August 16th Schedule of Events

All events will be held in Goergen Hall at the University of Rochester River Campus

8:30 – 9:00 AM: Coffee/Snacks and Poster Set-Up (Munnerlyn Atrium)

9:00 – 10:30 AM: Student Talks Session #1 (Moderator: Brandon Barnett; Goergen 101)

- 9:00 AM-9:10 AM **Opening Remarks** 9:10 AM-9:30 AM Low- and High-valent Actinide Complexes Supported by Pyridine Dipyrrolide Ligands: *Synthesis, Characterization, and Luminescence* Leyla Valerio (Matson) 9:30 AM-9:50 AM The Effects of a Rigid Void Space Surrounding a Ligated Metal Chris Hastings (Barnett) 9:50 AM-10:10 AM A Strongly Reducing sp² Carbon-conjugated Covalent Organic Framework Formed by N-Heterocyclic Carbene Dimerization Tristan Pitt (Milner) 9:50 AM-10:10 AM Catalytic Dehydration of Activated Alcohols to Olefins using Fused Oxazolidine-based Transition Metal Catalysts Aurodeep Panda (Jones) 10:10 AM-10:30 AM Addressing Challenges in Nickel-catalyzed Cross Coupling using Mechanism-guided Catalyst Design Medina Afandiyeva (Kennedy) 10:30 AM - 11:45 PM: Poster Session #1 (odd # posters; Munnerlyn Atrium) 11:45 PM – 12:30 PM: Lunch (Munnerlyn Atrium) 12:30 PM - 1:45 PM: Poster Session #2 (even # posters; Munnerlyn Atrium) 1:50 PM - 3:30 PM: Student Talks Session #2 (Moderator: Luis De Jesús Báez; Goergen 101) 1:50 PM-2:10 PM Insights into the Nucleation and Growth Mechanism and Electrochemical Behavior of Star-shaped Vanadyl Hydroxide Nanoparticles Jayanti Sharma (De Jesús Báez) 2:10 PM-2:30 PM Highly Water Soluble Iron(III) Coordination Cage as MRI-Active Carrier for Gold(I) Drugs Priya Ranjan Sahoo (Morrow) 2:30 PM - 3:10 PM Sustained Photochemical Hydrogen Evolution from a Minienzyme in Water Ryan Kosko (Bren)
- 3:10 PM-3:30 PMIn Vitro Assembly of Ammonia Monooxygenase from Recombinantly Expressed SubunitsAlexander Laughlin (Lancaster)

3:30-3:50 PM: Break/Snack and Poster take-down (Munnerlyn Atrium)

3:50 – 4:00 PM: Closing Remarks & Student Prizes (Munnerlyn Atrium)

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ABSTRACTS FOR ORAL PRESENTATIONS

Low- and high-valent actinide complexes supported by pyridine dipyrrolide ligands: synthesis, characterization, and luminescence properties

Presenter: Leyla Valerio (Ellen Matson)

Department of Chemistry, University of Rochester, Rochester NY

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. To this end, our group has synthesized high-valent uranyl adducts of the pyridine dipyrrolide ligand class, and have found that reduction of the metal center "switches on" photoluminescence in the reduced molecule. Moreover, isolation of actinide(IV) complexes, (MesPDPPh)AnCl₂(THF) and An(MesPDPPh)₂ has shown the impact that the availability of 5f orbitals in bonding has on the electronic structure of the use soft are nonemissive.

The effects of a rigid void space surrounding a ligated metal

Presenter: Christopher Hastings (Brandon Barnet)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. The design and fine tuning of secondary coordination spheres has become of increased focus within synthetic inorganic chemistry. Such strategies often include intramolecular H-bonding, large steric profiles, or exogenous Lewis acids. We propose ligand rigidity as a new design principle for the stabilization and characterization of reactive functional groups. By encapsulating a coordinatively unsaturated metal center, we have shown these complexes demonstrate selective ligation, increased thermal and hydrolytic stability as well as intermolecular E-H bond activation and intramolecular OAT. Characterization of such complexes has been achieved through an array of spectroscopic techniques (NMR, EPR, IR, UV-Vis) that are supported by XRD, providing insight into their electronic structures and reactivity.

A strongly reducing sp² carbon-conjugated covalent organic framework formed by Nheterocyclic carbene dimerization

Presenter: Tristan Pitt (Phillip Milner)

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

Abstract. Covalent organic frameworks linked by carbon-carbon double bonds (C=C COFs) are an emerging class of crystalline, porous, and conjugated polymeric materials with potential applications

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in organic electronics, photocatalysis, and energy storage. Despite the rapidly growing interest in sp2 carbon-conjugated COFs, only a small number of closely related condensation reactions have been successfully employed for their synthesis to date. We report the first example of a C=C COF, CORN-COF-1 (CORN = Cornell University), prepared by N-heterocyclic carbene (NHC) dimerization. In-depth characterization reveals that CORN-COF-1 possesses a two-dimensional layered structure and hexagonal guest-accessible pores decorated with a high density of strongly reducing tetraazafulvalene linkages. Exposure of CORN-COF-1 to tetracyanoethylene (TCNE, E1/2 = 0.13 V and -0.87 V vs. SCE) oxidizes the COF and encapsulates the radical anion TCNE⁻⁻ and the dianion TCNE²⁻ as guest molecules, as confirmed by spectroscopic and magnetic analysis. Notably, the reactive TCNE⁻⁻ radical anion, which generally dimerizes in the solid state, is uniquely stabilized within the pores of CORN-COF-1. Overall, our findings broaden the toolbox of reactions available for the synthesis of redox-active C=C COFs, paving the way for the design of novel materials.

Catalytic dehydration of activated alcohols to olefins using fused oxazolidine-based transition metal catalysts

Presenter: Aurodeep Panda (William 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 (AlCl₃) 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 [M^{II}(FOX)(OTf)₂] where M: Mn, Fe, Co, Ni, Cu. It was then observed that the [Cu(FOX)(MeCN)](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 catalytic process involves the dehydration of diverse allylic, tertiary, and benzylic alcohols. Moreover, the reaction is solvent specific (the reaction worked in toluene) and internal standard specific with commonly used NMR internal standards like 9,10 dihydroanthracene, 1,3,5-trimethoxybenzene, HMDSO, indane negatively impacting the catalytic reactions. 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.

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Addressing challenges in nickel-catalyzed cross-coupling using mechanism-guided catalyst design

Presenter: Medina Afandiyeva (Rose Kennedy)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Transition metal-catalyzed cross-coupling reactions are widely used in industry and academia. Ongoing research is focused on developing more efficient catalysts and user-friendly reagents that would enable a broader scope of these reactions and robust catalysis. In contrast with traditionally used palladium catalysts, electropositive nickel complexes enable activation of the more polar acyl C(sp2)–N and C(sp2)–O bonds found in abundant and less reactive amides and esters. Current methodologies for Ni-catalyzed cross-coupling often require high pre-catalyst loading and elevated reaction temperatures. To design catalysts that address these limitations, a detailed mechanistic understanding of Ni-catalyzed transformations through the identification of catalytically relevant organometallic intermediates is required. In this talk, I will describe a suite of NHC-supported bidentate [Ni] complexes and the role of tethered co-ligands in hydroboration and cross-coupling reactions. Preliminary evidence for unusual activation of NHC-pyridine-bound [Ni] pre-catalyst in cross-coupling between methyl benzoate and aniline will be provided. Current work on developing a milder synthetic approach toward a more efficient catalyst design for this transformation will be described highlighting the importance of organometallic chemistry for reaction development.

Insights into the nucleation and growth mechanism and electrochemical behavior of starshaped vanadyl hydroxide nanoparticles

Presenter: Jayanti Sharma (Luis De Jesús Báez)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Fundamental understanding of microstructure evolution during nucleation and growth of ternary materials is of utmost importance for the development of the next generation of functional devices. Case in point, growth of semiconducting particles with six-fold symmetry, so called star-shaped, could serve as an innovative morphology for application in neuromorphic, energy storage, and heterogenous catalysis devices. Herein, we present the discovery of how the synthetic route to produce orthorhombic star-shaped vanadyl hydroxide (VOOH) by using a hydrothermal reaction of orthovanadate and thioacetamide in an alkaline solution is highly dependent on time. For example, we observe that at 24h, we produce VS2 nanosheets with VOOH at the surface. A 36 h of reaction produce VOOH rods clustered in a single nucleating point and at 72 h of reaction VOOH stars can be observed in combination of clustered materials. Our current hypothesis stands that the clustered rods are a product of a condensation reaction between the vanadate precursor whereas the stars are seeded by the hexagonal symmetry of VS2 and further oxygenation and reduction of the vanadium center. Furthermore, we also elucidate the fundamental electrochemical behavior of these nanoparticles as capacitive electrodes for sodium-ion devices.

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A highly water soluble iron(III) coordination cage as an MRI-active carrier for gold(I) drugs Presenter: Priya Ranjan Sahoo (Janet Morrow)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Coordination cages are three dimensional supramolecular architectures that are prepared from organic linkers and metal ions. These coordination cages possess fixed cavity sizes with tunable features for guest encapsulation. Most popular applications of these metallocages include catalysis and sensing. Application of such cages in biomedical research remains challenging due to low water solubility. However, metallocages with a high overall charge have excellent water soluble properties and are robust toward dissociation. Gold complexes such as auranofin and its analog, Au(PEt3)Cl, exhibit promising in vitro anticancer activity. Yet, a majority of gold(I) complexes are insoluble in water, which makes their administration and biodistribution challenging. Therefore we are investigating an alternate strategy where encapsulation of a gold(I) metallodrug within a metallocage leads to tumor delivery and the cage is an MRI active carrier. Tetrahedral paramagnetic Fe(III) cages or diamagnetic Ga(III) analogs with encapsulated gold(I) phosphine complexes were prepared. Gold complexes encapsulated in the Ga(III) cages were characterized by using 1H, 31P NMR and FT-IR spectroscopic techniques. NMR studies including DOSY (Diffusion Ordered Spectroscopy) revealed that the gold complex is encapsulated within the polyhedral cage. Encapsulated gold complex exhibited pH dependent speciation and gold(I) release. Both 1H and 31P NMR spectroscopy studies suggested that the tetrahedral Ga(III) cage prevents binding of the gold drug to serum proteins for several hours. For the iron(III) metallocage, T1 relaxation measurements showed high relaxivity at 1.4 T with and without encapsulated gold drug and increased in the presence of serum albumin.

Catalytic dehydration of activated alcohols to olefins using fused oxazolidine-based transition metal catalysts

Presenter: Ryan Kosko (Kara Bren)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. A homogenous heavy-metal free system for visible light-driven hydrogen evolution in water is reported. This system uses Eosin Y as a metal-free photosensitizer, triethanolamine as a sacrificial electron donor and a synthetic cobalt mimochrome minienzyme (CoMC6*a) as a catalyst. This system avoids the use of heavy-metal containing photosensitizers and catalysts that are often employed to achieve high activity. Under optimal conditions, the system achieves a turnover number of 10,000 with respect to catalyst and remains active for 100 hours. Activity can be furthered by replenishment of excess dye and electron donor, supporting the robustness and stability of the synthetic protein catalysts. This uniquely high activity and longevity for a system utilizing Eosin Y is attributed to dyecatalyst binding that promotes catalyst activation by electron transfer from the photoexcited dye and disfavors dye degradation.

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In vitro assembly of ammonia monooxygenase from recombinantly expressed subunits **Presenter: Alexander Laughlin** (Kyle Lancaster)

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

Abstract. Nitrification, the biological oxidation of ammonia to nitrite and nitrate, produces metabolic reducing equivalents for ammonia-oxidizing bacteria and archaea. This metabolism is initiated by the selective oxidation of ammonia to hydroxylamine, implicating activation of a 107 kcal/mol N-H bond. This aerobic, copper-dependent transformation is catalyzed by ammonia monooxygenase (AMO), an integral membrane protein complex of trimeric heterotrimers and a member of the copper membrane monooxygenase family. AMO has never been purified in an active form. Presented here is the recombinant expression and purification of the individual AMO subunits. We have collected SDS-PAGE and mass spectrometry data verifying successful recombinant expression and purification of all AMO subunits. Furthermore, size exclusion and anion-exchange chromatography data suggest we have assembled the AMO complex in vitro using lipid nanodiscs. Additionally, we have shown with small angle x-ray scattering (SAXS) that the individual proteins and the assembly in nanodiscs are folded and not aggregated via Kratky and Guinier analysis. Further evidence of AMO isolation will be corroborated via activity assays and cryoelectron microscopy analysis.

ABSTRACTS FOR POSTER PRESENTATIONS

1. How much electron donation is there in transition metal 2 complexes? A computational study

Presenter: Augustine Obeng (Jochen Autschbach)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. The 'dative' covalent interactions between metals and ligands in coordination compounds, i.e., metal-to-ligand and ligand-to-metal donation, are manifestations of electron delocalization and subject to errors in approximate calculations. This work addresses the extent of dative bonding/donation in a series of closed-shell transition metal complexes. Several Kohn-Sham density functionals, representing different 'rungs' of approximations, along with post-Hartree-Fock methods are assessed in comparison to CCSD(T). Two widely used non-hybrid and global hybrid density functionals (B3LYP, PBE0) tend to produce notably too strong donation. Global hybrids with elevated fractions of exact exchange (40 to 50%) and the range-separated exchange functional CAM-B3LYP tend to perform better for the description of donation. The performance of a double-hybrid functional is found to be quite satisfactory, correcting errors seen in MP2 calculations. A fast approximate coupled-cluster model (DLPNO-CCSD) also gives a reasonable description of the donation, with a tendency to underestimate its extent.

2. How much electron donation is there in transition metal 2 complexes? A computational study

Presenter: Marina Zapesochny (Brandon Barnett)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Manganese and iron terminal oxo compounds have ample precedent in C-H functionalization in both enzymatic and synthetic systems. Isolating, characterizing, and studying terminal oxo compounds that are highly reactive toward activating strong C–H bonds can be a challenge due to their low kinetic stabilities. We have developed a ligand that localizes a rigid void around a metal coordination site, which we have used to isolate a high-spin iron(IV) oxo that possesses excellent kinetic persistence. We have now focused our efforts on accessing the corresponding terminal manganese oxo complex. Structures collected through XRD support an increased reactivity in the manganese complex. Through a complex array of spectroscopic techniques (IR, UV-Vis, EPR), further insight will be provided on the electronic structure and reactivity of the terminal manganese oxo complex.

3. Impact of engineered biocatalyst structure on hydrogen evolution from water **Presenter: Hafsa Irfan** (Kara Bren)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Concerns about climate change have accelerated the search for carbon-free fuels for energy storage. Molecular hydrogen, when produced from water in processes driven by

renewable energy, is a promising alternative to fossil fuels, with its high-energy density and clean combustion. In this project, we are developing cobalt-substituted heme proteins as catalysts for hydrogen production from water. We are investigating two cobalt-centered cyt c variants: Horse heart cyt c (Co-Hh cyt c) and Pseudomonas aeruginosa cyt c (Co-Pa cyt c). In electrochemical studies, Co-Hh cyt c shows higher activity than Co-Pa cyt c as manifested by double the charge and turnover number in a 24-h controlled potential electrolysis experiment. In photochemical studies, we pair these protein catalysts with three different photosensitizers: [Ru(bpy)₃]²⁺, CdSe quantum dots and Eosin Y. We find that Co-Hh cyt c outperforms Co-Pa cyt c with 2-3 times higher turnover numbers with all three photosensitizers. We present hypotheses as to how differences in structure of these proteins may contribute to differences in activity. This study provides a foundation for future rational design of robust and active proteins for hydrogen evolution catalysis.

4. Utilizing metal-organic frameworks for PFAS capture

Presenter: Irin Aby (Brandon Barnett)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Perfluoro compounds are recalcitrant chemicals and removing them from water sources is quite difficult. The project aims to use novel metal-organic frameworks for the remediation of fluoro compounds from water, especially perfluoro octanoic acid, which is an area of extensive research owing to its higher solubility in water and its prevalent use in industries.

5. Isolation of non-heme, high valent iron centers within rigid cavities

Presenter: Lucy Huffman (Brandon Barnett)

Department of Chemistry, University of Rochester, Rochester NY

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 (EPR, UV-Vis, IR). Intracavity binding of hydroxide is reported, a key intermediate in the radical rebound mechanism for C–H functionalization. Generation of this species also serves as a model for other linear ligands to bind high valent iron in unique geometries.

6. Capturing perfluorinated greenhouse gases with metal-organic frameworks Presenter: Bevan Whitehead (Brandon Barnett)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Perfluorocompound gases (e.g. CF_4 , C_2F_6 , and NF_3) play pivotal roles in semiconductor manufacturing as plasma etchants and deposition chamber cleaning

agents, however pose a severe global warming threat due to their long atmospheric lifetimes, intense heat-trapping capabilities and kinetic inertness to atmospheric conditions. Designing materials to capture them before they enter the environment is paramount. My research focuses on addressing this challenge through the testing or post-synthetic modification of existing frameworks to enhance their PFC capture. Through my work, I have been able to demonstrate that Zn(fba) has one of the highest CF_4 vs. N₂ selectivities for all known water-stable sorbents and the post synthetic modification of M_2 (dobpdc) with long fluorinated chains enhances the selectivity of the material for PFCs as chain length is increased. These two approaches offer insight into different methods for the capture of PFCs vs. N₂ along with information about the uptake kinetics and mechanism of these two different materials, which will allow us better design materials with larger CF₄ selectivities and more favorable kinetic profiles.

7. A cobalt complex with an outer-sphere secondary amine for selective CO_2/H^+ electroreduction in water

Presenter: Afsar Ali (Kara Bren)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. The global energy crisis has spurred an urgent quest for sustainable energy solutions. To meet these challenges, there has been a drastic shift toward developing renewable energy systems in the last few decades. The effective functioning of these clean energy systems relies heavily on multielectron and proton transfer reactions, which are critical for the selective electrochemical conversion of low-energy feedstocks into desired products. The CO2 reduction reaction has gained prominence because of the role of CO2 as a greenhouse gas. For precious-metal catalysts, CO2 reduction's faradaic efficiency declines in aqueous electrolytes due to the generation of CO2 competitive proton reduction reaction. Molecular CO2 reduction electrocatalysts have garnered considerable attention because of their tunability and high selective nature. In this work, we have developed two water-soluble cobalt molecular electrocatalysts (1 & 2) with an N4 type ligand framework and a secondary amine group in the second coordination sphere (complex 1). We have explored electrochemical CO2 reduction to CO by complexes 1 and 2 in buffers with variable pKa values. Complex 1 shows higher TON values compared to complex 2 under CO2 and nitrogen in all buffers. Under CO2, Complex 1 shows higher selectivity for CO generation in the higher pKa buffers (TON; 19924, FE; 95.0 %, CHES buffer) and complex 2 has yielded higher selectivity for proton reduction in the low pKa buffer (TON; 28284, FE; 88.50 %, MES buffer). We propose that complex 1 stabilizes a CO2-coordinated intermediate state due to bicarbonate ions being involved in hydrogen bonding with coordinated CO2 and proton of secondary amine. But, this type of interaction is not possible in the case of complex 2 because lack of a secondary amine in the second coordination sphere.

8. Strategic design of ligands to understand and control chemoselectivity in Ni-catalyzed amide bond activation

Presenter: Vivek Gangadharan Pillai (Rose Kennedy)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Ligands play an important role in influencing chemoselectivity in transition metalcatalyzed cross-coupling reactions. Recently, amides have gained significant attention as unconventional electrophiles for cross coupling owing to their abundant presence in biomass and drug-like compounds, as well as their straightforward synthesis. However, their potential is hindered by the lack of a comprehensive mechanistic understanding of amide bond activations, necessitating extensive screening of ligands and substrates to attain the desired selectivity. This study aims to elucidate the impact of ligand structure and electronics on the chemoselectivity in Ni-mediated C-N bond activation of amides and extend this knowledge to enable the selective formation of new C-C bonds. This will be carried out through the combination of stoichiometric organometallic synthesis, reaction kinetics, and spectroscopic analysis. Preliminary findings indicate that nickel supported by a pyridine-containing Nheterocyclic carbene (NHC) ligand can facilitate the decarbonylation of amides at room temperature. Conversely, monodentate ligands show a preference for carbonyl retention. The findings from the study can shed light into the interplay of ligand structure, leaving group identity, and catalytic function, enabling advances in the efficiency and chemoselectivity of nickel-catalyzed cross-coupling catalysis.

9. Anionic Fe(III) macrocyclic complexes with carboxylates or sulfonates as MRI probes Presenter: Anwita Roy (Janet Morrow)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Magnetic Resonance Imaging (MRI) is a noninvasive diagnostic method for producing high resolution images in preclinical animal studies and of the human body. Contrast agents are used to better visualize tissue and function, and Gd(III)-based contrast agents (GBCAs) are used in the clinic. However, there is a growing interest in safer alternatives that use transition metal ions. One promising alternative involves the use of iron, which is abundant and can be effectively sequestered and recycled by the body. Our research group has developed an iron complex called Fe-TASO, which shows improved water solubility, high kidney contrast within 5 minutes post-injection, and rapid renal clearance. Building on this development, our focus is on synthesizing and functionalizing 1,4,7-triazacyclononane (TACN) with anionic pendant groups (sulfonates and carboxylates) to enhance relaxivity and clearance rates comparable to GBCAs. Our primary aim is to optimize new synthetic pathways to create anionic macrocyclic complexes of high-spin Fe(III).

10. Fe(II)/Fe(III) high spin and low spin complexes as responsive MRI and MRS probes Presenter: Deepak Krishnan Balaji (Janet Morrow)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Magnetic resonance imaging (MRI) and Magnetic resonance spectroscopy (MRS) are non-invasive diagnostic techniques that use the principles of nuclear magnetic resonance (NMR) to visualize internal structures and soft tissues within the human body and for monitoring the biochemical processes that occur in living tissues. Contrast agents are paramagnetic metal complexes which alter the relaxation times of nearby water protons in surrounding tissues, thus creating image contrast, and enhancing the visibility of specific structures or pathologies during the MRI scan. ParaSHIFT agents are paramagnetic metal complexes which have highly shifted ligand proton resonances that are far from tissue proton resonances. Our studies involve high-spin Fe(II) and low spin Fe(III) couples as redox activated paraSHIFT agents or Fe(II) and high spin Fe(III) as redox activated relaxivity agents that could be triggered by biological oxidants prevalent at the site of inflammation. Both projects use 1,4,7-triazacyclononane (TACN) alkylated with heterocyclic pendant groups including derivatives of imidazole, pyrazole and pyridine. For paraSHIFT, large numbers of magnetically equivalent protons can be used with three pendant groups. Relaxivity agents have two pendants and a coordination site for bound water and a high-spin Fe(III) center. MRI contrast agents and paraSHIFT agents that are responsive to pH, temperature, and redox are under study. This presentation will focus on the design, synthesis, and characterization of macrocyclic Fe(II)/Fe(III) complexes with different heterocyclic pendants for MRI and MRS applications.

11. An octahedral iron(III) metal-organic polyhedron as T1 MRI probe Presenter: Aruni Dissanayake (Janet Morrow)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. The incorporation of multiple Fe(III) centers into a metal-organic polyhedron bridged by rigid ligands represents a powerful approach for designing MRI contrast agents with higher relaxivities. Here, the molecular rotation of the contrast agent in solution is slowed as a result of the significant increase in the size of the contrast agent and the rigidity of the supporting organic ligands, which govern the enhancement of the relaxivity per metal center. In this study, a new Fe(III) metal-organic polyhedron (MOP) was designed by coordination of six Fe3+ cations and four tris-acylhydrazone ligands. This MOP was synthesized, characterized, and studied for its potential as an MRI contrast agent with enhanced relaxivity in solution and in mice. Relaxivity studies suggested that the Fe(III) MOP has an enhanced r1 relaxivity of 11 mM-1s-1 and 18 mM-1s-1 per molecule at 1.4 T, 34 0C, pH 7.4 in the absence and presence of HSA, respectively. It binds strongly to serum albumin through mostly electrostatic interactions which will lead to a substantial increase in r1 relaxivity. Furthermore, the Fe(III) coordination cage is highly inert towards phosphate anions, EDTA, Zn(II) and transferrin. The coordination cage shows blood pool behavior in mice MRI studies and is cleared through a mostly hepatobiliary pathway.

12. Probing the dynamics of electrolyte system: an enabling tool toward designing improved flow batteries

Presenter: Mamta Dagar (Ellen Matson)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Emergent, flowable electrochemical energy storage technologies suitable for gridscale applications are often limited by sluggish electron transfer kinetics that impede energy conversion efficiencies. To address these current challenges in the development of nonaqueous redox flow batteries, we focus on titanium-doped polyoxovanadate-alkoxide clusters and tune their physicochemical properties by modifying surface capping ligands, altering the composition of the supporting electrolyte, and studying the effect of solvent system on the battery performance metrics. Our results illustrate that the one electron reduction and oxidation processes exhibit characteristically different rates, suggesting that different mechanisms of electron transfer are operative. We report that a 1:4 v/v mixture of propylene carbonate and acetonitrile can lead to a three-fold increase in the rate of electron transfer for one electron oxidation, and a two-fold increase in the one electron reduction process as compared to pure acetonitrile for the multimetallic assembly, $[Ti_2V_4O_5(OMe)_{14}]$. Furthermore, organic functionalization of the cluster core leads to enhanced solubility, and changing the supporting electrolyte can yield improved capacity retention. The results provide insight into the utility of probing the dynamics between the different components of the electrolyte system to systematically tune the design of next generation flow batteries.

13. What's on the inside matters: Dopant influences on proton coupled electron transfer in metal oxide clusters

Presenter: Shannon Cooney (Ellen Matson)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. The transfer of two H-atom equivalents to polyoxovanadate-alkoxide clusters results in the formation of a V(III)-OH2 site at the surface of the assembly. The effect of "dopant" incorporation (via ligand substitution and heterometal installation) in the thermodynamics and kinetics H-atom uptake are investigated. Inclusion of heterometal dopants into the assembly is found to have a substantial effect on the mechanism of the H-atom transfer, switching from a concerted proton/electron transfer to a stepwise transfer of the electron followed by the proton, highlighting the profound influence of cationic dopants on the mode of H-atom uptake.

14. Gram-scale, one-pot synthesis of a cofacial porphyrin bridged by ortho-xylene as a scaffold for dinuclear architectures

Presenter: Rachel Snider (Timothy Cook)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Herein, we report the reaction between four 1,2-dibromoxylenes and two tetra-3-pyridylporphyrins for the formation of a cofacial porphyrin core spanned by dipyridinium

xylene moieties. The metal-free organic nanocage (oNC) was synthesized in one twenty-four hour step at a gram-scale with a 91.5% yield. The free base oNC was subsequently metallated with cobalt(II) (Co-oNC), copper(II) (Cu-oNC), and nickel(II) (Ni-oNC) ions to furnish dinuclear complexes that were characterized by mix of mass spectrometry, NMR, EPR, electronic absorption spectroscopy, and for Co-oNC, single-crystal X-ray diffraction. The structure of the cobalt cage shows four-fold rotational symmetry with the porphyrin faces adopting an eclipsed conformation with 7.566(3) Å between the two metal sites. This metal-metal separation is consistent with EPR measurements of Cu-oNC establishing an s = 1/2 system where the Cu(II) ions are too far apart for significant coupling. The diamagnetic nature of NioNC enabled straightforward characterization by NMR methods, including variable temperature and diffusion techniques that predict a hydrodynamic radius of 11.9 Å for the solvated 8+ core balanced by eight hexafluorophosphate anions. Cofacial cobalt porphyrins are often active as catalysts for the Oxygen Reduction Reaction. Under heterogenous conditions in water, Co-oNC was 83% selective for the electrocatalytic 4 e⁻/4 H⁺ reduction of O_2 to H_2O over the 2 e⁻/2 H⁺ pathway that produces H_2O_2 . Additionally, homogeneous experiments using ferrocene as a chemical reducing agent revealed consistent selectivity for H₂O (88%) and helped to rule out a stepwise 2 + 2 pathway. This oNC core offers significant advantages over prisms formed by coordination-driven self-assembly: the dipyridnium-xylene coupling can furnish over 1 gram of material in a single synthesis and the tethering motif is robust, maintaining a cofacial architecture in acidic and basic solutions. We envision this approach may be generalized to other bis-bromobenzyl building blocks, providing a means to tune metal-metal separation and other structural and electronic properties.

15. Mechanistic investigation of Ni-catalyzed conjunctive cross couplings of C(acyl)-N electrophiles

Presenter: Kaycie Malyk (Rose Kennedy)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Carboxylic acid derivatives comprise a diverse class of acyl electrophiles prevalent in bioactive molecules, biomass, and polymers. As such, they provide an attractive alternative to organohalide electrophiles in cross-coupling for fine chemical synthesis. C(acyl)–N electrophiles (amides, imides) are of particular interest in Ni-catalyzed transformations due to their synthetic utility and ease of preparation/handling. However, current methods of crosscoupling using C(acyl)–N electrophiles have been limited due to the need for specific substitution patterns and high catalyst loadings, as well as a general lack of experimental mechanistic work. The overall mechanistic ambiguity in reported work provides a barrier to further advancements to address these limitations. A recent case study from our group demonstrated the catalytic efficiency of using single-component [Ni] systems to study mechanism. From this study, the kinetic accessibility of C(acyl)–N oxidative addition was determined, as well as the accessibility of Ni(0), Ni(II), and Ni(I) species. To build off these insights, olefin carbofunctionalizations, or conjunctive cross-coupling systems with these acyl electrophiles to form new C–C(sp3) bonds were evaluated next. This mechanistic case study evaluates the chemoselectivity-determining factors in these conjunctive cross-coupling systems, and aims to distinguish whether oxidative cyclization, a step common in [Ni]/NHC-catalyzed systems of aldehydes and a,β -unsaturated esters, is competitive with oxidative addition-type pathways. The insights provided by this work are anticipated to help design new catalytic methodologies using diverse C(acyl)–N electrophiles.

16. Advanced insights into the Te(II)/Te(IV) redox chemistry of telluroxanthylium dyes Presenter: Nanyanika Kalita (Timothy Cook)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. A tellurorosamine dye bearing a mesityl pendant (Te(II)) has been reported to undergo aerobic photo-oxidation resulting in self-sensitization and catalysis via the Te(II)/Te(IV) redox couple. Although Te(IV) species have been used in a number of oxidations of organic and inorganic substrates, knowledge of the complete photocatalytic cycle is obscured by the complexity of identifying key Te(IV)-oxo and Te(IV) bis-hydroxy intermediates. In this work, we have investigated the electronic structure and mechanism of formation of a Te(IV)-bis-hydroxy core (**Te(IV)-(OH)**₂). Under aerobic irradiation with visible light, **Te(II)** (λmax = 600 nm) transforms into a Te(IV) species (λ_{max} = 669 nm) cleanly, provided that water is also present. The resultant Te(IV)-species is not stable even in the absence of light or at -20°C, decomposing back to **Te(II)** along with other byproducts over the course of many hours. To eliminate the structural ambiguity of the Te(IV) photoproduct, we carried out spectroelectrochemical studies, wherein **Te(IV)-(OH)**₂ was electrochemically generated under anaerobic conditions. The electronic absorption of this **Te(IV)-(OH)**² matches that of the Te(IV) photoproduct of self-sensitization with water present. Since isosbestic points are maintained both photochemically and electrochemically, the oxo core, **Te(IV)-(O)**, that forms solely via the photochemical pathway must rapidly equilibrate with **Te(IV)-(OH)**₂. Calculations of free energies and electronic structure of the bis-hydroxy versus oxo species further corroborate that the equilibration is rapid and the spectra of the two species are similar. To further explore Te(IV) cores, two novel compounds Te(IV)-Cl₂ and Te(IV)-Br₂ were synthesized using PhICl₂ and Br₂ oxidants, respectively. Characterizations of these related Te(IV)-X₂ compounds were simplified since these halogenated cores have no analogue to the Te(IV)-(O)/Te(IV)-(OH)2 equilibrium, enabling clear and direct comparisons to the **Te(IV)-(OH)**₂ species. This work provides insights into the photophysical and electrochemical behavior of Te analogs of chalcogenoxanthylium dyes which are relevant for a broad range of photochemical application.

17. Synthesis of iron-layered double hydroxides (Fe-LDH) using microwave radiation, characterizations, and evaluation of oxygen evolution reaction (OER)

Presenter: Alysson Bermudez Garcia (Luis De Jesus Baez)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Tunable materials that can trap and react with specific chemicals are relevant to remediate emerging pollutants. Per- and poly-fluoroalkyl substances (PFAS) are anthropogenically generated chemicals with remarkable stability in air, water, and soil. These pollutants have garnered global attention due to their detrimental health effects and bioaccumulation in living matter. Recent reports on processes to mitigate PFAS highlight ion exchange and electrochemical treatment as feasible and developmentally mature methods to capture PFAS but require further research into the materials used to improve efficiency. This poster presents a systematic study of microwave-assisted synthesis of iron-layered double hydroxides. In contrast to previously reported methods, this method has demonstrated a diminished reaction time and a relationship between the amount of intercalated water content and the iron valence state of the material, as confirmed by XRD, FT-IR, and XAS. Furthermore, we explore the direct effect on bulk behavior, such as the performance of oxygen evolution reaction in alkaline media.

18. Molybdenum sulfide clusters as redox-active metalloligands for low-valent uranium Presenter: Kamaless Patra (Ellen Matson)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. The chemical and electronic interactions between actinide ions and redox-active surfaces is an important area of research, with implications in nuclear fuel cycle and catalysis. In this context, group(VI) chalcogenide materials demonstrate potential for selectively extracting uranium from seawater through beneficial soft-soft interactions and enhanced electronic communication with actinides. Motivated by the distinctive interactions between uranium and MoS₂ surfaces, we focus our investigation on synthesizing molecular analogues to model uranium uptake and reactivity at a redox-active support. Specifically, we present the redox-active metalloligand, ($Cp*_{3}Mo_{3}S_{4}$), serving as a single binding site for actinides, offering valuable insights into the unique interactions between actinide species and redox-active surfaces. To install a single actinide centre at the surface of the molybdenum sulphide hemicubane-based metalloligand, we opted to explore the coordination chemistry of Cp*Ul₂(THF)₃ with Cp*₃Mo₃S₄. This effort results in the successful synthesis of the [(Cp*₃Mo₃S₄)Cp*Ul₂] cluster and its reduced derivatives. We further investigated the reactivity of the reduced cluster towards the activation of small molecules, specifically the cooperative reduction of water, which models the reactivity of atomically dispersed uranium on MoS_2 surfaces. In summary, our comprehensive study sheds light on how cluster reduction influences the interaction dynamics between uranium and MoS₂ surfaces and the reactivity studies modeling U@MoS₂.

19. Synthesis of main group heterobimetallic complexes

Presenter: Jinwoo Jung (Kyle Lancaster)

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

Abstract. The transfer of two H-atom equivalents to polyoxovanadate-alkoxide clusters results in the formation of a V(III)–OH2 site at the surface of the assembly. The effect of "dopant" incorporation (via ligand substitution and heterometal installation) in the thermodynamics and kinetics H-atom uptake are investigated. Inclusion of heterometal dopants into the assembly is found to have a substantial effect on the mechanism of the H-atom transfer, switching from a concerted proton/electron transfer to a stepwise transfer of the electron followed by the proton, highlighting the profound influence of cationic dopants on the mode of H-atom uptake.

20. Progress toward Ni-catalyzed decarbonylative etherification of esters

Presenter: Abraham Ellenbogen (Rose Kennedy)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. The diaryl-ether motif is important to many biologically relevant molecules in agrochemicals and pharmaceuticals. Intramolecular decarbonylative etherification is a difficult transformation often limited to high temperatures and expensive palladium catalysts. The use of earth-abundant nickel catalysts and cheap ester starting materials make this an inviting strategy. Ongoing work from the Kennedy Research Group on decarbonylative amination has shown us that turnover of the Ni(0/II) cycle is challenging due to this catalyst poisoning by extruded carbon monoxide. We expect a similar challenge with decarbonylative etherification and therefore propose the use of a Ni (I/III) cycle to catalyze this transformation. To evaluate this strategy we utilize parallel structural and screening approaches of both single component Ni(I) and in-situ generation of Ni(I) species.

21. Synthesis, reactivity, and redox properties of pyridone-supported bimetallic Ni(I) complexes

Presenter: Hailemariam Mitiku (Rose Kennedy)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Pyridones make up an important class of ligands that can be involved in metalligand 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 render 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 and form Ni-Ni covalent bond. The complexes can engage in a one or two electron redox events in their dimeric form. The dinuclear Ni(I) complexes can undergo bimetallic oxidative addition into alkyl electrophiles, which will open the door for cooperative bimetallic reactivity.

22. Facilitating redox reactivity at Zr(IV) through a Lindqvist polyoxovanadate support Presenter: Becca Walls (Ellen Matson)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Redox-active ligands have been used as a method to facilitate redox reactivity at metal sites which are otherwise redox inactive, often employing biomimetic or highly aromatic ligand frameworks to achieve redox activity. Alternatively, a ligand framework with redox-active metal sites can be employed as redox reservoirs for reactivity and inactive metal sites. As such, we sought to investigate reactivity in heterometal doped polyoxovandate-alkoxide cluster assemblies, wherein the cluster assembly acts as an electron reservoir for redox reactivity at the Zr(IV) dopant site. Contrary to the Ti(IV)-doped assembly, the terminal alkoxide of the dopant site is labile in the Zr(IV)-doped cluster, allowing for ligand substitution at Zr(IV) with more reactive species, such as peroxides. Addition of hydrogen peroxide to the Zr(IV)-doped cluster resulted in cluster oxidation, as well as allowed for selective conversion of thioethers to the corresponding sulfoxide. Hammett parameters indicate the conversion occurs through a nucleophilic pathway, where electron-rich thioethers are converted more rapidly.

23. S-Nitrosylation catalyzed by Cytochrome P460

Presenter: Colby Gekko (Kyle Lancaster)

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

Abstract. Nitric oxide (NO) is an important signaling molecule whose concentrations must be tightly controlled due to its cytotoxicity and lability as a gas. One means of controlling NO concentrations is through S-nitrosylation, where NO is added to free thiols in proteins or small molecules, such as glutathione (GSH), to form RSNO groups. While the mechanisms of biological protein S-nitrosylation are still under investigation, it has been shown to occur via metal-nitrosyls or metal-assisted transnitrosylation from either nitrite or S-nitrosoglutathione (GSNO). GSNO is thought to be the primary non-protein nitrosothiol used by eukaryotes to store NO, and thus plays an important role in signaling. Our lab has previously shown that NO is an obligate intermediate of hydroxylamine oxidation and therefore is essential for the primary metabolism of ammonia oxidizing bacteria (AOB). Here, we show that the cytochrome P460 from the AOB Nitrosomonas europaea can catalyze S-nitrosylation of RSH species, in particular GSH to GSNO, via an electrophilic heme ferric nitrosyl ({FeNO}6) species. Importantly, this reaction generates Fe(II) cytochrome P460, which furnishes an electron upon oxidation which could be used for cellular respiration. This demonstrates the versatility of the cytochrome P460 active site and implicates a possible metabolic role of cytochrome P460.

24. Exploring the synthesis of a mixed ligand layered double hydroxide Presenter: Elliot Rivera (Luis De Jesús Báez)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. The list of emergent pollutants resulting from anthropogenic activity keeps increasing with little end on sight. Case in point, per- and poly-fluoroalkylated substances (PFAS), also known as "Forever Chemicals" are prevalent in our ecosystems and can take up to one hundred years to decay. For this, materials that are carefully tailored to uptake and degrade emergent pollutants in-situ are of utmost importance. To this end, layered double hydroxides (LDHs) are a class of inorganic lamellar nanomaterials comprised of divalent and trivalent metal centers with octahedrally coordinated hydroxyl groups that have demonstrated the capacity to capture and process pollutants. The capacity from LDHs to carry out this process is dependent on the chemical nature of the transition-metal and the intercalated anion; notwithstanding, changes on the ligand by stoichiometry exchange of the hydroxy groups is underexplored. In this work, we seek to further our understanding of LDH structures and how the modified ligands may influence behavior and overall morphology. In this study, we reacted an Fe-based LDHs with thioacetamide (TA) to incorporate sulfides within the system. We observed that the crystal structure of the LDH changed as we increased the amount of TA used for doping according to X-ray diffraction (XRD) data. This discovery is further supported by changes in sulfur's electronic structure according to X-ray absorption near-edge spectroscopy (XANES). Our results demonstrated fundamental changes in both the phase and the morphology of the material.

25. Engineering proton coupled electron transfer at the surface of polyoxotungstate clusters

Presenter: Zhou Lu (Ellen Matson)

Department of Chemistry, University of Rochester, Rochester NY

Abstract. Hydrogenation reduction is fundamental in chemical industry. High-pressure H₂ is often used as the hydrogen source with the adoption of noble metal catalysts, which possesses a large carbon footprint and makes it hard to recycle the expensive catalysts. To bypass the technological and economic limitations for hydrogenation, proton couple electron transfer (PCET) is conceptualized to achieve mild reaction conditions and high efficiency. One important class of materials that exhibit PCET activity is reducible metal oxides, while limited active sites brings open questions to engineer the surface for the reactivity. The understanding of how molecular geometry and/or electronic structure influence thermodynamics of surface E–H bonds is essential to design efficient catalysts for redox reactions. In this work, we describe the proton couple electron transfer (PCET) reactivity at the surface of polyoxotungstate clusters with different geometries and charge states, including Lindqvist-type [ⁿBu₄N]₃[VW₅O₁₉] (**VW**₅), Keggin-type [ⁿBu₄N]₃[PW^{VI}₁₂O₄₀] (**PW**₁₂) and [ⁿBu₄N]₄[SiW^{VI}₁₂O₄₀] (**SiW**₁₂), and [ⁿBu₄N]₄[W^{VI}₁₀O₃₂] (**W**₁₀). Through the constructions of potential-pK_a diagrams of

these polyoxotungstate clusters, the bond dissociation free energies (BDFE) of surface O–H groups that are *in situ* generated upon the reduction in the presence of organic acids are determined.

26. Elucidating the phase transformation mechanism to VO₂ via dehydration of VOOH nanostars

Presenter: TJ Kolpack (Luis De Jesús Báez)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. The rapid development of AI and machine learning technologies posits a unique opportunity to further improve so called 'smart switch' technologies that exist at the epicenter of neuromorphic computing. To this end, vanadium (IV) oxide (VO2) serves as a perfect system to evaluate smart-switching properties because it can undergo a canonical metal-to-insulator transition (MIT). Nevertheless, control over temperature range and hysteresis where the MIT occurs is of great application interest, where approaches such as doping with several transition metals, stabilizing ultrasmall particles, or morphology changes has been used as a knob to tailor these MIT conditions. Recent work in the De Jesús Báez lab has developed a synthetic route to multiple morphologies (nanorods and nanostars) of VOOH. VOOH being the hydrated form of VO₂ we seek to understand the phase transformation into VO₂ while retaining morphology. Herein, we present our current work on understanding this phase transformation by flash annealing at 120° Celsius to try to transform the material without impacting morphology. Our findings are showing effective transformation into other phases while maintaining the nanostar morphology.

27. Ruthenium catalyzed, hydroquinone, electrochemically assisted dehydrogenation of amines

Presenter: Ignacio Camarero Temino (William Jones)

Department of Chemistry, University of Rochester, Rochester NY

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

28. Nitrous oxide production via nitroxyl by a novel multicopper oxidase from a nitrifying archaeon

Presenter: Robert Voland (Kyle Lancaster)

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

Abstract. Multi-copper oxidases (MCOs) are a diverse class of metalloenzymes spanning all known kingdoms of life. Their known range of function in biology is expansive, ranging from laccase activity to chromophore synthesis to metal oxidation. Most canonical MCOs contain a type 1 (T1) blue copper site where the substrates are oxidized by either 1 or 2 electrons, where

the reducing equivalents are then shuttled through peptide bonds to a trinuclear cluster consisting of a type 2 (T2) and type 3 (T3) binuclear copper site which utilizes molecular oxygen (O₂) as the terminal electron acceptor. Interestingly, MCOs have been shown to be highly expressed and conserved in ammonia-oxidizing archaea (AOA). We have identified, recombinantly expressed, and characterized a MCO from marine archaeon Nitrosopumilus maritimus with a unique structure and reactivity which has been previously uncharacterized. This MCO is also quite promiscuous regarding substrate scope, acting as a laccase, phenoxazinone synthase, and hydroxylamine (NH₂OH) oxidase. This reactivity with NH2OH is of particular interest in the context of AOA, where NH₂OH is known to be a central metabolite and AOA primary metabolism is known to be a major source of oceanic nitrous oxide (N₂O) emissions. We show that this MCO selectively produces nitroxyl (HNO) via coupling oxidation of the obligate nitrification intermediate NH₂OH to O₂ reduction. This HNO undergoes several downstream reactions, although a significant fraction rapidly dimerizes to yield N₂O. These results afford a possible enzymatic origin of AOA-derived N₂O, and reveal a unique enzymatic reaction for producing the elusive HNO molecule.

29. Correlating surface functionalization with changes in optical properties of colloidal ternary spinel oxide nanocrystals

Presenter: Revathy Rajan (Kathryn Knowles)

Department of Chemistry, University of Rochester, Rochester NY

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 these nanocrystals in order to improve their function in a specific application. Here we use a series of gallium oxide spinel nanocrystals, namely γ -Ga₂O₃, CoGa₂O₄, NiGa₂O₄, and ZnGa₂O₄, 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 (Co²⁺, Ni²⁺, Zn²⁺).

30. The development of macrocyclic Co(II) complexes as ParaCEST probes for MRI Presenter: Jaclyn Raymond (Janet Morrow)

Department of Chemistry, University at Buffalo, Buffalo NY

Abstract. Chemical exchange saturation transfer (CEST) magnetic resonance imaging (MRI) contrast is generated from the attenuation of the bulk water proton signal intensity, which is

reduced upon proton exchange of the bulk water with saturated exchangeable protons of a CEST agent. An advantage of this method is the capability to use ratiometric methods to quantify parameters of interest (pH, temperature, redox) in the microenvironment of the agent for developing responsive probes. However, CEST agents possess limited sensitivity in vivo, and thus it is critical to increase CEST sensitivity for these probes to become clinically relevant. High-spin cobalt(II) complexes exhibit highly paramagnetically-shifted, sharp proton resonances which makes them ideal candidates for paramagnetic CEST applications. To ensure kinetic inertness, these complexes are based on macrocyclic ligands, and are appended with groups such as amides that contain exchangeable protons for CEST. For increased sensitivity, it's important that these complexes produce large hyperfine proton shifts, which arise from anisotropic arrangement of unpaired electrons on the metal ion that influences nuclear spins via through-bond and through-space interactions. Thus, the resulting coordination and geometry of these complexes is significant for producing effective paraCEST probes. The first project focused on the comparison of Co(II) complexes based on the macrocycles CYCLAM or CYCLEN with amide or hydroxypropyl pendants, or a mixture of both. Paramagnetic 1H NMR spectra and single-crystal X-ray diffraction studies were used to evaluate the complexes coordination and geometry. CEST studies showed that the most promising complexes were of 6-coordinate with pendants arranged in a cis- configuration. Next, analogous Co(II) complexes containing amide-glycinate pendants and a TACN-based amphiphilic complex were prepared for liposomal CEST applications.

31. Development of Sn-Rh bimetallics as hydrogenation platforms

Presenter: Benyu Zhou (Kyle Lancaster)

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

Abstract. The development of main group elements centered catalytic systems provides an important alternative to the dominant transition metal mediated industrial processes. Among the main group elements in interest, the uses of low valent heavy group 14 elements hydrides (tetrelene hydrides) have gained significant amount of attention due to several successful applications into highly efficient catalytic reductions of small molecules, such as CO₂ and carbonyl containing species. However, challenges still exist as such a reduction process often requires a strong terminal reductant for the regeneration of tetrelene hydrides. In this poster, we discuss the possibility of use dihydrogen as the terminal reductant for the tetrel element mediated catalysis by constructing bimetallic systems featuring both a tin(II) element and a rhodium center, which can behave as a dihydrogen activator and potentially a hydride transferring reagent. Structural and reactivity studies on such systems has provided insights into the cooperativity between the Sn-Rh centers and for the further development of hydrogenation reaction of small molecules.

32. Carbon capture from natural gas flue emissions and air via (bi)carbonate formation in a cyclodextrin-based metal organic framework

Presenter: Alexandra Lim (Phillip Milner)

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

Abstract. Carbon capture and utilization or sequestration (CCUS) from industrial point sources and direct air capture (DAC) are both necessary to curb the rising atmospheric levels of CO2. Amine scrubbers, the current leading carbon capture technology, suffer from poor oxidative and thermal stability, limiting their long-term cycling stability under oxygen-rich streams such as air and the emissions from natural gas combined cycle (NGCC) power plants. Herein, we demonstrate that the new, solvothermally prepared hydroxide-based cyclodextrin metal-organic framework (CD-MOF) Rb₂CO₃ CD-MOF possesses high CO₂ capacities from dry dilute streams at low temperatures and humid streams at elevated temperatures. Additionally, it displays good thermal, oxidative, and cycling stabilities and selective CO₂ capture under mixed gas conditions in dynamic break-through experiments. Unexpectedly, under dry, hot conditions, a shift in the CO₂ adsorption mechanism—from reversibly formed bicarbonate to irreversibly formed carbonate—is observed, as supported by gas sorption and spectroscopic studies. This mechanistic switch, akin to urea formation in amine-functionalized sorbents, has not been previously reported in a hydroxide-based material and sheds new light on the interplay between these two species. Our findings provide valuable insight for the design of next-generation materials containing oxygen-based nucleophiles for carbon capture applications.

August 16th Schedule of Events

PARKING INFORMATION

We are excited to host you at the University of Rochester on August 4th, 2023. Please see the following information about parking on campus.

Parking permits are required at the University of Rochester Campus from 7 am to 7 pm on weekdays.

Parking permits may be purchased for \$6/day at the information booth on Wilson Blvd.

Meter parking is available along Wilson Blvd.

Alternative parking is available across the Genesee River at Genesee River Valley Park.

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