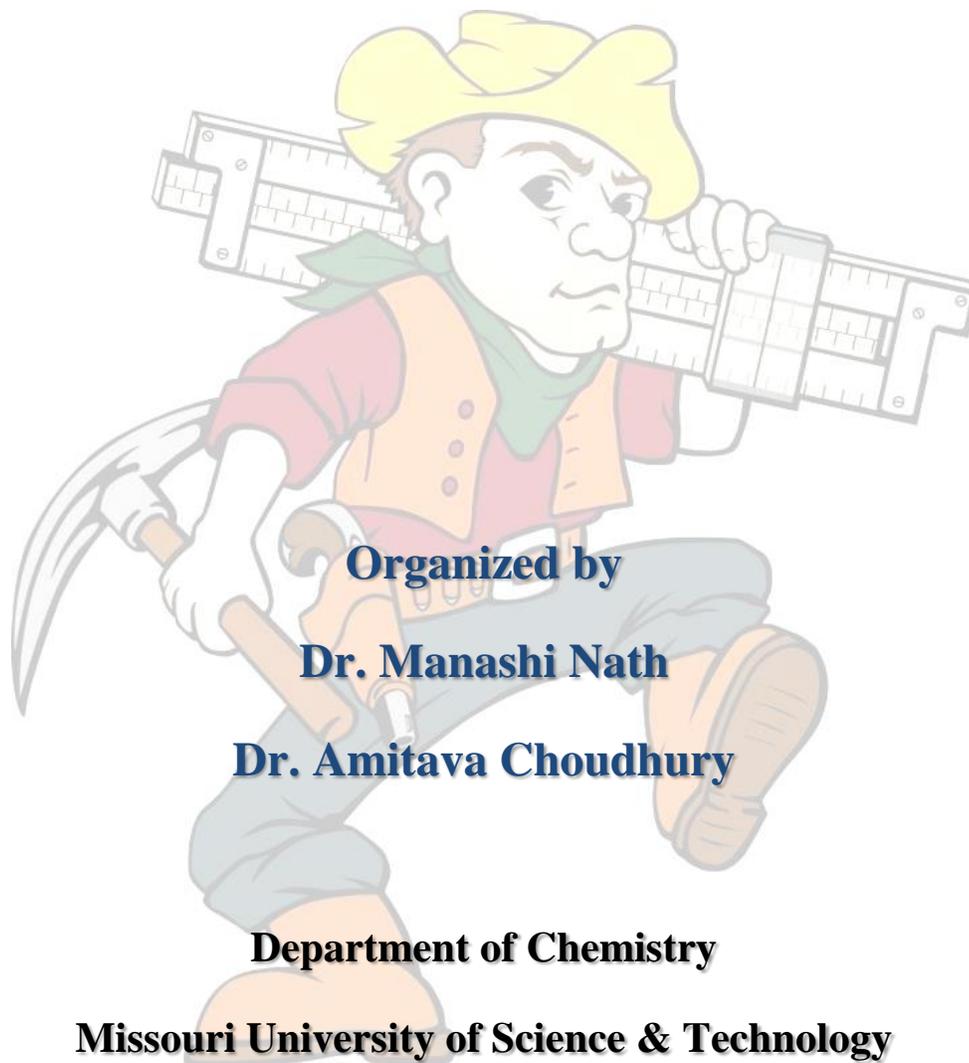


Missouri Inorganic Day 2013



Organized by

Dr. Manashi Nath

Dr. Amitava Choudhury

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Rolla, MO 65409

Date: 4th May 2013

Preface

The chemistry department of Missouri S&T, Rolla is proud to host the 26th Missouri Inorganic Day, MOID -2013. On this warm summer day right in the middle of everywhere we welcome you to enjoy a tantalizing session garnished with presentations about the various exciting inorganic chemistry research going on in and around Missouri. In today's world none of us has even the simplest doubt about the omnipresent role chemistry plays in our daily lives. Right from the water that surrounds us to the air that we breathe, the food that keeps us healthy to the medicines that keep us well, the plants that make oxygen to the soil that helps plants live, the ipod that stores music to the kindle that you can read, chemistry is everywhere. Inorganic chemistry, as we all agree forms one of the major pillars of chemistry that helps us understand the functioning of the world around us. Modern inorganic chemistry has come a long way in which it accommodates several areas of science like organic chemistry, materials science, nanoscience, biology and physical science, thereby playing an even greater unifying role and offering a glimpse of the broader picture. This year the Missouri Inorganic Day serves as a perfect platform to exemplify the vast coverage of modern day inorganic chemistry. The topics covered through oral and poster presentations range from traditional organometallic and catalysis, spectroscopic methods, coordination chemistry to materials and nano chemistry. The program includes plenary lectures by several eminent scientists, talks and poster presentations by senior and junior faculties, graduate researchers and post-docs. This year we have especially encouraged participation from all levels of researchers including undergraduates, graduates, post-doctoral associates and faculties. We are glad to report that we have a very good presence from all corners of Missouri and from all levels of researchers even including visiting scholars.

On behalf of the organizing committee, I would like to take this opportunity to thank the Chemistry Department Interim Chair, Prof. Klaus Woelk and the Interim Vice President for Academic Affairs, Prof. Phil Whitefield, for their generous financial support and encouragement. I would also like to thank Akshay Pariti for his help with constructing the website for this meeting.

Hope you all enjoy the Missouri Inorganic Day 2013 at Rolla, and have as much fun attending this symposium as we had in organizing the meeting.


Manashi Nath

Missouri Inorganic Day 2013
 4th May 2013, Missouri S&T Rolla

Time	Speaker	Topic
9 – 9:05 am	Welcome address	
9:05 – 10:15 am	<i>Magnetic Materials and Spectroscopy; Chair: Prof. Gary Long</i>	
9:05 – 9:35 am	Fernande Grandjean	<i>Synthesis and Fading of Eighteenth-century Prussian Blue Pigments: a Combined Study by Spectroscopic and Diffractive Techniques using Laboratory and Synchrotron Radiation Sources</i>
9:35 – 9:55 am	Stephen Holmes	<i>Tuning Magnetic and Optical Bistability in Cyanometalate Complexes.</i>
9:55 – 10:15 am	David Van Horn	<i>Positron Annihilation Spectroscopy for Materials Characterization.</i>
10:15 – 10:30 am	Coffee break	
10:30 am – 12pm	<i>The world of Coordination Chemistry; Chair: Prof. Pericles Stavropoulos</i>	
10:30 – 11:00 am	Paul Sharp	<i>Molecular Halogen Photoelimination from Pt(IV), or is it?</i>
11:00 – 11:20 am	Nikolay Gerasimchuk	<i>Bis-cyanoximes: new players on the field of multidentate acidligands</i>
11:20 – 11:40 am	Fengrui Qu	<i>Aerobic Oxidation of Me₃tacn PdII to PdIV</i>
11:40 – 12 noon	Jia Luo	<i>Oxidative Reactivity of (N₂S₂)PdIIRX Complexes (R, X = Me or Cl): Involvement of Pd(III) and Pd(IV) Intermediates</i>
12 – 2 pm	Lunch and Poster Session	
2 pm	Discussion about the next MOID venue and hosts	
2 – 3:20 pm	<i>Inorganic Materials Chemistry; Chair: Prof. A. Choudhury</i>	
2:00 – 2:20 pm	Gary Long	<i>Mössbauer Spectral Study of the Linear Two-Coordinate Fe[C(SiMe₃)₃]₂ Complex and its Reduced Anion, Fe[C(SiMe₃)₃]₂⁻</i>
2:20 – 2:40 pm	Alicia M. Beatty	<i>Hydrogen-bonded porous frameworks from molecular precursor</i>
2:40 – 3:00 pm	Justin Walensky	<i>The Softer Side of Actinide Chemistry</i>
3:00 – 3:20	Jakub Koza	<i>Template-Free Electrodeposition of Freestanding MnO₂ Nanowires and Their Pseudo-Capacitive Properties</i>
3:20 – 3:30 pm	Tea break	
3:30 – 5 pm	<i>Inorganic Nanostructures & their Applications; Chair: Prof. Jay Switzer</i>	
3:30 – 4:00 pm	Kattesh Katty	<i>Antioxidant Phytochemicals As Building Blocks In Green Nanotechnology: Implications In Chemistry, Engineering and Medicine</i>
4:00 – 4:20 pm	Xiaobo Chen	<i>Black Titanium Dioxide Nanocrystals</i>
4:20 – 4:40 pm	Sukhada Mishra	<i>Enhancement of Superconducting T_c in FeSe Nanostructures through Increased Interfacial Pressure</i>
4:40 – 5 pm	Jeffrey Winiarz	<i>Functionalization of Holographic Composites through the Inclusion of Inorganic Semiconductor Nanocrystals</i>

*A Plenary Lecture by Fernande Grandjean***Synthesis and Fading of Eighteenth-century Prussian Blue Pigments: a Combined Study by Spectroscopic and Diffractive Techniques using Laboratory and Synchrotron Radiation Sources**

Louise Samain,^{1*} **Fernande Grandjean**,^{2,3} Gary J. Long,^{3*}

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Prussian blue, a hydrated iron(III) hexacyanoferrate(II) complex, is a synthetic pigment discovered in Berlin in 1704. Because of both its highly intense color and its low cost, Prussian blue was widely used as a pigment in paintings until the 1970's. The early preparative methods were rapidly recognized as a contributory factor in the fading of the pigment, a fading already known by the mid-eighteenth century. Two typical eighteenth-century empirical recipes have been reproduced and the resulting pigment analyzed to better understand the reasons for this fading. X-ray absorption and Mössbauer spectroscopy indicated that the early syntheses lead to Prussian blue together with variable amounts of an undesirable iron(III) product. Pair distribution functional analysis confirmed the presence of nanocrystalline ferrihydrite, $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$, and also identified the presence of alumina hydrate, $\text{Al}_{10}\text{O}_{14}(\text{OH})_2$, with a particle size of *ca.* 15 Å. Paint layers prepared from these pigments subjected to accelerated light exposure showed a tendency to turn green, a tendency that was often reported in eighteenth- and nineteenth-century books. The presence of particles of hydrous iron(III) oxides was also observed in a genuine eighteenth-century Prussian blue sample obtained from a polychrome sculpture.

Acknowledgments: We thank Pauline Martinetto, Pierre Bordet, Jana Sanyova, and David Strivay for their help during the course of this work. The financial help of the Fonds National de la Recherche Scientifique, Belgium, is gratefully acknowledged.

Tuning Magnetic and Optical Bistability in Cyanometalate Complexes

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The systematic engineering of molecular complexes with atom-economical efficiency is an exciting area of world-wide research activity as realization of this goal may afford a diverse array of materials suitable for molecule-based electronic applications. These materials continue to be experience world-wide interest owing to their potential use in a variety of high-density information storage, sensor, display, and device switching applications. Among the more celebrated switchable molecule-based materials are those derived from cyanometalate anions. Using a building-block approach, molecular precursors are allowed to self-assemble towards a common structural archetype via the formation of $M(\square-CN)M'$ pairs. Using a variety of multidentate capping ligands, the directionality and numbers of coordination sites available for $M(\mu-CN)M'$ unit formation can be controlled at the single-ion level. This strategy allows for the deliberate and systematic preparation of structurally related polynuclear materials with tailored magnetic and optical properties. Recent efforts to understand optical (Figure 1a) and magnetic bistability (Figure 1b) in single-molecule magnets and photoresponsive complexes are described.

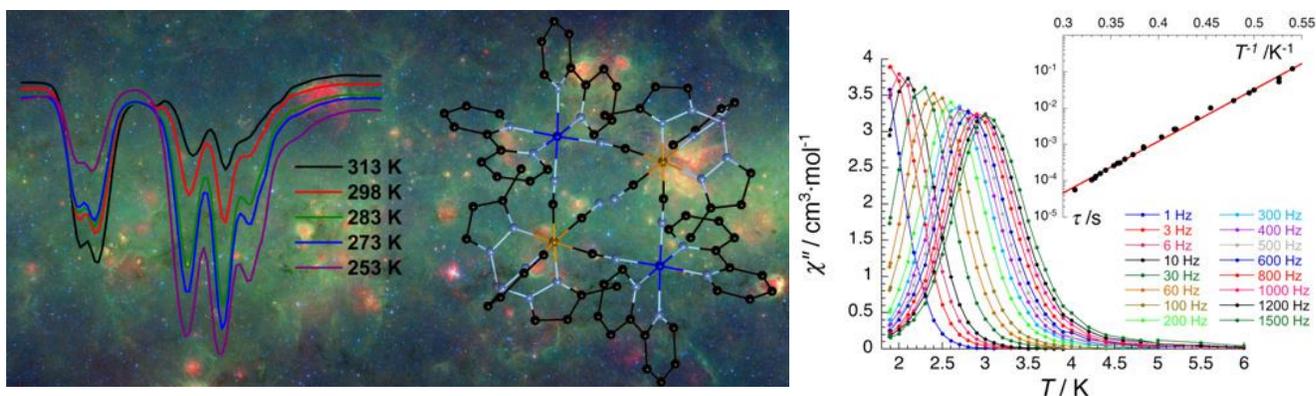


Figure 1. (a) Infrared spectra of a thermally- and photoswitched $\{Fe_2Co_2\}$ square. (b) Out-of-phase ac susceptibility data for a $\{Fe^{III}_4Ni^{II}_4\}$ single-molecule magnet.

Positron Annihilation Spectroscopy for Materials Characterization

David Van Horn

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Positron annihilation lifetime spectroscopy (PALS) is sensitive to the composition and free volume characteristics of a wide range of materials. The application of the technique to inorganic materials, surfaces, and interfaces will be presented with a focus on thin films, modified metallic foils, and on amorphous and crystalline minerals.

A Plenary Lecture by Paul Sharp

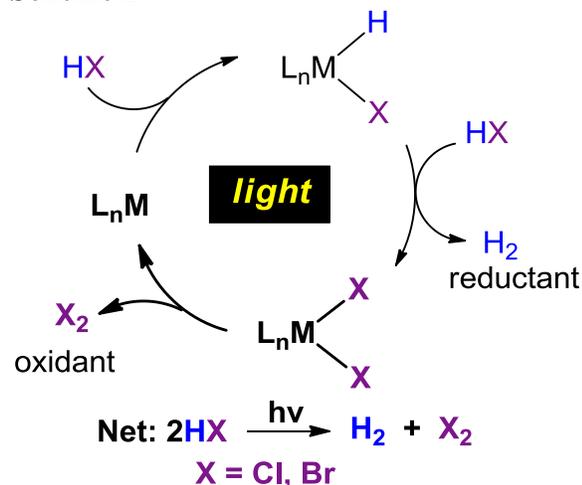
Molecular Halogen Photoelimination from Pt(IV), or is it?

Paul R. Sharp

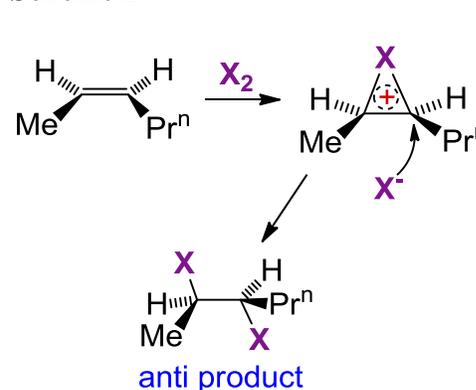
Department of Chemistry, University of Missouri, Columbia, MO 65211.

The endergonic photoelimination of molecular halogens (X_2) from transition metal dihalo complexes is an important step in potential solar energy conversion and storage through hydrogen halide (HX) splitting (Scheme 1). Studies of this photoelimination step are complicated by the favorable “back reaction” of X_2 with the reduced metal complex (L_nM). To prevent the back reaction halogen traps, usually alkenes, are added to react with the photogenerated X_2 . Observation of anti- X_2 addition to the alkene has been taken as evidence of free X_2 adding to the alkene through the halonium ion mechanism (Scheme 2).

Scheme 1



Scheme 2



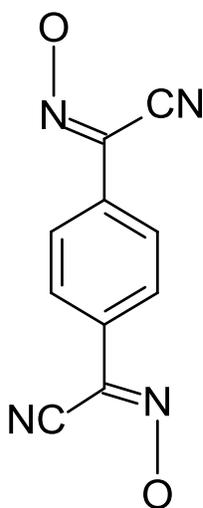
Our work on Pt(IV) systems and literature data suggest other possibilities for anti-addition product formation that do not involve free X_2 . These mechanistic possibilities will be discussed in light of the available data.

Bis-cyanoximes: new players on the field of multidentate acidoligands.

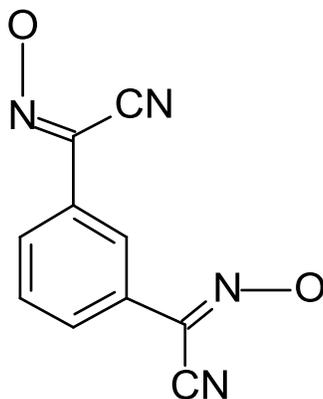
Nikolay Gerasimchuk

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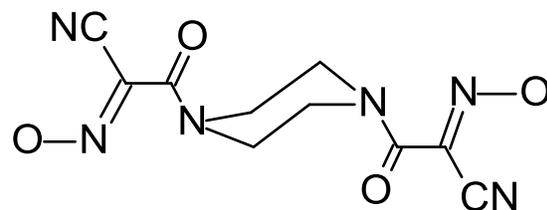
Three new shown below bis-cyanoximes, capable of formation of extended structures, were synthesized from respective bis-acetonitriles precursors using the nitrosation reaction with gaseous methylnitrite at basic conditions at room temperature. Compounds were characterized using spectroscopic methods (^1H , ^{13}C NMR, IR, UV-visible spectroscopy) and X-ray analysis. Both H(1,3-BCO) and $\text{H}_2\text{BiPipCO}$ have shown a very complex NMR spectra due to the presence of both geometrical isomers (*syn*- and *anti*-), and rotational conformers. Five different crystal structures of these three ligands were obtained and three contain the solvent of including due to the formation of pores and channels in crystals.



1,4-BCO



1,3-BCO



$\text{H}_2\text{BiPipCO}$

Several monovalent Tl and Ag complexes, and bivalent Cu, Ni complexes with metalloligands ML_2X_2 (M=Cu, Ni; X=Cl, Br) were obtained and studied as well using the above methods. Crystal structures also revealed presence of channels capable of hosting of molecules of gases of industrial importance.

Aerobic Oxidation of Me3tacn PdII to PdIV**Fengrui Ou**

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Two (Me3tacn)PdII complexes (Me3tacn = N,N',N''-trimethyl-1,4,7-triazacyclononane) were oxidized by O₂ to form the corresponding PdIV species. The products were fully characterized by X-ray, ESI-MS, and NMR spectrometry techniques. The dimethyl PdII complex (Me3tacn)PdIIMe₂ undergoes facile aerobic oxidation to yield the stable species [(Me3tacn)PdIVMe₃]⁺. Additionally, the structurally characterized complex [(Me3tacn)PdIVMe₃]I undergoes selective elimination of ethane at elevated temperatures. Overall, these two systems represent the very rare examples of aerobic oxidation of PdII organometallic precursors to yield the well-defined PdIV products, supporting the role of PdIV species as viable intermediates in Pd-mediated catalytic or stoichiometric aerobic oxidative transformations.

Oxidative Reactivity of (N₂S₂)Pd^{II}RX Complexes (R, X = Me or Cl): Involvement of Pd(III) and Pd(IV) Intermediates

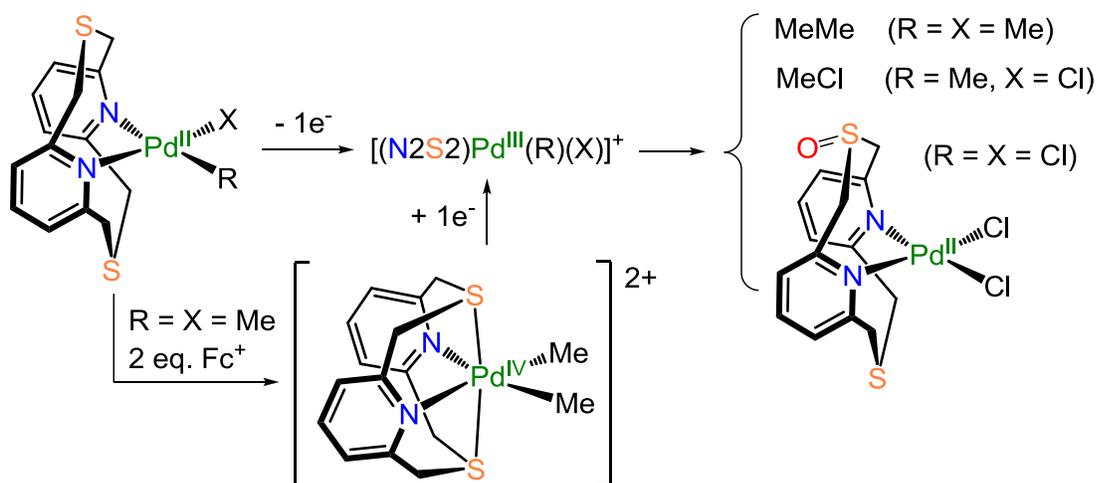
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A series of (N₂S₂)Pd^{II}RX complexes (N₂S₂ = 2,11-dithia[3.3](2,6)pyridinophane; R and X = Me or Cl) were synthesized and characterized by X-ray crystallography and cyclic voltammetry (CV). Electrochemistry studies suggest that the oxidation states of Pd(III) and Pd(IV) can be achieved by either electrochemical or chemical oxidation. The formation of Pd(III) species was monitored by *in situ* EPR, ESI-mass, and UV-vis spectroscopy upon one electron oxidation. In addition, [(N₂S₂)Pd^{IV}Me₂](PF₆)₂ was isolated and characterized by X-ray crystallography. Oxidative reactivity studies revealed clean MeMe and MeCl elimination from Pd^{II}-dimethyl and Pd^{II}-methylchloro complexes, respectively. The proposed mechanisms suggest the involvement of Pd(III) and Pd(IV) oxidation states as intermediates.



Mössbauer Spectral Study of the Linear Two-Coordinate $\text{Fe}^{\text{II}}[\text{C}(\text{SiMe}_3)_3]_2$ Complex and its Reduced Anion, $\text{Fe}^{\text{I}}[\text{C}(\text{SiMe}_3)_3]_2^-$

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The linear two-coordinate $\text{Fe}^{\text{II}}[\text{C}(\text{SiMe}_3)_3]_2$ complex and its reduced anion, $\text{Fe}^{\text{I}}[\text{C}(\text{SiMe}_3)_3]_2^-$, both exhibit single molecule magnet behavior under both a non-zero and a zero applied dc magnetic fields, respectively. [1,2] The energy barrier of $226(4) \text{ cm}^{-1}$ for $\text{Fe}^{\text{I}}[\text{C}(\text{SiMe}_3)_3]_2^-$ is the highest observed for a transition metal based single molecule magnet. Because $\text{Fe}^{\text{II}}[\text{C}(\text{SiMe}_3)_3]_2$ exhibits both a record large hyperfine field in its 4.2 K Mössbauer spectrum and a relaxation broadened 295 K spectrum, a Mössbauer spectral study of $\text{Fe}^{\text{II}}[\text{C}(\text{SiMe}_3)_3]_2$ and its reduced anion $\text{Fe}^{\text{I}}[\text{C}(\text{SiMe}_3)_3]_2^-$ between 4.2 and 295 K was carried out. Both complexes show spectra broadened by slow paramagnetic relaxation resulting from the hyperfine field reversal associated with the reversal of the magnetization, with a relaxation period comparable with the Larmor precession period of the iron-57 nuclear magnetic moment about the hyperfine field.

Changes in isomer shift and quadrupole splitting upon reduction are observed and can be understood through *ab-initio* calculations.

Arrhenius plots of the hyperfine field relaxation time observed above 70 K for $\text{Fe}^{\text{II}}[\text{C}(\text{SiMe}_3)_3]_2$ and $\text{Fe}^{\text{I}}[\text{C}(\text{SiMe}_3)_3]_2^-$ give activation energies of $288(10)$ and $386(10) \text{ cm}^{-1}$, respectively. The Arrhenius plots of the relaxation times obtained from ac-susceptibility studies between 20 and 29 K and Mössbauer spectra obtained above 70 K for $\text{Fe}^{\text{I}}[\text{C}(\text{SiMe}_3)_3]_2^-$ complement each other very well. The Mössbauer spectral hyperfine parameters may be best understood through the results of *ab-initio* calculations that indicate a very strong $4s-3d_{z^2}$ mixing and a virtually unquenched orbital contribution to the magnetic moment of both complexes.

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The Softer Side of Actinide Chemistry

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In order to satisfy the increasing energy demands, nuclear energy could provide a solution to a portion of this requirement. For nuclear energy to be viable, better separation methods are needed in order to reprocess spent fuel. Soft-donor ligands have been shown to provide better separation of actinides over lanthanides as well as middle trivalent actinides therefore we have examined the molecular and electronic structure of thorium and uranium complexes with soft-donor ligands such as sulfur, selenium, and tellurium and make comparisons with its hard-donor congener, oxygen. Our recent efforts in developing the chemistry of actinide complexes with soft-donor ligands will be discussed.

Title Hydrogen-bonded porous frameworks from molecular precursor

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While many coordination polymers (based on coordinate-covalent bonds between metals and bridging ligands) are known to form porous materials, porous hydrogen-bonded materials are rare. The talk will cover the strategy behind synthesizing porous solids from molecules containing hydrogen-bonding functionalities. Stability and properties of the materials will also be discussed.

Template-Free Electrodeposition of Freestanding MnO₂ Nanowires and Their Pseudo-Capacitive Properties

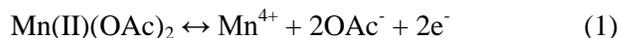
*Jakub A. Koza, Matthew M. Willmering, and Jay A. Switzer**

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Electrochemical capacitors store electrical energy using either ion adsorption (i.e., double-layer capacitors) or fast surface redox reactions (i.e., pseudo-capacitors).¹ Electrical capacitors can be fully charged or discharged in seconds. Their energy density (about 5 Wh/kg) is lower than that of batteries, but a much higher power delivery or uptake (10 kW/kg) can be achieved. RuO₂ is currently the best known pseudo-capacitor material.¹ It has multiple oxidation states within a 1.2 V voltage window, but rare Ru is an expensive element.¹ A lot of attention has been given to finding high capacity materials using earth abundant elements. MnO₂ is one of the most promising materials for positive electrodes in pseudo-capacitors with a predicted specific capacity of 1370 Fg⁻¹.¹ MnO₂ owes its high specific capacity to the fast surface redox reaction: MnO₂ + xC⁺ + yH⁺ + (x+y)e⁻ ↔ MnOOC_xH_y (where C is electrolyte cation).¹ The specific capacity is surface limited, hence it is strongly surface area dependent. Nanowires have a large surface area, which should be beneficial for pseudo-capacitor applications.

MnO₂ is electrodeposited from a Mn(II)acetate (OAc) solution (pH=5) at elevated temperatures. Electrodeposition is carried out in a standard three electrode setup. The deposits are obtained galvanostatically onto pyrolytic graphite substrates. The deposition is assumed to proceed according to the following reaction scheme:



X-ray diffraction showed the nanocrystalline nature of the deposits, and the structure matched best the orthorhombic R-MnO₂. Raman spectroscopy of films revealed that the structure is a mixture of R-MnO₂ and β-MnO₂ phases. Electrodeposited MnO₂ can be described by R-MnO₂ structure with β-MnO₂ blocks (De Wolf defects) in it which is assigned as γ-MnO₂. The morphology of deposits is affected by the deposition parameters. With increasing current density the morphology of samples changes from nanowires to 'star'-like, and eventually at high currents dense films are formed. By increasing the electrolyte temperature finer wires are obtained. The specific capacity of electrodeposited MnO₂ was measured in 1 M Na₂SO₄ by cyclic voltammetry and galvanostatic charge-discharge experiments. The specific capacity of films deposited at different conditions differs due to the changes of the active surface area available for the redox reactions.

Electrochemical deposition of MnO₂ nanowires gives an excellent contact to the substrate, i.e., it provides a continuous contact from the conductive electrode surface. Electrodeposition also allows for excellent control of the size, shape, structure, and morphology of the film,³ which makes it an attractive approach for synthesis of novel materials for super-capacitors.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant DE-FG02-08ER46518.

References:

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2. C. Julien; M. Massot; S. Rangan; M. Lemal; D. Guyomard; *J. Raman Spectr.* **33**, 223 (2002).
3. J.A. Switzer; G. Hodes; *MRS Bulletin* **35**, 743 (2010).

A Plenary Lecture by Kattesh Katti

Antioxidant Phytochemicals As Building Blocks In Green Nanotechnology: Implications In Chemistry, Engineering and Medicine

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Curators' Professor of Radiology and Physics

Margaret Proctor Mulligan Distinguished Professor of Medical Research

Director, University of Missouri Cancer Nanotechnology Platform University of Missouri

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Phytochemical extracts from leaves, fruits, seeds and roots have been a reliable source of nutrients with a host of medically-useful properties encompassing antioxidant, anti-tumor, and anti-depressant characteristics. The powerful antioxidant properties of phytochemicals derived from various fruits and vegetables, have constituted a vast class of chemopreventive agents including epigallocatechin gallate (EGCG), genistein, resveratrol, diallyl sulfide, S-allyl cysteine, allicin, lycopene, capsaicin, curcumin, 6-gingerol, ellagic acid, ursolic acid, silymarin, anethol, catechins and eugenol. The high redox potential of these agents have been successfully utilized to suppress cancer cell proliferating reactive free radicals, inhibit growth factor signaling pathways, induce apoptosis, inhibit NF- κ B, AP-1 and JAK-STAT activation pathways, inhibit angiogenesis, suppress the expression of anti-apoptotic proteins, inhibit cyclooxygenase-2, and many more untapped therapeutic characteristics. We hypothesized that several of these phytochemical agents possess appropriate redox potential for use in the reduction of metal precursors into their corresponding nanoparticles to create engineered nanoconstructs, through 'Green Nanotechnology', for plethora of applications within the biomedical, alternate energy and environmental restoration sectors. We have validated our hypothesis through a series of discoveries wherein we used phytochemicals from Cumin, Cinnamon, Soy, and Tea to synthesize well-defined homogeneously dispersed nanoparticles of gold. Our approach is 100% green as the overall process involves interaction of gold salt directly with raw phytochemicals sources (or purified phytochemicals) without the intervention of any toxic chemical. Complete life cycle analysis of the underlying chemistry of nanoparticles production further attests to the Green Nanotechnological innovation as all these processes proceed in aqueous media, often without the use of electricity. This presentation will discuss novel Green Nanotechnology approaches in drug discovery with direct implications in treating various forms of solid tumors. Development of Laminin receptor specific EGCg-AuNPs and their therapeutic efficacy in treating prostate tumors will be presented. This presentation will also focus on the interface of chemistry with Green Nanotechnology for the development of new nanotherapeutic approaches in drug discovery that will provide dual benefits of ablating primary tumors while controlling metastases. Several recent studies have demonstrated that just focusing on ablating primary tumors has not served complete clinical needs as the disease continues to propagate to other organs thus costing money and cancer patient lives. We will discuss the application of innovative Green Nanotechnology approaches, using Epigallocatechin gallate (EGCG) which is the most abundant catechin in Tea, for the development of tumor specific gold nanoparticles. Details on conjugation of Laminin receptor specific EGCg with inherently therapeutic radioactive gold nanoparticles provide prostate tumor specific nanotherapeutic agent EGCg-198-AuNPs. EGCg will direct and enhance the retention of therapeutic payloads of nanoparticles at Laminin receptors sites, over expressed in prostate tumors. Phytochemical chemical-based redox chemistry and its oncological applications through Green Nanotechnology in drug delivery and targeting will be discussed.

Acknowledgments: This work was supported by funds from the NIH and from the Research Offices of the University of Missouri. Collaborative efforts with Dr. Anandhi Upendran, Dr. Cathy S Cutler, Dr. Ravi Shukla, Dr. Nripen Chanda, Dr. Jeff Smith, Dr. John Lever, Dr. Ajit Zambre, Kavita Katti, Sagar Gupta, Dr. Jeffrey N. Bryan and Dr. Raghuraman Kannan, are gratefully acknowledged.

Black Titanium Dioxide Nanocrystals

Xiaobo Chen

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Titanium dioxide is known as photocatalyst. However, its large electronic bandgap limits its optical absorption properties for its applications in photocatalysis. Here we would like to present our recent effort in turning white titanium dioxide into black to maximize the optical absorption and their photocatalytic activity. The materials properties will be presented in details.

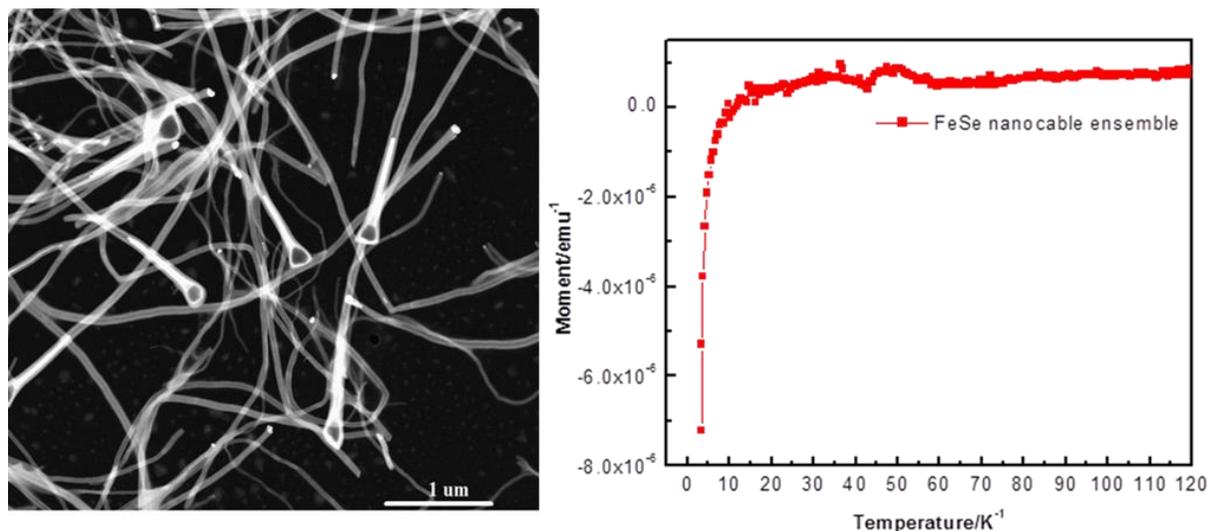
Enhancement of Superconducting T_c in FeSe Nanostructures through Increased Interfacial Pressure

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Superconductivity in iron selenide has attracted considerable attention due to the simplicity of composition, unconventional nature of superconductivity and ease of synthesis. We have synthesized superconducting FeSe@C nanocables and nanoparticles by a simple Au-Pd catalyst aided vapor transport reaction using iron acetylacetonate and elemental selenium as volatile precursors. The superconductivity was confirmed through magnetic measurements and T_c of ≈ 8 K was obtained for an ensemble of nanocables. Interestingly, significant enhancement was observed with onset $T_c \approx 32$ K for nanoparticles. Extensive high-resolution microscopy revealed that FeSe was adjacent to Pd/Se alloy formed in during the course of the reaction. There was considerable lattice contraction of 3.6% in the FeSe nanocable and 9% in FeSe nanoparticles, along the c-direction leading to a reduced spacing between the (001) lattice planes. The internal pressure effect caused due to Pd/Se-FeSe interphase and its contribution towards a higher T_c will be presented in detail.



The carbon encapsulated superconducting nanoneedles of FeSe@C

Functionalization of Holographic Composites through the Inclusion of Inorganic Semiconductor Nanocrystals

Jeffrey G. Winiarz

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The phenomenon of photorefractivity, which involves the creation of a reversible hologram generated by the crossing of two coherent beams in an appropriate medium, can be realized in polymeric composite materials which simultaneously exhibit photoconductive and electro-optic properties. The *nanocomposite* approach offers opportunities to produce high performance and relatively low cost optoelectronic media, suitable for many applications. Especially promising are nanocomposites of polymers and inorganic semiconductor nanocrystals commonly known as quantum dots. Initially, experiments focused on the optical absorption properties of quantum dots and their dependence on composition and size. The broad tunability of the spectral response and increased photo-charge generation efficiency were particularly interesting with respect to photorefractive composites. More recently, however, time-of-flight experiments have revealed that the mere inclusion of semiconductor nanocrystals significantly enhances the mobility of charge carriers in polymeric composites. This enhanced mobility translates into an improved response time; an issue which has plagued this class of materials since their inception and has precluded their use in many practical applications. This seminar will present experimental evidence confirming that through judicious selection of an appropriate semiconductor material, the enhanced charge-carrier mobility associated with nanocrystals can be more fully exploited, leading to improved response times.

Poster #1

ONIOM: A Route to Accurate Calculations of Dispersions on Large Molecular Systems

Penante Bruce-Vanderpuije, Charles Kirkpatrick

Department of Chemistry, St. Louis University, St. Louis, MO.

Weak/noncovalent intermolecular interactions provide understanding in areas of bulk properties of gases and solvent interactions. They are present in molecules with aromatic π - π interactions. Dispersion, a type of weak interaction results from electron correlation which are a great challenge to compute. Symmetry Adapted Perturbation Theory (SAPT) method, a solution to the electron-correlation problem, decomposes the interaction energy into electrostatic, exchange, induced and dispersion energy terms. We focus on accurately computing the interaction energies for model systems of Carbon nanotube (CNT) interacting with C₆H₅X. The effects of substituents are examined using an approximated method, ONIOM (Our-own-N-layer Molecular Orbital and Molecular Mechanics). The components of the interaction energy were studied using a QM: QM: QM ONIOM hybrid approach which allowed fragmentation of the large system into three layers. SAPT2 computations were performed on each fragment at different levels of theory and then merged to obtain a single interaction energy. The resulting ONIOM SAPT2 energies were found to be in agreement with energies obtained from a whole non-fragmented complexes using the standard full SAPT2 method. We justify that the fragmentation and ONIOM method can be used to calculate interaction energies for very large CNT systems at reduced computational cost. The knowledge of different energy contributions for substituents based on the SAPT2 and ONIOM method will aid in identification of a good organic solvent to disperse CNT based on the total SAPT2 interaction energies produced from π - π interactions between substituted benzenes and CNT.

Poster #2**Impact of Sterics on Metal Halide Assemblies**

Stephanie R. Cernicek, Alicia M. Beatty*

Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri-St Louis, Saint Louis, MO

Cadmium chloride and other metal halide compounds typically form 2-D networks when reacted with primary amines and anilines. However, it has been established in the Beatty group that it is possible to alter the metal halide assembly by changing the size of the substituent ortho to an aniline amine group. If that ortho group is too large, the assembly will not form layers, and instead will form 0-D and 1-D networks. To determine if this phenomenon occurs generally, we have used a variety of metal halides such as CdX_2 , PbX_2 , and CuX_2 (where $X = Cl$, or Br) with a number of ortho-substituted anilines and dianilines. Ammonium salts of tin iodide are also being studied; their 2-D and 1-D structures have been shown to have tunable band gaps. By controlling the steric aspects of the ammonium counterions a systematic study of the relationship between size and shape of the counterion and their electronic properties can be discovered. These clusters and/or layers could then be useful for applications in host-guest chemistry, catalysis, as superconductors, or as quantum dots.

Poster #3**First Bis-Cyanoximes: New Versatile Multidentate Building Blocks for MOFs****Scott Curtis***Department of Chemistry, Missouri State University, Springfield*

The first bis-cyanoximes have been synthesized by nitrosation of substituted acetonitriles. 1,3-bis(cyanoxime)benzene (1,3-BCO) and isomeric 1,4-bis(cyanoxime)benzene (1,4-BCO) represent the first phenyl non-chelating bis-cyanoximes. H₂BiPipCO represents the first bis-cyanoxime with both non-chelating and chelating potential. Compounds were characterized by several spectroscopic methods, TLC, and X-Ray analysis.

Poster #4

Synthesis, Characterization, and Reactivity of Thorium(IV) and Uranium(IV) Monoanionic Schiff Bases: A Non-Cyclopentadienyl but Multidentate Ligand

*Ashley N. Dame, Mohan S. Bharara, Charles L. Barnes, Justin R. Walensky**

Department of Chemistry, University of Missouri-Columbia, 65211-7600.

Uranium (IV) complexes of the form, $[RN=C(H)(tBu_2C_6H_2O)]_xUI(4-x)]$, R= C₉H₆N, C₆H₄N, C₆H₄SCH₃, have been synthesized, characterized using NMR, UV-Vis, and X-ray crystallography, and their reactivity has been explored. As sulfur-containing ligands have been shown to be effective in separating lanthanides and actinides in spent nuclear fuel, we have probed the uranium-sulfur interaction using X-ray Absorption Near-Edge Spectroscopy (XANES). These results and our efforts in synthesizing heteropolymetallic complexes will also be shown.

Poster #5

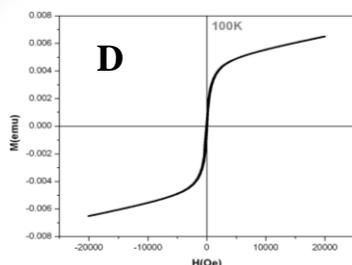
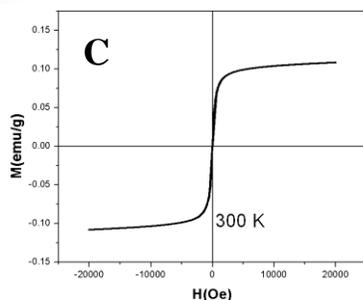
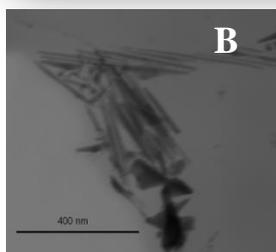
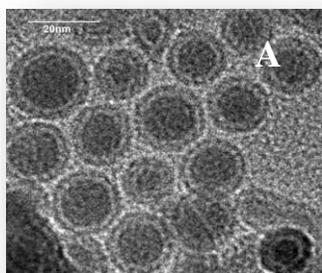
A generalized route for synthesis of Transition Metal arsenide nanostructures

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The discovery of iron based pnictide (AFEAs, where A= Na, Li) and oxypnictides (LnFeAsO, where Ln= La, Sm Gd) superconductors have brought transition metal pnictides especially FeAs under limelight. The iron pnictide layer is responsible for superconductivity in these compounds. Intercalation of the anionic FeAs layers with cationic Li⁺ and Na⁺ generate the 111 family of superconductors. We are attempting to synthesize these 111 nanostructured superconductors using the sacrificial template approach where nanostructured FeAs can act as a morphology directing agent. As a part of these efforts we have developed a method for the synthesis of FeAs nanoparticles and nanowires. This method can effectively be applied to the formation of metal arsenides alike CoAs and MnAs. The synthesis involved usage of transition metal carbonyls as a source of Fe, Co, Mn, a novel arsenic precursor, Triphenylarsine (TPA) and hexadecylamine (HDA) as a surfactant. Reaction proceeds by displacement of a carbonyl (CO) by the Triphenylarsine in transition metal carbonyls at low temperatures (300C). The close proximity of Tm (Fe, CO, Mn) and As in the formed intermediate is believed to aid in the internal redox therefore a reducing agent is not needed in this method. Hexadecylamine (HDA) due to its coordinating ability and melting point in the temperature range makes this synthesis a solvent-less method. For FeAs the synthesized nanoparticles are superparamagnetic with blocking temperature TB as high as 240K. The nanoparticles have a core and a shell. STEM, TEM, and XPS studies will be discussed with details of this simple, one pot synthesis of arsenide nanostructures using this novel method.



(A) shows FeAs @C core-shell nanoparticles. (B) CoAs one dimensional nanostructures and (C) M vs H for FeAs nanoparticles at 300K showing superparamagnetism and (D) for CoAs superparamagnetism at 100K.

Poster #6**Nanoworm Vanadium Oxide Aerogels via Epoxide-Assisted Gelation of VOCl_3**

Tyler Fears, *Shruti Mahadik-Khanolkar, Jeffrey G Winiarz, Chariklia Sotiriou-Leventis, Nicholas Leventis*

Department of Chemistry, Missouri University of Science and Technology, Rolla, MO - 65409

Nanoporous vanadia (VO_x) has applications in catalysis, Li intercalation, and low-density sacrificial energy absorption. The traditional method for synthesis of nanoworm VO_x aerogels is the controlled hydrolysis of expensive vanadium alkoxides. We present the first reported epoxide-assisted gelation of VOCl_3 , reducing the cost of aerogel fabrication by a factor of 10 while maintaining the nanomorphology of conventional methods. Mixed-oxide reduction during aging was followed via UV-Vis absorption spectroscopy, ^{13}C NMR, and ^{51}V NMR.

Poster #7

Low Coordinate Building Blocks for Single Molecule Magnets

Philip Ferko

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Single molecule magnets (SMM)s have attracted considerable interest as they are a confluence of multiple fields as well as the realization of a large body of theoretical predictions.¹ Early work focused on increasing the *S* value of clusters, the strength of coupling, and highlighted the importance of spin orbit coupling in *3d* metals for increasing the overall magnetic moment. More recently researchers have attempted to understand and predict physical structure and its influence on the uniaxial anisotropy term, *D*. This term is an indicator for SMM phenomena and synthetic control of it would provide a rational synthetic strategy.²

While coupling through other bridging atoms is on the average larger, cyanide bridges provide a degree of predictability and synthetic control that is as yet unrealized with some bridging ligands. Superexchange provides the magnetic interaction and can be altered by changing the metals as well as the pyrazolyl borate ligands used to complete the inner coordination sphere of said metals.

The current work presents SMM building blocks prepared from hydrido-tris(3-phenylpyrazol-1-yl)borates and first row transition metals. The phenyl rings act to occlude coordination sites so that three are occupied by the scorpionate and only a fourth actively bonds in the case of chlorides.³ This deviation from usual coordination perturbs the electronic structure of metal ions

and potentially modulates spin-orbit coupling. Structural and electronic characterization is presented as well as data from the ongoing effort to prepare multimetallic clusters from these building blocks.

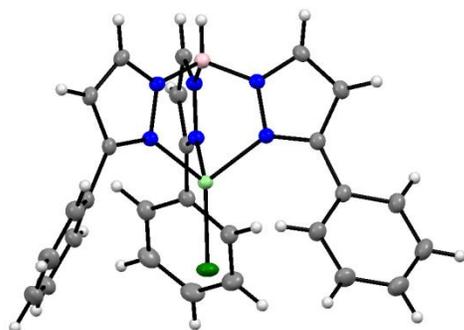


Figure 1. ORTEP diagram of $[(\text{Tp}^{\text{Ph}})\text{NiCl}]$ at the 50% probability level. The three phenylpyrazole moieties are crystallographically related about the Cl-Ni \cdots B-H axis.

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Poster #8

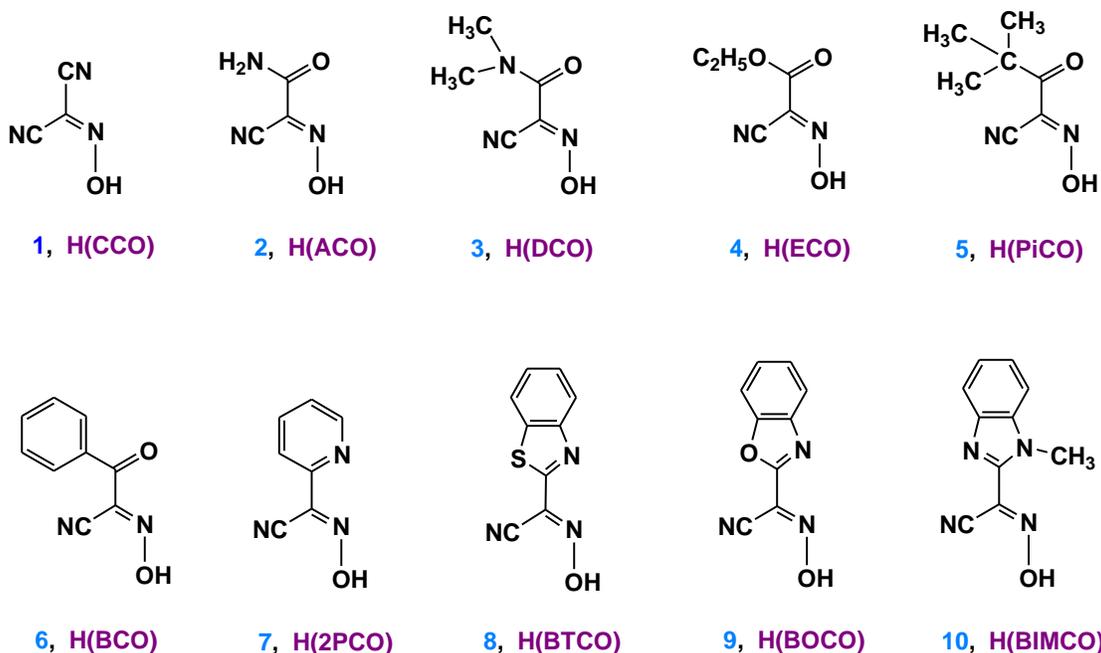
Light-insensitive Ag(I) cyanoximates as antimicrobial agents.

Mark Whited,¹ Korey Still,² Shalaka R. Lotikar,² Marianna Patrauchan² and Nikolay Gerasimchuk¹

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The number of patients requiring an internal fixation device or artificial joint has grown rapidly. In the United States alone, more than 4.4 million people have at least one internal fixation device and more than 1.3 million people have one joint. Bacterial infection induced by implant placement is a significant rising complication and is associated with considerable costs and morbidity. Clinical practice has shown that systemic antibiotics are unable to provide effective long-term treatment for implant-associated infections. A high dose of antibiotics applied locally at the bone-implant interface can prevent such bacterial infections.



Recently, we discovered a group of cyanoxime-based silver(I) coordination polymers of AgL composition that possess the above criteria. These complexes demonstrated pronounced antimicrobial activity, and can be mixed with polymeric light-curable composites applied as glues or adhesives during introduction of indwelling medical devices. These compounds will prevent infection from occurring and thus alleviate numerous cases of associated postoperative complications. The most current results of antimicrobial tests for silver(I) cyanoximates are presented and discussed.

Poster #9**First Principles Study of $[\text{AnO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]_n$ (An=U, Pu; n=0,-1) Reduction Potentials**

Michael Goshert

Department of Chemistry, University of Missouri, Columbia, MO.

Actinyl nitrates are common byproducts of the nuclear fuel cycle due to the use of nitric acid in the extraction process. There have been several incidents in recent history leading to the release of these compounds into the environment. Notable catastrophic examples include the steam explosion at the Chernobyl nuclear reactor and the leaking spent nuclear fuel storage drums at the Hanford site. These events illustrate the necessity for understanding these compounds' mobility in aqueous solution. Oxidation state plays an important role in species mobility. Therefore, understanding the energy required to reduce these compounds is crucial in clarifying how they will migrate over the years. Experimental data of these compounds can be difficult to obtain because of their variability in solution. However, computational methods have the capability to eliminate this issue and can be used to obtain the energy difference between oxidation states. Various computational methods have been used to calculate the thermodynamic parameters characterizing the reduction of $[\text{AnO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ to $[\text{AnO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]^-$; evaluated methods will include Hartree-Fock (HF) theory and Density Functional Theory (DFT) order perturbation theory.

Poster #10**Synthesis and Characterization of High Surface Area CuWO_4 and Bi_2WO_6 Photoelectrodes for Solar Water Oxidation****James Hill***Currently at Department of Chemistry, Missouri S&T, Rolla, MO 65409.*

Photoelectrochemical water splitting is promising as a renewable source of hydrogen and oxygen for use in a fuel cell. However, an ideal photoelectrode has not been found. CuWO_4 and Bi_2WO_6 are two n-type semiconductors that have not been extensively studied for use as a photoanode in a photoelectrochemical cell. A two-step synthetic method was used to produce these films. WO_3 was electrochemically prepared and subsequently converted to CuWO_4 or Bi_2WO_6 by annealing in the presence of solutions containing Cu^{2+} and Bi^{3+} , respectively. CuWO_4 has a band gap of 2.3 eV, smaller than the band gap of WO_3 (2.7 eV). The photoelectrochemical properties of CuWO_4 were evaluated in a 0.1 M borate buffer and it showed excellent photo-stability and photocurrent-to-oxygen conversion efficiency. Bi_2WO_6 has a band gap of 2.8 eV, which means it absorbs slightly less light than WO_3 . However, it has a conduction band better positioned for the water splitting reaction and thus has a lower photocurrent onset potential.

Poster #11**Synthesis and characterization of 1D platinum cyanoximes and nitrosonaphthols coordination complexes with semiconducting properties**

Michael Hilton, Nikolay Gerasimchuk

Missouri State University, Department of Chemistry, Temple Hall 456, Springfield, MO 65897

The objective of this research is to synthesize and characterize new platinum complexes with conducting properties. Platinum complexes with conducting properties have been studied extensively with notable compounds such as Magnus' Green Salt and KCP. With this research organic ligands are used instead, allowing for the complexes (ML₂) to be more tunable in their properties. These square planar complexes with cyanoxime/nitrosonaphthol ligands arrange themselves in 1D stacks which could allow for direct Pt-Pt interactions. Evidence for Pt-Pt interactions can be seen in their unique color (green, blue, purple) and in their conducting properties. Previously, two cyanoxime complexes have been studied for their conducting properties, Pt(PiPCO)₂ and Pt(MCO)₂. Eight additional cyanoxime complexes have been prepared and examined. The complexes were prepared by reacting the ligands with the platinum salt, K₂PtCl₄, in a basic solution. Characterization of these complexes includes UV-Visible, IR, ¹H ¹³C NMR spectroscopy, and DLS. Those complexes with possible Pt-Pt interactions (as evidenced by UV-Vis Spec.) will be examined further for their conducting properties.

Poster #12**Spectroscopic and structural characterization of a new ligand- N,N'-diethylamide-2-cyano-2-oximino-acetamide-and its first bivalent platinum and palladium complexes.**

Danielle Klaus, Nikolay Gerasimchuk

Department of Chemistry, MSU, Temple Hall 431, Springfield, MO 65897.

The previously prepared ligand H(DECO) was purified using filtration of the cyanoxime in absolute diethyl ether with Norite charcoal through Celite 545. The resulting off-white solution was concentrated on the rotary evaporator to a slightly yellow oil, which was left in the flask overnight at +4C to give clear prism-shaped crystals of pure cyanoxime H(DECO). The purified ligand was characterized by ^1H and ^{13}C NMR spectroscopy. Both instrumental analyses also indicated the absence of rotation of the N,N'-diethylamide group around the N-C amide bond. X-ray analysis showed that ligand crystallized in orthorhombic system and the geometry of the amide group indicated a partial double bond character in the C(O)-N fragment, which explains the absence of rotation around C-N bond identified in the previously mentioned NMR spectra. Upon further investigation, the variable temperature ^1H NMR studies allowed for the determination of the rotational energy barrier. The deprotonated ligand H(DECO) was complexed individually with K_2PtCl_4 and K_2PdCl_4 . The resulting square planer complexes (ML_2 , $\text{M} = \text{Pt}^{+2}$ or Pd^{+2} , $\text{L} = \text{DECO}^-$) of platinum and palladium were teal green and canary yellow respectively. The purity of the complexes was confirmed with the elemental analysis of C,H,N. Crystals structures were obtained for the ligand, the Pd complex, and the Pt complex. Crystals of ML_2 were obtained through the vapor diffusion of ether into acetonitrile. The ultimate purpose of these complexes is to be used in cytotoxic drug studies. Future analyses of these complexes will include in vitro for antiproliferating activity using human cervical cancer HeLa and WiDR colon cancer cells.

Poster #13

Resistance Switching in Electrodeposited Metal Oxides

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Resistance switching (RS) in metal oxides has been studied for decades.¹ However, reversible nonvolatile RS (memristive behavior) had not been demonstrated until Strukov et al.² showed that TiO₂ deposited onto crossbar-structures act as a nonvolatile memory. Since then, there has been extensive research on the use of metal oxides for highly-scalable resistance random access memory (RRAM).³ A lot of different novel logic architectures have also been proposed based on nonvolatile RS in TiO₂ such as latch switches and flip-flops.⁴ Co₃O₄ is one of the oxides, which undergoes filamentary, nonvolatile RS.⁵ It was shown for Co₃O₄ that by reducing its size by forming nanowires, the switching mechanism is altered. It changes from unipolar RS in films to bipolar RS in nanowires.⁵ Moreover, Co₃O₄ nanowires exhibit multistate RS (analog logic).⁵

In addition to *memristors*, it is also of interest to use transition metal oxides for novel logic applications as for example ultra-fast switches. In this case, a metal-to-insulator transition (MIT) can be utilized. There are numerous compounds that show MIT, however, from applicational point of view this number has to be limited to those oxides with MIT temperature above room temperature (RT) such as VO₂ or Ti₂O₃.⁶ VO₂ undergoes a sharp, first-order MIT at a temperature of ~68 °C⁶ which is accompanied by a structural change from an insulating, low-temperature monoclinic form VO₂(M) to a high-temperature, metallic rutile structure VO₂(R).⁷ The MIT near RT and the ultrafast (~fs) phase transition⁸ make this compound a very promising candidate for novel electronic applications, such as ultra-fast switches, oscillators, and Mott field-effect transistors.

The RS of the Co₃O₄ film was investigated by measuring the *I-V* characteristics, and by performing stability and endurance tests. Electrodeposited Co₃O₄ undergoes filamentary, nonvolatile RS. An endurance test has shown that the material can be switched back and forth hundreds of times. The low resistance state (LRS) and the high resistance state (HRS) are persistent for at least 10⁵ s. Electric transport measurements have shown that the filaments have metallic behavior. The resistance decreases as the temperature decreases. The HRS behaves as an insulator. The metallic behavior of filaments was further confirmed by impedance spectroscopy. Magnetic measurements revealed ferromagnetic nature of filaments. This strongly suggests that the filaments are Co.

The VO₂ films are prepared by electrochemically reducing V⁵⁺ ions complexed with triethanolamine (TEA) in aqueous electrolyte of pH of 6.5, followed by a short anneal at 400 °C in Ar atmosphere.⁹ The resistance vs. temperature measurements have shown that the film undergoes a MIT at the temperature of 322 K (on heating) and shows characteristic for VO₂ hysteresis. The *I-V* characteristics of the annealed VO₂ film measured at RT show a reversible, volatile RS (negative differential resistance – *NDR*).

The electrochemical approach for preparing thin oxide films is of interest because it introduces an easy and inexpensive method for depositing onto complex geometry substrates. Because electrodeposition is already used to fill up Si trenches with Cu, oxides could be electrodeposited directly onto Cu that could act as one of the contacts, omitting one of the lithographic steps necessary for physical deposition methods. Also, because electrodeposition is not a line-of-sight deposition method, it should also be possible to deposit conformal oxide films on nano-crossbar arrays for solid-state memory and novel logic.

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Poster #14**Oxidative Addition of S-2-bromophenyl-S-methylsulfoximine**

Yang Li, Michael Harmata, and Paul R. Sharp**

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The reaction of S-2-bromophenyl-S-methylsulfoximine with terminal alkynes gave two cyclization products. To get a better understanding of the reaction, oxidative addition of the sulfoximine to Pt(PEt₃)₄ was studied. The reaction resulted in multiple products at room temperature. A dimer with three metallacycle was formed when reacted at 120°C. The product's structure was confirmed by spectroscopy and X-ray crystal analysis. This poster will discuss the structures of the oxidative addition products.

Poster #15**Catalysis of the Oxygen Evolution Reaction on Cobalt Hydr(oxy)oxide**

Ying Chau Liu, Jay Switzer

Department of Chemistry, Missouri S&T, Rolla, MO 65409

The oxygen evolution reaction (OER) is the kinetic bottleneck in photoelectrochemical cells. The hydroxide, oxyhydroxide and oxides of cobalt have been known to exhibit catalytic activities toward OER. In our recent work, we have electrodeposited crystalline cobalt hydroxide, $\text{Co}(\text{OH})_2$ by reducing tris(ethylenediamine)cobalt(III) in alkaline solution. The oxyhydroxide and the oxides can be generated from $\text{Co}(\text{OH})_2$ electrochemically and thermally. The films were characterized by X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM). The reaction mechanisms were analyzed with cyclic voltammetry (CV) and the catalytic properties were studied by linear sweep voltammetry (LSV) and Tafel analysis. The enhanced OER by these films made them attractive candidates for the materials used in photoelectrochemical water splitting.

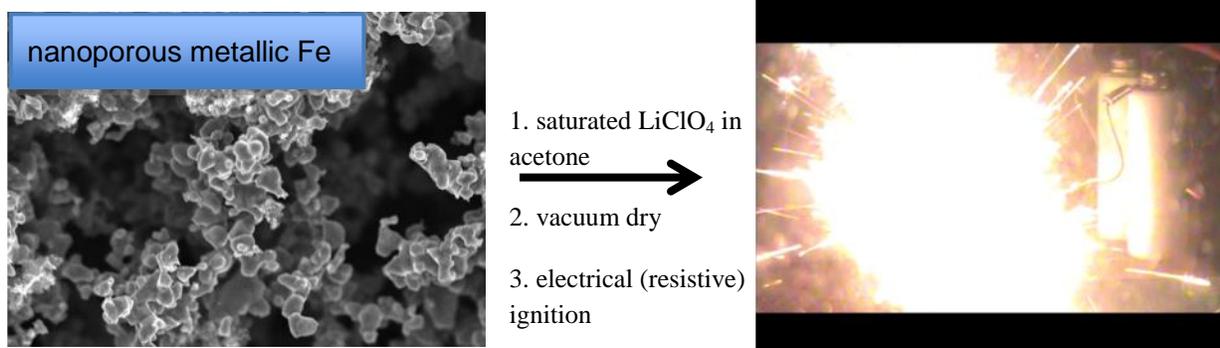
Poster #16

**Interpenetrating Polybenzoxazine-Iron Oxide (PBO-FeOx) Nanoparticle Networks:
Carbothermal Synthesis of Highly Porous, Monolithic Iron (Fe⁰)**

Shruti Mahadik-Khanolkar, Suraj Donthula, Chariklia Sotiriou-Leventis and Nicholas Leventis**

Department of Chemistry, Missouri S&T, Rolla, MO 65409.

We report a simple and safe fabrication method for almost pure (~97% w/w), highly porous (>90% v/v) monolithic iron by carbothermal reaction of interpenetrating polybenzoxazine and iron oxide nanoparticles. Interpenetration brings in close proximity the two reactants and is based on the ability of gelling iron chloride solutions to bring about acid-catalyzed polymerization of benzoxazine monomers. The pyrolysis product is sturdy and consists of interconnected sub-micron sized iron particles. Quantitative analysis, as well as a thorough chemical and material characterization were based on FTIR, TGA, SEM, N₂ sorption and XRD. Porous iron demonstrates the feasibility of producing nanostructured energetic materials with simple impregnation with oxidizing salts such as LiClO₄ or NaClO₄. Intimate contact between the oxidizer and the metal results in fast reaction. Those properties, considered together with the one-step synthetic protocol, render these materials ideal candidates for pyrotechnic applications as for example in thermites.



Poster #17**Photoelimination of Chlorine from Mononuclear Platinum(IV) Chloro Complexes****Tharushi Perera***Department of Chemistry, University of Missouri, Columbia, MO.*

Abstract Alternative energy sources like biomass, nuclear energy etc have limitations and or are insufficient to match growing global energy needs. Solar energy is the most promising carbon neutral energy source for the future. Splitting of simple molecules like HX (X = Cl, Br) an attractive way to store solar energy. Halogen photoelimination from metal centers is the most challenging step in HX splitting cycles using transition metal catalyst. We have synthesized the Pt(IV) chloro complexes $\text{trans-Pt}(\text{PEt}_3)_2\text{R}(\text{Cl})_3$ (R = Cl, aryl and poly cyclic aromatic fragments) which eliminate chlorine in the presence of a halogen trap when irradiated with UV-Vis light. The photo-efficiency of metal-halide bond activation is high showing up to a 58% quantum yield. DFT calculations suggest the photoeliminations of chlorine stores 22 to 33 kcal/mol of light energy.

Poster #18

Photochemistry of Platinum and Iridium Complexes

Andreas Ross, Paul R. Sharp

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Photolysis of (tripod)IrX₃ (tripod = 1,1,1-tris(diphenylphosphinomethyl)ethane and X = Cl, Br) yields an insoluble product. The proposed photochemical process is dissociation of an arm of the tripod ligand followed by coordination to another Ir center to give insoluble tripod-bridged structures. DFT (Density Functional Theory) calculation of the lowest energy triplet support phosphine arm dissociation. Furthermore, DFT investigation of (PNN)IrCl₃ (PNN = 2-(di-*t*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine) and (PNP)IrCl₃ (PNP = 2,6-bis(di-*t*-butylphosphinomethyl)pyridine) predicts dissociation of a halide from the iridium center in the triplet excited state. However, no photochemical activity has been observed experimentally. Under photolytic conditions (PNN)IrCl₃ is inactive and (PNP)IrCl₃ undergoes very slow (days), likely thermal, β -hydrogen elimination to form the iridacycle [2-[[[6-[[bis(1,1-dimethylethyl)phosphino- κ P]methyl]-2-pyridinyl- κ N]methyl](1,1-dimethylethyl)phosphino- κ P]-2-methylpropyl- κ C]dichloro iridium. Furthermore the photochemistry of [PtBr₆]²⁻ in dichloromethane was investigated. Photolysis in the presents of L resulted in heterolytic dissociation of bromide to form [PtBr₅L]⁻ complex (L = THF, DMSO and alkenes). The DMSO complex was characterized by standard ¹⁹⁵Pt-NMR spectroscopy and single crystal X-ray diffraction.

Poster #19**A Simple Model of Calculating Molecular Polarizability From SAPT Computations**

Bradley Welch, *Charles Kirkpatrick*

Department of Chemistry, St. Louis University, St. Louis, MO.

Current models of calculating polarizability are time consuming, and theoretically complicated. Here we present two simple models of calculating polarizability from SAPT calculations. Both models require no further computation besides the standard SAPT calculation. The second model uses the molecular dipole moment to determine the center of negative charge as the basis for the ion distances. It was found that both models do a good job at calculating polarizabilities w.r.t literature values. At the same time, the second model is a more accurate representation of reality despite requiring the calculation of the off-axis polarizabilities.

Poster #20

Pt^{IV} HYDROXO COMPLEX SYNTHESIS AND Pt^{IV} PHOTOCHEMISTRY

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Storing solar energy in chemical bonds is an important goal of transition metal photochemistry.¹ Toward this goal we have studied the photochemistry of Pt^{IV} complexes. Synthesis of trans-Pt^{IV}Cl₂(OH)R(PEt₃)₂(**1**) and trans-Pt^{IV}Cl(OH)(OOH)R(PEt₃)₂(**2**) (R= 4-trifluoromethylbenzene, Phenanthrene, Phenyl, etc) was done with concentrated H₂O₂ in ether. Crystal structures of compound (**1**) and (**2**) were obtained. Photolysis of mono-hydroxo Pt^{IV} (**1**) gives trans-Pt^{II}ClR(PEt₃)₂ and photoelimination of HOCl, H₂O₂ and H₂O₃ has been studied.

1. Karikachery. A.R.; Lee. H. B.; Masjedi. M.; Ross. A.; Moody. M. A.; Cai. X.; Chui. M.; Hoff. C. D.; Sharp. P. R. *Inorg. Chem.* **2013**, 52, 4113

Poster #21**Formation of TiO₂ nanomaterials via titanium ethylene glycolide decomposition**

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Titanium dioxide (TiO₂) nanomaterials show important applications in photocatalysis by different synthesis methods. In this study, TiO₂ nanomaterials were synthesized by reacting titanium isopropoxide with ethylene glycol under basic condition followed by calcinations at 200 °C, 400 °C, 550 °C respectively. We studied the structural, optical, and photocatalytic properties of the TiO₂ nanomaterials with x-ray diffraction, Raman spectroscopy, transmission electron microscopy, differential scanning calorimetry, Fourier-transformed infrared spectroscopy, x-ray and ultraviolet (UV) photoemission spectroscopy, UV–vis diffusive reflectance, and photocatalytic decomposition of methylene blue. We found that titanium ethylene glycolide was first formed, then decomposed at 330 °C, transformed into pure anatase TiO₂ around 400 °C, and the anatase phase further transformed into core/shell rutile/anatase TiO₂ composite 550 °C. This core/shell structure displayed the highest photocatalytic activity, which was attributed to the improved charge separation at the rutile/anatase n/n junction interface and its high crystallinity.

Poster #22

Synthesis, characterization and crystal structure of iron *Tavorite* phases, $\text{LiFePO}_4(\text{OH})_x\text{F}_{1-x}$ ($x = 1, 0.5,$ and 0), potential cathode materials for Lithium-ion Batteries

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During the past two decades, Li-ion batteries based on cobalt dioxide cathode have been successfully used mainly for powering portable electronic devices. However, scaling up of this battery type for high throughput applications like electric vehicle, renewable energy storage, etc. was lagging behind due to the safety issues and production costs. Introduction of LiFePO_4 as the cathode for Li-ion battery by Goodenough et al.¹ opened a new horizon for employing polyanion moiety-based materials with inherent higher safety, lower cost and lower environmental effects. With its relatively high operational voltage of about 3.5 V vs. Li/Li^+ , LiFePO_4 quickly became a good candidate for electric vehicle application. However, one major drawback of LiFePO_4 is the existence of one-dimensional Li-ion diffusion channels within the structure. *Tavorite* family of materials with the general formula of $\text{LiMPO}_4(\text{OH})_x\text{F}_{1-x}$ ($M = \text{Al}, \text{Fe}, \text{V}, \text{Mn}; x = 0 - 1$) present a solution to the problem mentioned above, as they provide 3-dimensional Li-ion diffusion channels in the crystal structure thereby making them suitable for high current applications. In this work, we have successfully synthesized employing soft chemical methods three phases of $\text{LiFePO}_4(\text{OH})_x\text{F}_{1-x}$ ($x = 1, 0.5,$ and 0) belonging to *Tavorite* structure type (Fig. 1), which has been quoted as a good cathode material.² The structure of the full hydroxo ($x = 1$) phase has been determined for the first time employing single-crystal X-ray diffraction. Powder X-ray diffraction was employed to confirm phase purity of each compound. FT-IR, Mössbauer spectroscopy, and TGA were used for further characterization. Basic electrochemical tests were conducted to evaluate the performance of each phase as the cathode material for Li-ion batteries.

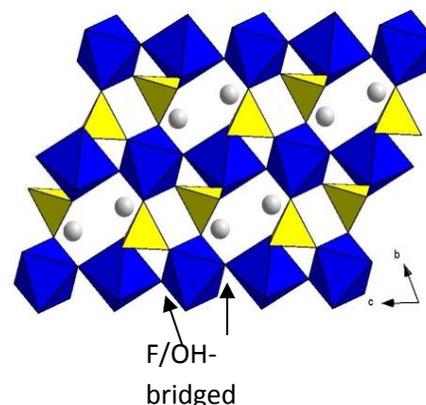


Fig. 1: Structure of Tavorite, $\text{LiFePO}_4(\text{OH})_x\text{F}_{1-x}$ ($x = 1, 0.5,$ and 0) ($\text{PO}_4 = \text{yellow}$ and $\text{FeO}_5\text{F} = \text{blue}$, grey = Li^+).

References:

1. Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. *J. Electrochem. Soc.* **1997**, *144*, 1188 - 1194.
2. Marx, N.; Croguennec, L.; Carlier, D.; Wattiaux, A.; Le Cras, F.; Suard, E.; Delmas, C. *Dalton Trans.* **2010**, *39*, 5108 - 5116.

Poster #23**Synthesis of Multifunctional Dumbbell-shaped Au-CoSe Nanoparticles through Chemical Vapor Deposition**

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Multifunctional nanoparticles are appealing to material scientists and chemists owing to their wide spread applications. These multifunctional nanoparticles consisting of two or more materials containing distinctively different functionalities can be used effectively in biomedical and catalysis applications. We have synthesized multifunctional dumbbell shaped Au-CoSe nanoparticles on Si substrate through catalyst aided chemical vapor deposition technique. A horizontal furnace equipped with mass flow controller was used to deposit the nanoparticles at 800°C under the steady flow of N₂. The technique utilized volatile cobalt acetylacetonate and elemental selenium as precursors while sputter coated Au-Pd (3:2) acts as a catalyst. The nanoparticles contain Au tip ranging 10-25 nm in size while CoSe size ranges from 50-75 nm. CoSe is a ferromagnetic, semiconducting material (band gap=1.53 eV) which is widely used in catalysis and as dilute semiconducting magnet. Detailed magnetic, optical and microscopy characterizations of Au-CoSe nanoparticles will be discussed in detail.

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MISSOURI
S&T Campus Map

CLASSROOMS/LABS

1. Butler-Carlton Civil Engineering Hall
2. Computer Science Building
3. Emerson Hall
4. Engineering Management Building
5. Fulton Hall
6. Gale Bullman Multi-Purpose Building
7. Harris Hall
8. Humanities and Social Sciences Building
9. Interdisciplinary Engineering Building

10. McNutt Hall
11. Physics Building
12. Pine Building
13. Rock Mechanics and Explosives Research Center
14. Rolla Building
15. Schrenk Hall
16. Toomey Hall

RESEARCH SUPPORT FACILITIES

17. Historic Bureau of Mines Building

18. Engineering Research Laboratory
19. Innovation Park
20. MSTR
21. Straumanis-James Hall
22. Curtis Laws Wilson Library

STUDENT HOUSING

23. Altman Hall
24. Farrar Hall
25. Holtman Hall
26. Kelly Hall
27. McAnerney Hall
28. Nagogami Terrace
29. Residential College #1

30. Residential College #2
31. Thomas Jefferson Residence Hall

CAMPUS & STUDENT SUPPORT

32. Algood-Bailey Stadium
33. Athletic Fields
34. Campus Housing and Dining Services
35. Campus Support Facility
36. Castleman Hall
37. Centennial Hall
38. Chancellor's Residence

39. Custodial and Landscape Services Building
40. General Services Building
41. Golf Course
42. Havener Center
43. Kummer Student Design Center
44. Miner Dome
45. Norwood Hall
46. Parker Hall
47. Power Plant
48. Rayl Cafeteria
49. Southwestern Bell Cultural Center
50. Student Health Services

51. Student Recreation Center
52. Temporary Facility A

CAMPUS LANDMARKS

53. E³ Commons
54. Millennium Arch
55. Missouri S&T Observatory
56. The Puck
57. Solar Village
58. Stonehenge