Western New York Inorganic Symposium 2025

August 15th Schedule of Events

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

9:00 – 10:50 AM: Catalysis and Catalyst Development (Moderator: Phil Milner)

9:00 AM – 9:10 AM	Opening Remarks
9:10 AM – 9:35 AM	*Metal–Metal Bonding Influences Hydride Reactivity in [Sn–Rh]*$^{3+}$ *and [Sn–Ni]*$^{2+}$ *Bimetallics* Benyu Zhou (Lancaster)
9:35 AM – 10:00 AM	*Coupling Plasma Chemistry and Electrocatalysis for Urea Production from Industrial Flue Gas* Mayuresh Janpandit (Li)
10:00 AM – 10:25 AM	*Defect-Engineered Metal–Organic Frameworks as Bioinspired Heterogeneous Catalysts for Amide Bond Formation* Bayu Ahmad (Milner)
10:25 AM – 10:50 AM	*Engaging Tethered and Untethered Nucleophiles in Direct and Remote Dual Functionalization of Dienes via the Formation of Palladium π–allyl Complexes* Owen Monteferrante (Paradine)

10:50 AM – 11:50 PM: Poster Session #1 (odd # posters)

11:50 AM – 12:45 PM: Lunch

12:50 – 2:05 PM: Applications of Inorganic Chemistry (Moderator: Brandon Barnett)

12:50 PM – 1:15 PM	*Effect of Coordination Environment and Electronic Coupling on Redox Entropy in a Family of Dinuclear Complexes* Daniela Carmona Perez (Thorarinsdottir)
12:50 PM – 1:10 PM	*Peroxide responsive Fe(II)/Fe(III) MRI probes* Deepak Krishnan Balaji (Morrow)
1:40 PM – 2:05 PM	*Structural and Spectroscopic Characterizations of Cavity-stabilized Nonheme High-Spiz {FeNO}*^{7} *and {FeNO}*^{6} *Complexes within a TREN-based Macrocyclic System* Bittu Chandra (Barnett)

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

3:15 PM – 4:30 PM: Materials and Extended Structures (Agnes Thorarinsdottir)

3:15 PM – 3:40 PM	*Ligand-Dependent Optical Properties of Colloidal Ternary Spinel Oxide Nanocrystals containing Transition Metals* Revathy Rajan (Knowles)
3:40 PM – 4:05 PM	*Tuning Charge Transfer Pathways in* Sb_2VO_5*/CdS-Zn(II) Porphyrin Ternary Heterostructures* Udani Wijethunga (Cook and Watson)
4:05 PM – 4:30 PM	*Creating a Liquid-liquid Interface Inside of a MOF* Lamisa Rahman (Liu)
4:30 PM	Closing Remarks & Student Prizes

ABSTRACTS FOR ORAL PRESENTATIONS

Metal–Metal Bonding Influences Hydride Reactivity in $[Sn–Rh]^{3+}$ and $[Sn–Ni]^{2+}$ Bimetallics

Presenter: Benyu Zhou (Kyle Lancaster)

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14850

Abstract. Heavier group 14 metal hydrides serve as key intermediates in catalytic transformations such as hydroboration. Possibilities of regenerating such intermediates via a clean hydride source like dihydrogen could provide such catalytic processes with an alternative that is more amiable to the environment. Herein, we report our efforts toward this goal using a Sn^{II}-Rh^{I} bimetallic system with the Rh^{I} center acting as a potential hydrogen activator. Reactivities of such a system have been studied with the target of introducing a hydride ligand to the bimetallic core, where a preference of the hydride ligand to be attached to the Rh center instead of the Sn has been discovered. Examination of the electronic structures of these complexes through theoretical and experimental evidence has revealed the electron acceptor nature of the Rh^{I} center within such bimetallic core and explained the preference for the hydride ligation.

Coupling Plasma Chemistry and Electrocatalysis for Urea Production from Industrial Flue Gas

Presenter: Mayuresh Janpandit (Chris Li)

Department of Chemistry, University of Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York, 14260

Abstract. Industrial flue gases, rich in CO_2 and nitrogen oxides, are major contributors to global greenhouse emissions. Transforming these emissions into useful chemicals, such as urea, presents an opportunity for carbon–nitrogen circularity. Flue gas primarily consists of carbon dioxide (CO_2), nitrogen (N_2), and water vapor, released during fossil fuel combustion. In recent years, plasma has emerged as an effective tool for activating N_2 by breaking its strong triple bond, enabling nitrogen fixation under mild conditions. In this study, we utilized a plasma reactor to activate nitrogen species present in flue gas, leading to the generation of NO, N_2O, and other NOx compounds, as confirmed by GC-MS analysis. The activated flue gas was then fed into an electrochemical reactor, enabling the synthesis of value-added products including urea, ammonia, and CO. To facilitate C–N coupling, we investigated a series of bimetallic catalysts for their ability to mediate interactions between NOx-derived nitrogen species and CO_2-derived carbon intermediates. Our results highlight that efficient CO_2 activation is a key step governing urea formation. These findings demonstrate the potential of integrating plasma activation with electrocatalysis for sustainable urea synthesis from flue gas. Ongoing efforts are focused on catalyst optimization and mechanistic understanding via in situ spectroscopy and DFT.

Defect-Engineered Metal–Organic Frameworks as Bioinspired Heterogeneous Catalysts for Amide Bond Formation

Presenter: Bayu Ahmad (Philip Milner)

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14850

Abstract. The synthesis of amides from amines and carboxylic acids is the most widely carried out reaction in medicinal chemistry. Yet, most amide couplings are still conducted using stoichiometric reagents, leading to significant waste; few synthetic catalysts for this transformation have been adopted industrially due to their limited scope and/or poor recyclability. The majority of catalytic approaches focus on a single activation mode, such as enhancing the electrophilicity of the carboxylic acid partner using a Lewis acid. In contrast, nature effortlessly forges and breaks amide bonds using precise arrays of Lewis/Brønsted acidic and basic functional groups. Drawing inspiration from these systems, herein we report a simple defect engineering strategy to colocalize Lewis acidic Zr sites with other catalytically active species within porous metal–organic frameworks (MOFs). Specifically, the combination of pyridine N-oxide and Zr open metal sites within the defective framework MOF-808-py-Nox produces a heterogeneous catalyst that facilitates amide bond formation with broad functional group compatibility from amines and carboxylic acids, esters, or primary amides. Extensive density functional theory (DFT) calculations using cluster models support that the formation of a hydrogen-bonding network at the defect sites facilitates amide bond formation in this material. MOF-808-py-Nox can be recycled at least five times without losing significant crystallinity, porosity, or catalytic activity and can be employed in continuous flow. This defect engineering strategy can be potentially generalized to produce libraries of catalytically active MOFs with different combinations of colocalized functional groups.

Engaging Tethered and Untethered Nucleophiles in Direct and Remote Dual Functionalization of Dienes via the Formation of Palladium π–allyl Complexes

Presenter: Owen Monteferrante (Shauna Paradine)

Department of Chemistry, University of Rochester, Rochester, NY 14627

Abstract. Diene difunctionalization reactions are often sought as they provide a more efficient addition of functional groups and molecular complexity than traditional functionalization. However, these types of reactions often have issues with selectivity, as it can be difficult to chemically differentiate the various potential functionalization sites. Transition metals, especially palladium, have been used in the past to allow for control of which sites are functionalized. Palladium can also undergo the process of chainwalking, allowing remote difunctionalization, increasing the scope of products that can be generated. So far, I have contributed to the development of three different dual functionalization methods, all with different types of nucleophiles.

Effect of Coordination Environment and Electronic Coupling on Redox Entropy in a Family of Dinuclear Complexes

Presenter: Daniela Carmona Perez (Agnes Thorarinsdottir)

Department of Chemistry, University of Rochester, Rochester, NY 14627

Abstract. In recent years, thermocells have caught attention as effective candidates for the recovery and utilization of medium- and low-temperature heat energy. A thermocell is an electrochemical system constructed from a pair of identical electrodes and a liquid electrolyte containing a redox pair. In this system, a thermoelectric potential is generated when a temperature gradient is applied between the two electrodes. The magnitude of the potential difference generated for a certain system at a given temperature gradient is called the temperature coefficient, and it determines the power output of a device. In efforts to increase the efficiency of thermocells, we need redox-active species that exhibit high temperature coefficients. Thus, our research focuses on identifying factors that affect the temperature coefficient in molecular systems, so we can design molecular compounds with target properties. As part of these efforts, we synthesized a series of isostructural homo- and heterometallic M2 (M = FeII, FeIII, ZnII) complexes supported by a phenoxo-centered tetrapyridyl ligand and ancillary carboxylate ligands that enabled independent change in (i) charge, (ii) coordination environment of the redox-active center, and (iii) electronic coupling strength between redox centers. Variable-temperature electrochemical analysis of the series revealed that the coordination environment and charge density change, rather than electronic coupling strength, are key parameters to consider for optimizing the temperature dependence of the redox potential. These results constitute the first examination of how electronic coupling influences the temperature dependence of the redox potential and provide important information for the design of molecular compounds with target redox properties.

Peroxide responsive Fe(II)/Fe(III) MRI probes

Presenter: Deepak Krishnan Balaji (Janet Morrow)

Department of Chemistry, University of Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York, 14260

Abstract. Magnetic resonance imaging (MRI) is a non-invasive diagnostic technique that uses the principles of nuclear magnetic resonance (NMR) to visualize internal structures and soft tissues within the human body. 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. Our studies involve high-spin Fe(II) and Fe(III) complexes as redox activated relaxivity agents that are triggered by biological oxidants prevalent at the site of inflammation. This project focuses on tuning the coordination environment to achieve an optimal redox potential to ensure that these complexes are only oxidized by oxidants

produced in inflammatory processes and not O_2. Therefore, macrocyclic ligands based on 1,4,7-triazacyclononane (TACN) alkylated with heterocyclic pendants including derivatives of pyridine and chiral pendant like hydroxy propyl are used to provide pentadentate and hexadentate coordination and kinetic inertness to the iron center. This presentation will focus on the design and characterization of macrocyclic Fe(II)/Fe(III) complexes and the kinetics and mechanism of oxidative activation of the Fe(II) probe.

Ligand-Dependent Optical Properties of Colloidal Ternary Spinel Oxide Nanocrystals containing Transition Metals

Presenter: Revathy Rajan (Kathryn Knowles)

Department of Chemistry, University of Rochester, Rochester, NY 14627

Abstract. Ternary spinel oxides of formula AB2O4 are semiconductors that possess compositionally and structurally tunable magnetic and optoelectronic properties that, when coupled with their extraordinary chemical and thermal stability, offer functional materials with applications in the fields of photocatalysis solar energy conversion, gas sensing, and photoelectrochemistry. Nanocrystals of these materials offer the additional advantages of high surfacearea-to-volume ratios and the ability to use surface functionalization as a plausible strategy for tailoring their optoelectronic properties to improve their function in a specific application. Here, we demonstrate that surface-bound species can dominate the absorption spectra of colloidal ternary spinel oxide nanocrystals. We show that the surface functionalization of cobalt-containing systems with thiol ligands leads to the growth of an intense peak centered at 2.4 eV (518 nm) in the absorption spectra, which arises due to the formation of cobalt-thiolate linkages on the nanocrystal surface. We demonstrate that the observed optical change can be used to track ligand exchange reactions and assess the relative binding affinity of thiol, amine, and carboxylate ligands to the nanocrystal surface. This work highlights the significant role that surface chemistry can play in determining the optical properties of ternary spinel oxide nanocrystals.

Tuning Charge Transfer Pathways in Sb_2VO_5/CdS-Zn(II) Porphyrin Ternary Heterostructures

Presenter: Udani Wijethunga (Tim Cook and David Watson)

Department of Chemistry, University of Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York, 14260

Abstract. We prepared ternary heterostructures composed of Sb2VO5 nanorods, CdS quantum dots (QDs), and zinc(II) 5-(3-carboxyphenyl)-10,15,20-(triphenyl)porphyrin (Zn3MCP), hereafter referred to as Sb_2VO_5/CdS-Zn3MCP triads and investigated their performance in photocatalytic CO_2 reduction. The CO_2 reduction reaction (CO2RR), which converts CO2 into value-added fuels and feedstocks, poses a significant challenge due to competition from the hydrogen evolution reaction (HER) and the presence of multiple possible multi-electrons, multi-proton pathways. We hypothesized that (a) photoexcited CdS QDs within the Sb_2VO_5/CdS-Zn3MCP triads would transfer electrons to Zn3MCP and holes to mid-gap states in Sb_2VO_5, (b) this directional charge separation would support subsequent redox half-reactions, and (c) Zn3MCP would function as a selective catalyst for CO2RR. To test these hypotheses, we studied both the excited-state charge-transfer dynamics and the photocatalytic behavior of Sb_2VO_5/CdS-Zn3MCP triads, along with their two-component analogues: CdS-Zn3MCP dyads and Sb_2VO_5/CdS heterostructures. In CdS-Zn3MCP dyads, energy transfer occurred from photoexcited CdS QDs to Zn3MCP. These dyads facilitated both CO_2RR producing CO and CH_4 and HER in photochemical tests. Similarly, Sb2VO5/CdS heterostructures enabled both CO_2RR and HER, but primarily generated H_2. Notably, the Sb_2VO_5/CdS-Zn3MCP triads exhibited selective photocatalytic CO_2 reduction, yielding HCHO, HCO_2H, CO, and CH_4 with complete suppression of HER. Increasing the Zn3MCP loading enhanced CH_4 production, the product of an eight-electron, eight-proton CO_2RR pathway suggesting cooperative interactions between porphyrin centers. These results support the proposed charge-separation mechanism and demonstrate that Sb_2VO_5/CdS-Zn3MCP triads are highly promising for selective CO_2 photocatalysis. More broadly, our findings illustrate how tuning the composition and interfacial architecture of heterostructures can unlock new reactivity and selectivity by modulating light-driven charge-transfer processes.

Creating a Liquid-liquid Interface Inside of a MOF

Presenter: Lamisa Rahman (Ken Liu)

Department of Chemistry and Materials Science, Rochester Institute of Technology, Rochester, New York, 14623

Abstract. MOF NU-1000 is highly periodic architecture with dual natured porosity: polar mesopores and non-polar micropores. This offers a unique platform to explore nanoscale liquid-liquid interfaces. These confined zones can enable molecular interactions and reactions that are typically hindered by the limited contact area between immiscible solvents. In this study, we selected water as the polar phase and heptane as the non-polar phase due to heptane's low toxicity and its favorable interaction with the MOF framework to study their adsorption in the MOFs. Difference electron density (DED) mapping at a relative pressure of 0.025 confirmed the adsorption of heptane into the micropores, while prior work has established the presence of water in the mesopores. These findings indicate successful formation of a stable liquid-liquid interface within NU-1000.

Structural and Spectroscopic Characterizations of Cavity- stabilized Nonheme High-Spiz $\{FeNO\}^7$ and $\{FeNO\}^6$ Complexes within a TREN-based Macrocyclic System

Presenter: Bittu Chandra (Brandon Barnett)

Department of Chemistry, University of Rochester, Rochester, NY 14627

Abstract. Nitric oxide (NO·) plays diverse roles in mammalian systems, functioning as a signaling molecule at nanomolar concentrations and as a component of immune defense at micromolar levels. Many of NO's biological effects are mediated through its interactions with metal centers, especially iron. While the binding of NO to both ferric and ferrous heme iron has been extensively investigated, its interaction with high-spin non-heme iron centers—particularly in the ferric state—remains less well characterized. In this presentation, I will describe the synthesis and structural and spectroscopic characterization of mononuclear, non-heme high-spin $\{FeNO\}^7$ and its one-electron oxidized form, $\{FeNO\}^6$, both supported by an anionic TREN-based macrocyclic ligand and embedded within a rigid cavity. Using this same ligand system, our group recently reported an exceptionally stable high-spin Fe^{IV}=O complex ($t_1/_2$ = 21 h at 70 °C in MeCN). The rare high-spin $\{FeNO\}^6$ species has now been stabilized and crystallized within the rigid macrocyclic cavity. A range of spectroscopic techniques—including UV-Vis-NIR, FT-IR, EPR, NMR, and cyclic voltammetry—has been employed to characterize these complexes. I will also discuss the role of the macrocyclic cavity in stabilizing biologically relevant, elusive intermediates, and compare its chemistry with that of a similar non-macrocyclic TREN-based system.

ABSTRACTS FOR POSTER PRESENTATIONS

1. **Realizing Multisite Proton–Coupled Electron Transfer through Polyoxotungstate Clusters**
   Presenter: Zhou Lu (Ellen Matson)
   Department of Chemistry, University of Rochester, Rochester, NY
   Abstract. Hydrogen atom transfer (HAT) reactions are fundamental in chemical industry, where noble metal complexes are often involved in, possessing a large carbon footprint and making it hard to recycle the expensive catalysts. Proton–coupled electron transfer (PCET) is one efficient pathway to bypass the technological and economic limitations to achieve mild reaction conditions and high efficiency. In light of designing HAT catalysts, the homolytic E-H bond strength can be estimated by Bordwell equation, where the bond-dissociation free energy (BDFE) is defined by summing the pKa and the redox potential to oxidize the resulting anion to neutral radical and reduce proton to H-atom. However, for a single molecule, these two key factors, pKa and E1/2, are inversely correlated. The existing leveling effect compensates the increasing basicity of conjugate base with decreasing oxidizing power, making it challenging towards efficient HAT reagents. The separation of e− and H+ offers more flexibility and tunability that redox potential of the electron donor and pKa of the proton donor varies independently. Here, we design multisite PCET (MS-PCET) dehydrogenation reaction realized by Keggin-Type polyoxotungstate clusters in corporate with organic bases. Fully-oxidized Keggin-type [VW12O40]3- and [PVoutW11O40]4- clusters are validated to dehydrogenate the 2,4,6-tritertbutyl-phenol into phenoxyl radical with the separate proton acceptors. This work sheds light on the affordable catalyst design to the H-atom transfer reactions.

2. **Nitroreductase activity of Nmar_1357 toward 2-Nitrophenol**
   Presenter: Zeinab Faraj (Kyle Lancaster)
   Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
   Abstract. Nitrification is a crucial microbial biological process by which ammonia oxidizing archaea (AOA) and ammonia oxidizing bacteria (AOB) convert ammonia (NH_3) to nitrite (NO_2^-) or nitrate (NO_3^-) deriving energy from the resulting reducing equivalents. AOA constitute one of the most abundant groups of microbes and produce nitrous oxide (N_2O) which is linked to environmental and atmospheric concerns. Our lab has previously shown that Nmar_1354 from *Nitrosopumilus maritimus,* an ammonia oxidizing archaeon, selectively oxidizes hydroxylamine (NH_2OH) to produce nitroxyl (HNO). Nmar_1357 is expressed within the same gene cluster as Nmar_1354 and is annotated as a nitroreductase, so we sought to characterize its reactivity to better understand its possible role in nitrification. Here, we show that Nmar_1357 demonstrates reactivity toward 2-nitrophenol (ONP), with the products of this reaction under investigation. The success of this project will aid us in better understanding AOA metabolism.

3. **Turning on Redox Mediation in Perylene Tetracarbonyl Derivatives**
   Presenter: Yujing Wang (Phillip Milner and Andrew Musser)
   Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY
   Abstract. The reductive functionalization of inert substrates is both significant and challenging for both environmental cleanup and organic synthesis. Conventional approaches

largely utilize catalyst photoexcitation to reach deeply reducing potentials. Here, we present that switch perylene tetracarbonyl derivatives to turn on catalytic redox mediation for the electroreductive radical borylation of aryl chlorides at relatively mild cathodic potentials.

4. **Ligand denticity and substrate chelating ability interact to control chemoselectivity in nickel-catalyzed amide cross-coupling**
Presenter: Vivek G. Pillai (Rose Kennedy)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. N-containing carboxylic acid derivatives, especially amides, are among the most common and accessible functional groups in pharmaceutical intermediates, APIs, and bio-based feedstocks. Despite their abundance, the use of amides in synthetic chemistry is limited by the inherent stability of the C(acyl)–N bond, which restricts efficient bond activation. Nickel/Nheterocyclic carbene (NHC) catalysis has emerged as a promising approach for milder activation of the amide C(acyl)–N bond compared to traditional harsh methods. However, current nickelcatalyzed systems often require high catalyst loadings (5–20 mol%), elevated temperatures, long reaction times, and suffer from limited substrate scope and chemoselectivity. These challenges mainly stem from unresolved mechanistic questions concerning the reaction pathway, intermediates, and factors influencing chemoselectivity. In this work, we address some of these mechanistic ambiguities in nickel-catalyzed amide cross coupling reactions. We hypothesized that both ligand denticity and the nature of the amide leaving group significantly affect chemoselectivity. To investigate this, we synthesized a series of single-component nickel complexes with varying steric bulk and coordination geometries to modulate the nickel environment, alongside amides bearing nonchelating and chelating leaving groups to probe substrate coordination effects. Stoichiometric and catalytic studies using Negishi coupling as a model system showed that monodentate ligands failed to induce chemoselectivity, whereas bidentate ligands strongly favored decarbonylative coupling under catalytic conditions. This study provides new insights into how ligand structure and chelating leaving groups influence reaction selectivity. Ultimately, these findings can serve as a foundation for developing guiding principles to predict and control chemoselectivity in nickel-catalyzed amide cross-coupling through the careful selection of ligands and substrates.

5. **Oriented MOF Thin Films for Controlling Electrode Microenvironment**
Presenter: Azina Rahmani & Vartika Jaiswal (Agnes Thorarinsdottir)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Heterogeneous electrocatalysts often suffer from uneven active site distribution and poor mass transport, limiting their selectivity and efficiency. To address these challenges, we are harnessing the well-defined structures and synthetic tunability of metal-organic frameworks (MOFs) to fabricate MOF-coated conductive substrates with optimized microenvironments for electrocatalysis. While MOFs are typically synthesized as powders, practical applications require thin films with controlled thickness and morphology. As crystalline materials, MOFs exhibit direction-dependent properties, making film performance highly sensitive to crystallographic orientation. Although various methods exist for preparing MOF films, they are often limited by poor control over structural features, low reproducibility, weak mechanical stability, and substrate incompatibility. Here, we report the fabrication of oriented MOF films, including ZIF-8, UiO-66, UiO66-NH_2, MOF-801, and MOF-808, on a variety

of conductive substrates. These films exhibit uniform thickness, full surface coverage, and defined crystallographic orientation. We characterized the films using PXRD, SEM-EDS, AFM, ICP, BET, and CV, and are systematically investigating their transport properties as a function of pore size, crystal structure, orientation, and thickness.

6. **Tuning Charge Transfer Pathways in Sb_2VO_5/CdS-Zn(II) Porphyrin Ternary Heterostructures**
   Presenter: Udani K. Wijethunga (Tim Cook and David Watson)
   Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY
   Abstract. We prepared ternary heterostructures composed of Sb_2VO_5 nanorods, CdS quantum dots (QDs), and zinc(II) 5-(3-carboxyphenyl)-10,15,20-(triphenyl)porphyrin (Zn_3MCP), hereafter referred to as Sb_2VO_5/CdS-Zn_3MCP triads and investigated their performance in photocatalytic CO_2 reduction. The CO_2 reduction reaction (CO2RR), which converts CO2 into value-added fuels and feedstocks, poses a significant challenge due to competition from the hydrogen evolution reaction (HER) and the presence of multiple possible multi-electrons, multi-proton pathways. We hypothesized that (a) photoexcited CdS QDs within the Sb_2VO_5/CdS-Zn_3MCP triads would transfer electrons to Zn_3MCP and holes to mid-gap states in Sb_2VO_5, (b) this directional charge separation would support subsequent redox half-reactions, and (c) Zn3MCP would function as a selective catalyst for CO2RR. To test these hypotheses, we studied both the excited-state charge- transfer dynamics and the photocatalytic behavior of Sb_2VO_5/CdS-Zn3MCP triads, along with their two-component analogues: CdS-Zn_3MCP dyads and Sb_2VO_5/CdS heterostructures. In CdS-Zn_3MCP dyads, energy transfer occurred from photoexcited CdS QDs to Zn_3MCP. These dyads facilitated both CO_2RR producing CO and CH_4 and HER in photochemical tests. Similarly, Sb_2VO_5/CdS heterostructures enabled both CO_2RR and HER, but primarily generated H_2. Notably, the Sb_2VO_5/CdS-Zn_3MCP triads exhibited selective photocatalytic CO_2 reduction, yielding HCHO, HCO_2H, CO, and CH_4 with complete suppression of HER. Increasing the Zn_3MCP loading enhanced CH_4 production, the product of an eight-electron, eight-proton CO_2RR pathway suggesting cooperative interactions between porphyrin centers. These results support the proposed charge-separation mechanism and demonstrate that Sb_2VO_5/CdS-Zn_3MCP triads are highly promising for selective CO_2 photocatalysis. More broadly, our findings illustrate how tuning the composition and interfacial architecture of heterostructures can unlock new reactivity and selectivity by modulating light-driven charge-transfer processes

7. **Transformations of Aromatic Amines by an Archaeal Multicopper Oxidase, Nmar_1354**
   Presenter: Thomas C. Arndt (Kyle Lancaster)
   Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
   Abstract. Nmar_1354 is a two-domain multicopper oxidase (2dMCO) found in the ammonia oxidizing archaea (AOA) *Nitrosopumilus maritimus,* which has recently demonstrated enzymatic conversion of hydroxylamine (NH_2OH) to nitroxyl (HNO) in a reaction that is coupled to the reduction of dioxygen (O_2). Nmar_1354 is characterized by a Type 1 blue Cu site responsible for substrate oxidation, a trinuclear Cu cluster responsible for O_2 reduction, and a dangling cupredoxin domain containing a type 1 Cu site of presently unknown function. *In vitro* studies of Nmar_1354 have shown the enzyme to be capable of activity similar to phenoxazinone-synthase, converting aromatic amines to substituted phenazine and

phenoxazinone products. In the presence of NH_2OH, Nmar_1354 is proposed to convert aromatic amines to the corresponding aromatic nitro-groups, potentially due to the ability of the enzyme to deliver HNO in aqueous solution. These aromatic transformations have been observed by UV-Vis spectroscopy and Direct-Analysis in Real Time (DART) mass spectrometry, allowing for putative identification of products.

8. **Realizing Functional Characterization of Enzymatic Activity in the Newly Identified Multicopper Oxidase Nmar_1354**
Presenter: Sucheta Ghosh (Kyle Lancaster)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
Abstract. The multicopper oxidase, Nmar_1354 from the ammonia-oxidizing archaeon *Nitrosopumilus maritimus*, has been recently purified and functionally characterized. Nmar_1354 has been shown to selectively produce nitroxyl (HNO) by coupling the oxidation of the nitrification intermediate hydroxylamine (NH_2OH) to the reduction of dioxygen.[1] Notably, preliminary investigations indicate that Nmar_1354 can also oxidize certain aromatic amines. UV–vis spectroscopy indicates that – o-aminophenol undergoes enzymatic conversion to nitro- aminophenol in the presence of hydroxylamine and dioxygen, suggesting that HNO intercepts canonical MCO products and delivers new products. Based on these findings, we hypothesize that Nmar_1354 mediates transformations unique from those known for MCOs; specifically, the conversion of aromatic amines to nitro compounds. Current efforts are directed towards establishing substrate scope as well as reaction mechanism.

9. **Nitrous Oxide Production via Nitroxyl by a Multicopper Oxidase from Nitrosopumilus maritimus**
Presenter: Robert W. Voland (Kyle Lancaster)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
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 metabolism of 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 studies of a multicopper oxidase (MCO) from the ammonia-oxidizing archaeon Nitrosopumilus maritimus comprising a novel structural class which is unique to AOA. We found that this MCO can perform the 2-electron oxidation of the central metabolite hydroxylamine to nitroxyl, which then goes on to produce the greenhouse gas nitrous oxide (N2O). The structure of this enzyme reveals a C-terminal cupredoxin domain containing a blue Cu site, giving each monomer of the enzyme five total Cu ions, different than the canonical four Cu ions found in most studied MCOs. Our studies have shown that this additional cupredoxin domain is both important for structural stability of the enzyme as well as cooperative with the canonical blue Cu site for oxidation of hydroxylamine. Understanding the

mechanism of hydroxylamine oxidation by this unique MCO will help us to better understand AOA metabolism in general as well as provide information on the mechanisms behind global N_2O flux.

10. **Harnessing Aluminum-Based Metal-Organic Frameworks for Hydrogen Sulfide Storage and Targeted Delivery**
Presenter: Priyadarshini Baidya (Philip Milner)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
Abstract. Hydrogen Sulfide (H_2S) has emerged as an essential gasotransmitter and therapeutic agent for various diseases. Current treatment depends on the use of small molecule donors such as NaSH, Na_2S, which are often limited by rapid release of H_2S and formation of toxic byproducts. Metal Organic Frameworks (MOFs) composed of organic linkers and metal nodes, offer high surface area and porosity, making them excellent candidates for gas storage and controlled delivery. Here, we have synthesized and screened various Aluminum-based MOFs using BET surface area measurements, H_2S adsorption isotherms, powder X-ray diffraction (PXRD), UV-Vis spectroscopy, and biological assay. These materials exhibit stability under ambient conditions, high H_2S uptake, and have potential for the delivery of H_2S.

11. **Utilizing Metal Organic Frameworks (MOFs) for Delivery of Gaseous Fluorinated Reagents as Powerful Fluorocarbon Building Blocks**
Presenter: Phuong Minh Nguyen (Philip Milner)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
Abstract. Fluorinated building blocks are indispensable in contemporary drug discovery, often enhancing molecular performance by increasing bioactivity and resistance to metabolic degradation. Despite their potential, fluorinated gases are underutilized in everyday synthetic chemistry due to practical barriers, including volatility, challenging containment, and ecological hazards. Traditional delivery methods, such as gas balloons or in-/ex-situ release from chemical precursors, often lack precision and are difficult to standardize across experiments, respectively. In our work, we address these limitations by employing Metal-Organic Frameworks (MOFs) to reversibly trap and release fluorinated gases in a controlled and quantifiable manner. This strategy allows us to safely incorporate fluorinated gases into a variety of transformations, expanding the toolkit for fluorocarbon synthesis while improving both safety and reaction reproducibility

12. **Synthesis and Reactivity of Group 9-Group 14 Heterobimetallic Complexes**
Presenter: Millie Trusler (Kyle Lancaster)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
Abstract. Heterobimetallic complexes that involve the coordination of both a main group metal as well as a transition metal can allow fine tuning of each metal center and a platform for more facile chemical transformations of small molecules. Previous work from the group has utilized a Sn-Ni bimetallic complex to perform sigma bond metathesis via the Sn center, with electronic tuning originating from the L type ligand bound to the Ni. This work focuses on the synthesis of analogous cobalt heterobimetallic systems consisting of the cobalt being paired with a main group metal, germanium or indium. These unique heterobimetallic

complexes are currently being probed to investigate their use as nitrogen oxyanion reduction catalysts through the attempted synthesis of their nitrate or nitrite complexes.

13. **Assessing structure, dynamics, and reactivity of iron complexes supported by Tris(amidate)amine ligands**
    Presenter: Lucy S. X. Huffman (Brandon Barnett)
    Department of Chemistry, University of Rochester, Rochester, NY
    Abstract. Tris(2-aminoethyl)amine (TREN) derived chelating ligand platforms can stabilize low coordination numbers and provide opportunities to tune the steric and electronic profile of the secondary coordination sphere. Our cavitand-inspired ligand allows for the isolation and characterization of a four-coordinate iron(III) species in a trigonal monopyramidal geometry. This is the first crystallographically characterized example of an iron(III) complex in this geometry. In addition, we have synthesized iron(III) fluoride and iron(IV) oxo species, studied their reactivity towards H-atom abstraction, and used MD simulations to probe the ligand dynamics. These simulations suggest negligible flexing of the rigid cavity opening, but also suggest a route by which exogenous ligands may bypass the rigid cavity opening yet still access the intracavity coordination site in $[MLOCH_2O]^n$ complexes via entry through the equatorial plane.

14. **Molybdenum Sulfide Clusters as Redox-Active Metalloligands for Actinide Ions**
    Presenter: Leyla Valerio (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 the processing of nuclear fuels. In this context, materials composed of group(VI) chalcogenides demonstrate great potential for selectively extracting uranium from seawater as a result of enhanced electronic communication between the actinide and redox-active surface. Motivated by these findings, our research group is investigating the synthesis of actinide-substituted molybdenum chalcogenide clusters. Starting from the redox-active dimeric complexes, $(Cp^*{}_2Mo_2S_4)$ and $(Cp^*{}_2Mo_2S_2SCH_2S)$, we find that low-valent actinide coordination (using $Cp^*UI_2(thf)_3$) is facilitated via electron transfer from the dimers to the uranium center, forming the adducts $(Cp^*{}_2Mo_2S_4)Cp^*UI_2$ and $(Cp^*{}_2Mo_2S_2SCH_2S)Cp^*UI_2$. The open coordination site in $(Cp^*{}_2Mo_2S_4)Cp^*UI_2$ allows for the incorporation of an additional metal, leading to the formation of heterotrimetallic hemi-cubane species that serve to probe the role of transition metal dopants in redox-active metal supports. The methylene backbone in $(Cp^*{}_2Mo_2S_2SCH_2S)Cp^*UI_2$ restricts reactivity to one face of the dimer, and is a good model for the edge site of MoS_2. With these complexes in hand, we aim to provide molecular insight into the interactions between group(VI) chalcogenide materials and actinide ions.

15. **Homogeneous Electrocatalytic Reduction of Nitrate by an Iron Complex in Water**
    Presenter: Kaye Kuphal (Kara Bren)
    Department of Chemistry, University of Rochester, Rochester, NY
    Abstract. The excessive concentration of nitrate in many natural bodies of water due to fertilizer usage to support the human population[1] is an environmental and health concern. As such, it is imperative to chemically transform nitrate into benign or industrially usable

nitrogenous compounds and thus mediate these issues. Nitrate reduction chemistry is difficult to perform given nitrate's kinetic stability and weak metal ligating properties. Furthermore, a number of reactive intermediates and products can be formed from its reduction, complicating studies on catalysis. Very few molecular compounds are reported to reduce nitrate, although activity has been shown by a few cobalt and chromium complexes. Here, we report electroreduction of nitrate using an iron electrocatalyst (FeN_5H_2) with a pentadentate ligand, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene. FeN_5H_2 was previously reported by our group to perform nitrite reduction in water and now is employed to catalyze the reduction of nitrate. This system is novel for employing a homogeneous iron catalyst at near-neutral pH in buffered water. Effects of the buffer on activity are reported, and the multielectron reduction of nitrate to hydroxylamine and ammonium is demonstrated.

16. **Bioinspired Photochemical CO_2 Reduction in Water Using the Synthetic MiniEnzyme CoMC6*a**
Presenter: Karishma B. Ramesh (Kara Bren)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Nature has mastered CO_2 reduction through photosynthesis, where plants efficiently harness sunlight to reduce CO_2 into energy-rich organic molecules. Despite significant advances in catalysis, replicating this process remains a major challenge due to the inherent thermodynamic and kinetic barriers to CO_2 activation. Moreover, achieving efficient CO_2 reduction in aqueous environments under light-driven conditions is particularly difficult due to the competing hydrogen evolution reaction, which is often exacerbated by activity of the photosensitizer. In this context, biomolecular catalysts offer an exciting nature-inspired approach, as they employ the active site architecture and secondary coordination environments of natural enzymes to enable selective, multi-electron transformations under mild conditions. In this work, we investigate one such biomolecular catalyst for photochemical CO2 reduction activity, cobalt mimochrome VIa (CoMC6*a), a synthetic mini-enzyme designed to mimic key features of natural metalloproteins. Paired with $[Ru(bpy)_3]^{2+}$ as a photosensitizer, CoMC6*a demonstrates selective CO production in optimized conditions, achieving turnover numbers of up to 400. This poster presents the photochemical CO_2 reduction activity of CoMC6*a with a parallel aim of understanding the factors that influence its catalytic selectivity. Specifically, we demonstrate how variables such as pKa of the exogenous proton donor, light intensity, and the concentrations of key system components affect the catalytic behavior to control selectivity of CO over H_2 production.

17. **Synthesis of tetra-porphyrin tubes for catalysis and host-guest chemistry**
Presenter: John Pinti (Timothy Cook)
Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY
Abstract. With the goal of moving away from coordination driven self-assembly, due to cost and limited abundance of precious metals (Rh, Ir, Ru), our lab is interested in exploring covalently linked porphyrin prisms for the use of small molecule activation and host-guest chemistry. To this end, we have synthesized a tetra-porphyrin tube with alkyl-pyridinium linkers by using tetra-3-pyridyl porphyrin and tetra-3-bromomethylphenyl porphyrin as starting materials. The free-base tube (FB4-tube) was characterized using 1D NMR, 2D NMR,

HR-MS, UV-Vis, and single crystal Xray diffraction. This architecture can be post-synthetically metalated with zinc(II) and cobalt(II) resulting in tetra-nuclear cores. We are also able to synthesize hetero-bimetallic prisms by metalating the two starting materials prior to the synthesis of the tube. We evaluated the tube as a homogenous ORR catalyst. The Co4-tube showed a $E^{cat}_{1/2}$ value of –1.0 V versus FcH^+/FcH. Additionally, porphyrin cages with large cavities have been used to sequester pollutants and other organic molecules like fullerenes. With our tube, encapsulation of C60 and C70 occurred with high binding affinity, which was verified via NMR and HR-MS. Due to the large cavity of the tube, the fullerenes sit off-centered, breaking the symmetry to C_{2v} from D_{2h}.

18. **Stabilizing High-Potential Mn(III) for Diverse Oxidative Chemistry**
Presenter: John Noel Maape (David Lacy)
Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY
Abstract. Manganese(III) possesses an intrinsically high redox potential, which is the driving force behind its crucial role in biological oxidation processes, such as photosynthetic water splitting and lignin degradation. However, this high potential also makes mononuclear Mn(III) species highly unstable in synthetic environments, leading to their rapid disproportionation or uncontrolled redox reactions. To address this challenge, we present a novel strategy that enables the stabilization of mononuclear Mn(III) halide and pseudohalide complexes without compromising their oxidizing power. This poster explores some of our recent findings in the consequences of this discovery including C–H functionalization and other intriguing inorganic phenomena.

19. **Semi-hydrogenation of alkynes catalyzed by Copper Iminopyridonate**
Presenter: Jin Hyeok Yoon (Rose Kennedy)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. The semi-hydrogenation of alkynes— selectively reducing a C-C triple bond to a double bond— is a key transformation in pharmaceutical development and industrial polymer synthesis. However, achieving high diastereo- and chemo-selectivity (avoiding over-reduction to alkanes) while catalyzing a wide range of alkyne classes remains a significant challenge. Traditionally, palladium-based catalysts have been mostly explored due to their high reactivity and broad applicability. Despite these advantages, their high cost and toxicity raise concerns for sustainable and large-scale industrial applications. Recently, copper-based catalysts emerged as a promising alternative, offering a more environmentally friendly and cost-effective solution. Additionally, studies have shown that the reactivity and selectivity of copper-based catalyst systems can be fine-tuned by modifying the ligand environment, enabling diverse catalytic behavior. We hypothesized that the (imino)pyridone copper complex can selectively reduce alkyne *via* a pyridone-O-assisted hydride delivery mechanism. Based on our preliminary results, we propose that the coordination between the pyridone oxygen and ammonia borane generates copper-hydride species. The hydride in this species then initiates migratory insertion to the alkyne, resulting in a copper-vinyl intermediate. With the addition of water, the intermediate undergoes accelerated protonolysis to yield the desired alkene products. This work aims to open a new avenue for designing efficient and selective hydrogenation reactions using Earth-abundant metals.

20. **Mechanistic investigations of iron-catalyzed reductive N-heterocycle formation**
Presenter: Jair Powell (Tom Driver)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. This poster examines three iron-catalyzed reductions of nitroarenes or *N*,*O*-heterocycles to afford different *N*-heterocycles using silane as a terminal reductant. Experiments were performed that provided insight into the mechanisms of these reactions. The resulting data were used to determine their rate equations, activation parameters, and the presence of any kinetic isotope effects. This, in turn, helped elucidate details on the catalytic cycles and their turnover-limiting steps, demonstrating the effect of changing the structure of the different *N*-aryl starting materials on the identity of the turnover-limiting step of the reaction.

21. **Metal-organic Frameworks for PFAS Abatement**
Presenter: Irin Aby (Brandon Barnett)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Per- and poly-fluoroalkyl substances (e.g., PFOA, PFHxA, GenX, PFOS) are widely used in materials such as upholstery, fire-fighting foams, food processing and packaging, textiles, semiconductor industry, etc. These are environmentally persistent, bio-accumulative, and potentially carcinogenic. Accordingly, there is a pressing need for materials that can mediate the selective capture and degradation of these chemicals from aqueous systems. Our research addresses this challenge by using a class of sorbent materials known as metal–organic frameworks (MOFs). This presentation will discuss the capture of perfluorooctanoic acid (PFOA) using two zinc-based MOFs. These materials can capture PFOA at low concentrations (parts per billion) from water and degrade PFOA into carbon dioxide and an alkane byproduct at fairly low temperatures. Efforts to regenerate the material for reuse will be discussed, as will insights into the mechanisms of uptake and degradation.

22. **A Tale of Metalation: Is Charge Incompatibility a Factor in (Medadi)M Syntheses?**
Presenter: Heather A. Arnold (Peter Wolczanski)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
Abstract. Previous work in these laboratories included synthesis and reactivity studies of first-row metals supported by a diamide–diimine chelate, dadi, a redox non-innocent ligand with access to five potential redox states. It was hypothesized that the installation of bulky alkyl groups into the diimine backbone of the dadi ligand could inhibit attack and rearrangement, leading to the synthesis of Medadi. First-Row Metals in columns 4-9 are able to be easily metalated, while columns 10 and 11 display charge incompatibility as predicted by CDVR. As a consequence, Ni(Medadi) is unstable and difficult to prepare and Cu(Medadi) is unable to be prepared.

23. **Modifying Quantum Dot Surface Environment for Improved Charge Transfer**
Presenter: Hannah N. Gorski & Chari Peter (Ellen Matson)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Semiconducting cadmium selenide quantum dots (CdSe QDs) are efficient charge carriers for applications such as photocatalytic H_2 generation but understanding the mechanisms behind charge transfer events occurring at the QD surface remains a challenge.

Our group has utilized CdSe QDs in conjunction with a wide variety of techniques to gain insight into surface-mediated charge transfer events to various molecular acceptors. Photoluminescence spectroscopy has been used to demonstrate and quantify the efficiency of hole transfer from QDs to a polyoxovanadate alkoxide cluster as a function of surface ligand density. We have also explored the importance of ligand presence and identity in effective photocatalytic H_2 production. Recent results from our lab have begun exploration into electrochemical techniques as a model for charge transfer of QD systems to redox-active mediators. Finding methods to better understand what components of a QD surface environment dictate efficient charge transfer is an ongoing part of our research.

24. **Ligand Design Influencing Stereocontrol in Ring-Opening Polymerization**
Presenter: Gabriel Goertz (Kyle Lancaster)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
Abstract. Zinc- and magnesium-catalyzed ring-opening polymerizations of cyclic esters have demonstrated considerable potential as a pathway to industrially relevant polymers; However, reliable and consistent stereocontrol of resultant polymers remains an area of potential improvement. Accordingly, the 1,8-disubstituted carbazole ligand framework suggests a possible solution: the conformation of a potential catalyst may be partially restricted or "locked" *via* sufficient steric encumberance by 1,8-diaryl substituents, which could introduce controlled tacticity in a zinc-carbazole-catalyzed polymerization. Preliminary results include the synthesis and structure of a bulky trigonal planar Zn(II) species.

25. **Synthesis and Reactivity of Low-coordinate Iron Transition Metal Complexes**
Presenter: Emma E. Lueders (Kyle Lancaster)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
Abstract. Low-coordinate complexes of iron and other first-row transition metals have garnered considerable attention due to their highly unsaturated coordination environments, which leave multiple valence orbitals open or singly occupied. This distinctive electronic structure supports a wide range of chemical reactivity, including substitution, addition, redox processes, and small molecule activation. Moreover, their electronic properties give res to intriguing magnetic behavior, highlighting their potential applications as single-molecule magnets (SMMs) and qubits in quantum computing.

26. **Leveraging a reduced polyoxomolybdate-alkoxide cluster for the formation of a stable U(V) sandwich complex**
Presenter: Dominic Sheils (Ellen Matson)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Polyoxometalates (POMs) have become a popular support for actinide centers. Often crystallizing easily, they allow researchers to develop series of isostructural actinide, lanthanide, and transition metal-containing complexes and characterization by single crystal X-ray diffraction allows the co-ordination preferences of actinides to be probed. However, a significant limitation of the use of POMs as "ligands" is that, until now, this has limited the solvent choice for synthesis and, more importantly, reactivity studies to water. Herein, we report the use of a preformed lacunary, Lindqvist-type, polyoxomolybdate-alkoxide cluster to provide access to first examples of actinide-polyoxomolybdate sandwich complexes to be

isolated under non-aqueous conditions. Incorporation of metal(IV) cations into this framework was found to "switch on" reversible redox chemistry at the {Mo_5} ligands, with the Zr and Hf containing complexes accepting up to two electrons, while the Th and U derivates accommodate as many as four additional electrons. The enhancement of the redox properties of the cluster upon actinide incorporation is an exciting observation, presenting actinide "doping' as a novel approach for accessing functional redox-active materials. Oxidation of the uranium containing sandwich complex $(TBA)_2[U\{Mo_5O_{13}(OMe)_4NO\}_2]$, chemically or electrochemically, allows facile access to the U(V) centered species, which was characterized both spectroscopically and by single crystal X-ray diffraction. This represents the first example of a U(V)-polyoxometalate sandwich complex to be isolated and structurally characterized.

27. **Adapting Metal-Organic-Frameworks for High Throughput Experimentation**
Presenter: Daniel Nakamura (Philip Milner)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
Abstract. Metal organic frameworks (MOFs) are versatile compounds with many applications including catalysis, gas absorption, and separations. Because of their insolubility, they are difficult to implement in a high throughput experimentation (HTE) setup without the use of expensive, specialized equipment. We have developed novel strategies to make MOFs compatible with HTE, both when using the MOF as a catalyst and when using it as a vessel to deliver a stoichiometric, gaseous reagent.

28. **N-Arylation by Nickel-Mediated Carbonyl Deletion from Carboxamides Enabled by Visible Light**
Presenter: Daniel Akuamoah (Rose Kennedy)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Carbon-nitrogen bonds are ubiquitous across medicinal compounds and natural products making aminations among the most important and utilized reactions in pharmaceutical chemistry. However, methods such as Buchwald-Hartwig amination require strong alkoxide bases and highly tailored ligands for each substrate class. These methods typically require aryl halide electrophiles, which have limited availability compared to carboxylic acid derivatives. The Curtius rearrangement is an alternative method for the generation of amines from carboxylic acids; however, safety concerns associated with explosive azides impede its broad application. We hypothesized that decarbonylative coupling of C and N fragments derived from a single starting material (amides) would circumvent catalyst inhibition by excess nucleophiles while bypassing the need to handle explosive intermediates. However, the two prior reports of this transformation both required high reaction temperatures (>150 °C) and had limited scope. Here in, we present a computation-guided approach for developing a mild carbonyl-deletion strategy that enables intramolecular N-arylation of readily accessible carboxamides, affording di- and triaryl amines. The transformation, facilitated by nickel and visible-light irradiation, proceeds at ambient temperature without the need for basic additives. Mechanistic investigations, supported by the isolation of key organometallic intermediates, validate computational predictions and shed light on the nature of the critical photochemical steps.

29. **S-Nitrosylation Catalyzed by Cytochrome P460**
Presenter: Colby E. 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 thiol (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.

30. **Strongly Reducing sp2 Carbon-Conjugated Covalent Organic Framework Formed by N-Heterocyclic Carbene Dimerization**
Presenter: Clarisse A. Doligon (Philip Milner)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY

Abstract. We have synthesized a covalent organic framework (COF) using N-heterocyclic carbene (NHC) dimerization. The tetraazafulvalene linkages give a strongly reducing property that allows reduction of tetracyanoethylene (TCNE) into radical TCNE· − and dianion TCNE2− that are encapsulated in the COF. The formation of this COF is currently limited by the formation of inorganic byproducts and the fragility of the framework. Dithiadiazafulvalenes linkages possess a promising ability to make a COF with better π-π stacking, milder dimeriza+tion conditions and better stability to make a strong electron donating COF.

31. **A Rigid Macrocyclic Ligand Framework Supports a High-Spin Fe(IV)-Oxo at Ambient Temperature**
Presenter: Chris Hastings (Brandon Barnett)
Department of Chemistry, University of Rochester, Rochester, NY

Abstract. The strategic design of secondary coordination spheres has long been of interest to synthetic inorganic chemistry, particularly for the stabilization and functionalization of high-valent metal–oxo species. While traditional approaches leverage pendant hydrogen-bond donors, exogenous Lewis acids, or steric bulk to modulate reactivity, we demonstrate an alternative strategy based on geometric confinement. By embedding an iron center within a narrow and rigid macrocyclic ligand, we access a high-spin Fe(IV)-oxo complex that is unusually stable at ambient temperatures. This design inhibits reactivity with O-atom acceptors but still allows for reactivity of substrates with acidic E-H bonds. A suite of spectroscopic techniques, including UV–vis, EPR, Mössbauer, IR, and THz spectroscopy, alongside X-ray diffraction and DFT calculations, provides a detailed picture of the electronic structure and reactivity profile.

These findings highlight geometric constraint as a powerful and underexplored axis for tuning high-valent reactivity in synthetic systems.

32. **Hydrogen evolution by C60-functionalized CdSe quantum dots through photoexcited charge transfer**

Presenter: Ben Parasch (David Watson)
Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY

Abstract. The growing energy demand, and the subsequent negative effects from the excessive use of fossil fuels, requires the use of solar-to-chemical energy conversion, including the photocatalytic production of hydrogen (H_2). A promising light-harvesting material for this process includes semiconductor quantum dots (QDs) due to their tunable electronic and surface chemistry properties. To create the most effective photocatalysts, QDs can be coupled with charge-accepting compounds, which extend the charge-separated-state lifetimes, increasing photocatalytic efficiencies and mitigating photoanodic corrosion of the QDs. We have synthesized, characterized, and evaluated the ability of CdSe QDs interfaced with benzoic acid-functionalized C60 (C60BA) to photoelectrochemically reduce H^+ to H_2. We have determined that photoexcited electrons are transferred from the QD to the adsorbed C60BA ligand, which extends the photoexcited charges lifetimes. Chronoamperometry experiments have revealed that the light-initiated mechanism can perform hydrogen evolution via reduction of H^+ to H_2. This presentation will highlight our results on the synthesis, characterization, photophysical properties, excited-state charge transfer, and photoelectrochemical reactivity of the CdSe-C60BA hybrids.

33. **Group IV Transition Metal Dopant Impacts on Proton-Based Reactivity in POValkoxide Clusters**

Presenter: M. Rebecca A. Walls (Ellen Matson)
Department of Chemistry, University of Rochester, Rochester, NY

Abstract. Polyoxometalate (POM) clusters have been invoked as multi-nuclear models of metal oxide surfaces. POMs are readily homogenized to offer an in situ picture of the surface of metal oxides materials, providing experimental insight into the active site and mechanism of reactivity of the surface for informed design. To understand the impact of single atom site defects, we derived a series of group IV transition metal doped polyoxovanadate-alkoxide (POV-alkoxide) clusters, where the dopant is capped with an alkoxide. In investigating the reactivity of hydrogen atoms with these clusters, we noted distinct differences in reactivity despite similar impacts observed in the molecular structures. Whereas Ti(IV) is shown to activate the adjacent vanadyls, promoting an electron led transfer of the hydrogen atom to the neighboring V=O bond, the larger coordination sphere of Zr(IV) can accommodate the binding of an acidic species, and subsequent displacement of the Zr(IV)-bound methoxide. Addition of excess water or stoichiometric 2,2,2-trifluoroethanol results in substitution of the methoxide for a hydroxide or 2,2,2-trifluoroethoxide ligand, respectively. This acidic proton driven substitution of the methoxide is then leveraged to access a relatively stable terminal peroxide bound to a POV-alkoxide supported Zr(IV) center. The reactivity of H_2O_2 at Zr(IV) sites can generate many species, including hydroxide, peroxide, and hydroperoxide terminated species. Isolation of the terminal peroxide complex thus allows for a unique perspective into the impact of the POV-alkoxide support on the activation of hydrogen peroxide at Zr(IV), through the steric protection and increased electron density in the POM core. While the isolated peroxide complex is inactive, the initial methoxy terminated Zr(IV) functions as a precatalyst, generating highly electrophilic oxidation conditions with hydrogen peroxide substrates, with a nucleophilic parameter of 0.09 ± 0.02. Thus, a high selectivity for sulfoxide products (95-99%) in the oxidation of thioethers in acetonitrile is observed, suggesting the highly reduced POV-alkoxide support prevents the over-oxidation of the sulfoxide at Zr(IV).

34. **Progress toward bimetallic copper(I)-mediated electrocatalytic CO_x reduction**
Presenter: Bappaditya Goswami (Rose Kennedy)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Global climate change, driven by the accumulation of CO_2 in the atmosphere, poses a serious threat to humanity, the environment, and the economy. Effective strategies for achieving net-negative CO_2 emissions must combine CO_2 capture and its conversion from chemical fuels to commodity and fine chemicals. Toward this aim, CO_2 valorization strategies are focused on electrocatalytic reduction of CO_2 to produce C1 or C2 products. However, even state-of-the-art systems exhibit low product selectivities and require high overpotentials. To address these issues, a deeper understanding of the mechanisms behind C2 product formation and selectivity is crucial. Herein, we discuss our effort towards the development of binuclear copper complexes by mimicking the heterogeneous copper electrocatalysts as tunable molecular models for elucidating selectivity-controlling features of CO_x reduction to C1/C2 products. The ongoing research on understanding the electronic structure, redox properties, and molecular-level insight into the factors influencing CO coordination and C–C bond formation in copper-mediated electrocatalytic CO reduction.

35. **Oriented MOF Thin Films for Controlling Electrode Microenvironment**
Presenter: Azina Rahmani (Agnes Thorarinsdottir)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Heterogeneous electrocatalysts often suffer from uneven active site distribution and poor mass transport, limiting their selectivity and efficiency. To address these challenges, we are harnessing the well-defined structures and synthetic tunability of metal-organic frameworks (MOFs) to fabricate MOF-coated conductive substrates with optimized microenvironments for electrocatalysis. While MOFs are typically synthesized as powders, practical applications require thin films with controlled thickness and morphology. As crystalline materials, MOFs exhibit direction-dependent properties, making film performance highly sensitive to crystallographic orientation. Although various methods exist for preparing MOF films, they are often limited by poor control over structural features, low reproducibility, weak mechanical stability, and substrate incompatibility. Here, we report the fabrication of oriented MOF films, including ZIF-8 and UiO-66, on a variety of conductive substrates. These films exhibit uniform thickness, full surface coverage, and defined crystallographic orientation. We characterized the films using PXRD, SEM-EDS, AFM, ICP, BET, and CV, and are systematically investigating their transport properties as a function of pore size, crystal structure, orientation, and thickness.

36. **Catalytic Dehydration of Activated Alcohols to Olefins using Fused Oxazolidinebased Transition Metal Catalysts**
Presenter: Aurodeep Panda (William Jones)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. The dehydration of biomass-derived alcohols provides a valuable route to key olefins. However, this transformation is often challenged by competing nucleophilic substitution reactions and the corrosive nature of acid catalysts used in industrial settings. To address these limitations, the Jones Group investigates alcohol dehydration using earth-abundant, environmentally benign transition metals in acid-free conditions. We have synthesized a series of fused oxazolidine (FOX)-based 3d metal complexes of the general formula $[M(FOX)](OTf)_2$ (M = Mn, Fe, Co, Ni, Cu). Among them, the $[Cu(FOX)(MeCN)](OTf)_2$ complex efficiently catalyzes the dehydration of 1-phenylethanol to styrene in 98% NMR yield in 5 hours, with only trace phenolic ethers and styrene dimers as side products. Further proton-NMR kinetic studies demonstrated that small quantities (~300 ppm) of water were crucial for catalyzing the transformation. This study emphasized the importance of accurately computing relaxation times (T_1) and delay times (d_1) to determine NMR yields. This catalytic system extends to a broad range of alcohols, including allylic, tertiary, and benzylic alcohols, as well as natural terpenols like geraniol and nerol. Our mechanistic studies suggest a 'carbocation-based' pathway, where carbocation stability dictates product distribution. To further elucidate the influence of electronic and steric effects on catalytic activity, we are developing a series of quinoline-fused FOX ligands. By introducing a π-system into the ligand framework, we aim to modulate electron density at the metal center and refine structure-activity relationships. Preliminary results show that the copper(II)-triflate complex achieves 88% styrene yield from 1-phenylethanol within 8 hours. Additionally, expanding the substrate scope to aliphatic alcohols, such as tert-butanol, reveals intriguing mechanistic trends compared to our previous studies with pyridine-fused FOX ligands, likely due to the altered electronic and steric properties of the quinoline moiety.

37. **Positional Tuning of Anchoring Groups to Enhance Energy Transfer in CdS QD–Zn-Porphyrin Diads**
Presenter: Ashrumochan Gouda (David Watson and Timothy Cook)
Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY
Abstract. Cadmium sulfide (CdS) quantum dots (QDs) are nanoscale semiconductors known for their tunable optical properties, strong photoluminescence, and high potential in solar energy conversion and photocatalysis. Their ability to absorb visible light efficiently makes them attractive materials for energy-related applications. On the other hand, porphyrins are planar, conjugated organic molecules with exceptional redox versatility, widely explored in electrocatalysis. Combining CdS QDs with porphyrins forms hybrid nanostructures that benefit from synergistic interactions, including improved light harvesting and enhanced charge separation. In this study, we report the synthesis and photophysical analysis of CdS QDs functionalized with two isomers of zinc porphyrins: 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin zinc (Zn-4MCP) and 5-(3-carboxyphenyl)-10,15,20-triphenylporphyrin zinc (Zn3MCP). Using steady-state fluorescence and time-resolved techniques, including time-correlated single photon counting (TCSPC), we investigated their emission behavior and energy transfer dynamics. The results reveal that CdS/Zn-4MCP hybrids exhibit faster

photoluminescence decay compared to their Zn-3MCP counterparts, indicating a more efficient energy transfer process likely due to stronger binding interactions with the QD surface. This efficiency is attributed to the anchoring behavior of carboxyl groups: the para-substituted Zn-4MCP shows more favorable surface orientation and higher loading onto CdS QDs than the metasubstituted Zn-3MCP. Energy transfer studies further confirmed the dominance of Förster-type interactions in the system and demonstrated that Zn-4MCP facilitates more effective energy transfer. These insights emphasize the critical role of anchoring group position in governing interfacial dynamics and offer strategic direction for designing next generation photocatalysts, particularly for CO_2 reduction applications.

38. **Octahedral M_6L_4 Coordination Cages of Co(II) and Ni(II) as paraSHIFT MRI Probes**
Presenter: Aruni Dissanayake (Janet Morrow)
Department of Chemistry, University at Buffalo, The State University of New York, Amherst, NY
Abstract. Highly symmetric, rigid, paramagnetic metal-organic cages with a large number of magnetically equivalent protons represent a powerful approach for designing paraSHIFT probes with enhanced sensitivity. In this study, octahedral M6L4-type metal-organic cages incorporating high-spin Co(II) or Ni(II) were prepared towards the development of paramagnetic coordination cages as MRI probes. Analogous bis-acylhydrazone Co(II) or Ni(II) complexes were also prepared for comparison of solution properties and structure with that of the coordination cages. Single-crystal X-ray analysis of the Co6L4 and Ni6L4 cages reveals that the six Co(II)/Ni(II) metal centers occupy the vertical positions of the octahedral framework, each coordinated by two planar tridentate N2O chelators, giving rise to a M6L4-type coordination cage. Similarly, the bis-acylhydrazone Co(II) or Ni(II) complexes also exhibit six- coordinate metal centers, with similar coordination environment around the metal centers. Solution 1H NMR studies showed sharp resonances for the Co(II) complexes and cages with nearly identical shifts dispersed within a range of +250 ppm to -72 ppm. Ni(II) complexes showed somewhat broadened proton resonances with the cage spectral linewidth larger at 500 mHz. Furthermore, the coordination cages were inert towards transmetallation or treatment with competing ligands. Encapsulation studies showed that simple molecules such as tetraethylammonium or tetraethyl phosphonium were guests within the Co(II) or Ni(II) cages. The lower limit of detection and high kinetic inertness suggest that the coordination cages are promising for further development as paraSHIFT probes.

39. **Co(II) and Fe(II) Macrocyclic Complexes as Anion Responsive paraSHIFT Probes**
Presenter: Anwita Roy (Janet Morrow)
Department of Chemistry, University at Buffalo, The State University of New York, Amherst, NY
Abstract. Paramagnetic chemical shift (paraSHIFT) agents enable frequency-encoded magnetic resonance imaging (MRI) of biochemical events, providing distinct spectral signatures for activated versus inactivated probes. While lanthanide-based paraSHIFT agents dominate the field, first-row transition metal complexes offer sustainable, potentially safer alternatives, though challenges remain in controlling solubility, oxidation state, and metabolite responsiveness. We report the design, synthesis, and characterization of sulfonate-functionalized triazacyclononane–with 2- methylpyridine pendants (STAMP) and its high-spin Fe(II) and Co(II) complexes as anionresponsive paraSHIFT agents. Both complexes feature an open coordination site for inner-sphere water, confirmed by variable-temperature

^{17}O NMR, with μeff values (Fe: 4.4 BM; Co: 4.3 BM) consistent with high-spin states. Notably, Co-STAMP displayed excellent aqueous solubility at physiological pH (20 mM). Although soluble at up to 10 mM at acidic pH, Fe-STAMP exhibited pH-dependent precipitation above pH 6; however, pyruvate or lactate binding stabilized the complex, restored solubility, and yielded reversible pKa transitions (~5.5, 7.8). ^{1}H and ^{19}F NMR metabolite titrations revealed direct coordination or outer-sphere interactions with lactate, pyruvate, malate, fluoride, and fluoro-lactate, inducing distinct hyperfine shifts. These results demonstrate that targeted ligand design can modulate first-row transition metal paraSHIFT probes for metabolite sensing, highlighting their potential as frequency-encoded MRI agents responsive to physiologically relevant anions.

40. **Realizing Influence of composition and cation distribution on the electrocatalytic capabilities of ternary spinel ferrites**
Presenter: Aida Gueye (Kathryn Knowles)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Ternary spinel ferrites (general formula AFe_2O_4) are promising electrocatalysts for a variety of transformations due to their electrochemical stability and their flexible composition. However, the impact of the identity of the A^{2+} metal cation, and the proportion of A^{2+} and Fe^{3+} ions in, respectively, tetrahedral and octahedral lattice sites (described by their inversion parameter) on the electrocatalytic properties of these materials is not well-understood. Here, we seek to investigate structure-function relationships (i) between the inversion parameter of ternary spinel ferrites and their ability to electrocatalyze a model reduction reaction, and (ii) between their composition and the Bond Dissociation Free Energy (BDFE) of surface O-H bonds. These BDFE values are important chemical descriptors for the ability of the oxide to participate in proton-coupled electron transfer reactions, which are key elementary steps in many electrocatalytic transformations. The electrochemically determined BDFE values (between 64-67 kcal/mol) does not vary significantly with the identity of the A (Co, Ni, Fe or Zn), potentially due to the fact that they correspond to the O-H attached to surface Fe sites. For $ZnFe_2O_4$, we found that small inversion parameters produce the largest catalytic currents for reduction of hydrogen peroxide and yield of hydroxyl radical as detected by a fluorescent assay. We also observe a correlation between the magnitude of the current measured in the presence H_2O_2 and that of the current measured for a redox event assigned to Fe^{3+}/Fe^{2+} reduction observed in the absence of H_2O_2. The data overall indicate that cation inversion controls the electrochemical availability of the catalytically active surface Fe^{3+} sites.

41. **Stabilizing High-Potential Mn(III) for Diverse Oxidative Chemistry**
Presenter: Ankita Kumari (David Lacy)
Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY
Abstract. Manganese(III) possesses an intrinsically high redox potential, which is the driving force behind its crucial role in biological oxidation processes, such as photosynthetic water splitting and lignin degradation. However, this high potential also makes mononuclear Mn(III) species highly unstable in synthetic environments, leading to their rapid disproportionation or uncontrolled redox reactions. To address this challenge, we present a novel strategy that enables the stabilization of mononuclear Mn(III) halide and pseudohalide complexes without compromising their oxidizing power. This poster explores some of our recent findings in the

consequences of this discovery including C–H functionalization and other intriguing inorganic phenomena.

42. **product selectivity in electrocatalytic nitrite reduction by molecular cobalt complexes in water**
Presenter: Afsar Ali (Kara Bren)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. Economic development and a growing population have required the production of artificial fertilizers on a scale that has impacted the global nitrogen cycle, with adverse effects on our ecosystem and human health. The development of new methods for the reduction of nitrite into nitrogen or ammonia is a pathway for the remediation of this toxic product. Copper nitrite reductase (CuNiR) and cytochrome C nitrite reductase (CcNiR) are two enzymes that reduce nitrite into nitric oxide and ammonium at physiological conditions. In CuNiR, aspartic acid provides hydrogen bonding and acts as a proton shuttle during nitrite reduction into nitric oxide. In CcNiR, His, Tyr, and Arg residues play pivotal roles in nitrite reduction to ammonium via the formation of extensive hydrogen bonding with the substrate. Inspired by these enzymes, in this work, we have deployed two water-soluble cobalt molecular electrocatalysts (1 & 2) with an N4 type ligand framework and either an -NH (complex 1) or an - NCH$_3$ (complex 2) in the secondary sphere for nitrite reduction. We have explored electrochemical nitrite reduction to ammonium along with hydroxylamine as a byproduct by complexes 1 and 2 in MOPS buffer at pH 7. In ongoing work, complex 2 shows higher TON values (TON(2)NH3:17000) with FE: 64.0 % for ammonium formation compared to complex 1 (TON(1)NH3: 4700, FE(1)NH3: 14.0 %). On the other hand, complex 1 has shown more selectivity for nitrite reduction into hydroxylamine (TON(1)NH$_2$OH: 48000, EF(1)NH$_2$OH: 95.0 %, TON(2)NH$_2$OH:14000, FE(2)NH$_2$OH: 34.0 %) under similar conditions. We propose that complex 1 stabilizes an NH$_2$OH coordinated intermediate state due to the secondary amine -NH in the secondary coordination sphere being involved in hydrogen bonding to NH$_2$OH, an interaction not possible in complex 2. These results demonstrate the ability to favor the producion of NH$_2$OH or NH$_4^+$ from nitrite in water by making a simple change in the catalyst structure.

43. **A Novel Method for Late-Stage N-Heterocyclic Carbene Functionalization**
Presenter: Abraham Ellenbogen (Rose Kennedy)
Department of Chemistry, University of Rochester, Rochester, NY
Abstract. N-Heterocyclic Carbene (NHC) ligands bound to metal centers have significant applications due to their structural modularity coupled with strong σ-donating character. Over the past decade, symmetric aryl-substituted NHCs have been utilized in nickel-catalyzed cross-coupling reactions. These studies have elucidated the importance of aryl substitution patterns on reactivity at the metal center. In addition, there are preliminary studies with unsymmetrical NHCs suggesting greater tunability and control of the reaction pathways. However, these unsymmetric aryl-NHCs are underexplored due to the lack of robust synthetic routes to ligand synthesis. To overcome this challenge, my work has been focused on the functionalization of NHC-bound nickel complexes via in situ cross-coupling with bench-stable and easily accessible aryl boronic acid nucleophiles. This poster will focus on the discovery and optimization of the nickel-mediated arylation in the 3 positions of the pyridyl moiety on the unsymmetric NHC

ligand, h IPrPy. My studies, supported by ^{1}H NMR, have shown the formation of the desired Ni(0) product, [(h^{I}PrPy$_{3}$-Ph)Ni(0)(cod)], from [(h^{I}PrPy)Ni(II)(-C$_{13}$H$_{8}$$^{\eta}$)]. Future studies will be conducted to appreciate the 3 utility of this methodology for late-stage ligand diversification for transition metal catalysis.

44. **X-ray Absorption Spectroscopic Investigation of Organometallic Systems**
Presenter: Gregory George (Kyle Lancaster)
Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY

Abstract: X-ray absorption spectroscopy (XAS) offers a powerful toolbox to interrogate the molecular and electronic structures of transition metal containing complexes. This work offers a brief primer on select X-ray absorption spectroscopies, i.e. metal and ligand K-edge X-ray absorption near edge spectra (XANES) and metal K-edge extended X-ray absorption fine structure (EXAFS). The utility and limitations of these techniques is discussed and their implementation in collaborative projects is presented. An analysis of the metal and ligand K-edge XANES of a series of PNP-carbazolide cobalt imido complexes demonstrates the capacity of XAS to provide insight into the electronic structure of organometallic systems. In addition, XANES and EXAFS are employed to probe the reaction of a bisthiolate iron(II) complex with dioxygen, including insight into the structure of a reaction intermediate.