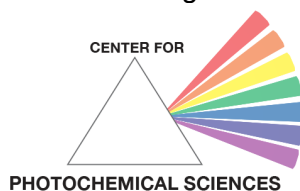




**2015 Ohio Inorganic Weekend
November 13-14, 2015
Bowling Green State University**

Oral Presentations

Saturday November 14, 2015
8:30- 4:20 pm
Math Sci Building Room 210



Talk #1

Moving Towards Multicomponent Chalcogenide Aerogels: Effect of Chalcogenide, Capping Agent and Crystal Structure on the Kinetics of Assembly

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Starting with well-established methods for single component metal chalcogenide (MQ) nanoparticle gels, we are establishing a practical method for co-gelation of different component particles with complimentary functionalities. We have demonstrated that the chemical mechanism for gel formation of MQ nanoparticles involves the oxidative loss of surface thiolate ligands (as disulfides) followed by oxidation of surface chalcogenides (Q^{2-}) to form $(Q_n)_2$ -interparticle linkages. For gel coupling of nanoparticles with differing Q ($Q = S, Se, Te$), we postulate that the relative redox characteristics of Q will govern the reaction rate, and affect the homogeneity of the composite. Moreover, we anticipate that judicious variation of capping ligands (chain length, polarity) will complement the redox characteristics, enabling reactivity tuning and control of the extent of heterogeneity in the resultant gel. Intriguingly, preliminary results indicate that crystal structure may also be playing a role, enabling even finer control over the product morphology. In this presentation, the roles of Q, capping ligand and crystal structure on the kinetics of assembly as probed by dynamic light scattering and 1H and ^{19}F NMR will be described and these data will be correlated with the observed morphology and photophysical properties of the resultant gels. The ability to exploit this knowledge for the programmable assembly of multicomponent gels with control of heterogeneity will be discussed in light of examples systems.

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Talk #2

Influence of Rotational Correlation Time and Magnetic Field Strength on the Relaxivity of Eu(II)-Containing Cryptates

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The purpose of this research is to study the influence of molecular parameters and field strength on the efficiency (relaxivity) of Eu(II)-containing cryptates as contrast agents for magnetic resonance imaging. Relaxivity is governed by several molecular parameters including rotational correlation time. The relaxivity of Eu(II)-containing cryptates with short and long rotational correlation times have been reported, but to understand how the interplay between rotational correlation time and field strength influences the relaxivity of Eu(II)-containing cryptates, complexes with intermediate rotational correlation times need to be studied. To fill this gap of knowledge, we synthesized host-guest adducts of biphenyl-functionalized cryptand with β -cyclodextrin and poly- β -cyclodextrin. We will present our results that compare rotational correlation time to relaxivity at a variety of field strengths. We expect that our results will be instrumental in the design of future Eu(II)-based contrast agents.

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Talk #3

Engineering Nickel-Substituted Azurin for Energy Conversion Reactions

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Nickel-containing metalloenzymes are highly relevant in the context of both environmental concerns and energy conversion reactions. Carbon monoxide dehydrogenase (CODH) reversibly interconverts carbon dioxide and carbon monoxide, and acetyl coenzyme A synthase (ACS) is responsible for the synthesis of acetyl CoA, a critical element in biological metabolic processes. The tightly coupled CODH/ACS complex offers a potential solution to present-day energy challenges and climate issues, as it is a promising system for carbon dioxide fixation and carbon-carbon bond-forming reactions, necessary for the generation of liquid fuels. However, these large, complex enzymes lack the stability to be extensively studied or widely applied. While significant progress has been achieved modeling other nickel-based enzyme systems, such as the [NiFe] hydrogenase and nickel superoxide dismutase, the development of models for understanding CO₂-converting enzymes is far behind.

We can overcome the limitations of fragile enzyme systems using existing metalloprotein platforms for protein redesign. In this work, the well-studied electron transfer protein, azurin, has been selected due to its robustness and versatility. We have recently shown that replacement of the native copper center with nickel generates a redox-active site with access to a reductive II/I couple closely matched to that of ACS. Spectroscopic and electrochemical techniques in conjunction with DFT calculations were used to probe the unique electronic and geometric structure. Comparison of these features to native nickel enzymes and functional model compounds provides insight into the key parameters required for enzymatic activity. Moreover, we have established the first protein model for the ACS enzyme.

Reference

1. Manesis, A. C.; Shafaat, H. S. Inorg. Chem. 2015

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Talk #4

A Square Planar Cu(I) and the Stabilization of an Entatic State Through Second Sphere Hydrogen Bonds

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The type-1 copper center in blue copper proteins (BCPs) exhibits extremely fast electron transfer rates (10^4 - 10^6 M⁻¹s⁻¹) through the cooperation of primary and secondary sphere interactions. Although Cu(I) and Cu(II) typically bind ligands in different geometries, BCP's impose an 'entatic state' on the Cu center whereby reorganization energy is minimized allowing for the fast rates of electron transfer. The interplay of both primary sphere and secondary sphere interactions, like hydrogen bonding, plays a critical role in the stabilization of this entatic state. As such, we have begun to study the effects of secondary sphere hydrogen bonding interactions on Cu(I) and Cu(II) geometries in synthetic metal-ligand constructs. Our lab has developed a ligand scaffold, based on the rigid terpyridine framework, that contains appended functionality in the form of hydroxy and anilido variants that can provide directed hydrogen bonding with metal-bound substrates. The meridonal binding of terpyridine combined with pendent hydrogen bond donors allows for the stabilization of a highly unusual square planar Cu(I) geometry. Furthermore, the planar geometry is maintained upon oxidation to Cu(II) providing a synthetic entatic state that exhibits electron transfer rates on the order of BCPs.

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Talk #5

Development of Photoactivatable Nitroxyl (HNO) Donors using the (3-Hydroxy-2-naphthalenyl)methyl Photolabile Protecting Group

Yang Zhou,[†] Ruth Cink,[‡] Nicola E. Brasch[‡] and Paul Sampson^{†*}

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The development of new nitroxyl (HNO) donors is receiving increasing attention primarily due to their promise as therapeutics for treating congestive heart failure. We are developing new HNO donors suitable for studying the fundamental bioinorganic chemistry of HNO, which rapidly release HNO via photoactivation. The synthesis of a new family of photoactivatable HNO donors based on the (3-hydroxy-2-naphthalenyl)methyl (HNM) phototrigger will be presented. HNO generation is demonstrated using aquacobalamin as a trapping agent. Detailed kinetic and mechanistic studies have also been carried out, and show that O-N bond cleavage occurs in addition to the desired pathway leading to HNO generation.

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Talk #6

Investigation of role group 13 & 15 superacids in the polymerization of chloropolyphosphazenes

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Polyphosphazenes make up the largest class of inorganic backbone polymers but due to synthetic challenges, their application has not reached its full potential. Lewis acids, such as AlCl_3 and PCl_5 , have been used in the ring opening polymerization of hexachlorotriphosphazene, but their role is not truly understood. A leading theory is that superacids are generated during the polymerization which has been shown to lower the polymerization temperature. Our group wanted to investigate the relative strengths of the superacids derived from selected group 13 (MCl_3) and group 15 Lewis acids (MCl_5). The strengths of the superacids were determined through the use of IR spectroscopy and variable temperature NMR. In our studies, we found that superacids are produced and they have the ability to protonate the poor nucleophilic nitrogen on the phosphazene ring.

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Talk #7

Two-Dimensional Tin Graphane Derivatives

Maxx Arguilla, W. McCulloch, S. Jiang, K. Krymowski, W. Windl, Y. Wu and J. E. Goldberger*
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Recent theoretical calculations suggested that two-dimensional honeycomb sp^3 -hybridized lattices of Group IV or V elements that possess high spin-orbit coupling have the prospect of being room temperature Quantum Spin Hall insulators. Here, we present our recent success in synthesizing various graphane-like two-dimensional (2D) derivatives of Sn via the topochemical deintercalation of an array of II-IV and I-IV-V Zintl phases. First, we show the synthesis of 2D $Ge_{1-x}Sn_xH_{1-x}(OH)_x$ alloys from the deintercalation of $CaGe_{2-2x}Sn_{2x}$ ($x < 0.09$) in HCl. In these two-dimensional alloys, the germanium atom is terminated with hydrogen while tin is terminated with hydroxide. With increasing Sn concentrations, the band gap systematically shifts from 1.59 eV in GeH down to 1.38 eV for $Ge_{0.91}Sn_{0.09}H_{0.91}(OH)_{0.09}$. To further understand the chemistry and the electronic properties of Sn in a puckered honeycomb lattice, we also synthesized various BN-like 2D Sn derivatives based on deintercalated I-IV-V Zintl phases, from the more electronegative group V component (P) to the least (Sb). We will discuss the optical and electronic properties and surface termination chemistry of this class of 2D materials.

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Talk #8

Cation Directed Synthesis of In-Derived 2,5-Thiophenedicarboxylate Metal Organic Frameworks: Tuning Dimensionality via Hydrogen Bond Donation.

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Template directed synthesis of metal organic frameworks (MOF) is of increasing interest. Herein we report the synthesis of six new MOFs synthesized from 2,5-thiophenedicarboxylic acid (TDC) and indium(III) chloride with one framework, YCM-22, containing to our knowledge an unprecedented dianionic node. The structural diversity represented by these materials is entirely controlled by the use of additives during the synthesis process. The role of these additives is briefly discussed with observed correlations of 1) hydrogen bonding capability to MOF dimensionality and 2) the presence of anionic counterions to coordination chemistry at the metal center.

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Talk #9

Catalytic Reductions Promoted by Solar Devices

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Fossil fuel depletion is a major issue in 21st century, thus the world needs to develop alternative energy sources. Dihydrogen has been identified as a good alternate energy carrier. Majority of dihydrogen production methods depend on fossil fuels, which is a finite, non-renewable resource. This also results in the release of carbon dioxide that causes harmful environmental impacts. Solar-driven dihydrogen production through water splitting offers a better choice as both solar energy and water are renewable and it is non-polluting process. However, this method is still in need of highly active non-noble catalysts to drive the reaction efficiently. This research examines the catalytic activity of nickel-based catalysts for the Hydrogen Evolution Reaction (HER). Nickel and nickel phosphide were electroplated onto stainless steel and their catalytic activity was compared with electroplated Pt, one of the best catalysts for HER. The aim is to apply these catalysts on the back side of the photovoltaic (PV) cell, where the reduction of water to hydrogen occurs and to develop an efficient system for dihydrogen production.

The knowledge gained can be extended towards the reduction of carbon dioxide to produce value added chemicals using PV devices, which would help to prevent environmental pollution through carbon dioxide emission. Also, the technique of electrodepositing metals on the PV device is expected to find use as a tool for water purification. The aim is to remove toxic metal ions such as arsenic, lead, mercury and chromium from water by subjecting the PV device to electrolysis in contaminated water.

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Talk #10

Light-triggered reversible change in mechanical stiffness in metallosupramolecular polymer materials

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Transition metal-ligand interactions offer a way to control mechanical properties of materials by tuning the photoreactivity and assembly of polymers. We have designed organic-inorganic metallopolymeric hybrid materials where new material properties were introduced due to unique interactions between a metal-binding terminus-group on the polymer and a metal ion. Specifically, the linkage of polymer molecules through metal-ligand interactions changed the mechanical properties of the material as well as added new features to the polymeric material. In the work presented here, telechelic hydrogenated poly(ethylene-co-butylene) polymers with ligand binding end groups coordinated to chromium(III) ions showed photoresponsive, viscoelastic response. Specifically, we showed tight control over the mechanical strength of prepared metallopolymers where 455 nm light radiation gave rise to reversible changes in the modulus of the materials. We attributed this photo-responsive behavior to the generation of an excited state of the chromium(III) metal center, which locally breaks the metal-coordination bonding in the polymer, leading to softening of the Cr(III)-based metallopolymers. The magnitude of this softening was observed up to 46 kDa in storage modulus G' . Once the light stimulus was removed, however, the initial matrix elasticity is fully recovered within a minute timescale. Current efforts are now aimed to create multifunctional supramolecular polymers with multi-modal self-assembly sites to introduce self-healing sites and maximize changes in mechanical stiffness of these materials upon light exposure.

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Talk #11

Establishing trends in high pressure behavior of scandium tungstate type materials

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Negative thermal expansion (NTE) materials have many potential applications in the engineering field as a means to control the overall thermal expansion of composites, increasing the durability and lifetime of its applications. The scandium tungstate, or $A_2M_3O_{12}$ family (in which A = a trivalent cation, and M = molybdenum or tungsten), is a well-known family of materials which exhibit this behavior in an orthorhombic structure. NTE behavior arises from the open framework crystalline structure of such materials, which also makes them susceptible to pressure induced phase transitions or amorphization. The high pressure behavior of these materials must be understood for their effective use, as NTE is not expected to be observed in the high pressure $A_2M_3O_{12}$ structures or amorphous material. Powder x-ray diffraction studies of several $A_2M_3O_{12}$ materials were conducted at the Advanced Photon Source from 5-7 GPa using a diamond anvil cell. These studies revealed that the high pressure behavior of these materials is quite complex, and several of the room temperature monoclinic compounds ($A_2 = Al_2, Fe_2, FeAl, AlGa$) underwent a similar sequence of reversible subtle phase transitions before undergoing a major structural transition to a common high pressure structure. The unit cell of this high pressure structure was successfully indexed, and all changes were found to be reversible on decompression. The phase transition pressure increased with decreasing cation radius.

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Talk #12

Lanthanum Catalysed Hydrophosphinylation of Imines and Nitriles

Miriam Basiouny and Joseph A.R. Schmidt*

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Hydrophosphinylation is the addition of H-P(O)R_2 across an unsaturated system. Hydrophosphinylation of alkenes and alkynes has previously been reported using palladium, nickel and magnesium but requires harsh conditions. Herein, a new lanthanum based catalyst was shown to be capable of single and double hydrophosphinylation of imines and common nitriles, respectively, under very mild conditions. The single hydrophosphinylation reactions of imines produced a new C-P bond for both alkyl and aryl imines. Surprisingly, the lanthanum catalyst was able to effect unprecedented double hydrophosphinylation of nitriles. Two regioisomeric products were observed depending on the nature of the starting nitrile. Initially, it was observed that phosphorus added to the carbon of alkyl nitriles twice, resulting in a P-C-P product with concomitant formation of a primary amine. Using the same conditions with aryl nitriles resulted in different addition products where one equivalent of the phosphine oxide was added to the carbon, while the second added to the nitrogen of the nitrile resulting in a P-C-N-P product. Further investigation of the catalytic cycle yielded evidence that aryl nitriles first undergo double addition at the carbon atom (deemed the kinetic product) that then undergoes isomerization to the final unsymmetric addition product (the thermodynamic product). All catalytic reactions were run neat or with very little solvent, required little workup and had high to moderate yields.

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Talk #13

Olefin Cyclopropanation Catalyzed by Metal Mesoporphyrins in Water: Towards Novel Metalloenzymes

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Small molecule transition metal complexes have proven to be effective catalysts in industrial organic synthesis, often catalyzing thousands of turnovers with high turnover rates and long catalyst lifetimes. However, many of these catalysts require expensive and environmentally-detrimental solvents to carry out these reactions and are inactive in water. By inserting metal complexes into water-soluble protein scaffolds, these new enzymes could lead to the development of “greener” and more stereo-selective organometallic catalysts. Metalloporphyrins can be inserted into a variety of small heme proteins, and can catalyze carbene, nitrene, and oxo transfer reactions. Synthetic porphyrins containing metals such as Ru, Rh, and Ir have been shown to catalyze these reactions with high turnover numbers, and studying these metalloporphyrins both in and out of the protein matrix is important if we are to develop a set of useful artificial metalloenzymes. Mesoporphyrin IX has been metallated with Ru(II), Rh(III), and Ir(III), and these porphyrins have been characterized by UV-vis and ¹H-NMR spectroscopy. Ru(II) and Ir(III) porphyrins have been shown to catalyze the cyclopropanation of ethyl diazoacetate and styrene in water, with the Ir(III) mesoporphyrin IX catalyst achieving >80,000 turnovers by GC/MS. Initial cyclopropanation studies have also been carried out with Ru(II) and Rh(III) inserted into myoglobin mutants, but more studies are needed in order to increase turnover numbers. Future studies will focus on further modifying the proteins through point mutations to induce altered reactivity, and examining other carbene, nitrene, and oxo transfer reactions with the metalloporphyrins and the reconstituted proteins.

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Talk #14

Using Femtosecond Time-Resolved Spectroscopy to Visualize Photoinduced Nitrile Dissociation from Ruthenium Metal Centers

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Ruthenium (II) metal centers with polypyridyl ligands such as 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy) have been previously shown to substitute nitrile functional groups in the complexes $[\text{Ru}(\text{phen})_2(\text{CH}_3\text{CN})_2]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$. This photosubstitution occurs by populating the triplet ligand field state of ruthenium, elongating the ruthenium acetonitrile bonds. Using ultrafast time-resolved infrared spectroscopy we have identified the shift of the nitrile bond in < 1 ps of excitation into the lowest triplet ruthenium-polypyridyl charge transfer manifold. This, alongside femtosecond transient absorption spectroscopic data, allows us to visualize the excited vibrational and electronic states of nitrile dissociation in ruthenium metal complexes. Understanding the excited states involved in ruthenium nitrile dissociation allows us to design more efficient compounds that can undergo light-induced drug release for applications such as photochemotherapy.

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