

Western New York Inorganic Symposium 2023

August 4th Schedule of Events

8:30 – 9:00 AM: Coffee/Snacks and Poster Set-Up

9:00 – 10:30 AM: Student Talks Session #1 (Moderator: David Lacy)

- 9:00 AM–9:10 AM Opening Remarks
- 9:10 AM–9:30 AM *Stereoconvergent Synthesis of (Z)-1,3-Dienes and Ring-Strain Assisted Ene-Yne/Olefin Metathesis*
Laurence N. Rohde (Driver)
- 9:30 AM–9:50 AM *Cobalt(III) Halide MOFs Drive Catalytic Halogen Exchange*
Tyler Azbell (Milner)
- 9:50 AM–10:10 AM *Selective Point Source Capture of Perfluorinated Gas using MOFs with Highly Fluorinated Pores*
Bevan Whitehead

10:10 AM – 11:10 PM: Poster Session #1 (odd # posters)

11:10 – 11:45 PM: Plenary Speaker, Christian Mueller (Moderator: Bill Jones)

News from the Chemistry of 5-membered Phosphorus-Nitrogen Heterocycles

11:45 AM – 12:45 PM: Lunch

12:50 – 1:30 PM: Student Talks Session #2 (Moderator: Agnes Thorarinsdottir)

- 12:50 PM–1:10 PM *Metal-based Inhibitors of the Mitochondrial Calcium Uniporter as Prodrugs and Supramolecular Guests*
Nicholas P. Bigham (Wilson)
- 1:10 PM–1:30 PM *Co(II) Complexes of Tetraazamacrocycles Appended with Amide or Hydroxypropyl Groups as paraCEST Agents*
Jaclyn Raymond (Morrow)
- 1:30 PM–1:50 PM *Elucidating the Mechanisms of Cofactor Maturation and Hydroxylamine Oxidation by Cytochrome P460*
Melissa Bollmeyer (Lancaster)
- 1:50 PM–2:10 PM *CO₂ Reduction Catalyzed by Biomolecular Cobalt Catalysts*
Alison Salamatian (Bren)

2:10 – 3:10 PM: Poster Session #2 (even # posters)

3:20 PM – 4:40 PM: Student Talks Session #3 (Moderator: Brandon Barnett)

- 3:20 PM–3:40 PM *Molybdenum-sulfide Clusters as Redox Active Metalloligands for Low-valent Uranium*
Kamaless Patra (Matson)
- 3:40 PM–4:00 PM *The Chemistry of Manganese(III) Chloride*
Ananya Saju (Lacy)
- 4:00 PM – 4:10 PM Closing Remarks & Student Prizes

ABSTRACTS FOR ORAL PRESENTATIONS

Stereoconvergent Synthesis of (Z)-1,3-Dienes and Ring-Strain Assisted Ene-Yne/Olefin Metathesis

Laurence N. Rohde Jr.; Elifnur Ylidiz, LiangZhan Li and Steven T. Diver

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract: In this talk, I will describe the stereoselective synthesis of 1,3-dienes via tandem ene-yne metathesis and photoisomerization. The stereopurity of (poly)olefins are of synthetic interest in natural products, bioactive molecules and functionalization reactions. 1,3-dienes are readily prepared via ene-yne metathesis, which is a selective bond reorganization reaction between an alkene and alkyne via Grubbs catalysts. However, ene-yne metathesis typically forms *E/Z* mixtures, which lowers the synthetic utility of the resultant diene. The stereopurity of the diene can be effected by thermodynamic control, but a stereoselective synthesis of the kinetic isomer is underdeveloped. More recently, uphill photocatalysis has emerged as a stereoconvergent method for the isomerization of *E/Z* mixtures to the *Z*-isomer. Photoisomerization of *E/Z*-1,3-diene mixtures furnished the desired *Z*-isomer and the scope of this method will be described. At the end, I will also introduce some of our latest work on ring-strain assisted ene-yne and olefin metathesis.

Cobalt (III) Halide MOFs Drive Catalytic Halogen Exchange

Tyler J. Azbell and Phillip J. Milner

Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY

Abstract: Fluorine and chlorine are two of the most essential elements in synthetic and process chemistry, present in > 30% of pharmaceuticals and > 40% of agrochemicals. However, the synthetic installation of these halogens is challenging due to the uncontrollable reactivity of halogenating molecules, which are often toxic gasses or prohibitively unstable solids. Metal-organic frameworks (MOFs) are porous, crystalline materials constructed from organic linkers and inorganic nodes with myriad potential applications in chemical separations, catalysis, and drug delivery. Using MOFs to sequester dangerous gasses is well-established in the literature, but few examples use MOFs as heterogenous catalysts for hazardous reagent delivery. Herein we report a family of halogenated MOFs competent in catalyzing nucleophilic aromatic substitution (S_NAr) in electron-deficient aromatic systems via the halogen-exchange (halex) reaction, a desirable transformation in the late-stage functionalization of pharmaceutical molecules. Traditional halex processes often require excessive heat and high equivalencies of the corresponding halogenating reagent, resulting in limited substrate tolerance. By utilizing a catalytic amount of MOF, the conversion of aryl bromides to aryl chlorides and fluorides is facilitated in competent yield. This catalytic system demonstrates functional group tolerance on a range of pharmaceutically relevant electron-deficient heterocycles. Additional ongoing experiments seek to apply this system in flow, taking advantage of the heterogenous nature of MOFs and their natural amenability to recyclable flow catalysis.

Selective Point Source Capture of Perfluorinated Gas using MOFs with Highly Fluorinated Pores

Bevan Whitehead and Brandon Barnett

Department of Chemistry, University of Rochester, Rochester NY

Abstract: A zinc-based metal organic framework was synthesized for the capture of perfluorinated semiconductor waste using halogen-halogen interactions. Perfluorinated compounds (PFCs), CF₄, NF₃, SF₆, and C₂F₆, are widely used as etching and cleaning agents for the fabrication of semiconductor

wafers, however, these gases pose severe environmental hazards due to their long atmospheric lifetimes and robust chemical bonds making them potent global warming gases. Through isotherms and IAST calculations, this material has been shown to be highly selective for CF₄ vs. N₂. We have also probed the uptake mechanism of this material for CF₄ using variable temperature single crystal gas dosing, kinetic measurements using single point uptake experiments, and solid-state NMR. Using these techniques, we have been able to show that this material has two types of pores, a cylindrical fluorinated 6 Å pore and a diamond shaped aryl pore 4.5 Å, both of which uptake CF₄. This is the first report of this type of behavior occurring for this material because all previous reports claimed that the smaller pore could not uptake any gas molecules.

Metal-Based Inhibitors of the Mitochondrial Calcium Uniporter as Prodrugs and Supramolecular Guests

Nicholas P. Bigham and Justin J. Wilson

Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY

Abstract: The mitochondrial calcium uniporter (MCU), a transmembrane protein residing on the inner mitochondrial membrane, is the primary transporter of calcium ions (Ca²⁺) into the mitochondrial matrix. Its implication in intracellular Ca²⁺ homeostasis is critical to cell survival and function. This channel has been linked to a number of pathological conditions that implicate mitochondrial Ca²⁺ (_mCa²⁺) overload, a phenomenon that triggers several downstream apoptotic processes, prompting the development of MCU inhibitors as potential therapeutic agents. Two dinuclear, metal-based inhibitors – Ru265 and Os245 – demonstrate nanomolar potency of the MCU with minimal off-target effects. In this work, the axial chlorido-ligands of these inorganic complexes have been exchanged with various carboxylate groups, leading to the development of several analogues of these complexes. These analogues have demonstrated prodrug activation by imparting slower aquation kinetics of the axial site, leading to delayed inhibitory activity. In addition, adding a hydrophobic adamantane carboxylate to the axial site has enabled these complexes to be encapsulated into supramolecular complexes such as cyclodextrin and cucurbituril, which has demonstrated both prodrug capability and significantly enhanced cellular uptake while still maintaining MCU inhibitory activity.

CO₂ Reduction Catalyzed by Biomolecular Cobalt Catalysts

Alison Salamatian, Jose Alvarez-Hernandez, Jiwon Han, Hafsa Mohamed, and Kara L. Bren

Department of Chemistry, University of Rochester, Rochester NY

Abstract: A semisynthetic electrocatalyst for carbon dioxide reduction to carbon monoxide in water will be discussed. Cobalt microperoxidase-11 (CoMP11-Ac) is shown to reduce CO₂ to CO with a turnover number of up to 32,000 and a selectivity of up to 88:5 CO:H₂. Higher selectivity for CO production is favored by a less cathodic applied potential and use of a higher pK_a buffer. A mechanistic hypothesis is presented in which avoiding the formation and protonation of a formal Co(I) species favors CO production. These results demonstrate how tuning reaction conditions impacts reactivity toward CO₂ reduction for a biocatalyst previously developed for H₂ production. Cobalt-mimochrome VI*a (CoMC6*a), a synthetic mini-enzyme, will be discussed as a leader in synthetic biomolecular catalysts for electrochemical CO₂ reduction in water. The catalytic turnover numbers reach ~2,100 for CO with a max selectivity of ~85%. Comparison of CoMC6*a with cobalt microperoxidase-11 (CoMP11-Ac) linked the enclosed active site of CoMC6*a with higher selectivity for CO₂ reduction. Selectivity for CO₂ over H⁺ reduction was also controlled through applied potential

and pKa. Leveraging the synthetic nature of CoMC6*a versus previously reported semi-synthetic CoMP11-Ac allowed for modifications to the structure which enhanced the activity without loss in selectivity. Herein, we discuss a highly active synthetic enzyme for CO₂ reduction along with methods to increase the selectivity of the system.

Elucidating the Mechanisms of Cofactor Maturation and Hydroxylamine Oxidation by Cytochrome P460

Melissa Bollmeyer and Kyle Lancaster

Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY

Abstract: Ammonia oxidizing bacteria rely on the oxidation of ammonia (NH₃) to nitrite (NO₂⁻) as their source of energy for life. The primary energy-producing step is carried out by the metalloenzyme hydroxylamine oxidoreductase (HAO), which harnesses a unique heme P460 cofactor to catalyze the oxidation of hydroxylamine (NH₂OH) to nitric oxide (NO). The only other metalloenzyme known to contain this cofactor is cytochrome (cyt) P460. Although cyt P460 is similar to HAO in that it oxidizes NH₂OH, it produces nitrous oxide (N₂O) and features a different active site architecture. The ability of cyt P460 to oxidize NH₂OH requires the covalent attachment of a lysine nitrogen to the porphyrin *meso*-carbon. In this work, we have shown that the lysine cross-link forms by a peroxide-dependent mechanism involving a ferryl intermediate. Outer coordination-sphere residues play an important role in promoting the heme ruffling distortion and controlling reactivity with peroxide to allow for the cross-link to form. Once the cross-link has formed, the outer coordination-sphere must also be tuned for NH₂OH oxidation. We have shown that a capping phenylalanine residue controls the rate-determining step of NH₂OH oxidation and consequentially product partitioning between NO and N₂O. These outer sphere influences provide insights into the difference in product selectivity between cyt P460 and HAO.

Molybdenum Sulfide Clusters as Redox-active Metalloligands for Low-valent Uranium

Kamaless Patra, William W. Brennessel, and Ellen M. Matson

Department of Chemistry, University of Rochester, Rochester NY

Abstract: Heterometallic clusters have significantly interested chemists because of their attractive structures and metal-metal synergistic effects in small-molecule activation and catalysis. However, reports of the isolation of heterometallic clusters with uranium remain very limited. Here, we describe coordination chemistry of the incomplete cubane cluster [Mo₃S₄] supported by Cp* ligands on molybdenum, to low-valent uranium centers. We present the synthesis and characterization of the heterometallic cubane-type cluster [(Cp*Mo)₃S₄Cp*U₂] (**1**). Our findings reveal an electron transfer from the U(III) center to the [Mo₃S₄] core, oxidizing the uranium center and reducing the [Mo₃S₄] core during the reaction of [(Cp*Mo)₃S₄] with Cp*U₂(THF)₃. Furthermore, a sequential reduction of **1** is performed, and the corresponding reduced products are isolated and characterized. We find that the [Mo₃S₄] cluster scaffold offers distinct advantages, such as electron storage and stabilization of low-valent uranium species, allowing the stored reducing equivalents to be harnessed for future chemical reactions. Notably, despite multiple metal centers held in place by similar auxiliary ligands in the heterometallic uranium cluster, low-valent uranium exhibits a preference for substrate activation. This observation further supports the importance of the 5f orbitals of the uranium center, which play a dominant role in its reactivity. Our work highlights the application of the [Mo₃S₄] core as a platform

for [Mo₃S₄U] cubes and sheds light on the intriguing reactivity of the [Mo₃S₄U] cluster towards the activation of small molecules through multi-electron processes.

The Chemistry of High Valent Manganese(III) Chloride

Ananya Saju and David C. Lacy

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract: High-valent Mn-based intermediates (oxidation states ≥ 3) are implicated in numerous chemical reactions. However, little is known about the chemistry of high-valent manganese species. A dearth of suitable precursors is one of the primary reasons for the limited exploration of high valent manganese chemistry. We aimed to synthesize a Mn(III) precursor that can serve as a synthon for accessing high valent Mn complexes. This was realized by the synthesis and characterization of MnCl₃(OPPh₃)₂ (**1**). In addition, a host of new and known Mn(III) chloride complexes with pnicogen supporting ligands were synthesized. Complex **1** is bench stable and easily prepared in gram scale from commercially available materials. **1** was used to synthesize other Mn(III) complexes, demonstrating its ability to act as a good synthon. Mn(III) chloride is also known to perform dichlorination of alkenes. Therefore, dichlorination of alkenes using **1** was investigated and observed to exhibit high selectivity and good functional group tolerance. C-H chlorination was also observed in few cases. The mechanism is radical-based, similar to previously reported Mn(III)-Cl halogenations. The result of these investigations will be presented in this talk.

ABSTRACTS FOR POSTER PRESENTATIONS

(1) Applying CDVR to Nitrosyl Ligands: Reconsidering the M-NO Charge Convention

Alexander A. D'Arpino, Thomas R. Cundari, Samantha N. MacMillan, Peter T. Wolczanski
Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY

Abstract. Metal nitrosyl complexes are well known for their electronic ambiguity. The non-innocent nature of the NO ligand allows for three possible redox states—NO⁺, NO[•], and NO⁻. This uncertainty in assignment, along with nitrosyls having an accessible spectroscopic handle, $\nu(\text{NO})$, allowed us to extend our previously developed system of charge distribution via reporters (CDVR) to M-NO species. First row transition metal nitrosyl complexes recorded in the Cambridge Structural Database were examined to look for correlations between the calculated cNO and several metrics, namely $d(\text{N-O})$ and $\angle\text{M-N-O}$. This comparative study allows for the connection of physical metrics and spectroscopic signatures to afford a phenomenological equation of charge for LnM-NO. We have applied this method to several novel, first-row mononitrosyl complexes that displayed puzzling and contradictory experimental metrics (e.g., XRD and IR analyses) relative to the IUPAC bent/linear convention.

(2) Tuning Carbon Dioxide Capture at Nucleophilic Hydroxide Sites in a Co(III) Metal Organic Framework

Alexandra Lim, Tyler Azbell, Donovan Cho, Phillip Milner
Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY

Abstract. Carbon capture and sequestration (CCS) and direct air capture (DAC) are key initiatives to minimize anthropogenic CO₂ emissions and combat global climate change. Current technologies are largely limited to aqueous amine scrubbers which are prone to oxidative and thermal degradation. Herein, we demonstrate rapid CO₂ capture with metal-azolate framework Co₂(OH)₂Cl₂(btdd) through HCO₃⁻ formation at nucleophilic OH⁻ sites within the framework pores. Oxidation of the parent Co(II) framework was performed with a range of oxidants and through a series of anion exchange pathways, resulting in a family of hydroxylated Co(III) frameworks as confirmed by Powder X-ray Diffractometry (PXRD) and SQUID magnetometry. CO₂ capture performance was evaluated via thermogravimetric analysis (TGA) and CO₂ sorption isotherm.

(3) Catalytic dehydration of alcohols to olefins using earth-abundant transition metal complexes of fused oxazolidine ligands

Aurodeep Panda, William D. Jones
Department of Chemistry, University of Rochester, Rochester NY

Abstract. Dehydration of biomass-derived alcohols presents a valuable route to access various important olefins. This pathway which involves the elimination of water has various nucleophilic substitution reactions as the competing side reactions. Moreover, the use of different acid catalysts to facilitate the reaction is corrosive to the present industrial machinery. Hence, in the Jones Group, we are investigating the catalytic dehydration of alcohols using earth-abundant environmentally benign transition metals in acid-free environments to exploit the vast library of important olefins. In this regard, a series of chiral and achiral fused oxazolidine (FOX) bicycles have been synthesized with yields higher than reported in the literature. It was observed that a weak acidic medium (acetic acid) gave

exclusively stable chiral isomers which upon introduction to relatively stronger Lewis acids(AlCl_3) resulted in isomerization to the achiral complexes. Moreover, metalation of the complexes resulted in the retention of the FOX skeleton in the crystalline metal complexes of the formula $[\text{M}(\text{FOX})(\text{OTf})_2]$ where M: Mn, Fe, Co, Ni, Cu. It was then observed that the $[\text{Cu}(\text{FOX})(\text{MeCN})](\text{OTf})_2$ complex catalyzed the dehydration of 1-phenylethanol to styrene 98 % yield (NMR yield) with trace amounts of phenolic ethers and styrene dimer as side products. The substrate scope was extended to different alcohols where it was found that the dehydration worked best with benzylic, allylic and 3^o- alcohols. Based on these results and a similar catalytic system, we propose a 'carbocation-based' catalytic pathway for the mechanism whose stability determines the product distribution.

(4) **Exploring the Emergent Redox Chemistry of Pd(II) Nodes with Pendant Ferrocenes: From Precursors, through Building Blocks, to Self-Assemblies**

Austin B. Gilbert, Matthew R. Crawley, Trevor J. Higgins, Yuguang C. Li, David F. Watson, Timothy R. Cook

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Energy-relevant small molecule activations and related processes are often multi-electron in nature. Ferrocene is iconic for its well-behaved one-electron chemistry, and it is often used to impart redox activity to self-assembled architectures. When multiple ferrocenes are present as pendant groups in a single structure, they often behave as isolated sites with no separation of their redox events. Herein, we study a suite of molecules culminating in a self-assembled palladium(II) truncated tetrahedron (TT) with six pendant ferrocene moieties using the iron(III/II) couple to inform about the electronic structure and, in some cases, subsequent reactivity. Notably, although known ferrocene-containing metallacycles and cages show simple reversible redox chemistry, this TT undergoes a complex multi-step electrochemical mechanism upon oxidation. The electrochemical behavior was observed by voltammetric and spectroelectrochemical techniques and suggests that the initial Fc-centered oxidation is coupled to a subsequent change in species solubility and deposition of a film onto the working electrode, which is followed by a second separable electrochemical oxidation event. The complicated electrochemical behavior of this self-assembly reveals emergent properties resulting from organizing multiple ferrocene subunits into a discrete structure. We anticipate that such structures may provide the basis for multiple charge separation events to drive important processes related to energy capture, storage, and use, especially as the electronic communication between sites is further tuned.

(5) **Photocatalytic Hydrogen Generation using Buckminsterfullerene Capped QDs**

Benjamin Parasch, Nuwanthi Suwandarathne, David F. Watson

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Modern fuel consumption often yields high levels of carbon byproducts, especially when burning the most common fuels in the forms of alkyl chains. To reduce these carbon emissions, there have been many approaches to alternative energy sources, including utilizing hydrogen gas as an efficient, carbon neutral fuel. Hydrogen gas synthesis is a limiting factor for the commercial use of H_2 fuel. It will often require more energy to create than is

environmentally and energetically favorable. The photocatalytic production of H₂ gas is a notable topic of research to create a carbon neutral fuel that can be synthesized by sunlight. One of the most efficient photocatalytic materials in research today are quantum dot (QD) heterostructures. Their light harvesting semiconductor core allows for easy electron excitation and transfer to a catalytic ligand. This poster will highlight research utilizing buckminsterfullerene (C₆₀) capped cadmium selenium (CdSe) quantum dots for photocatalytic hydrogen generation. It will focus on the spectroscopic characterization of the QDs, and the electron transfer capabilities of the C₆₀ capping ligand. It will also present NMR quantification methods for the adsorbed C₆₀ ligands on the CdSe core.

(6) **Catalytic Dehydration of Alcohols by Zn(FOX) Complexes**

Caz Wood, Aurodeep Panda, William D. Jones

Department of Chemistry, University at Rochester, Rochester NY

Abstract. We are interested in the catalytic behavior of Zn(FOX)Triflo complexes and their ability to dehydrate a series of alcohols. In this research, we synthesized three FOX ligand substituents and analyzed how they coordinated to the zinc(II) ion. We ran several reactions with our zinc metal complexes and explored the ligand effects on catalysis.

(7) **Surface Interactions between CdSe QDs and Polyoxovanadates that Influence Charge Transfer**

Chari Peter, Chayan Caramenate, Tood D. Krauss, Ellen M. Matson

Department of Chemistry, University at Rochester, Rochester NY

Abstract. Photocatalytic hydrogen (H₂) production is a process that converts solar energy into chemical energy by means of a suitable photocatalyst. Colloidal QDs have been widely utilized to harvest solar energy and to convert it into electricity or chemical fuel. This requires efficient separation of photoinduced electron-hole pairs (excitons) across the inorganic-organic interface. In this research we are focusing on hydrogen production where we are utilizing our artificial energy source CdSe quantum dots (QDs) with the help of a redox mediator polyoxovanadates (POV) to address the different barriers for efficient hydrogen production. These POV's act as hole scavengers in the QD-POV system where they are viewed as materials which remove photogenerated holes in the CdSe QDs.

(8) **Coordinatively Unsaturated Metallates Guarded by a Rigid and Narrow Void**

Christopher D. Hastings, Lucy S.X. Huffman, Chandan Tiwari, Jolaine Galindo Betancourth, William W. Brennessel, Brandon R. Barnett

Department of Chemistry, University at Rochester, Rochester NY

Abstract. Enzymatic systems and synthetic catalysts use defined channels to dictate reaction selectivities based on size and shape. However, this design element is challenging to replicate in homogeneous systems due to the flexibility of most small molecules. We present the synthesis of a tripodal ligand scaffold that orients a narrow and rigid cavity atop accessible metal coordination space. The permanent void is formed through a macrocyclization reaction which, when deprotonated and stirred with the appropriate metal(II) acetate, resulted in anionic trigonal monopyramidal complexes of divalent cobalt, nickel, iron, and zinc. We also report an analogous series of trigonal monopyramidal complexes with a non-macrocyclized

variant of the tripodal ligand. Physical characterization of the coordination complexes was carried out using various spectroscopic techniques, cyclic voltammetry, and X-ray diffraction. Our study shows that the macrocyclized ligand retains a rigid cavity upon metallation, precluding acetonitrile entry into the void and disrupting anticipated coordination at the intracavity site.

(9) Visible-light-mediated, Nickel-Catalyzed, Decarbonylative Amination of Amides

Daniel A. Akuamoah, C. Rose Kennedy

Department of Chemistry, University at Rochester, Rochester NY

Abstract. Decarbonylative amination of amides offers a highly efficient method for synthesizing C-N-containing compounds. However, existing approaches suffer from harsh reaction conditions (temperatures exceeding 150°C) and are limited to indoyl amides and pyridine amides. To address these limitations, we conducted computational studies utilizing density functional theory (DFT) to gain insights into the reaction energetics, identify the challenging steps, and guide our method development. Here in, we report a visible-light-mediated approach for nickel-catalyzed decarbonylative amination of amides.

(10) The Self-assembly Chemistry and Electrocatalysis of Bis-iron(III)- μ -oxo-porphyrins

Daoyang Zhang, Matthew R. Crawley, Timothy R. Cook

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Coordination-driven self-assembly allows for the facile and high-yielding synthesis of redox-active polynuclear metalloporphyrin-based catalysts for the Oxygen Reduction Reaction (ORR). Over the past few years, we have demonstrated that catalysts can be tuned based on geometry, rigidity, electronegativity, metal-metal distance, and the type of metal ion. The dinuclear cobalt porphyrin catalysts that have been developed over the course of these studies are among the most selective and active molecular catalysts for ORR. The iron active site of the cytochrome c oxidase inspires us to apply our structural platform to iron porphyrins for further ORR catalysis studies. By using coordination-driven self-assembly, a series of dinuclear iron porphyrin catalysts were rapidly synthesized and characterized. The geometries of these dinuclear iron porphyrins were established by ¹H NMR and single crystal X-ray diffraction techniques. Catalytic reactivity was explored electrochemically using cyclic voltammetry and rotating electrode methods. The H₂O versus H₂O₂ selectivity of these iron catalysts for ORR is sensitive to the molecular clip tethering the two porphyrin sites together and differs significantly from untethered μ -oxo structures.

(11) Redox-active Iron Macrocyclic Complexes as paraSHIFT Agents

Deepak Krishnan Balaji, Janet R. Morrow

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Magnetic resonance spectroscopy (MRS) is a non-invasive diagnostic technique that uses the principles of nuclear magnetic resonance (NMR) for investigating the biochemical processes that occur in living tissues by detecting and measuring the levels of different molecules and compounds within a biological sample and can provide valuable information on metabolic pathways, energy production, and neurotransmitter activity. ParaSHIFT agents are paramagnetic metal complexes which can shift the proton resonances far from the tissue

proton resonances being responsive to biological environment. When paraSHIFT agents are redox active, they can function as sensors for detecting physiological conditions such as inflammation where reactive oxygen species and peroxidases are prevalent. In the presence of such oxidants, redox active complexes are converted to a different oxidation and spin state which produces a change in the chemical shift of protons. Macrocyclic ligands based on triazacyclononane alkylated with heterocyclic pendants with large number of magnetically equivalent protons can be used as paraSHIFT agents. To ensure that these complexes are only oxidized by oxidants produced in inflammatory processes and not O₂, the redox potential of the complex can be tuned by designing appropriate pendants for the ligands. This poster presentation will focus on the design, synthesis, and characterization of ligands and potential complexes for MRS applications.

(12) **Machine Learning-driven Optimization of Ag⁺ Doping in Colloidal CdSe Nanoplatelets: Enabling Fine-tuned Optical Properties**

Farwa Awan, Jorge Medina, Andrew White, Todd D. Krauss
Department of Chemistry, University at Rochester, Rochester NY

Abstract. Colloidal CdSe nanoplatelets (NPLs) are nanoscale particles that possess a two-dimensional (2D) structure, with their exciton confined in one dimension along the thickness direction, perpendicular to the plane of the nanoplatelets. The thickness-dependent properties of nanoplatelets exhibit discrete emission wavelengths due to the quantum confinement effect. Modifying the composition of NPLs through post-synthetic impurity doping with isovalent or heterovalent cations enables control over their optical and electronic characteristics. However, achieving stable dopant levels and precise control of doping efficiency remains an area with limited understanding. Heterovalent Ag⁺ doping of four-monolayer CdSe nanoplatelets, which introduces a hole trap state for optically excited NPL excitons, necessitates intricate control of the doping process. Several reaction parameters, including temperature, concentration of the dopant solution, stirring time, and rate, as well as the optical density of the nanoplatelets, influence the success of the doping process. Machine learning (ML), a branch of artificial intelligence (AI), employs mathematical algorithms to analyze acquired data and infer meaningful relationships, independent of physical laws. By utilizing ML to model experimental results, we can elucidate the complex interdependencies between structure-property, composition-property, and reaction conditions-property relationships. This approach accelerates the design and optimization of nanomaterials with tailored properties. Motivated by the potential of ML, we have undertaken an investigation into utilizing machine learning techniques to regulate the behavior of the doping process. Our aim is to achieve accurate reproducibility of the desired optoelectrical properties in NPLs. By harnessing the power of ML, we anticipate making significant strides toward enhancing our understanding of the doping process and enabling efficient control over the optoelectronic properties of NPLs.

(13) **Synthesis, Reactivity, and Photophysical Properties of Pyridone-based Bimetallic Ni(I) Complexes**

Hailemariam Mitiku, Abhishek Kadam, C. Rose Kennedy
Department of Chemistry, University at Rochester, Rochester NY

Abstract. Pyridones make up an important class of ligands that can be involved in metal-ligand cooperativity (MLC). They form the reactive center in metalloenzymes such as [Fe]-hydrogenases and artificial catalyst systems. Pyridones, however, adopt various coordination modes as they can tautomerize and exist in both protonated and anionic state. This can consequently incur controlling complex speciation challenging. We have designed iminopyridones (IPyOH)—a bidentate pyridine-based ligands to resolve speciation challenges and employ cooperative reactivity. Metalation of neutral IPyOH with Ni(cod)₂ affords a bimetallic Ni(I) complex that are diamagnetic, form Ni-Ni covalent bond. They also exhibit interesting UV-vis absorption features in the near-IR region that are attributed to metal-to-ligand charge transfer (MLCT), rendering the complexes photoactive. Excited state lifetime (τ) of the complex has been elongated to 34 ps through ligand scaffold modification. Besides potential excited state reactivity, the dinuclear Ni(I) complexes exhibit reactivity towards carbene transfer and cooperative small molecules activations.

(14) Harnessing Phosphinate and Phosphonate Ligands for Enhanced Prodrug Properties and Potential MCU Probe Development

Haipei Zou, Justin J. Wilson

Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY

Abstract. Mitochondrial calcium uniporter (MCU) is a Ca²⁺ transporter located in the inner membrane of mitochondria that plays a crucial role in maintaining Ca²⁺ homeostasis. The known MCU inhibitor Ru265, which aquates at axial positions to form the active species Ru265⁺ to interact with MCU, has limitations in kinetic stability and cell permeability. In this work, two new Ru265 analogues are developed by attaching phosphinate or phosphonate ligands at the axial position, to overcome these issues. The first analogue incorporates a diphenylphosphinate ligand, enhancing cell permeability through increased lipophilicity. It also improves kinetic stability with an aquation half-life in the range of hours. The second analogue utilizes a methylphosphonate ligand. It exhibits pH-dependent thermodynamic stability, that the complex undergoes higher level of aquation at lower pH while remains mostly intact at physiological pH. Furthermore, during aquation asymmetric intermediates with different axial ligands (one aqua and the other phosphonate) are captured. This observation suggests the potential for developing MCU probes using aqua, phosphonate-capped Ru265 analogues, by incorporating a fluorophore or click-chemistry handle on the phosphonate ligand. In conclusion, this work harnesses phosphinate and phosphonate ligands to develop Ru265 analogues with better prodrug properties and potential for broader applications.

(15) Ruthenium Catalyzed, Benzoquinone, Electrochemically Assisted Dehydrogenation of Amines

Ignacio Camarero Temino, Kylie Ritz, William D. Jones

Department of Chemistry, University at Rochester, Rochester NY

Abstract. Dehydrogenation is an industrially relevant reaction for the formation of pharmaceutically relevant building blocks. This poster describes an electrochemically-assisted dehydrogenation of secondary amines using a combination of a ruthenium catalyst and benzoquinones.

(16) Mechanistic Insights into C(acyl)-N Functionalization Enabled by Single Component [Ni] Precatalysts

Kaycie R. Malyk, Vivek G. Pillai, William W. Brennessel, Elliot S. Silk, Roberto Leon Baxin, Daniel T. Nakamura, C. Rose Kennedy

Department of Chemistry, University at Rochester, Rochester NY

Abstract. In the past decade, carboxylic acid derivatives have been utilized as more sustainable electrophilic coupling partners in transition-metal catalyzed processes due to their abundancies and ease of preparation/handling. Carboxamides are of particular interest due to their prevalence in natural products, peptides, and biologically active molecules, though they exhibit high thermodynamic stability due to $nN \rightarrow \pi^*C=O$ conjugation. Ground-state distortion of this C(acyl)-N bond via inductive and/or steric effects allows for induced electrophilicity of carboxamides, which has been demonstrated in various Ni-catalyzed couplings with carbon and heteroatom nucleophiles. However, state-of-the-art methodologies generally are limited to specific substitution patterns as well as high catalyst loadings, mainly due to a lack of thorough experimental mechanistic studies. Herein, we report a detailed mechanistic case study of Ni-catalyzed C(acyl)-N functionalizations, in which competing electrophile-first and nucleophile-first manifolds are evaluated through stoichiometric and catalytic organometallic studies, crossover experiments, in situ spectroscopic measurements.

(17) Advances in Chelator Design: Enabling Encapsulation of Theranostic Pairs

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Abstract. Theranostics, an evolving field in nuclear medicine, combines therapeutic and diagnostic capabilities utilizing radionuclides for advanced cancer treatment. By harnessing the potential of theranostic pairs, clinicians can proficiently diagnose diseases, evaluate their progression, and administer targeted therapy. However, the development of bifunctional chelators accommodating both therapeutic and diagnostic radiometals poses a substantial challenge. Here we report the remarkable discovery of two macrocyclic ligands, py-macrodipa and dipy-macrodipa, which forms biologically stable complexes with Ac-225 and In-111 under mild conditions. These complexes exhibit exceptional promise for precise cancer treatment via Targeted Alpha Therapy and SPECT imaging. Notably, we achieved quantitative radiolabeling of both ligands with Ac-225 and In-111 within an impressive time frame of 5 minutes at ambient temperature, surpassing radiolabeling efficiency of over 95%. Moreover, human serum stability studies demonstrated that 98% of the complexes remained intact for up to 10 days, highlighting their robust stability under physiological conditions. Additionally, we identified unconventional radionuclides U-230 and V-48 as a novel theranostic pair, effectively broadening the horizons of nuclear medicine. By leveraging the similar coordination chemistry exhibited by uranyl and vanadyl ions, we demonstrated the potential utility of amidoxime-functionalized ligands for transforming U-230 and V-48 into theranostic radiopharmaceutical agents.

(18) Relating the Role of Metalloenzyme Hydroxylamine Oxidoreductase to the Energetic Outcomes of Ammonia Oxidizing Bacteria

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Abstract. Hydroxylamine oxidoreductase (HAO) is a key enzyme in mediating energy transduction from reactive nitrogen species during biological ammonia oxidation by ammonia oxidizing bacteria (AOB). HAO is an octaheme protein that features the unique, tyrosine-crosslinked c-heme variant "heme P460" that carries out 3-e⁻ oxidation of hydroxylamine (NH₂OH) to nitric oxide (NO), presumably via a ferric nitrosyl ($\{FeNO\}^6$) intermediate. Studies from our laboratory to date have advanced understanding of HAO reactivity via studies of a small, mono-heme cytochrome P460 that bears a related heme P460 cofactor. Cytochrome P460 generates an $\{FeNO\}^6$ that can react with nucleophiles. For example, a second equivalent of NH₂OH can attack to form N₂O. Alternatively, NO can dissociate and react with O₂ to form nitrite NO₂⁻. This route of NO₂⁻ production diverts one of the four net electrons liberated in nitrifier primary metabolism from the respiratory electron transport chain, and it is not consistent with the observed stoichiometric production of NO₂⁻ by AOB. Moreover, this reaction is inconsistent with evidence showing that the origin of the second oxygen in AOB-derived NO₂⁻ is from H₂O. These inconsistencies raise key questions concerning the subsequent chemistries NO can undergo at both the HAO and Cytochrome P460 active sites in AOB and how these organisms harness the electron liberated from NO. To this end, we are working to recombinantly express HAO to carry out mutagenesis studies towards understanding its differences from cytochrome P460 and to evaluate the possibility of reaction with alternate substrates.

(19) Synthetic Strategies for the Isolation of Low-coordinate Metal Centers within Rigid Cavities

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Abstract. Trivalent iron complexes tend to adopt high coordination numbers unless prohibited by steric constraints. In ligand environments that promote trigonal coordination environments, the overwhelming number of formally Fe(III) complexes exist in a trigonal bipyramidal geometry. Herein a novel, high-spin, trivalent iron is reported in a trigonal monopyramidal coordination environment. The paramagnetic properties are verified through various spectroscopic techniques (NMR, EPR, UV-Vis). Initial intracavity binding of linear gasses is reported. Creation of this species can serve as a model for other rigid ligands to bind high valent iron in unique geometries. An alternative ligand scaffold designed around trispyrazolylborate is also presented.

(20) Design Strategies for Enhanced Stability and Solubility of polyoxovanadate-alkoxides as Charge Carriers in Non-aqueous Redox Flow Batteries

Mamta Dagar, Daniel N. Kensler, Mevan D. Dissanyake, Molly Corr, Joshua McPherson, Ellen M. Matson

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Abstract. Redox flow batteries (RFBs) are garnering renewed interest for the development of new electrochemical energy storage technologies. The unique modularity and scalability of RFBs make them uniquely capable of meeting the variable needs of the grid. However, low energy densities of current RFB charge carriers preclude their widespread application. The

drive to improve energy density of RFBs has resulted in an increased focus on the design of charge carriers that are physically and electrochemically compatible with organic solvents. Herein, we report synthetic design strategies to enhance solubility and stability of multimetallic Ti-doped polyoxovanadate alkoxide clusters in organic media. Our results indicate an enhancement in solubility of these clusters upon organic functionalization of the metal core in acetonitrile. Substitution of d0 metal centers within the vanadium Lindqvist core increases the cell voltage of the system, while retaining the characteristic electrochemical reversibility and stability of the POV-alkoxide in non-aqueous conditions. We assess the capability of the proposed organometallic clusters to serve as charge carriers for application in non-aqueous RFBs through cyclic voltammetry, bulk electrolysis, and H-cell charge-discharge experiments. Our results indicate that both the solvent and supporting electrolyte can influence the performance of these active materials.

(21) Leveraging Sterics and Hemi-labile Interactions to Enforce Low-coordination of Late Transition Metals

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Abstract. Low-coordinate environments about transition metals imbues them with interesting electronic structures and reactivity. We are leveraging 1,8-diaryl carbazolido ligand platforms to enforce low-coordination via sterics and to enable access to uncommon molecular oxidation states via hemilabile interactions. Reduction of the four-coordinate Fe(II) complex, PAntLFeOTf(THF)₂, yields a masked two-coordinate Fe(I) complex stabilized by the hemilabile anthracenyl groups of the ligand. PAntLFe(THF) is a competent precatalyst for the direct intramolecular C—H amination of 2-azido-2-methylhexane. The major paramagnetic species formed during catalysis, PAntLFe(NR)₂ (R = 2-methylhexane), was isolated and characterized by a suite of structural and spectroscopic methods. This bis-imido Fe complex represents the only structurally characterized high-spin, formally Fe(V) species to date. Physical characterization and reactivity of the complex will be presented.

(22) Nature-inspired [Ni] Pyridone Complexes for Cooperative Catalysis and Mechanistic Insight

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Abstract. Pyridones are powerful ligands that play an important role in biological processes, such as dihydrogen (H₂) activation by [Fe] hydrogenase via a metal-ligand cooperative (MLC) mechanism. Analogous cooperativity has also been demonstrated in biological systems for reactions such as alcohol (de)hydrogenation. Nevertheless, limited access to single-component complexes hampers mechanistic insight and application in more complex systems. This poster will describe the synthesis, novel structural properties and hydroboration reactivity of highly electron-rich Ni(0) complexes supported by unsymmetric NHC-pyridone ligands.

(23) Ligand Exchange to Yield Phase Pure Zirconium Metal-organic Polyhedra

Meghan G. Sullivan, Heshali K. Welgama, Timothy R. Cook

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Abstract. Zirconium-based metal-organic polyhedra (ZrMOPs) represent an emergent class of materials that lend themselves to industrial applications because of their stability, high-yielding syntheses, inexpensive building blocks, and solubility relative to their metal-organic framework analogs (e.g. UiO-66). However, their utility is complicated by the presence of two ZrMOP architectures—the V_4L_6 “tetrahedron” and V_2L_3 “lantern.” Traditional synthetic methods yield a mixture of the two architectures, thus hindering elucidation of properties unique to either architecture. In this work, we synthesized a ZrCluster with benzoate capping ligands as a precursor to ZrMOPs. Following ligand exchange with dicarboxylate ligands, previously inaccessible phase pure ZrMOPs were isolated. The phase pure materials were found to have drastically different BET surface areas, with lanterns exhibiting significantly smaller surface areas (5 - 19 m²/g) than tetrahedral architectures (392 - 606 m²/g).

(24) Dinuclear Iminopyridone Nickel Complexes and their Aerobic Reactivity

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Abstract. Multiple metal active sites are commonly found in metalloenzymes; this motif has been imitated in bimetallic complexes that demonstrate reactivity beyond that observed in mononuclear systems. These multimetallic complexes are of interest because they may demonstrate cooperativity in catalysis. Mononuclear iminopyridines supported complexes and their corresponding dinuclear naphthyridine diamine complexes have been used to study the role of multimetallic cooperativity in transition metal catalysis. Lesser known are the effects of a pyridone oxygen on reactivity in such complexes. Using an electronically tunable iminopyridone ligand family, bimetallic Ni(I) complexes have been synthesized and reactivity is investigated. Such complexes may be oxidized upon exposure to O₂ resulting in a species with unexplored reactivity.

(25) Dinuclear Mn(I) Hydrogenative Catalysts with Bridging Phosphido and Hydrido Ligands

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Abstract. Ruthenium(II) complexes are well-established hydrogenation catalysts with a variety of applications in pharmaceutical synthesis. Manganese(I) has a similar ionic radius and electronic structure to that of Ru(II), thus Mn(I) may be a sustainable alternative to Ru(II) hydrofunctionalization catalysts. Dinuclear Mn(I) carbonyl complexes with bridging phosphido and hydrido ligands have been previously reported as effective catalysts in stereoselective (de)hydrogenation reactions. For example, the complexes $[Mn_2(CO)_8(\mu-H)(\mu-PR_2)]$ (R = Ph, iPr) were shown to undergo E-selective alkyne semi-hydrogenation (E-SASH) upon reaction with electron rich alkynes. The E-selectivity was shown to be an intrinsic property of the dinuclear Mn(I) catalysts, as the trans-alkene is formed directly with virtually no cis-to-trans isomerization observed. To account for this selectivity, it is hypothesized that a Mn carbenoid intermediate is involved. This hypothesis was formulated on the basis of trans-selective Ir and Ru systems that pass through carbenoid intermediates. Although such an intermediate has not yet been observed, Mn Fisher carbenes are known to be accessible on dimanganese(I)

phosphido complexes. This poster highlights the newest results from the Lacy group surrounding the hunt for these elusive carbene intermediates for the E-SASH reaction.

(26) Correlating Surface Functionalization with Changes in Optical and Electronic Properties of Cobalt Gallium Oxide Colloidal Nanocrystals

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Abstract. Ternary spinel oxides of formula AB_2O_4 are semiconductor materials that possess magnetic and optoelectronic properties that, coupled with their extraordinary chemical and thermal stability, offer functional materials applicable to the fields of photocatalysis, solar energy conversions, gas sensing, and photoelectrochemistry. The performance of these materials in these applications is further enhanced when they are made as nanocrystals due to the high surface area-to-volume ratios. Additionally, nanocrystalline morphologies enable the possible use of surface functionalization as an effective strategy for tailoring the optical and electronic properties of ternary spinel nanocrystals to improve their function in a specific application. Here we use a series of gallium oxide spinel nanocrystals, namely γ - Ga_2O_3 , $CoGa_2O_4$, $NiGa_2O_4$, and $ZnGa_2O_4$, as model systems to develop a fundamental understanding of (i) the effects of surface functionalization with thiol-containing ligands (RSH) on their optoelectronic properties, (ii) the role played by molecular oxygen in mediating these effects, and (iii) the dependence of these surface chemistries on the identity of the A cation (Co^{2+} , Ni^{2+} , Zn^{2+}).

(27) Structural and Biochemical Studies of Novel Metalloenzymes Implicated in Nitrogen Cycling

Rob W. Volland, Kyle M. Lancaster

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Abstract. Ammonia-oxidizing bacteria (AOB) and ammonia-oxidizing archaea (AOA) survive by oxidizing ammonia to nitrite to produce energy, however, there are many enzymological “black boxes” in these systems. While much is known about the metabolism of canonical AOB and the operative metalloenzymes involved, very little is known about the pathway and enzymes involved in the respective metabolisms of dirammox bacteria, which can convert ammonia to dinitrogen, or AOA. It is well known that hydroxylamine oxidoreductase (HAO) in AOB is responsible for the oxidation of hydroxylamine to nitric oxide (NO) using a c-type heme in a cytochrome P460 cofactor. The same is not true for AOA, as AOA lack c-type heme maturation machinery. Here, we show our structural and biochemical approaches to elucidate and study the metalloenzymes involved in both dirammox and AOA metabolic pathways. We have expressed, purified, and studied a diiron enzyme thought to be central to dirammox metabolism and successfully expressed and purified many AOA enzymes implicated in hydroxylamine and NO processing via genomic analysis. We have identified a multi-copper oxidase from the marine archaeon *Nitrosopumilus maritimus* with interesting reactivity toward phenolic amines and hydroxylamine and a seemingly novel structure containing a unique C-terminal cupredoxin domain. Understanding the operative metalloenzymes in these systems on a structural and biochemical basis can help us better understand how these

organisms perform such difficult chemistry and can help us better understand the evolution of these impressive organisms.

(28) High-concentration Self-assembly of Metal-organic Materials

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Abstract. Metal-organic frameworks (MOFs) are crystalline, porous solids constructed from organic linkers and inorganic nodes that are promising for applications in chemical separations, gas storage, and catalysis, among many others. However, a major roadblock to the widespread implementation of MOFs, including highly tunable and hydrolytically stable Zr- and Hf-based frameworks, is their benchtop-scalable synthesis, as MOFs are typically prepared under highly dilute (≤ 0.01 M) solvothermal conditions. This necessitates the use of liters of organic solvent to prepare only a few grams of MOF. Herein, we demonstrate that Zr- and Hf-based frameworks (eight examples) can self-assemble at much higher reaction concentrations than are typically utilized, up to 1.00 M in many cases. Combining stoichiometric amounts of Zr or Hf precursors with organic linkers at high concentrations yields highly crystalline and porous MOFs, as confirmed by powder X-ray diffraction (PXRD) and surface area measurements. Furthermore, the use of pivalate-capped cluster precursors avoids the formation of ordered defects and impurities that arise from standard metal chloride salts. These clusters also introduce pivalate defects that increase the exterior hydrophobicity of several MOFs, as confirmed by water contact angle measurements. Overall, our findings challenge the standard assumption that MOFs must be prepared under highly dilute solvothermal conditions for optimal results, paving the way for their scalable and user-friendly synthesis in the laboratory.

(29) Leveraging Vanadium Oxide Cluster Structure-function Relationships to Tune Reactivity of Surface Bound Hydrogen Atoms

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Abstract. Understanding how defects in metal oxides alter reactivity aids in future design of heterogeneous catalysts. Herein, a series of oxygen-atom deficient polyoxovanadate-alkoxide clusters with surface modifications (cationic/anionic dopants, ligand substitution) are investigated. Quantifying thermodynamic and kinetic factors that influence oxygen vacancy formation reveals how structural modifications change H-atom transfer at the cluster surface. Ultimately, the use of modified polyoxovanadate-alkoxides provides atomistic resolution to transformations that occur at surface interactions that occur on metal oxides.

(30) Bridging the Gap: Optimizing Electron Transfer in a Living Bio-Nano System for Sustainable Hydrogen Production

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Abstract. Developing light-driven chemistry to produce hydrogen fuel has the potential to revolutionize the production of clean and sustainable energy to fulfill society's growing needs.

A significant roadblock in the development of systems for artificial photosynthesis has been the need for high concentrations of sacrificial electron donors in the case when full water splitting is not accomplished. Here, we demonstrate an innovative strategy for light-driven hydrogen production that, in place of chemical electron donors, leverages extracellular electron transfer from electrogenic bacteria (*Shewanella oneidensis* MR-1) to cadmium selenide (CdSe) quantum dots that perform photocatalytic hydrogen evolution. Initial studies showed that this living bio-nano system sustains photocatalytic hydrogen production for over one week, resulting in $18.2 \pm 5.2 \mu\text{mol H}_2$ with a turnover number of $4,160 \pm 1,160$ with respect to CdSe without optimization of the system. To further evaluate the effects of quantum dots on the system, we looked at the effects of quantum dot size and observed an effect on hydrogen production, with smaller quantum dots we observed an increase in hydrogen production due to their unique electronic and optical properties, which influence their photocatalytic efficiency in hydrogen evolution reactions. To evaluate the effects of *Shewanella* membrane-bound cytochromes on activity, we measured hydrogen production in systems incorporating *Shewanella* strains in which genes involved in extracellular electron transfer were knocked out ($\Delta\text{omcA } \Delta\text{mtrC}$, ΔmtrA and ΔcymA). Our results showed ΔcymA produced $1.67 \pm 0.9 \mu\text{mol}$ of H_2 , ΔmtrA produced $4.7566 \pm 0.63 \mu\text{mol}$ and $\Delta\text{omcA } \Delta\text{mtrC}$ resulting in $7.167 \pm 0.14 \mu\text{mol}$ after 168hr irradiation with CdSe-MPA QDs. These results demonstrate how tuning properties of nanomaterials and bioengineering *Shewanella oneidensis* MR-1 is a promising approach towards optimizing hydrogen production in this bio-nano system.

(31) Development of Functionalized Chelators for Diagnostic and Therapeutic Approaches

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Abstract. Radioactive metals, or radiometals, are in growing demand for both the diagnosis (PET or SPECT) and therapy of oncological diseases by using particle emitting radiation. In recent years, combining these modalities into a single construct to afford so called theragnostic agents has become a powerful strategy for visualizing and monitoring the effectiveness during radiotherapeutic cancer treatment. To develop such theragnostic agents, radionuclide pairs comprising both a diagnostic and a therapeutic isotope are needed. However, for the development of effective theragnostic radiometal complexes several molecular properties need to be addressed before continuing preclinical research. For instance, the utilization of radiometals in nuclear medicinal approaches requires the formation of thermodynamically and kinetically stable metal complexes to prevent toxic effects of free metal ions. Up to now, radio-theragnostic metal complexes for nuclear medicinal field are scarcely reported. In particular, there is a need for alpha-emitting metal complexes with a diagnostic feature to monitor effectiveness of radiotherapeutic cancer treatment. Recently, the Wilson group established various efficient chelators for the complexation of lanthanides and actinides for diagnostic and therapeutic approaches in nuclear medicine. In our work, we present the development of novel chelators for the complexation of alpha-emitting radionuclides and the subsequent radiolabeling by using

clinically relevant PET radioisotopes. Our efforts have been focused on the synthesis of the chelators via multistep organic reactions and their chemical characterization. In our current work, we focus on the metal complexation with non-radioactive metals and efforts to introduce PET imaging relevant non-radioactive representatives is ongoing.

(32) A Structure-activity Study of Acid Modulation for the Synthesis of Zr-based Metal Organic Frameworks

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Abstract. Acid modulation is among the most widely employed methods for preparing metal-organic frameworks (MOFs) that are both stable and highly crystalline, yet there exist few guiding principles for selecting the optimal modulator for a given system. Using the Zr-based MOFs UiO-66 and UiO-68-Me₂ as representative materials, we performed an in-depth structure-activity study of acid modulators and identified key principles of modulation for the synthesis of highly crystalline Zr-MOFs. By applying whole pattern fitting of powder X-ray diffraction patterns as a technique for evaluating modulator efficacy, complemented by SEM, NMR, and TGA, we demonstrate that the key to effective modulation is competition between the linker and modulator for coordination to the Zr secondary building units (SBUs). Specifically, we illustrate that a close match in pK_a and structure between the linker and modulator favors larger and more well-defined crystallites, particularly with sterically unhindered aromatic acid modulators. By applying these criteria, we found two previously unstudied acids to be the most productive modulators evaluated in this study. These guiding principles have critical implications for the scalable and controllable synthesis of highly crystalline and stable MOFs relevant to chemical separations, gas storage, and catalysis.

(33) Zinc Porphyrin-coated Cadmium Sulfide Quantum Dots: Excited-state Charge Transfer Toward Efficient Visible Light-Driven Reduction of CO₂

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Abstract. Due to the high worldwide demand for energy, fossil fuel combustion has increased which releases excessive amounts of CO₂ into the atmosphere that leads to global warming. The photocatalytic reduction of CO₂ into valuable chemicals is an emerging strategy to overcome both energy and environmental issues. This presentation will focus on our development of Zn(II)-5,10,15,20-tetra(3-carboxyphenyl)porphyrin (metaZnTCPP)-coated cadmium sulfide (CdS) quantum dots (QDs) as photocatalysts to reduce CO₂ to C₁ and higher-order fuels and feedstocks in water. The photophysical properties of metaZnTCPP coated CdS QDs are studied by using steady-state and time-resolved emission spectroscopy. Emission and time-correlated single photon counting (TCSPC) measurements provide information on the electron transfer dynamics of the photocatalytic system. Measured electron transfer rates differed significantly with the position of the carboxylate anchoring group in metaZnTCPP and para-ZnTCPP. CdS-adsorbed metaZnTCPP exhibited a remarkably faster emission decay compared to paraZnTCPP, which we attribute to the acceleration of electron injection arising from the more inert and/or stable connection to the CdS QD surface through multiple carboxylic acid groups attached to the meso phenyl ring of the porphyrin. Differences in the

binding orientation of the porphyrin molecules on the CdS surface may also have contributed to differences in the electron injection rates. Our recent results pertaining to the CdS-metaZnTCPP photocatalyst and the photophysical findings have motivated us to further investigate the effect of different anchoring groups for electron transfer properties and subsequent reduction of CO₂ in photocatalytic experiments.

(34) Actinide Complexes Supported by Pyridine Dipyrrolide Ligands

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Abstract. Investigations into the chemical and electronic interactions between actinides, their ligand frameworks, and the surrounding chemical environment is vital to establishing effective processes for chemical separation of actinides and implementing methods for the long-term storage and use of radioactive waste. The Matson group is interested in understanding how we can leverage photochemistry and electrochemistry to 1) gain insight into covalency/electronic structure of actinide complexes, and 2) promote the activation of strong U-O bonds in the uranyl dication.

(35) Accelerating σ -bond Metathesis at Sn(II) Centers

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Abstract. Molecular main-group hydride catalysts are attractive as cheap, non-toxic, and Earth-abundant alternatives to transition-metal analogues. In the case of the latter, specific steric and electronic tuning of the metal center through ligand choice has enabled the iterative and rational development of superior catalysts. Comparatively, understanding of electronic- and steric- structure activity relationships for molecular main-group hydrides is lacking and improvements to these catalysts are often made empirically. Herein we report a modular Sn-Ni bimetallic system in which we systematically vary the ancillary ligand on Ni, which in turn tunes the Sn center. This tuning is probed using Sn L₁ XAS as a probe of electron density at the Sn center. We demonstrate that increased electron density at Sn centers accelerates the rate of σ -bond metathesis, and we employ this understanding to develop a highly active Sn based catalyst for the hydroboration of CO₂ using pinacolborane. Additionally, we are able to demonstrate that engineering London dispersion interactions within the secondary coordination sphere of Sn allows for further rate acceleration. These results show that the electronics of main group catalysts can be controlled without the competing effects of geometry perturbations, and that this manifests in substantial reactivity differences.

Western New York Inorganic Symposium 2023

August 4th Schedule of Events

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