator for a metal that usually quenches fluorescence. Our current results show that fluorescent intensity ratio Acceptor/Donor (‘A/D ratio’) of this indicator is proportional to concentration of Cu(II).

INOR 638
Copper(II) complexes of cyclodiphosph(v)azanes, [R(E)P(μ-N=NBu)2P(E)R] (R = NH2Bu; E = S, Se): Synthesis, characterization, and catalytic activity
Sandeep Kallapu, kallapusandeep@gmail.com, Perumalreddy Chandrasekaran. Department of Chemistry and Biochemistry, Lamar University, Beaumont, Texas 77710, United States

Bridging brididate sulfur and selenium donor ligands, [R(E)P(μ-N=NBu)2P(E)R] (R = NH2Bu; E = S, Se) based on cyclodiphosph(V)azanes have been prepared and their coordination chemistry with CuX (X = Cl, Br, I) have been investigated. Due to non-chelating ridged nature of these ligands supported by four membered P-N ring system leads to isolation interesting multinuclear Cu(II) complexes. X-ray crystal structure of copper complexes will be presented along with their catalytic activity in C(sp2)-S bond formation reactions.

INOR 639
Proton-coupled electron transfer and cofacial self-exchange of a nickel dithiolene complex
Steven Kennedy, srk232@psu.edu, Hemant Yennawar, Benjamin Lear. Department of Chemistry and Biochemistry, Penn State University, State College, PA 16801, United States

The proton-coupled electron transfer (PCET) process exhibited by a metal dithiolene complex [Ni(pdtt)$_2$]$^2+$(pdtt = 2,3-pyrazinedithiolate) was studied to understand the effect of protonation on localization of electron density on ligands disposed to the metal center. The electron transfer properties were explored using cyclic voltammetry (CV) and UV-Vis-NIR spectroscopy as functions of added acid. During titration, two sets of isosbestic points were observed in the UV-Vis-NIR spectra, indicating two protonation events occurred. The oxidized monoanion exhibited an intevalence charge transfer (IVCT) band in its UV-Vis-NIR spectrum. It is expected that titration of the oxidized monoanion will show that protonation localizes electron density on one of the ligands and alters the IVCT band. Future studies will attempt to understand electron transfer processes through cofacial n-stacked arrays in solution. A PCET scheme will be utilized to determine rates of intermolecular electron transfer within dyads of monomer complexes. The effect of protonation will enable control of the electron transfer process by changing the pH, which should grant greater control over ground state movement of charge. A competing mechanism between electron transfer and proton transfer will be established to determine the effect of simultaneous proton transfer on IVCT bands of cofacial aromatic dyads.

INOR 640
New class of multifunctional binolate ligand: Synthesis, characterization, and applications toward catalysis
Behzad Farajidizaji, beh.faraji@gmail.com, Kyle L Smith, Brian V Popp. C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States

Asymmetric bond transformations play a key role in contemporary organic chemistry. In order to mediate these processes, extensive research has been devoted to identifying chiral reagents capable of yielding high selectivities for broad classes of transformations. One such class of compound, binol, a
"privileged chiral ligand", has been used extensively for organo, early-to-mid transition-metal, and lanthanide-catalyzed processes. Conspicuously absent are studies applying this ligand to late-transition-metal catalyzed processes, which is likely due, in part, to the mis-match between hard-aryl oxide and soft-metal coordination characteristics. In order to make late transition metal binding more robust, we present a new class of L₃X₂ bionolate ligand that displays silyl-linked Lewis-basic residues at the 3,3'-positions. A modular synthetic approach has been identified to access these ligands by applying Geovgyan’s Rh₂[(OAc)₃]-catalyzed silane/aryl iodide coupling. Insights into the coordination characteristics of first and second-row late-transition metal complexes will be presented as well as preliminary insights into their ability to catalyze organic transformations.

INOR 641
Electron density modification at Ru⁴⁺ with Ru⁴⁺(tpy)(NN)X⁻⁻ via polypyridyl substituent and structure variation for electrocatalytic CO₂ reduction
Travis A White, travis.white@kemi.uu.se, Sascha Ott, Department of Chemistry, Ångström Laboratory, Uppsala University, Uppsala, Sweden

Converting thermodynamically stable, kinetically inert CO₂ into high-energy species capable of providing energy in a fashion similar to fossil fuels is of great importance in the quest for alternative fuel sources. Homogeneous, transition metal complexes are beneficial for CO₂ reduction in that the properties required for catalysis can be tuned by choice of metal, ligand set, and structural motif. One molecular architecture with minimal reports regarding use as a CO₂ reduction catalyst is [Ru⁴⁺(tpy)(NN)X⁻⁻] (tpy = 2,2’-6’,2’-terpyridine; NN = bidentate, polypyridyl ligand; X = monodentate ligand). This is somewhat surprising given the rich redox chemistry, strong UV and visible light absorption, and ease of polypyridyl ligand set modification. Altering the bidentate, polypyridyl ligand modifies the electron density at the Ru⁴⁺ center and provides insight into the lability and reactivity at the monodentate ligand coordination site. A series of [Ru⁴⁺(tpy)(NN)X⁻⁻] complexes (X = Cl⁻ or CH₃CN) with varying electron donating/withdrawing capabilities at the bidentate ligand has been synthesized and characterized. Analysis of the basic chemical properties and the proposed electrochemical mechanisms in the presence and absence of CO₂ will be discussed. The results presented provide a picture of the factors impacting electrocatalytic CO₂ reduction and is beneficial in the design of future catalysts using this architecture. The authors wish to thank the Wenner-Gren Foundation for their generous financial support of this research.

INOR 642
Computational study of cation coupled electron transfer in ferrate complexes
Kenneth A Jung, kj6821@gmail.com, Lizette Favela, llavela4@nmsu.edu, Micheal Johnson, Haobin Wang, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico 88001, United States

A mechanism is proposed, based on combined experimental and computational study, for the electron transfer reaction in ferrate complexes with a stable reaction intermediate. Computational evidence shows that this electron transfer can only occur with the help of cations to stabilize the complex. Thus the reaction can only occur in solutions with high ionic strength. This cation coupled electron transfer is studied in two systems each with ferrate complexing with a different anion. The computational results are consistent with experimental findings.

INOR 643
Vanadium spectroscopy and spectroelectrochemistry in alkali chloride melts
Ilya B. Polovov¹, polovov@pdpt.ustu.ru, Mikhail V. Chernyshov¹, Vladimir A. Volkovich¹, Boris D. Vasin², Andrey V. Chukin³, Trevor R. Griffiths³. (1) Department of Rare Metals and Nanomaterials, Ural Federal University, Ekaterinburg, Sverdlovsk reg. 620002, Russian Federation (2) Department of Theoretical Physics and Applied Mathematics, Ural Federal University, Ekaterinburg, Sverdlovsk reg. 620002, Russian Federation (3) Redstone Trevor Consulting, Ltd., Leeds, United Kingdom

Molten salts have a wide range of unique properties that make them particularly useful in many areas of technology. Spectroscopic techniques provide the insight into composition and structure of the complex ions formed in molten salts. The most valuable and reliable information can be obtained by combining spectroscopic and electrochemical methods.

In the present study the electronic absorption spectra (EAS) of soluble vanadium species were measured in 3LiCl-2KCl, NaCl-KCl and NaCl-2CsCl eutectic mixtures at 450-750 °C. Dissolution of VCl₃ in molten chlorides leads to the formation of V(III) species, VCl₃⁻⁻. A mixture of V(II) and (III) species is formed during dissolution of VCl₃ as a result of partial decomposing of vanadium(II)-containing chloro-species into V(III) and vanadium metal. Anodic dissolution of metallic vanadium is the best method for preparing vanadium(II)-containing melts. Increasing temperature and mean radius of the salt-solvent cation results in changes of EAS of vanadium(II)-containing melts. These changes were interpreted as a result of shifting VCl₄⁻⁻→VCl₅⁻⁻ equilibrium towards tetrahedral complexes.

It was shown that vanadium complexes are very sensitive to oxygen. Oxidation of vanadium(II)-containing melts leads to the formation of insoluble vanadium oxide based compounds containing alkali metals and vanadium in the oxidation state below four. Oxidation of VCl₅⁻⁻ complexes produces soluble vanadyl-based species. VO²⁻ containing ions are also formed during interaction of various vanadium oxides (V₂O₅; V₂O₆; V₂O₇) with HCl gas in studied chloride melts. The coordination environment of vanadyl-based ions depends on the cationic composition of the melt.

Vanadium(II) complexes are formed during electroreduction of vanadium(III)-containing melts. Further electrolysis leads to the deposition of vanadium metal. Insoluble oxygen-containing vanadium(III) species are the products of electrochemical reduction of vanadyl(IV) complexes, whereas their electrochemical oxidation does not affect vanadium speciation because the red-ox potential of VO³⁻/VO²⁻ couple is more positive than that of Cl⁻/Cl₂.

INOR 644
Effects of zeolite types and their different properties on proton exchange membrane
Viola SIM¹, Ka Wo LAM², kwilamaa@ust.hk, Ho Yee Timothy POON², Wei HAN², King Lun YEUNG¹,². (1) Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Hong Kong Special Administrative Region of China (2) Division of Environment, The Hong Kong University of Science and Technology, Hong Kong Special Administrative Region of China

Perfluorosulfonic acid (PFSA) membranes are the ‘gold standard’ commercial Nafion membrane because of its excellent proton conductivity and long term stability under fully hydrated conditions. Their efficiency is highly dependent on the hydration level of the membrane, leading to a sharp decline in performance with a decrease in hydration or an overﬂow of water causing a flooding in the membrane and hindering the reactant diffusion. As such, water management system is a crucial component of proton exchange membrane fuel cell.

As traditionally these membranes need external water regulating equipments and are unable to perform optimally at high temperatures, a membrane that can self humidify and can operate at a high temperature is-cis cite="mailto:Unknown%20Author" date-time="2013-10-07T00:55"> heavily researched on. Recently our lab reported a novel self-humidifying membrane that requires no humidifying aid by confining Nafion within zeolite-coated microsized pores on a stainless steel support, displaying superior performances compared to the commercial Nafion 117 membrane.

The novel membrane is fabricated by seeding and growing a thin silicalite-1 layer on a 50 µm-thick perforated stainless steel mesh before casting it with Nafion. The layer of zeolite serves as a water retention layer that enables the membrane to self-humidify. The MEA is then assembled by hot pressing the confined Nafion membrane between two gold-coated stainless steel plates with a thin layer of Pt/C brushed on. MEA performance was measured in
a home-made test unit and the electrical performance was monitored by CHI 660C electrochemical station with CHI 680 Amp Booster. Tests were ran to investigate the relationship between material property and call performances, e.g. testing the water retention of various zeolites, leaching of Al ions. The effect of different types of zeolites are explored in this work to investigate the role of confinement and choice of zeolitic materials with different properties on the performance of the self-humidifying PEMFC. The zeolite types include MFI, FAU (NaX and NaY) and BEA. The variable zeolite layers are grown on top of the silicalite-1 layer via template-free method before the confinement of the Naion.

INOR 645

Carbon nanofoams as porous scaffolds for iron-air battery electrodes

Marshall T McNally, lytlejc@plu.edu, Matthew R Pueringer, lytlejc@plu.edu, Hannah C Seal, lytlejc@plu.edu, Mark C Walsworth, lytlejc@plu.edu, Justin C Lytle. Department of Chemistry, Pacific Lutheran University, Tacoma, WA 98447, United States

Metal-air batteries store more energy per mass (specific energy) and per volume (energy density) than Li-ion batteries, but the rates of oxygen reduction and oxidation at metal anodes impede metal-air batteries from delivering energy quickly enough for power-hungry devices. We hypothesize that the specific power of metal-air batteries, as a class, would increase if the electrochemically accessible interfacial areas of metal anodes were greatly enlarged by supporting the redox-active metal component on nanostructured, porous current collectors. In such a design, a greater percentage of a metal’s atoms would be expressed on an electrode’s surface and would be simultaneously accessible to a liquid electrolyte that transports ions through a continuous pore network that is coupled with electronically conductive pore walls. We report a method to prepare sheets of carbon nanofoams that comprise a nanostructured carbon skeleton and micron-sized macropores within a bed of interleaved carbon fibers. A uniform coating of FeOx deposits from dilute K2FeO4 solution throughout the porous solid onto the pore walls of carbon nanofoams, and this rust coating can be electrochemically converted into iron metal. We demonstrate that these electrodes reversibly discharge and charge over several cycles, and that dilute additions of K2S to the electrolyte solution reduces the rate that the capacity fades upon cycling. In our study, iron-coated carbon nanofoams discharged more energy than similarly prepared, but nonporous electrode analogues at current densities between 0.01 – 1 mA cm-2.

INOR 646

Uranium electrochemical behavior and properties in LiCl-KCl-CsCl eutectic melt

Dmitry S Mal'tsev, Vladimir A Volkovich, volkovich@dtpt.unstu.ru, Evgeny N. Vladykin, Ilya B. Polovov, polovov@dtpt.unstu.ru, Boris D. Vasin. Department of Rare Metals and Nanomaterials, Ural Federal University, Ekaterinburg, Sverdlovsk reg 620002, Russian Federation

Pyrochemical technology is one of promising methods for reprocessing fast neutron reactors spent fuels after short cooling time. Working temperatures can be lowered by employing low-melting eutectic mixtures of alkali chlorides. Ternary lithium-potassium-cesium chloride eutectic has the lowest melting point (529 K) of all known alkali chloride systems.

The main objective of the present work was therefore studying the behavior and determining main electrochemical and thermodynamic properties of uranium (E(U(I-\tao)))_O, E(U(II)-\tao)O, ΔG of formation; D(UIII), D(UIV)) in LiCl-KCl-CsCl eutectic melt. The measurements were performed at 573–1073 K employing potentiometry, cyclic and square wave voltammetry. Uranium concentration in the melt and the average oxidation state were determined by chemical analysis after each experiment.

Uranium formal standard electrode potentials in LiCl-KCl-CsCl eutectic melt were determined using electromotive force method. E(U(II)-\tao)O linearly increases with temperature and between 576-1067 K is described by the following equation:

E(U(U))-\tao)O = -2.901 + 6.10-4\times T (± 0.029) V

From the results of the electrochemical measurements change of Gibbs free energy of the formation of uranium trichloride in LiCl-KCl-CsCl melt at 576-1067 K was calculated:

ΔG(UCl3) = -839.8 + 161.7\times 10^{-3} \times T (± 2.6) (kJ/mol)

Uranium(IV)/(III) electrochemical reduction was studied using cyclic and square wave voltammetry. Analysis of the experimental data showed that U(IV) → U(III) reduction is a reversible one-electron diffusion controlled process.

Information concerning diffusion of ions of the same metal in different oxidation states is important for explaining the mechanism of diffusion of polyvalent metal ions in molten salt media. In the present work the diffusion coefficients of uranium(III) and (IV) ions were determined between 573-1073 K employing cyclic voltammetry. The experimental results are satisfactorily described by the following equations:

log D(UIII) = -4341.809/T + 0.199 (±0.088) cm²/s

log D(UIV) = -3002.613/T - 1.541 (±0.047) cm²/s

INOR 647

Electrochemical sensing of hydrogen peroxide using various metal complexes supported on carbonaceous nanomaterials

Charlotte Felton, cmfelton@ualr.edu, Udaya B Nasini, Punnamchandar Ramidi, Ali U Shaikh. Department of Applied Science, University of Arkansas at Little Rock, Little Rock, Arkansas 72204, United States

Hydrogen peroxide (H2O2) sensors are used to detect low concentrations of H2O2 in food and pharmaceutical industries. Of the two types of sensors developed, enzymatic and non-enzymatic, the latter holds to be the more ideal route due to the catalytic ability was established using electrochemical studies and evaluated to be sensitive in low concentrations of H2O2. Role of carbon-based supporting materials (mulliwalled carbon nanotubes, graphene and carbon black) was established and we found that carbon nanotubes and graphene were more sensitive in detecting H2O2 compared to carbon black. The effect of various groups on the ligands was also electrochemically tested to determine the best detection system.

INOR 648

Electrochemical and local structural analysis of the Li1V2(2-x)Mg2PO4Cl/C cathode

Soojeeong Kim1, soojeeong@umich.edu, James Penner-Hahn1, Aniruddha Deb1, Li Yang2, Jizhang Chen2. (1) Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48105, United States (2) School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai, China

The electrochemically stable phosphate promises high reversible capacity, high operating voltage, and good ion mobility. New electrode design requires better understanding of their micro and nano-level structure which will help improvements in the storage capacity, battery-charging rate, and cycle life. Li1V2(2-x)Mg2PO4Cl/C composite phosphate cathode materials with different Mg doping for high reversible capacity, high operating voltage and good cycling stability. The ultimate goal of the experiment is to explore new technologically important Li-ion electrode materials that are electrochemically superior, environmentally friendly (Co-free) and affordable. These will ultimately lead to use in commercial large scale energy storage devices, for PHEV and EV applications. In order to understand the functioning of this cathode at the molecular level, we used In-situ x-ray absorption spectroscopy (XAS),
The XAS results verify for the charge compensation the V changes between V$^{3+}$ and V$^{2+}$ during charge/discharge cycling based on the different cut off voltage regions and that these are accompanied by local structure changes of the V and its neighboring atoms. Significant change has been shown in the pre-edge region of the XANES spectra when cut off is changed from 4.5V to 4.8V. Once, the electrode has been charged up to 4.8V cut off region, the structural change has been made which is irreversible during cycling.

INOR 649
Development of an electrochemical microRNA sensor
Siobhan G MacArldie, sgm2136@barnard.edu, Eileen R Smith, Marisa C Buzzeo, mbuzzeo@barnard.edu. Department of Chemistry, Barnard College, New York, NY 10027, United States
Several microRNAs have been linked to the occurrence of cancer, and thus the accurate measurement of these short, regulatory sequences could potentially serve as an early marker of disease. We seek to develop an electrochemical sensor that can detect relative miRNA levels through the indirect quantification of hybridization events at gold surfaces. Current efforts towards the design and optimization of this voltammetric detection platform will be presented.

INOR 650
Electrochemical characterization of diselenide bond reduction
Lindsey M Walker, lmw2145@barnard.edu, Faizunnahar Dewan, Marisa C. Buzzeo, mbuzzeo@barnard.edu. Department of Chemistry, Barnard College, New York, NY 10027, United States
We aim to better understand the potential role of diselenide bonds in the physiological setting. Efforts have focused on the voltammetric profile of selenocysteine with particular attention to surface interactions observed at bare gold and modified glassy carbon electrodes. Electrochemical and spectroscopic evidence of diselenide reduction will be presented and a mechanistic pathway proposed.

INOR 651
Directing polyaniline self-assembly using Laponite nanoparticles
Jared S. Mondschein1, mondschi@union.edu, Michael E. Hagerman2, Rebecca Cortez2. (1) Department of Chemistry, Union College, Schenectady, NY 12308, United States (2) Department of Mechanical Engineering, Union College, Schenectady, NY 12308, United States
Polyaniline (PANI) is a conductive polymer that shows excellent promise for numerous applications including gas sensors, electrodes and thin film bulk heterojunction solar devices. In order to improve photoefficiencies in organic polymer photovoltaics, it is crucial to understand how nanoparticle-polymer interactions affect composite nanoparticle morphologies and resultant physical properties. To this end we have employed Laponite nanoparticles, vanadium oxide, and varied morphosynthetic conditions to direct the facile self-assembly of PANI nanostructures within acidic aqueous phases. We have also incorporated Laponite-PANI films into bulk heterojunctions to study how localized nanoparticle/polymer morphologies influence photophysical properties. Herein we report atomic force microscopy (AFM) and scanning electron microscopy (SEM) studies to explore the effects of Laponite nanoparticle inclusion on the morphology of PANI domains. AFM, SEM, and single-molecule force spectroscopy (SMFS) experiments indicate that Laponite nanodiscs enhance water-processability and direct PANI self-assembly and dimensionality.

INOR 652
Target-specific stimuli-responsive MSN platform for the intracellular delivery of gemcitabine for pancreatic cancer treatment
Amir R Hashemi1, ahashem2@unc.edu, Alisa Geier1, Jimmy Pan1, Juan L Vivero-Escoto2,3. (1) Department of Chemistry, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States (2) The Center for Biomedical Engineering and Science, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States
Pancreatic cancer is one of the most aggressive types of cancer with a five year survival rate of only 6%. Current treatments for pancreatic cancer include the intravenous administration of gemcitabine and cisplatin; however the systemic toxicity and lack of specificity of these treatments produce several side effects. Recent advances in the development of multi-functional nanoparticles can overcome these major drawbacks for pancreatic cancer treatment. Mesoporous silica nanoparticles (MSN) are an attractive alternative for this treatment. The large surface area of MSNs allows for the loading of a large amount of drugs into the nanoparticles; moreover, they can also be functionalized with targeting agents such as small molecules and antibodies. In this work, we have developed a target-specific stimuli-responsive MSN-based carrier for the efficient intracellular delivery of gemcitabine. This platform contains a stimuli-responsive linker to chemically attach gemcitabine to the MSN material. The release of the drug can be triggered by reducing and acidic conditions, such as those found in cancer cells. The MSN material has been further functionalized with the MUC1 antibody to target the overexpressed MUC1 antigen on the surface of pancreatic cancer cells. The targeting ability and therapeutic effects of MUC1-MSN material has been successfully tested in MUC1-null (KCKO) and expressing MUC1 (KCM) pancreatic cancer lines. We envision that this MUC1-MSN platform can be used to alleviate some of the main issues of pancreatic cancer treatment.

INOR 653
Magnetic plasmon modes in Au nanorod trimer arrays
Yuting Tao, yttao@phy.cuhk.edu.hk, Lei Shao, Qileng Ruan, Jianfang Wang. Department of Physics, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong 00852, Hong Kong Special Administrative Region of China
Magnetic plasmon modes exhibit rich optical properties, which can be used to build optoelectronic multi-functional devices. Among various metamaterials, ordered plasmonic nanostructures possess tunable collective surface plasmon resonances, which allows for manipulating electromagnetic fields at nanoscale over a wide spectral range. Plasmonic nanostructures in specific geometries can also show intriguing optical-frequency magnetic responses, whose radiation loss during propagation is much lower than those of electric plasmons. Herein, we report on our study of the plasmonic properties of Au nanorod trimer arrays by both simulations and experiments. We utilize electromagnetic simulations to systematically study the plasmonic properties of a single Au nanorod, nanorod trimer, and trimer arrays. The nanorod trimers are formed by closely-spaced nanorods featuring trigonal symmetry. For a single Au nanorod, both longitudinal and transverse surface plasmon resonances are observed. For the nanorod trimer with decreasing interparticle gap distances, a new scattering peak emerges due to strong near-field coupling of the localized surface plasmons between the nanorods. The electric field intensity and charge density distribution contours exhibit a virtual current loop inside the trimer. The magnetic field intensity contour shows a confined magnetic field inside the trimer. The new peak can therefore be unambiguously assigned to the magnetic dipolar plasmon mode. For the nanorod trimer array, the magnetic plasmon mode can propagate along the array. Experimentally, Au nanorod trimer arrays are fabricated by electron beam lithography. The plasmonic properties of the trimer arrays are systematically studied by dark-field scattering spectroscopy. The scattering spectra are in good agreement with the simulation results. The moderate redshift and spectral broadening result from the increase of the refractive index and damping of the adhesion layer. The magnetic dipolar mode is further examined and corroborated by polarized scattering spectroscopy. Our results will be very helpful to the development of plasmonic devices based on magnetic plasmons.
INOR 654

Graphene-polyaniline-laponite nanocomposites for solar applications
Isaac A Ramphal, ramphali@union.edu, Michael E Hagerman. Department of Chemistry, Union College, Schenectady, New York 12308, United States

We are currently exploring the use of chemically modified graphene-polyaniline (PAG) nanocomposites to enhance charge transport within the active layer of bulk heterojunctions in polymer photovoltaic cells. Synthesis via in situ polymerization of aniline in colloidal dispersions of graphene oxide affords composites of polyaniline intercalated within graphene oxide sheets. We have employed an environmentally friendly iron-acid reduction of the graphene oxide to produce the conductive hybrid material. Laponite nanoparticles were incorporated to improve aqueous processability and film formation of these materials, thereby increasing viability for flexible solar-harvesting devices. Crystallinity and morphological studies were carried out using powder X-ray diffraction, atomic force microscopy and scanning electron microscopy. Host-guest interactions within PAG systems were studied with and without Laponite nanoparticle templating agents. Structure-property relationships were characterized using infrared and electronic absorption spectroscopies, thermogravimetric analysis and bulk conductivity measurements.

INOR 655

Silicon nanotube-based drug delivery/gene therapy
Yuan Tian1, yuan.tian@tcu.edu, Roberto Gonzalez-Rodriguez2, Jeffery L Coffer1, Giridhar R Akkaraju2. (1) Chemistry, Texas Christian University, Fort Worth, TX 76109, United States (2) Biology, Texas Christian University, Fort Worth, TX 76109, United States

Nanotubes of silicon have an enormous potential for development in biomedical applications, such as biosensing, tissue engineering, and drug delivery. Silicon nanotubes (SiNTs), hollow cylindrical nanostructures of this elemental semiconductor, are promising drug carriers offering selected advantages over other gene or drug delivery systems. First of all, SiNTs can effectively protect a given drug against denaturation or degradation in the delivery process. Second, SiNTs produce a negligible cytotoxicity in vitro. Furthermore, SiNTs have a tunable dissolution behavior in aqueous media by controlling the wall thickness and annealing time during synthesis, which makes it a perfect candidate for controlling drug release. Moreover, SiNTs have relatively large internal surface areas that can increase drug loading efficiency. Lastly, SiNTs have physically separated and tunable inner and outer surfaces, which can be differentially functionalized to load desired molecules inside, but impart targeted chemical features to the outer surface allowing for site-specific drug delivery.

In these experiments, the morphology of SiNTs was characterized by energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The cytotoxicity of these nanotubes was evaluated by their exposure to human embryonic kidney fibroblast cells (HEK 293) as a function of time and concentration, in conjunction with MTT and Trypan Blue Exclusion Assays. The dissolution behavior of SiNTs was evaluated by a Molybdate Silica Complexation Assay. The cellular uptake efficiency of SiNTs into HEK 293 cells was demonstrated by confocal fluorescence microscopy and gene transfection assays.

INOR 656

Silicon nanotubes: Fabrication, surface functionalization, and loading
Roberto Gonzalez Rodriguez, r.gonzalezrodriguez@tcu.edu.Chemistry, TCU, Fort Worth, Texas 76110, United States

Silicon (Si) remains the key material for electronic devices. The ability to fabricate silicon in nanostructure form is important not only to the next generation of such devices, but also in other applications relying on enhanced surface area, low dimensionality, and structural control, such as photovoltaics, battery technology, and biosensing/therapeutics.

In this presentation, we describe the basic fabrication steps for arrays of silicon nanotubes (SiNTs) based on (1) deposition of silane (SiH₄) on a preformed ZnO nanowire array template, followed by (2) sacrificial etching of the ZnO phase, resulting in the desired nanotube product. Hollow nanotube inner diameter is adjustable by size selection of the initial ZnO nanowire, while shell thickness control is achieved by concentration/duration of silicon deposition. Thermal annealing processes increase the crystallinity of the Si nanotubes; this crystallinity is reflected in the dissolution rate of the nanotube in water or phosphate-buffered saline (PBS).

Relevant to ultimate applications, we have also carried surface functionalization of the nanotubes using well-known alkyl amine-terminated silicon alkoxide reagents in conjunction with a fluorescent probe such as fluorescein isothiocyanate (FITC). We have also demonstrated proof-of-concept in terms of nanotube loading relevant to guided drug delivery systems by incorporating several sizes of superparamagnetic iron oxide nanoparticles into a range of Si nanotube structures.

All nanomaterials reported here were characterized by a combination of Scanning Transmission Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDX) and Transmission Electron Microscopy (TEM), along with confocal fluorescence microscopy in the case of the surface modified SiNTs.

INOR 657

Sustainable routes to porous silicon manufacture for drug delivery
Jhansil Kalluri1, J.KALLURI@TCU.EDU, Whitney Cosey1, Roberto Gonzalez2, Phil Hartman2, Armando Loni2, Leigh T Canham2, Jeffery L Coffer1. (1) Chemistry, Texas Christian University, Fort Worth, Texas 76129, United States (2) Biology, Texas Christian University, Fort Worth, Texas 76129, United States (3) PSI Medica Ltd, Malvern, Worcestershire WR14 3 SZ, United Kingdom

Porous silicon (PSi), with its nanoscale architecture, acts as a very promising resorbable biomaterial for a broad variety of possible uses: in vivo biosensors, tissue engineering, and carrier material for controlled drug delivery. The most conventional methods for preparing porous silicon are electrochemical etching and stain etching, but these require solid elemental crystalline silicon feed stocks, the use of corrosive hydrofluoric acid and organic solvents, along with somewhat specialized apparatus. As an alternative, we have recently investigated an eco-friendly process for manufacturing porous silicon from terrestrial plants, Horsetail (Equisetum arvense L.), Great Horsetail (Equisetum telmateia), and Tabasheer (Bambuseae), all of which are well-known silicon accumulators.

The extraction of silicon from these plants was achieved by washing a given dried plant with hydrochloric acid (10%) to remove any metallic residue (deposited during the plant grinding process), followed by calcination to extract biogenic silica from this HCl washed dried plant. The silica extract from the plant was subsequently converted to elemental silicon by simple reduction of the silica with magnesium powder at 600°C under an argon atmosphere. To maintain porosity, sodium chloride was added to the reaction mixture, this acting as a thermal moderator. Any residual magnesium phases were removed by washing with hydrochloric acid, and the final product was characterized by a combination of scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM). The oxide content in the Mg-reduced Tabasheer was estimated by etching with 40% hydrofluoric acid.

This presentation will focus on the fabrication and characterization of the above nanostructures, as well as initial investigations of the ability of this plant-derived porous silicon to deliver antibacterial agents in a sustained fashion.

INOR 658
Metal phosphide electrocatalysts for clean energy technologies
Eric J Popczun, ezp5064@psu.edu, Raymond E Schaak.Department of Chemistry and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

Transition metal phosphide nanoparticles have received much attention due to their stability at high temperatures and resistance to corrosive acids. Because of this, many phosphides have been attractive catalysts for a variety of harsh industrial processes. Recently, we have extended the catalytic portfolio of transition metal phosphides by showing that nanoparticles of nickel phosphide (Ni₃P) are electrocatalysts for the hydrogen evolution reaction (HER), which is traditionally facilitated most effectively by noble metals such as platinum. The Ni₃P nanoparticles have among the highest HER activity of any non-noble metal electrocatalyst reported, while producing H₂(g) with nearly quantitative faradaic yield, and affording stability in aqueous acidic media. This presentation will include our most collaborative efforts towards the synthesis and characterization of Ni₃P and related nanoparticles as HER electrocatalysts.

INOR 659
Advanced nanocomposite innovation with Pixelligent’s nanotechnology
Robert Wiacek, rwiacek@pixelligent.com, Wei Xu, Yijun Wang, Xia Bai, Selina Thomas, Linfeng Gou, Brian Wehrenberg, Jun Xu, Zhiyun Chen, Greg Cooper, Serpel Gonen-Williams.Pixelligent Technologies, LLC, Baltimore, Maryland 21224, United States

The incorporation of Pixelligent’s zirconium oxide nanocrystal dispersions creates next-generation nanocomposites with superior properties and new functionalities. The novelty of nanocomposites is that the enhanced properties gained by the addition of the nanocrystals present significantly less trade-offs when compared to traditional composites. Pixelligent's nanocrystals can improve extremely diverse properties, including optical (significantly increased refractive index, high transparency, low haze), mechanical (improved scratch resistance, increased mechanical strength, improved lubrication properties), and chemical (increased chemical etch resistance, improved thermal properties, increased oxidation/aging resistance).

Pixelligent achieves the highest quality dispersions through a combination of our proprietary nanocrystal synthesis, where we can control the size and shape of our zirconium oxide nanocrystals, and our capping methodologies. Our capping methodology enables Pixelligent to control the surface chemistry of the nanocrystal where we chemically bond materials to the nanocrystals that are compatible with the target polymer system. This capping process is one of the key reasons our nanocomposites are highly loaded, perfectly dispersed, and fully scalable. Using our dispersion technology, Pixelligent can disperse nanocrystals into numerous polymer families including acrylics, SOGs, siloxanes, polyesters, epoxy resins, and silicones.

Pixelligent nanocrystals are dense, which means on average we will only be contributing 2%-30% of the total volume of a completed nanocomposite. This translates into delivering a disruptive technology that significantly increases the value of your product, while minimizing the incremental cost impact.

INOR 660
1H NMR characterization of association of single-walled carbon nanotubed with alcohols
Donna J Nelson, Logudurai Radhakrishnan, logudurairou.edu, Ravi Kumar.Department of Chemistry & Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, United States

Investigation of the interactions of small molecules with the single-walled carbon nanotubes (SWCNTs) is of great interest in order to understand the enhancements of its dispersion, solubility, and applications of single-walled carbon nanotubes (SWCNTs). Herein, we report the effect of SWCNTs association with various alcohols (R-OH) by using 1H NMR spectra in order to determine the nature and magnitude of their interaction. The changes in the 1H NMR chemical shift values of alcohols with SWCNTs indicate that the hydroxyl (-OH) group is in close proximity than the other parts of the alcohol because larger changes in chemical shift values were observed for the protons adjacent to the hydroxyl functional group. Thus the results from 1H NMR spectroscopy help us to understand the nature of association and orientation of the small molecules on the SWCNTs surfaces. The effect of SWCNTs association with alcohol and 1H NMR results will be discussed and presented.

INOR 661
Reversible Li capacity of thermally- and chemically-reduced graphene oxide nanoribbons
Phillip A Medina IV, medin1pa@cmich.edu, Chananate Uthaisar, David J Hicks.Science of Advance Materials, Central Michigan University, Mount Pleasant, Michigan 48859, United States

The search for better energy storage devices is essential in our goal of fossil fuel independence. Fossil fuel emissions have detrimental effects on our environment; water supplies, health and greenhouse affects. Alternative energy can be the power source we need to help slow or stop this damage caused by fossil fuel. No matter the alternative fuel source, be it solar, wind, geothermal, biomass or biofuel it is essential for a proper energy device that can make the energy portable, cheap, and safe.

In this work, multiwall carbon nanotubes (MWCNTs) are evaluated for their potential as an anode material for Li ion batteries. MWCNTs of varying sizes were oxidized using a modified Tour's method, giving oxidized graphene nanoribbons (oGNR). These oGNR were tested for their electrochemical properties, and unlike graphene oxide (GO) which showed good Li capacity, oGNR capacity was poor. The oGNRs were then reduced, both thermally and chemically. The thermally reduced oGNR Li capacity was greatly improved, whereas the reduced GO capacity was significantly less. Chemically reduced oGNR, using hydrazine, show different characteristics than the thermally reduced nanostructures.

INOR 662
Development of pattern hiding layer with silica nano particle for graphene anode on transparent devices
Fredrick Kim1, fxx110230@utdallas.edu, Duck Joo Yang2, Chan Jae Lee2. (1) Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United States (2) Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United States (3) Korea Electronics Technology Institute, Republic of Korea

In recent years, graphene, two dimensional form of graphite, has brought many attentions to the researchers as new and revolutionary substitute for some of the currently used materials. Its good characteristics such as high transparency, high electrical and thermal conductivity, and mechanical strength have suggested that it will be an ideal material as anode of transparent devices, especially for flexible devices. Although graphene has high transmission over 97%, there is a difference in transmittance between the graphene with electrode pattern and the one without the pattern. This difference in transmittance produces non-clear images. In order to decrease the difference in transmittance, we have studied the pattern hiding layer (PHL) by using nano composite layer with nano scattering particles. We are aiming to reduce the difference between the transmittance of the patterned and non-patterned graphene.
In order to synthesize 100–400nm spherical silica particles, we added 100mL of ethanol, 50mL of deionized water, 1.0-1.5mL of oleylamine (OA), 0.3-5.2mL of NH₂OH and 1.5mL of tetraethyl orthosilicate (TEOS), which was heated at 60°C for two hours. Sizes were controlled by either increasing or decreasing the concentration of each material. We then mixed the synthesized nano particles into polymer resin. The mixture was coated on a polycarbonate film with patterned graphene.

The transmission is measured by using UV-VIS spectroscopy in visible range. We were able to decrease the difference up to 60% in visible range by using PHL with 400nm particles.

**INOR 663**

**Diameter control of electrospun yttrium doped cerium oxide nanowires**

Anne D’Achille, a.moffitt@tcu.edu, Jeffery Coffer. Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, United States

Cerium oxide, or ceria, has a high ion conductivity that may enable improved conductivity values at lower temperatures relative to other metal oxides. Furthermore, the dual Ce³⁺/Ce⁴⁺ oxidation state results in a metal oxide with a high number of oxygen vacancies that can act as a free radical scavenger and anti-oxidant. The addition of yttrium oxide, or yttria, to cerium oxide increases the overall stability at high temperatures and enhances the oxygen vacancy density. This combination of properties gives yttrium-doped cerium oxide (YDC) possible relevance to a broad range of technologies, including nanoscale therapeutics.

To date, our research has focused on the synthesis of diameter-controlled YDC nanowires via a combination of electrospinning techniques and thermal annealing. Precursor fibers were produced by electrospinning yttrium and cerium nitrates in a DMF-methanol solution using polyvinylpyrrolidone (PVP) as a polymer template. Subsequent calcination of these precursor fibers resulted in the formation of crystalline YDC nanowires.

It is found that increasing the polymer template concentration resulted in larger average nanowire diameter, due to an increase in solution viscosity. This can be achieved by varying the mass of DMF used; for example, average YDC nanowire diameter can be tuned from 80 nm to 200 nm as the DMF content decreases from 35 wt% to 26 wt%. Similarly, changes in the mass of methanol used results in increases in nanowire diameter, ranging from 109 to 212 nm as the methanol content decreases from 68 wt% to 35 wt%. Variations in the DMF:methanol mass ratio yields additional diameter control, with mean diameter values shifting from 95 nm to 187 nm with ratios of 0.55 to 0.25 respectively. The data obtained from these investigations will be used for evaluating size effects in various applications.

**INOR 664**

**Preparation of a magnetite-immobilized cyclam copper(II) complex for heterogeneous phosphate ester hydrolysis**

Eric Thomas Amerling, etamer10@smumn.edu. Department of Chemistry, Saint Mary's University of Minnesota, Winona, MN 55987, United States

Progress was made on the development of an easily-recoverable metal-containing heterogeneous catalyst for phosphate ester hydrolysis. The synthetic strategy was to begin by creating a monoalkylated cyclam with a pendant triethoxysilyl group. Condensation of those groups onto magnetite nanoparticles, followed by metallation with copper(II), resulted in a material whose hydrolytic activity against phosphate esters and recoverability from solution using a magnetic field were studied. Synthetic details, product characterization, and preliminary kinetic and magnetic recoverability data will be presented.

**INOR 665**

**Significant proximity effect in heterobimetallic Ti⁴⁺/Cr³⁺ catalysts for ethylene polymerization**

Shaofeng Liu, shaofeng-liu@northwestern.edu, Alessandro Motta², Aidan R. Mourat², Massimiliano Delferro³, Tobin J. Marks¹. ¹ Department of Chemistry, Northwestern University, Evanston, IL 60208, United States ² Dipartimento di Scienze Chimiche, Università di Catania and INSTM, Catania, Italy

New heterobimetallic complexes, (Ti- CO-C⁴(SNS)) (Ti- C⁴H₂₃-C⁴(SNS)) and (Ti- C⁴H₄-C⁴PNP) and (Ti- C⁴-C⁴(SNS)) are synthesized, characterized and employed as olefin polymerization catalysts.

With ethylene as the only feed, both of (Ti- CO-C⁴(SNS)) and (Ti- C⁴H₂₃-C⁴(SNS)) afford linear low-density polyethylene (LLDPE), similar to the analogue (η⁵-indenyl)[1-Me₂Si(Bu)NTCl][C₂H₅-\{N-N-bis(2-(ethylthio)ethyl)amine\}CrCl] (Ti- C⁴H₄-C⁴(SNS)). However, (Ti- C⁴H₄-C⁴(SNS)) and (Ti- C⁴-C⁴(SNS)) produces LDPE and HDPE under identical conditions, respectively. Considering both of activity and selectivity, the SNS-based catalysts are superior. In ethylene homopolymerization, (Ti- CO-C⁴(SNS)) produces higher molecular weights and branching density polyethylene vs (Ti- C⁴H₂₃-C⁴(SNS)), while (Ti- C⁴H₂₃-C⁴(SNS)) acts in a reverse manner. In the ethylene + 1-pentene competition experiments, (Ti- CO-C⁴(SNS)) incorporates α-propyl branches as long as 5.5% in total branches, while the numbers for (Ti- C⁴H₂₃-C⁴(SNS)) and (Ti- C⁴H₂₃-C⁴(SNS)) are 34.8% and 55.1%, respectively. Both homopolymerization and copolymerization results argue that achievable Ti- Cr spatial proximity significantly enhances the bimetallic cooperative effects in terms of molecular weights and comonomer enrichment selectivity.

**INOR 666**

**Kinetics of phosphine substitution in CpRu(PPh₃)₂X (X =Cl, Br, I, N₃, NCO, and SCN)**

Rein Kirss¹, r.kirss@neeu.edu, Miles Clark¹, mils39@gmail.com, Connor Delaney¹, delaney.connor@gmail.com, David Hill¹, Matthew Eaton¹, Olivia Hendricks². ¹ Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115, United States ² Department of Chemistry, Wellesley College, Wellesley, MA 02481, United States

The rate of phosphine substitution of PPh₃ by PMePh₂ in CpRu(PPh₃)₂X (X =Cl, Br, I, N₃, NCO, and SCN) was measured in CDCl₃ under pseudo-first order conditions over the temperature range 25-70°C. The relative rates of reaction are observed to be: 1 > 4 > 2 > 5 > 3 > 6. No reaction is observed for X=F, SnCl₂ and H under these conditions. The activation parameters are similar (ΔH° = 24-30 kcal/mol, ΔS° = 21-38 cal/mol-K) and consistent with an i₂ mechanism. The observed order of the rates does not correlate with the size, the electronegativity of X but correlates reasonably well with the electrochemical potentials of 1-6 and may reflect differences in τ-donor ability of the X group with the best τ-donors having the fastest rate.

**INOR 667**

**Aerobic oxidative C-C bond formation from novel Pd complexes: Ligand effects by a theoretical study**

Qian Peng, qian.peng@mail.chem.tamu.edu, Michael B Hall. Texas A&M University, college station, TX 77840, United States

 Palladium-catalyzed C-C coupling reactions are among the most important transformations in synthetic organic chemistry. Recently, Mirica and his coworkers have reported on several exciting Pd complexes of new tetradequate ligands. These Pd(II) complexes are able to oxidatively couple their methyl groups to produce ethane at low temperature. Such a facile reaction is unprecedented.
Hereby, we propose to make a thorough computational study of this reaction to understand the reaction mechanism via calculations of possible transition states and the thermodynamics quantities for proposed intermediate. In our preliminary study, the reaction involves three major transformations – that is: 1. Pd(II) complex oxidized by O₂, 2. Me transfer between two Pd center and 3. Reductive elimination from Pd(IV) complex. The novel tetradentate ligand can exhibit “chair” or “boat” conformation to coordinate Pd center during the whole mechanism that will stable related transition state and intermediate. Through these studies we would be able to interpret the significant role in this reaction and discover a new ligand that will enhance the desired reactivity of this important breakthrough reaction.


INOR 668
Light enhanced displacement of methylacrylate from iron carbonyl: Investigation of the reactive intermediate via rapid-scan FTIR and computational studies
Muhammad Sohail1, muhammad.sohail@qatar.tamu.edu, Salvador Moncho1, Edward N Brothers1, Ashfaq A Bengali1, Bo Li2, Samuel J Kyran2, Donald J Daresbourg2. (1) Department of Chemistry, Texas A&M University, Doha, Qatar (2) Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, Texas TX 77843, United States
The thermal displacement of methylacrylate from Fe(CO)₅(η²-CH₂=CHCOMe) by phosphine ligands is a relatively slow reaction requiring several hours at elevated temperatures. In the present study, it is observed that photolysis of the tetracarbonyl complex with UV light activates the process such that the reaction is complete within a few seconds. This rate enhancement is due to the formation of an intermediate η⁶ complex where the organic C=O and C=C units of methylacrylate occupy axial and equatorial coordination sites on the Fe center, respectively, following photochemical CO loss. The displacement of methylacrylate from this photolytically generated intermediate is facile with a remarkably low barrier of 8.7 kcal/mol. DFT calculations support these experimental observations.

INOR 669
Catalytic hydrosilylation of carbonyl compounds using Fe- and Co-complexes
Ashleigh Smith, ashleigh.smith@ttu.edu, Anu Saini, Michael Findlater. Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409, United States
Six pre-catalysts were screened for activity in the catalytic hydrosilylation of carbonyl-containing substrates. In-situ activation of the Fe and Co complexes of the pincer ligands 40-PNP and 30-PONOP and the diimine ligand 40-BIAN affords catalytically active species.

INOR 670
Ruthenium-catalyzed amine alkylation using alcohols under mild conditions via the borrowing hydrogen methodology
Arrey Enyong, abe4@georgetown.edu, Bahram Moasser. Department of Chemistry, Georgetown University, Washington, District of Columbia 20057, United States
Amine alkylation reactions for the formation of C-N bonds are important in the fields of organic, inorganic and biochemistry. Typical alkylation reactions require the use of stoichiometric amounts of toxic alkyl halide compounds or the use of stoichiometric amounts of strong reducing agents through reductive amination. Transition metal-catalyzed alkylation using alcohols, via the borrowing hydrogen methodology, is an attractive alternative since water is the only byproduct of this reaction. The earliest examples by Grigg and Watanabe required high reaction temperatures (150-180°C) but the reaction conditions have been improved by several research groups over the past two decades (typically 100-130°C, as low as 70°C).
Herein we present the ruthenium-catalyzed alkylation of amines using alcohols under mild conditions, as low as room temperature. Using amino-amide ligands derived from commercially available amino acids, with the alcohol as the solvent, we are able to alkylate aliphatic and aromatic amines, using primary aliphatic and aromatic alcohols and also diols. The selectivity of these alkylation reactions was good for most of the reactions, yielding mainly the monoalkylated product. Aromatic amines required the highest temperatures (65°C) and catalyst loading (8 mol%) whereas the alkylation of aliphatic amines were carried out at 45-55°C for the first time with 6-8 mol% catalyst loading. Room temperature alkylation reactions were also achieved for the first time though a high catalyst loading (12%) was needed. Using this system, alkylation was also carried out using near stoichiometric amounts of alcohol but required high temperatures (110°C).

INOR 671
Comparison of an in situ generated, air stable, and recyclable aqueous phase nitrile hydration catalyst with [RuCl₃PTA]₁
Whalmany Ounkham, wounkham@yahoo.com, Jason A. Weeden, Wei-Chih Lee, Brian J Frost. Department of Chemistry, University of Nevada, Reno, Reno, NV 89501, United States
RuCl₃[PTA]₁(PTA=1,3,5-tri-aza-7- phosphadadamantane) was recently reported as a highly active catalyst for aqueous phase nitrile hydration at 100 °C in air.¹ Recently we have explored in situ generated catalysts, such as RuCl₃·3H₂O with 6 PTA, for aqueous phase nitrile hydration. Both [RuCl₃PTA]₁ and RuCl₃·3H₂O/6 PTA are highly active, air stable, recyclable, aqueous phase nitrile hydration catalysts. The in situ generated catalyst demonstrated similar, near quantitative, conversion of aromatic, alkyl, and vinyl nitriles to their respective amides with a wide substrate tolerance. Analogous to [RuCl₃PTA]₁ the in situ catalyst was stable in solution for weeks and could be reused more than five times without significant loss of activity. Catalyst loading down to 0.001 mol% was explored. Turnover numbers greater than 20,000 and turnover frequencies of over 60 h⁻¹ have been obtained under various conditions. The effects of PTA concentration, pH, and salt have been explored and will be discussed.


INOR 672
Role of the metal and ligand environment in designing catalysts for water-gas shift reaction
Adriana Dinescu, adriana.dinescu@wilkes.edu, Joshua Fox. Department of Chemistry, Wilkes University, United States
Molybdenum-containing carbon monoxide dehydrogenase catalyses a reaction similar to water-gas shift reaction. Density functional theory and pseudopotentials have been employed to design biomimetic catalysts that could be used for hydrogen production and carbon dioxide activation. In this research, energy profiles of the reaction pathway have been calculated for redox-active analogs of the molybdenopterin cofactor and different metalloclusters. While the model based on the native enzyme involved a very stable intermediate, by replacing molybdenum with tungsten the energetics became more favorable. In addition, the redox-active diimine ligand showed a more favorable behavior (formed less stable intermediates) than the dithiolen ligand, which mimics the molybdenopterin ligand.

INOR 673
Cyclometalated Ru(II) complexes catalyzed enyne coupling and alkene dimerization
Pinjing Zhao, Jing Zhang, pinjing.zhang@ndsu.edu. Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108-6050, United States

Cyclometalated Ruthenium(II)-imine and -ketone complexes with C2 symmetry were synthesized and characterized by NMR and XRD. The Ruthenium-imine complexes were proven to be effective catalysts and catalyst precursors for enyne coupling reaction with acrylates/acylamides and internal and terminal alkynes under relatively mild and redox-neutral reaction conditions. This method is amenable to larger scale reactions and grams of 1,3-diene could be prepared. Besides, alkene dimerization could also be catalyzed by these novel cyclometalated Ruthenium complexes.

INOR 674
Progress towards asymmetric hydrosilylation of ketones using a Zr/Co heterobimetallic complex
Noam I Saper, nsaper@brandeis.edu, Seth L Marquard, Wen Zhou, Christine M Thomas. Department of Chemistry, Brandeis University, Waltham, MA 02453, United States

In the past several years, the Thomas group has been studying a Zr/Co heterobimetallic system featuring a unique dative metal-metal interaction with reactivity substantially different from the corresponding monometallic compounds. Notably, catalysts of the form (THF)Zr(AnNP)Co–N2 have been shown to undergo one-electron redox processes and efficiently affect the hydrosilylation of various ketones in high yield. We believe that this proceeds via homolytic cleavage of the Zr-Co bond and one-electron reduction of the ketone to form a Zr-bound ketyl radical intermediate. This proposed mechanism is supported by the isolation of a tetrametallocene asymmetric isobenzenesacral product upon reaction with benzophenone. It is highly desirable to us to induce selectivity at the newly formed sterocenter by altering the ligand environment around the radical species. We describe our recent progress towards preforming this transformation asymmetrically.

INOR 675
C-H activation and functionalization of long chain and substituted aromatic hydrocarbons effected by Cp^+W(NO)(CH2CMe3)(η^2-CH2CHMe) and a comparison of the reactivity of Cp^+W(NO)(alkyl)(η^2-allyl) complexes with aldehydes and ketones
Monica V Shree, mshree@chem.ubc.ca, Peter Legzdins. Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

The 18-electron complex, Cp^+W(NO)(CH2CMe3)(η^2-CH2CHMe), loses neopentane at ambient temperatures and forms the η^2-diene intermediate, Cp^+W(NO)(CH2CMe3)(η^2-CH2=C=C=CMe). The 16-electron η^2-diene intermediate initiates selective C-H activation processes. For example, its reactions with n-pentane, and mesitylene all result in a single product resulting from activation at the terminal CH3 position of the hydrocarbon. These C-H activation processes will be compared to that exhibited by Cp^+W(NO)(alkyl)(η^2-allyl) complexes with related ketones and aldehydes. After activation of the long-chain hydrocarbons, the resulting Cp^+W(NO)(alkyl)(η^2-allyl) complexes can be functionalized by migratory insertion of CO exclusively into the W-allyl linkages.

INOR 676
Synthesis of bifunctional catalyst and its application in CO2/epoxide copolymerization
Fu-Te Tsai, fu-te.tsai@mail.chem.tamu.edu, Donald Jude Darensbourg. Department of Chemistry, Texas A&M University, College Station, Texas 77840, United States

Selective transformation of carbon dioxide (CO2) into biodegradable polycarbonates by the alternating copolymerization with epoxides presents a green, promising polymerization process for potential large-scale utilization of CO2 in chemical synthesis. Because of high activity and selectivity for polycarbonate production, bifunctional electrophile-nucleophile catalyst 1 consisting of (1R,2R-Salen)Co(III)(DNP) and a quaternary ammonium salt was synthesized for the asymmetric coupling of CO2 with racemic 3,4-epoxy-1-butene (figure 1). In addition, post-polymerization modification of the produced polycarbonate 2 with 2-mercaptoundehanol in the presence of azobisisobutyronitrile (AIBN) was demonstrated.

INOR 677
Synthesis and characterization of a cis-directed 4-electron/4-proton transfer agent.
Estelle L Lebeau, lebea1el@cmich.edu, Michael Roy Stenzel. Department of Chemistry, Central Michigan University, Mount Pleasant, MI 48858, United States

Although some monomeric dioxo species are strong oxidizing agents, not all are able to control the spatial conformation of the complex. We describe here the preparation and characterization of a new, highly reactive cis-directed dioxo ruthenium catalyst complex that incorporates the bidentate ligand 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DMPPP). The synthetic route to the preparation of [(DMPPP)Ru(O)2]3(CO2), including the preparation of the dichloro and diaqua precursors, is described. The complexes have been characterized using x-ray crystallography, IR/Raman, UV-visible spectroscopy, elemental analysis and NMR. We will present the results of pH-dependent electrochemical potential studies.

INOR 678
Photocatalytic conversion of CO2 to CO and acrylic acid
Eric Oweggi, eoweggi@gmail.com, Venugopal Komreddy, D. Paul Rillema. Department of Chemistry, Wichita State University, Wichita, KS 67260, United States

The synthesis of various rhenium complexes was followed by an investigation of their capacity to reduce CO2 photocatalytically to CO. Re(bpy)(CO)3X (X = Cl, NCS; bpy = 2,2'-bipyridine) was irradiated in a CO2 saturated DMF-TEOA solution in a Pyrex tube capped with a serum cap. The CO produced in the reaction was trapped using a gas chromatograph fitted with a molecular sieves column. This was followed by examining the reactivity of carboxylated Re(dcbpy)(CO)3X (dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine) dye derivatives in the same manner. The objective was to attach the rhenium dye to TiO2.
using it as a photoanode in a photoelectrochemical cell to produce electricity and at the same time reduce CO₂ and CO catalytically. Secondly CO₂ insertion into olefin-metal bonds was also studied. Molybdenum and tungsten complexes were synthesized and coupled with CO₂ to form acrylic acid.

INOR 679

1D, beta-cyclodextrin and carbonaceous coated oxide nanofibers for photocatalytic membrane filtration

Jairah Shaikh, maoy@utpa.edu, Yuanbing Mao, Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78539, United States

Environmental problems have increasingly become a matter of serious concern. Nanotechnology is used in this work to resolve the low effectiveness, slow decontamination rate and poor cyclability of current options for decomposing and removing contaminants and microorganisms from polluted water. Here a type of novel titanate@C@β-cyclodextrins (CDs) nanowire membrane with enhanced photocatalytic activity was developed using a cost effective procedure to resolve many of the problems involving water purification and quality, including to simultaneously enhance photocatalytic degradation efficiency and adsorption by coupling the functionalities of these components. In this presentation, we will present the successful synthesis and characterization of the compositionally controlled nanocomposite membranes, also the investigation of the dependence of photocatalytic ability and separation performance on the characteristics of the nanowire membranes and the fabrication parameters.

INOR 680

Preparation of sol-gel-immobilized cyclam metal complexes for heterogeneous phosphate ester hydrolysis

Alexander C Thomas, acthom10@smumn.edu, Brett R. Bodsgard, Chemistry, Saint Mary’s University of Minnesota, Winona, MN 55987, United States

Progress was made on the synthesis of a series of sol-gel-immobilized cyclam metal complexes to act as heterogeneous catalysts for phosphate ester hydrolysis. The synthetic strategy was to first prepare a monoalkylated cyclam with a terminal alkyl functional group, preceded by a novel protection reaction. After monoalkylation and subsequent deprotection, a hydrosilation reaction created a terminal triethoxysilane moiety through which a sol-gel can be created. After metallation of the covalently-linked embedded cyclam ligands, the resulting material was tested for its phosphate ester hydrolysis activity. Synthetic details and analysis, along with preliminary kinetic data, will be presented.

INOR 681

Synthesis and characterization of carbonic anhydrase active-site mimics for CO₂ hydration

Deepshikha Gupta¹, deepshikha.gupta@uky.edu, Cameron A. Lipper², Anitha Vishrojawar¹, John P. Selegue¹, Joseph E. Remias², Kunlei Liu². (1) Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, United States (2) Center for Applied Energy Research, Lexington, KY 40511, United States

The catalyzed enhancement of CO₂ absorption is a critical component to reduce the capital cost of CO₂ capture. Specifically, an effective catalyst will increase the CO₂ hydration rate, thereby decreasing the size of the absorber tower needed. We are exploring complexes of zinc(II) and similar metal ions with ligands such as 1,4,7,10-tetraazacyclododecane (cyclen), 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet a), tris(benzimidazolylmethyl)amine (BIMA) and anionic tris(pyrazolylborates) that mimic the enzyme, carbonic anhydrase. [Zn(cyclen)(H₂O)]·2H₂O is found to catalyze CO₂ hydration in aqueous solvent mixtures under both pH-drop screening and stopped-flow conditions. However, under pH-drop which has conditions similar to industrial post combustion capture, activity of [Zn(cyclen)(H₂O)]·2H₂O drops as compared to observed in stopped-flow conditions. We are focusing our efforts on designing other catalysts that show high CO₂ hydration rate similar to carbonic anhydrase while showing superiority towards temperature, pH and inhibitors.

INOR 682

Characterization of transition metal substituted polyoxometalates in aprotic solvents and their activity toward carbon dioxide reduction

Adam J Dannenhoffer, dannenha@canisius.edu, Skyler Sweeney, Mariusz M Kozik, Steven H Szczepankiewicz, szczepas@canisius.edu. Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY 14208, United States

Our recent work demonstrated that transition metal substituted heteropoly tungstates in nonpolar solvents have a tendency to form dimers. This behavior is confirmed with ³¹P NMR spectroscopy. Theoretical calculations confirm the thermodynamic stability of certain isomeric dimer structures. Evidence for catalytic activation of carbon dioxide is observed by cyclic voltammetry in acetonitrile solutions. The feasibility of electrolytic reduction of carbon dioxide, along with reduced product analysis, is discussed.

INOR 683

Computational investigation of the polymerization of phenylacetylene by rhodium scorpionates

T. Ryan Rogers¹, trogers6@uc.edu, Richard M. Tarkka¹, Patrick J. Desrochers¹, Charles E. Webster². (1) Department of Chemistry, University of Central Arkansas, Conway, AR 72035, United States (2) Department of Chemistry, University of Memphis, Memphis, TN 38152, United States

Trispyrazolylborate ligands (TpR), also known as scorpionates, have a long and rich history. The steric and electronics of TpR can be tuned by varying the R substituents. Rhodium-scorpionate complexes catalyze the polymerization of acetylenes. More recent work from our laboratory has focused on anchoring variants of Tp catalysts on resin supports, in an effort to create recyclable heterogeneous catalysts. We will present our findings on the exploration of various mechanistic pathways of phenylacetylene polymerization by TpRh(cod) catalysts. Our results are also used to aid in the design and development of heterogeneous-supported catalysts with novel TpR analogues.
INOR 684
Stereoselective-induced variable aggregation and photocatalysis of fluorinated phthalocyanines lacking C-H bonds
Hemanthbhai H. Patel, hemantbhai.patel@student.shu.edu, Sergiu M. Gorun. Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07102, United States
We report the stereoselective synthesis of the cis isomer of F40PcZn, a perfluorophthalocyanine peripherally substituted by both aromatic, F, and aliphatic, R, groups. In F16Pc, F40Pc, and F64Pc scaffolds, the 8 peripheral positions are substituted to 0, 50, and 100% extents by R, groups, respectively, thus defining a substitution parameter S with values 0, 0.5 and 1. For S = 0.5 a single crystal X-ray structure reveals the formation of dimers exhibiting π-stacking of the type expected for S = 0. Aggregation of F40PcZn in solution is solvent dependent, likely limited by the bulkiness of the moiety of the type found for S = 1. The generation of singlet oxygen was also demonstrated to occur at rates comparable with that observed for S = 1, about twice that observed for S = 0.

The fluorinated environment insures the high stability of the phthalocyanine macrocycle during the production of singlet oxygen and oxidation of β-citronellol to hydroperoxides, thus recommending the F40Pc for additional catalytic processes developments using aerobic pathways.

Acknowledgment
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INOR 685
Ammonia as the high-density solar fuel of the future
Daniel J Little, littled5@chemistry.msu.edu, Jason M Thornton, Thomas W Hamann. Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States
Due to the combination of the worlds increasing energy demand and concerns of fossil-fuel combustion induced climate change, there is an imminent need to switch to carbon-free renewable energy sources such as solar. Solar irradiation is diurnal and intermittent, however, making it essential to store a large fraction of the converted energy. For these reasons photochemical water splitting to generate renewable hydrogen has attracted a lot of attention. Storage of the low-density gas is problematic, however, making the conversion to higher energy density fuels attractive. One option is the storage of renewable hydrogen as ammonia since it has a relatively high energy density, is carbon-free, and can potentially be decomposed back to nitrogen and hydrogen with the application of less than 0.1 V (compared to over 1.23 V for water electrolysis) or used in a direct ammonia fuel cell. In practice, however, large overpotentials are required to drive the overall ammonia electrolysis reactions resulting in poor energy conversion efficiencies. We have recently begun investigating reducing the ammonia electrolysis overpotentials through homogeneous and heterogeneous catalysis. Results of electrocatalytic ammonia splitting in organic solvents as well as in liquid ammonia at metal and metal oxide surfaces will be discussed. We found a striking dependence of the catalytic performance on the electrolyte composition in liquid ammonia. In addition, ammonia oxidation via a series of ruthenium poly-amine complexes will be presented.
Synthesis and reactivity studies of novel tris(pyrazolyl)boratocobalt complexes
Shawn G. Ridlen, shawn.ridlen@mavs.uta.edu, Muhammed Yousufuddin, H.V. Rasika Dias. Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019, United States

Cobalt(I) is being increasingly studied for its role as a catalyst for many organic reactions and inert bond activation. In many cases, Cyclopentadienyl (Cp) is used as a supporting ligand. In particular, CpCo(I) has been shown to mediate reactions such as C-H bond activation and cyclomerization. However, the tunability of these complexes is limited. This limitation can be overcome by using functionalized tris(pyrazolyl)borate (Tp) ligands. Our efforts on developing new TpCo(I) complexes will be presented.

INOR 687
Hydrogen transfer catalyst design inspired by thermodynamics
Zachariah M. Heiden, zachariah.heiden@wsu.edu. Department of Chemistry, Washington State University, Pullman, WA 99164, United States

Currently, most ketone and imine reductions involve the use of stoichiometric reagents such as LiAlH₄, NaBH₄, or NaBH₄CN. Although these reagents work well, their use on industrial scales can generate waste disposal issues. While metal-based catalysts have been shown to promote the reduction of ketones and imines, new guidelines of United States Pharmacopeia have dramatically lowered the allowable metal impurities such as Pd, Pt, Ru, Ir, Rh, and Os in pharmaceuticals. This has prompted new interest in the development of base metal and metal-free hydrogenation processes. This poster will discuss the thermodynamics of current metal based and metal-free hydrogen transfer catalysts and describe how this analysis can be used as guidelines for future catalyst development for imine and ketone reduction.

INOR 688
[FeFe]-hydrogenase active site mimic with an annulated terthiophene group as an approach to a visible light absorbing photocatalyst for hydrogen production
Steven M Sil1, sili1986@email.arizona.edu, Gabriel B Hall1, Laura M Stratton1, Richard S Glass1, Dennis L Lichtenberger1, Dennis H Evans2. (1) Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona 85721, United States (2) Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

Recent work on [FeFe] hydrogenase active-site mimic catalysts has focused on generating a photocatalytic complex by coupling the 2Fe2S core with a chromophore to facilitate the reduction of protons to molecular hydrogen. A (2,5-bis(2,2’-thiophene-2-yl)-thiophene-μ-3,4-dithiolato)diiron hexacarbonyl complex (1) has been prepared using a dithiol ketone resulting in a 54% yield, compared to current methods for this class of compounds which involve harsh conditions to deprotonate the dithiols. The catalytic ability of the complex to reduce protons from acetic acid to H₂ was investigated via electrochemical and computational methods. The complex 1 was found to have a reversible two electron reduction. Compared to the related catalysts, benzene- and thiophenedithiolato-diiron hexacarbonyl (2, 3), 1 displayed an improved catalytic peak. UV-vis analysis of 1 shows a broad absorption band in the 400-500 nm range with a λmax at 430 nm and an ε of 6500 M⁻¹ cm⁻¹, which is more prominent than is observed for 2 and 3. DFT calculations performed on 1 show that the electron density of the HOMO of the complex is primarily located on the terthiophene ligand and the LUMO is primarily iron-based, while 2 and 3 have displayed a HOMO that is metal-sulfur based.

INOR 689
Study on stability of new primary phosphines
Shanshan Wu, sxw325@case.edu, John D. Protasiewicz. Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, United States

Primary phosphines are a class of important molecules in diverse applications, which usually possess bulky groups to improve air stability. A primary phosphine 3,5-di-tert-butyl-2-phenophenophenol has been prepared. But the presence of a sterically demanding tert-butyl group adjacent to the PH₂ center renders the molecule very sensitive to loss of PH₃ and 3,5-di-tert-butylphenol. This work mainly discussed efforts on interpretation of this decomposition mechanism. Also several new phosphinomethylpheno1s were prepared, and their stabilities were studied.

INOR 690
N-substituted amine-boranes as liquid-phase hydrogen storage fuels
Asa E Carre-Burritt, asac@lanl.gov, Benjamin L Davis, Brian D Rekken. Los Alamos National Lab, Los Alamos, New Mexico 87545, United States

The transition to a hydrogen (H₂) based economy has many hurdles to overcome in reaching targets for onboard hydrogen storage as determined by the Department of Energy. Of critical importance, the material must exhibit a liquid phase before and after dehydrogenation. To address this, the compounds, 3-methoxymethylamine-borane and hexylamine-borane, have been developed as viable hydrogen storage materials. H₂ evolution by controlled heating of the amine-boranes produces a liquid, dehydrocoupled trimer. The amount of usable H₂ was increased in these materials by
blending the amine-boranes with ammonia-borane. Co-oligomeric products of the two components feature slight increases in their respective molecular weights that are proportional to the amount of ammonia borane incorporated into the system. Evolved gas measurements reveal the differences in volatile products between the pure amine boranes and the ammonia-borane blends. Products are further characterized by $^1$H and $^{11}$B NMR spectroscopy, gel-permeation chromatography, and other complimentary techniques.

INOR 691

**Aluminum-α-dimine complexes: Redox-active aluminum systems**

Bren E Cole1, bren.cole001@albright.edu, Connor A Koelner1, Nicholas A Pira2, William G Dougherty2, W Scott Kassef, Christopher R Graves1, cgraves@alb.edu. (1) Albright College, Reading, PA 19612, United States (2) Villanova University, Villanova, PA 19085, United States

A series of Aluminum-α-dimine ligand complexes exhibiting multi-electron redox chemistry have been prepared. α-Dimine ligands of the type ArNC(Me)(Me)N-Ph (Ar = substituted aromatic) were synthesized and their coordination chemistry to aluminum was investigated. Singly ((dimine)AlCl2) and doubly ((dimine)2AlCl(THF)) reduced α-dimine complexes of aluminum were prepared for ligands incorporating substitution in the ortho positions of the aromatic side groups. Complexes were characterized by €H NMR spectroscopy, X-ray diffraction, and DFT. The redox behaviour of the complexes was investigated using electrochemistry and the cyclic voltamograms showed rich redox behaviour. Aluminum complexes with α-dimine ligands lacking ortho substitution incorporated two ligands: The fully neutral ligand compounds [((dimine)2AlCl2][AlCl4]) and the fully reduced ligand complexes M[(dimine)2]2Al] (M = alkali metal) were both prepared and characterized and the redox behavior was investigated.

INOR 692

**Reactions of diiminopyridine ligands with boron halides**

Abigail Africa, Caleb D. Martin, caleb_d_martin@baylor.edu.Department of Chemistry and Biochemistry, Baylor University, Waco, TX 76798, United States

There has been significant interest in the chemistry of transition metal complexes featuring diiminopyridine ligands (DIMPY) as many of these species are great catalysts for a variety of transformations. The chemistry of DIMPY with the main group elements remains far less developed. In fact for boron, no reactions have been reported. In this regard, we herein examine the reactivity of DIMPY ligands with the boron halides. The synthesis, characterization and reactivity of the new complexes will be evaluated.

INOR 693

**Silylanilino derivatives containing boron**

Kyralysa Hauger, k.hauger@tcu.edu, Robert H Neilson.Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, United States

Boron compounds containing silicon-nitrogen functional groups have a wide variety of derivative chemistry. Current research interests involve investigating compounds containing Si-N groups attached to a 4-substituted Ph group to afford silylanilino derivatives. Due to the variety of reactions that can occur on the boron, these compounds hold the potential to be precursors to new inorganic-organic hybrid polymers and/or novel ring system. We report the synthesis, characterization and reactivity of some representative examples of (silylanilino)boranes of types 1 and 2.

INOR 694

**Heterolytic cleavage of molecular dihydrogen via an "inverse" frustrated Lewis pair (FLP) approach**

Sureshbabu Mummadi, suresh.mummadi@ttu.edu, Hui Li, Adelia Aquino, David Cordes, Fernando Hung-Low, William Hase, Clemens Kremper.Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas (TX) 79415, United States

The heterolytic cleavage of H2 via frustrated Lewis pairs (FLP’s) represents a new concept in sustainable chemistry that has the potential of replacing expensive, less abundant and toxic precious metals. One of the major disadvantages, however, is that the currently available FLP’s capable of cleaving H2 are largely limited to highly fluorinated boranes such as B(C6F5)3 and RB(C6F5)3 and synthetic procedures to these expensive Lewis acids involve hazardous or explosive materials (C6F3Li).

It will be demonstrated that strong and sterically encumbered Brensted bases such as zwitterionic and non-zwitterionic carbanions, N-heterocyclic carbenes and phosphonium ylides form intermolecular FLPs with fluoride free boron-containing Lewis acids capable of cleaving H2. Our experimental and computational results clearly show that even poor Lewis acids engage in H2 cleavage provided that the present base is sterically encumbered and of sufficiently high Brensted basicity. This FLP approach - weak Lewis acid combined with a strong base - is inverse to that pioneered and exhaustively studied by Stephan, Erker and others the latter utilizes FLPs composed of the exceptionally strong Lewis acids B(C6F5)3 or RB(C6F5)3 and weakly basic amines and phosphines.

INOR 695

**Tetrahedral and octahedral organotin showing a dependence on geometry for activity as biocides**

Jonathan A Muniz, jamuniz@miners.utep.edu, Keith H Pannell, Armando Varela, Renato Aguilera.Department of Chemistry, University of Texas At El Paso, El Paso, Texas 79936, United States

Organometallic compounds have been widely used as cytotoxic materials for cancer cells and have provided promising results in the treatment for cancer. Organotins specifically result in a good variant as they are very cytotoxic, although they lack cytoselectivity. On the other hand, cytotoxic compounds of ruthenium have shown a low cytotoxic activity, but high cytoselectivity. It was hypothesized that the creation of a ruthenium-tin-chlorine backbone should yield both cytotoxic and cytoselective. As a preliminary study we have used some tetrahedral and octahedral tin compounds dissolved in DMOSO at milli-micro-molar concentrations and tested against different cell lines, including MDA-MB231 cancer cell lines, grown on DMEM media. The techniques used were the classic cytotoxic assays with readings after 24 and 48 hours using Propidium iodide and Hoechst staining to determine the cytotoxicity. The most cytotoxic tetrahedral compounds are [(C5H5)2Fe(CO)2]2SnMe2 with a CC50 of 0.107 milimolar, (t-butyl)3SnCl2 with a CC50 of 0.33 milimolar, and [(C5H5)Fe(CO)2]Sn(t-butyl)2Cl with a CC50 of 0.74 milimolar. The observation of the activity of the iron-tin complex not containing the normally requisite Sn-Cl bond is a novel result from the literature. Four molecules that have an octahedral geometry have been synthesized with three of
them having a general framework \([\text{o-MeEC}_3\text{H}_4\text{CH}_3\text{SnCl}_3]\) where \(E = O, S, \text{CH}_2\). The usage of those octahedral molecules has indicated that the tetrahedral geometry is required to maintain a high cytotoxicity.

**INOR 696**

Syntheses and characterization of Sb(III) and Sb(V) di(benzothieno)stiboles  
**Anna M DeLaRosa.** anna.delarosa@chem.tamu.edu, Masato Hirai, Francois P Gabbai. Department of Chemistry, Texas A&M University, College Station, TX 77842, United States

The synthesis of an Sb(III) phenyl di(benzothieno)stibole was accomplished in high yield and the product fully characterized by spectroscopic methods and X-ray crystallography. This compound features an antimony atom incorporated into a rigid benzannelated framework comprised of five fused rings with a high degree of π conjugation. This dithiennostibole is oxidized to various corresponding Sb(V) dithiennostiboles by direct reaction with orthochloranil and by a peroxide oxidation method with vicinal diols including pinacol and perfluoropinacol. These compounds have also been fully characterized and retain the rigid fused-ring framework around the oxidized antimony atom.

**INOR 697**

Reactivity of \([\text{Ru(tpy)}(\text{dpdz})(\text{NO})_2])^+\) in model physiological conditions with DNA  
**Nicole O Lahanas.** nicoleirene.lahanas@student.shu.edu, Victoria S Lonnay, Matthew Mongelli, Wyatt R Murphy. Department of Chemistry and Biochemistry, Seton Hall University, South Orange, New Jersey 07079, United States

The synthesis of the bifunctional complex \([\text{Ru(tpy)}(\text{dpdz})(\text{NO})_2])^+\) (tpy = 2,2',6,2'-terpyridine; dpdz = dipyridophenazine) will be reported. This complex contains the strongly DNA intercalating ligand dpdz, and the NO2 ligand, which can act as a precursor to nitric oxide under acidic and hypoxic conditions. The complex is being studied for DNA binding, conversion of the nitro ligand to nitrosyl, and reduction to NO and NO2. Solutions mimicking the physiological environment of normal and cancer cells will be used to study the behavior of the complex in the presence and absence of polymeric DNA. Gel electrophoresis will be used to determine if strand scission has taken place. Binding studies of the compound such as the characterization of the binding constant and binding site size, and kinetic data will be also reported.

**INOR 698**

Investigation of synthetic pathways of \([\text{Ru(bpy)}_2(\text{NO})_2(\text{OH})_2])^+\)  
**Victoria S Lonnay, victoria.lonnay@student.shu.edu, Nicole-Irene O Lahanas, Wyatt R Murphy, Jr.** Department of Chemistry and Biochemistry, Seton Hall University, South Orange, New Jersey 07079, United States

Covalent binding of ruthenium polyphenyl complexes with labile ligands to N-7 of guanine is a motif that may lead to anticancer pharmaceuticals. This binding alone can be enhanced by including a reactive group such as NO, which results from acid conversion of the nitro to nitrosyl, followed by reduction with NADH, vitamin C or similar agents. Generally the nitro form of ruthenium polyphenyl complexes is significantly favored at pH 7, which is advantageous in that it will remain relatively inactive in normal healthy tissue (the area surrounding tumor cells tends to be more acidic). \([\text{Ru(bpy)}_2(\text{NO})_2(\text{OH})_2])^+\) was prepared via literature methods by Murphy, Meyer, et al. (1983) as a potential binding-reactive site bifunctional complex. This compound has been successfully bound to the N7 site of guanosine as proven by UV-VIS and NMR. Results of studies with adenosine, cytidine, thymidine and polymeric DNA will be reported. The effect of coordination of the complex to the nucleobase on the nitro/nitrosyl equilibrium and formation of NO will be reported.

**INOR 699**

Heterocyclic platform ligands with a PO/CMPO pendant arm: Synthesis and coordination with Ln(III) ions  
**Sabrina Ouizem, souizem@unm.edu, Daniel Rosario Amorin, Sylvie Pailloux, Diane A Dickie, Benjamin P Hay, Laetitia H Delmau, Robert T Paine.** (1) Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131, United States (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Increasing concerns toward the permanent disposal of nuclear wastes has been a major motivation for developing new selective extractant ligands efficient for separation of f-block metal ions from aqueous solutions via solvent extraction process. In comparison to the well-known CMPO type ligands, NOPOPO type ligands, developed in our laboratory, that incorporate a pyridine N-oxide fragment show remarkable extraction power toward lanthanide and actinide ions.

Continuing studies have been based on the development of CMPO-N-oxide pyridine compounds that combine both platforms where the CMPO is attached by the nitrogen. As it has been observed in the literature on various preorganized multi-CMPO ligands, we expect that such ligands would display improved extraction performance compared with the parent CMPO. We are also interested in the development of a polymer-supported phosphinopyridine N-oxide, that could allow application of the ligand as a selective immobilized extractant. Finally, we considered taking advantage of the amino group to introduce functional groups known to coordinate Ln(III) ions.
INOR 700

Design, synthesis and coordination chemistry of new ligands with potential interests for LLE applications

Daniel Rosario-Amorin¹, drosari@unm.edu, Sabrina Ouzem², Diane A Dickie², Benjamin P Hay², Julien Podair², Laetitia H Delmauf², Sean D Reilly³, Andrew J Gaunt², Brian L Scott². (1) Department of Chemistry and Chemical biology, University of New Mexico, Albuquerque, NM 87131, United States (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States (3) Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States (4) Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States

The development of multidentate ligands suitable for liquid-liquid extraction (LLE) of minor actinides from nuclear spent fuel remains a considerable challenge. In this context, pyridine N-oxide platforms bearing methyl phosphine oxide groups 1-2, have proven to provide improved extraction performance compared to the well-known CMPO class of ligands. Recently we extended this functionalization approach to additional heterocyclic receptors including dibenzofuran, thiophene, dibenzothiophene and their sulfone analogues. Some of these were found to be more efficient and selective for LLE process than the two individual classes of extractants.

INOR 701

Synthesis, structural characterization, and magnetic properties of dinuclear, tetraneurul, and heptaneurunl lanthanide(III) complexes of a tri-functional hydrazine ligand

Santokh S. Tandon¹,², standon@kent.edu, Scott D. Bunge³, Laurence K Thompson³. (1) Chemistry and Biochemistry, Kent State University, Salem, OH 44460, United States (2) Chemistry and Biochemistry, Kent State University, Kent, OH 44242, United States (3) Chemistry, Memorial University, St. John's, NL A1B3X7, Canada

The reactions of a tri-functional (vanilin-hydrazine-oxime) ligand (L) with lanthanide (Ln) salts result in the formation of a variety of different products, depending on the reaction conditions. Reactions of LnX₃ (X = NO₃ or Cl) with L in the presence of triethylamine (TEA) and trimethylacetic acid ([(CH₃)₂CO]₂) form dinuclear complexes, [Tb₂L₄(CH₃)₂CO₂]₂(NO₃)₂(1), [Tm₂L₄(CH₃)₂CO₂]₂(H₂O)₂(2), tetraneurul complexes, [Eu₂L₄(CH₃)₂CO₂]₂(H₂O)₂(C₂H₅OH)₂(3), [Gd₂L₄(CH₃)₂CO₂]₃(H₂O)₂(C₂H₅OH)₂(4), and a heptaneurul complex, [Dy₂L₂(CH₃)₂CO₂]₄(H₂O)₆(5). Reactions of Ho(NO₃)₃ with L in the presence of TEA and benzoic acid (C₆H₅CO₂H) or acetic acid (CH₃CO₂H) form a dinuclear complex [Ho₂L₄(C₆H₅CO₂)₂(NO₃)₂]₆(6) and a hexaneurul complex [Ho₂L₄(OH)(CH₃CO₂)₄]₇(7) respectively. The reaction of Tb(NO₃)₃ with L in the presence of TEA and sodium azide (NaN₃) forms a tetraneurul complex [Tb₂L₄(N₃)₄]₈(8). The x-ray crystal structures, spectroscopic, and magnetic properties of these complexes will be reported.

INOR 702

Structural, photoluminescence, and energy transfer properties of lanthanide dicyanoaurates containing terpyridine ligands

Frankie White¹, fdw701@jagmail.southalabama.edu, Lam Pham¹, Kang Rui Xiang¹, Rylee Thomas¹, Paul Vogel¹, Richard Sykora¹, rsyskora@southalabama.edu, Zerihun Assefa¹. (1) Department of Chemistry, University of South Alabama, United States (2) Department of Chemistry, North Carolina A&T State University, United States

Lanthanide cyanometallates are an interesting and important class of materials, due to their optical properties, that exhibit diverse types of metallophilic interactions. More specifically, the structural and spectroscopic properties of lanthanide cyanometallates have been extensively studied. The two-dimensional extension of the aurophilic interactions in these compounds can lead to strong visible emissions or energy transfer with select Ln³⁺ ions. We have previously shown that the structural and electronic properties of lanthanide cyanometallates can be modified through the incorporation of additional ligands around the Ln³⁺ sites. The tridentate ligand 2,2’-6’,2’-terpyridine has also proven to be effective in this regard and it substantially alters the structural and photoluminescent properties of the lanthanide dicyanoaurate compounds containing it. [Ln(C₅H₁₁N₂)(H₂O)(NO₃)]₂Au(CN)₂[Ln = Eu, Tb, Dy, Ho, Er, Yb], LnAu, form an isostructural series as established by single-crystal X-ray diffraction studies. The structural studies of these compounds reveal dimeric aurophilic interactions and terpyridine π-stacking that are both present with distances of ∼3.5 Å. These dimers lead to strong, broad emission bands in the visible region that are characteristic of excimers. However, in select compounds, EuAu and TbAu, these excimer bands can be quenched via intramolecular energy transfer because of a reasonable energy match. The photoluminescence measurements also demonstrate that EuAu displays enhanced Ln-based emission due to intramolecular energy transfer from the coordinated ligands.

INOR 703

Synthesis and design of supramolecular self-assembled lanthanide cages
The synthesis, structures and properties of a remarkable new class of discrete self-assembled molecules, which feature both lanthanide (4f) and d-block transition metals will be described. The use of specifically designed ligands results in the formation of cage-like supramolecular architectures which possess drum or barrel like structures. The ligands “L” are derived from a Schiff-base ligand of the “salen” type but which contain 5 or more methylene (CH₂) units in the backbone linking the metal binding N,O terminals. The compounds were structurally characterized by single crystal x-ray diffraction studies and their photophysical properties investigated. So far the compounds feature stoichiometries in which there is a Ln:Tm ratio of 1:3 (Ln = lanthanide ion; Tm = d-block transition metal). Examples include [Ln₂Cd₆L₁₃(OAc)₁₄] and [Ln₆Cd₁₃L₁₀O₆(OAc)₂₂].

INOR 704

Synthesis, in vitro testing, and encapsulation of novel organometallic compounds for cancer treatment

Sandugash Yespolayeva, sandugash.yspolayeva@nu.edu.kz, Gulzhan Kamitova, Aisulu Zhanbossoina, Salimgerey Adilov, sadilov@nu.edu.kz. Department of Chemistry, Nazarbayev University, Astana, Aqmola 010000, Kazakhstan

Organometallic compounds have been extensively used for cancer treatment over the past few decades. However, major clinical problems, including high toxicity to normal healthy cells, low selectivity, and acquired or intrinsic resistance, often lead to the fail of complete cancer remission and numerous undesirable side effects. In order to overcome these problems, we designed and synthesized new organometallic compounds based on ferrocene, ruthenium metals with indole, resorcinol, PTA derivatives. Currently, these compounds are at the stage of in vitro testing for anticancer activity. These compounds are furnished with functional groups which expected to induce programmed cell death and show high selectivity to cancer cells. Furthermore, to reduce the toxicity and to deliver an anticancer agent directly to the target cell we will encapsulate synthesized complexes with the synthetic biodegradable and biocompatible polymers. With further studies we wish to examine the mode of actions of compounds to see the interaction with DNA and impact on the cell cycle.

INOR 705

Varying the steric of an azaferrocene Lewis base donor: Synthesis and structures of azaferrocene-boranes

Sarah B. Krause¹, tbrunker@towson.edu, Jason R Smith¹, Arnold L Rheingold², Tim J Brunker². (1) Department of Chemistry, Towson University, Towson, MD 21252, United States (2) Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093, United States

Three different azaferrocenes (Cp*FePyr) have been prepared which vary in the number of alpha-methyl substituents on the pyrrolyl ring, and hence the steric environment of the Nitrogen-donor: These azaferrocenes are PMAF (Pyr = pyrrolyl), 6MAF (Pyr = 2-methylpyrrolyl) and HMAF (2,5-dimethylpyrrolyl). The borane adducts (BX₃; X = H, F, Cl, C₆F₅ and 9-bora-bicyclo[3.3.1]nonane (9-BBNH)) of these azaferrocenes have been synthesized and characterized by IR and NMR spectroscopy and, in some cases, X-ray crystallography. In this set, only the HMAF adduct of 9-BBNH has not been isolated, presumably due to steric hinderance of the alpha-methyl groups in HMAF. However, with the smaller acceptor, BF₃, no difference in N-B bond length is found between the X-ray structures of PMAF-BF₃ and HMAF-BF₃. The structure of HMAF-B(C₆F₅)₂ was also determined and shows a classical Lewis acid-base adduct albeit with considerable distortion of the azaferrocene moiety. ¹⁻ and ¹⁴N NMR solution studies show that the azaferrocene-B(C₆F₅)₂ adducts remain intact in solution and display restricted rotation about N-B and/or B-C bonds: The lack of reactivity of these adducts with H₂(g) also supports the conclusion that these are not frustrated Lewis acid/base pairs. Efforts to further increase the steric bulk of the azaferrocene Lewis base will be outlined as will other reactivity studies of these borane adducts. Electrochemical characterization of HMAF and 6MAF will also be reported.

INOR 706

Copper(I) complexes of “click”-derived abnormal carbenes and their applications in catalysis

Stephan Hohloch, Stephan.Hohloch@fu-berlin.de, Biprajit Sarkar. Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin, Germany

Copper(I) complexes with NHC ligands (NHC = N-heterocyclic carbene) are known to be highly active catalysts in various transformation. [1] We have prepared a series of neutral and cationic copper(I) complexes of the general formula [Cu(αNHC)ₓ][L] (x = 1 or 2) or [[αNHC]₂Cu]⁺ (αNHC = triazolylidene type abnormal carbene). Formation of the desired complex can be controlled by varying the counter-ion of the triazolium salt used. All complexes were studied by methods like NMR spectroscopy, mass spectrometry and X-Ray diffraction. Structural analysis revealed interesting coordination motifs for the different compounds. The complexes have been investigated for their catalytic properties in the azide-alkyne cycloaddition reaction. Thereby the cationic systems were found to be more active than their neutral counterparts. It was possible to convert challenging substrates at short reaction times using these systems at low catalyst loadings. [2] [3]
INOR 707
Frustrated Lewis pairs as ligands for organometallic catalysis
Brian R Nichols, bnichol3@mix.wvu.edu, Brian V Popp.C Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States
A great deal of research has explored the structural consequences of ambiphilic ligand environments on the coordination sphere of inorganic and organometallic complexes. Far less is known, however, about their impact on catalytic activity. The application of frustrated Lewis pairs with organometallic catalysts may provide new opportunities for small molecule activation and catalyst development. We have prepared and characterized a variety of new rhodium and iridium complexes containing the β-phosphinoethylborane ligand. Preliminary insights from stoichiometric and catalytic studies of these complexes will be presented that provide a conceptual foundation for developing new catalytic systems in the future.

INOR 708
Density-functional analysis of N-heterocyclic carbene compounds
Ruth A Juarez1, padre@nmsu.edu, Wei-Tsung Lee2, Jeremy Smith2, Haobin Wang1. (1) Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico 88001, United States (2) Chemistry, Indiana University Bloomington, Bloomington, Indiana 47405, United States
Electronic structure calculations are carried out to study a class of N-heterocyclic carbene compounds employing density functional theory (DFT). The calculated vibrational frequencies for the N-O stretch, which is the experimental probe of electron donating strength of the donor ligand, are in excellent agreement with the experimental values. The underlying mechanism of such a measure of the electron donating strength is analyzed in terms of electronic structures and thermodynamic properties. Furthermore, the DFT results are used to predict the outcome of some of the reactions involving similar compounds.

INOR 709
Organometallic complexes with tethered hydrazone and pyridyl ligands as model photochromic complexes: A density functional theory study
Roger G. Letterman, rgltmn@memphis.edu, Jermaine O. Johnson, Theodore J. Burkey, Charles Edwin Webster. Department of Chemistry, The University of Memphis, Memphis, TN 38152, United States
Our labs have been developing organometallic photochromic systems with tethered, derivatized hydrazone and pyridyl (or phenyl) functional groups. We will present both experimental and computational studies related to the pathway for the thermal isomerization between chelates of the tethered functional groups. Various experimental and computational spectroscopic data (IR, NMR, UV-vis) for the identification of photoproducts will also be presented and discussed.

INOR 710
Fluorescent organotin systems based on O-N-O ligands: Synthesis, characterization, and cell imaging applications
Maria C Garcia1, mcgl170@hotmail.com, Blanca M Muñoz2, Victor M Jimenez1, Rodrigo A Chan1, Arturo Chavez2. (1) Quimica de los materiales, Universidad Autonoma de Nuevo Leon, San nicolas de los garza, Nuevo leon 66451, Mexico (2) Centro de investigacion y de estudios avanzados, Apodaca, Nuevo leon 66600, Mexico
A series of substituted 2-hydroxyalicyclidenbenzohydrazides were converted into their diorganotin complexes in good yields upon reaction with di-n-butyl or diphenyltin. All organotin compounds were full characterized by NMR (1H, 13C, and 119Sn), UV, IR, and mass spectrometry. The X-ray structures of four complexes showed the tin atoms with trigonal bipyramidal geometry. The 119Sn parameters for 1-4 indicate pentacoordinated tin centers. The photophysical properties of organotin compounds exhibit quantum yields below 5% with lifetimes in the range 10^-10^-11s. Preliminary results by confocal microscopy fluorescent imagen of B16F12 cells in the present of 2 showed yellow fluorescent after being for 2 hours and reveals its potential applications as a fluorescent imaging material.
INOR 711
Synthesis and DNA-binding studies of Re(I)-pentylcarbonato and related complexes
Brent V Powell1, bpow3@morgan.edu, Saroj K Pramanik2, Santosh K Mandal2. (1) Chemistry, Morgan State University, Baltimore, Maryland 21251, United States (2) Biology, Morgan State University, Baltimore, Maryland 21251, United States

Rhenium(I) tricarbonyl diimine complexes have been established as cytotoxic agents. We have synthesized numerous rhenium(I) diimine pentylcarbonato complexes where the diimines are 2,9-dimethyl, 4,7-dimethyl, 5,6-dimethyl, and 3,4,7,8-tetramethyl-1,10-phenanthroline complexes. The parent dirhenium decacarbonyl and the corresponding methyl-substituted 1,10-phenanthrolines were refluxed in 1-pentanol in the presence of carbon dioxide to obtain the corresponding pentylcarbonato complexes. The pentylcarbonato complexes have been characterized spectroscopically. The pentylcarbonato complexes containing the diimine ligands 2,9-dimethyl-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline have been characterized through X-ray crystallography. The DNA-binding study of the pentylcarbonato complexes through electronic spectroscopy and electrophoresis reveal that some of these complexes bind the DNA in an intercalative mode.

INOR 712
Electrochemical durability of nanocrystal-based energy storage materials
Natacha Krins1, Ajay Singh1, Linping Xu1, Brett A. Helms1, Jordi Cabana1,2, Delia J. Milliron1,3, dmilliron@lbl.gov. (1) Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (2) University of Illinois, Chicago, IL 60612, United States (3) Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States

We assemble electrochemically active colloidal inorganic nanocrystals into well-controlled mesoscale architectures to correlate structure and composition on multiple length scale with cycling stability and thereby derive design rules for robust battery electrodes. Nanocrystals with well defined size, shape, and crystal phase are arranged into mesoporous films through block copolymer templating or embedded in an inorganic matrix to form nanocrystal-in-glass composites. Comparing anatase titania nanocrystals of different sizes and shapes, we find that a small minimum particle dimension and a porous network both contribute to accommodate the strain of the lithium-induced phase transition out to at least 1000 cycles in nanorod-based mesoporous films. By contrast, tin nanoparticles are observed by ex situ TEM to fragment after only one lithiation cycle. The cycle stability of tin nanoparticle electrodes can be dramatically improved by encasing the particles in a thin inorganic glassy matrix.

INOR 713
Inorganic synthesis of titania-based nanomaterials for high power, safe Li-ion battery anodes
Bart M Bartlett, bartmb@umich.edu. Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States

Maximizing the electrical energy stored in, and drawing high power from titanium-based materials for safer Li-ion battery anodes requires preparative methods that generate high purity nanomaterials. Although low temperature synthesis methods known to generate nanoscale materials have been adapted for promising candidates, their electrochemical performance is often plagued by point defects, particle aggregation, and impurity phases—all of which can be minimized if one has a thorough understanding of and appreciation for inorganic reaction chemistry. I will highlight two specific examples currently under investigation in my laboratory: 1) lithium titanate spinel nanocrystals synthesized by a templated sol-gel processing method; 2) bronze-phase TiO2 microflowers synthesized by hydrothermal synthesis followed by aqueous work-up. I will provide details of the synthetic chemistry used to generate these materials along with guidelines that can be applied to other solid oxides. In addition, I will show that electrodes composed of titania nanomaterials show excellent energy density and stability. Most important, the rate capability (power) is superior due to the small particle sizes we obtain from our synthesis methods.

INOR 714
Carbon coated silicon nanowires for lithium ion battery electrodes
Timothy Bogart, Daichi Oka, Xiaotang Lu, Brian A Korgel, korgel@che.utexas.edu. Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712, United States
Silicon (Si) nanowires were synthesized in solution using tin seeds and phenylsilane reactant. The nanowires form with a polyphenylsilane shell that can be transformed by pyrolysis to an electrically conductive carbon coating. These nanowires were tested as slurry anodes with poly(acrylic acid) binder in lithium (Li)-ion batteries. The anodes exhibited capacities over 2000 mAh g⁻¹ for 100 cycles when cycled slowly at C/10 and over 1200 mAh g⁻¹ when cycled quickly at 1C. In situ TEM experiments showed that the conductive carbon coating increases the lithiation rate, but limits the extent of lithiation by constraining the volume expansion. Segments of nanowires without the carbon coating freely expand and contract, but are much more prone to structural degradation.

INOR 715
Mechanisms of solar-driven charge separation and H₂ generation in multifunctional colloidal nanorod-catalyst heterostructures
Tianquan Lian, tian@emory.edu. Department of Chemistry, Emory University, Atlanta, GA 30322, United States

Quantum confined semiconductor nanocrystals have been widely investigated as light harvesting and charge separation components in photovoltaic and photocatalytic devices. The efficiency of these semiconductor nanocrystal-based devices depends on many processes, including light harvesting, carrier relaxation, charge separation and charge recombination. The competition between these processes determines the overall solar energy conversion (solar to electricity or fuel) efficiency. Compared with single component quantum dots (QDs), semiconductor nanoheterostructures, combining two or more materials, offer additional opportunities to control their charge separation properties by tailoring their compositions and dimensions through relative alignment of conduction and valence bands. Further integration of catalysts (heterogeneous or homogeneous) to these materials form multifunctional nanoheterostructures. Using CdSe/CdS/Pt, dot-in-rod nanorods(NRs) with Pt tips, as a model system, we are examining the mechanism of long-lived charge separation and H₂ generation in the presence of sacrificial electron donor. The rates of electron transfer, hole transfer and charge recombination are directly monitored by transient absorption and time-resolved fluorescence spectroscopy. In this talk, we will discuss the mechanism of exciton dissociation and the dependence of the rates of elementary charge transfer processes on the dimension (size and length) and band alignment in these materials.

INOR 716
Photochemical upconversion and its applications in solar energy capture, conversion, and storage
Felix N Castellano, fncastel@ncsu.edu. Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, United States

Semiconductors suffer from the inability to harvest photons with energy lower than their bandgap, therefore limiting their efficiency in solar energy applications. To mitigate this problem, photons of low energy can be upconverted into higher energy light at low flux through sensitized triplet-triplet annihilation, resulting in sub-bandgap sensitization of semiconductors without any chemical modification of the latter. This presentation will describe numerous examples of upconversion phenomena realized in solution and solid-state polymeric materials along with emerging classes of acceptor/annihilator chromophores. Triplet fusion processes will be shown to operate at high efficiencies with concomitant linear incident power density response, demonstrated in both theory and experiment using non-coherent photons. Finally, upconversion-based photoaction observed in water splitting photoelectrochemical cells and operational photovoltaics will be discussed.

INOR 717
Electron transfer as a probe of the permeability of monolayers at nanoscopic interfaces
Kathryn Knowles, Michal Malicki, Mario Tagliazucchi, Emily Weiss, e-weiss@northwestern.edu. Northwestern University, United States

This paper describes the influence of the size and shape of alkyl-substituted benzoxazine (s-BQ) acceptors on the efficiency with which they participate in static and collisional photoinduced electron transfer (PET) with oleate-coated PbS quantum dots (QDs) in dichloromethane solution. Efficient extraction of photogenerated charge carriers from colloidal semiconductor QDs is essential to their application as photovoltaic and photocatalytic active materials. The organic ligand shell that electronically passivates and solubilizes colloidal QDs also presents a physical barrier that impedes a molecular redox partner’s approach to the QD surface, and limits the number of available sites per QD for its adsorption. We have shown that the ability of a molecular redox partner to adsorb to the inorganic surface of a QD, where it can participate in photoinduced charge transfer on the single-picosecond timescale, depends on the density and permeability of the native ligand shell, and that these properties are sensitive to the absolute concentration of the QDs and the binding headgroup of the native ligands. Here, we take the first step toward designing organic adlayers to control this redox activity by examining the rates of both static and collisionally gated photoinduced electron transfer processes as a function of the size and shape of the molecular acceptor.

INOR 718
Fabrication of TiO₂ nanofibers for photocatalytic degradation of environmental toxins
Danielle L McCarthy¹, dmcart5@binghamton.edu, Jian Liu¹, Julia B Tolli¹, Jared B Decoste³, William E Bernier², Wayne E Jones². (1) Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902, United States (2) Leidos, Inc., Gunpowder, Maryland 21010, United States

Environmental sustainability is gaining momentum as a topic of interest in the scientific community. Nanotechnology can provide novel systems for rapid decontamination and sustainability. Electromagnetic radiation in the form of visible and ultra-violet light, typically provided by sunlight, can be used to achieve self-cleaning photodegradation of environmental toxins such as, toxic industrial chemicals (TICs), toxic organic dyes, biopharmaceuticals, and chemical warfare agents (CWAs). TiO₂ nanofibers represent an alternative approach to conventional composites used in photocatalytic degradation. The one dimensional morphology of TiO₂ nanofibers is desired compared to spherical TiO₂ nanoparticles; due to its excellent mobility of charge carriers, high surface area, the existence of pores enhancing the accessibility of electrodes to the hole transporting materials and hence enhanced charge collection and transport. The fabrication process takes advantage of electrospinning, a non-mechanical, electrostatic technique that can produce fibers in the nanometer range using electrically driven jets of polymer sol-gel solution followed by a calcination process under thermally controlled atmospheric conditions. The results are hypothesized to provide modifications leading to improvement of photocatalysis with priority in decontamination of selected templates of environmental toxins. Fabrication, catalytic mechanism, and application of electrospun TiO₂ nanofibers will be further discussed.

INOR 719
Tuning noble gas separations in metal formates with temperature dependent selectivities
Keith V Lawler, keith.lawler@unlv.edu, Paul M Forster. Department of Chemistry, University of Nevada Las Vegas, Las Vegas, Nevada 89154, United States

Gas separations are critical throughout industrial processes: The primary parameter by which sorbents are assessed is their selectivity for a specific gas from the mixture from which it is to be separated. We previously demonstrated with single gas adsorption measurements that the metal formates (M=Co, Ni) should be good candidates for the separation of krypton and xenon. Here, we analyze the metal (M=Mg, Mn, Fe, Ni, Co, Zn) formate family of metal-organic frameworks for their ability to separate mixtures of noble gases by means of multi-component gas mixture grand canonical monte carlo simulations. Simulations are compared to supporting single gas adsorption measurements that have been analyzed with ideal adsorbed solution theory. We find that the metal formates are more selective than other compounds in the literature for the heavier noble gas in the mixture, and that formates with
smaller pores tend to be more selective. The temperature and loading dependence of the selectivity are explored to find optimal conditions for pressure swing adsorption applications of the metal formates. The selectivities are highest at low loadings and colder temperatures, but appear practical over a wide range of conditions. The temperature and composition of the heat of adsorption of the noble gases into the formates is analyzed in order to show that gas mixture adsorption data needs to be evaluated for accurately estimating PSA.

**INOR 720**

Surface functionalized zirconium phosphates: A unique class of functional materials

**Agustin Diaz**, diaz@chem.tamu.edu, Brian M. Mosby, Abraham Clearfield. Department of Chemistry, Texas A&M University, College Station, TX 77842, United States

The list of uses and potential uses of α-zirconium phosphate (ZrP) is quite extensive, but among the most promising ones are ion-exchange, catalysis, photoinduced charge separation, drug delivery, biosensors, and fuel cells, among many others. In order to improve the applicability of these materials, surface modifications of the nanoplatelets are highly desirable. Each modification can be tailored for a specific application. We will describe the modification of the surface of ZrP with different groups, such as silanes, epoxides and different metals. The resulting materials were characterized by XRPD, FTIR, AFM, TEM, XPS, and SIMS, among other techniques. The synthesized materials were used for different applications, including drug delivery, emulsifiers, nanofillers in polymer based nanocomposites and as compatibilizing agents in non-compatible polymer blends. The complete synthesis, characterization, and applications of these materials will be presented.

**INOR 721**

Exploring C-C coupling reactions using peptide-capped Pd nanoparticles

**Beverly D. Briggs**, bbriggs@umiami.edu, Nicholas M. Bedford1,2, Rajesh R. Naik2, Marc R. Knecht1. (1) Department of Chemistry, University of Miami, Coral Gables, FL 33146, United States (2) Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, Ohio 45433, United States

Biomimetic approaches to nanoparticle synthesis have been explored to mimic materials made in Nature with precise size and shape control. This control can be exploited to precisely tailor nanoparticles for a variety of applications. In our work, peptide-capped Pd nanoparticles have been synthesized using the Pd4 peptide, which was determined to have a strong affinity for Pd metal. Spherical and nearly-monodisperse Pd nanoparticles were generated, yielding nanoparticles with an optimized surface-to-volume ratio for catalytic applications. These nanoparticles, previously shown to be reactive for Stille coupling under ambient conditions with low catalyst loadings, are shown now to be active for Suzuki coupling, where the activity was found to have a unique correlation to the transmetalation agent structure. By comparing the reactivity of the same particles for both Stille and Suzuki coupling, unique mechanistic information can be addressed, suggesting a significant effect at the transmetalation step. Furthermore, both of these coupling reactions using these peptide-capped Pd nanoparticles have been suggested to operate under an atom-leaching mechanism, where recent work using EXAFS and SAXS has provided compelling evidence to support this theory. Finally, initial steps in exploring the functionality of these peptide-capped Pd nanoparticles attached at surfaces will be discussed for a completely heterogeneous system.

**INOR 722**

Synthesis and characterization of metal deposited CZTS nanostructures for use in catalysis

**Patrick S Dilsaver**, pdilsave@iastate.edu, Javier Vela, Malinda Reichert. Department of Chemistry, Iowa State University, Ames, Iowa 50010, United States

CZTS is a relatively non-toxic semiconductor material made of earth-abundant elements compared with other materials. The direct bandgap of ~1.5 eV means that it can absorb a large part of the visible region of the solar spectrum, and is an interesting candidate for photocatalysis. Semiconductor nanorods have several advantages for use in catalysis, including a high surface area and lower electron-hole recombination rates. Metal deposited on the surface of semiconductors is also thought to aid in catalysis, slowing recombination and may also lead to selectivity in products. Here we report the deposition of metal islands onto CZTS nanorods using photodeposition techniques as well as thermal pathways. Deposition was studied using metal precursors, as well as pre-formed metal nanoparticles. The resulting heterostructures were characterized with a variety of methods, including UV-Vis, TEM, EDS, XPS, Powder XRD and others. These heterostructures were also screened for reactivity for a variety of reactions under various photocatalytic conditions. Results of this part of the research are ongoing and will be discussed further once studies are complete.

**INOR 723**

DNP surface enhanced NMR spectroscopy for the characterisation of metal-surface interactions in catalysts

**Lyndon Emsley**, lyndon.emsley@ens-lyon.fr, Institut de Sciences Analytiques, Center for High Field NMR, Ecole normale supérieure de Lyon, Villeurbanne, France

Surface enhanced NMR spectroscopy (SENS) can be achieved by using dynamic nuclear polarization (DNP). In this approach, electron polarization is transferred from an organic radical to the rare nuclei (at natural isotopic abundance) at the surface, yielding more than a hundred-fold signal enhancement for surface species in silica frameworks. Here we show the full characterisation by DNP SENS of a hybrid organic-inorganic silica material containing homogeneously distributed Pd-NHC complexes that is active for the Z-selective hydrogenation of alkynes. The results confirm the well-defined uniform environment of the Pd-complex on the surface silica material.

We then go on to determine secondary interactions that are demonstrated to direct the stability of well-defined Ru-NHC based heterogeneous alkene metathesis catalysts. Specifically, we determine the interactions between the metal center (active site) and the surface functionality of the support. The interactions are present only when the metal center is attached at the surface via a flexible linker (a propyl group), which allows the active site to either react with the substrate or relax – reversibly – to the surface, thus providing stability. In contrast, the use of a rigid linker leads to a well-defined active site far away from the surface, and we show that this leads to faster decomposition and deactivation of the catalysts.

**INOR 724**

Synthesis of peptide-templated bimetallic nanostructures for enhanced catalytic reactivity

**Nicholas A Merrill**, n.merrill@umiami.edu, Nicholas M Bedford1,2, Rajesh R Naik2, Lawrence Drummy2, Marc R Knecht1. (1) Department of Chemistry, University of Miami, Coral Gables, FL 33146, United States (2) Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio 45433, United States

Bio-inspired approaches for the formation of metallic nanomaterials have been extensively employed for a diverse range of applications including self-assembly, biomedical diagnostics, and catalysis. A significant benefit of these materials for catalytic applications is that they can often be used under benign and ecofriendly conditions that do not require harmful solvents or high temperatures; however, it is often challenging to control the material size, morphology, and composition simultaneously. To overcome these limitations, we have employed the R5 peptide that forms a 3D scaffold in solution to direct the size and linear shape of metallic nanomaterials. While Pd, Pt, and Au monometallic templated materials have been shown to be highly reactive for a variety of reactions, the catalytic activity can be significantly enhanced via the formation of bimetallic structures. To this end, bimetallic PdAu and
PdPt materials have been prepared using a self assembling peptide template that alter the electronic properties of the materials, resulting in a catalytic reactivity increase. The morphology and composition of the materials are controlled by varying the metal to peptide and metal to metal ratios to generate highly controlled structures with a linear morphology. The catalytic activity of the final materials was studied using the hydrogenation of allyl alcohol to 1-propanol as a model reaction. In general, a significant increase in the reaction turnover frequency was noted for bimetallic materials containing 33.3% Au in PdAu structures and 16.7% Pt in PdPt materials as compared to their monometallic Pd counterparts.

INOR 725
Metal-based supramolecular ordering in liquid crystalline phases
Rachel J Allenbaugh, rallenbaugh@murraystate.edu, Michael G Hyatt, McKenna L Morgan. Department of Chemistry, Murray State University, Murray, KY 42071, United States

Although metalophilic interactions, where metal d⁸ and d¹⁰ centers stack at less than van der Waals distances, have been noted in liquid crystalline phases, this type of interaction has not been systematically studied as a supramolecular ordering motif in liquid crystalline systems. A series of functionalized bipyridine derivatives of Ag(I), Ni(II), Pt(II), and Pd(II) will be discussed in light of how metal-center selection and ligand functionalization affects the formation of metalophilic interactions. In some cases, room temperature metalomesogenic phases can be produced. Characterization of the complexes via X-ray diffraction, differential scanning calorimetry, and NMR spectroscopy will be presented. Additionally, a more efficient, less expensive, and more environmentally friendly mechanochemical synthetic method will be discussed.

INOR 726
Designable architectures on nanoparticle surfaces: Zirconium phosphate nanoplatelets as a platform for tetravalent metal and phosphonic acid assemblies
Brian Mosby, brian.mosby@chem.tamu.edu, Mark Goloby, Agustín Díaz, Abraham Clearfield. Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

α-Zirconium phosphate (ZrP) nanoparticles were functionalized through a two-step ion exchange and self-assembly procedure. Metal ions, such as Hf(IV) and Sn(IV), were deposited on the surface of ZrP nanoparticles through an ion exchange reaction with the protons of the surface phosphate groups followed by complexing the metal ions with phosphonic acid ligands. The presence of the metal ion layer and further organic functionalization was verified by powder X-ray diffraction, electron microprobe, XPS, MAS/CP NMR, FTIR, and TGA. It was found that use of bisphosphonic acids led to the ability to build multilayer materials from the nanoparticle surface in a layer-by-layer fashion. This approach allows designable architectures to be built on the nanoparticle surface; the synthesis and applications of these materials will be discussed.

INOR 727
Electroless approach to atomic layer deposition on noble metal powders
Patrick J Cappillino, pcappil@sandia.gov, George M Buflieben, Maher Salloum, John L Stickney, David B Robinson. (1) Energy Nanomaterials Department, Sandia National Laboratories, Livermore, CA 94551, United States (2) Department of Chemistry, University of Georgia, Athens, GA 30602, United States (3) Scalable and Secure Systems Research, Sandia National Laboratories, Livermore, CA 94551, United States

Palladium has important applications in an array of fields including hydrogen storage and sensing, chemical catalysis and fuel cells. It offers high volumetric power density in metal hydride batteries and pseudocapacitors. However, the kinetics of hydride formation and hydrogen release in such applications are often limited by the high stability of the surface hydride formed with Pd. Theoretical and experimental reports suggest that adlayers of metals that form weaker surface Pd-H interactions can destabilize the surface hydride, which should facilitate hydrogen transport.

We have developed an electroless (chemical) atomic layer deposition technique in which we grow such layers on palladium powder. Exposing a suspension of powder to dilute hydrogen/nitrogen gas mixtures causes a surface hydride to form. Subsequent addition of a solution containing noble metal salts displaces the surface hydride with the reduced metal in a surface layer fashion. This approach allows designable architectures to be built on the nanoparticle surface, the synthesis and applications of these materials will be discussed.
metal salts displaces the surface hydride with the reduced metal in a surface limited reaction. This process can be repeated, and the thickness of the surface coverage increases, as shown by XPS. This technique requires no specialized equipment and makes use of benign reagents. It is surface-limited in nature, but is not limited to an electrode. This confers important advantages of high scalability and compatibility with complex surface topologies and conductive substrates are not required. We also feel that this versatile technique could be widely applied by synthetic chemists to take advantage of enhanced catalytic properties of near surface alloys.

In addition to details on the preparation and characterization of Pd powder with adlayers of other noble metals, we will show evidence of enhanced hydrogen transport in these samples. A kinetic model for this process that includes gas flow, solid-state hydrogen diffusion and surface hydride formation will also be presented.

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INOR 728
Discovering Ce-rich oxygen evolution catalysts, from high throughput screening to water electrolysis
Joel A. Haber1, jahaber@caltech.edu, Suho Jung1, Dan Guevarrat, Chengxiang Xiang1, Slobodan Mitrovic2, Eitan Anzenberg3,5, Christian Kisielowski1,4, Junko Yano4,5, Jian Jiri2, John M. Greigore6. (1) Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA 91125, United States (2) Engineering Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (3) National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (4) Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

Discovering improved electrocatalysts for the oxygen evolution reaction (OER) is of great importance for efficient solar fuels generation, electrowinning of metals, regenerative fuel cells, and recharging metal air batteries. The slow kinetics of the 4-electron OER requires large overpotentials to drive water oxidation at appreciable current densities. Among the numerous compositions investigated, mixed metal oxides in the (Ni-Fe)Ox and (Ni-Co)Ox composition spaces are among the most active and most studied OER catalysts. Although this technologically important reaction has been studied for more than 50 years, many of the mechanistic details remain under investigation. Lacking a robust fundamental understanding of the basic science and mechanistic details of multi-electron heterogeneous electrocatalysis, an efficient high-throughput synthesis and property screening methodology is well-suited to discovering the requisite new catalytic materials. We have established high throughput methods to systematically investigate the performance of pseudo-quaternary material libraries as OER electrocatalysts. We report a new Ce-rich family of active catalysts composed of earth abundant elements, which was discovered using high-throughput methods to produce 5456 discrete compositions in the (Ni-Fe-Co)Ox composition space. The activity and stability of this new OER catalyst was verified by re-synthesis and extensive electrochemical testing of samples in a standard format in 1.0 M NaOH, as well as by operation in a photovoltaic-powered electrolyzer for more than 100 hours. The most interesting variations in activity lie in a pseudoternary cross-sectional plane containing 665 compositions. Our detailed investigation of this pseudoternary cross-section has revealed systematic trends in Tafel slopes and electrochemical signals with composition, which provide a connection between the previously known Ni-Fe and newly discovered Ni-Co-Ce catalysts. Characterization of selected compositions by XRD, XPS, TEM, EDS, XRF, and EXAFS, both as-synthesized and after electrochemical testing, reveal important differences in nanostability and nanoscale catalytic activity, and the observed differences in electrochemical performance under OER conditions.

INOR 729
Coordination chemistry of metal chalcogenide nanocrystals
Jonathan S Owen, jso215@columbia.edu, Nicholas C Anderson, Mark P Hendricks, Joshua J Choi, Department of Chemistry, Columbia University, New York, New York 10027, United States

Surfaces dominate the properties of colloidal semiconductor nanocrystals. Characterizing and controlling surface coordination chemistry is therefore crucial to their application in optoelectronics and fluorescence labeling. I will describe our picture of nanocrystal surface structure as well as a carboxylate for chloride exchange method that allows us to fabricate high mobility semiconductor films using solution techniques. Using NMR spectroscopy we have discovered a novel ligand exchange mechanism where the surface layer of excess metal cations on metal chalcogenide nanocrystals is displaced in the presence of L-type ligands. We further show this reaction is rapid and reversible leading to nanocrystal stoichiometries that depend sensitively on the solution concentration. The importance of this behavior to luminescence quantum yields and nanocrystal synthesis will be discussed.

INOR 730
Chromium and cobalt, carbonyl, carbanions, and carboxylates: Organometallic chemistry through the years
Richard R Schrock1, Linda H Doerrer2, doerrer@bju.edu. (1) Department of Chemistry, Massachussetts Institute of Technology, Cambridge, MA 02139, United States (2) Department of Chemistry, Boston University, Boston, MA 02215, United States

A brief overview of chemistry from vanadium carbonyls to redox active ligands and the latest in ethylene polymerization will be given.

INOR 731
Selective transformations of organic compounds mediated by transition metal complexes
Robert G Bergman, rbergman@berkeley.edu, Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720-1460, United States

Many stoichiometric and catalytic reactions are now known in which metal complexes mediate the synthesis of new organic compounds. These processes have been used to convert simple organic compounds into more complex functionalized materials, in many instances with substantial selectivity. Mechanistic experiments have played an important part in bringing us to the current understanding of these transformations, providing rational ways to improve them, and guiding the development of new reactions. The content of the lecture will be chosen from exploratory and mechanistic research that has been carried out most recently. Examples will be taken from studies focused on the activation of carbon-hydrogen and carbon-carbon bonds in organic compounds and organic and organometallic reactions that take place in the cavities of self-assembled clusters.

INOR 732
Zincacarbatranes: Organozinc compounds that feature terminal hydride, fluoride and bicarbonate ligands
Wesley Sattler, Serge Ruccolo, Gerard Parkin, parkin@columbia.edu, Chemistry, Columbia University, New York, New York 10027, United States
INOR 733

O-O bonding in metal-dioxygen adducts

William Tolman, wtolman@umn.edu. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States

Inspired by the unusual active site structures and reactivities exhibited by copper enzymes, we seek to prepare and characterize synthetic complexes in order to test hypotheses developed to explain the novel functions of the biological sites. In collaborative work with Klaus Theopold, comparisons were drawn about the nature of O-O bonding in a variety of side-on metal-dioxygen adducts relevant to postulated intermediates in oxidation catalysis. Aspects of this work will be reviewed, and key lessons learned from correlations of O-O stretching frequencies and X-ray crystallographic data will be presented.

INOR 734

Hybrid nanoreactors comprising enzymatic and water stable organometallic co-catalysts

Trevor Douglas1a,b, tdouglas.ii@gmail.com, Dustin Patterson2, Ethan Edwards1. (1) Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, United States (2) Department of Chemistry, Indiana University, Bloomington, IN 47405, United States

Catalytic materials, either biological or synthetically derived, have the ability to perform a vast array of chemical transformations. Biological catalysts, typified by enzymes and optimized by evolutionary adaptation, are synthesized at the level of gene expression, which makes production relatively simple. Synthetic catalysts require more extensive design and synthetic development but can possess unique physical and functional properties, such as simpler chemical structure, greater thermal stability, and tunable properties, not found in their biological counterparts. By combining both enzymatic and synthetic catalysts together, new hybrid materials can be produced incorporating the best of both catalytic systems. We have constructed a hybrid catalyst nanomaterial through the co-incorporation of a redox enzyme and a small organometallic catalyst. The enzyme alcohol dehydrogenase D (AdhD) from *Pyrococcus furiosus* utilizes NADH to reduce 3-hydroxy-butan-2-one (acetoin) to 2,3-butanediol and represents a useful and important industrial biocatalyst. Many commercially relevant enzymes utilize the NADH cofactor and small molecule catalysts that can regenerate this cofactor, in close proximity to the enzyme, would be advantageous. We have used a rhodium catalyst, 

Cp*Rh(phen)Cl,

to convert NAD+ to NADH using formate as a reductant. Coupling of the two activities provides an illustration of initial steps towards the design of a semi-synthetic metabolic pathway. We have previously shown that the monomeric AdhD enzyme can be incorporated into a protein cage architecture derived from the bacteriophage P22 by heterologous expression in E. coli, producing nanoparticles with a high-density packaging of enzymes that retain their overall high catalytic efficiency. The Cp*Rh(phen)Cl

catalyst is water stable and with modifications to the phenanthroline group to incorporate a thiol reactive iodoacetamide group it can be covalently incorporated onto the protein architecture in close proximity to the AdhD enzyme.

INOR 735

Adventures in low-coordinate phosphorus chemistry

John Protasiewicz, protasiewicz@case.edu. Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44140, United States

Low coordinate and multiply bonded phosphorus compounds form the basis of reactive materials for the construction of new complexes and conjugated materials. In this presentation our work on the coordination chemistry of phosphinidenes (RP), phosphaalkenes (RP=CR=) and diphosphenes (RP=PR) will be presented. Phosphinidenes are analogues of carbones (R,C), and as such will form complexes will both transition metals and main group species. In particular, chemistry of the phophine stabilized phosphinidenes Ar=PR3 aka, phospha-Wittig reagents will be highlighted.

INOR 736

Manipulating MRI contrast by catalytic exchange of protons in slow water exchange complexes

A. Dean Sherry1a,b, dean.sherry@utsouthwestern.edu, Yunkou Wu1, Mary Evbuomwan2, Bunyong Sombunsakdikun2, Todd Soesbe1. (1) Advanced Imaging Research Center, University of Texas Southwest Medical Center, Dallas, Texas 75396 (2) Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75083, United States

A key parameter in determining the efficiency of a metal-based MRI contrast agent is the rate of water exchange between an inner-sphere water coordination position and bulk solvent. This is true not only for gadolinium-based T1 agents, especially targeted agents, but also for paramagnetic chemical exchange saturation transfer (paraCEST) and T2 exchange (T2exch) agents. Although slow water exchange can limit contrast enhancement in Gd-based T1 agents as molecular rotation become restricted, this feature is highly advantageous for paraCEST and T2exch Contrast mechanisms. In this study, we prepared a series of DOTA-tetraamide ligands having from one to four extended primary amino groups at various distances away from the metal center. An examination of the T1 relaxation and CEST properties of various paramagnetic lanthanide complexes with this ligand series as a function of pH revealed that the CEST contrast is absent or weak at pH values near 7.4 but substantially enhanced at lower pH values. Similarly, the T2exch contrast properties of the dysprosium and ytterbium complexes were also highly dependent on pH. Further investigations of the mechanism of these effects showed that the appended amino groups catalyze proton exchange from the single, slowly exchanging lanthanide ion-bound water molecule into the pool of solvent protons, effectively turning these slow water exchange agents into fast proton exchanging systems (advantageous for T1 relaxation but not for CEST). As the appended amino groups become protonated at lower pH values, they are no longer able to base catalyze proton exchange from the bound water molecule such that T1 contrast becomes less efficient while CEST contrast is turned on. Interestingly, the T2exch Contrast mechanism can either be turned on or off at lower pH dependence upon which lanthanide complex is chosen. These combine observations had led to new insights into how to create efficient MRI reporters of tissue pH.

INOR 737

Design of nanoparticles for magnetic resonance molecular imaging: A multidisciplinary task

Robert N MULLER, robert.muller@umons.ac.be. Laboratory of NMR and Molecular Imaging, University of Mons, Mons, BelgiumCenter for Microscopy and Molecular Imaging, Gosselies, Belgium

Molecular imaging is a young and growing discipline that aims at the development of new diagnostic technologies using specific reporters for the visualization of molecular processes in vivo, in particular those involved in pathological mechanisms. Their early detection may represent a decisive advantage for the choice and the follow-up of the therapeutic strategies.

Among the contemporary methods of medical imaging, MRI offers the unique advantage of being non-invasive and of furnishing simultaneously - and with a high spatial resolution -anatomical, physiological, and molecular information. Nevertheless, the quite low efficiency of currently available MRI...
contrast agents represents a challenge with respect both to the improvement of more efficient reporters, as well as to the development of MR protocols adapted to their detection.

A contrast agent for MR molecular imaging (MRMI) is a complex assembly made of a magnetic reporter, the “contrastophore”, linked to a vectorizing moiety specific to the structure to be targeted.

Parallel to the development of paramagnetic complexes, large efforts are devoted to the production of superparamagnetic nanoparticles carrying a high payload of relaxivity. Those require new synthetic approaches as well as new characterization protocols.

The specific molecular vector further linked to the nanoparticle can be selected among peptides identified by phage display or among the non-peptidic mimetics proposed in the literature.

This lecture will present an overview of the current state of the field.

**INOR 738**

How coordination chemistry affects water exchange, and vice versa, in lanthanide(III) DOTA-type chelates

*Mark Woods*, mark.woods@pdx.edu. Department of Chemistry, Portland State University, Portland, Oregon 97201, United States

Advanced Imaging Research Center, Oregon Health and Science University, Portland, Oregon 97239, United States

The ability of Gd³⁺ chelates to shorten the T₂ of solvent water protons is strongly influenced by the exchange of protons between the inner coordination sphere and the solvent water. This inner-sphere relaxation effect is described by the theory of Solomon, Bloembergen and Morgan (SBM). It is now widely accepted that the rate of inner sphere proton exchange in the Gd³⁺ chelates used as clinical agents is slower than optimal. Such slow exchange kinetics limits the effectiveness (or relaxivity) of these agents. There has therefore been considerable interest in better understanding and improving the inner sphere proton exchange characteristics of Gd³⁺ chelates. One of the problems in developing a highly detailed picture of exchange is the inherently flexible coordination chemistry of lanthanide complexes. It is common to find multiple coordination species present in solution, each with their own exchange characteristics, for a single Gd³⁺ chelate. This has traditionally frustrated attempts to paint a picture of exchange in anything other than broad strokes. By rigidifying the DOTA ligand structure and isolating single coordination species we have been able to gain some significant insights into how coordination chemistry affects water exchange in these chelates. We will examine the effect of relatively remote changes in the ligand structure on water exchange.

We will also examine how changes in water exchange can affect the perceived coordination chemistry of a Gd³⁺ chelate. Finally we will examine the effect of these changes on the relaxivity of these chelates; discovering that, in direct contradiction of traditional SBM analyses, an “optimal” water exchange rate (at 1.5 T) actually affords lower relaxivity than sub-optimal (slower) exchange. We will conclude by examining the implications of these discoveries for maximizing relaxivity.

**INOR 739**

Recent developments in Eu(II)-based contrast agents

*Matthew J. Allen*, mallen@chem.wayne.edu, Levi A. Ekanger, M. Meser Ali, E. Mark Haacke, Lisa A. Polin. (1) Department of Chemistry, Wayne State University, Detroit, MI 48202, United States

(2) Department of Radiology, Henry Ford Health System, Detroit, MI 48202, United States

(3) Department of Radiology, Wayne State University, Detroit, MI 48201, United States

(4) Department of Oncology, Wayne State University, Detroit, MI 48201, United States

Eu³⁺-containing cryptates have been demonstrated to have great potential as alternatives to Gd³⁺-based contrast agents for magnetic resonance imaging (MRI). Important questions about these agents include the relationship among ligand structure, complex stability, toxicity, and imaging efficiency. We have been pursuing these issues, and we will present data relevant to toxicity, relaxivity, ligand structure, and oxidation. The presented results are expected to be useful in future design of contrast agents for MRI.

**INOR 740**

CatalyCEST MRI contrast agents that detect enzyme activities

*Marty D Page*, mpagel@u.arizona.edu, Byunghee Yoo, Dina V Hingorani, Iman Daryaei, Paul J Akhenblit. (1) Chemistry and Biochemistry, University of Arizona, Tucson, Arizona 85719, United States

(2) Biomedical Engineering, University of Arizona, Tucson, Arizona 85724-5024, United States

(3) University of Arizona Cancer Center, University of Arizona, Tucson, Arizona 85724-5024, United States

(4) Athinoulia A. Martinos Center for Biomedical Imaging, Massachusetts General Hospital and Harvard Medical School, Boston, MA 02129, United States

Chemical Exchange Saturation Transfer (CEST) MRI is a relatively new contrast mechanism that can be exploited for molecular imaging. This presentation will briefly review the physical chemistry of CEST MRI to demonstrate how multiple MRI contrast agents can be selectively detected during the same scan session. To apply CEST MRI for molecular imaging, we have developed catalyCEST contrast that can detect enzyme activities. These catalyCEST agents show a change in the chemical shift, amplitude, or chemical exchange rate after an enzyme catalyzes a covalent change in the agent’s structure.

We have developed paramagnetic CEST agents that detect proteases. We have demonstrated that a responsive catalyCEST agent and an unresponsive CEST agent can be dynamically monitored during in vivo studies of a mouse tumor model, and the comparison of the two agents can improve the detection of in vivo protease activity. We have also developed paramagnetic CEST agents that detect an “anti-protease” which creates an amide bond. We have also developed polymers that are triggered by enzyme activity to spontaneously disassemble into monomers that have different CEST properties, which amplifies the detection of enzyme activities. We have also developed non-metallic, diamagnetic CEST agents that detect enzyme activities, and this presentation will compare the merits and limitations of paramagnetic and diamagnetic CEST agents for molecular imaging. Together, these examples constitute a comprehensive overview of the emerging research field of catalyCEST MRI.

**INOR 741**

DOTAM-based chelates for the development of paraCEST contrast agents

*Robert H.E. Hudson*, robert.hudson@uwo.ca. Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada

Recently, non-Gd³⁺ lanthanides have been used to develop MRI contrast agents using the technique of paramagnetic chemical exchange saturation transfer (ParaCEST). The amount contrast generated relies on chemical exchange processes which are dependent on pH, temperature and details of the structure. Typical ParaCEST contrast agents use a chelated Eu³⁺ ion with a bound water that is shifted approximately 50 ppm away from bulk water. While these agents are excellent at producing contrast there are still limitations for their use in vivo. The magnetization transfer generated during in vivo ParaCEST imaging decreases the overall sensitivity of agents that are not shifted far enough (>100 ppm) and water exchange is not exceptionally sensitive to pH changes. More recently it was found that a T₁relaxation induced by the exchangeable water is detrimental to observing the ParaCEST effect.

To overcome these limitations, we have examined agents that rely on highly shifted exchangeable amide protons. We have shown that Tm³⁺ t-butyl-DOTAM can mitigate MT effects due to its exchangeable amide signal appearing past 100 ppm at 37°C. The chemical shift of this signal was also sensitive to temperature within the physiologic range and may permit a direct readout of in vivo temperature. We have also recently found that some Tm³⁺ DOTAM anilides possess highly shifted amide signal and likely exist in the TSAP⁺ conformation meaning that metal bound water exchange is...
limited and thus minimizing the erosion of SNR due to T$_{2u}$. These aforementioned agents ultimately have limited potential as in vivo ParaCEST agents due to poor solubility and their tricationic nature. We have used chemical modification of the structures to address these problems and have found that reduction of charge to +1, makes the agents suitable for in vivo imaging by both direct injection (leg muscle) as well as iv injection (tail vein).

INOR 742

Electrochemical growth of copper(I) oxide nanorods on F-SnO2 substrates via polymer templating

Keith M. Haynes, kmh0277@gmail.com, William J. Youngblood, Teresa D Golden. Department of Chemistry, University of North Texas, Denton, TX 76210, United States

Vertically aligned cuprous oxide nanorods can currently be grown only with the assistance of anodic aluminum oxide membranes (AAOs), which are time-consuming to prepare and expensive to purchase. This research focuses on developing a simple and inexpensive ‘nanocasting’ method for copying the morphology of a nanostructured film and replicating that morphology for different materials. Starting from zinc oxide nanorods, which can be easily grown using hydrothermal methods, we are able to create a polymer template and electrochemically grow cuprous oxide into the template with the same morphology as the original ZnO nanorods. The polymer membrane is easily removed leaving hexagonal cuprous oxide nanorods, which have good electrochemical contact to the electrode substrate and are photocatalytically active within prototype regenerative solar cells.

INOR 743

Modulated nanotopography and optical properties of nonpolar gallium nitride via surface in-situ functionalization with cysteamine and phosphoric acid

Albena Ivanisevic, ivanisevic@ncsu.edu. MSE, NC State University, Raleigh, NC 27695, United States

In-situ functionalization of nonpolar a-plane gallium nitride (GaN) surface was achieved by adding cysteamine to phosphoric acid, aiming to modulate its optical properties. The emission properties and oxide formation were explored through surface characterization with atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and water contact angle. Nonpolar a-plane bulk GaN sample sliced from a GaN boule and nonpolar a-plane GaN thin layer heteroepitaxially grown on r-plane sapphire were used to elucidate the effects of in-situ functionalization of identical surface orientation of GaN crystals with different defect ensembles. The addition of cysteamine to the phosphoric acid solution was found to result in: (i) increased surface roughness, (ii) no change to hydrophobicity, (iii) decreased oxygen content at high solution temperatures and increased gallium and nitrogen content versus phosphoric acid solutions at similar temperatures without cysteamine. The in-situ functionalization resulted in enhanced PL intensity from the nonpolar bulk GaN, while the PL intensity from the nonpolar heteroepitaxially grown GaN layer on sapphire was significantly reduced. The opposite PL modulation was explained by the effects of different defects present in the two samples on the nonradiative recombination.

INOR 744

Synthesis of copper indium disulfide nanoplatelets

Linjia Mu, mu.linjia@wustl.edu, William E. Buhro. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States

Nanocrystals of the I-III-VI$_2$ semiconductors are of potential interest for solar-energy applications, due to their high absorption coefficient in the red to near-infrared region. In this study, CuInS$_2$ nanoplatelets are prepared from a variety of precursors in primary-amine solvents. The platelets exhibit both rectangular and hexagonal morphologies, and have lateral dimensions in the range of 20 – 30 nm. XRD analyses establish the wurtzite rather than the (bulk) chalcopyrite crystal structure for the nanoplatelets. The characterization and spectroscopic properties of these nanoplatelets will be presented.

INOR 745

Oriented growth of 1D CdSe and 0D Bi quantum structures from vertical sub-10nm hard templates

Yi-Hsin Liu$^1$, frfkimo@gmail.com, Fudong Wang$^3$, William E Buhro$^2$, Chung-Yuan Mou$^{2,3}$. (1) Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Taiwan Republic of China (2) Center for Condensed Matters and Sciences, National Taiwan University, Taipei, Taiwan 106, Taiwan Republic of China (3) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States

Oriented growth of 1D CdSe and 0D Bi quantum structures from vertical sub-10nm hard templates

Yi-Hsin Liu$^1$, frfkimo@gmail.com, Fudong Wang$^3$, William E Buhro$^2$, Chung-Yuan Mou$^{2,3}$. (1) Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Taiwan Republic of China (2) Center for Condensed Matters and Sciences, National Taiwan University, Taipei, Taiwan 106, Taiwan Republic of China (3) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States

Orientation of quantum structures rectifies efficiencies of conductivity properties that improve merits of all thermoelectric and solar devices. Unfortunately, current synthetic methods in gas phase, such as CVD, cannot easily produce uniform 1D structures below sub-10nm regimes, while those in solution phase are in lack of adequate substrate interaction to align the structure growth in vertical fashions. Recent discovery of vertical mesoporous films ideally provides rigid hosts to anchor catalysts that are consecutively used to grow dense 1D quantum arrays. It is known that bismuth performs thermoelectrical efficiency while it also serves as the best low-melting point and high-efficient catalysts to initiate growths of semiconducting quantum structures in a mild solution phase (via SLS mechanism). Based on this idea, we develop the idea of anchoring Bi quantum dots (~5 nm)

to grow CdSe 1D quantum wires upon mesoporous silica thin films (MSTF) hierarchically
Advances in electron microscopy have enabled the imaging of dynamics at atomic-level resolution. Nanocrystals present well-defined systems to study fundamental transient phenomena which are well defined in bulk materials. Cadmium chalcogenides (CdS, CdSe, and CdTe) are one of the most extensively studied and understood nanocrystals systems. These materials have been applied to a variety of optical and optoelectronic applications such as display phosphors, biological markers, and photovoltaics. Many first order phase transitions such as melting point and pressure-induced structural changes for these materials have been investigated through indirect spectroscopic methods; direct observation of phase changes in anisotropic structures have not been reported. In this work, we present the first direct observation of sublimation in CdSe nanorods. We observe the dynamics of sublimation in bright field TEM with atomic-level resolution at 10^7 Torr at four different temperatures. We found that vaporization occurs exclusively from the (001) and (00-1) planes. At a temperature just below the sublimation point, the electron beam heats the rod inducing vaporization from both ends in process which is limited by nucleation rather than vaporization. At temperatures much higher than the sublimation point, vaporization proceeds rapidly from only one end of the rod and does not appear to be nucleated limited. We believe that at these elevated temperatures, the sublimation behavior may be strongly influenced by a roughening transition.

INOR 746
High-resolution TEM of CdSe nanorod sublimation
Daniel J Hellebusch1,2, dhell@berkeley.edu, A. Paul Alivisatos1,2,3. (1) Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, United States (2) Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, United States (3) Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

We describe a novel strategy to perform low-temperature nanocrystal synthesis via the intermediacy of nanoclusters. Crystalline CdSe quantum platelets are obtained at room temperature in primary-amine, secondary-amine co-solvent mixtures. Their crystallinity is established by XRD, high-resolution TEM, and their sharp extinction and photoluminescence spectra. Reaction monitoring establishes the magic-size nanocluster (CdSe)34 as a key intermediate in the growth process, which converts to CdSe quantum platelets by first-order kinetics with no induction period. The results are interpreted to indicate that the critical crystal-nucleus size for CdSe under these conditions is in the range of (CdSe)32 to (CdSe)34. Thus the nucleation barrier is nearly surmounted in the formation of this magic-size nanocluster. The nanocluster is obtained in isolated form as [(CdSe)34(n-octylamine)16(di-n-pentyllamine)33], which is proposed to function as crystal nuclei that may be stored in a bottle.

INOR 747
Magic-size nanocluster (CdSe)34 as a low-temperature nucleant for cadmium selenide nanocrystals: Room-temperature growth of crystalline quantum platelets
Yuanyuan Wang, wangyuanyuan@wustl.edu, Ying Zhang, Fudong Wang, Daryl E. Giblin, Jessica Hoy, Henry W. Rohrs, Michael L. Gross, Richard A. Loomis, William E. Buhro. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130-4899, United States

The development of small electronic components is fundamental in our highly technology dependent society. Currently, the electronic industry is rapidly approaching the limit of silicon-based complementary metal-oxide-semiconductor (CMOS) technology. In consequence, the development of new technologies to replace silicon has rapidly become a hot topic not only in the academic community but also in industry. This new Holy Grail of electronic materials has to perform better than silicon at smaller scales (>10 nm) and if possible add new functionalities for electronic devices such as flexible electronics. In this direction, single layer transition metal dichalcogenides (TMDs) have recently emerged in nanoelectronics, although the study of layered TMDs beyond MoS2/WX2 is still incipient.

We studied the electronic structure of Ti, Zr, Hf, Ni, Pd and Pt 2D TMDs and nanoflakes/nanodiscs were investigated via periodic density functional theory and density-functional based tight-binding calculations. For group X TMDs, disulfide monolayers are indirect band gap semiconductors while the diselenides and ditellurides analogues present significant band gap reduction and can even become semimetallic or metallic materials. We also explored the stacking effects of these materials. A mechanical strain of these materials leads rapidly to a metallic electronic structure if compressed, but to quasibound band gap semiconductors if stretched. This behavior could be exploited towards the application of these materials in nanoelectronics. On the other hand, diverse group IV TMD nanoflakes/nanodiscs shapes up to 10nm were explored and their properties (electronic structure, interlayer interaction, edge composition...) were compared with the pristine mono- and multilayer 2D materials.

INOR 748
Single layer materials beyond MoS2
Pere Miro Ramirez, pere.miro@gmail.com, Mahdi Ghorbani-Asl, Thomas Heine. School of Engineering and Science, Jacobs University Bremen, Bremen, Germany

INOR 749
Modular approach to colloidal CdSe nanocrystal ligand exchange with chalcogenenols generated via the in-situ reduction of dialkyl and diaryl dichalcogenides
We have employed a simple modular approach to install small chalcogenol ligands on the surface of CdSe nanocrystals. This versatile modification strategy provides access to thiol and unique selenol and tellurol ligand sets via the in-situ reduction of \( \text{R}_2\text{E}_2 \) (\( \text{R} = \text{Bu, Bn, Ph}; \text{E} = \text{S, Se, Te} \)) by diphenylphosphine (\( \text{Ph}_2\text{PH} \)). The ligand exchange chemistry was analyzed by solution NMR spectroscopy, which demonstrates that reduction of the \( \text{R}_2\text{E}_2 \) precursors by \( \text{Ph}_2\text{PH} \) directly yields the active chalcogenol ligands that subsequently bind to the surface of the CdSe nanocrystals.

Thermogravimetric analysis, FT-IR spectroscopy, and energy dispersive X-ray spectroscopy provide further evidence for chalcogenol addition to the CdSe surface with a concomitant reduction in overall organic content. Time-resolved and low temperature photoluminescence (PL) measurements showed that, like thiol ligands, the selenol and tellurol ligands induce a fast, thermally activated quenching of the nanocrystal exciton population. This PL quenching is likely due to hole transfer to a ligand-induced excited state and is more efficient at low temperature for the selenol and tellurol ligands.

**INOR 750**

**Incorporation of dopant ions in II-VI molecular clusters**

**Kevin R. Kittilstved**, kittilstved@chem.umass.edu, Swamy Pittala.Department of Chemistry, University of Massachusetts Amherst, Amherst, MA 01003, United States

The physical properties of colloidal semiconductor quantum dots (QDs) are strongly coupled to the intended or unintended formation of intrinsic and extrinsic defect sites. To understand how extrinsic defects are formed during the growth of colloidal QDs we have started an effort using molecular analogs of II-VI QDs as model systems of the active surfaces of QDs. These molecular analogs are the well-known metal chalcogenide molecular clusters with the general formula \([\text{M}_x\text{E}_y\text{E}_2\text{H}_z\text{O}_w]^2−\) and \([\text{M}_x\text{E}_y\text{E}_2\text{R}_z]^2+\) (\( \text{M} = \text{Zn, Cd, Co, Mn and E = S, Se} \)) and have long been used as single-source precursors for producing QDs and transition metal doped QDs. Our current studies deal with the metal exchange reactivity and electronic structures of extrinsic defects in these molecular clusters. We have confirmed incorporation of Co\(^{2+}\) into the [Cd\(_x\)S\(_y\)P\(_z\)H\(_w\)]\(^2−\) and [Zn\(_x\)S\(_y\)P\(_z\)]\(^2−\) clusters at low temperature by \(^1\text{H}-\text{NMR}, \text{EPR}, \text{high-resolution mass spectrometry, and variable-temperature variable-field magnetic circular dichroism spectroscopy. However, differences in the NMR spectra and MS data of the doped tetrameric clusters strongly suggests that the equilibrium constants for [Zn\(_x\)S\(_y\)P\(_z\)H\(_w\)]\(^2−\) and [Cd\(_x\)Co\(_y\)S\(_z\)P\(_w\)]\(^2−\) are significantly different. Efforts to understand the stabilities and formation mechanism of these doped clusters as a function of temperature using \textit{in situ} spectroscopic techniques are currently underway.**

**INOR 751**

**Consequences of surface treatment on the transport properties of II-VI semiconductor nanowire devices**

**Pravin Paudel**, paudep@email.sc.edu, Bobby Barker, Christopher W Pinion, Andrew B Greytak.Department of Chemistry and Biochemistry, University of south carolina, Columbia, South Carolina 29208, United States

Semiconductor nanowires have been widely studied due to their unique properties like widely adjustable surface to volume ratio and high carrier mobility. These unique properties make them a suitable candidate for various electronic devices like photovoltaics, photodiodes, photodetectors, and field effect transistors. The performance of these devices depends on the surface of nanowires, because of the high surface to volume ratio. In this work, CdS nanowires, grown via the high-temperature vapor liquid solid mechanism, are treated following growth with solution phase reagents to control the chemical state of their surfaces. These solution phase treatments are correlated with changes in electronic properties as determined from field effect transistor (FET) and photocurrent measurements.

**INOR 752**

**Seeded growth of semiconductor nanocrystals from conducting metallopolymers: A novel approach to material fabrication for hybrid photovoltaics**

**Minh T. Nguyen**, mnguyen@cm.utexas.edu, Matthew T. Rainford, Kristin J. Suhr, Bradley J. Holliday.Department of Chemistry, The University of Texas at Austin, Austin, TX 78712, United States

Inorganic nanocrystals (NCs) of various binary, ternary, and quaternary semiconductors have been synthesized from metal centers interacting directly with the conjugated system of polythiophene-based conducting metallopolymers. The metal ions that are incorporated into the conducting metallopolymers serve as nucleation or seed points upon which the NCs can grow directly within the preformed polymer structure. This fabrication method, termed the seeded growth approach to bulk hybrid materials, provides materials with direct bonds between the inorganic NC and the conducting polymer backbone and therefore results in direct electronic communication between the donor and acceptor for effective charge transfer. Additionally, the seeded growth approach eliminates the need for organic capping ligands to stabilize the NC structures from aggregation. The size and distribution of the semiconductor NCs were controlled systematically by varying the concentration of metal centers in the initial conducting metallopolymers, the thickness of the polymers, and the number of NC growth cycles. The formation, size, and shape of inorganic NCs were studied by UV-Vis spectroscopy, transmission electron microscopy (TEM) and electron dispersive spectroscopy (EDS). Charge separation studied by light-induced electron paramagnetic resonance (L-EPR) shows charge transfer between materials, indicating promise for application in optoelectronic devices.

**INOR 753**

**Sequential chemistry of semiconductor nanocrystals through purification, stoichiometry, and measurement**

**Andrew B Greytak**, greytak@sc.edu.Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

Our group has introduced preparative gel permeation chromatography (GPC) as a method to separate natively-capped nanocrystals from small molecules including weakly-bound ligands. The GPC method provides highly purified nanocrystals with low and consistent ligand populations that we can use to study the effects of impurities on ligand exchange and shell growth, and as a well-defined initial state from which to examine the thermodynamics of ligand binding and interactions. We have also investigated the formation of CdS shells on CdSe nanocrystals under alternating layer addition conditions to evaluate the proposed selective ionic layer adhesion and reaction (SILAR) mechanism of shell growth. Through experiments such as these we aim to identify metrics for QDs and anisotropic nanocrystals and nanowires that enable subsequent reaction chemistry and physical properties to be predicted with confidence.

**INOR 754**

**N-heterocyclic carbene-stabilization of highly reactive beryllium complexes**

**Robert J. Gilliard, Jr.**, gilliard@uga.edu, Yuzhong Wang, Gregory H. Robinson.Department of Chemistry, The University of Georgia, Athens, GA 30602, United States

Recent efforts of this laboratory have resulted in the experimental realization of unusual main group molecules stabilized by N-heterocyclic carbenes. Notable examples include diborene (\( \text{H}—\text{B}—\text{B}—\text{H} \)), disilicon (\( \text{Si}_2 \)), diporphosorus (\( \text{P}_2 \)), and diarsenic (\( \text{As}_2 \)). We recently synthesized a carbene-stabilized analogue of the elusive beryllium borohydride monomer, \( \text{L}—\text{Be}(\text{BH}_4)_2 \) (\( \text{L} = \text{N-Heterocyclic Carbene} \))—the first structurally characterized compound.
containing the highly reactive Be(BH4)2 moiety. This talk will highlight our most recent results concerning the synthesis, structure, and reactivity of novel organoberyllium complexes.

INOR 755
Structural insights and characteristics of novel alkaline earth metal organic frameworks based on isonicotinic acid and isomers
Peter J Rosado, pjosado@syr.edu, Karin Ruhlandt. Department of Chemistry, Syracuse University, Syracuse, NY 13210, United States

Microporous materials in form of metal-organic frameworks (MOFs) have recently found use in areas as diverse as catalysis and gas storage for fuel cells. While a significant number of transition metal MOFs have been realized, inquiry into s-block metal MOFs remains largely unexplored, although several highly attractive applications, based on the unique properties of the metals are evident. We are especially intrigued by low weight of the metals, paired with a large affinity towards hydrogen under potential hydride formation, suggesting that the resulting MOF’s might be suitable hydrogen storage agents.

The lack of studies involving s-block metals may be a result of the absence of systematic pathways towards desired complexes. In this work, the impact of ligand topology and synthetic conditions on resulting framework dimensionality in two new magnesium based MOF’s containing the pyridinecarboxylic acid (Hin) and m-pyridinecarboxylic acid (Hnic) ligands have been explored. ([Mg(in)2]2·DMF)≈ (1) and [Mg4(in)8]≈ (2) were prepared by acid base reactions in vacuum sealed Carius tubes, using magnesium nitrate and acetic acid. The structural principles of the target compounds were explored via single crystal X-ray crystallography. It was found that both compounds show coordination through the nitrogen in the pyridil ring and carboxylate moiety yet their resulting structures differ depending on the location of the nitrogen in the ring. In 1, the structure propagates via nitrogen and carboxylate moieties forming a 3D network exhibiting thromboid shape cavities. These open cavities host disordered DMF molecules which can be replaced by polar solvents such as acetonitrile or THF by changing the reaction conditions. Contrary to 1, compound 2 displays intertwining chains to afford a dense 3D network without cavities. TGA experiments and temperature dependent PXRD were conducted to examine the temperatures of desolvation (of 1) and thermal stability, complemented by guest exchange experiments. An overview of this work will be presented.

INOR 756
From bisimidazole to N-alkylated bisimidazoles: The incremental ligand field increase leads to spin crossover in homoleptic Fe(II) complexes
Hoa V Phan, Jeremy J Hudrka, Michael Shatruk, shatruk@chem.fsu.edu. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States

Tris-homoleptic complexes of Fe(II) with bisimidazole (bim) are known to exist only in the paramagnetic high-spin (HS) state, which in general places bim in the range of weak-field ligands. We have recently demonstrated [1] that a combination of bim with a stronger tetradentate ligand, tris-(2-pyridyl)methylamine (tpma), affords a heteroleptic complex [Fe(tpma)(bim)](ClO4)2 that undergoes spin-crossover (SCO) between the HS and low-spin (LS) states. In the course of this study we also discovered SCO behavior for the analogous complex [Fe(tpma)(xbim)](ClO4)2 with N-alkylated ligand, 1,1'-(a.o.r'-oxy)-2,2-bimimidazole (xbim). Optical absorption studies also revealed that xbim was a slightly stronger ligand than bim. Now we report that the use of three xbim ligands results in the sufficient increase in the ligand-field strength to push the resulting tris-homoleptic complexes with Fe(II) into the SCO range. The complexes exhibit interesting crystal packing with important intermolecular interaction between the xbim ligands that should influence the abruptness of the spin transition.


INOR 757
Development of a new bispyrrolylpyridine pincer ligand that enforces unusual geometries at iron
Keith Searles1, ksearles@sas.upenn.edu, Skye Fortier2, Patrick J Carroll3, Chun-Hsing Chen2, Maren Pink1, Daniel J Mindiola3, Kenneth G Cautero. (1) Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States (2) Department of Chemistry and Molecular Structure Centre, University of Indiana, Bloomington, Indiana 47405, United States (3) Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968, United States

In our continued efforts of investigating the pyridylpyrrole ligand class, we have developed a new pincer-type ligand to prevent common demetallation pathways that have previously been observed in our chemistry. We have incorporated an additional pyrrole to the pyridylpyrrole moiety, yielding a tridentate bispyrrolylpyridine ligand that enforces a meridional coordination environment at the metal center. This talk will describe the synthesis of a particular bispyrrolylpyridine ligand and the unusual coordination environment observed in several monomeric and dimeric iron complexes. Additionally, investigation of chemical oxidations and reductions involving a divalent iron complex will be discussed.

INOR 758
Electronic structure and redox properties of bimetallic units with open coordination sites
Dino Villagran, dino@utep.edu. Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968, United States

The accessibility of bimetallic units with available and open coordination sites may provide useful inorganic platforms for small-molecule activation through multireactional cooperativity. We present the syntheses and structural characterization of several bimetallic units with open coordination sites with, M2 (where M = Cr, Mo, W, Rh, Ru, Au), bridged by bulky formamidinate and guanidinate ligands. We have explored their redox chemistry through electrochemical methods and through appropriate reducing and oxidizing agents. Some of these compounds show interesting electronic structures, such as the possibility for high bond orders (M = Cr, Mo, W), second-order Jahn-Teller distortions (M = Au), and interesting magnetic behavior (M = Ru). We finally show proof of principle results of multi-metallic cooperativity through their reactivity with alkyl reagents.

INOR 759
Second generation tris(2-pyridyl)borate ligands: toward supramolecular polymeric materials
So Yi Jeong, ssooyii@gmail.com, Chengzhong Cui, Patrick O. Shipman, Frieder Jaekle. Chemistry, Rutgers University-Newark, Newark, NJ 07102, United States

We have recently introduced tris(2-pyridyl)borates (Tpyb) as a new class of tridentate ligands.[1] These “scorpionate”-type ligands are promising because of their strong coordinating ability toward main group and transition metals, the chemical tunability, and the high stability in comparison to commonly used tris(2-pyrazolylborates). Based on these considerations, numerous applications in the fields of materials chemistry and catalysis are anticipated. We will focus on the development of a 2nd generation of tris(2-pyridyl)borates that contain additional functional groups X for further elaboration. Moreover, a bitopic derivative is presented that may serve as building block for functional metal-containing polymers. The synthesis, characterization and metal complexation behavior of this new class of ligands will be discussed.

INOR 760
Synthesis, characterization and investigation of low coordinate transition metal compounds and their magnetic properties

Aimee M. Bryan, aimeebryan@gmail.com, Philip P. Power. Department of Chemistry, University of California Davis, Davis, California 95616, United States

Low coordinate, paramagnetic transition metal complexes have been synthesized and characterized in order to study their bonding and magnetic behavior. A goal of this research is to synthesize novel compounds that have single molecule magnet (SMM) behavior and have reversal of magnetization barriers (\(U_{\text{eff}}\)) above \(kT\) (where \(T = 300 \, \text{K}\)). SMMs are a topic of intense research because of their potential applications in magnetic memory, high-density information storage and quantum computing technologies. A major theme of SMM research has been to design molecules that exhibit large negative axial zero field splitting \((D)\) which directly influences \(U_{\text{eff}}\). Currently, the various factors that determine \(D\) are not well understood but orbital angular momentum can be a primary contributor. Most recently, we have found unexpectedly large \(D\) values in the range of -60 to -80 cm\(^{-1}\) for three and four coordinate cobalt (II) complexes.

INOR 761
Polyoxometalate-supported polyion complex that mimics the mineralization in ferritin

Xikui Fang, xfang@ameslab.gov. Ames Laboratory, Ames, Iowa 50011, United States

Iron storage within the protein shell of ferritin is a venerable area of biorganic chemistry. The exact structural nature of the iron(III) oxide hydroxide core therein, however, is poorly defined. Here we present a polynuclear iron(III) complex supported by polyoxometalate ligands. These inorganic scaffolds inhibit nonspecific iron hydrolysis and prevent the formation of insoluble aggregates, a function similar to that of the ferritin protein shell. The complex also features a number of characteristics that closely resemble the ferritin core: (1) It is water-soluble. (2) It contains compact layers of iron(III) oxide hydroxides. (3) The iron core of the model complex includes unusual, 4-coordinate iron centers. The ferritin core itself, suggested by EXAFS data, is a 1/3-2/3 mix of tetrahedral and octahedral iron sites. (4) The core structure features bridging phosphate groups, which are also present in the natural systems.

INOR 762
Zwitterionic carb- and silyl anions: Synthesis, structure, reactivity and FLP chemistry

Clemens Krempner, clemens.krempner@ttu.edu. Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, United States

We have been developing the chemistry of zwitterionic carb- and germyl anions also referred to as zwitterionic metal tetrelides. These organometallic species represent a structurally novel class of rigid zwitterions, in which the cationic metal center is rigidly locked and charge-separated from the tri-coordinated tetrelide anion by internal polydonor bridges. In striking contrast to the well-documented family of tetra-coordinate borate-based zwitterions, our tri-coordinate tetrelide zwitterions have a stereochemically active electron pair localized at the central tetrelide anion, which is available for additional metal binding and allows for the convenient generation of hetero-bimetallic zwitterions. For example, reactions of the silylides and germanides with metal carbonyls, \(\text{M(CO)}_n\) give with loss of one molecule of CO stable hetero-bimetallic zwitterions. In the presence of Lewis acidic organoboranes, \(\text{BR}_3\), novel zwitterionic borates are formed.

Remarkably, our zwitterionic carbanions form frustrated Lewis pairs (FLP’s) with a variety of boranes ranging from \(\text{Mes}_2\text{BF}\) and \(\text{BPH}_3\) to weakly Lewis acidic alkyl boranes (\(\text{BR}_3\)) and alkyloborates, \(\text{B(OH)}_2\). Cleavage of dihydrogen with these novel FLP’s occurs readily to give alkali metal borate salts. The synthetic utility and reactivity of this novel class of FLP’s will be discussed.

INOR 763
Survey of the coordination chemistry of a new bis(pyridyl)selone

Lizeth Hernandez, lhernan4@uncc.edu, Daniel Rabinovich. Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States

The synthesis and coordination chemistry of a rare mixed-donor ligand featuring two pyridines and one N-heterocyclic selone, the bis(pyridyl)selone (2-py)_2se, will be described in this presentation. A series of group 12 metal complexes \{(2-py)_2se\}MX_3 (M = Zn, Cd, Hg; X = Cl, Br, I) and \{(2-py)_2se\}MX_2 (M = Cd, X = I; M = Hg, X = Cl, Br, I), has been prepared and fully characterized and their structures illustrate the different coordination modes and versatility of this N=Se donor ligand. In addition, a series of related complexes of copper(I), silver(I), indium(III), tin(IV), lead(II), antimony(III) and bismuth(III) have been synthesized and will be compared with the corresponding bis(pyridyl)thione analogues that we have previously isolated.

INOR 764
Heterobimetallic effects for enhanced α-olefin incorporation in ethylene polymerization catalysis

Massimiliano Delferro*, m-delferro@northwestern.edu, Shaofeng Liu†, Alessandro Motta‡, Aidan R. Mouat*, Tobin J. Marks*. (1) Chemistry, Northwestern University, Evanston, Illinois 60208, United States (2) Dipartimento di Scienze Chimiche, Università di Catania and INSTM, Catania, Italy

The synthesis and characterization of heterobimetallic \((\eta^5\text{-indenyl})\)\(\text{[Ti}_2\text{Me}_2\text{Si(BuN)TiCl}_3\text{][3-MeN-bis(2-ethylthio)ethyl]amine}[\text{CrCl}_3]\) \((\text{Ti-C2-Cr})\) and \((\eta^5\text{-indenyl})\)\(\text{[Ti}_2\text{Me}_2\text{Si(BuN)TiCl}_3\text{][3-MeH}_2\text{N-bis(2-ethylthio)ethyl]amine}[\text{CrCl}_3]\) \((\text{Ti-C2-Cr})\) are presented. In ethylene homopolymerization, both of \((\text{Ti-C0-Cr})\) and \((\text{Ti-C6-Cr})\) afford linear bis-low density polyethylene (LLDPE) using ethylene as the only feed, similar as the analogue \((\eta^5\text{-indenyl})\)\(\text{[Ti}_2\text{Me}_2\text{Si(BuN)TiCl}_3\text{][3-MeH}_2\text{N-bis(2-ethylthio)ethyl]amine}[\text{CrCl}_3]\) \((\text{Ti-C2-Cr})\). \((\text{Ti-C0-Cr})\) produces higher molecular weights and branching density polyethylene vs \((\text{Ti-C2-Cr})\) under identical conditions, while \((\text{Ti-C6-Cr})\) acts in a reverse manner. In the ethylene + 1-pentene competition experiments, \((\text{Ti-C0-Cr})\) incorporates \(n\)-propyl branches as low as 5.5% in total branches, while the numbers for \((\text{Ti-C2-Cr})\) and \((\text{Ti-C6-Cr})\) are 34.8% and 55.1%, respectively. With \(\text{Bu}_3\text{Al/Ph}_2\text{CB(C}_6\text{H}_5\text{F})_3\) as the activator/cocatalyst, linear polyethylene without branches detectable was yielded for all three catalysts.
When polar solvent COCl₂ is used as the polymerization medium, higher activity and lower product branching densities are observed. Both homopolymerization and copolymerization results argue that achievable Ti:Cr spatial proximity significantly influences chain transfer rates and selectivity for comonomer enchainment and that such proximity effects are highly cocrystal and solvent sensitive.

INOR 765

Development of thermally stable nickel(II) α-diimine catalysts for ethylene polymerization

Jennifer L. Rhinehart, rthinehart.jenn@gmail.com, Lauren A. Brown, Nolan Mitchell, Brian K. Long. Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States

Nickel-based olefin polymerization catalysts bearing α-diimine ligands offer the ability to produce high molecular weight polyethylene, to incorporate polar co-monomers, and to produce multiple polymer topologies. These benefits quickly disappear at elevated reaction temperatures (70-110 °C) as most group 10 α-diimine catalysts rapidly decompose at these temperatures. To avoid this shortcoming, sterically demanding α-diimine ligands derived from 2.6-bis(diphenylmethyl)-4-methyl aniline were used and evaluated at temperatures up to 100 °C. These catalysts were found to have remarkable thermal stability up to 90 °C, which was supported by constant turnover frequencies and steady productivity over 20 minutes, ultimately reaching molecular weights above 500,000 g/mol.

INOR 766

(\(\text{CH}_3\))\(_3\text{M}(-\text{L}^1)^{-}\cdot(\text{OCH}_3)\text{M(\text{CH}_3)}_2\): Synthesis and function as MAO mimic complexes in syndiotactic styrene polymerization (M = Al, Ga; \(\text{L}^1 = 3,5\)-di(2-pyridyl)-1,2,4-triazole; \(\text{L}^2 = 3,5\)-di(2-pyridyl)pyrazole)

Issam Kobrsi, i.kobrsi@pi.ac.ae. Department of Chemistry, The Petroleum Institute, Abu Dhabi, United Arab Emirates

The reaction of \(\text{L}^1\) with excess Al(CH\(_3\))\(_3\) and excess Ga(CH\(_3\))\(_3\) afforded Al(CH\(_3\))\(_2\)(\(\text{L}^1\))·3Al(CH\(_3\))\(_3\) (1) and Ga(CH\(_3\))\(_2\)(\(\text{L}^1\))·Ga(CH\(_3\))\(_3\) (2) respectively. (1) and (2) have been fully characterized structurally and spectroscopically, are extremely air sensitive and readily react with O\(_2\) to produce the analogous dimeric complexes (\(\text{CH}_3\))\(_2\)M(\(\mu\)-(\(\text{L}^1\))·(\(\mu\)-OCH\(_3\))·M(\(\text{CH}_3\))\(_2\)), where M = Al (3) and Ga (4). The reaction of \(\text{L}^2\) with excess Al(CH\(_3\))\(_3\) and then exposure to O\(_2\) afforded (\(\text{CH}_3\))\(_2\)Al(\(\mu\)-(\(\text{L}^2\))·(\(\mu\)-OCH\(_3\))·Al(\(\text{CH}_3\))\(_3\)) (5). 3, 4 and 5 are unusually air stable for tetrahedral group 13 complexes with non-bulky alkyl groups. They have the Al and Ga in a 4-coordinate environment and the O in a 3-coordinate environment, which is analogous to the theoretically predicted structure of methylalumoxane (MAO). For this reason, 3 and 5 can be thought of as well-defined MAO mimics. Both 3 and 5 were successful as cocatalysts with Cp\(_2\)TiCl\(_2\) in the polymerization of styrene when used in 1:1 to 5:1 ratios of 3 or 5 to Cp\(_2\)TiCl\(_2\). However, the yields of the polymerizations were low and elevated temperatures were required for the reactions to begin.

INOR 767

Bis(imino)pyridine iron bis(alkoxide) catalysts for redox-controlled polymerization of cyclic esters

Ashley B. Biernesser, ashleyb@bc.edu, Jeffery A. Byers. Department of Chemistry, Boston College, Chestnut Hill, MA 02467, United States

The synthesis of bis(imino)pyridine iron bis(alkoxide) complexes is reported. Preformed iron(II) alkoxides and iron(II) alkoxide complexes for the polymerization of (rac)-lactide. Catalysts containing more electron rich alkoxides resulted in faster polymerization rates. The reaction displayed characteristics of a living polymerization including low molecular weight distributions, a linear relationship between molecular weight and conversion, and polymer growth observed for up to fifteen sequential additions of lactide monomer to the polymerization reaction. Mechanistic experiments revealed that the number of propagating polymer chains depended on the identity of the initiating alkoxide: aliphatic alkoxides resulted in two propagating polymer chains while aromatic alkoxides resulted in one propagating polymer chain. Unlike the iron(II) catalyst precursors, a catonic iron(III) bis-alkoxide complex was completely inactive towards lactide polymerization. However, catalysis could be switched off and turned back on during lactide polymerization upon oxidation and reduction of the iron catalyst, respectively. Application of this catalyst system for the controlled polymerization and copolymerization of (rac)-lactide with other monomers will be discussed.

INOR 768

Electronic design principles of metal-organic frameworks for photocatalysis, gas-storage and light harvesting

Christopher H. Hendon, c.hendon@bath.ac.uk, Aron Walsh. Department of Chemistry, University of Bath, Bath, Somerset BA2 7AY, United Kingdom

Metal-organic frameworks (MOFs) have gained popularity for their diverse applications, notably as candidates for gas-storage, photocatalysts and as light harvesters.[1,2] The current status of MOF design is focused on creating large surface area materials for gas-storage, however no frameworks have been proven to have the absorption capacity, chemical stability and simplicity of synthesis to be viable replacements for pressurised gas. There have been marginally better results for MOFs as catalysts, with many examples of organic reactions being performed inside the pore, or on the framework itself. Since catalytic function is determined by the electronic structure we modify these through intelligent design of both the organic and inorganic motifs.[3]
Using two prototype frameworks, MIL-125 and UiO-67, we focus on the electronic factors that influence their photocatalytic applications. MIL-125, a TiO$_2$ based framework, has catalytic capabilities controlled by organic modifications; the valence band of MIL-125-NH$_2$, shown, left.[4] UIO-67 is unusual as its inorganic subunit, ZrO$_2$, is insulating thus acting as only a structural motif and does not contribute to frontier electronic states. This provides scope for intra-MOF catalysis through heterometal-coordination to bipyridine-modified UIO-67 ligands. A truncated section of UIO-67 functionalised with bipyridine is shown, right. As a result, we provide methods for both organic and inorganic electronic manipulation emphasise the importance understanding the electronic structure for application based MOF design.


INOR 769
Selective reactions of chlorosilanes: Applications in degradable and dendritic materials
Abyy R Jennings, aroth@smu.edu, David Y Son.Department of Chemistry, Southern Methodist University, Dallas, TX 75275, United States
A library of multi-functional silyl-thiols was synthesized through the selective reaction of various chlorosilanes and mercaptoethanols. Degradable cross-linked networks were prepared via the thiol-ene reaction between the multi-functional thiols and various –ene containing compounds. Degradation studies were performed under physiological conditions and the degradation products were analyzed using $^1$H NMR and GC-MS spectroscopies. Furthermore, a number of dendritic precursors were synthesized via the selective thiol-ene reaction of various vinylchlorosilanes and mercaptoethanols.

INOR 770
Copolymerization of CO$_2$ and dihydronaphthalene oxide with Cr(III) and Co(III) catalysts
Samuel J Kyran, sam.kyran@tamu.edu, Donald J Darensbourg.Department of Chemistry, Texas A&M University, College Station, TEXAS 77843, United States
Poly carbonates derived from CO$_2$ and epoxides such as poly(propylene carbonate) and poly(cyclohexene carbonate) are well-studied in literature and have been commercialized in recent years. A cheap, non-toxic and renewable resource, utilization of CO$_2$ as a monomer provides a sustainable chemistry for the production of polymeric materials. Our group newly reported the synthesis of poly(indene carbonate) having a glass-transition temperature ($T_g$) of 138 °C, the highest observed so far for polycarbonates obtained via CO$_2$ and epoxide coupling. We are currently investigating epoxide monomers with bulkier backbones that might further increase $T_g$ in addition to showing better selectivity towards polymer formation with the right catalysts. This presentation will cover our current efforts in copolymerizing CO$_2$ with naphthalene derived epoxide (see figure). Polymer selectivity versus cyclic carbonate formation will be discussed with regards to employing binary (salen)M(III)X/cocatalyst and newer asymmetric bifunctional M(III) catalysts, where M = Cr, Co.


INOR 771
Copolymerization of cyclopentene oxide with CO$_2$ utilizing bifunctional cobalt(III)- and chromium(III)-salen catalysts
Wan-Chun Chung, wan-chun.chung@chem.tamu.edu, Donald J. Darensbourg.Department of Chemistry, Texas A&M University, College Station, Texas 77840, United States
Copolymerization of epoxides and CO\textsubscript{2} represents a green pathway for the production of polycarbonates utilizing a renewable, abundant and non-toxic resource. Poly(cyclopentene carbonate) is one such polycarbonate. Upon degradation, it reverts to its comonomers (CO\textsubscript{2} and cyclopentene oxide), whereas degradation of other polycarbonates gives cyclic carbonates that are unable to be repolymerized.\textsuperscript{1,2}

This special property makes poly(cyclopentene carbonate) an attractive polymer due to its ease of recyclability. However, this polymer is not accessible using conventional salen chromium catalyst/cocatalyst systems; cyclic cyclopentene carbonate is the only product.

Bifunctional salen metal complexes bearing tethered cocatalyst have been reported to have high activity and polymer selectivity in catalyzing epoxide/CO\textsubscript{2} coupling. Unlike the binary system, bifunctional salen cobalt and chromium catalysts are able to yield poly(cyclopentene carbonate). In this presentation, the investigation of epoxide/CO\textsubscript{2} coupling catalyzed by salen metal complexes will be discussed.\textsuperscript{3}

References

(2) Darensbourg, D. J.; Wei, S.-H.; Yeung, A. D.; Ellis, W. C. Macromolecules 2013, 46, 5850.

INOR 772
Synthesis, characterization, and photophysical studies of exceptionally stable phosphorescence polymeric microspheres with Pt(II) complexes for biomedical applications

Prabhat K Upadhyay\textsuperscript{1}, upadhyay.u@gmail.com, Sreekar Marpu\textsuperscript{2}, Mohammad Omary\textsuperscript{1}. (1) Department of Chemistry, University of North Texas, Denton, Texas 76201, United States (2) Intelligent Optics Systems, Los Angeles, California 90505, United States

Pt(II) complexes with square planar geometry can be water soluble and emissive at room temperature. Metal-metal intramolecular or intermolecular interactions often influence the emission properties. The emission of some Pt(II) complexes is very sensitive to oxygen in aqueous solutions, which can be utilized for the sensing of oxygen (O\textsubscript{2}) in biological systems to probe hypoxic conditions during cancer growth and other abnormalities. The presence of oxygen drastically quenches the emission of a representative complex we investigated. In our research group, we are utilizing such complexes for the bio-imaging of worm and fish models under various degrees of hypoxic conditions. Stability in aqueous water, however, is rather limited and the representative complex starts decomposition within a day at room temperature. To overcome this stability problem in aqueous systems at room temperature, we have incorporated the Pt(II) complex into the polymer matrix of polyacrylonitrile (PAN) in order to increase its long-term stability. Incorporation of the Pt(II) complex within PAN leads to the formation of phosphorescent microspheres with diameter in the 0.1-1 micron regime according to dynamic light scattering and fluorescence microscopy. Presence of this polymer exceptionally enhanced the stability of the Pt(II) complex in aqueous suspension at room temperature without compromising the photophysical properties in terms of band energy. All compositions and sample variations examined were exceptionally stable at room temperature for more than 2 years. These polymeric microspheres have significantly enhanced the luminescence intensity, lifetime, and quantum yields compared to the native Pt(II) complex in water, which was limited to minutes spectroscopically and hours visually in the absence of polymers. The resulting hybrid polymeric/molecular phosphorescent microspheres exhibit lower oxygen sensitivity and enhanced thermal stability vs. the dissociated components. The phosphorescent microspheres' particles size can be tuned with temperature and relative or absolute concentration of the two components. The so formed phosphorescent microspheres are promising candidates for both biological and environmental applications including protein labeling, bio-imaging and sensing applications.

INOR 773
Making and breaking bonds using new group 5 metal catalysts

John Arnold, arnold@berkeley.edu, Thomas L Gianetti, Robert G Bergman.Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

This presentation will focus on the reactivity of new group 5 complexes incorporating 'nacnac' supporting ligands. We will summarize our recent work with these species, targeting both stoichiometric and catalytic reactivity towards small molecules and C-F bonds.

INOR 774
Unusual structures in metal complexes with heavy group 14 atoms

Odile Eisenstein, odile.eisenstein@univ-montp2.fr, Christophe Raynaud.Institut Charles Gerhardt, CNRS and Université Montpellier 2, Montpellier, Languedoc Roussillon F-34095, France
The structures of organometallic complexes are overall well understood. However changing an organic ligand bonded by a carbon to a metal by a heavier atom of the same group induces some remarkable structural changes. Several factors contribute to the change such as i) the decreased electronegativity of the heavier Group 14 element which can induce electron redistribution notably at the metal center, ii) the ability of go hypervalent, iii) the ability to go to a lower valence. Selected examples will be presented relating when possible structures and reactivity.

INOR 775

Transition metal catalyzed activation of the SiH bond: New insights into the dual SiH effect
Keith H Pannell, kpannell@utep.edu. Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968-0513, United States

Despite the fact that the hydroboration reaction has been known for decades, this widely used synthetic tool still throws up interesting challenges and opportunities. Our use of Karstedt’s catalyst to study of the reduction of DMF (Me₂NCHO) by the popular “dual SiH” containing tetramethyldisiloxane, HMMe₂SiOSiMe₃H, has revealed that the first step in the process involves a single initial hydroboration to form HMMe₂SiOSiMe₃OCH₃NMe₂. This intermediate is readily isolated and purified via distillation at 50°C/15mm Hg. In the presence of a series of transition metal catalysts, including Karstedt’s, this material readily transforms to trimethylamine, Me₃N, and a transient material that we propose is (Me₂SiO)₂, D₂, that itself transforms to (Me₂SiO)n, n = 4, D₄, and n = 6, D₆. The result demonstrates that the “dual SiH” effect may come about by virtue of the facile intramolecular elimination of the amine Me₃N from 1, indicating that a single molecule of 1 effectively reduces the amide rather than 2 for the monosilanes. Despite this reactivity 2 can also be used to perform the expected metal-catalysed hydroboration chemistry of the SiH group as well as reactions of the SiOCH₃NMe₂ functionality involving siloxane chain extension.

INOR 776

Magnesium(II)-catalyzed hydroboration of carbonyl compounds
Aaron D Sadow, sadow@iastate.edu. Department of Chemistry, Iowa State University, Ames, IA 50011, United States

To⁴MgMe (To⁴ = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) is a precatalyst for addition reactions of pinacolborane (HBpin) and esters (RCO₂R') resulting in C-O cleavage to give RCH₂OBpin and ROBpin. A number of functional groups are compatible with the catalyst system, including nitro, nitrile, halide, and thiophene. However, aldehydes and ketones are readily hydroborated under the catalytic conditions. The rate law for ester hydroboration, measured for ethyl acetate and isobutyli isobutyrate as -d[ester]/dt = k[To⁴MgMe][ester] 2, rules out both ester/catalyst interactions (i.e. insertion) and HBpin/catalyst reactions (σ-bond metathesis) as the turnover-limiting steps in the catalytic cycle. Interestingly, the rate law for To⁴Mg-catalyzed addition of isobutyraldehyde and HBpin reveals that neither insertion nor σ-bond metathesis are rate-limiting. Instead, the turnover-limiting step is unimolecular and involves conversion of a species containing all three reactive components, namely To⁴MgX, RCHO, and HBpin. This turnover-limiting step characterizes both aldehyde and ester hydroboration reactions.

INOR 777

Synthesis, bonding and reactivity of uranium (IV-VI) imido complexes
James M. Boncella1, boncella@lanl.gov, Neil C. Tomson1, Robert E. Jilek1, Ryan S. Shook1, Brian L. Scott1, Enrique R. Batista2. (1) Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States (2) Theory Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States

We have discovered convenient synthetic procedures for the preparation of mononuclear imido complexes of uranium (IV, V and VI). These compounds have allowed us to explore and compare the reaction chemistry and bonding in uranium complexes that have the same or very similar ligand sets in three different oxidation states. The redox chemistry of these compounds will be discussed as will the reactivity of the imido groups with electrophiles. Changes in the reactivity of the imido groups as a function of oxidation state correlate with changes in the calculated U-N orbital interactions that make up the uranium-nitrogen multiple bonds in these compounds. The relationship between the observed reactivity and the evolving view of covalency in U-L bonding will be discussed.

INOR 778

Early transition metals in hydroaminoalkylation: Catalytic C-C bond formation via C-H activation
Laurel L Schafer, schafer@chem.ubc.ca. Department of Chemistry, The University of British Columbia, Vancouver, BC V6T 1Z1, Canada

Hydroaminoalkylation is a 100% atom-economic C-C bond forming reaction using simple unprotected amines and alkenes as starting materials while avoiding the use of stoichiometric reagents. This reaction affords selectively substituted secondary amines with excellent regioselectivity, diastereoselectivity and even enantioselectivity. Most importantly this transformation takes advantage of the high reactivity, low cost and low toxicity of early transition metals. Recent developments in this C-H functionalization reaction include the direct synthesis of α-substituted heterocycles, the development of new phosphoramidate ligated complexes for room temperature reactivity and achieving intramolecular variants of this transformation. Mechanistic insights that guide efforts to develop robust, easy to use early transition metal complexes for application in organic synthesis will be discussed.

INOR 779

Microwave assisted synthesis of unusual noble metal nanocatalysts
Simon M. Humphrey, smh@cm.utexas.edu, Stepanhny Garcia, Graham W. Piburn, Pranaw Kunal, Graeme A. Henkelman, Liang Zhang. Department of Chemistry, The University of Texas at Austin, Austin, TX 78712-1224, United States
Microwave heating allows for the preparation of noble metal nanoparticles, in which catalytically important properties (size, surface structure, surface chemistry) are significantly enhanced versus conventionally-prepared nanoparticles. Programmable injection of molecular precursors under microwave irradiation also allows for the easy and rapid formation of alloy nanoparticles using classically ‘immiscible’ metals. These include RhAg and RhAu nanoparticles, which show dramatic catalytic enhancement in hydrogenation chemistry versus pure Rh nanoparticles. Theoretical calculations support the observed enhancement in reactivity of the alloys, and indicate that few-atom ensembles play an important role in H-binding energies on the nanoparticle surfaces.

INOR 780

Don, Cp"Yb(bipy), and 547 Latimer Hall

Richard A. Andersen, raandersen@lbl.gov. Department of Chemistry, University of California, Berkeley, California 94720, United States

Don prepared Cp"Yb(bipy) sometime in his first or second-year as a graduate student at Berkeley in 1978 or 1979, but the compound did not see the light of print until some 23 years later (Schultz, Boncella, Berg, Tilley, and Andersen, Organometallics, 2002, 21, 460). A model for the electronic structure of its ground state as a multiconfigurational, closed-shell singlet, in which the ytterbium is intermediate valent, took 7 more years to unravel (J. Am. Chem. Soc., 2009, 131, 6480 and 2010, 132, 17537). This presentation will describe the evolution of the electronic structure by successive students working in room 547 Latimer Hall and how an understanding of the electronic ground state of the general class of ytterbocene adducts with heterocyclic-nitrogen bases leads to new reactivity patterns.

INOR 781

Reactivity of a diphosphine with persistent phosphinyl character in solution and advances in carbene-stabilized group 14, 15, and 16 systems

Jason D. Masuda, jason.masuda@smu.ca. Department of Chemistry and the Atlantic Centre for Green Chemistry, Saint Mary’s University, Halifax, Nova Scotia B3H 3C3, Canada

The first part of the presentation will discuss the work of my research group on the preparation and reactivity of a diphosphine/phosphinyl-based system with a variety of elements, small molecules and functional groups.

The second part will discuss our recent advances in the reactivity of singlet carbenes with group 14, 15 and 16-based molecules that lead to a number of unique molecules including a new S\(_2\)N\(_2\)-carbene adduct, as well as an introduction to new radical-containing systems.

INOR 782

Diversifying the coordination chemistry of p-block acceptor elements

Neil Burford, nburford@uvic.ca. Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada

We have recently demonstrated that homotopic coordination chemistry offers a versatile approach to P-P bond formation, and a variety of synthetic methods are now available, allowing for the systematic development of catena-phosphinophosphonium cationic frameworks. Extrapolation of coordination chemistry to bonds between other p-Block elements provides approaches for general non-metal element-element bond formation. More importantly, in the context of the coordination chemistry of the transition metals, a potentially diverse and extensive coordination chemistry for non-metal element acceptors can be envisaged, as illustrated (L = neutral ligand, X = halogen) for the tetrals (E = Si, Ge, Sn) and the pnictogens (Pn = P, As, Sb, Bi). The synthesis, structure and bonding for new complexes involving non-metal acceptors with nitrogen or phosphorus centered ligands will be described.


INOR 783

Stable radicals of the heavy group 14 elements: From phantom species to isolable compounds and their application

Akira Sekiguchi, sekiguch@chem.tsukuba.ac.jp. Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Being considered just a few decades ago only as fleeting reactive intermediates, silyl, germyl and stannyl radicals, cations and anions now constitute an important class of real, observable and in many cases isolable and fully characterizable compounds. In this symposium, the chemistry of stable free radicals on the heavier group 14 elements (Si, Ge, Sn) will be focused; the first one concerns the chemistry of the stable neutral radical species of cyclic and acyclic radicals, the second one is devoted to the charged radical species, the third one is chemistry of the heavy group 14 centered biradicals with singlet and triplet states. The electronic and crystal structural features of these radicals and ion radicals, both in the solid state and in solution, are compared with each other. The most important parameters affecting the stability, geometry and electronic configuration of the radicals are discussed. The interconversion between the heavy cations–radicals–anions is very important for the development of material science.

INOR 784

Phosphine-stabilized Si(II) complexes

Antoine BACEIREDO, antoine.baceiredo@chimie.ups-tlse.fr. LHFA, Université de Toulouse, Toulouse, France

Antoine BACEIREDO

Université de Toulouse, Laboratoire Hétérochimie Fondamentale et Appliquée

Antoine.baceiredo@chimie.ups-tlse.fr

http://hfa.ups-tlse.fr

Recently we have developed an efficient method for the preparation of phosphine-stabilized Si(II) complexes, which present an enhanced silylenoid character. In particular they react reversibly with unactivated alkenes in a [2+1] cycloaddition process. In the case of Si(II) hydride derivative 1, the oxidative addition of diphenylacetylene led to the quantitative formation of the corresponding silirene 2, which rearranges into the first sila-cyclopropylidene 3 via an unprecedented Si(IV)→Si(II) rearrangement in very mild conditions.
Silica-cyclopropylidene 3 reacts, in mild conditions, with small molecules like N_2O, and O_2 to generate the corresponding donor stabilized silacyclopropanone and sila-b-lactone, respectively. In addition, 3 is an excellent ligand for transition metals.

References:

INOR 785
Stabilization of small fragments with NHC and CAAC ligands
Gernot Frenking, frenking@chemie.uni-marburg.de.Fachbereich Chemie, Philipps-Universität, Marburg, Germany
The lecture reports about quantum chemical calculations of small electronically unsaturated fragments which are stabilized by the donor ligands NHC (N-heterocyclic carbene) and CAAC (cyclic alkyl amino carbene).

INOR 786
Reactivity of carbene-stabilized diatomics
Gregory H. Robinson, robinson@uga.edu. Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556, United States
This laboratory has been interested in the main group chemistry of N-Heterocyclic carbene (L) for some time. While our early efforts largely concerned the synthesis of carbene-stabilized main group diatomics such as L:Si=Si:L, L:P-P:L, and L:As-As:L, recent studies have concentrated on the reactivity of these molecules. This presentation will concern our recent efforts on the synthesis and molecular structure of novel molecules resulting from these studies.

INOR 787
Developing quantum dot solids for thin-film photovoltaics
Matt Law, lawm@uci.edu. Chemistry, University of California, Irvine, Irvine, CA 92697, United States
Colloidal semiconductor quantum dots (QDs) are attractive building blocks for solar photovoltaics (PV). In this talk, I will provide an overview of our ongoing efforts to design lead salt QD thin film absorbers for next-generation PV. Basic requirements for QD absorber layers include efficient light absorption, charge separation, charge transport, and long-term stability. I will first discuss several methods used to make conductive QD films by solution deposition and ligand exchange. Studies of carrier mobility as a function of basic film parameters such as inter-QD spacing, QD size, and QD size distribution have led to a better understanding of charge transport within highly disordered QD films. Efforts to improve carrier mobility by enhancing inter-dot electronic coupling, passivating surface states, and implementing rudimentary doping will be highlighted. Engineering the inter-QD matrix to produce QD/inorganic or QD/organic nanocomposites is introduced as a promising way to optimize coupling, remove surface states, and achieve long-term environmental stability for high-performance, robust QD films. To obtain large photocurrent from QD solar cells, it is critical to increase the minority carrier diffusion length to rival the optical absorption length, possibly by harnessing band-like transport through extended electronic states. The relative roles of superlattice order, energy disorder, and surface states in this regard will be summarized. New results from in situ spectroscopic studies of QD field-effect transistors will be discussed.

INOR 788
Electronic and phonon transports in bulk quantum dots engineered semiconductors
Pierre Ferdinand Poudou Poudou, ppoudoup@umich.edu. Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States
One of the major roadblocks to large improvements in the thermoelectric figures of merit (ZT) of leading candidate thermoelectric materials such as the Bi_xTe_y, PbTe, CoSb_2, and half-Heusler (HH) based systems remains the difficulty in making meaningful simultaneous improvements in both the electrical conductivity (σ) and thermopower (S) of these materials through doping and/or substitutional chemistry. In conventional semiconductors, both materials parameters (S and σ) are fundamentally coupled adversely through the concentration, n, of charge carriers. Therefore, the maximization of one parameter by tuning the carrier concentration (n) via doping and/or substitutional chemistry inevitably results in the minimization of the other. Recently, we show that by coherently embedding sub-ten nanometer scale inclusions within a semiconducting half-Heusler matrix, large enhancements of the thermopower (S) and the mobility (μ) can be achieved simultaneously in both n-type and p-type nanocomposites. The enhancement in thermopower originates from large reductions in the effective carrier density (n) coupled presumably with an increase in the carrier effective mass (m^*_e). The surprising enhancement in the mobility is attributed to an increase in the mean-free time (τ) between scattering events (phonon-electron scattering, ionized-impurity scattering and electron – electron scattering). Using X-ray powder diffraction, electron microscopy, and electronic transports data, we will discussed the mechanism of phase formation and transformation, at the sub-nanometer scale, in bulk half-Heusler (HH) matrix and the mechanism by which the embedded nanostructures regulate electronic charge transport within the semiconducting HH matrix to achieve unprecedented combinations of physical properties such as, large enhancements in the carrier mobility (μ), thermopower (S) and electrical conductivity (σ) simultaneously with drastic decrease in thermal conductivity (κ) at high temperatures.

INOR 789
Microwave assisted synthesis of Ge nanoparticles and their application in quantum dot TiO_2/Ge heterojunction solar cells
INOR 790
Fiat colloidal semiconductor nanocrystals
Yuanyuan Wang, Paul J. Morrison, Linjia Mu, Yang Zhou, William E. Buhro, buhro@wustl.edu. Department of Chemistry, Washington University, St. Louis, MO 63130, United States
Pseudo-1D nanocrystals such as quantum wires (QWs) and quantum belts (QBs, nanoribbons) are in principle capable of transporting energy (excitons) and charge over long distances, and thus may have applications in solar-energy conversion and other technologies. However, excitons and charge carriers in QWs and QBs sample extremely large surface areas and thus have a high probability of encountering surface trap sites, precluding efficient transport. Surprisingly, the optical properties of QBs and quantum platelets (QPs) are quite good, despite their large surface areas, which is indicative of excellent passivation and low defect densities on their broad surfaces. Thus, excitons are efficiently delocalized over the entire dimensions of the nanocrystals, and the photoluminescence efficiencies are as high as 40%, rivaling those of quantum rods. The synthesis and properties of CdSe, PbS, and CulnS2 QBs and QPs will be discussed.

INOR 791
Substituted thioureas: A tunable precursor library for colloidal nanocrystal synthesis
Jonathan S Owen, jso2115@columbia.edu, Mark P Hendrickx. Department of Chemistry, Columbia University, New York, New York 10027, United States
Thioureas with organic substituents are conveniently prepared in a single step from commercially available amines and organosulfenylcyanate or thio phosphogene derivatives. Reaction of these thioureas with metal surfactant complexes produces metal sulfide nanocrystals in quantitative yields. Their conversion rate is readily tuned by adjusting the organic substituents, allowing this family of precursors to be useful for nanocrystal synthesis over a range of more than 100 °C in reaction temperature. Fine control over the conversion rate allows a desired nanocrystal size to be prepared in quantitative yield at a single temperature. The relationship between the precursor conversion rate and crystal nucleation as well as size distribution focusing will be described.

INOR 792
Molecular control of nanoscale composition, morphology and function: From compositionally graded nanorods to surface doped quantum dots
Javier Vela, vela@iastate.edu. Chemistry, Iowa State University, Ames, Iowa 50010, United States
Part I. The exact composition, size and morphology of semiconductor nanocrystals precisely determine their opto-electronic properties (band gap, exciton lifetime and decay pathways, carrier mobility). While researching the synthesis of binary CdE nanocrystals and ternary CdE′ alloys (E, E′ = S, Se), we found that the relative ease of formation of different nanocrystalline phases is a direct consequence of the reactivity of their molecular precursors. Using a series of closely related molecular precursors, we are building a working scale of chemical reactivities for chalcogenide, pnictide and cationic precursors. This could obviate the need for time-consuming testing of several different reaction conditions or unrelated precursors as is currently practiced in the field of solution phase nanocrystal synthesis.

Part II. Controlling the degree of functionalization or valence per nanocrystal remains an unsolved challenge in colloidal semiconductors. Surface modification is routinely performed by exchanging the nanocrystal’s native ligands with excess carboxylate- or amine-terminated thiols. This ligand exchange approach fails to control the extent of surface modification. We are investigating fundamentally new surface ligand doping strategies that enable to control the degree of functionalization or valence per nanocrystal while retaining its original colloidal and photo stability. As part of this goal we also investigate changes in ligand organization, surface chemistry and nanocrystal properties that result from surface modification. The extent of surface coverage by a particular functional group has a large impact on a nanocrystal’s surface affinity and permeability, and thus on its ability to localize, penetrate, and be transported across specific biological tissues, cellular and subcellular structures.

INOR 793
Hybrid small molecules using lipoic acid as antioxidant chelators designed to target amyloid and the molecular features associated with neurodegenerative diseases
Kayla N Green, kayla.green@tcu.edu, Paulina M Gonzalez, Kimberly M Lincoln, Giridhar Akkaraju. Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, United States
Alzheimer's disease (AD) is the most common form of dementia affecting over 5 million people in the United States, and this number is expected to double by the year 2050. Neither the exact cause nor a cure for AD have yet to be found despite years of interdisciplinary research. One common feature of AD is the production of oxidative stress due in part to buildup of amyloid (Aβ) plaques in the brain of patients. This is known to lead to death of neurons and loss of cognitive function. Mounting evidence links metal ion dyshomoeostasis and miscompartmentalization with subsequent deposition of Aβ and concomitant free radical generation as one source of this stress which causes neuronal death although others exist as well. When redox active metal ions bind to amyloid, Fenton chemistry cascades to produce a plethora of reactive oxygen species (ROS) known to cause lipid, DNA, and protein oxidation, impaired synaptic and axonal communication, neuronal death, and mitochondrial dysfunction. This body of work has established the role of metal ions as a component of the amyloid cascade hypothesis to form the “metal hypothesis of Alzheimer's disease,” which notes that the interactions of Aβ and metal ions, along with atypical metal ion homeostasis, are coupled with the neuropathogenesis of AD. Our group has developed new molecules composed of N-heterocyclic amines that are designed to bind the metal-ions associated with AD as well as engender antioxidant capacity. Our work will show that these novel ligand systems have low toxicity in multiple cell lines and provide protection against both amyloid and metal-induced assaults in neuronal cell culture. Moreover we will focus on the interaction of the molecules with amyloid peptide provided by fluoroscence and 15N-SOFAST NMR Spectroscopy.

INOR 794
Ruthenium(II) polypyridyl complexes synthesis and studies of DNA binding, photocleavage, cytotoxicity activity
Yata Praveen Kumar, naninizam@gmail.com, Sirasani Satyanarayana.DEPARTMENT OF CHEMISTRY, OSMANIA UNIVERSITY, HYDERABAD, ANDHRA PRADESH 500007, India

In this study three new Ru(II) poly(pyridyl) complexes, [Ru(phen)2(dpphz)]2+ (1) [dpdphz dipyrdo[3,2-a:2',3'-c] phenazine-11-hydrazide, phen = 1,10-phenanthroline], [Ru(bpy)2(dpphz)]2+ (2) [bpy = 2,2'-bipyridine] and [Ru(dmb)2(dphe)]2+ (3) [dmb = 4,4'-dimethyl2,2'-bipyridine] have been synthesized and characterized. Their DNA binding behavior has been explored by various spectroscopic titrations, viscosity measurements, which indicated that all the complexes could bind to CT-DNA by means of intercalation with different binding strengths. The light switch properties of these complexes have been evaluated. The antimicrobial activities of these three complexes have been investigated. For these complexes Photo induced DNA cleavage studies have been done. All the complexes exhibited efficient photocleavage of pBR322 DNA upon irradiation. The cytotoxicity of these complexes has been evaluated by MTT assay with HeLa tumor cell lines.

INOR 795
Extending the utility of platinum-based anticancer agents using nanodelivery

Timothy C. Johnston, timothyj@mit.edu, Stephen J. Lippard.Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Nanodelivery provides a means to access the therapeutic range of platinum-based anticancer agents. We describe recent efforts to understand factors that govern encapsulation of platinum complexes within polymeric nanoparticles comprising poly(lactic-co-glycolic acid)-block-poly(ethylene glycol) (PLGA-PEG). Included is an investigation of the effect of ligand lipophilicity on the encapsulation efficiency of hydrophobic Pt(IV) produgs, formed by oxidative addition of two additional ligands to a Pt(II) precursor such as cisplatin, cis-[Pt(NH3)2Cl2]. The latter is then regenerated in cells by reducing agents such as glutathione. A PLGA-PEG nanoparticle construct was also developed to encapsulate the hydrophilic produg mitaplatin, c.c.t: [Pt(NH3)2Cl2(O2CCHCl)2]. The effects of encapsulation were investigated and included monitoring its influence on the growth of murine xenograft tumors derived from human triple-negative breast cancer cells. Finally, we describe a nanoparticle construct designed to encapsulate the potent monofunctional Pt(II) complex phenanthriplatin, cis-[Pt(NH3)2(P)(Cl)]2+, where P is phenanthridine. Treatment of tumor-bearing mice with the unencapsulated compound had no effect on tumor growth, in strong contrast to the potent anticancer activity observed in tissue culture assays. Nanoparticle encapsulation restored the activity of the complex in vivo. This work was supported by a grant from the National Cancer Institute.

INOR 796
Reactivity of kiteplatin with biothiols and nucleic acids

Emanuele Petruzzella1, epetruzz@emich.edu, Nicola Margiotta2, Giovanni Natili3, James D Hoeschele3. (1) Department of Chemistry, Eastern Michigan University, Ypsilanti, Michigan 48197, United States (2) Department of Chemistry, Università degli Studi di Bari, Bari, Bari 70125, Italy

Kiteplatin, [PtCl2(cis-1,4-DACH)], where DACH = diaminocyclohexane, is a potential new platinum-based anticancer drug. It was found to be active against cisplatin- and oxaliplatin-resistant tumor cell lines.1[1]

The resistance to platinum antitumor drugs is multifactorial and can be caused by modifications of the uptake and/or the efflux mechanisms, detoxification operated by platinophiles, such as intracellular thiols, and reparation of platinum-induced DNA lesions.[2]

The interaction of platinum antitumor drugs with intracellular thiols, such as the tripeptide glutathione (GSH), and proteins rich in cysteine (cys) and methionine (met) residues, can decrease the activity of platinum complexes. Under physiological conditions, the Pt−S bond is preferred to the Pt−N bond,[3] where N is the N7 of the guanine residue of DNA, the preferential binding site of anticancer Pt drugs, necessary for the antitumor activity.[4] High intracellular levels of glutathione, in fact, have been correlated to cisplatin-resistance.[5]

We investigated the reaction between kiteplatin and glutathione in order to clarify its metabolic fate. We found that kiteplatin reacts with glutathione forming a dimeric (2 : 2) and a macrochelate (2 : 1) adduct, similar to oxaliplatin,[6] however, in the case of kiteplatin, the macrochelate adduct is a reactive species that undergoes a ring-opening process.

We also proved that kiteplatin is able to bind to DNA models, i.e. 5′−GMP, after first reacting reaction with glutathione. This finding could be a potential explanation of the activity of kiteplatin also in cisplatin- and oxaliplatin-resistant tumors.


INOR 797
Microwave-assisted synthesis of cisplatin

James D. Hoeschele, hoeschel@msu.edu, Emanuele Petruzzella, Cristian Chirosca.Department of Chemistry, Eastern Michigan University, Ypsilanti, MI 48197, United States

We have initiated a broad synthetic program to investigate the synthesis of selected precious metal complexes (e.g., Pt, Rh, Ir, Ru) using a microwave-assisted approach. We present here a summary of our work on the microwave-assisted synthesis of Cisplatin, a potent anticancer drug known globally. The goals of our studies were (1) to explore the use of microwave technology to synthesize Cisplatin and (2) to develop a rapid, microscale synthesis of pure Cisplatin in order to facilitate the incorporation of the short-lived radioisotope, 155Pt (t1/2 = 1.41 d), and thereby maximize the useful life of radiolabeled Cisplatin in biological studies.

Initial syntheses were modeled after the conditions of the Lebedinskii-Golovnya method and under exposure to microwave radiation (2450 MHz), K2PtCl6 (0.05 to 0.2 millimoles) was the starting material in all reactions. Reaction parameters (scale of synthesis, reaction time, temperature, ratios of reactant concentrations relative to Pt(II) & various NH4+ salts) were varied systematically while under the influence of the microwave radiation to achieve the highest yields and purity of cisplatin.

The optimized procedure permits yields of > 40% of highly pure Cisplatin on a scale of 50-200 mmol. While the synthesis requires a microwave irradiation time of 15 min at 100 °C at millimolar ratios of NH4+/K2PtCl6 = 4, and KC1/K2PtCl6 = 2, the purification of the crude product requires an additional hour. Purification is achieved by fractionation of the major impurity, [Pt(NH3)2Cl]2Pt(NH3)Cl2 using K2PtCl6 to form the insoluble salt, [Pt(NH3)2Cl4]2K2PtCl6. Reaction products were evaluated by 1H-NMR, HPLC, and UV-Vis spectroscopy. While the optimal yield is less than that obtained using the Dhara method, the preparation time is shorter.

References

Cytotoxicity studies of a new series of dirhodium (II,II) compounds containing mixed bridging ligands

Amanda David, amanda.david@chem.tamu.edu, Bruno Peña, Jean-Philippe Pellois, Kim R. Dunbar. 1. Chemistry, Texas A & M University, College Station, TX 77843-3255, United States 2. Biophysics and Biophotonics, Texas A & M University, College Station, TX 77843-2128, United States

Many efforts have been devoted to the design and synthesis of metal-based anticancer agents. Our group has shown that Rh₂(µ-O₂CCH₃)₂ and other derivatives containing electron accepting ligands can bind in vitro to nucleotides, form intra-strand DNA cross-links and interact with other biologically relevant molecules. 1, 2 As part of our interest in this, we have synthesized a series of dirhodium (II,II) complexes with different types of bridging ligands in the same molecule. 3 Reactions of Rh₂₄(F-form)(µ-O₂CCH₃)₂(CH₂CN)₂ (1) (F-form = N,N-di-o,2,6-difluorophenylformamidinate) with electron accepting chelating ligands (N,N) namely, dpdz (dipyrido[3,2-a:2′,3′-c]phenazine) (2), dpdz (dipyrido[3,2-a:2′,3′-c]phenazine) (3) and dpdz (benzo[d]pyrido[3,2-a:2′,3′-c]quinoline) (4) to form [Rh₂(F-form)(µ-O₂CCH₃)(N,N)]OAc₂ were studied. 4 The cytostatic effect of compounds 1-4 against cervical cancer cells was studied in the dark and also upon irradiation. Fluorescence probes were used to elucidate possible cell death mechanisms of action. HeLa cells were incubated with compounds 1-4 for 2 h in the dark and then irradiated for 1 h. Compound 4 ([Rh₂(F-form)(µ-O₂CCH₃)(dpdz)]OAc₂) is the most effective at inhibiting cell growth with an IC₅₀ value of 64 ± 7 µM in the dark and 11 ± 4 µM upon irradiation. The results of a JC-1 assay indicate that compound 4 induces changes in the mitochondrial membrane potential as early as 2 h as observed from a time lapse experiment, indicating that the complex may induce cell death through mitochondrial-mediated pathways.


Synthesis, characterization and structure-activity relationships of novel ruthenium(II) poly(pyridyl) complexes

Eugenia S Nahr, eugenia.nahr@mavs.uta.edu, Frederick M MacDonnell.Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, Texas 76019, United States

The novel mononuclear ruthenium(II) poly(pyridyl) complex (RPC) ([phen]₄Ru(tadbp)]Cl₂ (B) (where tadbp is 9,11,20,22-tetraazadiquinoxalino[3,2-a:2′,3′]dibenzo[3,2-o:2″,3″-n]pentacene) was synthesized and characterized. The structural difference of an open chelated site between the mononuclear ruthenium complex ([phen]₄Ru(tadbp)]Cl₂ (MP) (where tap is 9,11,20,22-tetraazatetrapyrdo[3,2-a:2′-c:3″,2″-1,2″-3″-pentacene) and B plays a role in their redox potential and biological activity. The promising DNA cleavage activity, cytotoxicity and anticancer potential of B in comparison to MP are investigated. Furthermore, this paper will present the development of novel related ruthenium(II) poly(pyridyl) complexes consisting of varying aromatic bridging ligands.

Dna protection by the bacterial ferritin Dps via DNA charge transport

Anna R Arnold, anordstr@caltech.edu, Jacqueline K Barton.Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

Dps proteins, bacterial mini-ferritins that protect DNA from oxidative stress, are implicated in the survival and virulence of pathogenic bacteria. These proteins are thought to protect DNA by depleting ferrous iron and hydrogen peroxide, which can otherwise produce damaging hydroxyl radicals via Fenton chemistry. We seek to elucidate more specifically the mechanism of E. coli Dps protection of DNA. DNA charge transport (CT), whereby charge is effectively conducted through the base pair π-stack, is proposed to be utilized within the cell in, for example, the long-range activation of redox-active transcription factors. Can the DNA-binding protein Dps similarly utilize DNA CT to protect the genome from a distance? That is, must oxidizing equivalents diffuse specifically to the di-iron ferroxidase sites of Dps, or can Dps also become oxidized through a distance within DNA CT? We employ an intercalating ruthenium photooxidant to generate oxidative DNA damage via the flash-quench technique. The injected electron hole localizes to guanine repeats, the sites of lowest potential in DNA. Because the lifetime of the guanine radical is long relative to the timescale of DNA CT, the guanine radical can interact with DNA-bound redox-active proteins. We find that Dps loaded with ferrous iron significantly attenuates the yield of oxidative DNA damage, in contrast to Apo-Dps and ferric iron-loaded Dps which lack reducing equivalents. In this manner, ferrous iron-loaded Dps is selectively oxidized to fill guanine radical holes, thereby restoring the integrity of the DNA. Luminescence studies indicate no direct interaction between the ruthenium photooxidant and Dps, supporting the DNA-mediated oxidation of ferrous iron-loaded Dps. Thus DNA CT may be a mechanism by which Dps efficiently protects the genome of pathogenic bacteria from a distance.

Treatment of Alzheimer’s disease with bimodal hybrid heterocyclic amine ligands: A closer look into the oxidative pathways and copper misregulation in the disease

Paulina Gonzalez, p.gonzalez8@tcu.edu, Giridhar Akkaraju, Kayla Green.Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, United States

Neurodegenerative diseases such as Alzheimer’s, Parkinson’s, Huntington’s and prion disease have certain chemical and biological mechanisms in common, including the aggregation of protein. Some theories postulate that aggregation of the β-Amyloid protein due to misregulation of copper and other metals could play a role in the development of neurodegenerative disorders such as Alzheimer’s disease. In addition, metal ion misregulation is often associated with the production of tissue-damaging reactive oxygen species. The focus of this project is the synthesis of the hybrid heterocyclic amine LC molecule, which can act as a ligand that can rescue the copper misplaced in amyloid plaques, thus restoring solubility of these aggregates. The compound examined herein is also constructed to quench radical species as a means to reducing neuronal damage associated with Alzheimer’s disease as well. Both, biological and chemical experiments are presented in order to analyze the activity of LC in relation to the molecular features associated with this neurodegenerative disorder. These results indicate that the molecule can quench radical species in vitro and in vivo. Western Blotting, TEM, fluorescence and NMR techniques show that LC is also capable of reversing amyloid fibril formation induced by exposure to copper ions.
Recent coordination chemistry featuring N- and N,C-donor chelates will be presented, some of which possess features of redox non-innocence. The presentation will focus on the synthesis, structure, and reactivity of cobalt and chromium species in honor of Klaus Theopold, whose contributions in this area are prominent.

**INOR 803**

**Study of an amphiphilic poly(organosiloxane) nanocage: Behavior of Co ions in a bio-inspired confined nanoreactor with defined array of multifunctional reactive groups in confined space**

Jingmei Shen, jingmei.shen@northwestern.edu, Zhongliang Shen, Zhen Wang, William A. Gunderson, Mayfair Kung, Brian M. Hoffman, Harold Kung. (1) Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, United States (2) Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

The catalytic function of enzymes is mainly a consequence of cooperative interaction between an array of multifunctional groups with substrate/product within nanometer-size confines. One bio-inspired soluble nanocage structure was designed and synthesized by template-directed method with a spherocilicate as a template. The resulted 2 – 5nm – diameter nanocage has the hydrophilic interior with carboxylic acid and silanol groups, and hydrophobic carbosilane shell. The reaction between the nanocage and excess of Co(CO)₃ in toluene afforded orange nanocage-Co₅(CO)₉ specie. ¹H NMR, IR, and UV-vis spectra confirmed the complexation of Co₅(CO)₉ by nanocage. Approximate four cobalt per nanocage was calculated based on ICP analysis. The magnetism and EPR study suggested that the formal oxidation state of Co in the nanocage was +1. The catalysis behavior of the Co ions in a nano confined space was explored. Size and polarity selectivities of the porous amphiphilic shell were also observed in this study, comparable with that of other similar structures.

**INOR 804**

**Mechanistic investigations of acetonitrile, chloromethane, and alcohol activation by Tp’RhL complexes**

William D Jones, jones@chem.rochester.edu, Yunzhe Jiao. Department of Chemistry, University of Rochester, Rochester, NY 14627, United States

Reaction of acetonitrile with the [Tp’Rh(CNneopentyl)] fragment led only to C-H activation products. Irradiation of Tp’Rh(PMe₃)H₂ or heating of Tp’Rh(PMe₃)PH in acetonitrile gives both Tp’Rh(PMe₃)(CH₂CN)H and Tp’Rh(PMe₃)Me(CN). Use of a low temperature thermal precursor for [Tp’Rh(PMe₃)] in acetonitrile leads to the η¹-adduct Tp’Rh(PMe₃)(NCMe), which gives C-CN product upon heating to 100 °C. Reaction of the thermal precursor with chloromethane leads to C-H activation products, which then convert to Tp’Rh(PMe₃)(Me)H at 30 °C. Additional activations of a variety of alcohols will also be described.

**INOR 805**

**Chemistry of old and new perfluoropinacolate complexes**

Sarah E Specht, Laleh Tahsini, Joshua J M Nelson, Alexandra F Long, Holly Hajare, Linda H Doerrer, doerrer@bu.edu. Department of Chemistry, Boston University, Boston, MA 02215, United States

Past work has demonstrated that transition metal compounds with fluorinated aryloxide and alkoxide ligands have distinct structural and electronic properties. The reduced O-atom basicity supports lower coordinate metal environments and relatively more sigma, less pi donation from the O atoms to the metal center. Two highly unusual, high-spin square-planar complexes, [M(pinF)₂]²⁻, with M = Fe, Co have previously been reported (ACIE, 2012, 51, 1000) with the perfluoropinacolate ligand. In this contribution, we will present further examples of {M(pinF)} complexes, including V, Cr, and Mn derivatives as well as electrochemistry from Ni and Cu species.
that demonstrate reversible M(III)/M(II) redox couples. Some of the [M(pinF)2]- chemistry is cation dependent and will be discussed. We will also describe an unusual transformation of the perfluoropinacolate ligand into two propane diolate groups within the Co system. This reverse-pinacol coupling reaction is solvent dependent and sheds light on the robustness and vulnerabilities of the perfluoropinacolate ligand.

INOR 806
Small molecule activation with monovalent by nickel complexes
Glenn P. A. Yap, William L Green, Jessica Wallick, Charles G Riordan, riordan@udel.edu. Chemistry & Biochemistry, University of Delaware, Newark, DE 19716, United States
This report will highlight recent advancements from this laboratory in the activation of small molecules, specifically O₂, S₈, and Se, by nickel(I) coordination complexes. Emphasis is placed on elucidating the electronic and geometric structures of reactive intermediates and correlating these structures with chemical reactivity, with a focus on C-H oxidation.

INOR 807
Expanding the coordination geometry and enhancing the photophysical features of Re(I) with redox non-innocent pincer ligands
Darrin Richeson, darrin@uottawa.ca, Tom Woo, Philip Bulsink, Prajesh Joshi, Titel Jurca, Ilia Korobkov. Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N6N5, Canada
The photochemical and photophysical properties of α-dimine Re(I) compounds have been recognized since the mid 1970's. In particular, these species possess exceptional photocatalytic ability to function as unique CO₂ reduction catalysts without the requirement of additional complexes as photosensitizer or catalyst. However, the development of Re(I) chemistry has been restricted by the limited structural and electronic variability of the common pseudo-octahedral fac-[ReX(CO)₅]L₂ (L₂ = α-dimine) products. We address this constraint by reporting the preparation and characterization of tridentate pincer ligand compounds possessing bis(mino)pyridine and terpyridine ligation, κ³-LRe(CO)₅X (L = 2,6-(ArN=CR)=2H), 2,2'-6',2''-terpyridine; X = Cl-, Br-, OTf-. Single crystal X-ray analyses document the new coordination environment for Re(I) carbonyl chemistry where the metal center is supported by a planar, tridentate pincer ligand. The photophysical features of these compounds show significant elaboration in both number and intensity of the d-n° transitions observed in the UV-Vis spectra relative to the bidentate starting materials; these spectra were analyzed using time-dependent DFT computations. Electrochemical analysis indicated an increase in electrostatic stabilization of the reduced ligand in the tridentate conformation.

INOR 808
MRI contrast agents: Toward a second generation
Kenneth N. Raymond, raymond@socrates.berkeley.edu, Sylvie L. Pailloux, Stephen David Köster. Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720-1460, United States
Since the advent of modern medical MRI imaging in the 1980's, the commonly used field-strength has been 1.5 Tesla. Improvements in instrumentation using superconductive technology have generated powerful 3.0 Tesla magnetic fields, which become increasingly popular due to the strength anymore, making the development of new MRI contrast agents an important research goal.

In recent years health concerns have arisen due to the high concentrations of Gd-based contrast agent that have to be administered to reach acceptable contrast enhancement. As a result, a higher per Gadolinium relaxivity has been one of the leading themes in the development of MRI contrast agents in order to reduce dosage. Based on mixed HOPO (hydroxypyridonate)-TAM (Terephtalamide) ligands, the Raymond group has developed small molecule contrast agents with an optimum water exchange rate, high numbers of coordinated water molecules and high thermodynamic stability. In an effort to further improve these contrast agents, we have recently functionalized them to enable conjugation to macromolecules and nanosupports. We demonstrated that conjugation of our small-molecule contrast agents to MS-2 virus capsids and biodegradable esteramide dendrimers significantly increases the per Gadolinium relaxivity by the reduction of molecular tumbling. Ongoing and future research includes the immobilization of these small-molecule contrast agents on gold nanoparticles to reach even higher loadings and relaxivities and the possibility of targeted MRI imaging.

INOR 809
Gd-free MRI contrast agents based on a Mn-porphyrin platform: Improving the sensitivity and modulating the pharmacokinetics
Inga E Haedicke1,2, Weiran Cheng1, Xiao-an Zhang1,2, xazhang@utsc.utoronto.ca. (1) Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada (2) Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Ontario M1C 1A4, Canada (3) Department of Biological Sciences, University of Toronto Scarborough, Toronto, Ontario M1C 1A4, Canada

As a noninvasive and versatile biomedical imaging technique, magnetic resonance imaging (MRI) is widely applied in clinical diagnosis and fundamental research throughout the life sciences. Currently gadolinium (Gd)-based T₂ contrast agents (CAs) play a crucial and dominant role in contrast-enhanced MRI studies. Challenges are emerging, however, as clinical Gd-agents have been implicated in nephrogenic systemic fibrosis (NSF), a rare but severe adverse effect related to the toxicity of free Gd³⁺ ions released in vivo. In addition, the contrast enhancement efficiency (relaxivity) of typical Gd CAs decreases with increase of magnetic field strength. Since clinical MRI scanners are progressively being replaced by 3 T or even higher field instruments it is highly desirable to develop new CAs that circumvent these intrinsic limitations of Gd.

We have developed a different class of Gd-free T₂ CAs based on manganese(III) porphyrins (MnP). Unlike Gd, Mn is an endogenous micronutrient, and is tightly bound by the rigid porphyrin ligand as a +3 oxidation state complex with remarkable stability. Despite the presence of only four unpaired electrons in Mn₁⁸⁺ (S = 2) compared to seven in Gd³⁺ (S = 7/2), anomalously high T₂ relaxivity (r₂) was observed on certain water-soluble MnPs. Through rational design, we can modify the structures of MnPs to further improve the r₂ at high fields and finely tune the pharmacokinetics in a controllable manner. In this talk, I will present three different types of CAs based-on MnP specifically engineered for different applications:

(1) Extracellular fluid agent with rapid renal clearance suitable for high-field applications;
(2) Blood-pool agent with long circulation time for vascular imaging;
(3) Cell-permeable and trappable Tₐgent for cell labelling.

Overall, MnP is a versatile platform for developing next generation CAs with high sensitivity, optimal biocompatibility and tunable pharmacokinetics.

INOR 810
Linking fundamental undergraduate f-element research to real-world applications: Development of pyridine/phosphonate based MRI contrast agents
The pursuit of high-relaxivity Gd-based MRI contrast agents presents an excellent opportunity in the undergraduate research laboratory for students to acquire knowledge and skills in the area of lanthanide coordination chemistry while pursuing the goal of developing practical imaging agents. Our lab is presently investigating a series of multidentate, pyridine containing ligands linked through a tripodal backbone to afford lanthanide complexes with hydration numbers of two to three. The syntheses of the ligands can be carried out via straightforward procedures, and in one case in only one, solventless step. This is important both in terms of the potential commercial applications but also in allowing meaningful contributions to be made by undergraduates with limited and often fragmented blocks of time to devote to research. Among the ligands examined thus far is the tris-imino/pyridine ligand (TRIPy) which forms a Gd(III) complex in aqueous solution with an average hydration number of 2.3. This value, combined with relatively fast water exchange, is consistent with relaxometric characterization and has inspired the synthesis of new derivatives incorporating phosphate binding groups to enhance stability and fully exploit the potential of this novel class of complexes.

INOR 811
Design of protein MRI contrast agents for temporal and spatial molecular imaging of cancer biomarkers

Jenny J. Yang1,2, jenny@gsu.edu, Jingjuan Qiao1, Shenghui Xue1, Fan Pu1, Jie Jiang1, Natalie White1, Zhi-Ren Liu2. (1) Department of Chemistry, Georgia State University, Atlanta, GA 30303, United States (2) Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, GA 30303, United States (3) Department of Biology, Georgia State University, Atlanta, GA 30303, United States

The major barriers limiting the application of MRI to detect small lesions and metastasis at the early stage and patient selection for targeted therapy based on molecular imaging of disease biomarkers, are due to the lack of desired MRI contrast agents capable of enhancing the contrast between normal liver tissues and tumors with high relaxivity, tumor targeting, high intra-tumoral distribution and no toxicity. To address the critical need, we have developed a novel class of protein-based MRI contrast agents (ProCas) with significant improvement of both r1 and r2 relaxivities and in vivo dose efficiency in mouse models. Several key factors for relaxivity, such as correlation time, exchangeable water numbers from first coordination shell and secondary/outer sphere are improved by protein design of Gd3+ binding site(s) in stable proteins and protein modification. Our recent studies have shown that the Gd3+ binding constant of ProCas is comparable to DTPA but metal selectivity for Gd3+ over physiological metal ions such as Ca2+, Mg2+ and Zn2+ are ~10000 fold than DTPA and there is no detectable cellular and animal toxicity. It enables non-invasive early detection primary liver tumors and metastatic tumors at 0.2 mm from the current threshold of 20 mm or larger. In addition, we developed ProCas enable the 100 fold increase of detection size of metastatic liver tumors by MRI from the current threshold of 20 mm or larger with high confidence using our established melanoma metastatic mouse model. Furthermore, we have designed several MRI contrast agents that specifically targeting to cancer biomarkers including HER2, EGFR and GRPR that expressed on various types of cancers using animal models. These new classes of targeted MRI probes exhibit advantages in crossing the endothelial boundary, tissue distribution, and tumor tissue retention as demonstrated by even distribution of the imaging probe across the entire tumor mass. The capability to spatially and temporally visualize intratumoral distribution as well as quantification of the levels of major disease biomarkers would greatly improve our ability to track the change of the biomarkers during tumor progression, monitor treatment efficacy, aid in patient selection, and further develop novel targeted therapies for clinical application.

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INOR 812
Iron oxide nanoparticles as theranostic agents for siRNA and microRNA therapies in cancer

Anna Moore, amoore@helix.mgh.harvard.edu. Department of Radiology, Massachusetts General Hospital, Charestown, MA 02129, United States

Superparamagnetic iron oxide nanoparticles have an inherent capacity for noninvasive imaging and obtaining semi-quantitative information about nanoparticle bioavailability in target tissues. As theranostic agents they can serve as vehicles for delivery of various therapeutic agents. This presentation will focus on utilizing iron oxide nanoparticles for delivery and noninvasive monitoring of siRNA and microRNA therapies in cancer.

RNA interference is an innate cellular mechanism for post-transcriptional regulation of gene expression in which double stranded ribonucleic acid inhibits the expression of genes with complementary nucleotide sequences. Its potential for tumor therapy is indisputable, considering that one can use this mechanism to silence virtually any gene, including genes implicated in tumorigenesis, with single-nucleotide specificity. Magnetic nanoparticles were used for delivering and monitoring siRNA to tumors.

MicroRNA are a class of post-transcriptional regulators that have been implicated in various cell functions including metastatic potential. Several microRNAs that mediate the process of tumor cell migration and tissue invasion have been identified. In our laboratory we used iron oxide nanoparticles for targeting miR-10b implicated in breast cancer metastasis.

In both cases magnetic nanoparticles served not only as imaging reporters but also as protective delivery vehicles for oligonucleotides. Information obtained using these nanoparticles in potential clinical scenario could provide directions for treatment on a patient-by-patient basis, opening up the possibility for designing individualized therapeutic regimens.

INOR 813
Multifunctional inorganic nanocrystal based contrast agents for medical imaging

David P Cormode, davidcormode@gmail.com. Department of Radiology, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

Over the past ten years, nanoparticle-based contrast agents medical imaging has become a topic of intense interest. Nanoparticles possess a range of advantages over small molecules as contrast agents. For example, nanoparticles can carry high payloads of contrast generating material, have long circulation half-lives, be efficiently targeted and it is relatively easy to integrate multiple properties into the same platform. In this presentation I will focus on methods we have devised to achieve the latter goal.

In this presentation I will describe our latest results in developing multifunctional nanoparticle contrast agents for a range of techniques, including magnetic resonance imaging (MRI). We synthesize inorganic nanocrystals such as gold, iron oxides, quantum dots and upconverting nanoparticles. We integrate these nanocrystals with lipids, polymers, proteins, fluorophores, drugs and other functional components to create complex architectures. For example, I will describe an approach to integrate gold, iron oxides and quantum dots into the shell of polymer based microbubbles to provide contrast for ultrasound, MRI, computed tomography and fluorescence-based methods. The applications of such multi-functional nanostructures in targeted imaging, cell tracking and as ‘theranostic’ agents in cardiovascular disease and cancer will be described.

INOR 814
Application of photoexcited states of Re (l) metal complexes to solar energy conversion

Venugopal Komreddy, vxkomreddy@wichita.edu, Jim Yoder, Cameron Wilkinson, Huy Nguyen, Navanitha Subbayan, D. Paul Rilee. Department of Chemistry, Wichita State University, Wichita, KS 67260, United States
Dye sensitized solar cells (Grätzel Cell) have attracted significant attention as promising next generation photovoltaic devices. In a photovoltaic cell, the dye sensitizers anchored to mesoporous thin films made of the broad band gap semiconductor TiO₂, absorbs the incident photons and the excited electrons transfer into the conduction band of TiO₂. The efficiency of a dye sensitized solar cells (DSSC) could potentially be improved by changing the dyes used as sensitizers. Toward this end, a series of Re(I) complexes, Re(dcbpz)(CO)X, Re(dcbpz)(CO)X, [Re(dcbpz)(CO)X(py)]PF₆, [Re(9-cphe)(CO)₃Cl] and [Re(dfo)(4-isonicotinic-py)(CO)₃]PF₆ (where X = Cl, Br, I, CN, SCN; dcbpz = 4,4’-dicarboxyl-2,2’-bipyridine; dcbpz = 5,5’-dicarboxyl-2,2’-bipyrizine; py-pyridine; 5-cpe = 5-carboxyl-1,10-phenanthroline, dfo = 4,5-diazolofluorene-9-one) have been synthesized, and their photophysical properties characterized. The band at lower energy shows the typical metal-to-ligand charge transfer (MLCT) due to the d⁷ → π* transitions consistent with Re(I) dicarboxylated-bipyridine systems located in the 390 nm to 436 nm region, and these compounds have long life times in solution at room temperature (τ < 50 ns). The dye efficiencies were calculated by anchoring the dicarboxylated complexes to the wide band gap semiconductor TiO₂. The efficiency of the DSSC was near 1% compared to about 9 % for the best known N3 dye. To increase the efficiency, we plan to synthesize dyes that absorb energy at higher wavelengths in the visible region of the spectrum by changing the metal centers and ligands attached to them.

New iridium luminophores combining tunability and enhanced photostability

Danielle N. Chirdon, dichirdon@andrew.cmu.edu, Wesley J. Transue, Husain N. Kagalwala, Aman Kaur, Andrew B. Maurer, Tomislav Pintauer, Stefan Bernhard. (1) Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States (2) Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, United States

Leading iridium photosensitizers of the form [Ir(ppy)2(bpy)]+ (ppy=2-pheny1pyridine and bpy=2,2’-bipyridine) are vulnerable to decomposition through dissociation of their bidentate bipyridine ligand. Here, a new architecture is explored in which bpy is replaced with a more stable, tridentate ligand while cyclometalation is maintained to create a long-lived mixed excited state. Straightforward modification of all ligand sites in the new architecture has been achieved, and the geometric arrangement of the ligands is unambiguously assigned via X-ray crystallography. The rich electrochemistry of the complexes is presented via cyclic voltammetry and shows that ligand modification affords control of electrochemical behavior and electronic structure. Effects of ligand tuning are also shown in solution-based photophysical measurements. These measurements reveal intense room temperature phosphorescence with quantum yields ranging from 3-28 % and emission lifetimes in the μs range. Electrochemical and photophysical trends are elucidated through DFT calculations. Meanwhile, oxygen quenching and photocatalytic hydrogen generation studies highlight the robustness of the new materials and their potential for broad future application.

Novel lanthanide-containing 12-MC-4 complexes

Curtis M Zaleski, cmzaleski@ship.edu, Department of Chemistry, Shippensburg University, Shippensburg, PA 17257, United States

Nine single crystal X-ray structures of the LnIII·Na(OAc)·[12-MC₁₂H₂₄N₄O₄]·[H₂O]₆·DMF complex, where “OAc is acetate, shi” is salicylhydroximate, DMF is N,N-dimethylformamide, and LnIII is PrIII, NdIII, GdIII, TbIII, DyIII, HoIII, ErIII, TmIII, and YbIII will be presented. These complexes demonstrate the first inclusion of LnIII ions into the 12-MC-4 framework. The X-ray structures reveal that the identity of the LnIII ion affects the structural 12-MC₁₂H₂₄N₄O₄ framework. The largest LnIII in terms of ionic radius, PrIII, causes an expansion of the 12-MC₁₂H₂₄N₄O₄ framework as evident in longer cross cavity MnIII – MnIII distances, cross cavity oxime oxygen – oxygen distances, and average adjacent MnIII – MnIII distances. Thus, the PrIII·Na(OAc)·[12-MC₁₂H₂₄N₄O₄]·[H₂O]₆·DMF complex has the largest metalallocrown cavity. In addition, the PrIII causes the 12-MC₁₂H₂₄N₄O₄ framework to be the most bowled as evident in the largest bond angles about the axial coordination of the ring MnIII ions and the greatest distance difference of the LnIII between the oxime oxygen mean plane and the manganese mean plane.

Rational post-synthetic modification of phosphorous based porous coordination materials for gas uptake and luminescence applications
Chromogenic detection of Sarin by discolouring decomplexation of a metal coordination complex

Alexandre Carella\(^1\), alexandre.carella@cea.fr, Lucie Ordonneau\(^2\), Miroslav Pohanka\(^2\), Jean-Pierre Simonato\(^2\).  (1) Department of Nanomaterials Technologies, CEA, Grenoble, France (2) Faculty of Military Health Sciences, University of Defence, Hradec Kralove, Czech Republic

Fears that the Syrian regime might use chemical agents, and in particular Sarin, against rebel forces have been widely reported recently. Nerve agents, like Sarin, were reported to be used against Kurds in 1988, and was also employed as a deadly weapon during the terrorist attack of Tokyo’s subway in 1995. In order to protect both military and civilian people from such warfare agents, it is necessary to develop sensing devices with high sensibility and specificity to traces of organophosphorus nerve agents (OPs), like Sarin, in ambient air.

We developed an innovative concept for the detection of OP nerve agents thanks to the discolouration of a coordination complex containing ligands with specific reactivity. When this complex is exposed to OP molecules, cyclisation of the ligands prevents further metal coordination which leads to the disappearance of the light absorbing MLCT band, and thus causes discolouration of the OP sensitive colorimetric sensor.

Experiments carried out with Sarin simulant showed high reactivity both in the liquid and vapour phases. When real Sarin was used, discolouration was achieved in liquid phase.


INOR 820
Cyclometallation of aza-dipyrromethene on neutral Ru8 complexes: Toward new chromophores with extended NIR absorption properties for light-harvesting applications

André Bessette1,2, andre.yvon-bessette@umontreal.ca, Janaina G. Ferreira1, Mihaela Cibian1, Francis Bélanger2, Denis Désilets2, Garry S. Hanan1. (1) Department of Chemistry, Université de Montréal, Montréal, Québec H3C 3J7, Canada (2) St-Jean Photochemicals Inc., St-Jean-sur-Richelieu, Québec J3B 8J8, Canada

As analogues of porphyrinoids and dipyrromethene families of dye, aza-dipyrromethene (ADPM) derivatives exhibit exciting photophysical properties. Their high absorbance (ε up to 100 000 M⁻¹cm⁻¹) and strong near-IR (NIR) luminescence are especially interesting in the context of designing new light-harvesting materials. In the present study, we introduce the first examples of ADPM cyclometallation on neutral ruthenium complexes bearing either bpy 1 or terpy 2 and demonstrate the latter support further chemical modifications toward the achievement of new photosensitizers 3 for dye-sensitized solar cells (DSSC). Photophysical characterization and modelization studies will be presented to assess the origin of the bathochromic shift in the NIR region observed in the absorption spectra. Electrochemistry of the complexes will also be discussed in the perspective of optimization toward the specific energetic levels required for photovoltaic applications such as DSSC and OPV.

INOR 821
Homogeneous and immobilized Ni tripod complexes: Syntheses, 2D liquid- and solid-state NMR, and catalysis

Kyle J. Cluff, kyle.cluff@chem.tamu.edu, Nattamai Bhuvanesh, Janet Bluemel. Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

The success of homogeneous and immobilized Ni catalysts is crucially dependent on the nature of the phosphine ligands. Ni complexes with tripod ligands, e.g. (Ph3P)2CH2, or (Ph2P)2Si(OEt), have been synthesized to (a) suppress nanoparticle formation, (b) reduce leaching of immobilized catalysts, and (c) prevent interactions of the immobilized metal complexes with the reactive support and premature decomposition. All complexes have been characterized by liquid- and solid-state NMR. The 31P CSA patterns have been correlated with the single crystal X-ray crystallography data of the complexes. Besides the expected tri-, bidentate coordination can be achieved selectively, leaving one phosphine group uncoordinated. This phosphine group can be coordinated to different metals, yielding well-defined heterobimetallic complexes, which will serve to identify cooperative effects in catalysis. All Ni tripod and heterobimetallic catalysts are studied in the cycloolimerization of phenylacetylene, and the surprising results will be presented in this contribution.

INOR 822
Macroyclic ligands with heterocyclic pendent groups for Fe(II) and Co(II) paraCEST MRI contrast agents

Pavel B Tsirovich, paveltsi@buffalo.edu, Janet R Morrow. Department of Chemistry, University at Buffalo, SUNY, Amherst, NY 14260, United States

The CEST (Chemical Exchange Saturation Transfer) MRI experiment is based on alterations in image contrast produced by transfer of selectively saturated spins from a chemical pool of contrast agent (CA) to a pool of bulk water. The magnetization of the exchangeable protons (H2O, -NH, -OH) of CA is modulated by a presaturation pulse, and the water signal decreases upon exchange of the partially saturated protons.

Fe(II) and Co(II) transition metal (TM) ions form paramagnetic complexes with TACN (1,4,7-triazacyclononane) or CYCLEN (1,4,7,10-tetraazaacyclododecane) macrocycles with pendent heterocyclic donor groups that are suitable for CEST contrast. TACN-based ligands containing 6-methyl-2-picolyl/5-amino-6-methyl-2-picolyl produce paramagnetic six-coordinate complexes with Fe(II) and Co(II). These complexes are stabilized in a single diamagnetomer form and have hyperfine shifted proton resonances (-20 to +200 ppm) with narrow line widths (60-800 Hz) in water. CYCLEN derivatives with four 6-methyl-2-picolyl/6-amino-2-picolyl arms also stabilize paramagnetic states of Fe(II) and Co(II) in aqueous solution. The hyperfine shifted proton resonances in these complexes span from -130 to +330 ppm. 1,7-Disubstituted CYCLEN with 6-methyl-2-picolyl pendant demonstrates similar hyperfine shifted proton resonances, suggesting a six-coordinate geometry of CYCLEN-based complexes. Structurally similar CYCLEN-based complexes containing amino-picolyl pendants produced a paramagnetic CEST (paraCEST) effect with large chemical shift.

Other heterocyclic donor groups including 1H-benzimidazol-2-ylmethyl and 1H-pyrazol-3-ylmethyl with TACN/CYCLEN macrocycles have been studied. Reported Fe(II) and Co(II) CA are kinetically inert over a wide range of pH 5.0-8.5, as well as in the presence of physiologically relevant cations and anions. A great variety of heterocyclic donors could be used to tune redox potential of Fe(II) and Co(II) complexes to physiological range (-100 to -300 mV) for redox-responsive MRI imaging. The large shift of paraCEST peaks is promising in overcoming background from magnetization transfer (MT) effects in tissues.

INOR 823
Theoretical investigations of supramolecular chemisorption adducts of volatile small molecules with a trinuclear silver(I) nitrated pyrazolate complex: DFT modeling of dipole-quadrupole interactions

Sammer M Tekari1, stekari@yahoo.com, Vladimir N Nesterov1, Mohammad A Omary1, Rossana Galassi2, Simone Ricci2, Alfredo Bunn2. (1) Department of Chemistry, University of North Texas, Denton, Texas 76203, United States (2) School of Science and Technology, University of Camerino - Via Sant’Agostino, Camerino, Macerata I-62032, Italy
A comparative study on the tendency of a new trinuclear silver(I) pyrazolate, namely \([\text{N,N}-(3,5\text{-dinitro-pyrazolate})\text{Ag}_3]\) (1) and a similar compound known previously, \([\text{N,N}-(3,5\text{-bis(trifluoromethyl)pyrazolate})\text{Ag}_3]\) (2) to adsorb small volatile molecules was performed. It was found that 1 has a remarkable tendency to form adducts, at room temperature and atmospheric pressure, with acetone, acetylacetone, ammonia, pyridine, acetonitrile, triethylamine, dimethylsulfide, and tetrahydrothiophene while CO, THF, alcohols, and diethyl ether were not adsorbed. On the contrary, 2 did not undergo adsorption of any of the aforementioned volatile molecules. Density Functional Theory (DFT) results (polarizability, electrostatic potential profiles, kinetics and thermodynamics, and positive point charge calculations) are consistent with the chemisorption model, explain the experimental adsorption selectivity for 1, and the lack of similar adsorption by 2 upon proper selection of the density functional. The M06 method in conjunction with CEP-31G basis set provides good agreement with the experimental data both qualitatively and quantitatively compared to B3LYP/CEP-31G. The results suggest that the adsorption of Lewis basic vapors occurs mainly by kinetic effects. The high vs. low binding energies calculated for the adducts of 1 with acetonitrile vs. CO manifest the experimental findings. The findings in this project suggest that this class of quadrupolar macromolecular complexes may exhibit potential for toxic industrial chemical (TIC) removal applications already known for porous organic polymers.

**INOR 824**

**Interesting pulse radiolytic studies on cobalt(II)- and ruthenium(II)-containing complexes in acetonitrile**

Michael J. Celestine, mcele002@odu.edu. Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia 23529, United States. Applied Physics, University of Michigan, Ann Arbor, Michigan 48108, United States. Department of Chemistry and Biochemistry, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States. Mountain View College, Dallas, Texas 75211, United States. Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, United States.

Pulse radiolysis studies were carried out on \([\text{Co(dmgBF}_3\text{(H}_2\text{O})_2]_2}\) 1 (where dmgBF = difluoroboryldimethylglyoximato), \([\text{Co(dmgBF}_3\text{(H}_2\text{O})_2]_2}\) (where dmgBF = difluoroboryldimethylglyoximato), \([\text{Co(dmgBF}_3\text{(H}_2\text{O})_2]_2}\) (where dmgBF = difluoroboryldimethylglyoximato), \([\text{Co(dmgBF}_3\text{(H}_2\text{O})_2]_2}\) (where dmgBF = difluoroboryldimethylglyoximato), \([\text{Co(dmgBF}_3\text{(H}_2\text{O})_2]_2}\) (where dmgBF = difluoroboryldimethylglyoximato), \([\text{Co(dmgBF}_3\text{(H}_2\text{O})_2]_2}\) (where dmgBF = difluoroboryldimethylglyoximato), \([\text{Co(dmgBF}_3\text{(H}_2\text{O})_2]_2}\) (where dmgBF = difluoroboryldimethylglyoximato), and \([\text{Co(dmgBF}_3\text{(H}_2\text{O})_2]_2}\) (where dmgBF = difluoroboryldimethylglyoximato).

Post-radiolysis absorbance spectra of complexes 1 and 2 were similar, and believed to result from the formation of a cobalt(II)-containing species, which is in contrast with a different spectrum obtained from complex 3 (this isbelieved to result from the formation of a ruthenium(I)-containing species). At 600 nm the transient spectra of complexes 4 and 5 (at 30 ns) were roughly similar with that of complex 3 at 9 µs. We concluded that this is due to the decay of a ruthenium(I)-containing species without the corresponding formation of a cobalt(II)-containing species due to the electron being transferred to the bridging ligand prior to transfer to the cobalt(II) metal center in complexes 4 and 5.

**INOR 825**

**Trapped in imidazole: How to accumulate multiple photoelectrons on a black absorbing ruthenium complex**

Benjamin Dietzek¹, benjamin.dietzek@ipht.jena.de, Linda Zedler², Ines Rabelo de Moraes¹, Stephan Kupfer². 1) Functional Interfaces, Institute of Photonic Technology Jena, Jena, Thuringia 07745, Germany. 2) Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller-University Jena, Jena, Thuringia 07743, Germany.

The charge transfer reaction mechanism in functional Ruthenium polypyridine complexes used for solar-energy conversion are studied by combining UV-Vis absorption, resonance Raman spectroscopy and electrochemical methods. This combination of methods in concert with quantum chemistry calculations allow detailed insights into the structural and electronic properties of electronic intermediates, which might be of functional importance in the overall solar-energy conversion achieved by the transition metal complexes investigated.

In this study light induced excitation has been mimicked by electrochemical reduction and the intermediate redox state has been characterized spectroscopically. In particular we focus on systems baring an imidazole ligand coordinated to the Ru-ion, which – due to their unusually red-shifted absorption – present promising candidates for sensitizers in dye-sensitized solar cells. The spectroelectrochemical approach used deciphers the structure of the Ru complexes upon photoinduced charge accumulation.
The work presented is supported by the Thüringer Ministerium für Bildung, Wissenschaft und Kultur (grant no.: B514-09049 and grant no.: 2011 FE9096). Further financial support from the Fonds der chemischen Industrie (B. D.) is gratefully acknowledged. We acknowledge the COST Action CM 1202 Perspect-H2O.

INOR 826
Sensing amyloid protein aggregation using ruthenium probes: The effect of Δ and Λ enantiomers
Angel A. Marti, amarti@rice.edu, Nathan P. Cook. Chemistry, Rice University, Houston, TX 77005, United States

The onset of a considerable number of neurodegenerative diseases, including Alzheimer’s, Parkinson’s and Hutchinson’s diseases, has been linked to protein aggregation into fibrillar structures. These fibrillar aggregates are typically called amyloid, and possess a common cross β motive. Amyloid fibrils form insoluble depositions in cells and tissue depending on the disease. Here we will give an overview on the advances we have made in the use of photoluminescent dipyridophenazine ruthenium(II) complexes to monitor protein fibrillization. These ruthenium complexes present a remarkable increase in photoluminescence when bound to aggregates such as amyloid-β and α-synuclein fibrils. We will show how these molecules bind to amyloid-β and why they present photoluminescence in the presence of fibrils and no otherwise. Additionally, we will present our latest results on what is the effect of using enantiomerically pure complexes in for the detection of protein aggregation.

INOR 827
Combined XANES, Mössbauer, and DFT analysis of Cu-Fe and Zn-Fe heterobimetallic complexes featuring polar metal-metal bonds
Malkanthi K Karunananda¹, mkarun3@uic.edu, Soma Chattopadhayay²,³, Tomohiro Shibata²,³, E Erçan Alp⁴, Wenli Bi⁴, Neal P Mankad¹. (1) Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States (2) CSRRI-IIT, Argonne National Laboratory, Argonne, Illinois 60439, United States (3) Physics Department, Illinois Institute of Technology, Chicago, Illinois 60616, United States (4) Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States

Cu-Fe and Zn-Fe heterobimetallic complexes with polar metal-metal bonds have shown catalytic activity in organometallic and small molecular activation reactions. However, the contribution of the electronic environment of each metal in the mechanism remains a hypothetical. This study probes the electronic structure of the metal centers in a series of heterobimetallic complexes with the metals Fe, Cu and Zn containing Cp, CO and N-heterocyclic carbene ligands using K-edge XANES (X-Ray Absorption Near Edge Structure), Mössbauer Spectroscopy and DFT calculations. The analysis is aimed to uncover the role of the individual metal redox changes in catalytic reactions that use metal-metal cooperativity. The potential to incorporate this enhanced understanding of electronic structure in future catalyst designs will also be discussed.

INOR 828
Tuning excited state isomerization dynamics through ground state structural changes in analogous ruthenium and osmium sulfoxide complexes

Komal Garg, kg150509@ohio.edu, Jeffrey J. Rack. Department of Chemistry and Biochemistry, Ohio University, Athens, OH 45701, United States

The photochemistry and photophysics of polypyridine metal transition complexes is a continuing area of interest in inorganic photochemistry. Ruthenium sulfoxide complexes, a class of such chromophores, may be used in solar cells, or as molecular switches in a variety of information storage devices. Herein, we report the synthesis and spectroscopic properties of [Ru(bpy)3(pyESO)]2− and [Os(py)(pyESO)]2+, where bpy is 2,2′-bipyridine, pyESO is 2-(propane-2-sulfinyl)ethylyl)pyridine. We found that by simply increasing the chelate ring size from 5 to 6 leads to dramatic photoreactivity changes in these complexes. There is a striking increase in the quantum yields of isomerization (Φs-o) for complexes with a six-membered chelate ring relative to a five-membered chelate ring. For the osmium compound, we report that isomerization may only be triggered by electrochemical oxidation. The compounds have been analyzed by X-ray crystallography, 1H-NMR, UV-Visible absorption and ultrafast transient absorption spectroscopy. Analysis of data reveals quite important features in the electronic structure of these complexes. These data and other details for both complexes will be discussed.

INOR 829

Use of iron tricarbonyl complexes as dynamic probes of local chemical environments

Benjamin J Lear, bu14@psu.edu, Andrea N Giordano. Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

The IR and Raman spectra of η4-diene coordinated iron tricarbonyl complexes can be used as probes of either the thermodynamic or dynamic environments in which the complexes find themselves. We find that use of norbornadiene results in a spectrum that is sensitive to the dynamic properties of the local environment. In particular, the three carbonyls undergo a turnstile excitation on the picosecond timescale that results in a dynamic vibrational spectra. This spectra can be used in order to determine how the dynamic parameters (ie. moment of inertia, viscosity, etc) of the surrounding solvent affect the rate of this carbonyl exchange. At the same time, use of cyclooctatetraene results in a complex in which the carbonyl exchange is too slow to give rise to dynamic effects in the vibrational spectra. This provides a means by which to examine the control over the spectra exerted by the thermodynamic properties of the solvent. Together, these two complexes allow for deconvolution of dynamic and static effects, and give us a detailed molecular view of how parameters such as viscosity, solvent relaxation, and dipolar interactions come together to control ultrafast ground state processes of molecules.

INOR 830

Perturbation analysis of the (0,0) band of the A2Π→X2Σ+ transition in ZrN

Kaitlin A Womack1, kwomack@siue.edu, Taylor N Dahms1, Leah C O’Brien1, James O’Brien2. (1) Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, Illinois 62025, United States (2) Department of Chemistry and Biochemistry, University of Missouri St. Louis, St. Louis, Missouri 63121, United States

The (0,0) band of the A2Π→X2Σ+ transition of ZrN is known to be perturbed. Both homogeneous and heterogeneous perturbations are observed in the spectrum. PGOPHER is used to explicitly analyze these perturbations, and the perturbing states are analyzed as A and Σ states. ZrN was produced in a hollow cathode sputter source, and the spectrum was recorded in emission by a high resolution FT spectrometer. Results of the analysis will be presented.

INOR 831

Analysis of a new electronic transition of MoO in the near-infrared

Jack C Harms, jharms@siue.edu, Kaitlin A Womack, Leah C O’Brien. Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62025, United States

A new electronic transition of molybdenum monoxide, MoO, was observed near 6735 cm⁻¹. This transition is tentatively assigned as the (0,1) band of the A2Π→X1Σ+ transition. PGOPHER is used analyze the line positions observed in the spectrum. MoO molecules were produced in a Mo-lined hollow cathode sputter source, and the spectrum was recorded in emission using the high resolution spectrometer associated with the McMath-Pierce Solar telescope at Kitt Peak, AZ. Results of the analysis will be presented.

INOR 832

Magnetic excitations in metalloporphyrins by inelastic neutron scattering and determination of zero-field splittings

Seth C. Hunter1, shunte16@utk.edu, Andrey A. Podlesnyak2, Zi-Ling (Ben) Xue1. (1) Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, United States (2) Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37996, United States

Inelastic neutron scattering (INS) has been used to study magnetic excitations in metalloporphyrins [MII(TPP)Cl] (M = Mn, Cr; TPP = tetraphenylporphyrin) and [MIII(TPP)] at the Cold Neutron Chopper Spectrometer (CNS) at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory. Inelastically scattered neutrons transfer energy to molecules in the sample of each compound, leading to transitions between the energy levels. Zero field splitting parameters D for these complexes have been obtained. The work shows that magnetic excitations below ~30 cm⁻¹ could be determined using non-deuterated samples.

INOR 833

Femtosecond transient absorption anisotropy study on photochromic ruthenium and osmium sulfoxide complexes

Lei Wang, lw138009@ohio.edu, Jeffrey J Rack. Department of Chemistry and Biochemistry, Ohio University, Athens, OH 45701-2979, United States

Transient absorption polarization measurements report on the orientation of the transition dipole moment relative to the excitation dipole moment, and it has been employed to study the excited-state dynamics in polypyridylRu(II) and Os(II) complexes following photoexcitation to a metal-to-ligand charge transfer (MLCT) state. We found that the anisotropy decay rates were (5ps)⁻¹ and (50ps)⁻¹ in [Ru(bpy)3]²⁺ in acetonitrile consistent with previous reports. Our previous studies on photochromic ruthenium and osmium sulfoxide complexes indicated an excited state absorption ascribed to S(0) → Ru²⁺ or Os²⁺-dtr ligand-to-metal charge transfer (LMCT). We will report on our polarization anisotropy studies of these complexes with an aim to understand the motion of the sulfoxide along the triplet excited state potential energy state following excitation.

INOR 834

Ultrafast spectroscopy of ruthenium and osmium sulfoxide complexes

Jeffrey Rack, rackj@ohio.edu, Komal Garg, Albert King, Lei Wang. Department of Chemistry and Biochemistry, Ohio University, Athens, OH 45701, United States

Photochromic compounds are light-activated molecular switches that convert photonic energy to potential energy for specific and selective excited state bond breaking and bond making reactions. Our examination of ruthenium and osmium polypyridine complexes containing sulfoxide ligands demonstrate that S-to-O isomerization is efficient, and can occur rapidly both in solution. Picosecond transient absorption spectroscopic data show that S-to-O
isomerization time constants may be as fast as 45 ps. Recent studies of ruthenium polypyridine complexes containing chelating sulfoxides illustrate that two different colors of light may be used to trigger between the two ground states. These investigations also show that isomerization occurs in a non-adiabatic fashion. These results and others will be presented and discussed.

INOR 835
Investigating ultrafast linkage isomerizations in a new ruthenium sulfoxide two-color photochrome
Albert W King, ak342610@ohio.edu, Jeffrey J Rack. Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, United States
Among photochromic compounds, polypyridyl ruthenium sulfoxide complexes which undergo reversible S → O linkage isomerizations are of particular interest due to their tunable MLCT absorption maxima, high quantum yields and rapid (Ultrafast) isomerization time constants. Few examples exist of ruthenium sulfoxides which are specifically two-color photochromes, due to the balance of complex excited state features of largely unknown character which must be present in such molecules. A new two-color reversible ruthenium sulfoxide photochrome featuring a chelating benzimidazole-sulfoxide moiety is reported here, and the characterization of the complex is discussed. Excited state isomerization dynamics have been interrogated by Ultrafast transient absorption spectroscopy. Additionally, minor modification of the chelate ring size of the benzimidazole-sulfoxide ligand is observed to substantially accelerate the isomerization event, which is complete in ~100 ps, and the dynamics and characterization of the modified complex are described in comparison to the parent complex.

INOR 836
Water oxidation catalyzed by a dinuclear Cobalt polypyridyl catalyst Co-Hbpp: How does it differ from Ru-Hbpp?
Nora Planas1, noraplanas@gmail.com, Sukanta Mandal1, Mathew L Rigby2, Antoni Lieb3, Shannon S Stahl1, Laura Gagliardi3, Christopher J Cramer1. (1) Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States (2) Institut of Chemical Research of Catalunya, Tarragona, Spain (3) Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States (4) Department of Chemistry and Nano Science, Ewha Womans University, Seoul, Republic of Korea
The in-in[(Co(II)trpy)(μ-O3)(μ-bpp)] (Co-Hbpp) catalyst was investigated by means of density functional theory and multi-reference methods. M06-L and M11L density functionals were utilized to examine the possible water oxidation pathways in the gas phase. SMD continuum solvation model was used to account for the bulk solvation effects. The proposed mechanisms and predicted activation barriers based on these calculations were compared with the experimental studies as well as with the previously studied Ru-Hbpp catalyst.

INOR 837
Electro- and photocatalytic H2 production by Co complexes with pentadentate ligands
Xuan Zhao1, xzhaot@memphis.edu, Manohar Vennapalli1, Chialiu Que1, Teera Baine1, Min Zhang1, Guangchao Liang1, John C Bollinger2, Charles E Webster1. (1) Department of Chemistry, University of Memphis, Memphis, TN 38152, United States (2) Department of Structural Biology, St. Jude Children’s Research Hospital, Memphis, TN 38105, United States
The production of H2 for future use as a clean and renewable fuel has inspired the design of metal complexes as catalysts for proton reduction, as Co, Ni, and Fe complexes. We have shown that mononuclear Co complex with pentadentate ligand, N,N-Bis(2-pyridinylmethyl)-2,2’-Bipyridine-6-methanamine (DPA-Bpy), can catalyze electro- and photocatalytic production of H2 in aqueous solution. In order to improve the catalytic efficiency, the design, synthesis, and characterization of Co complexes with new ligand scaffolds to modify their electronic and structural features will be reported, and their effects on catalytic H2 evolution will be discussed.

INOR 838
Threefold-symmetric cobalt complexes for oxidation catalysis
Marika Wieliczko, Christian M Wallen, Christopher C Scarborough, scarborough@emory.edu. Department of Chemistry, Emory University, Atlanta, GA 30322, United States
The search for effective base-metal catalysts continues to drive much of inorganic chemistry. Progress is often facilitated by the design of novel ligand architectures that are informed by ligand field and molecular orbital theories. This lecture will describe the design, synthesis, and catalytic activity of a series of cobalt complexes in threefold symmetry that contain redox-innocent Group I or II ions in the second coordination sphere. The role of the redox-innocent ions in catalysis and the scope and mechanism of catalytic substrate oxidation will be discussed.

INOR 839
Theoretical insights into the mechanisms of peptide hydrolysis by metal-cyclen and metal-cyclodextrin complexes
Tingting Zhang, t.zhang7@umiami.edu, Rajeev Prabhakar. Department of Chemistry, University of Miami, Coral Gables, FL 33146, United States
The selective hydrolysis of the extremely stable peptide or amide bond of peptides and proteins is required in a wide range of biological, biotechnological and industrial applications. We have employed quantum mechanics (QM) and hybrid quantum mechanics/molecular mechanics (QM/MM) techniques to investigate the mechanisms of peptide hydrolysis by metal-cyclen and metal-β-cyclodextrin (CD) complexes. Firstly, the mechanisms of Co(III)- and Cu(II) containing complexes of cyclen and oxacyclen and the effects of the ligand environment, pendant and metal ion (Co(III), Cu(II), Ni(II), Zn(II), Cd(II) and Pd(II)) on the energetics of this reaction have been elucidated. Secondly, the exact reaction mechanism, the location of CD (number of -CH2 groups downstream from the metal center), conformation of CD (primary or secondary rim of CD facing the substrate), the number of CD (one or two) and the optimisation metal ion (Pd2+, Zn2+ or Co3+) of the metal-β-Cyclodextrin (CD) complex have been suggested.

INOR 840
Hydroxide-promoted catalytic hydrodefluorination by ruthenium in aqueous media
Michael M Konnick, mkonnick@scripps.edu, Roy A Periana, Brian G Hashiguchi. Department of Chemistry, The Scripps Research Institute - Scripps-Florida, Jupiter, FL 33458, United States
The utility of organofluorine compounds across the chemical industries cannot be understated. This unique position in modern chemistry is derived from both the incredible thermodynamic and kinetic stability of the C-F bond. However, these same features have historically made the degradation of organofluorine compounds challenging, allowing fluorocarbons to persist in the environment for extended periods of time; several of which are bio-accumulative and toxic or highly potent greenhouse gases. To address this, the conversion of fluorocarbons into benign hydrocarbon products (hydrodefluorination, HDF) has received increasing focus over the past decades. While many of the existing catalytic HDF systems are efficient, many also suffer from the need for either high reaction temperatures/pressures or exotic and expensive reducing reagents to achieve high reactivity. Hydrogen (H2) would be the ideal reductant for HDF, as H2 is atom economical, inexpensive, readily available, and can be formed with sustainable energy processes. Unfortunately, H2 is generally less reactive than many other hydrogen sources, and concomitant HF generation during catalysis can interfere with the overall HDF reaction. Addressing the concerns listed above, we recently designed a novel and practical approach to utilize of H2 in KOH/H2O media for catalytic HDF, mediated by Ru metal catalysts. In this study, a variety aryl-fluorocarbons and perfluorocarbons were observed to be rapidly defluorinated at low temperatures (<100 °C) to generate hydrocarbon products. Additionally, alkyl fluorocarbons (such as CH3F2) could also be
Using reduced catalysts for oxidation reactions: Mechanistic studies of the "Periana-Catalytica" system for CH₄ oxidation

Oleg A Mironov, Steven M Bischof, Michael M Konnick, mkonnick@scripps.edu, Brian G Hashiguchi, Vadim R Ziatdinov, William A Goddard, Marten Ahlquist, Roy A Periana. 1) Department of Chemistry, The Scripps Research Institute - Scripps-Florida, Jupiter, FL 33458, United States 2) Department of Chemistry, University of Southern California, Los Angeles, CA 90089, United States 3) Department of Chemistry, California Institute of Technology, Pasadena, CA 91125, United States

Designing oxidation catalysts based upon CH activation with reduced, low oxidation state species is challenging given the proclivity for catalyst deactivation by over-oxidation. This dilemma has been recognized in the Shilov system where reduced Pt²⁺ is used to catalyze methane functionalization. Thus, it is generally accepted that the key to replacing Pt²⁺ in that system with more practical oxidants is ensuring that the oxidant does not over-oxidize the reduced Pt²⁺ catalyst. The "Catalytica" system, which utilizes (bpym)PtCl₂ in concentrated H₂SO₄ solvent at 200 °C, is a highly stable catalyst for the selective, high yield oxy-functionalization of methane. In lieu of the over-oxidation dilemma, the high stability and observed rapid oxidation of (bpym)PtCl₂ to Pt³⁺ in the absence of methane would seem to contradict the originally proposed mechanism involving CH activation by a reduced Pt²⁺ species. Mechanistic studies show that the originally proposed mechanism is incomplete and that, while CH activation proceeds with Pt²⁺, the system provides a solution to the over-oxidation dilemma. Importantly, contrary to the accepted view (to minimize Pt²⁺ over-oxidation), these studies indicate that increasing the rate of Pt²⁺ oxidation could actually increase the rate of catalysis and enhance system stability if catalysts are designed to facilitate a rapid Pt²⁺ + Pt³⁺-R reaction. The mechanistic basis for this counterintuitive prediction could help to guide the design of new catalysts for alkane oxidation that operate by CH activation.

\[ \text{A: C-H Activation} \]
\[ \text{B: M-R Oxidation/Catalyst Repair} \]
\[ \text{C: M-R Functionalization} \]

Novel heterogeneous core/shell nanostructured photocatalysts for high efficient waste water treatment

Jennifer Bravo, maoy@utpa.edu, Yuanbing Mao. Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78539, United States

The health and welfare of people, especially of vulnerable groups such as children, the elderly and poor, are closely connected to the availability of adequate, safe and affordable water supplies. Water quality in a wide variety of industrial, municipal and agricultural sources has been seriously tainted due to increasing pollution of ground and surface water from these sources, severely reducing the supply of freshwater for human use. Hence, there is a clear need for the development of innovative technologies and new materials whereby challenges associated with the provision of safe portable water can be addressed. Here we developed novel core/shell nanostructured photocatalysts using a cost effective procedure to resolve many of the problems involving water purification and quality. In our designed hierarchical TiO₂@C core/shell nanostructured photocatalyst, the carbonaceous shell provides large amount of hydroxyl groups and adsorbed molecular oxygen, which increase the trapping sites for not only photogenerated holes, but also photogenerated electrons by adsorbing more molecular oxygen, resulting in more hydroxyl radicals to participate the photocatalytic reaction. These functional products were characterized in details in terms of their structure and morphology using XRD, SEM, EDX, and TEM among others. Moreover, their high photocatalytic properties for destruction of toxic dye molecules were studied carefully. We also will present our studies on establishing the basic photodegradation mechanisms, identifying the effective disinfection factors, and investigating the disinfection kinetics for practical purposes.

Catalytic oxidation of alcohols by nickel phosphine complexes with pendant amines

Charles J Weiss, Charles.Weiss@pnnl.gov, Monte L Helm, Aaron M Appel, Parthapratim Das. Pacific Northwest National Laboratory, Richland, WA 99352, United States

The electrocatalytic oxidation of alcohols is of great interest for both synthetic and energy storage applications. We are developing a series of homogeneous nickel electrocatalysts of the formula Ni(PT²⁺₃Nₓ)₃(CH₃CN)₃(BF₄)₂ (R = tBu, Bn, or Ph; x = 2-3) with phosphine ligands containing pendant amines to act as internal bases to facilitate the movement of protons. Studies using Et₃N and Cp₂FeBF₄ as the base and oxidant, respectively, demonstrate that the catalysts are able to effectively oxidize both primary and secondary alcohols to their respective aldehydes and ketones. An examination of rates found that with more basic pendant amine bases, significantly higher catalytic rates are observed suggesting involvement of the pendant amines in the oxidation reaction. Additional results from kinetic and mechanistic studies will be presented.

Hexadecacobalt-substituted polysilicotungstate water oxidation catalyst
A new polysilicotungstate containing 16 adjacent cobalt centers, $K_2[H_2[Co_{16}((OH)_5(PO_4))_4(SiW_{34}O_{114})] 37H_2O$, has been synthesized and characterized by X-ray crystallography, infrared and UV-vis spectroscopies, elemental analysis and cyclic voltammetry. It is an effective water oxidation in a photo-driven system with $[Ru(bpy)_3]^2^+$ as photosensitizer and Na$_2$S$_2$O$_8$ as the sacrificial electron acceptor. Several arguments are consistent with the hexadecacobalt-substituted polyoxometalate being the dominant water oxidation catalyst. The work was funded by DOE Solar Photochemistry (grant DE-FG02-07ER15906).

**INOR 845**

**Oxidation and oxygenation catalysis with metal-organic ligands lacking C-H bonds**

Hemanthbhai H Patel, Andrei I Loas, Karpagavalli Ramji, Sergiu M. Gorun, sergii.gorun@shu.edu. Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079, United States

The catalytic transformation of organic substrates using air is a topic of current interest. Organic-based catalytic materials capable of energy or electrons accumulations, followed by their transfer to dioxygen are rendered labile by their C-H bonds. We report the synthesis of a new class of organic-metal complexes derived from phthalocyanine ligands, heme analogues, complexes that exhibit only C-F bonds. Several representatives, exhibiting a stepwise increase in steric bulkiness imparted by an increase in the number of perfluoro isopropyl substituents have been synthesized. Single-crystal X-ray structures reveal the onset of solid-state p-stacking aggregation, as well as the counterintuitive, preferential formation of cis-type, sterically crowded isomers. Variable aggregation in solution is also noted. The closed-shell zinc complexes transfer solar energy to O$_2$ to generate singlet oxygen that can either constructively oxygenate or destructively oxidize organic substrates. The open-shell cobalt complexes oxidize C-H and S-H bonds to form C=O or S-S links, respectively. The substitution of aromatic fluoro groups by aliphatic ones, a process that diminishes the extent of π-stacking appears to be the key factor in imparting the favorable catalytic properties. Furthermore, the catalysts appear very stable under both oxidation and oxygenation conditions, thus meeting a challenge in homogeneous catalysis, namely the rational design of reactive molecules that are not only active, but resist self-oxidation as well.

**ACKNOWLEDGMENTS**

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**INOR 846**

**Protonation of mono-N$_2$ complexes: A DFT investigation**

Aaron W Pierpont, aaron.pierpont@pnnl.gov, Michael T Mock, Roger Rousseau, William G Dougherty, Scott Kassel, Morris Bullock. (1) Center for Molecular Electrocataylsis, Pacific Northwest National Laboratory, Richland, Washington 99354, United States (2) Department of Chemistry, Villanova University, Villanova, PA 19085, United States

Recently, several low valent Cr(0)-N$_2$ complexes exhibiting stoichiometric production of hydrazine and/or ammonia upon treatment with acid have been synthesized. These complexes are supported by macrocyclic phosphorus based ligands containing pendant amines, which along with the Cr(0) center are significantly more basic than the coordinated N$_2$. In this presentation, DFT computations are performed to evaluate the thermodynamics of protonating these complexes, and ligand modifications are proposed in order to direct the thermodynamics toward preferential N$_2$ protonation in an effort to develop a Cr based N$_2$ reduction catalyst.

**INOR 847**

**Non-line-of-sight deposition of nanoscale separator/electrolytes for 3D all-solid-state batteries**

Megan B. Sassin, meganbou@msn.com, Jeffrey W. Long, Debra R. Rolison. Chemistry, U.S. Naval Research Laboratory, Washington, DC 20375, United States

All-solid-state 3D batteries are poised to offer unprecedented combinations of energy and power in a single device, but their realization is currently hindered by challenges associated with the separator/solid-state electrolyte component, which must be ultrathin, pinhole-free, electronically insulating, ionically conducting, and electrochemically stable. In addition to achieving these physical properties, the electrolyte component must be incorporated within complex 3D battery architectures, necessitating the use of non-line-of-sight fabrication methods. Previously, we demonstrated that electropolymerization via electro-oxidation of phenol-based monomers produces nanoscale, conformal, pinhole-free, electronically insulating polymer coatings on ultraporous complex electrode architectures that function as a separator/solid-state electrolyte. To expand the library of separator/solid-state electrolytes and increase fabrication versatility, we are also exploring electropolymerization via electro-reduction. As a preliminary example, we electrodeposited siloxane-based polymer films from 1,3,5-trivinyl-1,3,5-trimethylcyclosiloxane (D$_3$V$_3$) on 2D planar and 3D macroporous electrode architectures. The low electronic conductivity and high dielectric strength render siloxane-based polymers as ideal battery separator candidates, while the ether groups in the D$_3$V$_3$ monomer promote Li$^+$ solvation and transport, providing sufficient ionic conductivity for function as a solid-state separator/electrolyte.

**INOR 848**

**In-situ neutron diffraction of lithium vanadium oxide cathodes**

Tyler M Fears, tmf9rc@mst.edu, Nicholas Leventis, Chankila Sotiriou-Leventis, Jeffrey G Winiarz, Haskell Taub, Helmut Kaiser. (1) Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409, United States (2) Department of Physics and Astronomy, University of Missouri - Columbia, Columbia, Missouri 65211, United States (3) University of Missouri Research Reactor, University of Missouri - Columbia, Columbia, Missouri 65211, United States

The performance of Li-ion battery electrodes is dependent upon the crystal structure of the intercalation material and its evolution during cycling. Methodology for structural studies under realistic operating conditions has been developed using synchrotron radiation for in-situ x-ray diffraction in coin cells. Neutron diffraction has the advantage of being sensitive to Li, which is transparent to x-rays; additionally, vanadium is practically transparent under neutron diffraction, allowing independent refinement of V-O and Li-O lattices in lithium vanadium oxides (Li$_x$VO$_3$) using complementary diffraction techniques, as illustrated below (note 1.81, 2.66, and 2.79 Å$^*$).
The limiting factor in in-situ neutron diffraction is incoherent scattering from hydrogenous components, which reduces signal and increases background intensity. Deuteration and fluorination of hydrogenous components reduces incoherent scattering, e.g. replacing polyvinylidene difluoride with polytetrafluoroethylene as the electrode binder. The major source of hydrogenous material in a typical Li-ion cell is the carbonate-based electrolyte. Unfortunately, deuteration and fluorination of these carbonates is not feasible due to cost and reactivity, respectively. Other advanced electrolyte systems, such as ionic liquids, do not mitigate these issues, necessitating the development of novel electrolyte systems specifically for in-situ neutron diffraction.

This presentation will discuss in-situ neutron diffraction in Li-ion electrode materials in the context of Li$_x$VO$_x$. Focus will be placed on the neutron scattering properties and electrochemical performance of deuterated perfluorocarboxylate esters as electrolyte solvents, e.g. d$_3$-methylheptafluorobutyrate (CF$_3$CF$_2$CF$_2$COOCD$_3$).

INOR 849
Polyoxometalates as electron mediators for better Li-S cell performance
Wonsung Choi, Dongmin Im, dongmin.im@samsung.com, Min Sik Park, Dong Joon Lee, Young-Gyoon Ryu, Seung Sik Hwang. Energy Lab, Samsung Advanced Institute of Technology, Yongin, Gyeonggi-do 446-712, Republic of Korea

Li-S battery is being considered a candidate as a future power source for electric vehicles since it can potentially provide a very large energy density. Nonetheless, the formation of soluble intermediate species such as polysulfides makes the redox chemistry of sulfur less reversible and therefore restricts the practical use of Li-S battery. While most approaches pursue the confinement of polysulfides in nanostructured conductive networks, this study explores a feasibility of using electron mediators to convert polysulfide species away from the conductive network. A Keggin-type polyoxometalate has been selected as the mediator based on the redox potential calculation using a density functional theory (DFT) method. The DFT study has also shown how the selection of composing elements affects the electronic properties of Keggin compounds. A series of electrochemical cell tests reveal that only a small amount of mediator molecules (10 mM) in nonaqueous electrolyte can significantly improve both the reduction and the oxidation reactions of Li-S chemistry.

INOR 850
New methods for modification of electrodes by metal complexes
Matthew V. Sheridan¹, mvsherid@uvm.edu, Kevin Lam², William E. Geiger¹. (1) Department of Chemistry, University of Vermont, Burlington, VT 05405, United States (2) Department of Chemistry, Nazabayev University, Astana, Kazakhstan

Methods will be described for electrode modification by wide range of molecules bearing a terminal alkyne or alkene group. For the former, either direct anodic oxidation of the alkynyl group or oxidation of the lithio-activated alkyne may be employed:

\[
\text{M} \rightarrow n\text{-BuLi} \text{ and/or } - e^- \rightarrow \text{M}
\]

M = organometallic complex

A number of metallocenes have been covalently attached to various metal surfaces and characterized by their electrochemical responses. Porphyrins and metallo-porphyrins have also been covalently attached. Fundamental aspects of the electrode modifications will be examined and possible applications to catalysis and sensing will be discussed as time permits.
**INOR 851**

**Electrochemically driven functionalization of metal oxide surfaces using aryl iodonium salts**

**Kristin J. Suhr**, kristin.suhr@cm.utexas.edu, **Matthew R. Charlton**, **Keith J. Stevenson**, **Bradley J. Holliday**. Department of Chemistry, The University of Texas at Austin, Austin, TX 78712, United States

Indium tin oxide (ITO) is a ubiquitous transparent conducting oxide that can easily be deposited into thin films for applications in electronics, light-emitting diodes, solar cells, and other optoelectronic devices. However, various materials (e.g., PEDOT:PSS) are commonly used to ease the work function transition between the inorganic oxide and functional organic thin film layers in device architectures. Although these types of materials are widely commercially available, batch to batch inconsistency and supplier variations can often be problematic for the reproducible fabrication of devices. One approach to circumvent these issues involves electrode surface modification by chemical functionalization. This approach utilizing grafting of molecular compounds to transparent thin film conductors, such as ITO, titanium dioxide, and graphene, is attracting increasing research interest. Generally, aryl diazonium salts have been previously used to chemically modify electrode surfaces, however spontaneous grafting can occur and there is little control over the reaction rate. In contrast, iodonium salts have more negative reduction potentials and have shown electrochemically initiated bonding to a variety of substrates. Electrochemical reduction and subsequent dissociation of aryl iodonium salts results in grafting of an electrically insulating layer of the aryl moiety onto the metal oxide surface. Passivation of the electrochemical reactivity of the metal oxide can be seen, along with an increase in the work function. In this way, the judicious design of aryl iodonium salts can potentially lead to a new strategy to functionalize metal oxide surfaces and provide a bridge between the work function of inorganic metal oxides and the organic device active layer. The synthesis, characterization, and electrochemistry of several aryl iodonium salts will be discussed.

**INOR 852**

**Enhancing tungsten trioxide photoanodes through electrochemical doping**

**Jing Zhao**, jjzhao@ucdavis.edu, **Frank E. Osterloh**. Department of Chemistry, University of California, Davis, Davis, California 95616, United States

Tungsten oxide (WO₃) with a bandgap of 2.6-2.7 eV has drawn frequent attention as a photoelectrode material for water oxidation — an important step in generating hydrogen fuel from sunlight and water. Here, we present a reduction-induced activity enhancement by 5-10 fold, when a WO₃ photoanode is conditioned at -0.04V vs. NHE for 60 seconds. Both macro- and nanostructured WO₃ electrodes can be successfully activated through this mild reduction, but a greater boost in photocurrent was observed in WO₃ electrode of larger average particle size, as characterized by SEM and TEM. The activation is not due to the change in charge injection kinetics, but the increase in carrier concentration and film conductivity, as verified by overpotential and electrochemical impedance measurements on both macro- and nanostructured WO₃ electrodes. As revealed by UV–Vis, W⁶⁺ species are formed upon reduction, which effectively dope the WO₃ film and enhance its n-type characteristic, leading to the observed photocurrent increase. The activated performance remains stable both in air and under the cell operating condition after 60 minutes. Besides, this activation methodology is also applicable to BiVO₄ photoanodes.
INOR 853
Reduction potentials and hyperfine electron affinities of O₂
Edward C M Chen¹, edcmchen@gmail.com, Sunil Pai², Herman Keith³, Edward S. Chen⁴. (1) Natural and Applied Sciences, University of Houston, Clear Lake, Houston, TX 77025, United States (2) Department of Physics, Stanford University, Stanford, California 93405, United States (3) none, Wentworth Foundation, Houston, TX 77025, United States (4) Department of Molecular and Human Genetics, Baylor College of Medicine, Houston, TX 77030, United States
The presentation demonstrates how hyperfine electron affinities for the dioxygen molecule can be determined by conducting several cyclic voltammetry scans over the temperature range of 298 K to 409 K. It was discovered that electrochemical data can be assigned to the 27 bonding quantum mechanical spin states for the superoxide radical (O₂⁻) that have been observed in the gas phase. Also, relative anion bond orders and the electron correlation of the hydride anion the estimation of the stabilities of the 54 spin electron affinities for the dioxygen molecule predicted by quantum mechanics that are used to calculate anion Morse potentials.

INOR 854
Electrocatalytic water oxidation with a manganese pyrophosphate compound
Toshihiro Takashima¹, ttakashima@yamanashi.ac.jp, Yuki Hotori², Hiroshi Irie¹⁵. (1) Clean Energy Research Center, University of Yamanashi, Kofu, Yamanashi 4008511, Japan (2) Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Kofu, Yamanashi 4008511, Japan (3) Japan Science and Technology Agency/CREST, Japan
Development of an active electrocatalyst for the oxidation of H₂O to O₂ has been an intensive research subject owing to its importance to construction of artificial photosynthetic systems. To realize efficient O₂ evolution under neutral pH conditions, a notable number of water oxidation catalysts including simple and mixed-metal oxides and organometallic complexes have been synthesized. On the other hand, few studies have been reported concerning O₂ evolving activity of polyanion-based metal compounds which have been extensively studied as a positive electrode material of a Li-ion battery. In this study, we examined the capability of pyrophosphate-bridged manganese compounds to drive water oxidation reaction electrochemically, and CaMnP₂O₇ was found to be a promising candidate for an active O₂ evolution electrocatalyst under neutral pH conditions where a conventional first-low transition metal oxide electrocatalyst shows a moderate activity as shown in Figure 1.

INOR 855
Multielectron transfer processes in strongly coupled bis(pyridinium) systems
A series of phenylene-bridged bis(pyridinium) compounds was prepared by reaction of the appropriate alkyl or aryl amine with the corresponding bis(pyrylum) species. For most p-phenylene-bridged derivatives, cyclic voltammetry reveals a fully reversible reduction, and peak separations are suggestive of a two-electron process. This has been confirmed by the covalent attachment of ferrocenyl moieties as internal electron counters. For the m-phenylene-bridged derivatives, initial reduction is split into two closely spaced one-electron processes. Both p- and m-phenylene-bridged isomers also display a second, generally quasi-reversible multielectron reduction peak, the position of which is sensitive to the nature of the N substituent.

Quantum calculations were employed to examine the molecular and electronic structures of the parent bis(pyridinium) dications, as well as the corresponding one-electron and two-electron reduced species (cation radicals and neutrals, respectively). The lowest energy state of the neutral species for all meta derivatives was a triplet, while for para derivatives, it was a singlet. Further, the neutral para systems show a distinct and pronounced bond length alternation pattern, indicative of a quinoidal structure.

Finally, a detailed spectroelectrochemical investigation of the p-phenylene-bridged compounds indicates the presence of radical cation only at low conversion, suggesting that the inherent stability of the quinoidal form drives a rapid and efficient disproportionation.

INOR 856
Na storage and diffusion in bulk and nanostructured C, Si, Ge, and Sn-based anode materials

Oleksandr I. Malyi1, mpeom@nus.edu.sg, Fleur Legrain1, Vadym V. Kulish2, Teck L. Tan3, Sergei Manzhos1. (1) Department of Mechanical Engineering, National University of Singapore, Singapore, Singapore (2) Singapore University of Technology and Design, Singapore, Singapore (3) Institute of High Performance Computing, Singapore, Singapore

The search for high capacity anode materials for metal-ion batteries is an active area of research. Group IV (C, Si, Ge, and Sn) based electrodes can provide ultra-high specific capacities and volumetric energy densities for metal-ion batteries. Nevertheless, diffusion anisotropy induced by dopant-dopant interactions or/and by high insertion barriers can make the theoretical capacities unreachable at high charge/discharge rates [1, 2]. Using first-principles calculations, we study the interaction of Na atoms with bulk (crystalline and amorphous) and nanostructured group IV (C, Si, Ge, and Sn) materials. We show that the chemical interactions are sensitive to bulk-nanostructure transition [3, 4], anode preamorphization, and/or phase transition. For instance, the charge transfer from Na atom to Si nanosheet and Si bulk are ~0.90e[3] and ~0.75e[1], respectively. Such differences in Na-anode interaction affect both Na storage energetics and the dependence of the diffusion barrier on dopant-surface distances [4]. Moreover, in some cases, the insertion of Na atoms becomes thermodynamically and kinetically unfavourable [3]. Based on the calculations, we show that the insertion of Na atom in pure Si and C anode is limited but could be enhanced by anode amorphization or doping/alloying. In contrast, both bulk Sn and nanostructured Sn anodes are suitable for Na-ion batteries [5].

References

INOR 857
Tris(alkyne) complexes of coinage metal ions

Animesh Das1, animeshd@uta.edu, Mehmet Ali Celik2, Gernot Frenking2, Muhammed Yousufuddin1, H. V. Rasika Dias1. (1) Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, United States (2) Fachbereich Chemie, Philippus-Universitat Marburg, Marburg, Germany

Coinage metal (Cu, Ag, Au) mediate many organic transformations involving alkynes are believed to be initiated by the π complexation of alkyne to the electrophilic coinage metal(I) center. Therefore, isolable coinage metal–alkyne adducts are of considerable interest. Molecules with more than one π-bonded ligand on coinage metals are extremely rare and structural data on such systems are not readily available. We have synthesized a series of tris(alkyne) adducts of copper(I), silver(I) and gold(I) using cyclooctyne as the alkyne moiety. To elucidate the nature of coinage metal-alkyne interaction, detailed computational studies have been carried out. Herein, the synthesis, characterization and computational details of these rare adducts will be discussed. Moreover, gold catalyzed various reactions of alkyne are also presented.

INOR 858
Phosphorescent C^C* cyclometalated Pt(III) NHC emitters

Alexander Tronnier, alexander.tronnier@chemie.tu-dresden.de, Thomas Strassner. Physical Organic Chemistry, TU Dresden, Dresden, Saxony 01069, Germany

Over the past ten years phosphorescent transition-metal complexes have emerged as an interesting class of compounds for application as emitters in organic light-emitting devices (OLEDs). Due to the effect known as triplet harvesting, quantum yields of up to 100% are possible, which makes them more efficient than fluorescent lumophores.

We report on a series of mono- and bimetallic N-heterocyclic C^C* cyclometalated platinum(III) complexes as a new class of efficient phosphorescent emitters for OLED applications. Due to different substitution patterns the electronic nature of the emitting state can be altered, which allows to tune the emission behaviour. The synthesis, solid-state structures and photophysical properties are presented together with quantum chemical DFT calculations.

INOR 859
Cyclometalated Pt(II) complexes based on phenyltriazol-5-ylidenes

Mario Tenne, mario.tenne@chemie.tu-dresden.de, Thomas Strassner. Physical Organic Chemistry, TU Dresden, Dresden, Saxony 01069, Germany

Cyclometalated platinum(II) complexes represent a promising class of phosphorescent emitting molecules for application in organic light-emitting diodes (OLEDs) due to their luminescence properties.

We present two new classes of heteroleptic platinum(II) complexes [Pt(C^C*)(O^O)] [O^O = pentane-2,4-dionato, acac] containing cyclometalating ligands based on 1-phenyl-1,2,4-triazol-5-ylide and 4-phenyl-1,2,4-triazol-5-ylide. Both types of complexes are emissive in the blue region of the spectrum. They are sensitive to the electronic properties of substituents at the phenyl ring. The synthesis of these new complexes, their molecular structures and photophysical properties are reported.

INOR 860
Lewis acid promoted formation of acrylate from nickelalactone complexes

Dong Jin, dongjin@brown.edu, Wesley Bernskoetter. Department of Chemistry, Brown University, Providence, RI 02912, United States

Transition metal mediated methods for the conversion of CO$_2$ has the potential to provide more sustainable and economically attractive syntheses for acrylate and other commodities. Among the leading avenues of exploration has been the conversion of the nickelalactone complexes, formed by coupling of CO$_2$ and ethylene, to the corresponding nickel n$^2$-acrylic acid species via $\beta$-hydride elimination. This key step in acrylate formation at nickel has remained elusive with few known examples. Lewis acids, such as tris(pentfluoropheny1)borane, tetrakis[3,5-trifluoromethyl]phenyl]borate, were found to induce $\beta$-hydride elimination from these nickelalactone complexes. Following treatment with select Bronsted bases, nickel n$^2$-acrylate complexes were produced, completing a net conversion of nickelalactone to acrylate. Our on-going investigations of the technique and its development toward catalytic methods of CO$_2$ functionalization will be discussed.

INOR 861

Reduction of carbon dioxide to acrylate, formate and propionate at Triphos molybdenum complexes

Yuanyuan Zhang, yuanyuan_zhang@brown.edu, Wesley Bernskoetter. Department of Chemistry, Brown University, Providence, RI 02912, United States

The functionalization of carbon dioxide at transition metals is one potential method of enhancing the sustainability of commodity chemicals. With this interest, our laboratory has prepared TRIPHOS molybdenum hydride complexes from sodium triethylborohydride reductions molybdenum chloride compounds and used them to promote CO$_2$ functionalization. Characterization of molybdenum hydride complexes and exploration of their reactivity towards CO$_2$ and ethylene have been investigated. In addition, efforts toward the elimination of CO$_2$ functionalized organic product from molybdenum will be discussed.

INOR 862

Ferracarborane-ruthenium tris(bipyridyl) complexes as optical small cation sensors

Scott S Graham, sgraham9@slu.edu, Paul A Jelliss, Rebecca J Callahan. Department of Chemistry, Saint Louis University, St. Louis, MO 63108, United States

Here we present the synthesis and application of various ferracarborane and tris(bipyridyl) ruthenium(II) complexes. Preliminary studies have shown that the ferracarborane complex NHMe$_3$[Fe(3,1,2-C$_2$B$_9$H$_{11}$)$_2$] can act as a phosphorescence quencher for [Ru(bipy)$_3$]([PF$_6$]).

The quenching mechanism was investigated by monitoring the efficiency of triplet state quenching at various viscosities through variation of solvent and solvent temperature. These studies revealed that quenching primarily occurs through dynamic quenching, where the ferracarborane acceptor depletes energy from the triplet state donor through non-radiative collisional impacts in solution. Other preliminary work on the ferracarborane complex [3,3’:Fe-1,2-C$_2$B$_9$H$_11$-8-O(CH$_2$)$_n$(CH$_2$)$_n$OH$^+$][Et$_3$NH]$_3$-1,2-C$_2$B$_9$H$_{10}$] has revealed that the pendant aminothioether chain can function like a crown ether, effectively chelating to small cations. In this work we aim to create a tethered ferracarborane-ruthenium complex that takes advantage of this to act as an optical sensor for small cations such as Li$^+$. Other ferracarborane applications include shifting the reduction potential of the Fe$^{III}$/II center to match the reduction potential of FAD, the cofactor of glucose oxidase. A successful anodic shift in reduction potential was observed through replacement of B-H bonds with B-Br bonds on the carborane cages to create a mono- and dibrominated complex.

INOR 863

Rhenacarboranes: Toward their use as drug delivery vehicles

Daniel G. Pruitt, dpruitt1@slu.edu, Paul A. Jelliss. Department of Chemistry, Saint Louis University, St. Louis, Missouri 63103, United States

Rhenacarboranes and their derivatives provide an attractive area of research due to their ability to cross over the blood-brain barrier (BBB). As potential drug-delivery vehicle candidates, an array of these rhenacarboranes can be synthesized and functionalized via coupling to various amino acids and polypeptides. In application, a rhenacarborane has the potential to attach to biologically active cargo that does not have the ability to penetrate and passively diffuse across the BBB and deliver it into the central nervous system (CNS). Due to the robust nature of metallacarboranes, they are not readily metabolized, which eliminates risks of heavy metal poisoning and other side effects. Our foremost objective is to synthesize a rhenacarborane complex functionalized with a pendant oligoether side-chain containing a terminal target functional group (-OH/NH$_2$) that will be able to bind with the desired polypeptide Met-enkephalin. When connected to the rhenacarborane, opioid growth factor (OGF) could be transported past the BBB and then enzymatically cleaved off the vehicle, allowing for distribution into the CNS. We also report the development of a synthetic protocol for a radiolabeled rhenacarborane derivative to assess physiological distribution as well as approached coupling strategies to link Met-enkephalin and Boc-protected tyrosine to the vehicle candidates. All complexes and intermediates were characterized by IR and NMR spectroscopy.
**INOR 864**

Mesoporous crystalline lattice, for the adsorption and fluorescent sensing, of biological compounds

**Kenneth J. MacKenzie**, kjm103020@utdallas.edu, Anne M. Marti, Kenneth J Balkus Jr.*. Department of Chemistry, University of Texas at Dallas, Richardson, Tx 75080, United States

Metal-Organic-Frameworks (MOF’s) are a class of crystalline materials known for their low densities, high surface areas, and high thermal stability. MOF’s to date have been employed for gas separations, chemical sensing, and enzyme immobilizations. A subclass of MOF’s, known as bio-Metal-Organic-Frameworks (bio-MOF’s), use zinc-adenine building unit’s (ZABU’s), as opposed to the metal ions or metal-carboxylate cluster found in many MOF’s. Many of the bio-MOF’s reported to date, have been mesoporous structures, primarily studied for their CO₂ separation capabilities. One bio-MOF in particular, bio-MOF-1, utilizes ZABU’s connected by 4,4-biphenyldicarboxylic acid (BPDC) linkers, forming a 3D, luminescent crystalline structure. In the past, bio-MOF-1 has been studied for the timed release of procainamide, an anti-arrhythmic drug. In this work, we will demonstrate bio-MOF-1’s ability to bind nucleotides, such as uracil and thymine, through the free amine functional moieties on the ZABU. Changes to bio-MOF-1’s structure were monitored quantitatively using; fluorescence, X-ray diffraction, thermogravimetric analysis, FT-IR, and UV-Vis spectroscopy.

**INOR 865**

Hydrogenation of CO₂ using non-precious metal complexes

**Marie A Barnes**, marie.barnes@chem.queensu.ca, Jianzhong Jiang², Jiasheng Lu¹, Alan Lough³, Philip G Jessop¹. (1) Chemistry, Queen’s University, Kingston, Ontario K7L 3N6, Canada (2) School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, China (3) Chemistry, University of Toronto, ON M5S3H6, Canada

Formic acid, a useful chemical feedstock for the production of valuable chemicals, currently produced from syngas, and derived from non-renewable feedstocks. In contrast, CO₂ is a cheap, benign, renewable and readily available alternative for the synthesis of formic acid.

The most studied catalysts for this reaction have been based on precious metals, with the most successful being ruthenium², rhodium and iridium phosphine complexes that can obtain high turnover numbers (TONs) and turnover frequencies (TOFs).³ However, due to the cost and scarcity of these metals, recent research has focused instead on non-precious metals. Of specific interest to our group are bisphosphine complexes of iron, cobalt and nickel. We reported our first success, a Ni catalyst, some time ago, but now we report many more examples. The use of molybdenum, indium, zinc, tungsten, manganese and niobium for CO₂ hydrogenation will also be discussed.

Catalyst = FeCl₂(dmpe)₂, NiCl₂(dmpe)₂, CoCl₂(dmpe)₂, FeCl₂ + DMPE, CoCl₂ + DMPE, NiCl₂ + DMPE, Fe(OAc)₂ + DMPE, Co(OAc)₂ + DMPE, Ni(OAc)₂ + DMPE, MCl₂ + DMPE, MCl₃ + DMPE, WCl₆ + DMPE, MnCl₃ + DMPE, NbCl₆ + DMPE.

H₂ + CO₂ → HCOOH

Our initial efforts were to identify a catalytically active species which can obtain high TONs and TOFs. We report the results, including several new catalyst precursors, and characterization of the precatalysts was accomplished through NMR spectroscopy, x-ray crystallography, high resolution mass spectrometry and elemental analysis.

References:

**INOR 866**

Ratiometric detection of nitric oxide by fluorescent organometallic Re-phenanthroline complexes

**Lissette I. Lozano-Lewis**, liloza009@fiu.edu, Kumpal Madras², Nikolaos M. Tsoukias², Konstantinos Kavallieratos¹. (1) Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199-0001, United States (2) Department of Biomedical Engineering, Florida International University, Miami, FL 33174, United States

Despite the importance of Nitric Oxide (NO) in physiology and medicine, its quantification at intracellular environments is still a topic of intense research interest and some controversy. There are several fluorescent dyes for NO detection with DAF-FM (Nagano et al; Advanced Materials, 2000, 12, 763) and Cu-FL (Lippard et al.; Nature Chemical Biology, 2006, 2, 375) being the sole commercial examples. Ratiometric dyes for NO detection are still extremely rare. Another challenge for existing dyes is determining their mechanism of action. The complex (phen)(Re(THF)(CO)₂(OTf)) shows ratiometric response upon NO addition (added in the form of NO-donor MAHMA-NONOate). FT-IR, NMR and fluorescence spectroscopy of this and analogous isolable complexes has provided evidence of possible intermediates and has helped us elucidate to an extent a mechanistic pathway for the reactivity of this new ratiometric NO dye. The NO-sensing properties of other organometallic analogs will also be discussed.

**INOR 867**
Platinum(II) assisted chlorine photoelimination from platinum(IV) chloro complexes

Tharushi A Perera, tap53t@mail.missouri.edu, Mehdi Masjedi, Paul R Sharp.Department of Chemistry, University of Missouri Columbia, Columbia, MO 65211, United States

Solar energy is the most promising carbon neutral energy source for the future. Splitting of simple molecules like HX (X = Cl, Br) has become an attractive way to convert and store solar energy. Halogen photoelimination from metal centers is the most challenging step in photochemical HX splitting cycles. We have synthesized Pt(IV) chloro complexes trans –Pt(PEI$_3$)$_2$R(Cl)$_2$ (R = Cl, aryl and PAH fragments), which eliminate chlorine in the presence of halogen cycles when irradiated with uv-vis light. The photo-efficiency of Pt–chloride bond activation increases in the presence of Pt(II) complexes trans –Pt(PEI$_3$)$_2$R(Cl)$_2$ suggesting the absence of molecular chlorine from reductive elimination of Pt(IV) chloro complexes. Also, we propose that the mechanism of halogen photoelimination from Pt(PEI$_3$)$_2$X$_3$R (X = Cl, Br) (R = aryl, Cl, PAH) complexes is cis elimination via radical abstraction.

INOR 868

Oxygen atom insertion into iron phenyl and methyl bonds

Jiajun Mei1, jm29xg@virginia.edu, Steven E. Kralman1, T. Brent Gunnoss1, Thomas R. Gundar2, Michal Sabat2. (1) Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States (2) Department of Chemistry and center for advanced scientific computing and modeling, University of North Texas, Denton, TX 76203, United States

Oxygen atom insertion into metal carbon bonds is a key step for metal-mediated hydrocarbon partial oxidation. Few examples have been reported, especially oxy-insertion into non-d$^2$ metal complexes. Cp*Fe[Cr(OCH$_3$)$_3$]$_2$(Ph) (Cp* = pentamethylcyclopentadienyl) reacts with Me$_2$NO in THF (THF = tetrahydrofuran) under photolysis or ambient light to ultimately form PhOH. Studies indicate that photolysis assists with dissociation of P(OCH$_3$)$_3$CEt. With other oxidants (e.g., periodate), the C$-$C coupling product Cp*Ph is observed. The analogous CpFe[P(OCH$_3$)$_3$]CEt[Ph and Cp*Fe[P(OCH$_3$)$_3$]CEt]Me exhibit similar reactivity.

INOR 869

Design and engineering of man-made protein maquettes for diverse functions.

Goutham Kodali1, kodalg@med.upenn.edu, Lee A Solomon1, Michael T Englander2, Bruce R Lichtenstein2, Tammer A Farid1, JL Ross Anderson3, Molly M Sheehan1, Nathan M Ennist1, Bryan A Fry1, Chris Bialas2, Joshua A Mancini1, Zhengyu Zhao1, Bohdana M Discher1, Christopher C Moser2, P Leslie Dutton1. (1) Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, PA 19104, United States (2) Max Planck Institute for Developmental Biology, Spemannstr. 36, 72076 Tübingen, Germany (3) School of Biochemistry, University of Bristol, Bristol, United Kingdom

 Developing man-made proteins that possess both customarily functions and the efficiency of natural enzymes is a major challenge of synthetic biology. Engineering such man-made enzymes would be extremely useful for the enhancement of human health and for the fulfillment of mankind's energy needs. Working towards these goals, we have designed a monomeric four-a-helix protein maquette, which can serve as a platform for a diverse set of oxidoreductase related functions. We describe the progressive design steps taken from the simplest a-helical peptide, designed using first principles, towards functionalized proteins designed using iterative rational design. We call this process of iterative rational design the maquette approach. We will present our strategies for assembly of natural cofactors such as hemes, flavins, iron-sulfur clusters and light active cofactors (porphyrins, chlorins, bilins) and many more synthetic analogues with a control over the distance and orientation that allow tuning for specific selected function. This maquette platform has considerable latitude for external charge patterning and internal control of stability, both globally and locally. We demonstrate that this platform can accomplish a variety of functions, including electron transfer to natural proteins, O$_2$ binding, CO and NO sensing, millisecond superoxide bursts and triplet excited state-driven nanosecond charge-separation followed by micro to millisecond electron tunneling reactions with minimal changes. These maquette proteins are expressed in E.coli in high yields and can be altered to assemble in water, membranes or on a range of surfaces including titania. Such versatility makes this protein platform suitable for further iterative designs for light energy harvesting, photochemical charge separation, oxygen transport, P450 catalysis and oxidative metabolism as well as for understanding of fundamental properties of enzyme activity, stability, and folding.

INOR 870

Flexible glutamine regulates catalysis within toluene/o-xylene monooxygenase

Alexandra Deliz Liang, adliang@mit.edu, Alexandra T Wrobel, Stephen J Lippard.Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Toluene/o-xylene monooxygenase (ToMO) is a carboxylate-rich diiron enzyme within the bacterial multicomponent monooxygenase family. The diiron active site is located in the hydroxylase component of ToMO (ToMOH), buried 12 Å from the surface of the protein. We describe the progressive design steps taken from the simplest o-helical peptide, designed using first principles, towards functionalized proteins designed using iterative rational design. We call this process of iterative rational design the maquette approach. We will present our strategies for assembly of natural cofactors such as hemes, flavins, iron-sulfur clusters and light active cofactors (porphyrins, chlorins, bilins) and many more synthetic analogues with a control over the distance and orientation that allow tuning for specific selected function. This maquette platform has considerable latitude for external charge patterning and internal control of stability, both globally and locally. We demonstrate that this platform can accomplish a variety of functions, including electron transfer to natural proteins, O$_2$ binding, CO and NO sensing, millisecond superoxide bursts and triplet excited state-driven nanosecond charge-separation followed by micro to millisecond electron tunneling reactions with minimal changes. These maquette proteins are expressed in E.coli in high yields and can be altered to assemble in water, membranes or on a range of surfaces including titania. Such versatility makes this protein platform suitable for further iterative designs for light energy harvesting, photochemical charge separation, oxygen transport, P450 catalysis and oxidative metabolism as well as for understanding of fundamental properties of enzyme activity, stability, and folding.

INOR 871

Copper(II) and copper(III) in copper-dioxygen systems for tyrosinase models

John B Gary, jbgary@stanford.edu, T. Daniel P. B Stack, Peng Kang.Department of Chemistry, Stanford University, Stanford, CA 94303-4401, United States

The dinuclear copper enzyme tyrosinase activates dioxygen to form a side-on peroxodicopper(II) complex, which is capable of oxidizing phenols to catechols. Several synthetic side-on peroxodicopper(II) complexes created with simple diamine ligands will be discussed that faithfully reproduce the spectrum of oxygenated tyrosinase, yet convert to Cu(II)-bis-oxide species upon phenolate addition at extreme solution temperatures. These species decay with hydroxylation of the aromatic ring by a mechanism that shares the hallmarks of an electrophilic aromatic substitution mechanism, as seen with tyrosinase. Experimental calibrated DFT calculations on these system support strongly that the bis-mu2-oxodicopper(III) species serves as an electrophilic agent in this oxidation. Overall, the evidence for sequential O=O bond cleavage and C-O bond formation suggests an alternative mechanism to the concerted or late-stage O-O scission generally accepted for phenol hydroxylation by tyrosinase. Insights into ligand and substrate binding modulation of copper(II) versus copper(III) will be discussed.

INOR 872

Enzyme immobilization in a gyroidal metal-organic-framework
Metal Organic Frameworks (MOFs) are porous crystalline structures constructed by metal centers and connected by organic linkers. MOFs are unique compared to other porous solids due to their large surface areas, high porosity, chemical and thermal stability, and tunability. By interchanging the organic linkers and or metal ions, various porous MOFs are constructed with different topologies. MOFs typically are used for gas storage/separations, chemical sensing and catalysis, and enzyme immobilization. Enzymes show high selectivity for reagent binding and exhibit low thermal stability as well as low stability in organic solvents. By using MOF's as a matrix for the enzyme, the stability issues can be overcome. Through immobilization, the enzyme is expected to thrive at higher temperatures, and in a wide range of solvent systems, thus preventing denaturation.

MOFs have been used for gas storage/separations, chemical sensing and catalysis, and enzyme immobilization. Enzymes show high selectivity for reagent binding and exhibit low thermal stability as well as low stability in organic solvents. By using MOFs as a matrix for the enzyme, the stability issues can be overcome. Through immobilization, the enzyme is expected to thrive at higher temperatures, and in a wide range of solvent systems, thus preventing denaturation.

STU – 1 is a gyroidal MOF, in which its framework has a unique minimal surface, with no straight lines and/or edges. It has high surface area (1225 m²/g) and extra large pores (27.3 × 15.4 Å). It also exhibits exceptional thermal stability (420 °C), and permanent porosity. STU-1 is constructed using zinc nitrate hexahydrate and the synthesized linker Blm.

The enzyme Microporoxidase 11 (MP-11) which has a size of 17.5 Å. The presence of the iron-heme group in MP-11 allows for the oxidation of organic molecules such as AmplexUltraRed to Resorufin [2].

STU-1 has promising characteristics that allow it to be a suitable host for MP-11. STU-1 will prevent degradation of the enzyme and prolong its catalytic activity. We expect our matrix to have improved catalytic activity as a result of the tight fit of MP-11 in the pores of STU-1, therefore the framework will protect the enzyme from denaturing in solution within the pores as well.

INOR 873

**BS-DFT calculations of µ-oxo bridge EPR parameters applied to Mn⁴⁺Mn⁴⁺ model complexes and Photosystem II**

*William M Ames¹,², ames@juniata.edu, Leonid Rapatskiy², Anton Savitsky³, Thomas Weyhermüller², Frank Neese⁴, Wolfgang Lübitz², Nicholas Cox². (¹) Department of Chemistry, Juniata College, Huntingdon, PA 16652, United States (²) Max-Planck-Institut für Bioanorganische Chemie, Mühlheim an der Ruhr, NRW D-45470, Germany*

The electron paramagnetic resonance (EPR) parameters of µ-oxo bridges have been calculated using broken-symmetry density functional theory (BS-DFT). Two dimeric Mn⁴⁺Mn⁴⁺ model complexes, BIPY and DTNE, which contain similar structural motifs seen in bioinorganic metalloproteins, were initially investigated. The comparison of raw, as calculated, BS-DFT hyperfine coupling constants (HFCCs) with experiment requires a well-known spin projection. The application of this spin projection is a simple matter for atoms that are part of only a single spin system. However, µ-oxo bridges are by their very nature part of two separate metallo-centered spin systems. As such, a new spin projection was developed to facilitate a comparison between theory and experiment. These new as-projected, calculated values, are in good agreement with experimental values (~7 MHz) obtained from ¹⁷O exchanged µ-oxo bridges probed with W-band electron-electron double resonance detected NMR (¹⁷O-EDNMR). The extension of the method to spin systems with more than two spin centers is discussed. Finally, a comparison between experimental ¹⁷O-EDNMR and BS-DFT projected values is made for the µ-oxo bridges contained in the tetra-Mn oxygen evolving complex (OEC) of photosystem II (PSII).

![BIPY and DTNE](image)

INOR 874

**Diiron hydrogenase active site models outfitted with pendant redox-active units**

*Allen M Lunsford, allen.lunsford@mail.chem.tamu.edu, Marcetta Y Darenbourg. Department of Chemistry, Texas A&M University, College Station, Texas 77845, United States*

Scientists have sought the use of H₂ as a renewable energy source for years, but as of now the cost of producing H₂ outweighs the benefits. The development of diiron constructs that are synthetic analogues of the [FeFe]-hydrogenase active site as base metals for proton reduction has attracted much attention recently. In our lab, N-heterocyclic carbenes, with allyl-ferrocenyl groups, have been prepared and attached to the diiron carbonyl model as a surrogate for the 4Fe4S cluster in the H-cluster. The 1-Imes analogue, see graphic, has almost identical ν(CO) IR bands, indicating that the pendant mesitylene or ferrocenyl groups have very little electronic influence on the neutral diiron complexes. However, the single irreversible cathodic event is some 250-300 mV more negative for the bis-ferrocenyl NHCl as compared to the 1-Imes complex. In the anodic region, the 1-Imes has a prominent quasi-reversible wave at +510 mV. The 2Fc complex displays a reversible, apparently two electron process likewise shifted negatively as compared to the 1-Imes complex with a second reversible anodic wave at +780 mV. The ferrocenes of the neutral form (2Fc) shows no influence on the electronics of the [FeFe]-H₂ase model complex as compared to 1-Imes. Four new complexes of this type have been prepared in order to establish the effects of a redox center, seated in the second coordination sphere, on the electronic and structural parameters of the 2Fe₂S core.
INOR 875
Deciphering the mechanism of carbon monoxide induced elimination of disulfide from a dinitrosyl iron complex: Hammett correlations of a series of para substituted (NHC)(SPhX)Fe(NO)₂ compounds
Randara Pulukkody¹, randara.pulukkody@chem.tamu.edu, Michael Drummond², Samuel J Kyran¹, Chung-Hung Hsieh², Donald J Daresbourg¹, Marcetta Y Daresbourg¹, (1) Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012, United States (2) Department of Chemistry, Tamkang University, New Taipei city, Tamsui District 25137, Taiwan Republic of China (3) Department of Biology and Chemistry, Azusa Pacific University, Azusa, California 91702, United States
Dinitrosyliron complexes (DNICs) are organometallic-like compounds of biological significance in that they appear in vivo as products of NO-degradation of iron-sulfur clusters or derived from the cellular chelatable iron pool (CIP); synthetic analogues have potential as NO storage and releasing agents. Their reactivity is expected to depend on ancillary ligands and the redox level of the distinctive Fe(NO)₂ unit: paramagnetic {Fe(NO)₂}⁹, diamagnetic dimerized forms of {Fe(NO)₂}¹⁰ and diamagnetic {Fe(NO)₂}²¹ DNICs (Enemark-Feltham notation). We reported (J.A.C.S, 2013) an interesting process of carbon monoxide (CO)/RS• ligand substitution from an N-Heterocyclic Carben (NHC) stabilized DNIC. Kinetic studies indicated an associative mechanism and computational investigations indicated a unique role for the delocalized frontier molecular orbitals of the Fe(NO)₂ unit, resulting in a 5-coordinate, 19-electron intermediate with the NO ligands accommodating the excess charge. To further test the computationally proposed mechanism, (NHC)(SPhX)Fe(NO)₂ derivatives with varying para-substituents at the phenyl thiolate were synthesized and characterized. The series included p-OCH₃, p-CH₃, p-Cl, p-CF₃ and p-NO₂ derivatives. Hammett correlations were analyzed to study the effects of the electron density at the N-Fe-N site on the rate of reaction. In accordance with the computational mechanistic proposal, rate enhancement was observed with electron donating substituents, while rates were seen to decrease with electron withdrawing substituents.

INOR 876
Recent advances in microwave irradiation for novel materials
David Gunn, d.gunn@milestonesci.com.Chemistry, Milestone inc, Shelton, CT 06484, United States
Microwave synthesis has been one of the most utilized tools in the last 20 years. Moving from traditional organic synthesis to materials science has transformed the way labs conduct research. Conventional heating in the formation of new nanoparticles, new catalysts and complex mixed metal organic frameworks (MOF) has now been replaced with microwave processes due to the speed with which desired products can be made. Unfortunately, conventional microwave reactors have presented challenges for conducting research such as the need to batch reactions, limited pressure capabilities and slow and uncontrolled cooling times. Single reaction chamber (SRC) microwave synthesis is a relatively new technique that offers significant benefits over traditional microwave technology, including the ability to scope reaction solvent, catalyst, reactant and reagent stoichiometry or the ability to run multiple independent reactions simultaneously in a single operation. Utilization of metal cross-linked cyclodextrin catalysts, the formation of grafted single-walled carbon nanotubes and transition metal oxyfluorides using SRC technology will be presented.
INOR 877

Dissolution of silica from rice hull ash (RHA) and other biogenics and the distillation of an alkoxysilane right out of the pot

Richard M Laine1, talsdad@umich.edu, Vera Popova2, David Pan1, Phi Doan1. (1) Macromolecular Science and Eng. and Department of MSE and Chemistry, University of Michigan, Ann Arbor, MI 48109-2136, United States (2) Mayaterials Inc, Ann Arbor, MI 48108, United States

A grand challenge in silicon chemistry is the depolymerization of silica using chemical means to produce silicon-containing compounds without first having to reduce SiO2 with C using carbothermal reduction in an electric arc furnace at 1900°C to produce metallurgical grade silicon or Si\textsubscript{met} and then oxidize it back to Si(OR)\textsubscript{4} as a means to make a distillable compound that offers access to high purity materials including precipitated silicas of use in applications ranging from polishing materials for the planarization of silicon wafers, to hard coatings for optical applications, to optical grade quartz as well as food grade silica (think toothpaste).

Silica depolymerization has been studied on and off for the last 80 years with no success in producing distillable aryl or alkoxyl silanes. We now report success in this matter using RHA and other biogenic silica sources.

RHA is produced in 100,000 ton/year quantities in the U.S. alone from the burning of rice hulls, a byproduct of rice milling. This high surface area (20+ m\textsuperscript{2}/g), amorphous, biogenic silica (typically 90 wt %) can be dissolved at temperatures of only 150-200°C using minimal amounts of base in the correct medium. Following concentration of the reaction solution, the base can be recovered and recycled. The dissolved silica can be precipitated using a variety of traditional techniques to provide silicas with surface areas ranging from 150-800 m\textsuperscript{2}/g with a variety of pore sizes and size distributions and pore volumes. We are also able to distill alkoxysilanes directly from the reaction pot to produce high purity materials for multiple applications now served by Si(OE)\textsubscript{4} produced from Si\textsubscript{met}.

This approach represents a potentially new paradigm in the production of alkoxysilanes and precipitated silicas in high purity and at very low cost compared to the traditional Si\textsubscript{met} and sodium silicate processes currently used commercially world-wide.

INOR 878

Thermotropic liquid crystalline Pt(II) complexes with a single side chain

Markrete Krikorian, mk16@mit.edu, Shuang Liu, Timothy Swager. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Liquid crystals have been studied for the last century and a half, but have only recently been explored as emissive or conductive materials. Metallomesogens benefit from the optoelectronic properties of the metal centers and the mesogenic behavior of the organic component. Here we present a series of luminescent cationic bis-cylometallated Pt(II) complexes that form hexagonal columnar mesophases. These complexes display thermotropic columnar liquid crystalline behavior in spite of only having a single sidechain. Crystals also undergo mechanochromic transformations that can be reversed with solvent.

INOR 879

Effect of cations and polar additives on the crystallinity and morphology of FAU zeolite

Shaneela Nosheen, shaneela17@yahoo.com. School of Chemical and Materials Engineering, National University of Sciences & Technology, Islamabad, Capital 44000, Pakistan

We report high crystallinities and novel changes in the morphologies of Faujasite zeolites. Faujasites (FAU) were synthesized by hydrothermal reactions of sodium aluminate and silica solutions without any seed or template. The structure and morphology of FAU was greatly altered by the addition of
different cations and polar solvents. Changes in the crystal structures and morphologies were verified with the change of alkali group members from Na, K, to Ca and use of polar solvents as additives from ethanol, propanol to ethylene glycol, propylene glycol, and glycerol. Crystal structure and morphologies were investigated by XRD, SEM, FTIR, AFM, and BET techniques. Microwave heating was used only in the nucleation phase during the synthesis of FAU to enhance the kinetics of nucleation reaction and to study the effects of dielectric constant and presence of single, double, and triple OH functional groups of polar organic additives. The use of microwave heating for nucleation reaction greatly improved the kinetics of reaction and thus greatly impacted on the crystallization of the end product especially when used additives having double and triple OH functional groups. Hydrothermal reaction without using any additives ended up in the FAU phase. However, an increase of OH ions and a change of cations played an important role in the formation of different phases and morphologies of resulting zeolites.

INOR 880
Comparative studies on fire-rated and standard gypsum wallboard
Harika Javangula1, hankajavangula@gmail.com, Quentin Lineberry2. (1) Chemistry, Western Kentucky University, Bowling Green, Kentucky 42101, United States (2) Chemistry, Western Kentucky University, Bowling Green, KY 42101, United States

ABSTRACT
Gypsum has been one of the most widely used since ancient times. Gypsum wallboard consists mainly of gypsum, i.e. calcium sulfate dihydrate, CaSO4·2H2O. In buildings, the chemical, mechanical and thermal properties of gypsum wallboard play an important role in delaying the spread of fire. This fire resistance property is mainly attributed to the absorption of energy related with the loss of hydrate water going from the dihydrate (CaSO4·2H2O) form to the hemihydrate (CaSO4·H2O) and from the hemihydrate to the anhydrous form (CaSO4) in a second decomposition. The present paper is a comparative study of commercially available standard, fire-rated type X and type C gypsum wallboards. Type X wallboards are typically reinforced with non-combustible fibers so as to protect the integrity of the wallboard during thermal shrinkage while the type C wallboards are incorporated with more glass fibers and an additive, usually a form of vermiculite. These type C wallboards have a shrinkage adjusting element that expands during the process of thermal shrinkage. Differential scanning calorimetry (DSC), thermogravimetric analysis–mass spectroscopy (TGA-MS), thermomechanical analysis (TMA), scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) were used to characterize and compare the materials. Various properties such as the heat flow, weight loss, gases evolved, dimensional changes and crystalline structures of the gypsum wallboards were studied using these instruments. The results of these tests will be presented

Keywords: gypsum, Calcium Sulfate; dehydration; thermal shrinkage; thermal decomposition.

INOR 881
Mechanism of conversion of precursors to binary semiconductor nanomaterials at low temperature
Kui Yu, kui.yu@nrc.ca. Emerging Technologies., National Research Council Canada, ottawa, Ontario K1A 0R6, Canada

Semiconductor nanomaterials are much in demand for their technologically potential in various areas. At the same time, there is a compelling need to improve their synthetic reproducibility and particle yields at low reaction temperature. Accordingly, it is of critical importance to fill in the gap in our knowledge of the fundamental chemistry involved in conversion of nanocrystal (NC) precursors to nanocrystals (NCS). In this oral presentation, I will discuss our latest experimental and computational efforts towards such fundamental understanding. The Se exchange between tri-n-octylphosphine (P(C8H17)3 or TOP) and diphenylphosphine (HPPh2 or DPP), i.e. Se-P(C8H17)3 + HPPh2 = P(C8H17)3 + Se-PhP2H, has been acknowledged to be heavily weighted toward the left. With CdSe in 1-octadecene (ODE) (at ambient temperatures) as a model systems, the mechanism of conversion of the precursors in Reaction (1) at low temperature to CdSe NCS can be more rationally investigated by reaction (3) than Reaction (2), the two reactions of which share a single conversion mechanism. We envision that our proposed mechanism, which should be generally applicable to ME semiconductor NCS, offers a practical mean to assist the design of low-temperature approaches to various binary ME and alloyed semiconductor nanomaterials.

Cd(OCC6H5)2 + Se=P(C6H5)3 + HPPh2 = CdSe NCS (1)
Cd(OCC6H5)2 + Se=PhP=H =CdSe NCs (2)
Cd(Se=PhP=H) + Cd(OCC6H5)2 + HPPh2= CdSe NCS (3)

INOR 882
Low temperature solvent processing of SnS thin films for light harvesting applications
Priscilla D Antunez, pantunez@usc.edu, Richard L. Brutchey. Department of Chemistry, University of Southern California, Los Angeles, CA 90089, United States

The sun’s potential to fulfill the increasing global energy demand in a secure, clean, and sustainable manner is hindered by the high fabrication cost of solar energy technologies. In order to address this issue, we have applied a low temperature solvent processing system for the fabrication of tin monosulfide (SnS) thin films. Recently, SnS has been reported as a highly efficient photocatalyst for water splitting. Splitting from being comprised of earth abundant elements, SnS is a relatively stable and nontoxic semiconductor. In addition, the direct (Eg = 1.07 eV) and indirect (Eg = 1.32 eV) band gaps of SnS make it attractive for light harvesting applications. We present a method to dissolve bulk material to produce semiconductor thin films that can be easily processed via spin-coating and a mild annealing step. The solution processing method preserves the material’s crystal phase and purity in addition to its optical band gap, demonstrated by comparing XRD, SEM-EDS, and UV-vis of the material before and after processing; whereas FT-IR shows the organic content in the films is eliminated after mild annealing. The material’s potential for light harvesting applications will be discussed.

INOR 883
Metal-organic routes to functional ceramics: Single source precursor approach for synthesis of alkaline earth metals and first row transition metal salts of 2-hydroxy-carboxylic acids (e.g. lactic acid, 2-methyl-lactic acid, mandelic acid, and benzilic acid) with solid MoO3 or V2O5. XRD analysis has shown that the thermal decomposition of these single source bimetallic precursors produces the target materials.

INOR 884
Tailoring organic growth modifiers of calcium oxalate monohydrate crystallization

Jihae Chung, jhchung2@gmail.com, Jeffrey D Rimer. Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204, United States

Kidney stones are one of the most common types of urinary tract diseases with the number of afflicted people on the rise. In the United States, ca. 12% of men and 6% of women develop kidney stones in their lifetime, and approximately 50% of previous stone-formers are inclined to experience reoccurrence of formation of stones. Unfortunately, there has not been any substantial improvement in therapeutic treatments over the last 30 years. Calcium oxalate monohydrate (COM) is the most common component in human kidney stones. There are four critical steps in stone formation: Crystal nucleation, growth, aggregation, and retention. Inhibiting any of these steps is sufficient to suppress stone pathogenesis. There are, in fact, many urinary components that play a crucial role in preventing stone formation, such as osteopontin, Tamm-Horsfall protein, and nephrocalcin. These components are rich in anionic groups, which promote inhibitor-crystal interactions. Moreover, the crystallographically distinct faces of COM crystals exhibit different spatial distribution and densities of calcium ions, which invoke site-specific binding of growth inhibitors. Here, we will present our studies employing a series of small organic molecules, termed organic growth modifiers (OGMs), which we benchmark against citrate (a current therapeutic agent and moderate growth inhibitor). Bulk crystallization studies were used to observe the effect of OGMs on crystal size and morphology, while the efficacy of OGMs was quantified by kinetic studies. In situ atomic force microscopy (AFM) was used to monitor COM crystal surface growth. Time-resolved AFM images provide microscopic validation of OGM efficacy and molecular recognition for different COM crystal surfaces. Collectively, these studies establish a platform for the rational design of crystal modifiers and new drugs for stone disease.

INOR 885
Formation of zero-valent metal salt-hydride complex and its unique use for nanoparticle synthesis

Michael P Rowe, michael.rowe@tema.toyota.com, Daniel Herrera, Rana Mohtadi. Toyota Research Institute of North America, Ann Arbor, MI 48105, United States

Complex hydrides have a variety of applications from reagents for chemical synthesis of nanomaterials to hydrogen storage media. Balancing the notions of functionality and stability, without losing sight for ease of synthesis, can be a difficult effort. Here we report a new complex hydride that demonstrates a very unique configuration and an opportunity for a new means of nanoparticle synthesis. When zero-valent manganese metal powder is ball-milled with lithium borohydride, a chemical change occurs (not simply a physical change), and a new reagent complex is formed. Remarkably, the Mn region of the XPS spectrum shows a reduction of the Mn 639eV peak by approximately 3eV (shown in the XPS spectrum of Mn(LiBH4)) included here). Solid state NMR analysis of the 7Li in the complex indicates an interaction between the Li and Mn. This is consistent with an intimate composition of zero-valent manganese metal and the lithium borohydride. Both FT-IR and solid state NMR indicate the BH4 ion is not reacting and is retaining its tetragonal geometry. In spite of holding onto its overall BH4 - structure, boron XPS of the Mn(LiBH4) complex does show a distinct change to the reported boron peaks versus authentic LiBH4. The Mn(LiBH4), synthetic parameters of manganese versus lithium borohydride stoichiometry, as well as, the length of ball mill processing time were investigated and are reported. The utilitarian function of this Mn(LiBH4), reagent complex to form nanoparticles of manganese alloyed with other metals is reported.

INOR 886
Molecular organometallic Pd, Cu, and Rh catalysts immobilized on oxide supports

Janet Bluemel, bluemel@tamu.edu, Johannes Guenther, Jacqueline Pope. Department of Chemistry, Texas A&M University, College Station, TX 77843, United States

Catalysts immobilized on oxide supports such as silica by bifunctional linker molecules ideally combine the recyclability of heterogeneous catalysts with the activity and selectivity of homogeneous systems. Here, we present novel di-, tri- and tetraphosphine ligands, which tether Pd, Cu, and Rh complexes to the support via ethoxysilane or phosphonium groups. Some linkers incorporating short alkyl chains display surprising reactivity with the organometallic precursors, providing a wealth of mechanistic insights gained by multinuclear NMR spectroscopy in solution. Classical CP/MAS (Cross Polarization/Magic Angle Spinning) and HPRMS (High-Resolution MAS) NMR of slurries are used to investigate the nature and mobility of all surface-bound species, providing again a plethora of unprecedented results. Based on these insights, surface-bound catalyst systems, which are prevented from deactivation by dimerization or contact with the reactive oxide surface, have been obtained. Immobilized organometallic catalysts will be presented, that can be recycled batchwise for 30 times without major loss of activity or selectivity. Based on the successful systems, as compared to less active ones with shorter lifetimes, general prerequisites and characteristics for a “winning” immobilized molecular catalyst are identified.

INOR 887
Arene ruthenium(II) and iridium(III) complexes of pyridyl-triazoles, bis-triazoles and bis-triazolyldienes: Synthesis, characterization, and catalysis

Stephan Hohloch, Stephan.Hohloch@fu-berlin.de, Lisa Suntrup, Biprajit Sarkar. Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin, Germany
Avoiding molecular hydrogen is one of the major goals in modern organic synthetic chemistry. Catalytic transfer hydrogenations have proven to be a valuable alternative to the use of molecular hydrogen. [1] In this contribution we will present the synthesis, characterization and application of new cationic arene-complexes of ruthenium(II) and iridium(III) having the general formula \([\{\text{Cym} \}\text{Ru}(\text{L}\text{Cl})^\text{+} \] or \([\{\text{Cp}'\}\text{Ir}(\text{L}\text{Cl})^\text{+} \] (Cym = p-Cymene, \(\text{Cp}' = \) pentamethyclopentadienyl) with L being bipyridine or a “click”-derived ligand like pyridyl-triazole, bis-triazole or bis-triazolylidene (abnormal carbenes). The use of these complexes as (pre)catalysts for the transfer hydrogenation of Nitrobenzene in isopropanol will be presented. [2] The influence of ligand substitution, metal substitution, and temperature variation on catalytic activity and selectivity has been investigated in this work. Furthermore mechanistic investigations will be presented to understand the reaction pathways. This is, to the best of our knowledge, one of the rare examples for the generation of azobenzene from nitrobenzene in a homogeneous catalytic pathway. [3]

In OR 888

Hybrid platinum complex – based systems for tandem aerobic methane – to methanol conversion

**Daoyong Wang**, dywang@um.edu, Andrei N. Vedernikov.Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States

In this work various combinations of two Pt(II) complexes are used to achieve aerobic methane – to – methanol conversion where one metal complex is responsible for methane activation and the second complex allows for aerobic Pt(II)Me – to – MeOH functionalization.

In OR 889

Nickel-catalyzed transformations of CO₂ into value added products

**Juventino J Garcia, juvent@unam.mx, Facultad de Quimica, Universidad Nacional Autonoma de Mexico, Mexico City, Coyoacan 04510, Mexico**

The reaction of CO₂ silanes catalyzed by low valent nickel complexes afforded in the case of Et₂SiH the reduction products Et₂SiOCH(OH)(CH₃)₂ (12 %), Et₂SiOCH₂(H)₂ (3 %) and CO, which were characterized by standard spectroscopic methods. Part of the generated CO was found as the complex [(dppe)Ni(CO)]₂ and characterized by single-crystal X-ray diffraction. When the same reaction was carried out in the presence of a Lewis acid, such as Et₂B, the hydrosilylation of CO₂ efficiently proceeded to give the silyl formate (Et₂SiOC(O)H) in high yields (85-89 %), at 80 °C for 1 h. Further reactivity of the silyl formate to yield formic acid, formamides and alkyl formates was also investigated. The use of PhSiH₃ allowed the catalytic preparation of products derived from a tandem process of reduction of CO₂ to CO and -CH₂ derivatives, to produce methyl ureas and methylamines in the presence of amines.

In OR 890

Organolanthane-catalyzed atom-efficient and regioselective dearomatization of substituted aromatic N-heterocycles

**Massimiliano Delferro**, m-delferro@northwestern.edu, Alexander S. Dudnik¹, Victoria L. Weidner², Alessandro Motta², Tobin J. Marks². (1) Chemistry, Northwestern University, Evanston, IL 60208, United States (2) Dipartimento di Scienze Chimiche, Università di Catania and INSTM, Catania, Italy

Organolanthane complex [Cp'*LaH] (1) serves as effective catalyst for the rapid and regioselective dearomatization of pyridine and its derivates using an equimolar amount of pinacolborane ([HBpin]). Remarkably, the organolanthane catalyst 1 is tolerant to polar (ester, ether, amine) and halogen (F, Cl, Br, I) substituted groups. Standard Eyring and Arrhenius kinetic analysis yield activation parameters \(\Delta H^\text{a} = 15.72 \text{kcal/mol}, \Delta S^\text{a} = -27.16 \text{cal/mol}, E_a = 16.34 \text{ (0.4) kcal/mol suggesting a highly organized transition state. The reaction rate law of dearomatization of pyridine is first-order in [1 ], “fractional” order in [pyridine], and inverse-first order in [HBpin]. These mechanistic data implicate intramolecular turnover-limiting insertion of C=N unsaturation into the Ln-H bond, in agreement with DFT calculations.**

In OR 891

Iron-catalyzed synthesis of phosphines from primary phosphines

**Justin Kane Pagano**, jkpagano@uvvm.edu, Rory Waterman. Department of Chemistry, University of Vermont, Burlington, Vermont 05405, United States

Despite the ready availability and ease of synthesis, primary phosphines remain underutilized as synthons in preparation of value-added organophosphines. Herein, we report the catalytic synthesis of phosphines with an iron catalyst CpFe(CO)₂Me (Cp = η⁵-C₅H₅). Reaction of primary aryl or alkyl phosphines with either diene or 2 equiv. of alkyne forms the corresponding phosphine in modest to high yields. This work provides a compliment to recent reports of catalytic phosphine syntheses with palladium by use of an earth-abundant catalyst and avoiding pre-fabricated P=C bonds in the substrate as well as previous work where electrochemical, metal-supported phosphinidenes allowed stoichiometric access to phosphines. The observed reactivity is most akin to α-elimination, or the extrusion of a low-valent fragment. Indeed, reaction of primary phosphate with catalytic CpFe(CO)₂Me in the absence of unsaturated substrate afford dehydrocoupling products. Exploration of catalysis scope and mechanism will be presented.

In OR 892

Heterobimetallic complexes for catalytic alkene carboxylation

**Vaishali Vajpayee**, vaishali.vajpayee@mail.wvu.edu, Trevor W Butcher, Brian V Popp.C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States

Catalytic transformation of CO₂ from a harmful greenhouse gas into useful organic compounds, has received considerable attention as a cheap and abundant carbon source. Although a variety of catalytic systems have been reported for CO₂ fixation, transition-metal-catalysed carboxylation of alkenes to generate carboxylic acids, a biologically important class of organic molecule, has remained relatively unexplored. Building upon recent work by Greenhalgh and Thomas (J. Am. Chem. Soc. 134, 11900) illustrating the success of iron complexes ligated by the pyridinediimine (PDI) pincer for
stere carbonylation, we have designed a new multifunctional PDI-phosphate ligand framework capable of forming heterobimetallic complexes. Preliminary insights into the scope and mechanism of alkene carbonylation will be discussed.

INOR 893

Correlation of ligand donicity with catalytic activity in a series of gold(I) carbene and phosphine complexes

Yohlan N Mathota Arachchige1,2, mathota@okstate.edu, James Le1, LeGrande M Slaughter1,2. (1) Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United States (2) Department of Chemistry, University of North Texas, Denton, Texas 76203, United States

Catalytic activities of transition metal complexes are influenced by both steric and electronic effects arising from ancillary ligands. In the case of linear gold(I) complexes, the available evidence suggests that ligand electronic effects are more important. However, available methods to investigate the donor abilities of ligands are not easily conducted with gold(I) complexes. In this study, the donor abilities of selected carbene ligands, including N-heterocyclic carbenes (NHCs), abnormal N-heterocyclic carbenes (aNHCs), and acyclic diaminocarbenes (ADCs), as well as phosphine ligands, at a gold(I) center were studied. Methyl isocyanide adducts and 1,3-disopropylbenzimidazolin-2-ylidine (Pr2-bimyl) adducts of a series of gold complexes were synthesized as IR probes and 13C NMR probes, respectively. The gold-catalyzed intramolecular cyclization of alkynes, which is known to be accelerated by strong donor ligands, showed an inverse relationship between the δν of the MeNC IR probe and the reaction rate. The same trend was observed with the 13C NMR probe, but the MeNC IR probes gave a better correlation with catalytic rates. Explanations of the observed donicity trends in terms of bonding effects will be discussed.

INOR 894

Dehydrocoupling of amine boranes and subsequent transfer hydrogenation of alkenes and alkynes via triamidoamine-supported zirconium catalysts

Karla Erickson, karla.erickson@uvm.edu, Rory Waterman. Department of Chemistry, University of Vermont, Burlington, Vermont 05405, United States

The dehydrocoupling of amine boranes has been intensely studied due to interest in their application as a hydrogen storage material. Our interest and studies focus on how amine boranes are dehydrocoupled via non-traditional dehydrocoupling catalysts. This has mechanistic implications in the design of novel and active catalysts. Herein, we present the use of triamidoamine-supported zirconium catalysts, N2N2X (N = N(CH2CH2NSiMe3)2, X = Me2S, Cl2, OBu2), in the formation of borazines and borazanes from RR'NHBH2 (R = R' = Me, H; R = 'Bu, R' = H), in good yields and under mild conditions. As these catalysts cannot participate in α-bond metathesis due to the strong Zr–X bond, it is proposed that this occurs via a ligand-assisted mechanism which also can participate in transfer hydrogenation of unsaturated organic substrates of varying electronics and sterics. This is a rare example of a group 4 hydrogenation catalyst and has been demonstrated for a range of alkenes and alkynes using amine boranes as a source of hydrogen. In this presentation, the full substrate scope and mechanistic details of both processes will be described.

INOR 895

Synthesis and reactivity of phosphinite-amino (NCP) complexes of rhodium

Jaime A Flores, ja3655@rci.rutgers.edu, Thomas J Emge, Alan S Goldman. Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854, United States

The ligand precursor 1,3-(di(t-butyl)phosphino-0xy)(di(isopropyl)amino)methyl]benzene (“NCP-H”) has been used to synthesize pincer (kappa-3-NCP) rhodium complexes, including (NCP)RhHCl. A comparison of their reactivity with the corresponding PCP pincer complexes, with respect to both the differences engendered by a coordinated amino group vs. a phosphino group, as well as the possibility of hemilability resulting from dissociation of the amino group, has been initiated.

INOR 896

Exploiting P22 virus-like particles as contrast agents for magnetic resonance imaging (MRI)

Trevor Douglas1,2, tdougla.iu@gmail.com, Shefaz Qazi2, Masaki Uchida2, Janice Jucon2, Ethan Edwards2. (1) Department of Chemistry, Indiana University, Bloomington, IN 47405, United States (2) Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, United States

We have explored virus-like particles (VLPs), derived from the bacteriophage P22, as macromolecular T1-enhanced contrast agents for magnetic resonance imaging. We have utilized the large interior volume of the P22 capsid by growing a functionalizable polymer, constrained to the interior volume of the capsid and attached multiple metal ion chelates to complexes to polymer. To accomplish this we have exploited two different polymerization techniques, both of which allow for high loading of the metal ion and result in extremely high relaxivities.

In one approach we used an iterative azide-alkyne click reaction to grow a branched polymer inside the P22 cavity and attach multiple Gd-DTPA complexes. This resulted in a payload of 1,900 Gd per P22 with high relaxivities and an optimized rotational correlation time for this system. The stepwise nature of this approach made it inefficient for full utilization of the interior cavity of P22. A second approach used a one-step atom transfer radical polymerization (ATRP) reaction to incorporate a cross-linked polymer consisting of poly(2-aminoethyl methacrylate) (AEAM) monomers attaching 9,100 Gd per P22. Significantly more Gd is incorporated than in previous reports using virus capsules, placing this construct at the upper end of observed macromolecular relaxivities. As an alternative to Gd-based agents, we have investigated the attachment of manganese protoporphyrin complexes (MnPP) onto the ATRP polymer. Using simple EDC/NHS coupling, we loaded 1,200 Mn/capsid. While these have lower ionic relaxivities than the Gd-DTPA P22, they do exhibit high per particle relaxivity.

These approaches highlight the use of P22 in the development of VLP-based MRI contrast agents. Current efforts are towards addition of peptide ligands on the external surfaces of P22 for targeting and imaging atherosclerotic plaque. These agents can potentially be administered at low doses and still provide high contrast images, meeting an important criterion for next-generation diagnostic tools.

INOR 897

Enzyme-responsive PARACE and T1 probes based on a self-immolative approach

Eva Toth1, eva.jakabtoth@cnrs-orleans.fr, Sara Lacerda1, Jiefang He2, Celia Bonnet1, Thomas Chauvin1, Bernard Badef1, Philippe Durand2. (1) CNRS, Center of Molecular Biophysics, Orleans, France (2) CNRS, Institut of Chemistry of Natural Substances, Gil/lyvette, France

Enzymes have a special importance in biological processes and represent a major class of molecular biomarkers in imaging. MRI probes can be useful to detect enzymatic activities associated to a disease state. Importantly, enzymatic activation of a pro-MRI agent can circumvent the problem of low sensitivity, as the transformation of a large amount of the agent can be realized through multiple enzyme catalytic cycles.

We have previously developed a versatile platform of enzymatically activated PARACE agents based on coupling an enzyme specific substrate to a lanthanide chelating unit via a self-immolative spacer (1,2). We report here a new generation of self-immolative probes that provide an enzymatic response both in PARACE and relaxivity (Figure 1). The Gd analogue shows an increase of 300 % in relaxivity upon enzymatic reaction thus functions as a switch on/off probe. This relaxivity variation has been rationalized in terms of an increase in the hydration number from zero for GdL1 to...
one for GdL2. Among the analogues formed with other paramagnetic lanthanides, nine complexes present a PARACEST effect either before or after enzymatic cleavage.

**Acknowledgements**

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**References**


**INOR 898**

Signal amplification by reversible exchange (SABRE): An avenue for “steady-state” hyperpolarization?

Karlso X Moreno¹, karlos.moreno@utsw.edu, Warren Goux¹², Khaled Nasr¹, Zoltan Kovacs¹, Dean Sherry¹². (1) Advanced Imaging Research Center, University of Texas Southwestern Medical Center, Dallas, TX 75390, United States (2) Department of Chemistry, University of Texas - Dallas, Richardson, TX 75083, United States

The detection and diagnosis of disease non-invasively is achieved with varying success by several technologies. Magnetic resonance (MR) spectroscopy is one of the more non-invasive modalities but is an insensitive method, even for proton. The low sensitivity of MR limits the technology to mostly structural information of tissue. To gain metabolic information, a nucleus such as carbon-13 would be ideal due to its large chemical shift dispersion, but it suffers from low natural abundance and has \( \sim \frac{1}{2} \) the sensitivity of proton. Nearly a decade ago, the process of liquid-state dynamic nuclear polarization (DNP) was introduced which increased the sensitivity of \(^{13}\text{C}\) MR >10,000 fold by changing the distribution of nuclear spins to a non-Boltzmann state (Figure 1). DNP technology offers great enhancements of MR signal, but suffers from long polarization times and is available for only a ‘single-shot’ of polarized material. More recently, a different method of polarization was developed, Signal Amplification By Reversible Exchange (SABRE), wherein the target substrate is polarized through the scalar coupling with parahydrogen bound to an iridium-based catalyst. SABRE provides shorter polarization times; tens of seconds. Current technology of SABRE provides enhancements of several hundred. Here we describe methodology for catalyst development, such as solid supported catalysts, for increased polarization of biologically relevant substrates. Solid supported catalysts allow for a continuous flow of substrate and paraghydrogen, thus leading to ‘steady-state’ hyperpolarization studies of biochemical pathways.

**INOR 899**

Molecular imaging probes for investigating cell patterning and recognition events

Thomas J. Meade, tmeade@northwestern.edu. Chemistry, Northwestern University, Evanston, IL 60208, United States

The quest to understand fundamental biological questions has driven technological advances in an emerging, and rather fast changing area of research known as molecular imaging. One technique that has been a powerful tool in clinical and biological settings is magnetic resonance imaging (MRI). It is non-invasive and yields a true volume rendering of the subject with cellular resolution (10 microns).

To permit the direct observation of ongoing developmental events in living embryos, the descendants of individual precursors in an intact embryo are labeled by microinjection of a stable, nontoxic, membrane impermeable MRI lineage tracers. Since a complete time-series of high-resolution three-
dimensional MR images can be analyzed forward or backward in time, one can fully reconstruct the cell divisions and cell movements responsible for any particular descendant(s). Unlike previous methods, where labeled cells are identified at the termination of the experiment, MR imaging allows the entire kinship relationships of a clone to be determined.

We have been investigating the development of molecular MR probes that are bio-activated (in-vivo) and report this information in the form of an acquired 3D-MR image. The agents modulate fast water exchange with the paramagnetic center, yielding distinct "strong" and "weak" relaxivity states. The modulation is triggered by two types of biological events: i. enzymatic processing of the contrast agent and, ii. the reversible binding of the ions Ca(II) and Zn(II).

INOR 900

Dual-frequency MRI contrast agents for visualization of biological processes

Goran Angelovski, goran.angelovski@tuebingen.mpg.de. Max Planck Institute for Biological Cybernetics, Tuebingen, Germany

Magnetic resonance imaging (MRI) is one of the most important tools in clinical diagnostic and biological research. Lately, the development of 19F based MRI methods has been receiving increased attention due to its ability to overcome specific drawbacks associated with standard 1H MRI techniques. When combined, 1H and 19F MRI provide the opportunity to generate complementary information by using common expertise and instrumentation.

We prepared a series of macrocyclic, fluoride-containing aryl-phosphonates and a range of their complexes with paramagnetic and diamagnetic ions. We also investigated various physico-chemical properties of the obtained molecules using a number of techniques. Thermodynamic and kinetic stability studies render them suitable for further in vivo characterization. The complexes exhibit high proton longitudinal relaxivities while displaying an increase in 19F relaxation rates which are favourable for 19F MRI experiments. Their potential was finally examined in the respective MRI phantom experiments.

Subsequently, responsive complexes that contain Ca2+ chelator in between paramagnetic and fluorine-containing moieties are prepared. favourably, they are capable of reporting the changes in Ca2+ concentrations simultaneously by 1H and 19F MRI. Extensive studies revealed mechanisms which underline the intramolecular changes triggered by Ca2+, and are responsible for the alternation of MRI signals at both frequencies.

A new generation of dual-frequency probes suitable for both 1H and 19F MRI opens novel perspectives in MRI. Agents with high longitudinal relaxivity at 1H, and enhanced relaxation rates at 19F frequency, respectively, allow gathering of critical information simultaneously with two different MRI methods. The responsive dual-frequency agents hold great promise for development of novel methods to successfully assess Ca2+ in living organisms and study essential physiological processes. The ability to observe its concentration changes in a non-invasive fashion would be of paramount importance for MRI methodology advancements and biomedical research in general.

INOR 901

GdAAZTA complexes as building blocks for the development of multimetric and supramolecular assemblies

Mauro Botta, mauro.botta@unipmn.it, Lorenzo Tei, Giuseppe Gambino, Jonathan Martellini. Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale “Amedeo Avogadro”, Alessandria, Italy

There is an ongoing interest in developing high-relaxivity Gd-based MRI contrast agents to overcome the low sensitivity issue inherent to the technique. The relaxivity enhancement can be pursued by: a) increasing the hydration number Q; b) optimizing the mean residence time τQ; c) lengthening the rotational molecular correlation time τR. Hexa- and heptadentate ligands for stable complexation of Gd(III) ions have been actively investigated in order to increase the hydration state (Q=1) and enhance the relaxivity, r1, of the paramagnetic complexes. One of the most promising example is represented by AAZTA, a chelator formed by a seven-membered ring with two endocyclic and one exocyclic nitrogen atoms and four carboxymethyl side arms, which represents an intermediate family between the open chain DTPA and macrocyclic DOTA ligands.[Gd(AAZTA)] shows excellent properties in terms of thermodynamic stability and relaxivity, associated with the presence of two inner sphere water molecules that are not displaced by endogenous bidentate anions and feature a short residency time.

Two AAZTA derivatives containing a reactive functional group were synthesized and used as building blocks for the development of multimetric, high relaxivity MRI contrast agents. We investigated: a) a series of multimetric GdL1 complexes (n = 2-32) covering a broad range of molecular weights (1200-25000 Da) and allowing a systematic investigation of the relationship between rotational dynamics and relaxometric behavior at high magnetic fields; b) a dimeric Gd-complex bearing an adamantly group (GdL2) able to form strong supramolecular adducts with specific hosts such as β-cyclodextrin, poly-β-CD, HSA and functionalized PAMAM dendrimers; c) lipophilic Gd-AAZTA multimetric complexes (GdL1 and GdL2) suitable for incorporation in liquid nanoparticle systems such as micelles and liposomes with the aim to combine the slow tumbling motion of these systems with the low rotational flexibility of the multimetric probes.

INOR 902

Peptide effects at nanoparticle surfaces

Marc R Knecht, knecht@miami.edu, Zhenghua Tang, Nicholas M. Bedford, J. Pablo Palafox-Hernandez, Yue Li, Tiffany R. Walsh, Paras N. Prasad, Mark T. Swihart, Rajesh R. Naik. (1) Department of Chemistry, University of Miami, Coral Gables, FL 33146, United States (2) Institute for Frontier Materials, Deakin University, Geelong, Victoria 3216, Australia (3) Department of Chemistry, University at Buffalo (SUNY), Buffalo, NY 14260, United States (4) Department of Chemical and Biological Engineering, University at Buffalo (SUNY), Buffalo, NY 14260, United States (5) Materials and Manufacturing Directorate, Air Force Research Laboratories, Wright-Patterson Air Force Base, OH 45433, United States

Biomolecular recognition represents new approaches for the fabrication of nanomaterials with control over the size, shape, composition, and functionality of the inorganic structures. Interestingly, specificity in the binding ability likely arises during the biocombinatorial selection process, where only minimal understanding of this binding event is presently understood. By achieving this fundamental understanding, the de novo design of new sequences could be possible, thus expanding the application of these important materials. Recently, we have quantitatively demonstrated both enthralic and entropic factors that govern the binding of a variety of peptides to Au metallic surfaces. These peptides were then used for the fabrication of spherical Au nanoparticles where differing particle sizes and morphologies were observed based upon these differences in binding events. As a result, changes to the morphology of the Au nanoparticle surface were observed, that could be correlated to the biomolecular binding event. These results suggest that changes in the particle surface can be controlled via peptides, which could be important for applications such as plasmonics and catalysis that are dependent upon the surface structure of inorganic nanomaterials.

INOR 903

New and novel synthesis for the formation of oxide-free tin nanoparticles

Michael P Rowe, michael.rowe@tema.toyota.com, Daniel Herrera, Nikhilendra Singh. Toyota Research Institute of North America, Ann Arbor, Michigan 48105, United States

Gram-scale formation of oxide-free tin nanoparticles has been facilitated in a facile manner through the formation of a new zero-valent tin lithium borohydride complex. Via ball-milling tin metal and lithium borohydride together, a new and unique SnLiBH4 complex is formed. Interestingly, XPS analysis of this new complex shows that the zero-valent tin metal peaks have been reduced by approximately 2eV each versus the authentic tin sample. When this new complex is dispersed in a solution of THF and octylamine, Sn nanoparticles are formed. These Sn nanoparticles are shown by XRD to be
markedly free of oxide contamination, and only 11nm in size. This very simple nanoparticle preparation is remarkable for its straightforwardness and self-cleaning nature for the elimination of oxides. Such a scalable preparation is excellent for oxide sensitive applications in secondary rechargeable batteries. Recent results displaying the battery application, and capability, of these oxide-free tin nanoparticles will be presented and discussed.

INOR 904
Unusual noble metall alloy nanoparticles for enhanced and cost-effective hydrogenation catalysis
Stephany Garcia, stephanygarcia87@utexas.edu, Liang Zhang, Graeme Henkelman, Simon M Humphrey, Department of Chemistry & Biochemistry, University of Texas at Austin, Austin, TX 78712, United States

Nanoparticles (NPs) with non-equilibrium configurations have been synthesized with the aid of microwave irradiation. Microwave-assisted synthesis has allowed for the successful and facile alloying of two metals that are classically immiscible. It has also been possible to tune the composition of these NPs in order to have an impact on the kinetics of hydrogenation catalytic processes performed. It has been observed that due to ensemble effects, alloyed NPs of Rh and other noble metals (Ag & Au) are catalytically more active than pure Rh NPs for hydrogenation catalysis. Thus, cost effective catalysts have been synthesized by diluting a precious metal such as Rh with abundant and relatively inexpensive metals, also yielding higher turnovers even when one of the metals is catalytically inactive.

INOR 905
Optical rotation measurements of enantioselective separation on chiral Au nanoparticles
Nisha Shukla1, nisha@andrew.cmu.edu, Nathaniel Ordeck1, Nathan Khosla2, Alex Pettit2, Andrew J Gellman2. (1) ICES, Carnegie Mellon University, Pittsburgh, PA 15213, United States (2) Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Adsorption of chiral compounds on chiral surfaces is the initial step in enantioselective processes such as separations and catalysis. There has been a significant effort over the past decade aimed at the preparation of chiral nanoparticles based on metallic cores modified by chiral ligands. In principle, these can serve as the basis for enantioselective chemical processing. In this work we demonstrate a simple measurement of enantioselective adsorption on chiral metal nanoparticles using a method that can yield quantitative measures of the enantiospecific adsorption equilibrium constants [1]. The surfaces of chemically synthesized Au nanoparticles have been modified with D- or L-cysteine to render them chiral and enantioselective for adsorption of chiral molecules. Their enantioselective interaction with chiral compounds has been probed by optical rotation measurements when exposed to racemic propylene oxide. The ability of optical rotation to detect enantiospecific adsorption arises from the fact that the specific rotation of polarized light by R- and S-propylene oxide is enhanced by interaction Au nanoparticles. This effect is related to previous observations of enhanced circular dichroism by Au nanoparticles modified by chiral adsorbates. More importantly, chiral Au nanoparticles modified with either D- or L-cysteine selectively adsorb one enantiomer of propylene oxide from a solution of racemic propylene oxide, thus leaving an enantiomeric excess in the solution phase. Au nanoparticles modified with L-cysteine (D-cysteine) selectively adsorb the R-propylene oxide (S-propylene oxide). A simple model has been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-PO adsorption on the chiral Au nanoparticles.


INOR 906
Controlled synthesis and catalytic performance of gold intercalated in the walls of mesoporous silica
Yazhou Ji1, richard@mines.edu, Xue Wang2, Ryan M. Richards2,3. (1) Materials Science Program, Colorado School of Mines, Golden, CO 80401, United States (2) Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, United States

Gold nanoparticles intercalated in mesoporous silica (GMS) was successfully synthesized and catalytic properties of the materials were investigated. Varied parameters were adopted in the synthesis of mesoporous silica to control pore size, connectivity and wall thickness, followed by intercalation of gold nano particles into the walls of the supporting silica. Physisorption, transmission electron microscopy and X-ray diffraction were utilized to characterize the porosity, morphology and structure of the gold intercalated mesoporous silica. The results showed a stable structure of mesoporous silica after gold intercalation along with surface increasing to ~1000 m²/g and pore sizes ranging from 20 to 50 angstroms. The materials were used as catalysts in both oxidation and reduction reactions. The potential of this system for substrate selectivity has also been investigated.

INOR 907
Chemical relevance of the photothermal effect of strongly absorbing nanoparticles
Benjamin J Lear, bulb14@psu.edu, Kaitlin M Haas, Robert JG Johnson. Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, United States

The photothermal effect of nanoparticle systems provides a means by which to control the application of heat on a time (nanoseconds) and length (nanometers) scale similar to that of reactive chemical systems. We will present our work on model chemical systems designed to test the chemical relevance of this heat, as well as to determine the parameters of the nanoscale system that allow fine control over the generation and evolution of this heat. Specifically, we examine the decomposition of polypropylene carbonate around both gold and iron oxide nanoparticles. We find that the extent of this decomposition depends on the nanoparticle concentration, size, and the identity of the surfactants on the nanoparticles.

INOR 908
Intercalation of aggregation-resistant metal nanoparticles in the walls of mesoporous silica for applications in catalysis
G. Jeremy Leong1,2, jleong@mines.edu, Maxwell C. Schulze1, mschulze@mines.edu, Vincent S. Delaney1, vdelaney@mines.edu, Ameen Ghavami1, Xue Wang2, Brian Trevyn2, Ryan M. Richards1. (1) Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, United States (2) Chemical and Materials Science Center, National Renewable Energy Laboratory, Golden, CO 80401, United States

Catalyst durability is of great concern when considering the design of next generation materials. Recently reported synthetic routes towards shape and size control of metal nanoparticles has shown promising activity and selectivity due to the enhanced catalytic properties attributed from surface faceting.
However, the main challenge with highly active surfaces is the fact that often times, structure rearrangement and sintering takes place under catalytically pertinent reaction conditions which is a large cause of deactivation. Herein, we report a novel route towards the intercalation of metal nanoparticles in mesoporous silica frameworks for developing highly active, robust, aggregation-resistant catalyst materials showing improved thermal and chemical stability. To date, we have reproducibly intercalated Pt, Pd and Au nanoparticles in the walls of various mesoporous silica frameworks. Thermal and chemical stability studies were carried out through calcinations and catalyst recycling, respectively while observing changes in the metal nanoparticle structure via TEM, BET and XRD.

**INOR 909**

Platinum-based single-site catalyst tethered onto mesoporous carbon nanoparticles for C-H activation chemistry

Madhura Joglekar¹, joglekar@mines.edu, Tristan S Gray², T Brent Gunnoe³, Brian G Trewyn¹. (1) Department of Chemistry, Colorado School of Mines, Golden, CO 80401, United States (2) Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States

Currently used methods for surface functionalization of mesoporous carbons involves the use of strong oxidants such as hot, concentrated sulphuric and nitric acids which not only decrease the selectivity of functionalization by generating multiple oxygen containing functionalities on the surface but also produces side reactions in catalysis. In order to circumvent the drawbacks associated with this oxidation method, we report a lithium mediated approach to selectively functionalize the surface of uniform monodispersed mesoporous carbon nanoparticles and for the first time demonstrate its utility to tether a platinum-bipyridine single-site catalyst onto the surface. This carbon-based single-site heterogeneous catalytic system has been applied to C-H activation chemistry.

**INOR 910**

Formation principles for templated vanadium selenides

Alexander J Norquist, anorquis@haverford.edu. Department of Chemistry, Haverford College, Haverford, PA 19041, United States

A set of formation principles governing organically templated vanadium selenides are describe in the context of a series of new compounds. First, the compositions of the reaction mixtures dictate the form of the secondary building units from which the inorganic structures are constructed. Second, the strengths of hydrogen-bonding networks formed between inorganic anionic and organic cationic components are maximized. Third, orientations of selenium stereoreactive lone pairs are driven by the minimization of internal void space. Fourth, compound symmetry can be affected by the use of chiral reaction components.

**INOR 911**

Symmetry-guided synthesis of highly porous metal-organic frameworks with desired topology for clean energy applications

Muwei Zhang, muwei.zhang@mail.chem.tamu.edu, Ying-Pin Chen, Mathieu Bosch, Hong-Cai Zhou. Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

Metal-Organic Frameworks (MOFs) have gained a tremendous amount of attention in the past few decades. Due to the tunable nature of their ligand geometry, their enormous surface area and their large uptake capacities, MOFs are widely applied in many areas such as gas storage, gas separation, CO2 capture, catalysis, drug delivery, sensors, photosensitve materials and magnetic materials. However, rational design of MOFs with desired characteristics still remains largely challenging. A careful inspection of the framework topology from the atomic level may provide a novel insight to the rational design of MOFs. In this work, we have demonstrated a successful implementation of symmetry-guided design of stable, non-interpenetrated MOFs with the expected topology from the atomic level, and reported a series of isoreticular MOFs with high porosity, large stability and desired topology. In particular, PCN-521 possesses the largest cavity size (20.5 × 20.5 × 37.4 Å), BET surface area (4040 m2g−1) and solvent accessible volume (78.50%) among all the published MOFs from tetrahedral ligands. Second, it is the first examples of non-interpenetrated MOFs synthesized from the MTBC ligand. Third, it is the first example of Zr MOFs constructed from tetrahedral ligands.

The successful synthesis of PCN-521 has provided a general way of making stable, non-interpenetrated MOFs with large porosities. New structures can be obtained by varying both the organic linkers and the metal SBUs. An isostructural MOF, PCN-523, was obtained by replacing the 8-connected Zr clusters with Hf clusters. This Hf MOF also possesses a high chemical and thermal stability. Due to the non-interpenetrated nature of fluoroite-topology framework, it is suggested that a further elongation of the tetrahedral ligands may result in MOFs with even larger cavities. PCN-524 was obtained by combining the Zr clusters with a further elongated tetrahedral ligand. It possesses a cavity size of 22.8 × 22.8 × 40.2 Å. This work not only illustrates a successful case of designing MOFs with a desired topology from the atomic level, but also provides a systematic way to construct stable, non-interpenetrated MOFs with large porosities.

References:

**INOR 912**

Facile chemical etching induced structure evolution of cuprous oxide microcrystals and their SERS application

Chao Qiu, chao.qiu@usd.edu, Ying Bao, Nathan L Netzer, Chaoyang Jiang. Department of Chemistry, University of South Dakota, Vermillion, SD 57069, United States

Morphology, composition, and structure of semiconductor nanomaterials play important roles in determination of their unique physical and chemical. In this presentation, a facile chemical etching method will be introduced to tune the structures of cuprous oxide microcrystals which resulted in excellent performance in surface-enhanced Raman scattering (SERS). Microscopic and spectroscopic techniques were utilized to investigate the structures of cuprous oxide during the chemical etching, as well as the assessment of the SERS sensitivity. Such chemical approach can significantly enhance the SERS capabilities of the Cu2O microcrystals with an enhancement factor up to 106. The increasing SERS sensitivity is attributed to the generation of Raman hot spots related to the etching-induced rough surface, sharp tips and edges, as well as the strong chemical interactions between the probe molecules and the SERS substrates. Our work provides a simple method to modify the semiconductor nanomaterials and induce SERS activity, thus expanding cuprous oxide microcrystals into even broader applications.

**INOR 913**

Investigations of processing parameters that affect transparency of silica aerogels for thermal insulation systems

Metin Karayilan¹, metin.karayilan@gmail.com, Can Erkey². (1) Department of Chemical and Biological Engineering, Koç University, Istanbul, Turkey (2) Koç University Tüpraş Energy Center, Koç University, Istanbul, Turkey

Transparency in thermal insulation systems is of great practical importance since transparent insulation materials would provide efficient insulation that can replace conventional window glazing. Silica aerogels are promising candidates to be used in such insulation systems because they are transparent and have very low thermal conductivity (10-15 mW/m.K). Silica aerogels are synthesized by sol-gel chemistry, gelled in a mold and dried by supercritical
extraction with CO$_2$ to get highly porous (porosity > 90%), low density aerogels. The purpose of this study was to investigate the effects of synthesis parameters such as type and composition of solvents, and type of molds to achieve optimum thermal conductivity and transparency values. Pore diameters, surface areas, and pore size distributions of the synthesized silica aerogels were measured with N$_2$ adsorption-desorption analysis. Optical properties were determined with using UV-VIS spectrophotometer. Transient Hot-Disk plane source and steady-state Guarded Hot Plate methods were used for analyses of thermal properties. It was found that decreasing the molar ratios of the solvents added in the sol mixture increases transparency. Theoretical calculations on thermal conductivity showed that the lowest values can be reached when the density of the aerogel is between 100-200 kg/m$^3$. Based on this information, a large scale (30x30x1.2 cm$^3$) transparent silica aerogel panel was synthesized with density of 180 kg/m$^3$. Transparency ratio and thermal conductivity of the aerogel were measured as 88% (at 600 nm) and 16 mW/mK, respectively.

INOR 914
Kinetic isotope effect studies of the template effect on the mechanism of crystallization of the halozeotype CZX-1
Feier Hou, fhou@ncsu.edu, Eric D. Dill, Jacob C. W. Folmer, James D. Martin. Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, United States
CZX-1, halozeotype, is a templated derivative of ZnCl$_3$ with the formula [HN(CH$_3$)$_3$]CuZnCl$_4$. It is isosstructural with sodalite. The [HN(CH$_3$)$_3$]$^+$ cations balance charge and serve as a structural template, forming hydrogen bonds to the metal halide framework. Previously, kinetic measurements of CZX-1 crystallization were studied with time-resolved X-Ray Diffraction and Differential Scanning Calorimetry (DSC). That work demonstrated that the velocity of the phase boundary increases above the glass transition temperature to a maximum, then decreases until it drops to zero at a temperature that is about 11 °C below the melting point. To investigate the role of the template on the mechanism of crystallization of CZX-1, a series of H/D kinetic isotope effect (KIE) measurements has been investigated. The crystallization rates are measured with DSC for the d$_1$, d$_2$, d$_3$ and d$_{12}$-CZX-1 with isotopically substituted [(H/D)NC(H/D)$_3$]$^+$ templates. The crystallization rates at high temperature are measured by crystallization from quenched melt, while crystallization rates at low temperature are measured by cold crystallization. Comparative isotopic labeling can differentiate the impact of template reorientation and template-framework hydrogen bonding on crystallization. The results demonstrate that both impact the crystallization rates, the temperature of the maximum crystallization rate, and the maximum rate of crystallization. The differential role of nucleation on the rate of cold and hot crystallization will also be discussed.

INOR 915
Morphological control in Pechini synthesis via polymerization-induced phase separation
Stephen G Rudisill, rudio047@umn.edu, Sammy Shaker, Andreas Stein. Department of Chemistry, University of Minnesota - Twin Cities, Minneapolis, MN 55455, United States
Mechanisms driving microstructure formation in template-confined Pechini-type gel systems involving ceramic oxides are investigated. Three-dimensionally ordered macroporous microspheres and more extended bicontinuous networks with hierarchical porosity can be synthesized directly from a Pechini sol–gel precursor within a colloidal crystal template. The type of morphology generated is related to the mechanisms of phase separation in the precursor, namely, nucleation and growth vs spinodal decomposition. These mechanisms are, in turn, determined by the citric acid concentration in the initial precursor solution and by electrostatic interactions of the precursor with the polymeric template. Microspheres generated by the nucleation-and-growth pathway can be produced between 1–3 μm in size, with polydispersities below 15%. They retain the ordered porous network left by removal of the template. This work demonstrates the heavy dependence of the morphology on molecular weight of the precursor gel; details attempts to generalize the synthesis to a variety of metal oxides; and attempts to shed light on the complex relationship between size and charge of cations, complexation, and molecular weight of the resulting precursor.

INOR 916
Crystal structure and morphology control of metal carbide nanomaterials synthesized from an amine-metal oxide composite
Brian M Leonard, bleona5@uwyo.edu. Department of Chemistry, University of Wyoming, Laramie, WY 82072, United States
Metal carbides have received significant interest in recent years as catalysts for several energy conversion processes due to their low cost, enhanced stability, and high activity. However, one of the main challenges that still exist in metal carbide synthesis is overcoming the high reaction temperatures traditionally used and lowering these temperatures to make high surface area nanomaterials. By combining molybdenum oxides with organic amines, we can create composite precursor materials that are readily transformed into metal carbides at temperatures as low as 600°C. These composite materials conveniently combine a metal oxide, amine reducing agent, and a carbon source in a templated structure that provides morphology control over the final product. While hexagonal Mo$_2$C is the most stable and commonly studied phase, our new reaction process allows us to make several phases in the Mo-C system giving us access to more complex and unstudied phases. We are currently investigating the mechanism of these reactions including the morphology of the composite, extension to other metal carbides including bimetallic carbides, and control over the crystal structure. In addition, we are studying these materials as catalysts for energy related reactions.
INOR 917

Rotating linkers as a guest-dependent breathing mechanism in anisotropic MOFs

Christopher R. Murdock1, cmrdock@hotmail.com, Nicholas W. McNutt2, David J. Kefler3, David M. Jenkins1. (1) Department of Chemistry, University of Tennessee - Knoxville, Knoxville, TN 37996, United States (2) Department of Chemical and Biomolecular Engineering, University of Tennessee - Knoxville, Knoxville, TN 37996, United States (3) Department of Materials Science and Engineering, University of Tennessee - Knoxville, Knoxville, TN 37996, United States

The existence of multiple stable states in breathing MOFs has led to a variety of selective sorption applications and, therefore, an increased interest in their design and synthesis. We are utilizing semi-rigid ligands to design breathing MOFs which place the hinges or “kneecap” solely on the ligand rather than the metal-ligand interface. Placing the “kneecap” on the ligand allows for a new approach to breathing in which an aryl moiety of the linker can rotate between fixed positions to open and close the pore as a function of guest. An additional advantage for this breathing mechanism is that the rotating subunit can be monitored directly by solid state NMR. Progress in the design and synthesis of a series of these anisotropic MOFs will be discussed.

INOR 918

Synthesis and characterization of [Fe(CO)3(dppe)]2[Rh(CO)Cl]2: A unique compound

Hayley E Hudson1, HE-Hudson@wiu.edu, Bryn L Lutes2, Wen Zhang3, Brian J Beilott4, Richard L Keiter2, Ellen A Keiter2, Arnold L Rheingold3. (1) Department of Chemistry, Western Illinois University, Macomb, IL 61455, United States (2) Department of Chemistry, Eastern Illinois University, Charleston, IL 61920, United States (3) Department of Chemistry, University of California San Diego, La Jolla, CA 92033, United States

The unique physical and chemical properties of macrocyclic molecules have made them a synthetic target for decades. Research concerning macrocyclic complexes has increased the knowledge pool of the scientific community, and has opened the door for the discovery of vital applications ranging from powerful reaction catalysts to using macrocyclic complexes as biological oxidation agents. However, synthesis of such complexes has proven to be challenging, time consuming, and costly, due to the vast number of possible conformations these systems can adopt. The synthesis of [Fe(CO)3(dppe)][Rh(CO)Cl]2 has been achieved in three steps. The first step was synthesis of the iron complex trans-Fe(CO)3(Ph2PCH=CH2)2 from iron pentacarbonyl and diphenyl vinyl phosphine. This reaction was optimized with 85.9% yield, and characterized via FTIR, 1H NMR, 13C NMR, and melting point. In the second step, Fe(CO)3(dppe) was synthesized from the product of the first reaction and diphenylphosphine, achieving an efficiency of 72%, and characterized via FTIR, 1H NMR, melting point, and x-ray crystallography. Finally, [Fe(CO)3(dppe)][Rh(CO)Cl]2 was synthesized using the product of the preceding synthesis. This novel compound has excellent application regarding hydrogenation and/or oxidation catalysis, due to the nature of iron phosphine complexes in the presence of rhodium or palladium. Computational data on the nature of the carbonyl bonding interactions are explored.

INOR 919

Terminal nitride of titanium

Rick R Thompson1, rick@ias.upenn.edu, Dan J. Mindiola1, Maren Pink2. (1) Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States (2) Department of Chemistry and Biochemistry, Indiana University, Bloomington, Indiana 47401, United States

Despite their prevalence for groups 5-8, isolation of a terminal nitride for group 4 metals has yet to be realized. Herein we report the synthesis and characterization of the first ever terminal titanium nitride via deprotonation of a related parent imido. Preliminary reactivity shows the nitride to be a potent nucleophile capable of forming unique heteroatom substituted imidos. Exploration of the nitride as a potential N-atom source will also be discussed.

INOR 920

New developments involving N-heterocyclic phosphonium pincer ligands bound to first row transition metals

Sadie E Knight, knightse@brandeis.edu, Christine M. Thomas. Department of Chemistry, Brandeis University, Waltham, MA 02453, United States

The coordinative unsaturation of the phosphorus atom of N-heterocyclic phosphonium cations (NHP’s), and the presence of both a lone pair and an empty p orbital enable NHP’s to act as suitable ligands for low valent late transition metals. Incorporation of NHP’s into chelating frameworks provides unique stability to resulting transition metal complexes. The ability of NHP’s to perform two-electron redox processes at the central phosphorus atom has been recently demonstrated with platinum and palladium complexes, in which the NHP ligand oxidizes the metal by two electrons, resulting in NHP phosphido ligands. In an effort to target cooperative metal-ligand redox activity, we have begun targeting first row transition metal complexes supported by the chelating NHP-diphosphine pincer ligand developed on our laboratory. The synthesis of first row metal-NHP complexes and their reactivity and electronic properties will be presented.

INOR 921

Novel coordination chemistry of first-row transition metals enabled by the bulkiest triazacyclononane derivatives

Arumugam Thangavel, Gregory J Karahalis, Cassandra T Buru, Christopher C Scarborough, scarborough@emory.edu, Department of Chemistry, Emory University, Atlanta, GA 30322, United States

A wealth of coordination compounds in various oxidation states has been made accessible by saturated aza-macroyclic ligands, pure sigma donors that resist oxidative degradation. However, these compounds have been limited to pseudo-four-fold symmetry because tridentate saturated aza-macroyclic ligands (derivatives of 1,4,7-triazacyclononane (tacn)) cannot enforce coordination numbers fewer than five. We have recently prepared the first
derivatives of tacn bearing tertiary alkyl nitrogen substituents, which are the bulkiest tacn derivatives to date. These ligands enforce 4-coordinate pseudo-tetrahedral geometries for a variety of first-row transition metals, opening the door to new coordination chemistry and reactivity enabled by this redox-inert ligand. The progress of this research area will be disclosed.

INOR 922
Comparing covalent multiple bonds in chromium-m (m = Cr, Mn, Fe) complexes
Paul A Rudd, rudd00067@umn.edu, Nora Planas, Laura Gagliardi, Connie C Lu.Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States
Homo- and heterobimetallic chromium-metal (metal = Cr, Mn, Fe) complexes have been prepared in multiple oxidation states in a trigonal, “double decker” ligand. The rich redox profiles of these complexes allows isolation of species with d6, d10, d11, or d12 electron counts. These complexes were investigated with multiple techniques, including X-ray crystallography, to determine whether the bimetallic unit is more sensitive to the identity of the heterometal or the overall electron count. The covalency of the metal-metal bond is also investigated theoretically.

INOR 923
N-heterocyclic thiones (NHTs): Synthesis and structures of mercury(II) complexes
Marissa S. Styron, mstyron@uncc.edu, Daniel Rabinovich.Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States
This presentation outlines the synthesis and initial reactivity studies of two new N-heterocyclic thione (NHT) ligands bearing large substituents on the nitrogen atoms. The 2,6-diisoproplyphenyl and 2,6-xylyl derivatives IPrS and IXyS have been prepared and structurally characterized. Reactivity studies have led to the preparation of both three- and four-coordinate mercury(II) complexes of general formulas LHgX2 and LHgX3 (X = Cl, Br, I), some of which have been structurally characterized. This presentation will also describe preliminary work aimed at isolating new NHT complexes of copper(II) and gold(II) with potential catalytic applications.

INOR 924
Assembly of interpenetrated MOFs through “molecular stitching” of pre-formed 2D layers
Zixuan Zhang, zhangzixuan0207@gmail.com, Jinxiang Chen, Wenhua Zhang, T.S. Andy Hor.Institute of Materials Research and Engineering, Singapore, Singapore
Modifying pre-formed MOFs allows us to introduce desirable functionality in a predictable manner or to obtain novel structures that may otherwise be unfeasible from direct metalliggand assembly[1, 2]. However, it is challenging to maintain the crystallinity of MOFs after such disruption. Herein, we report a Cadmium-based two-dimensional coordination polymer with bulky diethylformamide (DEF) solvates that exhibits channels for dipyridyl bridging ligands to diffuse into the crystal lattice. Such ditopic ligands act as “needles” that thread through the pores of one layer and substitute the surface DEF molecules on the neighbouring layers to stitch alternate layers into interpenetrated MOFs (Figure 1). A class of bridging ligands with different lengths such as 4,4′-bipyridine (bpy, 7.1 Å), 4,4′-azopyridine (azopy, 9.0 Å) and trans-1,2-bis(4-pyridyl)ethylene (bpe, 9.4 Å) are used. The crystallinity of the molecular layers is maintained throughout the stitching process to yield a series of flexible interpenetrated MOFs with decent performance in carbon dioxide adsorption.

References

INOR 925
Alkane dehydrogenation and alkene isomerization catalyzed by CCC-pincer complexes of iridium
Anthony R Chianese, achianese@colgate.edu.Department of Chemistry, Colgate University, Hamilton, NY 13346, United States
Iridium complexes of CCC-pincer bis-N-heterocyclic carbene ligands were synthesized and found to be active catalysts for the acceptorless dehydrogenation of alkanes, giving up to 100 turnovers for cyclooctane and n-undecane. Selective production of terminal alkenes from linear alkane substrates was not achieved, as the same complexes are highly active catalysts for the isomerization of terminal alkenes to the internal isomers. Mechanistic studies indicate that alkene isomerization proceeds through pi-allyl intermediates for a mesityl-substituted precatalyst.

INOR 926
Dual reactivity of pincer iridium complexes toward hydrazine
Kathleen D Field, kfield13@eden.rutgers.edu, Tian Zhou, Karsten Krogh-Jespersen, Alan S Goldman.Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854, United States
The synthesis of ammonia via the Haber-Bosch process is one of the most important industrial processes in the world today. Unfortunately, it is also one of the most energy intensive processes accounting for more than 1% of the world's energy consumption. Hydrazine (N2H4) is potentially a key intermediate in the conversion of N2 and H2 to ammonia and it has also been claimed to be a promising hydrogen storage material. We report both the dehydrogenation of hydrazine by PCP-pincer iridium type catalysts to N2 and H2 as well as the N-N bond cleavage reaction to give ammonia and N2. Experimental evidence will be discussed in reference to a proposed computationally derived mechanism.

INOR 927
Iridium (III) pincer complexes in catalytic aerobic methane oxidation
Meng Zhou1, meng.zhou@rutgers.edu, Alan S Goldman1,2, Robert J Nielsen2, Samantha I Johnson2, William A Goddard2. (1) Department of Chemistry, Rutgers University, Piscataway, New Jersey 08854, United States (2) Department of Chemistry, California Institute of Technology, Pasadena, CA 91125, United States
The practical and direct catalytic oxidation of methane to methanol, a liquid fuel, remains a grand challenge in chemistry. The reaction is preferably carried out by air or an air-regenerable oxidant. We present our recent experimental and computational studies using iridium (III) pincer complexes as catalysts and air as the oxidant.

INOR 928
Aryl halide coupling reactions with pincer complexes of group 9 metals
Oleg V Ozerov, ozerov@chem.tamu.edu, Samuel D. Timpa, Christopher J. Pell.Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States
Pincer-supported Rh complexes can undergo a number of oxidative addition (OA) and reductive elimination (RE) reactions that mirror the reactivity Pd and Ni. For Rh, this involves the +1/+3 or oxidation states in contrast to 0/+2 for Pd chemistry. Unsaturated, three-coordinate, T-shaped (pincer)Rh fragments are critical for this chemistry as intermediates in OA and RE and are analogous to the role of unsaturated LpdO intermediates. This presentation will demonstrate how judicious selection of the pincer ligand can allow parlaying the requisite stoichiometric reactions into successful catalysis. For example, we will discuss the use of (PCP)Rh complexes in C–C and other C–heteroatom coupling reactions. The presentation will also address the potential for extending the chemistry observed with Rh to its lighter and cheaper congener, cobalt, and the specific challenges associated with implementing Co(I)/Co(III) chemistry in the pincer context.

INOR 929
Application of new P^OCOP, P^OCOSH and P^OCCHOP pincer complexes of iridium for catalytic C–H bond functionalization
Loren P. Press, loren.press@chem.tamu.edu, Billy J. McCulloch, Chris J. Pell, Oleg V. Ozerov. Department of Chemistry, Texas A&M University, College Station, Texas 77840, United States

Catalytic functionalization of C–H bonds under mild conditions and low catalyst loadings is of paramount importance for the production of value-added chemicals from abundant hydrocarbon feedstocks. To this end, various P^OCOP and PCP pincer complexes of iridium have been investigated for the direct catalytic functionalization of aromatic C–H bonds. We have developed new P^OCOP, P^OCOSH, P^OCCHOP and PCP pincer ligands for use with late transition metals, with the aim of performing catalytic C–H bond functionalization.

INOR 930
Activation of C–H bonds via iridium pincer complexes: New motifs in protected M(I) low-valent catalysts
Laci Singer, laci.singer@ttu.edu, Michael Findlater. Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79416, United States

Alkanes, as the most abundant hydrocarbons, represent an attractive chemical feedstock. However, the inert nature of C–H bonds renders their conversion to useful products difficult. Our group is focused on the activation of C–H bonds using late transition metal complexes based upon a pincer ligand motif. It is now well accepted that a 14-electron metal center (Ir(I)) is the active catalyst in most cases. Synthetically, our approach to access low oxidation state metal centers takes advantage of labile phosphine ligands (i.e., PPh3 and PCy3), which can be easily displaced. Using this strategy, we have employed Ir(I) pincer complexes to perform transfer dehydrogenation in substrates such as cyclooctane and silyl-piperidine.

INOR 931
Mechanistic studies of intramolecular hydroamination of alkylamines by a zirconium(IV) CCC-NHC pincer complex
Katherine N. Leigh1, kleigh1@memphis.edu, Wesley D. Clark2, T. Keith Hollis2, Charles Edwin Webster2. (1) Department of Chemistry, The University of Memphis, Memphis, TN 38152, United States (2) Department of Chemistry, Mississippi State University, Mississippi State, MS 359762, United States

Hydroamination is an atom-economical method to produce alkylamines, including N-heterocyclic species. The combination of an amine and an electron-rich unsaturated bond has a high energetic barrier, and a variety of catalysts have been utilized to overcome it. A Zr-based CCC N-heterocyclic pincer carbene has successfully catalyzed the production of five- and six-membered rings with various substituents. Plausible mechanisms for this reaction have been studied using density functional theory calculations. Cycloaddition, insertion, and concerted-type cyclization mechanisms will be compared. The effects of halogen ligands and substrate substitution will also be discussed.

INOR 932
Ambiphilic ligands for late-transition-metal catalysis
Brian V Popp, Brian.Popp@mail.wvu.edu. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States

Multifunctional ligand environments are a hallmark of metalloenzymes, and allow for the preorganization of Lewis basic residues in appropriate conformations to bind a metal (or group of metals). In addition, both basic and acidic donors sit poised in the proximity of the active site to mediate catalytic transformations of organic or small molecule substrates. In recent years, significant attention has been directed toward a class of molecules termed “frustrated Lewis pairs” for non-metal-catalyzed small-molecule activation. These molecules feature both a Lewis basic and Lewis acidic moiety that are incapable of forming robust Lewis pairs due to conformational constraints, making them interesting molecules for study as ligands for transition metals since they place a Lewis acidic moiety in the secondary coordination sphere of the metal and potentially offer an avenue for enzyme mimicry. While the coordination chemistry of these ligands has been extensively explored by a number of groups, application to catalytic transformations has been explored to a lesser extent. This presentation will highlight some of our recent progress toward utilizing previously reported phosphino-borane and novel NNN-pincer-borane ligands in late-transition-metal catalysis.

INOR 933
Synthesis of PCS bis-pincer complexes and their reactivities
Wei-Chun Shih, g9623505@gmail.com, Loren P Press, Chandra Mouli Palit, Oleg V Ozerov. Department of Chemistry, Texas A&M University, College Station, TX 77840, United States

Hydrogenolysis of primary alkyl alcohols into alkanes and water is one of most important steps to convert triglycerides derived from biomass into second generation alkane biodiesel. This transformation remains an unsolvable challenge due to the stabilities of alkyl C–O bonds. In order to cleave these types of inert alkyl C–O bonds, binucleating pincer complexes containing metal centers of differing electronic properties may prove essential to overcome these difficulties. Previously, our group reported binuclear palladium complexes supported by PNN and PCN bis-pincer ligands with C2 and C4 alkyl linkers.

Here we synthesized PCS bis-pincer complexes supported by a more rigid linker, 1,3-bis-methyl phenyl group
Recent work in our group has demonstrated the viability of the PNP scaffold to support the synthesis of group 9 metal fluorocarbynes. We now look to extend this work to include the preparation of analogous siloxycarbynes through the application of silylium reagents to pincer-supported transition metal carbonyls. Recent investigations into this area will be presented, to include examples of metal-bound silylium adducts. Preliminary studies of related systems for hydrogen oxidation will also be shown.

INOR 935
Contributions of BrCl, BrOCl, and Br₂O toward bromination rates of aromatic compounds in solutions of aqueous free bromine: Implications for water disinfection
John D. Sivey, jsivey@towson.edu, Daniel A. Victor, Mark A. Bickley. Department of Chemistry, Towson University, Towson, Maryland 21252, United States

Bromide is ubiquitous in aqueous environmental systems. Recent increases in anthropogenic discharges of bromide (e.g., from wastewater effluents, hydraulic fracturing, and road salts) into sources of drinking water have renewed concerns over the formation of brominated disinfection by-products (DBPs) during drinking water treatment. When bromide-containing waters are disinfected with free chlorine, bromide is readily oxidized into free bromine, primarily as HOBr (pKₐ = 8.7) at near-neutral pH. Free bromine can subsequently react with organic compounds in the water to form potentially toxic brominated DBPs.

The vast majority of previous research on mechanisms of DBP-precursor bromination assumes HOBr is "the" active brominating agent. We present evidence that other brominating agents (including BrCl, BrOCl, and Br₂O) in equilibrium with HOBr can significantly influence regioselective bromination rates of methoxy-substituted benzenes, employed herein as model DBP precursors (Figure 1).

Our results suggest that the greater electrophilicities of BrCl, BrOCl, and Br₂O can more than compensate for their lower concentrations relative to HOBr during bromination of aromatic compounds of somewhat modest nucleophilicity. Equilibrium concentrations of BrCl, BrOCl, and Br₂O are proportional to the concentrations of Cl⁻, HOCl, and HOBr, respectively. Accordingly, we also discuss how changes in solution chemistry can influence bromination rates, particularly during chlorination of drinking water and wastewater. We also explore how the structure of aromatic compounds influences the relative importance of BrCl, BrOCl, and Br₂O as active brominating agents.

INOR 936
High water oxidation activity of suspended BiVO₄/Co₃O₄ nanocomposite photocatalyst under visible light
Jiaurui Wang, wjrwang@ucdavis.edu, Frank E Osterloh. Department of Chemistry, University of California, Davis, Davis, California 95616, United States

BiVO₄ has been of interest as a photoanode material for solar water photoelectrolysis. Here we demonstrate visible light (380 mW cm⁻², >400 nm) driven photocatalytic water oxidation with suspended BiVO₄ nanoparticles using NaIO₄ as a sacrificial electron acceptor. After modification with Co₂O₃ cocatalyst, the activity reaches 11 mmol g⁻¹ h⁻¹ of O₂, one of the highest values ever reported for a suspended water oxidation photocatalyst. Powder XRD and electron microscopy show that BiVO₄ is of monoclinic Scheelite structure with a particle size of ~100 nm. UV-Vis Spectroscopy observes the indirect band gap at 2.45 eV and the direct band gap at 2.62 eV. Photoelectrochemical measurements on thin films immersed in 0.1 M aqueous Na₂SO₄ solution and exposed to 435 nm light (7.4 mW cm⁻²) confirm anodic photocurrents above +0.32 V vs NHE. Addition of 1 mol% Co₂O₃ cocatalyst by thermal annealing of Co(NO₃)₂ at 673 K increases the photocurrent and reduces the water oxidation overpotential by 0.9 V. Surface photovoltage spectroscopy observes hole injection from BiVO₄ into Co₂O₃ at photon energy of >2.6 eV. These results illustrate the significant potential of nano-BiVO₄-Co₂O₃ for the construction of a tandem photocatalyst for overall water splitting and the production of hydrogen fuel from sunlight.

INOR 937
Synthesis, energetics and charge separation in rhodium-doped strontium titanate nanocrystals for visible light driven water splitting photocatalysis
Jiaurui Wang, wjrwang@ucdavis.edu, Benjamin A nail, Jing Zhao, Frank E Osterloh. Department of Chemistry, University of California, Davis, Davis, California 95616, United States

The ability to control the optical and electronic properties of inorganic nanocrystals is essential for many branches of technology, incl. microelectronics, photovoltaics, and photocatalysis. Here we show that the majority carrier type and band gap of SrTiO₃ nanocrystals, an important photocatalyst material, can be controlled via doping with rhodium. SrTiO₃ nanocrystals with 1-3 mol% Rh dopants were obtained by hydrothermal synthesis. According to powder XRD and TEM, the crystals are of perovskite structure type and form a cubic morphology with edge length between 35 and 40 nm. UV-Vis Spectroscopy observes the direct band gap at 2.7 eV and the indirect band gap at 2.3 eV, compared to 3.4-3.3 eV for the non-doped nanocrystals. Photoelectrochemical measurements on nanocrystal films immersed in 0.1 M aqueous Na₂SO₄ solution at pH=3.5 and exposed to 435 nm light (7.4 mW cm⁻²) confirm cathodic and anodic photocurrents below +0.2 V and above +0.6 V vs NHE, respectively. These potentials are 1.1 V and 0.8 V away from the conduction and valence band, respectively, suggesting that Rh doping diminishes the n-type character and mildly increases the p-type character of the material. The ability of the nanocrystals to catalyze visible light (112 mW cm⁻², >400 nm) driven proton reduction in 20vol% aqueous methanol was measured as a function of Rh doping and Pt, Ru cocatalyst loading. The activity increases in the order 1% Rh doping < 3% Rh doping, and 1% Ru < 1% Pt < 2% Pt cocatalyst loading and reaches up to 95 μmol g⁻¹ h⁻¹. Surface photovoltage spectroscopy suggests that the improvement with Pt is due to better charge separation at the SrTiO₃-Pt interface.

INOR 938
ZnO nanoforest: Morphology-tunable synthesis and applications in solar energy conversion
Yuanbing Mao, maoy@utpa.edu, Xing Sun. Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78539, United States

Sunlight is an abundant, inexpensive, pollution-free and endlessly renewable source of clean energy. Converting solar energy into an easily usable form has also attracted considerable interest in the last several decades. Among different technologies for solar energy conversion, photocatalysis has been used to split water in hydrogen and oxygen without any emission of byproducts. However, the conversion efficiency today remains low (e.g. lower than that of photovoltaics), and is limited mainly by the low performance of the photoelectrodes. To develop better photoelectrodes and more efficient devices, one of the main strategies is the nanostructuring strategy by exploiting scaling laws and specific effects at the nanoscale to enhance the efficiency of existing semiconductors and metal oxides. It has gained significant interest in the last twenty years. In this study, three-dimensional (3D) ZnO nanoforests were successfully shape-programmed fabricated via a facile hydrothermal route. The respective and synergistic influence of ammonia and polyethyleneimine on the architectures of ZnO nanoforests were systematically investigated. The in-depth understanding of mechanism of hydrothermal method is substantial for advancing this facile approach and control over special 3D nanostructure into a versatile large-scale nanomanufacturing industry. More importantly, the incredible architecture characteristics endowed the willow large dimensional (3D) ZnO nanoforests miraculous PEC water splitting performance, including small charge transfer resistance, long photoelectron lifetime, paramount photocurrent density 0.919 mA cm⁻² at +1.2 V, vs. Ag/AgCl, and more importantly “champion” photoconversion efficiency (0.299% at 0.89 V, vs. RHE), which leads the realm of homogeneous ZnO nanostructures. In all, this work opens up an unprecedented avenue by governing desirable 3D ZnO nanostructures based on demands, and broadens the application potentials of 3D nanotechnology to both minimized functional and large-scale industry devices.

INOR 939
Optimal ratio of polypyrrole decoration on V₂O₅ nanopipers as electrode materials for energy storage
Xing Sun, maoy@utpa.edu, Yuanbing Mao. Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78539, United States

Growing demands for rapidly powering portable electronics and electric vehicles has triggered substantial efforts on high-energy and high-power density energy storage devices. Based on the charge storage mechanism, supercapacitors are classified into two main categories: electrical double-layer capacitors (EDLCs) and pseudocapacitors. The former store electrical energy via electrostatic accumulation of charges at the electrode/electrolyte interfaces (non-faradaic process). Pseudocapacitance is based on fast and reversible redox reactions occurring at the surfaces of electroactive materials (faradaic process). Because of the difference in their energy storage mechanisms, pseudocapacitors deliver higher specific capacitance and energy density than EDLCs. To further improve the performances of pseudocapacitors, numerous hybrid nanomaterials were designed by engineering electrically conductive polymers and transition metal oxides. In this report, core/shell structured V₂O₅@polypyrrole (PPy) nanopipers were successfully synthesized as electrode materials of supercapacitors and the optimal mass ratio of PPy on V₂O₅ was determined around 40% with high specific capacitances and excellent rate capability. Overcoating of PPy weakened the adherence between electroactive materials and current collector and retained the integral performances of electrodes. Respective contributions of double layer capacitance and pseudocapacitance were explored at different PPy/V₂O₅ ratios, further ascertaining the function of PPy shells on V₂O₅ nanopipers. This work lays the foundation for outperformed hybrid electrode materials in aqueous supercapacitors.

INOR 940
Photosensitization of a molecular iron catalyst for water oxidation using semiconductor electrodes
Benjamin M Klepser, bklepser@umich.edu, Bart M Bartlett. Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States

Solar water splitting is desirable for generating hydrogen from non-fossil-fuel sources. The major challenge to realizing solar water splitting is the slow four-electron water oxidation half-reaction. Molecular water oxidation catalysts (WOCs) can help overcome the kinetic limitations of water oxidation and typically generate oxygen faster than semiconductor photocatalysts. However, molecular WOCs typically require sacrificial oxidants (e.g.—Ce⁴⁺ or S₂O₅²⁻), and they only operate in the dark unless a separate photosensitizing component is added. To address these drawbacks, a molecular iron WOC, Fe(tebppmcn)Cl₂ (1, tebpmpcm = tetraethyl N,N'-bis(2-methylpyridyl)-4-phosphonate)-N,N'-dimethyl-cyclohexyldiamine) has been tethered to semiconducting WO₃ through its phosphonate linker to generate a solar-responsive oxygen-evolving system (1-WO₃). The photocurrent density in 1-WO₃ is 50% higher than that of WO₃. In addition, the 1-WO₃ electrode exhibits a 61% increase in selectivity for water oxidation in acidic sulfate solution.
Finally, varying the anchor and the oxide semiconductor allows for electron transfer between the molecular catalyst and the photosensitizer to be optimized. These efforts present a new avenue toward simultaneously photosensitizing molecular catalysts and removing sacrificial oxidants specifically for effecting solar water oxidation.

INOR 941

Reactions of hydrated nitrates and rare earth oxides with formamide: Relevant to recycling rare metals

Pradeep W. Samarakseke, pwsamara@central.uh.edu, Xi Qiu, Allan J. Jacobson. Department of Chemistry, University of Houston, Houston, Texas 77023, United States

The direct reactions of both hydrated metal nitrates and lanthanide oxides with formamide have been studied. Fifteen lanthanide formate frameworks were obtained under mild solvothermal reactions, nine were isostructural compounds with the composition [Ln(HCOO)x]·[(HCONH)y][LnFA: Ln = Y, Sm, Eu, Gd, Tb, Ho, Yb, and Lu] and six were isostructural metal frameworks with the composition [(CH(NH2)2)Ln(HCOO)4] (LnFMD; Ln = Y, Sm, Ho, Tb, Yb, and Lu). All the compounds contain metal ions in square antiprismatic coordination by oxygen atoms connected by anti-anti formato ligands to form frameworks. The lanthanide ions in the LnFA structure are six coordinated by oxygen atoms from six formate ligands; two oxygen atoms from two coordinating formamide ligands complete the eight coordination and protrude into the neutral Ln(HCOO)x cavity. The lanthanide ions in LnFMD structure consist of eight coordinated by oxygen atoms from eight formate ligands to give a negatively charged Ln(HCOO)x cavity. Formamidate cations formed in-situ occupy the empty space in the cavity and balance the framework negative charge. The luminescence properties of the four members SmFA, EuFA, TbFA and SmFMD were investigated using solid state photoluminescence spectroscopic methods in the range 300 nm – 800 nm. On the excitation with UV light, the compounds show typical but intense characteristic emission bands for the respective metals. The spectra of three rare earth formate families, lanthanide formate, LnFA, and LnFMD containing Sm, Eu, and Tb are compared. We have successfully extended the chemistry demonstrated for the simple oxides and hydrated nitrates to include rare earth oxides found in end-of-life materials such as CRT displays and fluorescent light bulbs.

INOR 942

Pore size tailored metal-organic frameworks with ultrahigh methane uptake

Dawei Feng, dawei.feng@chem.tamu.edu, Hong-Cai Zhou. Chemistry, Texas A&M University, College Station, Texas 77840, United States

Metal-organic frameworks (MOFs) as a new class of porous materials have received great attention for gas storage. The readily tunability is one of the most characteristics of MOFs. Especially, methane adsorption is considered to be highly related to the pore size distribution and pore shapes. Based on a metal-organic polyhedral constructed MOF, we designed a series of new isoreticular MOFs by tailoring the pore size. One of these MOFs exhibit extremely high methane uptake and record high working capacity (5.8 bar to 65 bar) at room temperature among all the porous material.

INOR 943

Synthesis of water stable MOFs by post-synthetic exchange of unstable MOFs

Tianfu Liu, liutianfu010@gmail.com, Lanfang Zou, Yingpin Chen, Hongcai Zhou. Department of Chemistry, Texas A&M University, College station, Texas 77840, United States

Metal-organic frameworks (MOFs) have garnered tremendous interest in recent decades due to their promising performance in a lot of important applications. Compared with some other porous materials, MOF is easily designed and functionalized by judicious choice of metal nodes and organic linkers. However, one of the shortcomings of MOFs may be ascribed to their low hydrothermal and chemical stability that undoubtedly limit their uses in industrial applications with large scale. On account of the “hard base” character of carboxylate group, hard acid metal ions such as Fe(III), Cr(III) and Zr(IV) are usually considered to be good candidates to construct stable MOFs. This method has become the focus of some research efforts but still relatively few stable MOFs have been obtained up to now. The reason for this may be that the MOFs based on these metal ions are usually poor crystalline and hard to predict and control. These drawbacks have led us to consider the post-synthetic metal exchange as an option for the preparation of stable MOFs.

Some unique examples relating metathesis of hard acids metal ion were reported. However, in this case the metal ions are merely partially exchanged. In order to get the fully exchanged, stable MOFs, we synthesized an unstable MOF as a protocol to exchange with Fe(III) and Cr(III) ions. Followed with oxidized by air flow, water stable Fe(III)-MOF and Cr(III)-MOF were obtained and characterized by X-ray single crystal diffraction. This study shows an example of post-synthesis of stable MOFs from unstable ionic MOFs without destroying the single crystalline. This single crystal to single crystal transmetalation provides a new strategy to readily synthesize water stable MOFs and single crystal of Cr-MOF was first time determined by X-ray diffraction.

INOR 944

Photochemistry of PtIV hydroxy complexes and mechanistic studies

Lasantha A. Wickramasinghe, lawr87@mail.missouri.edu, Paul R. Sharp. Chemistry, University of Missouri-Columbia, Columbia, MO 65211, United States

Storing solar energy in chemical bonds is an important goal of transition metal photochemistry. Toward this goal we have studied the photochemistry of PtIV complexes shown below. Trans-PtIV(Cl(OH)R)(PET3)2(1) and trans-PtIV(Cl(OH)O(R)(PET3))2(2) (R = 4-trifluoromethylphenyl, 9-phenanthryl, phenyl, etc) were synthesized via oxidative addition of H2O2 to trans-PtIVCl(PET3)2. Characterization was done by 31P NMR, 1H NMR, 195Pt NMR, 19F NMR and X-ray crystallography. Photoelimination of HOCl and H2O2 has been studied under various conditions. Photolysis of 1 & 2 at 77K in a frozen matrix was also carried out for more mechanistic information (Scheme 1).

INOR 945

Pushing forward the adoption of H2 and CH4 in metal-organic-frameworks: A theoretical investigation
Microporous metal–organic frameworks (MOFs) have recently emerged as a promising gas-storage materials due to their exceptionally high surface areas and chemically-tunable structures. In the context of alternatives fuels for automotive applications, their ability to store hydrogen and methane is especially important.

Together with our experimental collaborators, in a joint effort to devise MOFs with higher uptake capacity, we seek to understand the fundamental mechanism underlying the adsorption processes for hydrogen and methane into MOFs. By studying the weakly interacting complexes of methane or hydrogen with structural elements of MOFs we are able to gain insights into their adsorption mechanisms.

Equilibrium structures, adsorption enthalpies and entropies are calculated for several of post-modified MOF linkers and metal clusters. Other than providing an estimate of adsorption free energies and capacities, our result also show that charge transfer interactions have a significant contribution to the adsorption of hydrogen to metals and that isoelectronic Ca or Mg complexes may display different qualitative behaviors of methane adsorption. Practical issues such as the effect of solvent molecules present in the MOF are also discussed.

INOR 946
Studies of aluminum borohydride: From stabilized adducts to a novel hypersalt material

Douglas A Knight1, knight65202@yahoo.com, Robert Lascola1, Rana Mohtadi2, PremKumar Sivasubramanian2, Devleena Samanta3, Puru Jena3. (1) Hydrogen Technology Research Laboratory, Savannah River National Laboratory, Aiken, SC 29808, United States (2) Materials Research Department, Toyota Research Institute of North America, Ann Arbor, MI 48105, United States (3) Department of Physics, Virginia Commonwealth University, Richmond, VA 23284, United States

Aluminum borohydride, [Al(BH4)3], possesses almost 17 wt. % hydrogen available for desorption; yet is seen as a volatile, Pyrophoric liquid that is difficult to handle under normal conditions. Limited studies showing that Al(BH4)3 can form a more stable solid material through either adductation with a Lewis base ligand or through complexation with other metal borohydrides. Raman data has revealed that the adducted aluminum borohydride becomes increasingly ion in nature; bring about the materials increase in stability. While, further studies show that the Al(BH4)3-(NH3)n adduct follows a decomposition mechanism similar to that seen with ammonia borane. Complexation of Al(BH4)3 with KBH4 also brings about a stable solid, K[Al(BH4)4]. Computational and experimental methods reveal that with the formation of the highly electronegative [Al(BH4)4: anion, the K[Al(BH4)4]] is identified as a new member in a unique class of materials called hypersalts. These types of energetic materials promise to have a multitude of applications above and beyond those of standard hydrogen storage materials. Presented is the experimental synthesis and characterization with an in-depth comparison to computational results. Select materials' hydrogen sorption capabilities are measured using a standard Sieverts apparatus with additional thermal characteristics examined by TGA coupled with residual gas analysis with further analysis performed by Raman spectroscopy. Included are structural features as determined by way of single crystal and high resolution powder X-ray diffraction.

INOR 947
Watching a photocatalyst function: Spectroscopic implications for the design of supramolecular photocatalysts for the production of H2

Benjamin Dietzek1, benjamin.dietzek@ipht-jena.de, Sven Rau2. (1) Functional Interfaces, Institute of Photonic Technology Jena, Jena, Thuringia 07745, Germany (2) Institute of Inorganic Chemistry I, Ulm University, Ulm, Germany

Our recent progress in understanding the function-determining photoinduced reaction steps in Ruthenium-polypyridin based dinuclear complexes for the photocatalytic hydrogen production is discussed. The work combines Resonance-Raman-scattering with electrochemistry, theoretical chemistry, X-ray absorption spectroscopy and time-resolved spectroscopy. The photoinduced electron transfer processes within Bis{4,4’-di-tert-butyl-2,2’-bipyridine} ruthenium(II)-µ (tetrapyrido[3,2-a:2’,3’c:3’-h:2”′,3”′-]phenazine) dichloro-Palladium(II)(Ru-tphzh-Pd) and Ru-tphzh-PT are characterized in detail by resonance Raman1 and ultrafast time-resolved absorption spectroscopy. By comparing the photophysics of the complexes to model complexes the individual electron transfer steps are assigned to kinetic components and their solvent dependence is discussed.2 The resonance Raman data reveal that the initial excitation of the molecular ensemble is spread over the terminal tbbpy (4,4’-Di-tert-butyl-2,2’-bipyridine) and the tphzh (tetrypyrido[3,2-a:2’,3’c:3’-h:2”′,3”′-]phenazine) ligands.3 To decipher the electronic structure of long lived intermediates within the catalytic cycle, resonance Raman-spectroelectrochemistry is employed.4 The results reveal a distinct influence of the second metal ion, i.e. Pd or Pt, on the electrochemical properties of the complexes and – hence – on the nature of the intermediates formed. Furthermore, X-ray absorption measurements indicate the nature of the catalytically active species to be different in RuPd and RuPt. The comprehensive spectroscopic approach enables to watch the individual steps of the catalytic function of the dinuclear complexes and infer design strategies for the photocatalyst.

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INOR 948
Porous supramolecular boronates: Towards selective adsorption and detection of benzene

John J. Lavigne, lavigne@sc.edu. Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States

Boron is a metalloid, having properties intermediate between those of metals and nonmetals. Given the empty p-orbital found on neutral boron, most boron containing species can serve as Lewis acids that are capable of coordinating Lewis bases. As such, coordination between boron and amines has long been used to generate supramolecular assemblies, though little has been reported towards advancing the utility of these compounds. Described here, coordination between boronate diesters and diamines produced polymorphic material with solvent-dependent structures ranging from macrocycles to linear polymers to extended crystalline networks. Some of these materials contain persistent pores and show selective guest uptake, for example adsorbing benzene over toluene, ethylbenzene or xylene (BTEX). Other structures undergo a color transition upon guest binding, affording unique and highly selective sensors. One such compound changes from dark red (burgundy) to bright yellow upon exposure to benzene vapor, yet does not show any color transition when exposed to other aromatic guests. Based on these novel supramolecular boronates, applications for both the selective adsorption and detection of benzene will be presented.

INOR 949
Spectroelectrochemical characterization of metal verdazyl complexes

David J. R. Brook, david.Brook@sjsu.edu, Dorothy Chung, Erik Johnson. Department of Chemistry, San Jose State University, San José, California 95192, United States

Verdazyl radicals make interesting ligands as a result of the magnetic interaction between radicals and metal ions, combined with the potential for valence tautomerization resulting in species with complex and unusual electronic structure. Dipyridyl substituted verdazyls show unusually strong magnetic exchange and radical metal interaction as a result of the central location of the verdazyl ring within the ligand. We report detailed studies of the first row transition metal complexes of this ligand, in particular electrochemical and spectroelectrochemical studies that highlight their unusual electronic structure.

INOR 950
Enhancing zero field splitting parameters in mononuclear vanadium complexes

Mohamed R Saber1,2, mohamed.saber@chem.tamu.edu, Stephen Hill3, Komalavalli Thirunavukkuaras2, Kim R Dunbar1. (1) Chemistry Department, Texas A&M University, College Station, Tex 77840, United States (2) Chemistry Department, Fayoum University, Fayoum, Fayoum 63111, Egypt (3) NHMF, Tallahassee, Florida FL 32310, United States

Considerable efforts are being devoted to designing enhanced molecular magnetic materials, in particular single molecule magnets (SMMs), that can meet the requirements for future technologies such as quantum computing and spintronics. One of the current trends in the field is to enhance the global anisotropy in metal complexes using single-ion anisotropy. This work is devoted to study the importance of tuning the local coordination environments of metal ions in order to ensure enhanced single ion anisotropy.

INOR 951
Magnetic, spectroscopic, and structural properties of a trans-μ-[TCNQ-TCNQ]2 bridged zinc complex

Juyeong Kim1, jyk5304@psu.edu, Robert Fraleigh2, Hemant P. Yennawar1, Nitin Samarth2, Benjamin J. Lear1. (1) Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States (2) Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

The vanadium (III) ion can give rise to strong ferromagnetic interactions and often exhibits large zero-field splitting D up to ~20 cm−1. This makes it a very promising building block for SMMs. A family of axially distorted mononuclear vanadium (III) compounds of general formula, A[L3VCl4] (3-9) (X = F, Cl or Br, A+ = EtN+, nBuN+ or PPN+, L3 = Tp or Tp* (Tp = tris-(3,5-dimethyl-1-pyrazolyl)borohydride), Tp* = tris(3,5-dimethyl-1-pyrazolyl)(borohydride)), were studied (Figure 1). Replacement of the Tp ligand in 3 with the stronger π-donor Tp* results in a near doubling of the magnitude of the axial zero-field splitting parameter D (D = -16.0 cm−1 in 3, and -30.0 cm−1 in PPN[TpVCl4] 4) as determined by magnetic measurements. Such findings support the notion that control of the axial crystal field distortion is an excellent way to control single-ion anisotropy. High Field-High Frequency EPR measurements on 4 revealed an even higher D value, -40.0 cm−1.

Interestingly, compound 4 exhibits evidence for an out-of-phase signal under a dc applied field indicating the first mononuclear vanadium single molecule magnet.

3. Juyeong Kim1, jyk5304@psu.edu, Robert Fraleigh2, Hemant P. Yennawar1, Nitin Samarth2, Benjamin J. Lear1. (1) Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States (2) Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
We report the first example of a single molecule (Zn dimer) containing a $\alpha$-dimerized 7,7,8,8-tetracyanoquinodimethane (TCNQ). Zn dimer was synthesized via slow diffusion of Zn(NO$_2$)$_2$, 2,2$'$-bipyridine (bpym) and Li(TCNQ) in methanol, and formed leaf-like purple crystals. The solid state properties were analyzed using single X-ray diffraction, IR spectroscopy, UV-visible near IR diffuse reflectance spectroscopy, and SQUID. It is composed of two zinc metal centers, each of which is coordinated octahedrally with two bpym and one TCNQ$^-$. The zinc metal centers are bridged by a dimerized TCNQ ([TCNQ-TCNQ]$^2$). In each moiety, two bpym ligands are cis disposed to each other, leaving TCNQ$^-$ and [TCNQ-TCNQ]$^2$ cis disposed to each other. In the IR spectrum, ν(C≡N) stretch mode is shifted to lower energies, and δ(C-H) bend mode validates the presence of [TCNQ-TCNQ]$^2$. The UV-vis near IR spectrum shows signals caused by π-stacking of TCNQ, which is supported by the packing diagram. TCNQ$^-$ and [TCNQ-TCNQ]$^2$ are positioned alternatively, forming staircase-shaped stacking pattern. SQUID data suggests that unpaired electrons of TCNQ$^-$ might attribute a very weak paramagnetic property to Zn dimer. In addition, the solution phase behavior was investigated using cyclic voltammetry, UV-vis spectroscopy and IR spectroscopy. The first two techniques demonstrate identical properties to a single molecule, TCNQ$^-$. The IR spectrum of the chemically reduced species displays disproportionation of Zn dimer.

Figure 1. Crystal structure of Zn dimer. All hydrogen atoms are removed for simplicity.

INOR 952

Accurate calculation of relative energies between different spin states in coordination complexes using density functional methods

Jordi Cirera, jcireafernandez@ucsd.edu, Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093, United States

Density Functional Theory (DFT) has had a major impact as a complementary tool for experimental inorganic chemists. The use of DFT calculations allow gain insight into the electronic structure of transition metal compounds and its implications in structure, reactivity and physical properties. In this communication we present our results for the application of the meta-hybrid GGA functional TPSSh$^1$ for the accurate calculation of relative energies between different spin states in transition metal complexes. Our methodology has been tested in the theoretical calculation of transition temperatures ($T_c$) for the [Fe(spy)_2(NCX)_2] (X = S, Se, BH$_4$) family of spin crossover systems with unprecedented accuracy. Fundamental insights into the dependence of $T_c$ on the nature of the axial ligands are obtained from the direct analysis of the underlying electronic structure in terms of the relevant molecular orbitals.$^3$ This methodology has also been applied to the study of the [Fe(TMP)CN]$^-$ anion to unravel the reasons for the thermally accessible high-spin state.$^4$ The reported methodology can be used to get quantitative information in processes where the electronic structure of the metal center changes qualitatively and more than one spin state become relevant.

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INOR 953

Tuning the spin transitions in hexacyanometallate containing magnetic materials

Codi A Sanders, codi.sanders@chem.tamu.edu, Heather Stout, Catalina Achim, Doros Petasis, Kim R Dunbar. (1) Department of Chemistry, Texas A&M University, College Station, TX 77843, United States (2) Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States (3) Department of Physics, Allegheny College, Meadville, PA 16335, United States

Prussian blue type materials are known to behave as high temperature magnets and to exhibit rich magnetic phenomena including spin-crossover, cyanide-linkage isomerism, charge-transfer-induced spin-transition and photomagnetic behavior. It has been shown by our group that discrete cyanide molecules of general formula [M$^0$(tmpphen)$_2$][M$^0$(CN)$_6$]$_2$ (tmpphen = 3,4,7,8-tetramethylphenanthroline) with a trigonal bipyramidal (TBP) geometry are able to mimic the magnetic properties of Prussian blue analogues but with several distinct advantages over the extended structures such as higher solubility for processing into films, ease of tuning vis-à-vis the properties and, most importantly, they allow for modeling of magnetic phenomena.

One of our efforts in this area involves the use of trivalent hexacyanometallates of cobalt, ruthenium and osmium to prepare TBPs that undergo spin state changes due to either spin-crossover or electron transfer. It has been found that spin-crossover and charge-transfer-induced spin-transitions can be finely tuned in TBPs that undergo solvent exchange or solvent loss. The DC temperature dependent magnetic susceptibility data for the TBP [Fe$^0$(tmpphen)$_2$][Ru$^0$(CN)$_6$]$_2$ shown below illustrates the significant changes in the spin transition behavior as the interstitial solvent is varied. These and related results will be presented and discussed.
INOR 954

Underexplored magnetic architectures based on trivalent titanium and molybdenum

Andrew J Brown, andrew.brown@chem.tamu.edu, Kim R Dunbar. Department of Chemistry, Texas A&M University, College Station, TX 77843, United States

Much interest in nanoscale electronics stems from the possibility of quantum information processing, molecular spintronics, and high density data storage. Highly promising candidates for these applications are a subclass of molecular nanomagnets known as single-molecule magnets (SMMs). These materials exhibit bistability, magnetic hysteresis, and relaxation dynamics of a molecular origin. The main challenge is to increase the temperature at which SMMs exhibit a memory effect, as the current record is still well below liquid nitrogen temperatures (a benchmark for application feasibility).

Because the field is still in its fundamental stages, underexplored transition metals with specific ligand fields are being sought to afford higher single-ion anisotropy with an easy-axis for the magnetization. In this work, molecules containing trivalent titanium ions (d^1) with trigonal symmetry were synthesized with the new starting material, (Et_3N)[Tp^*Ti(CN)_3]. Titanium(III) capped by tris(3,5-dimethylpyrazolyl)borohydride (Tp^*) can exhibit a degenerate ground state, which would lead to a strong spin-orbital contribution – a leading source of single-ion anisotropy. Additionally, only two heteronuclear molecules are known to date that contain titanium(III). Another metal building block that is being pursued is heptacyanomolybdate, which exhibits large anisotropic exchange along the axial direction.

The incorporation of these starting materials into molecules along with their full magnetic characterization will be presented.


INOR 955

Copper(I) and silver(I) complexes of an amido ligand with two pendent carbenes

Venkata A.K. Adiraju, venkata.adiraju@mavs.uta.edu, Muhammed Yousufuddin, H.V. Rasika Dias. Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065, United States

New CNC pincer ligands based on N-heterocyclic carbenes and amido groups will be presented. The pincer salts were deprotonated to form the corresponding lithium amido complexes. The successful transmetallation to the copper(I) complex was accomplished by treating these lithium salts with copper(I) triflate. Solid-state structures of the copper(I) pincer complexes were characterized by a variety of techniques including X-ray crystallography. Additionally, the isolation of the silver(I) pincer complexes were accomplished upon transmetallation with silver(I) triflate or silver(I) chloride. Structures and properties of these adducts will be discussed.

INOR 956

Polymeric metal complexes for multi-electron reactions

Gabriel Menard, gmenard@fas.harvard.edu, Theodore A. Betley. Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

The multi-electron conversion of small molecules is readily accomplished in Nature at high spin polynuclear metal assemblies nestled in metalloenzyme cores (e.g., nitrogenase, oxygen evolving complex). The close proximity of several metal centers in these complexes provides multiple metal-substrate binding sites, while facilitating multi-electron redox processes associated with small molecule conversion.

Our approach has focused on using flexible multinucleating ligands composed of weak-field hexa-amine binding sites (1,3,5-C_3H_6(NHPh-ortho-NHSiMe_3)Bu); and LH_k) to direct the formation of predesigned multinuclear architectures, such as the reported [^M_LFe(thf)] (M = Fe, Mn) or mixed-metal [^MFeLFeMn(thf)] complexes. This talk will describe recent progress in the synthesis of complexes with two transition metals and a redox inactive Lewis acid (LA) incorporated in the same proximal space. Incorporation of a LA (Ca or Sr) has resulted in the stabilization of a [^MFeLFeLA(µ-O)] species, previously inaccessible using the ^MFeLFe(thf) platform. Further efforts to synthesize LA-stabilized reactive linkages, such as Cu–O–Cu or Fe–C–Fe, through oxidative multi-electron group transfer chemistry will be described, as well as their subsequent reactivity with small molecules.


INOR 957

Investigations of group 11 metal-ethylene complexes

Kristine Klimovica, kristine.klimovica@gmail.com, Olafs Daugulis. Department of Chemistry, University of Houston, Houston, Texas TX-77204, United States

Transition-metal alkene complexes are of significant interest due to their intermediacy in many catalytic reactions. In this work, we report synthesis and characterization of a new group 11 metal-ethylene complexes. Comparison between ethylene exchange in copper, silver, and gold complexes will be presented.

INOR 958

Organometallic chemistry with a hammer: Mechanochemical synthesis of bulky allyl metal complexes containing electropositive metal centers
A solid-state mechanochemical approach has been investigated as a solvent-free synthetic route for metal allyl complexes of electropositive metals with sterically demanding allyl ligands. Compounds of the form A'M (A' = [1,3-(SiMe3)2C6H4]) are traditionally synthesized by salt metathesis in ethereal solvents (e.g., Et2O, THF). The use of such ethers can often lead to products containing coordinated solvent molecules that are not always subsequently removable, either in whole or in part. The presence of such solvents may limit product reactivity, influence bonding modes of the bulky allyls, or even redirect reaction pathways, so that desired products do not form. The synthesis and characterization of A'M complexes formed in the absence of reaction solvent will be described.

INOR 959
Investigation of mechanistic pathways for N-N bond cleavage with group 5 and 6 dinuclear pentamethylcyclopentadienyl amidinate dinitrogen complexes of general formula, ([η^5-C5Me5]M[N(i-Pr)C(X)N(i-Pr)]2[η^1-η^1-N2]), for M = V, Nb, Ta, Mo and W
Andrew J. Keane, akeane@umd.edu, Brendan L. Yorke, Jonathan P. Reeds, Phil P. Fontaine, Masakazu Hirotsu, Peter Y. Zavali, Lawrence R. Sita.Dept. of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States
This talk will provide the results of extensive experimental and theoretical studies of the N-N bond cleavage pathways for the titled complexes that occur under thermal conditions for group 5 metal derivatives and via photolysis for group 6 metal analogs to provide the corresponding dinuclear bis-(nitrido) complexes, ([η^5-C5Me5]M[N(i-Pr)C(X)N(i-Pr)](μ-N2)), in each case except for M = V. Results from detailed kinetic and crossover experiments for M = Nb and Ta will be discussed. In the case of M = Mo and W, quantitative N-atom functionalization chemistry has been developed that provides access to the corresponding mononuclear group 6 imido complexes, (η^5-C5Me5)M[N(i-Pr)C(X)N(i-Pr)](NR), that can engage in catalytic imido group transfer reactions. Finally, a discussion of remaining obstacles that must still be overcome to achieve catalytic dinitrogen fixation using the present metals and supporting ligand environment will be presented.

INOR 960
Isolation and reactivity of neutral mono- and dinuclear coinage metal complexes of Cyclic (Alkyl)(amino) carbenes
David S Weinberger, dsweinberger@ucsd.edu, Mohand Melaimi, Guy Bertrand.Dept. of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92033, United States
The nucloephilicity and electrophilicity of cyclic (alkyl)(amino) carbenes (CAACs) has been utilized to stabilize neutral mono- and dinuclear gold complexes. These complexes are readily available by one electron reduction from the corresponding (CAAC)Au+ (CAAC)MC+ (M=Cu, Ag, Au), respectively. The above-mentioned complexes represent the first neutral monomeric and dimeric coinage metal complexes. These complexes have been studied by x-ray diffraction and electron paramagnetic resonance demonstrating that the additional electron is both on the metal and ligand. In addition, the Au-Au dimer has shown interesting reactivity with alkenes, alkenes, isocyanides, and boranes as well as activation of small molecules (i.e. P2).

INOR 961
Steric protection of polyynes within rotaxane assemblies
Zuzana Baranova, zbaranova@chem.tamu.edu, Alex Kalin, John A. Gladysz.Dept. of Chemistry, Texas A&M Univ., College Station, TX 77842, United States
The one dimensional sp hybridized species "carbyne", (C≡C)n, a less explored allotrope of carbon, has been fascinating numerous scientists. The stability of polyyne chains decreases as they become more accessible to reagents with increasing length. An increase in stability has been achieved by capping the polyynediyl with organometallic endgroups such as [trans-(Cp^*)2(μ-tol)2P]= by sterically insulating the macrocyclic rotors. Longer polyyne chains provide more freedom for the translational motion of the macrocycle. Thus, longer axles and variously modified rotors have been employed via an active metal template approach featuring a copper(I) complex. Multinuclear NMR, UV/vis spectroscopy, single crystal X-ray diffraction, etc. exposed the properties of these compounds. Progress in the understanding of these polyyne-containing supramolecular assemblies will be presented.

INOR 962
Mechanistic insight into inorganic click (iClick) reactions: Cycloadditions between gold(I)-azides and gold(I)-acetylides
Andrew R Powers, arpowers@ufl.edu, Khalil A Abboud, Adam S Veige.Dept. of Chemistry, University of Florida, Gainesville, Florida 32611, United States
Inorganic click, or iClick reactions represent a viable synthetic methodology for the realization of novel hetero- and homo-multimetallic complexes. Similar to the Huisgen 1,3-dipolar cycloaddition of organic azides to organic acetylides, the iClick reaction is capable of yielding substituted triazolate species, but in this specific reaction motif, the organometallic starting materials that yield a triazole which acts as bridge between two metal centers. In this talk, current advancements highlighting homonuclear gold(I) iClick reactions are demonstrated. The results of a kinetic investigation study fuel insight into a mechanistic discussion of such a gold-gold iClick reaction, as well as the parallels it draws to the more studied copper catalyzed azide alkyn cycloaddition (CuAAC) class of reactions.

INOR 963
Platinum(0) complexes derived from molecular gyroscopes: Synthesis, characterization, and reactivity
Tobias Fiedler, tobias.fiedler@mail.chem.tamu.edu, John A. Gladysz.Dept. of Chemistry, Texas A&M University, College Station, TX 77840, United States
Since their first appearance in the literature, "molecular gyroscopes" have been synthesized with a wide variety of metals, ligands, and coordination geometries. Such assemblies which are comprised of ML2rotors enclosed in cage-like dibridgehead diphosphine stators resemble the symmetry of macroscopic toy gyroscopes. The key synthetic step - the assembly of the stator's spokes - has been achieved by olefin metathesis in all cases. Herein we describe synthesis, characterization, and reactivity of a highly reactive platinum(0) complex obtained via reduction from the corresponding platinum(II) gyroscope (see Scheme). Spectroscopic data of this complex as well as derived complexes will be presented and discussed.
INOR 964
Niobium-mediated disassembly of benzylic CF3 groups
Thomas L Gianetti, tlg1369@berkeley.edu, John Arnold, Robert G Bergman. Department of Chemistry, UC Berkeley, Berkeley, California 94703, United States
Recently, we reported the formation of arene niobium complexes [Nb(BDI)(NtBu)(arene)] (BDI = N,N'-diisopropylbenzene-β-diketiminate) via hydrogenolysis of the dimethyl complex [Nb(BDI)(NtBu)(Me)2] in aromatic solvent. These complexes were found to undergo dissociative arene exchange consistent with the formation of a transient low coordinate trivalent niobium complex "Nb(BDI)(NtBu)". The study presented here describes the reactivity study of these d2 masked Nb arene complexes toward C-F bond activation.

INOR 965
Chemistry of coordinatively unsaturated tantalum alkylidyne
Rodrigo Ramirez, rramirez@mail.chem.tamu.edu, Oleg V Ozerov. Department of Chemistry, Texas A&M University, College Station, Texas 77840, United States
This talk will focus on the chemistry of coordinatively unsaturated, cationic early metal alkylidyne complexes and the study of their potential application as catalysts for alkylene metathesis. In particular, this study is centered around the tantalum systems Ta(η5-C5(CH3)5)(CC6H5)(P(CH3)3)Cl and Ta(η5-C5H5)(CC6H5)(P(CH3)3)2Cl, described by Schrock et al.1 We have attempted the synthesis of electrophilic species of these complexes by halide abstraction using the sodium salts of the weakly coordinating anions [HCB11Cl11]− and [B(3,5-C6H3(CF3)2)4]−. Upon abstraction of chloride, a mixture of cationic species can be observed. Two of the components are two isomeric products of cyclometallation of one of the P(CH3)3 ligands. One of such isomers is the alkylidene [Ta(η5-C5(CH3)5)(CHC6H5)(P(CH3)3)(CH2P(CH3)3)][BuCB11Cl11] (1), which was characterized by X-ray crystallography. Another component of this mixture is the cation [Ta(η5-C5H5)(CC6H5)(P(CH3)3)]+ (2), which is the product of redistribution of the P(CH3)3 ligands. When such mixture was treated with excess P(CH3)3, only 2 can be observed by 1H and 31P NMR. When the mixture of cations is treated with 3-hexyne, the corresponding cationic tantalacyclobutadiene [Ta(η5-C5(CH3)5)(CHC6H5)(P(CH3)3)(CH2P(CH3)3)][HCB11Cl11] (3) is formed cleanly. This compound was isolated and characterized by NMR spectroscopy and X-ray crystallography. To the best of our knowledge, this compound represents the first example of an isolated and crystallographically characterized tantalum metallacyclobutadiene.

References

INOR 966
Syntheses, structural characterizations and low temperature magnetic studies on paramagnetic trimeric vanadium(IV) and dimeric cobalt(II) clusters

Rudy L Luck1, rluck@mtu.edu, Matthias Zeller2, John S Maass3. (1) Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931, United States (2) Department of Chemistry, Youngstown State University, Youngstown, OH 44556-3663, United States

Metal oxide clusters are one of the more well-established areas of chemistry. The syntheses of nonclassical vanadium trimer compounds where low temperature magnetic measurements reveal very weak interactions between the d\(^1\) metal centers will be featured. We have also produced a dimer of trimers as depicted in the diagram using the bidentate ligand N,N\'-dipyridyl oxalamide. Research with the element cobalt (recently discovered to be useful for the activation of water) have resulted in a variety of geometries featuring mononuclear, dinuclear and polymeric species. Dinuclear species feature two tetrahedral cobalt centers as well as two octahedral sites have been synthesized. Additionally, asymmetric dinuclear clusters featuring tetrahedral and octahedral cobalt geometries will be discussed as well as low temperature magnetic measurements on the d\(^2\) Co(II) species, which are difficult to interpret.

INOR 967
Theoretical studies of the complexation process of lanthanides in separations by solvent extraction

Deborah A Penchoff1, dpenchoff@utk.edu, George K Schweitzer2, Bruce E Bursten3, Robert J Harrison2,3. (1) Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States (2) Computational Sciences Center, Brookhaven National Laboratory, Long Island, NY, United States (3) Institute for Advanced Computational Science, Stony Brook University, Stony Brook, NY 11790, United States

Optimization of separation methods for lanthanides has become crucial since lanthanides play a vital role in advanced technology, supplies are limited, and their separation is particularly challenging. Our work provides a theoretical model for a fundamental understanding of coordination preferences involved in the extraction process. The theoretical protocol implemented in our study includes an in-depth analysis of the step-wise reactions involved in a two-phased extraction by considering different possible coordination environments, thereby gaining essential knowledge of the mechanism of complex formation. This unique computational analysis provides thermodynamic and structural information that complements experimental observations in greater depth than previous studies.

A step-wise mechanism in the separation of lanthanides between solvent phases as a function of solvent and complexing agent will be presented with emphasis on acetylacetone, butyric acid and substituted forms of this acid.

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INOR 968
Extraction of uranyl from the lanthanide elements in acidic media using dithiophosphinate based ionic liquids

Lani A Seaman1, lseaman@lanl.gov, Bill Ewing1, George S Goff2, Wolfgang H. Runde2. (1) Inorganic, Isotope, and Actinide Chemistry, Los Alamos National Laboratory, Los Alamos, NM 87505, United States (2) Science Program Office - Office of Science, Los Alamos National Laboratory, Los Alamos, NM 87505, United States

Soft donor extractants for use in separations of the actinide elements from the lanthanide elements in spent nuclear fuel has been of interest for many years. Ionic liquids have shown promise in actinide/lanthanide extractions due to their selectivity and chemical stability. We have been exploring the use of soft-donor containing phosphonium dithiophosphate ionic liquids (ILs) for separation purposes. The ionic liquids [P(6,6,6,14)][BuPS\(_2\)] and [P(6,6,6,14)][Cyranex 301] (Cyranex 301 = 'BuCH\(_2\)CHMeCH\(_2\)PS\(_2\)) have been shown to selectively extract the uranyl moiety from the lanthanide elements in nitric acid solutions. In all extractions, the uptake of uranium into the ionic liquid phase was quantitative and the lanthanide elements remained in the aqueous phase. Speciation of the uranyl species was investigated by NMR and Raman spectroscopies. Additionally, we studied the effects of uranyl uptake by varying pH and in the presence of increased NO\(_3\)\(^-\) and Cl\(^-\) concentrations.

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INOR 969
Quinoxalinol salens for actinide sensors and sensing polymers

Anne E. V. Gorden, anne.gorden@auburn.edu, Michael A DeVore, Charmaine D Tutson, Branson A Maynard, Spencer Kerns. Department of Chemistry and Biochemistry, Auburn University, Auburn, Al 36849, United States
Increasing the use of nuclear fuels for power production is one proposal to limit our dependence on fossil fuels and atmospheric emissions; however, fuel remediation is made more difficult by gaps in our understanding of actinide chemistry. There is a tremendous need to develop a better fundamental understanding of the underlying factors that control ligand selectivity. New ligands are required that can coordinate, sense, and purify actinides for use in sensors or decontamination applications. This will both allow us to develop new separations and sensor technologies and further our understanding of the chemistry of the lanthanides and the radioactive actinides (the F-Elements).

Chemosensors for actinides have the potential to allow for rapid in-field visual identification and thus increase ease of decontamination. We have developed ligands incorporating quinoxalines or imine azo-donors into a salen-like backbone. The addition of a quinoxaline to the salen imparts the fluorescence to the quinoxaline and alters the coordination site. We have used these complexes to probe the contributing factors toward selectivity, signal intensity, and the differentiation between actinides (like uranium and thorium) and transition metals (like copper or cobalt) as the basis of new chemosensors or fluorescent sensors to allow for rapid in-field visual identification.

INOR 970

Unconventional metal-organic frameworks (UMOFs) for separation of lanthanides from actinides and americium from curium

Rita Silbernagel1, Rita.Silbernagel@chem.tamu.edu, Jonathan D. Burns1, Thomas C. Sheheen2, David T. Hobbs2, Abraham Clearfield2. (1) Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States (2) Savannah River National Laboratory, Aiken, South Carolina, United States

Our research is directed towards carrying out separations of lanthanides from actinides and americium from curium. The ability to do these separations stems from our discovery of a remarkable group of M(IV) phosphate-phosphate ion exchangers that are selective for ions with high charge of 3+ or 4+ but sorb very little of those with lower charge (1+, 2+). Both the actinides and lanthanides exist as 3+ ions but the actinides can be oxidized to AnO2+ with charge of 1+. The lanthanides and also curium under these conditions remain in the 3+ state and can be separated from the actinides by ion exchange sorption. An ideal composition of this material is M(O2PCH2PO4)2.5(HPO4)nH2O where M is Zr(IV) or Sn(IV). By utilizing Na2 PO4 in place of H2PO4 in the preparation, some NaPO4 replaces a portion of the HPO4 resulting in a partial sodium phase of the material. A new variety of potassium phases have been prepared and comparisons to the sodium and proton phases will be included.

The goal in the separation is to oxidize the actinides to oxidation state five to obtain AcO2+ that yields low K0.5 values and the UMOFs take up the lanthanides and Cm that have very high K0 values at pH 2-3. This report will include information on the preliminary separation of Am from Cm. Work in separating lanthanides from actinides in mixtures of ions is in progress. Our preliminary results indicate the possibility of achieving excellent separation of lanthanides from actinides by control of pH and oxidation states of the actinides.

INOR 971

Optimization of lanthanide separations using Eichrom’s LN resin

Leah M Arrigo1, leah.arrigo@pnnl.gov, Chelsie L Beck1, Erin C Finn2, Zachary S Finch3, Stephanie J Gregory3, Brienne N Seiner1, Lanee A Snow1, Lori A Metz1. (1) Radiochemical Analysis, National Security Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, United States (2) Radiochemical Science, Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, United States

Radioactive lanthanides are produced during nuclear fission, often in high yield. The intergroup separation of the lanthanide actinide mixture is in progress. Our preliminary results indicate the possibility of separating lanthanides from actinides and americium from curium. The goal in the separation is to oxidize the actinides to oxidation state five to obtain AcO2+ that yields low K0.5 values and the UMOFs take up the lanthanides and Cm that have very high K0 values at pH 2-3. This report will include information on the preliminary separation of Am from Cm. Work in separating lanthanides from actinides in mixtures of ions is in progress. Our preliminary results indicate the possibility of achieving excellent separation of lanthanides from actinides by control of pH and oxidation states of the actinides.

INOR 972

Thorium mediated synthesis of 2,3-diaminophenazine

Branson A Maynard, branson@auburn.edu, Anne E. V. Gorden.Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849, United States

Oxidative coupling of α-phenylenediamine has been previously reported via Lewis acid catalysis or activity with horseradish peroxidase in the presence of hydrogen peroxide. The electronic properties of 2,3-diaminophenazine in conducting oligomers and polymers, and a separate report of nanoparticles for detection of H2O2 have gained interest recently. Corresponding to these reports alternative methods of synthesizing these large aromatic compounds are sought. Accounts of actinide assisted reaction pathways are more prevalent now than in the past and actinide alkoxo complexes are reported to promote the Tschitschibabin reaction. Few records exist with thorium as the reactive metal and because of the empty 5f6 little reactivity is expected from the Th6+ ion. However, Th6+ is readily available and easily accessible as the nitrate salt. Our interest lies in the less often reported chemistry and subsequent reactivity of the thorium ion. Here we present the oxidative coupling of α-phenylenediamine forming 2,3-diaminophenazine in the presence of thorium nitrate in aqueous solution.

INOR 973

What do uranyl-peroxide nanocapsules have in their pockets?

Pere Miro Ramirez1, p.miro@jacobs-university.de, Bess Vlasavjevich1, Adria Gil1, Peter C. Burns3, May Nyman2, Carles Boi2, Laura Galgardi1. (1) University of Minnesota and Superconducting Institute, Minneapolis, MN 55455, United States (2) Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Tarragona 43007, Spain (3) Dept Chem & Biochem, Univ Notre Dame, Notre Dame, IN 46556, United States (4) Department Physical and Inorganic Chemistry, University Rovira i Virgili, Tarragona, Tarragona 43007, Spain (5) Department of Chemistry, Oregon State University, Corvallis, OR 97330, United States

Nowadays, a wide variety of nanocapsules has been characterized and, although the growth processes are not fully understood yet, experimental evidence suggests that alkali metal cations, internal waters and other small ions in solution are fundamental in the stability and ultimate topologies of the nanocapsules. Herein, we present a theoretical study on the electronic structure of a series of diverse uranyl-peroxide nanocapsules, specifically ([UO2]6(O2)10O10(3-) (UO3)(3+)), ([UO2]6(O2)10(OH)3(OH)(2)2(2-) (UO2)) and ([UO2]6(O2)10(2)28H2O). We also shed some light onto the effects of the encapsulated species on their stability, electronic structure and other relevant properties. We have studied the encapsulation of diverse alkali counterions (such as Li+, Na+, K+, Cs+, Ca2+, ...), solvent molecules (H2O), and other small molecules (such as SO42-, [UO2]6(OH)43-, Ta(O2)5 and Nb(O2)3). Our results will be compared with the latest results from our experimental collaborators.
INOR 974

Synthesis and characterization of a new ligand for uranium capture

Karl J. Bernstein1, kberne@utk.edu, Chi-Linh Do-Thanh1, Deborah Penchoff1, Christopher R. Murdock1, S. Alan Cramer1, Zheng Lu1, Robert J. Harrison2,3, Jon P. Camden1, David M. Jenkins1. (1) Chemistry, University of Tennessee Knoxville, Knoxville, Tennessee 37996, United States (2) Institute for Advanced Computational Science, Stony Brook University, Stony Brook, New York 11794, United States (3) Computational Sciences Center, Brookhaven National Laboratory, Brookhaven, New York 11719, United States

Seawater uranium sequestration has seen a significant increase in research interest due to the projected depletion of terrestrial ores within our lifetime. Seawater contains roughly 4.5 billion tons of uranium, a thousand times the known terrestrial reserves, making it an essential and extensive source of raw material for decades to come. A significant stumbling block to seawater sequestration has been the separation processes of uranium from the complexation agent which involves concentrated acid baths. The baths rapidly degrade the media reducing the duty cycle and increases the processing cost to impractical levels.

Initial findings suggest that the addition of an aromatic sub structure ("backbone") can increase the durability of the ligands during processing. For this reason, we have chosen a molecule with a significant aromatic "backbone" for which we have designed a synthetic route and produced pilot quantities for study. This compound was characterized natively and complexed with uranium by nuclear magnetic resonance spectroscopy (NMR), mass spectroscopy (MS), elemental analysis, x-ray crystallography, infrared spectroscopy (IR) and Raman spectroscopy. Further understanding of the system's electronic character and predictions of the uranyl stretching frequency have been gathered from density functional theory (DFT) studies. Our ligand readily binds with uranium as have previous compounds, however our molecule exhibits a 1:1 binding motif verses the previously encountered 2:1 ligand : uranium binding. This is a beneficial development that should theoretically cut the number of binding sites required by half and doubling the amount of uranium captured per cycle. The improved binding ratio demonstrated by this new molecule represents a significant improvement upon previous uranium binders of this functional group. In addition the expected enhanced resistance to hydrolysis of this ligand stands to make it a significant advancement in uranium capture.

INOR 975

Insights into the bonding of Ln-DTPA chelates: A combined experimental/theoretical study

Lindsay E Roy1, lindsay.roy@srnl.doe.gov, Jennifer J Pittman1, Christopher L Klug2, Leigh R Martin2. (1) Savannah River National Laboratory, Aiken, SC 29808, United States (2) Georgia Regents University, Augusta, GA 30904, United States

Chelating agents have been used extensively to bind metal ions in several industrial processes and biological systems. One of the most commonly used chelators, diethyleneetriaminepetaacetic acid (DTPA), is used as the hold-back agent in the Trivalent Actinide-Lanthanide Separation by Phosphorous reagent Extractant from Aqueous Complexes process (TALSPHAK). Additional uses of DTPA exist in the medicinal arena as a carrier for contrast media. While DTPA is widely used in a variety of applications, the fundamental chemistry for these interactions is still not completely understood. To date few studies have focused on understanding the basic principles of DTPA chelation. This talk focuses on our efforts into understanding the structure and bonding of M-DTPA speciation, specifically La-DTPA, within the pH range of 3-8. The use of Raman spectroscopy coupled with theoretical calculations is unique as there are no reports in the literature pairing these two approaches to develop an understanding of the metal ion speciation at specific pH. The results will be used to develop an understanding of the changes in the La-DTPA chelation at relevant pHs by understanding changes in the electronic structure and metal-ligand bonding structure.

INOR 976

Assembly of mixed ligand lanthanide coordination polymers

Ralph Zehnder, ralph.zehnder@angelo.edu. Department of Chemistry & Biochemistry, Angelo State University, Angelo, TX 76909, United States

Previous examinations of extended series of lanthanide coordination polymers showed that the rigidity of the linking system seems to have a direct influence on the structural continuity of the resulting products as ionic radii decrease towards the heavier Ln-elements. Transition from purely inorganic anionic entities to various organic linker systems allows for the introduction of larger pores into the resulting coordination polymers.

Simple organic spacer units such as terephthalic acid, glutaric acid, and their derivatives readily form isostructural extended series of the corresponding lanthanide coordination polymers. While the integration of such small organic entities produces networks with very limited cavity sizes the combination of two or more organic ligand systems is expected to assist in customization of network topology as well as enlargement of pore sizes. However, so far we have obtained only a very few of the targeted Ln-coordination mixed ligand polymers. We are currently seeking for answers why the synthesis of these systems that incorporate more than one organic spacer unit turned out to be much more challenging as compared to systems that have only one ligand entity integrated.

INOR 977

Copper-promoted cyanation of the closo-CB11− cluster: Synthesis and reactivity of 12-CN-closo-CHB11H10 and 7,12-(CN)2-closo-CHB11H6

Marcus A Juhasz2, juhaszma@whitman.edu, Aaron J Rosenbaum2, Douglas H Juers2, Gregory E Dwulet1, Hannah R Midgett1. (1) Department of Chemistry, Whitman College, Walla Walla, WA 99362, United States (2) Department of Physics, Whitman College, Walla Walla, WA 99362, United States

The 1-carba-closo-dodecaborate(1-) carborane anion (closo-CB11−), has potential uses in medicine, as a non-interfering counter-anion for cationic catalysts, and in optical and electronic materials, but relatively few synthetic methods exist for preparing useful derivatives of this cluster. In an effort to expand the synthetic repertoire of closo-CB11−, we have developed a copper-promoted cross-coupling method for cyanating boron vertices of this anion. Clusters with one or two cyano groups can be prepared efficiently by this strategy: 12-CN-CHB11H10 and 7,12-(CN)2-CHB11H6 were each synthesized in yields of over 80%. These anions are the first examples of boron-cyanated derivatives of closo-CB11−, and their salts were fully characterized by NMR, IR, MS, and X-ray crystallography. The CN group is synthetically versatile and its attachment to the closo-CB11− cluster opens the door to a variety of new derivatives. The cyanation method and subsequent reactivity of cyanated closo-CB11− derivatives will be discussed.
INOR 978
Luminescent organoboron compounds derived from salicylidenebenzohydrazide: Synthesis, characterization, structure, and photophysical properties
Rodrigo A Chan1, aldor_81@hotmail.com, Víctor M Jímenez1, Blanca M Muñoz2, Ivanna Moggio2, Eduardo Arias2, María C García1.

(1) Quimica de Materiales, Universidad Autonoma de Nuevo Leon, San Nicolas de los Garza, Nuevo León 66451, Mexico
(2) Materiales Avanzados, Centro de Investigacion en Quimica Aplicada, Saltillo, Coahulia 25294, Mexico

Reaction of the 2-hydroxysalicylidenebenzohydrazides derivatives 1-4 and phenylboronic acid in benzene provided the new four cyclic boron complexes in good yields. All compounds were full characterized by NMR, UV-vis, IR and mass spectrometry. The δ11B NMR spectra to 5-8 show one signal between 7.5 and 7.9 ppm indicative of tetracoordinated boron atoms. The geometry around boron was supported by the X-ray diffraction studies.

Photophysical properties of the free benzohydrazide ligands and their boron complexes have been determined and display quantum yields below 1 % with lifetimes in the range 10^10-10^11 s.

INOR 979
Reactivity of acyclic silylenes toward alkenes and alkynes
Felicitas B Lips, flips@ucdavis.edu, Philip P Power.
Department of Inorganic Chemistry, UC Davis, Davis, CA 95616, United States

Silacycles, obtained by the addition of alkenes and alkynes to silylenes, are an important field in main group chemistry and in organic chemistry due to their application to form heteroatom ring compounds.
The reactivity of the acyclic silylenes Si(SArMe6)2 (ArMe6 = C6H3-2,6(C6H2-2,4,6-Me3)2) and Si(SArPri4)2 (ArPri4 = C6H3-2,6(C6H3-2,6-Pri2)2) toward alkenes and alkynes have been investigated.

Several siliranes and silirenes have been prepared by direct reaction under ambient conditions and characterized by 1H, 13C and 29Si NMR spectroscopy as well as X-ray crystallography. The factors that govern the reversibility of such reactions will be discussed.

INOR 980
Synthesis and reactivity of stable nucleophilic boron species
David A Ruiz, druiz@ucsd.edu, Mohand Melaimi, Guy Bertrand.
Department of Chemistry and Biochemistry, UC San Diego, La Jolla, CA 92093, United States

Boranes and borohydrides are generally regarded as archetypical Lewis acids and hydride donors, respectively. Consequently, stable nucleophilic boron compounds have eluded chemists for decades. Since their first isolation by Yamashita, Nozaki, and co-workers in 2006, only a few other boron centered nucleophiles have been described. Quite recently, we have developed unique synthetic routes leading to novel types of neutral and anionic nucleophilic boron species. Their synthesis and reactivity towards metals and electrophiles will be presented.

INOR 981
An "inverse" frustrated Lewis pair (FLP) approach toward the activation and heterolytic cleavage of molecular dihydrogen
Hui Li, hui.li@ttu.edu, Clemens Krempner, Adelia J. A. Aquino, David B Cordes, Fernando Hung-Low, William L Hase.
Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409, United States

The heterolytic cleavage of H2 via frustrated Lewis pairs (FLP’s) represents a new concept in sustainable chemistry that has the potential of replacing expensive, less abundant and toxic precious metals. One of the major disadvantages, however, is that the currently available FLP’s capable of cleaving H2 are largely limited to highly fluorinated boranes such as B(C6F5)3 and RB(C6F5)2 and synthetic procedures to these expensive Lewis acids involve hazardous or explosive materials (C6F5Li).
We will demonstrate that strong and sterically encumbered Brønsted bases such as zwitterionic and non-zwitterionic carbanions and N-heterocyclic carbene form intermolecular FLPs with fluorine free boron-containing Lewis acids capable of cleaving $\text{H}_2$. Our experimental and computational results clearly show that even poor Lewis acids engage in $\text{H}_2$ cleavage provided that the present base is sterically encumbered and of sufficiently high Brønsted basicity. This FLP approach - weak Lewis acid combined with a strong base - is inverse to that pioneered and exhaustively studied by Stephan, Erker, and others the latter utilizes FLPs composed of the exceptionally strong Lewis acids B(C$_6$F$_5$)$_3$ or RB(C$_6$F$_5$)$_2$ and weakly basic amines and phosphines.

INOR 982
Coordination non-innocence in transition metal stibine complexes
James S Jones, james.jones@chem.tamu.edu, lou-sheng Ke, François Gabbaï, Department of Chemistry, Texas A&M University, College Station, Texas 77840, United States

Several classes of ligands exhibit the ability to modify their electronic properties via nucleophilic attack or electrophilic addition at one of more of the ligand atoms. Examples of such behavior include nucleophilic attack on metal carboxyls to form acyl ligands or carbones, as well as alkylolation of metal cyamine to form the corresponding isocyanides. As part of our group's continuing interest in redox-active, main group-transition metal platforms, we have begun to investigate whether stibine ligands may display analogous behavior in conjunction with a transition metal center. Changes in the electronic properties of metal-coordinated stibines upon coordination of anions to the antimony center, as well as potential applications of these anion-induced changes will be discussed.

INOR 983
Organoantimony(V) Lewis acids as colorimetric and turn-on fluorescence fluoride sensors
Masato Hirai, masato.hirai@chem.tamu.edu, François Gabbaï, Department of Chemistry, Texas A&M University at College Station, College Station, TX 77843-3012, United States

Water fluorination is widespread in the US but excessive exposure to fluoride can trigger serious conditions such as skeletal fluorosis. To prevent such side effects, fluoride anion sensors that can be used in water are desirable. Lewis acidic main group compounds including boranes such as Mes$_2$B and silanes such as Ph$_3$SiF bind fluoride in organic solvents but not in water. In this presentation we will describe an alternative approach based on the use of organostiboranes such as ($\text{C}_2$-C$_6$H$_4$)$_2$PhSb(O$_6$C$_2$F$_5$Cl) (1), a square-pyramidal stiborane first isolated by Holmes. NMR and UV-Vis monitoring shows that stiborane 1 readily binds fluoride under both biphasic (water/CH$_2$Cl$_2$) and homogeneous (water/THF) conditions. Unfortunately, 1 does not give any notable photophysical response when converted into [1- $\text{F}^-$. In this presentation, we will show that this issue can be resolved by replacing the tetrachlorocatecholate ligand of 1 by a chromophore such as alizarin red.


INOR 984
Synthesis and characterization and isolation of a stable carborane-fused triazole radical anion
Matthew Asay, masay001@ucr.edu, Christos E Kefalidis, Laurent Maron, Vince Lavallo, (1) Department of Chemistry, University of California, Riverside, Riverside, CA 92521, United States (2) Department of Chemistry, Université de Toulouse, Toulouse, France

Recently, we reported the synthesis of a family of unusual 1,2,3-triazoles that are fused with icosahedral carborane anions such as the phenyl substituted compound 1 (figure 1, unlabeled vertices = B-Cl). Interestingly, both the carborane and five-membered-triazole portions of these molecules independently feature aromatic characteristics. The electrochemical properties of 1 have been investigated to ascertain if a radical anion is accessible but due to the electron rich nature of the carborane reduction is not possible. With this fact in hand it seemed reasonable that if the negative charge of 1 were masked, by the formation of a zwitterion, its electrochemical properties may be altered sufficiently to make one electron reduction feasible. Hence, anion 1 was alkylated with methyl triflate to afford the zwitterionic species 2 in excellent yield. Reduction of this species with cobaltocene led to a radical species that could be detected as one broad signal at $g=2.003$ by EPR spectroscopy.

To confirm the formation of the radical anion 3 and compare its structural features with those of the unreduced zwitterion 2, we obtained crystals suitable for single-crystal X-ray diffraction studies of both compounds. Spectroscopic and computational data have been used to ascertain that the radical is localized on the triazolium portion. This represents the first isolable and fully characterized 1,2,3-triazolium species.

INOR 985
Two-electron redox chemistry at the dinuclear core of a SbPt platform: Chlorine photoreductive elimination

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Metal complexes that support two-electron redox processes are attracting a great deal of interest because of their importance in the domain of catalysis and energy conversion. Recent developments in this field have witnessed the advent of bimetallic complexes and their use for the photocatalytic splitting of HX molecules. While such complexes usually contain two noble metals, the Gabbai group has recently shown that heterobimetallic compounds containing a noble metal (Pt) as well as a heavy main group element (Te) may also have a potential in this area. As part of our developing passion in redox-active main group/transition metal platforms for energy applications, we have investigated platinum/ammonium complexes of general formula R$_2$Sb[PtI]Cl with [PtI] = L$_2$Pt. Such complexes can be oxidized by addition of an equivalent of chlorine to afford complexes of general formula (R$_2$Sb)[Pt-Cl]. Remarkably, some of these oxidized complexes can be reduced back to the original complex when irradiated with UV-light in the presence of a radical trap such as 2,3-dimethyl-1,3-butadiene. Depending on the antimony substituents, the quantum yield of the photooxidative elimination can be as high as 15.3%.

INOR 986
Reactivity studies of carbonyl-decorated carboranes with group 15 element-containing compounds
Todd W Hudnall, th40@txstate.edu, Antonio J Torres, Roberta R Rodrigues, Christopher L Dorsey. Department of Chemistry and Biochemistry, Texas State University, San Marcos, TX 78666, United States
We and others have recently shown that the introduction of carbonyl groups into the backbone of N-heterocyclic carbenes (NHCs) greatly enhances the n-acidity of the carbene by lowering the LUMO energy. This modification results in carbenes which can be regarded modest electrophiles and poor nucleophiles. This presentation, will discuss how the unique electronic properties of carbonyl-decorated carbenes (CDCs) alters their reactivity toward chlorinated group 15-element containing compounds. Specific attention will be devoted to the reactions of diaminocarbenes and monoamidoamino carbenes with phosphorus, arsenic, and antimony chlorides including PCl$_3$, AsCl$_3$, SbCl$_3$, PhPCl$_3$ and PhSbCl$_3$. As a part of this discussion will also be new synthetic methodologies that we have developed to overcome some of the limitations regarding the reactivity of CDCs toward group 15 chlorides.

INOR 987
Synthesis and reactivity study of an efficient precursor for transition-metal-free 1,3-dehydoro-ocarbaborane
Da Zhao, zxie@cauhk.edu.hk, Zuowei Xie. Department of Chemistry, The Chinese University of Hong Kong, Hong Kong, Shatin, New Territories, Hong Kong Special Administrative Region of China
1,2-Dehydoro-ocarbaborane (o-carbaborane) 1, a very reactive intermediate reported first in 1990, is regarded as a three-dimensional relative of benzene (1) and known to undergo [4+2] cycloaddition reaction with polycyclic and hetero aromatics. 1,3-Dehydoro-ocarbaborane (1,3-o-carbaborane) 3, which might feature a cage C-B multiple bond, however, remained less developed. The only reported preparation of 3 is from 3-ido-1-lithio-ocarbaborane mediated by palladium(0). 3-Diazionio-ocarbaborane tetrafluoroborate 4 were prepared as a transition-metal-free precursor for the generation of 3. Such reactive intermediate could be trapped by various alkylbenzenes to afford [4+2] and ene products in moderate to good yields by treatment of 4 with one equiv of lithium disopropanylamine (LDA) as shown in the scheme.

INOR 988
Core@Shell RE:A$_2$O$_3$@A'B'O$_2$ nanoparticles: Synthesis and luminescence properties
Yuanbing Mao, mao@utpa.edu. Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78539, United States
In order to improve the luminescence efficiency of nanomaterials doped with RE$^{3+}$ ions, a lot of approaches have been developed. In this study, trivalent europium doped lanthanum zirconate (La$_2$Zr$_2$O$_7$:Eu$^{3+}$) core nanoparticles (NPs) were first synthesized morphology-controllably via a facile molten salt synthetic process, and were coated with yttrium orthoborate (YBO$_3$) shell in the next step. These novel formed heterostructured La$_2$Zr$_2$O$_7$:Eu$^{3+}$@YBO$_3$ core@shell NPs were characterized mainly using power x-ray diffraction, transmission and scanning electron microscopes, and their photoluminescence was carefully studied. More importantly, the effect of different experimental processing parameters on the structure, morphology and luminescence properties of these core@shell nanoparticles was explored. The core nanoparticles possess a unprecedented high concentration quenching, which is ~32.5% of europium dopants in the La$_2$Zr$_2$O$_7$ host due to the even distribution of Eu$^{3+}$ ion enabled by our facile synthetic process. Moreover, luminescent enhancement was observed after the La$_2$Zr$_2$O$_7$:Eu$^{3+}$ core NPs were coated with the thin YBO$_3$ shell. Based on optical transition property analysis and fluorescent decay measurement, the improvement of non-radiative transition rate is possibly responsible for the luminescent enhancement. Moreover, the improvement of the symmetry around the Eu$^{3+}$ ions in the La$_2$Zr$_2$O$_7$:Eu$^{3+}$ core NPs was found after the YBO$_3$ shell coating. These special properties allow these nanoparticles as excellent candidates for broad applications in various many fields, such as lasers, signal storage, bio/medical imaging and diagnostics, solar energy conversion, and disinfection of surfaces and water.

INOR 989
Linking the anomalous magnetic properties of iron oxide nanocubes to their defect structure: Topotaxial oxidation of Fe$_{14}$O([Fe$_{3}$O$_{4}$] core(shell nanocubes to single-phase particles
Erik Wetterskog, Cheuk-wai Tai, Jekabs Grins, Lennart Bergström, German Salazar-Alvarez, german@mrnk.su.se. Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden
Magnetic nanoparticles have emerged as potential candidates for e.g., magnetic storage and a range of biomedical applications. However, their magnetic properties are often below the theoretically expected values. In this work we study how the microstructure and magnetic properties evolve when biphasic core@shell Fe$_{14}$O([Fe$_{3}$O$_{4}$] nanoparticles synthesized by thermal decomposition topotaxially oxidizes to single-phase nanoparticles. Geometric phase analysis of high-resolution electron microscopy images reveals a large interfacial strain at the core@shell interface and the presence of anti-phase boundaries. Dark-field transmission electron microscopy images and powder x-ray diffraction concur that, as the oxidation proceeds, the interfacial strain is released as the Fe$_{14}$O core is removed, but that the anti-phase boundaries remain. The perseverance of the anti-phase boundaries results in anomalous magnetic behavior, i.e., a reduced saturation magnetization, and emergence of exchange-coupling effects. Our results indicate that internal defects and not only surface effects play an important role in dictating the magnetic properties of iron oxide nanoparticles.

INOR 990
Tuning thermoelectric properties of Yb$_2$MnSb$_2$, by RE substitution: Synthesis, structure and thermoelectric properties of Yb$_{14}$RE$_2$MnSb$_2$(RE=Pr and Sm, 0<x<1)
Yufei Hu1, yihu@ucdavis.edu, Susan Kauzlarich1, Sabah K Bux2, Maxsuda N Abdusalyamova3. (1) Department of Chemistry, University of California, Davis, Davis, California 95616, United States  (2) Department of Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, United States  (3) Institute of Chemistry of Tajik, Dushanbe, Tajikistan

Thermoelectric materials, which can convert heat into electricity, have attracted much attention in potential applications for waste-heat to electricity conversion. Yb14MnSb11 is the only known high efficiency p-type thermoelectric material at high temperatures. Substitution of other rare earth elements for Yb provides a method to optimize its thermoelectric property and study its magnetic properties. Single crystals of Yb14RE,MnSb11 (RE = Pr and Sm, 0≤x≤1) were synthesized by Sn flux. Structural study and magnetic measurement were carried out on the single crystals. The Pr is site selective in the structure. As x increases, the ferromagnetic ordering temperature is reduced while the saturation moment falls into a small range. Powder samples of Yb14RE,MnSb11 (RE = Pr and Sm, 0≤x≤1) have been synthesized by annealing at 1375K for one week. Electron microprobe was used to verify the molecular formula. Thermoelectric properties of these samples were measured to 1275K. The zT value of these samples are 10% to 20% percentage larger than Yb14,MnSb11.

INOR 991

3D conjugated acceptors: Azadipyrromethene based homoleptic Zn(II) complexes
Wasana Senevirathna, wus@case.edu, Jun Gu, Zhenghao Mao, Geneviève Sauvé. Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106, United States

Organic photovoltaic is a promising technology for solar energy harvesting. The power conversion efficiency (PCE) of solution-processed bulk heterojunction (BHJ) cells has reached over ~10%. In many studies, fullerene and its derivatives have been the most investigated acceptor. However, fullerene derivatives have disadvantages: (i) weak absorption in visible and near IR range, (ii) limited energy tunability. Promising alternative non-fullerene acceptors are limited, and the best efficiency achieved so far is ~5%.

In this study, we introduce 3D conjugated homoleptic Zn(II) complexes of azadipyrromethene (ADP) based molecules as promising candidates for use as electron acceptors in organic photovoltaics. The degree of conjugation in ADP was extended by installing phenylacetylene, ethynylthiophene and thiophene groups at the pyrrolic positions of the ADP core using Stille coupling. 3D structures of these molecules were synthesized by chelating with Zn(II). These new molecules show broad intense red to near infrared absorption with onsets around 760 nm. The estimated LUMO energy level of Zn(II) complexes ranged from -3.60 to -3.85 eV. The electron accepting properties were studied by fluorescence quenching experiments using poly(3-hexylthiophene) (P3HT) as the donor. These metal complexes quench the fluorescence efficiently in both solutions and film. DFT calculations show that all the metal complexes have distorted tetrahedral structures, and that the two ADP ligands are π-stacked with each other. Additionally, the Zn(II) complexes have very low internal reorganization energy with high electron affinity. These ADP based Zn(II) complexes show photovoltaic properties in organic solar cells.

INOR 992

Supramolecular aggregates of single-molecule magnets
Tu N Nguyen1, nguyen@chem.ufl.edu, Tuhin Ghosh1, Muhandis Shiddiq2, Wolfgang Wernsdorfer2, Stephen Hill2, Khalil Abboud3, George Chistou1. (1) Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States  (2) High Magnetic Field National Laboratory, Tallahassee, Florida 32310, United States  (3) Institut Néel, CNRS, Grenoble, France

Single-molecule magnets (SMMs) are molecules with a large ground-state spin, S, and a magnetooanisotropy of the Ising-type (negative D). As a result, they display the classical magnetic property of a magnet, hysteresis loops in magnetization vs applied magnetic field scans. SMMs represent a molecular approach to nanoscale magnetic materials, and also display interesting quantum properties, such as quantum tunneling of magnetization and quantum phase interference. SMMs with various structures have been prepared using a variety of ligands. Linking two or more SMMs together in order to introduce weak exchange interactions between them is important for potential applications, such as qubits in quantum computing. Recent investigations into the use of dioximes and dicarboxylic acids as potential bridging ligands have resulted in new supramolecular SMMs with interesting structures. The syntheses, structures, magnetic characterization and supramolecular properties of these SMMs will be described.
INOR 993
Interlinking STEM disciplines in the search for new mesoscopic magnetic materials

Christos Lampropoulos, c.lampropoulos@unf.edu, John M Cain. Department of Chemistry, University of North Florida, Jacksonville, Florida 32224, United States

The field of molecular magnetism is intrinsically interdisciplinary, since the properties of molecular magnetic materials straddle between the classical and quantum regimes. In the search for new molecular magnets and their use in molecule-driven devices, chemistry, physics, and engineering are interlaced: chemistry for the materials synthesis, physics for their characterization, and engineering for the device development. An overview will be given on our cross-disciplinary efforts towards magnetic materials and molecular sensors.

INOR 994
Light-induced radical trapping (LIRT): Toward photomagnetic switching at room temperature

Hoa Phan¹, hphan@chem.tus.edu, Kristina Lekin², Stephen M Winter², Richard T Oakley², Michael Shatruk². (1) Florida State University, Tallahassee, Florida 32310, United States (2) Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Trapping of metastable paramagnetic states generated by photoexcitation is one of the most fascinating phenomena in the study of photoresponsive molecular materials. The magnetic state switching holds potential for being used in memory devices, sensors, or radiation detectors. Although this phenomenon has been studied extensively in transition metal complexes, no examples of long-lived metastable states (on the order of days) paramagnetic states have been reported in solid state organic materials. Herein, we demonstrate our first observations of such switching in hypervalent 4-center 6-electron S···S−S···S bridged σ-dimers of a bisdithiazolyl radicals. The results are very encouraging, as the photogenerated paramagnetic state exhibits an unusually high relaxation temperature, remaining stable to nearly room temperature before converting back to the diamagnetic dimer form. The radical-dimer interconversion under irradiation has been monitored by magnetic susceptibility measurements, optical absorption spectroscopy, and single crystal X-ray diffraction.

INOR 995
Halide substituent effects on difluoroboron diketonate mechanochromic luminescence

William A Morris, wam8wr@virginia.edu, Tiandong Liu, Christopher A DeRosa, Cassandra L Fraser. Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States

Many difluoroboron 8-diketonate (BF₂-dbdk) dyes display mechanochromic luminescence (ML). Furthermore, various substituents can influence these properties. For example, the difluoroboron iododibenzoylemethane derivative, BF₂-dbdk(1)OC₂H₅, exhibits mechanochromic luminescence quenching (MLQ). That is, when thin films of the emissive dye are smeared under air, the perturbed regions become dim. Under a nitrogen atmosphere, however, the emission from the smeared regions is not quenched. Green fluorescence and orange phosphorescence are observed, with a significant increase in phosphorescence intensity in mechanically perturbed regions. This suggests that applying mechanical force to the dye facilitates crossover to the oxygen sensitive triplet state. In this study, we seek to better understand the effects of halide substituents on ML. A series of dyes of the form BF₂-dbdk(X)OC₂H₅, where X = F, Cl, Br, I and H was synthesized. The luminescence properties of the dyes were studied in CH₂Cl₂ solution, as thin films on weighing paper substrate, as well as thin spin-cast films on microscope cover glass slides. All of the dyes exhibit ML and MLQ to varying degrees. The MLQ effect was found to increase with heavier halogen substituents. Therefore, MLQ is not limited to BF₂-dbdk(1)OC₂H₅ and can be tuned by using differing halogen substituents. Furthermore, the emission from these dyes is quite sensitive to annealing temperature. The F, Cl, and Br variants require higher temperatures to achieve ordered states with blue-shifted emissions than do the H and I variants. Finally, spin-cast films of the dyes on microscope cover glass were studied using atomic force microscopy (AFM), revealing a change from an amorphous material in the as-spun state to an ordered, crystalline state after annealing.

INOR 996
Investigating the formation of thermoelectric nanomaterials synthesized by a modified polyol process

Evan E Rugen, Cameron F Holder, Mary E Anderson, meanderson@hope.edu. Chemistry, Hope College, Holland, MI 49423, United States

Reaction pathways have been determined for the formation of two thermoelectric materials, PbTe and Bi₂Te₃, synthesized by a modified polyol process. Thermoelectric materials have excellent alternative energy potential, most notably for the conversion of waste heat into usable electricity. Conversion efficiencies have been shown to be improved by modifying the material to be nanostructured; and synthetic methods are being investigated to reduce production costs for economic viability. Presented here is a modified polyol process for the formation of thermoelectric nanoparticles that reduces production cost and energy consumption by using a solution phase “bottom-up” approach. This method uses sodium borohydride to reduce starting materials from metal ions to atoms while mixing them together in a high boiling point polyol solvent (tetraethylene glycol) to form intermetallic nanoparticles. These thermoelectric nanomaterials were characterized by powder x-ray diffractometry, scanning electron microscopy, and energy dispersive x-ray spectroscopy. By generating a range of samples as a function of time and temperature, reaction pathways were determined mapping out changes in elemental composition, crystal structure, and morphology. Growth mechanisms for both PbTe and Bi₂Te₃ have been compared and contrasted to investigate what growth stages are common to the synthetic method and which are specific to the compound being fabricated. For these two compounds, the reaction begins similarly with lead or bismuth ions, respectively, being reduced as the reaction begins and then incorporated into the tellurium material. This incorporation occurs very differently for these two systems and dramatic morphological transitions are observed as intermediate products are formed and converted. Production of the two target materials occurs at similar temperatures, but as temperature is elevated...
the effect on morphology differs. Further research is underway to investigate the effect of different tellurium starting materials, to study other telluride containing compounds, and to appreciate nuances in reaction pathways for different polyol solvents.

INOR 997

Phenomena observed in solid-state NMR spectroscopy when adsorbing phosphines, phosphine oxides, and metallocenes on silica surfaces
Janet Bluemel, bluemel@tamu.edu, Kyle J. Cluff, Casie R. Hilliard. Department of Chemistry, Texas A&M University, College Station, TX 77843, United States

The adsorption of molecular species on oxide surfaces represents the crucial first step in many synthetic processes and purification procedures. Solid-phase synthesis, chromatography, ion exchange, or catalysis are typical fields involved. Here, we present new, surprisingly general and common characteristics regarding the surface mobilities and phase transitions of species as diverse as phosphines, phosphine oxides, and metallocenes, when they are adsorbed on silica surfaces. The nature and mobility of each adsorbed species is optimally investigated by multinuclear solid-state NMR spectroscopy. Classical \(^{31}P\) and \(^{13}C\) CP/MAS (Cross-Polarization/Magic Angle Spinning) and \(^{2}H\) MAS investigations of dry materials, as well as HRMAS NMR (High-Resolution MAS) of slurries, reveal the CSA (Chemical Shift Anisotropy), the chemical shift, the quadrupolar coupling constant, and the residual halfwidth, on going from the molecular crystalline to the adsorbed species. Interestingly, the adsorption can be achieved in all cases not only from solution, but also by grinding together the dry components (with high melting points!), phosphines, phosphine oxides, and metallocenes, with silica. Surprising quantitative insights about the diverse modes of mobility on the silica surface will be presented for all adsorbed species.

INOR 998

Photomechanical effects in polymers containing photochromic compounds
Lauren Loftus, Yuhuan Jin, Jeffrey Rack, rackj@ohio.edu. Department of Chemistry and Biochemistry, Ohio University, Athens, OH 45701, United States

We have prepared polynorbornene and polydimethylsilane samples which contain photochromic ruthenium sulf oxide complexes. Upon irradiation these polymer samples undergo reversible and repeatable shape change. For polynorbornene, this shape change is macroscopic and results in dramatic bending induced by light. We will discuss a bilayer cantilever model to explain these results. For polydimethylsilane, the polar ruthenium complexes aggregate forming coronae within the apolar silane polymer. Upon irradiation this shape change results in significant topological changes with coronae rising on the order of 30 nm. In the dark, these topological features reverse. These cycles are reversible and repeatable for many cycles. These studies and others will be discussed and a model to explain these results will be presented.

INOR 999

Luminescent aluminum salophen complexes incorporated into conducting metallopolymers
Lauren A. Mitchell, averyle@utexas.edu, Sarah F. Swingle, Bradley J. Holliday. Department of Chemistry, The University of Texas at Austin, Austin, TX 78712, United States

OLED devices are typically composed of a cathode, an electron transport layer, an emitting layer containing small molecule fluorophores such as platinum or iridium containing complexes, a hole transport layer, and then finally a transparent anode. Many devices also contain additional buffering layers and injection layers to improve device performance. Each layer requires laborious and therefore expensive deposition processes. Often the emissive layers of these device architectures suffer from aggregation of the emitters, non-uniform films, and the need for a composite material. Our approach to these issues is to create a polymeric system based upon a conducting polymer backbone to eliminate the need for a composite material, with covalently bound luminescent centers to prevent emitter aggregation. Additionally we specifically chose electropolymerization because the polymerization process creates a thin film directly on an electrode, eliminating the need for the processing of bulk material into films. Schiff base ligands, such as salophen are easily synthetically accessible and can bind to a wide array of metal ions. Aluminum salophen complexes in particular have been found to exhibit blue emission, which is promising as an economic alternative to the widely studied blue emitters which often contain precious metals such as platinum and iridium. The specific system selected for this study is an ester functionalized salophen ligand flanked by electropolymerizable bithiophene groups. Additionally, alkyl chains were appended to the phenyl backbone to overcome solubility issues with the material. Presented herein will be the synthesis and characterization of the salophen ligand, aluminum-salophen monomer, and the resulting polymeric materials. Both electrochemical studies and the absorption and emission spectroscopy of the ligand, monomer, and polymeric materials will be discussed.

INOR 1000

Self-Propelled Mg-based micromotors for environmental remediation
Wei Gao, gaowei2009@gmail.com, Xiaomiao Feng, Allen Pei, Yonge Gu, Jinxing Li, Joseph Wang. Department of Nanoengineering, University of California, San Diego, La Jolla, CA 92093, United States

The propulsion of synthetic nanoscale objects represents a great challenge and opportunity. Unfortunately, the requirement of the toxic chemical fuels or extreme environments greatly impedes many practical applications of such chemically-propelled micro/nanoscale motors. We describe here the use of seawater as fuel to propel Janus micromotors. The new micromotors consist of biodegradable and environmentally friendly magnesium microparticles and a nickel–gold bilayer patch for magnetic guidance and surface modification. Such seawater-driven micromotors, which utilize macrogalvanic corrosion and chloride pitting corrosion processes, eliminate the need for external fuels to offer efficient and prolonged propulsion towards diverse applications in aquatic environments. The important related roles of the gold coating and the ionic (particularly chloride-rich) environments have been discussed. We also demonstrated the first example of a surface-functionalized water-driven micromotor towards practical applications in realistic environments. SAM-modified hydrophobic Mg micromotors were thus applied successfully for oil cleaning in seawater and show considerable potential for environmental remediation. The new water-driven motion capability should greatly expand the scope of applications and environments of chemically powered nanomachines.
INOR 1001
Integration of molecular and enzymatic catalysts on graphene for biomimetic generation of antithrombotic species
Teng Xue1, tengxue@ucla.edu, Yu Huang1, Xiangfeng Duan2, Mark E Meyerhoff3. (1) Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, CA 90095, United States (2) Department of Chemistry, University of California, Los Angeles, Los Angeles, CA 90095, United States (3) Department of Chemistry, University of Michigan, Ann Arbor, Ann Arbor, MI 48109, United States

The integration of multiple synergistic catalytic systems can enable the creation of biocompatible enzymatic mimics for cascading reactions under physiologically relevant conditions. Here we report the design of a novel graphene-hemin-glucose oxidase (GOx) conjugate as a tandem catalyst, in which graphene functions as a unique support to integrate molecular catalyst hemin and enzymatic catalyst GOx with retained functionality for biomimetic generation of antithrombotic species. We show that the monomeric hemin can be conjugated with graphene through π-π interactions to function as an effective catalyst for the oxidation of endogenous L-arginine by H2O2. Furthermore, we show that GOx can be covalently linked onto graphene for local generation of H2O2 through the oxidation of blood glucose. Thus, the integrated graphene-hemin-GOx catalysts can readily enable the continuous generation of nitroxy, an antithrombotic species, from physiologically abundant glucose and L-arginine. Lastly, we demonstrate the conjugates can be embedded within polyurethane to create a novel, long-lasting antithrombotic coating for blood contacting biomedical devices.

INOR 1002
Optimization of the Fe2O3 (hematite) nanocrystal: NaIO4 photocatalytic water oxidation system
Bronwyn L Harrod, Nicholas Brune, Christopher Wong, Frank E Osterloh, fosterloh@ucdavis.edu. Department of Chemistry, University of California, Davis, CA 95616, United States

While nanostructured Fe2O3 (hematite) photoelectrodes are now well established as a means to convert solar energy into fuel via the water splitting reaction, the photocatalytic water oxidation properties of suspended Fe2O3 photocatalysts have not been thoroughly studied. We recently reported that visible irradiation (>400 nm) of suspended Fe2O3 nanocrystals produces oxygen with up to 0.77 mmol h	extsuperscript{-1} g	extsuperscript{-1}, when silver nitrate is used as a sacrificial electron acceptor. But, reductive deposition of silver deactivates the nanoparticles completely within 18h. Prolonged O2 evolution with only minor catalysts deactivation is possible with NaIO4 as electron acceptor (E\textsuperscript{\circ}=+1.6 V vs NHE). This allows a systematic investigation of the photocatalytic reaction system. Here we show that the activity increases linearly with illumination intensity, as expected from thermodynamics. It increases asymptotically with sacrificial electron acceptor concentration up to a final threshold that is defined by the water oxidation kinetics. A similar asymptotic dependence is observed with the Fe2O3 concentration, due to shading. Higher solution pH promotes oxygen evolution, based on thermodynamic reasons.

INOR 1003
Self-assembly of catalytic Janus nanomotors
Wei Gao, gaowei2009@gmail.com, Joseph Wang. Department of Nanoengineering, University of California, San Diego, La Jolla, California 92093, United States

Locomotion of synthetic nano-/microscale objects through fluid environments is one of the most exciting and challenging areas of nanotechnology. Inspired by animal interactions, the ability of synthetic nanoscale motors to produce self-organized structures is of considerable interest, owing to their future implications in nanomedicine, nanomachinery, transport systems, and chemical sensing. Organized self-assemblies of Janus catalytic motors, induced by hydrophobic surface interactions involving multiple motor/motor and motor/nonmotor particles, display controlled coordinated self-propulsion. These assemblies were prepared by octadecytrichlorosilane (OTS) modification of the surface of a silica microparticle and addition of a catalytic Pt hemispheric coating. The influence of the self-assembled structures upon the motion behavior is investigated. Different bonding orientations between these hydrophobic Janus motors induce different forms of motion. The relative orientation of each motor in the assembly changes its contribution to the net propulsion force and rotational moment. The hydrophobic interactions between individual micromotors and micromotor assemblies can promote a continuous growth of the assembly during its movement and lead to dynamic changes in the motion behavior. Organized assemblies of multiple motor/nonmotor particles are also illustrated toward optimal cargo transport and delivery. Such controlled structures and motion of chemically powered Janus nanomotor assemblies hold considerable promise for the creation of intelligent nanomachines that perform collective tasks.
Design of hybrid nanostructures for efficient electron-hole separation in photocatalytic CO₂ reduction and water splitting

Yujie Xiong, yjxiong@ustc.edu.cn. School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, China

Photoexcited electrons should be efficiently separated from holes in semiconductors, allowing their delivery to specific regions for half-reactions in photocatalysis. In competition with charge transfer is electron and hole recombination, which has been a key process for limiting quantum efficiency in related applications. In order to suppress the recombination, an effective solution is formulation of Schottky junctions by integrating an electron-extracting agent with the semiconductor. In this presentation, I will demonstrate two approaches to efficient electron-hole separation for CO₂ reduction and water splitting, respectively, by formulating Schottky barrier in semiconductor-based hybrid nanostructures. In the first approach, a semiconductor-metal-graphene design has been implemented to efficiently extract photoexcited electrons through the graphene nanosheets. Ultrafast spectroscopy characterizations exclusively demonstrate that the accumulation of “hot” electrons at the interface of semiconductor and metal can be substantially avoided, enabling superior efficiency in water splitting. The second approach is to utilize the capabilities of metal-organic frameworks (MOF) in capturing CO₂ and transferring electrons, leading to greatly improved activities of semiconductor in CO₂ reduction. It is anticipated that this work opens a new window to rationally designing hybrid systems for photo-induced applications.

Nanofabricated, nanostructured LiCoO₂ thin film cathode for Li ion batteries

Mark A Poyner, mark-poyner@utulsa.edu, Dale Teeters. Department of Chemistry and Biochemistry, The University of Tulsa, Tulsa, Oklahoma 74104, United States

Li ion batteries provide a viable power source for numerous applications including but not limited to mobile devices, laptop computers and electric vehicles. The demand for more complex technologies continues to increase the need for smaller, lighter and higher capacity Li ion batteries. Using nanotechnology to improve Li ion battery performance has gained significant interest as battery applications continue to grow. These unique properties appear dependent on the amount of surface area exposed by the nanomaterial. Using techniques that increase an electrode material's surface area should result in more electrode-electrolyte contact, Li ion intercalation and ultimately higher capacities. Anodized aluminum oxide (AAO) nanoporous membranes having pores that are 200 nm in diameter were used as templates to make a LiCoO₂ nanostructured electrode material. The nanostructured LiCoO₂ was formed by using RF magnetron sputtering of the lithium ion electrode material on the AAO template, and this nanofabrication technique makes an electrode system in a configuration that is immediately ready for thin film battery applications. These nanoporous electrodes exhibit six times the surface area of traditional thin film electrodes, making for increased electrode-electrolyte contact. The resulting enhanced electrode performance will be discussed. The characterization techniques used to study nanostructured LiCoO₂ include ac impedance, infrared and Raman spectroscopy. The crystal structure was studied using X-ray diffraction and surface structure was investigated by atomic force microscopy and scanning electron microscopy. SEM was used to investigate the structure change upon lithium deintercalation (charging) and intercalation (discharging). Nanostructured LiCoO₂ cathodes will be discussed in comparison to a standard thin-film cathode with no nanostructuring.

Exciton-plasmon energy exchange in non-epitaxial Au/CdS core/shell nanocrystals

Mikhail Zamkov, zamkovm@bgsu.edu, Scott Lambright, Pavel Moroz, Shannon Ibarra, Natalia Razgoniaeva. Physics, Bowling Green State University, Bowling Green, OH 43403, United States

The dynamics of exciton-plasmon interactions in non-epitaxial Au/CdS core/shell heteronanocrystals has been studied using ultrafast transient absorption spectroscopy. The hybrid interface of metal and semiconductor domains in these structures was designed to prevent an excessive lattice strain. As a result, the rate of carrier trapping on defect sites was found to be substantially reduced (lifetime, τ ~ 300 ps) in comparison with Au/CdS heterostructures grown via a conventional, Au-salt reduction approach (τ < 0.02 ps). Remarkably, it was found that the rate of CdS exciton dissociation due to trapping on defects or charge transfer across non-epitaxial Au/CdS interfaces was sufficiently slow to allow for ultrafast (< 0.7 picosecond) exciton-plasmon interactions to fully unfold before defect-related energy losses took place. It is hypothesized that unusually long lifetimes of excitons in non-epitaxial Au/CdS NCS should be attributed to the formation of an interstitial alloy layer (either Au₂S or Ag₂S) at the boundary of Au and CdS phases, which prevents a “backward” flow of charges into the metal domain.
Water splitting using semiconductor-based heterogeneous photocatalysis plays a key role in a promising path to clean and sustainable energy production. Domen’s group has reported that the band gap of GaN can be reduced to absorb visible instead of UV light by alloying GaN with ZnO. The band-gap-narrowed GaN/ZnO alloy is an efficient visible-light photocatalyst, although microscopic models for reaction sites and mechanisms remain as important open questions. Using density-functional-theory-based molecular dynamics, we investigate the microscopic structural and electronic properties of aqueous interfaces of nonpolar Wurtzite facets of GaN, ZnO, and representative GaN/ZnO alloy structures. We find that water adsorption is substantially dissociative. At the equilibrated interfaces, most of the surface anions are protonated, while many surface cations are bonded to hydroxide ions. Surface N-sites show stronger basic character and are protonated more readily than surface O-sites. All surface Ga atoms are bonded to hydroxide ions while about 50% of surface Zn atoms are bonded to hydroxide ions. Our earlier work suggests that water oxidation at the GaN-water interface is driven by the localization of photogenerated holes on the adsorbed hydroxides. We analyze the propensity for such hole localization by means of the projected density of states. At pure GaN and ZnO aqueous interfaces, holes are equally likely to localize on the adsorbed hydroxides and protonated anions. However, at GaN/ZnO alloy aqueous interfaces, holes tend to localize on protonated N atoms and nonprotonated O atoms suggesting that additional reaction barriers related to hole adsorption might be involved.

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INOR 1008

Interconnected 3D caterpillar-like ZnO networks: Novel structural evolution and enhanced photoelectrochemical water splitting performance

Yuanbing Mao, maoy@utpa.edu, Qiang Li, Xing Sun.Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78539, United States

Sunlight is an abundant, inexpensive, pollution-free and endlessly renewable source of clean energy. Converting solar energy into an easily usable form has also attracted considerable interest in the last several decades. Among different technologies for solar energy conversion, photoelectrolysis has been used to split water in hydrogen and oxygen without any emission of byproducts. However, the conversion efficiency today remains low (e.g. lower than that of photovoltaics), and is limited mainly by the low performance of the photoelectrodes. To develop better photoelectrodes and more efficient devices, one of the main strategies is the nanostructuring strategy by exploiting scaling laws and specific effects at the nanoscale to enhance the efficiency of existing semiconductors and metal oxides. Here a hierarchical “caterpillar-like” ZnO nanoarchitecture was demonstrated with densely packed nanowire branches on seed-assembled nanofibers. The networks composed of multilayered ZnO catapillars possess high-level spatial distribution of crystalline nanowires and hence build vital 3-D interconnected conduction pathways to improve the overall solar conversion efficiency. The photoelectrodes achieve a maximal photocurrent density of 0.72 mA cm\(^{-2}\) at +1.2 V versus Ag/AgCl under 1 sun illumination (100 mW cm\(^{-2}\) AM 1.5G). This protocol is substantially beneficial to hydrogen generation by means of (i) greatly increased light-harvesting/trapping capability, (ii) improved electron migration to back contact confirmed by longer photoelectron lifetime, and (iii) optimum charge separation and hole transfer at the electrode/electrolyte interface validated by photoelectrochemical impedance spectroscopy study.

INOR 1009

Imparting stability to MgO(111) via carbon coating processes

G. Jeremy Leong\(^{1,2}\), jeong@mines.edu, Zachry R. Gertig\(^{1}\), zgertig@mines.edu, Maxwell C. Schulze\(^{1}\), Ameen Ghavam\(^{1}\), Ryan M. Richards\(^{1}\). (1) Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, United States (2) Chemical and Materials Science Center, National Renewable Energy Laboratory, Golden, CO 80401, United States

Carbon-coating has been shown to effectively provide protection to MgO under conditions that would normally cause decomposition and deactivation. In particular, it would be desirable to utilize the properties of MgO in aqueous and acidic environments. Previously reported methods towards carbon coating MgO (CC-MgO) utilized resorcinol or gaseous hydrocarbons as the carbon precursors which often times produces heterogeneous coatings. Herein, we report a green, facile, scalable and reproducible method of carbon coating via a two step synthetic route. Glucose is polymerized via solvothermal treatment, and then carbonized under inert conditions using systematically controlled temperature profiles and reaction times, yielding specific carbon thicknesses. Glucose has been used to carbon coat other ceramic and composite materials like MnO\(_2\), LiCoO\(_2\), and LiFePO\(_4\). Characterization of materials was performed using TEM, BET, XRD, TGA, and Raman spectroscopy. Stability studies were carried out under aqueous and acidic environments by observing changes in pH upon CC-MgO addition.

INOR 1010

How does the surface area of metal-air anodes affect their rate of discharge?

Marshall T McNally, Matthew R Pueringer, Hannah C Seal, Mark C Walsworth, Justin C Lytle. lytlejc@plu.edu.Department of Chemistry, Pacific Lutheran University, Tacoma, WA 98447, United States

The challenges of meeting the energy and power demands of modern electron applications have motivated the battery community to incorporate nanostuctured features and throughconnected porosity into battery electrodes and thereby greatly amplify an electrode’s interactions with its surrounding electrolyte. This approach has been successfully applied to electrodes in Li-ion batteries, as numerous studies have demonstrated that porous nanomaterials can greatly increase the rates of an electrode’s charge and discharge. Metal-air batteries and other chemical formulations are also appealing because they can store even larger amounts of energy per mass and volume. Metal-air batteries are limited, though, in the current densities they can bear without polarization because the rates of oxygen reduction at the cathode and metal oxidation at the anode can limit the overall power of these batteries. We hypothesize that the specific power of metal-air anodes will improve by distributing metal nanoparticles on the pore walls of current collectors that are themselves porous and have abundant interfacial areas. To test this hypothesis, we prepare macroporous carbon nanofoam sheets using an existing methodology with phenolic resin and carbon fiber paper, and subsequently deposit rust onto nanofoam pore walls from dilute K\(_2\)FeO\(_4\) solution. Iron oxyhydroxide is present throughout the aerogel-like carbon nanofoam pore network (SEM, EDS), and can be electrochemically reduced into metallic iron (CV, XRD) in order to charge the electrode. In subsequent steps, the iron coating can reversibly charge and discharge in strongly alkaline solution in the presence of a dilute K\(_2\)S additive that impedes the dissolution of iron. We note that the nanofoam’s pore network and electronically conductive framework act in tandem to deliver electrochemical species to and from the iron coating, such that iron-coated nanofoam electrodes discharge more energy per square centimeter than nonporous electrode analogues at current densities between 0.01 – 1 mA cm\(^{-2}\).

INOR 1011

Single-walled carbon nanotubes wrapped by helically chiral, ionic, semiconducting polymers: New nanoscale compositions for energy capture, conversion and storage

Jean-Hubert Olivier\(^{1}\), jo Olivier@duke.edu, Jaehong Park\(^1\), Pravas Deria\(^1\), Amar S. Kumbhar\(^2\), Maria Andrian-Albesu\(^2\), Michael J. Therien\(^1\). (1) Department of Chemistry, Duke University, Durham, North Carolina 27708, United States (2) Department of Applied Physical Sciences, University of North Carolina at Chapel Hill (UNC-CH), Chapel Hill, North Carolina 27599, United States
Highly charged semiconducting polymers that feature a 2,2’-(1,3-benzyloxy)-bridged (b)-1,1’-bi-2-naphthol unit have been shown to single-chain wrap the nanotube surface with fixed helical chirality and pitch length. We demonstrate that chiral anionic semiconducting polymers that feature a perylene diimide (PDI) electron acceptor as an integral part of the polymer repeat unit provide polymer-SWNT superstructures for light-driven energy conversion reactions. Femtosecond pump-probe transient absorption spectroscopic experiments show that excitation into the SWNT E$_{11}$ transition generates SWNT hole polaron [(6,5) SWNT$^{•+}$] and PDI radical anion (PDI$^{•-}$) states. These studies demonstrate for the first time a photoinduced electron transfer process involving a SWNT and a semiconducting polymer in which: (i) the charge-separated products, and (ii) photoinduced charge separation and thermal charge recombination dynamics, are fully characterized. To fully exploit these polymer-SWNT hybrids in energy conversion applications, we have developed solution-based processes to structure dense, highly aligned arrays of these nano-objects on solid substrates. We show that ionic self-assembly approaches afford solid-state SWNT-based materials from solution that feature aligned, individualized nanotubes at high mass fraction per unit volume. The ability to modulate polymer electronic structure by design, used in conjunction with facile hierarchical organization, offers exceptional promise for the development of new types of optoelectronic nanomaterials.