

# Ohio Inorganic Weekend

Virtual Conference 2020

November 13 – 14



**Friday November 13<sup>th</sup> 6:30 PM – 8:30 PM**

**Saturday November 14<sup>th</sup> 8:30 AM – 5 PM**

Hosted by Dr. Jimmy Jiang and the Jiang group at the University of Cincinnati

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## Ohio Inorganic Weekend Oral Presentations

### **Friday November 13<sup>th</sup> 6:30 PM – 8:30 PM**

WebEx meeting link:

<https://ucincinnati.webex.com/ucincinnati/j.php?MTID=m07e8e12d9ac4272e2eaef150b9327aeb>

#### **Session 1 – Hosted by Dr. Matt Allen (Wayne State University)**

- |         |   |
|---------|---|
| 6:30 pm | <b>Copper-mediated Direct Fluorination of Alkyl C-H Bonds</b><br><i>Jamey Bower</i><br>The Ohio State University  |
| 6:50 pm | <b>High-Efficiency Photoluminescence in Double Perovskite Phosphors</b><br><i>Matthew Gray</i><br>The Ohio State University   |
| 7:10 pm | <b>Synthesis of Iron(II) Complexes Bearing an NHP<sup>+-/-</sup> Containing Pincer Ligand and their Reactivity Towards H<sub>2</sub> and the Catalytic Hydroboration of C-O Double Bonds</b><br><i>Greg Hatzis</i><br>The Ohio State University |
| 7:30 pm | <b>Exploring the Limits of Dative Boratrane Bonding: Iron as a Strong Lewis Base in Low-Valent Non-Heme Iron-Nitrosyl Complexes</b><br><i>Hai T. Dong</i><br>University of Michigan   |
| 7:50 pm | <b>Computational Raman Study of Organic Adsorbent on Graphene</b><br><i>Sajjad Afroseheh</i><br>Bowling Green State University  |
| 8:10 pm | <b>Enhanced Molecular CO<sub>2</sub> Electroreduction Enabled by a Flexible Hydrophilic Channel for Relay Proton Shuttling</b><br><i>Caroline Williams</i><br>University of Cincinnati  |

## **Saturday November 14<sup>th</sup> 8:30 am – 5 pm**

WebEx meeting link:

<https://ucincinnati.webex.com/ucincinnati/j.php?MTID=m531c423976f409087f270aa8a9c05321>

### **Session 2 – Hosted by Dr. Charles McCrory (University of Michigan)**

- 8:30 am     **Nickel-Templated Reductive Phosphine Substituent Replacement of a Tetradentate Bisamido-bisphosphino Ligand  $^{4\text{Ph}}[\text{PNNP}]^{2-}$**   
                *Kyounghoon Lee*  
                The Ohio State University
- 8:50 am     **Encapsulation of Tricopper Cluster in a Protein-like Cryptand Enables Facile Redox Processes from  $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$  to  $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$  States, Mimicking the Redox Behaviour of Multicopper Oxidases**  
                *Weiyao Zhang*  
                The Ohio State University
- 9:10 am     **Blue Light Photochemistry in the Curious Case of Cyclobutadiene Formation at a Zirconium Center**  
                *P. Minh N. Do*  
                West Virginia University
- 9:30 am     **Meet the Editors with Chemical Science and Dalton Transactions**  
                *Francois Gabbai, Christine Thomas, Jennifer Griffiths*  
Join us for an interactive panel discussion about publishing with editors of two Royal Society of Chemistry journals. Prof. Francois Gabbai, Associate Editor of Chemical Science, and Prof. Christine Thomas, Associate Editor of Dalton Transactions, will share insight into how editors make decisions. They'll give advice how to write your article to meet the standards of high-impact journals and give insight into what goes on "behind the scenes" during the peer review process. Questions can be submitted in advance to [griffithsj@rsc.org](mailto:griffithsj@rsc.org), or bring them to the session to ask directly!
- 10:15 am    Break

### **Session 3 – Hosted by Dr. Shiyu Zhang (Ohio State University)**

- 10:30 am    **Fluorinated  $\text{Gd}^{\text{III}}$ -based Contrast Agent for Magnetic Resonance Imaging Thermometry**  
                *S. A. Amali S. Subasinghe*  
                Wayne State University

- 10:50 am **Three-in-One Catalyst Design: Dramatically Enhancing Electrocatalytic Activity at Lower Effective Overpotentials for CO<sub>2</sub> Reduction by Simultaneously Modulating Three Substituent Effects in a Single Molecular Catalyst Structure**  
*Weixuan Nie*  
University of Michigan
- 11:10 am **Synthesis and Magnetism of Cubic and Distorted 5d<sup>1</sup> Double Perovskite oxides**  
*Victor Barbosa*  
The Ohio State University
- 11:30 am **Origin of Magnetic Anisotropy of the Five Coordinated Co(II) Complexes**  
*Nuwanthika Kumarage*  
Miami University
- 11:50 am Break for lunch

**Session 4 – Hosted by Dr. Nate Szymczak (University of Michigan)**

- 1:20 pm **C-H Bond Activation Facilitated By a Zirconium-Cobalt Heterobimetallic Complex**  
*Nathanael Hunter*  
The Ohio State University
- 1:40 pm **Br-mediated Production of Renewable Biopolymer Precursor from Furfural and CO<sub>2</sub>**  
*Xiao Shang*  
University of Cincinnati
- 2:00 pm **Fatty Acid-like Pt(IV) Prodrugs Overcome Cisplatin Resistance in Ovarian Cancer by Harnessing CD36**  
*Amarasooriya Jayawardhana*  
Kent State University
- 2:20 pm **Modulation of LUMO/Fermi Energy Gap in Polypyridine-based Metal Complexes for Molecular Current Rectification**  
*Samudra Amunugama*  
Wayne State University
- 2:40 pm Break

**Session 5 – Hosted by Dr. Jimmy Jiang (University of Cincinnati)**

- 3:00 pm     **Real-time Viscosity Monitoring in Adhesives using luminescent Cu(I) Phenanthroline Molecular Sensors**  
*Ankit Dara*  
Bowling Green State University
- 3:20 pm     **Reversible Photoresponse in Vanadium(V)-tartrate Clusters Containing a Mixed-valent Intermediate**  
*Kalani D. Edirisinghe*  
Bowling Green State University
- 3:40 pm     **Exploration of Novel Binding Modes in Pincer-Ligated N-Heterocyclic Phosphenium/Phosphido Nickel Complexes**  
*Leah Oliemuller*  
The Ohio State University
- 4:30 pm     **Presentation winner announcement and closing remarks**

## Copper-mediated Direct Fluorination of Alkyl C-H Bonds

*Jamey Bower, Andrew Cypcar, Brenda Henriquez, Chantal Stieber, Shiyu Zhang*

The Ohio State University

Advisor: Shiyu Zhang

Approximately 20% of all new pharmaceuticals contain at least one carbon-fluorine bond, but selectively adding fluorine atoms to organic molecules remains a prominent synthetic challenge. The direct replacement of a C-H bond with a C-F bond is an efficient and atom-economical route to rapidly incorporate fluorine in carbogenic frameworks. We report a new system that accomplishes alkyl C-H fluorination by capitalizing on the electronic structure synergy between copper and fluorine. The first discrete, formally copper(III) fluoride complex, LCuF, was synthesized by oxidation of a copper(II) fluoride precursor, and was fully characterized, including by single crystal X-ray diffraction. Advanced quantum chemical computations (CASSCF) revealed that LCuF is best described as copper(II) bound to a fluorine atom. In accordance with the electronic structure, LCuF performs C-H fluorination of allylic, benzylic, and  $\alpha$ -ethereal C-H bonds (seven examples). Mechanistic experiments reveal that LCuF rapidly activates the C-H bonds of 9,10-dihydroanthracene on par with other high-valent first row metal complexes. Furthermore, LCuF captures carbon-centered radicals generated from homolysis of azobisisobutyronitrile (AIBN) and Gomberg's dimer to furnish the corresponding C-F bond. Together, the data fully support a radical mechanism in which two molecules of LCuF sequentially perform hydrogen atom abstraction and fluorine atom transfer to generate the C-F bond. This report demonstrates that the formal copper(II)/(III) redox couple is suitable to enable the incorporation of fluorine directly into hydrocarbons.

## **High-Efficiency Photoluminescence in Double Perovskite Phosphors**

*Matthew Gray, Jackson Majher, Noah Holzapfel, San Liu, Patrick Woodward*

The Ohio State University

Advisor: Patrick Woodward

The photoluminescent properties of a lead-free double perovskites  $\text{Cs}_2\text{NaInCl}_6$  and  $\text{Rb}_2\text{RbInCl}_6$  doped with  $\text{Sb}^{3+}$  are explored. Both compounds are wide band gap semiconductors comprised of alternating  $[\text{InCl}_6]^{3-}$  octahedra and alkali metal ions. Differences in the host crystals are explored via diffraction methods and through changes in photoluminescent characteristics that arise from localized transitions on  $\text{Sb}^{3+}$  centers. The lower electronic dimensionality in  $\text{Rb}_2\text{RbInCl}_6:\text{Sb}^{3+}$  caused by noncooperative tilting of isolated  $[\text{InCl}_6]^{3-}$  octahedra results in an increase in photoluminescence quantum yield from 79% to > 90% and a red-shifted emission maxima, in comparison to the cubic double perovskite  $\text{Cs}_2\text{NaInCl}_6:\text{Sb}^{3+}$ .

**Synthesis of Iron(II) Complexes Bearing an NHP<sup>+-</sup> Containing Pincer Ligand and their Reactivity Towards H<sub>2</sub> and the Catalytic Hydroboration of C-O Double Bonds**

Greg Hatzis

The Ohio State University

Advisor: Christine Thomas

To facilitate multi-electron chemistry at Earth-abundant first row transition metals, the development of reactive ligands that allow bond activations and subsequent eliminations across metal-ligand bonds has been an active area of research. Such metal-ligand cooperative reactions with iron(II) complexes bound to pincer ligands have been extensively studied, but most examples feature reactivity across iron-nitrogen bonds and there are few examples involving reactivity across iron-phosphorus bonds. Our group has utilized a pincer ligand bearing a central N-heterocyclic phosphonium/phosphido (NHP<sup>+-</sup>) moiety (PPP) to achieve challenging bond activations and catalytic reactivity with cobalt(I) complexes and here we turn our attention to the chemistry of this ligand bound to iron(II). We explore the coordination chemistry and subsequent reductions of the NHP unit when bound to iron, then explore the reactivity of these complexes towards activating H<sub>2</sub> and the catalytic hydroboration of a variety of C-O double bond containing substrates.

## **Exploring the Limits of Dative Boratrane Bonding: Iron as a Strong Lewis Base in Low-Valent Non-Heme Iron-Nitrosyl Complexes**

*Hai T. Dong; Matthew J. Chalkley; Paul H. Oyala; Jiyong Zhao; E. Ercan Alp; Michael Y. Hu; Jonas C. Peters; Nicolai Lehnert*

University of Michigan

Advisor: Nicolai Lehnert

We previously reported the synthesis and preliminary characterization of a unique series of low-spin (1s)  $\{\text{FeNO}\}^{8-10}$  complexes supported by an ambiphilic trisphosphineborane ligand,  $[\text{Fe}(\text{TPB})(\text{NO})]^{+/-}$ . Herein, we use advanced spectroscopic techniques and density functional theory (DFT) calculations to extract detailed information as to how the bonding changes across the redox series. We find that, despite the highly reduced nature of these complexes, they feature an  $\text{NO}^+$  ligand throughout with strong Fe-NO pi-backbonding and essentially closed-shell electronic structures of their FeNO units. This is enabled by an Fe-B interaction that is present throughout the series. In particular, the most reduced  $[\text{Fe}(\text{TPB})(\text{NO})]^-$  complex, an example of a 1s- $\{\text{FeNO}\}^{10}$  species, features a true reverse dative  $\text{Fe} \rightarrow \text{B}$  bond where the Fe center acts as a strong Lewis-base. Hence, this complex is in fact electronically similar to the 1s- $\{\text{FeNO}\}^8$  system, with two additional electrons “stored” on site in an Fe-B single bond. The outlier in this series is the 1s- $\{\text{FeNO}\}^9$  complex, due to spin polarization (quantified by pulse EPR spectroscopy), which weakens the Fe-NO bond. These data are further contextualized by comparison with a related  $\text{N}_2$  complex,  $[\text{Fe}(\text{TPB})(\text{N}_2)]^-$ , which is a key intermediate in  $\text{Fe}(\text{TPB})$ -catalyzed  $\text{N}_2$  fixation. Our present study finds that the  $\text{Fe} \rightarrow \text{B}$  interaction is key for storing the electrons needed to achieve a highly reduced state in these systems, and highlights the pitfalls associated with using geometric parameters to try to evaluate reverse dative interactions, a finding with broader implications to the study of transition metal complexes with boratrane and related ligands.

## **Computational Raman study of organic adsorbent on graphene**

*Sajjad Afroseeh and Alexey Zayak*

Bowling Green State University

Advisor: Alexey Zayak

Surface-enhanced Raman spectroscopy presents a unique and keen approach for studying complex heterogeneous interfaces. Chemical Enhancement (CE) is known to report information about the interfacial electronic coupling, however a substantial learning curve is ahead before that information can be fully understood. The case of Graphene Enhanced Raman Spectroscopy (GERS) appears to be particularly intriguing. A delocalized  $\pi$  electron system of graphene coupled with localized electronic states of organic molecules decorating the surface of graphene introduce a significant challenge for Raman spectroscopy. We present a systematic computational study of Tetracyanoquinodimethane (TCNQ) physisorbed on graphene. The study involves computations of surface-enhanced Raman spectra supported by the electronic structure analysis, focusing on the interfacial charge transfer and electron-phonon coupling. Application of a wide range of external electric biases allows us to modulate the charge transfer across the interface and reveal its role in corresponding changes of Raman spectra. Presented results may enable using Raman as a characterization technique for charge-transfer dipole layers in heterogeneous interfaces.

# Enhanced Molecular CO<sub>2</sub> Electroreduction Enabled by a Flexible Hydrophilic Channel for Relay Proton Shuttling

*Caroline Williams, Amir Lashgari, Jingchao Chai, Jianbing “Jimmy” Jiang*

University of Cincinnati

Advisor: Jianbing “Jimmy” Jiang

The effects of primary and second coordination spheres on molecular electrocatalysis have been extensively studied, yet investigations of third functional spheres are rarely reported. Here we report an electrocatalyst (**ZnPEG8T**) with a hydrophilic channel as a third functional sphere that facilitates relay proton shuttling to the primary and second coordination spheres for enhanced catalytic CO<sub>2</sub> reduction. Using foot-of-the-wave analysis, the **ZnPEG8T** catalyst displayed CO<sub>2</sub>-to-CO activity (TOF<sub>max</sub>) thirty times greater than that of the benchmark catalyst without a third functional sphere. A kinetic isotopic effect (KIE) study, in conjunction with voltammetry and UV-Visible spectroscopy, uncovered that the rate limiting step is not the protonation step of the metallocarboxylate intermediate, as observed in many other molecular CO<sub>2</sub> reduction electrocatalysts, but rather the replenishment of protons in the proton shuttling channel. Controlled-potential electrolysis using **ZnPEG8T** displayed a Faradaic efficiency of 100% for CO<sub>2</sub>-to-CO conversion at -2.4 V vs Fc/Fc<sup>+</sup>. Our work validates a strategy for incorporating higher functional spheres for enhanced catalytic efficiency in proton-coupled electron transfer reactions.

**Nickel-Templated Reductive Phosphine Substituent Replacement of a Tetradentate Bisamido-bisphosphino Ligand  ${}^{4\text{Ph}}[\text{PNNP}]^{2-}$**

*Kyoungsoon Lee, Curtis E. Moore, Christine M. Thomas*

The Ohio State University

Advisor: Christine Thomas

Multidentate phosphine ligands are one of the most versatile ligand platforms used in the field of homogeneous catalysis and organometallic chemistry due to their strong donor properties and tunability. Synthetic strategies have developed along with the increasing demand for phosphine ligands, but it is still challenging to prepare some chelating alkyl-phosphine or cyclized phosphine ligands. Here we report the Ni(II)-templated facile replacement of phenyl substituents on a tetradentate bisamido-bisphosphino ligand  ${}^{4\text{Ph}}[\text{PNNP}]^{2-}$  with alkyl groups. A nickel complex  ${}^{4\text{Ph}}[\text{PNNP}]\text{Ni}$  (**1**) was treated with 3 equiv KH, forming a bisphosphide complex  $\{\text{K}(\text{THF})_x\}_2{}^{2\text{Ph}}[\text{PNNP}]\text{Ni}$  (**2**). The further treatment of the bisphosphide **2** complex with 2.5 equiv MeI formed  ${}^{2\text{Me},2\text{Ph}}[\text{PNNP}]\text{Ni}$  (**3**), an analogue of **1** with one methyl and one phenyl substituent on each phosphine arm. The additional treatment of **3** with 3 KH exclusively expelled phenyl groups by forming a methyl phosphide complex  $\{\text{K}(\text{THF})_x\}_2{}^{2\text{Me}}[\text{PNNP}]\text{Ni}$  (**4**), and the subsequent treatment of **4** with 2.5 MeI formed  ${}^{4\text{Me}}[\text{PNNP}]\text{Ni}$  (**5**). All four P-phenyl groups in **1** were substituted with methyl groups in **5** following a two-step procedure. The treatment of **5** with excess KCN eliminated nickel to form  $\text{H}_2{}^{4\text{Me}}[\text{PNNP}]$  (**6**), and subsequent coordination with  $\text{PdCl}_2$  in the presence of  $\text{NaO}^\circ\text{Bu}$  formed  ${}^{4\text{Me}}[\text{PNNP}]\text{Pd}$  (**7**), demonstrating the versatility of the Ni-templated synthetic method. In addition, the treatment of **2** with 1,3-dibromopropane formed a cyclized complex  ${}^{2\text{Ph,propylene}}[\text{PNNP}]\text{Ni}$  (**8**). Overall, the sequential treatment with KH and alkylhalide replaced phenyl with alkyl substituents, which facilitates the challenging syntheses of multidentate alkyl or macrocyclic phosphine ligands.

**Encapsulation of tricopper cluster in a protein-like cryptand enables facile redox processes from Cu<sup>I</sup>Cu<sup>I</sup>Cu<sup>I</sup> to Cu<sup>II</sup>Cu<sup>II</sup>Cu<sup>II</sup> states, mimicking the redox behaviour of multicopper oxidases**

*Weiyao Zhang, Curtis E. Moore and Shiyu Zhang*

The Ohio State University

Advisor: Shiyu Zhang

Synthetic tricopper clusters have been a prominent synthetic target for (bio)inorganic community over the past few decades, since tricopper centers were identified/proposed as essential active sites for biological reduction of O<sub>2</sub> to H<sub>2</sub>O in multicopper oxidase (MCO) and aerobic hydroxylation of methane in particulate methane monooxygenase (pMMO). Understanding factors governing the redox of tricopper clusters as a single unit is fundamental to their development as biomimetic catalysts in fuel cell technology and functionalization of alkanes. However, the majority of synthetic tricopper clusters reported to date have limited redox capability, and only isolated at a single oxidation state. The redox of Cu<sup>II</sup>/Cu<sup>I</sup>, in an unconstrained solvent-exposed environment, often results in significant geometric rearrangement. Herein, we showed a one-pot reaction of tris(2-aminoethyl)amine, [Cu<sup>I</sup>(MeCN)<sub>4</sub>]PF<sub>6</sub>, and paraformaldehyde affords a mixed-valent [TREN<sub>4</sub>Cu<sup>II</sup>Cu<sup>I</sup>Cu<sup>I</sup>( $\mu_3$ -OH)](PF<sub>6</sub>)<sub>3</sub>. The tricopper cluster is fully encapsulated in a macrocyclic azacryptand TREN<sub>4</sub> ligand, exhibiting several reversible single-electron redox events. The distinct electrochemical behaviors of [TREN<sub>4</sub>Cu<sup>II</sup>Cu<sup>I</sup>Cu<sup>I</sup>( $\mu_3$ -OH)](PF<sub>6</sub>)<sub>3</sub> and its solvent-exposed analog [TREN<sub>3</sub>Cu<sup>II</sup>Cu<sup>II</sup>Cu<sup>II</sup>( $\mu_3$ -O)]Cl<sub>4</sub> suggest that isolation of tricopper core in a cryptand enables facile electron transfer, allowing potential application of synthetic tricopper complexes as redox catalysts. For the first time, a synthetic tricopper cluster was isolated and fully characterized at Cu<sup>I</sup>Cu<sup>I</sup>Cu<sup>I</sup>, Cu<sup>II</sup>Cu<sup>I</sup>Cu<sup>I</sup>, and Cu<sup>II</sup>Cu<sup>II</sup>Cu<sup>I</sup> state, providing structural and spectroscopic models for many intermediates in MCOs. Indeed, the fully reduced [TREN<sub>4</sub>Cu<sup>I</sup>Cu<sup>I</sup>Cu<sup>I</sup>( $\mu_3$ -OH)](PF<sub>6</sub>)<sub>2</sub> can reduce O<sub>2</sub> under acidic conditions. Recent study showed that the protonation of [TREN<sub>4</sub>Cu<sup>I</sup>Cu<sup>I</sup>Cu<sup>I</sup>( $\mu_3$ -OH)](PF<sub>6</sub>)<sub>2</sub> by strong acid affords [TREN<sub>4</sub>Cu<sup>I</sup>Cu<sup>I</sup>Cu<sup>I</sup>( $\mu_2$ -OH<sub>2</sub>)](PF<sub>6</sub>)<sub>3</sub>, resembling the fully reduced state of MCOs. Further study is under investigation to enable its binding with O<sub>2</sub>.

# **Blue light photochemistry in the curious case of cyclobutadiene formation at a zirconium center**

*P. Minh N. Do and Carsten Milsmann*

West Virginia University

Advisor: Carsten Milsmann

Reduced early transition metal (ETM) compounds are inherently reactive and undergo distinct transformations compared to late TM analogs. This divergence is advantageous for designing new and complementary stoichiometric and catalytic reactions. State-of-the-art synthetic routes toward low-valent ETM complexes often involve strong chemical reductants, thermal activation of high-valent organometallic precursors, or high-energy UV light and broad-spectrum light source in the case of organozirconium. Our prior work with zirconium complexes containing electron-rich pyridine monopyrrolate (PMP) ligands explored the importance of ligand-to-metal charge transfer (LMCT) bands for visible light excitation that facilitates C-C bond formation by formal reductive elimination at zirconium. These studies prompted the synthesis and photochemical investigation of  $(^{Me}PMP^{Me})_2ZrBn_2$  ( $^{Me}PMP^{Me}$  = 3,5-dimethyl-2-(2-pyridyl)pyrrolide, Bn = benzyl) as a precursor to low-valent intermediates.

Absorption spectroscopy in benzene showed one strong band in the visible region with a maximum at 415 nm ( $\epsilon = 12\ 300\ M^{-1}\ cm^{-1}$ ). Time-dependent density functional theory (TD-DFT) calculations revealed the hybrid nature of the absorption band: LMCT/ligand-to-ligand charge transfer (LLCT). Ligand contribution came from either  $^{Me}PMP^{Me}$  or Bn. Within minutes of exposure to 462-nm LED, the bibenzyl coupling product was formed and opened the coordination sphere for further reactivity. Photolysis in excess diphenylacetylene lead to the unexpected half-sandwich complex  $(^{Me}PMP^{Me})_2Zr(\eta^4-C_4Ph_4)$ , confirmed by X-ray crystallography. Under the same reaction condition,  $(^{Me}PMP^{Me})_2ZrBn_2$  and 4-methylbenzyl bromide generated  $(^{Me}PMP^{Me})_2ZrBr_2$ . Bibenzyl by-products (bibenzyl, 4-methylbibenzyl and 4,4'-dimethylbibenzyl) were identified by GC-MS and various NMR experiments, which suggested a radical mechanism. Preliminary photoreactions with other unsaturated hydrocarbons (phenylacetylene and 1-phenyl-1-propyne) resulted in alkyne trimerization.

## **Fluorinated Gd<sup>III</sup>-based contrast agent for magnetic resonance imaging thermometry**

*S. A. Amali S. Subasinghe, Jonathan Romero, Cassandra L. Ward, Matthew D. Bailey,  
Donna R. Zehner, Prakrut J. Mehta, Fabio Carniato, Mauro Botta, Jason T. Yustein,  
Robia G. Pautler, and Matthew J. Allen*

Wayne State University

Advisor: Matthew J. Allen

Fluorinated probes for magnetic resonance imaging (MRI) are useful in generating images inside living organisms with no observable background signal. Temperature mapping has many medical applications because of the close inter-relationship between tissue temperature, metabolism, and physiology. Existing thermometric methods are mostly invasive or report only absolute temperatures instead of reporting a range of temperatures. Thermometry using MRI is a noninvasive method that can be used to accurately determine heterogeneously distributed temperatures in living organisms. A recent report describing a fluorinated Eu<sup>II</sup>-based redox-active multimodal contrast agent for MRI, that responds to both hypoxia and temperature based on intramolecular fluorine interactions, inspired us to think about isolating temperature detection by using a metal that was not redox active under physiological conditions. We chose gadolinium because Gd<sup>III</sup> can have large relaxivity values to enhance contrast while remaining inert to reduction or oxidation *in vivo*. We hypothesized that if <sup>19</sup>F nuclei are clustered close to Gd<sup>III</sup> ions, that they would interfere with water exchange (and hence contrast enhancement) at low temperatures but not at high temperatures. Our results demonstrate that fluorinated Gd<sup>III</sup>-containing complex modulates water exchange around body temperature or higher. Accordingly, this Gd<sup>III</sup>-containing fluorinated analog increasingly enhances contrast in MRI with increasing temperature between 30 and 40 °C. The observed fit with Solomon Bloembergen Morgan theory for a system that increases water exchange as a function of temperature. This strategy is expected to enable temperature probes for MRI.

**Three-in-One Catalyst Design: Dramatically Enhancing Electrocatalytic Activity at lower effective overpotentials for CO<sub>2</sub> Reduction by Simultaneously Modulating Three Substituent Effects in a Single Molecular Catalyst Structure**

Weixuan Nie, Drew E. Tarnopol and Charles C. L. McCrory

University of Michigan

Advisor: Charles McCrory

The electrocatalytic activity for CO<sub>2</sub> reduction is greatly enhanced for Co complexes with pyridyldiimine-based ligands through the stepwise integration of three synergistic substituent effects: extended  $\pi$ -conjugation, inductive effects from incorporating electron-withdrawing groups, and intramolecular electrostatic effect. The stepwise incorporation of these effects into the catalyst structures results in a series of complexes that show an atypical inverse scaling relationship for CO<sub>2</sub> reduction,—the maximum activity of the resulting catalysts increases as the onset potentials are driven positive due to the ligand substituent effects. Incorporating all three effects simultaneously into the catalyst structure results in a Co complex with dramatically enhanced activity for CO<sub>2</sub> reduction, operating with an estimated intrinsic activity TOF<sub>0</sub> ~ 6.3 s<sup>-1</sup> with > 95% Faradaic efficiency for CO production in acetonitrile using 11 M water as the proton source. This makes it among the most active molecular catalysts reported for the CO<sub>2</sub> reduction reaction. Our work highlights a three-in-one ligand design strategy for molecular CO<sub>2</sub>RR catalysts,—enhancing catalytic ability of a catalyst by tuning three synergistic substituent effects simultaneously in a single catalyst structure.

## **Synthesis and Magnetism of Cubic and Distorted 5d<sup>1</sup> Double Perovskite oxides**

Victor Barbosa, Phuong Tran, Jie Xiong, Patrick Woodward

The Ohio State University

Advisor: Patrick M. Woodward

Double perovskites oxides containing 5d<sup>1</sup> cations in the B-site are known for being highly influenced by spin-orbit coupling, which leads to exotic magnetic behavior. The magnetic behavior in double perovskites is highly dependent on the bond angles and bond lengths. Most cubic at room temperature 5d<sup>1</sup> double perovskites oxides, such as Ba<sub>2</sub>NaOsO<sub>6</sub> ( $T_c \sim 7K$ ) and Ba<sub>2</sub>MgReO<sub>6</sub> ( $T_c \sim 18K$ ) are ferromagnetic. Surprisingly, isostructural and isoelectronic Ba<sub>2</sub>LiOsO<sub>6</sub> ( $T_N \sim 8K$ ) is antiferromagnetic. Furthermore, previous reports on double perovskites containing 5d cations have shown that distorting the crystal structure from the ideal cubic lattice significantly impact the magnetic properties of the material. For example, substituting barium by strontium induces an out-of-phase tilting along the c-axis, which lowers the symmetry from  $Fm\bar{3}m$  to  $I4/m$  and changes the magnetic ground state from an antiferromagnet to a spin glass in Sr<sub>2</sub>LiOsO<sub>6</sub> ( $T_g \sim 30K$ ). In this work, synthesis, magnetic properties and low-temperature neutron structures of Ba<sub>2</sub>NaOsO<sub>6</sub>, Ba<sub>2</sub>LiOsO<sub>6</sub> and Sr<sub>2</sub>LiOsO<sub>6</sub> are reported, in order to accurately determine the crystal structure near their magnetic transition temperatures.

## **Origin of magnetic anisotropy of the five coordinated Co(ii) complexes**

*Nuwanthika Kumarage and David Tierney*

Miami University

Advisor: David Tierney

Five coordinate cobalt(II) complexes have garnered interest recently for applications as magnetic materials, owing to inherently large magnetic anisotropy. However, the relationship between physical and electronic structure for five-coordinate Co(II) complexes remains only moderately understood. We will present a determination of the orientation of the magnetic axes of three five-coordinate Co(II) complexes - [TpPh,Me)Co(maltolato)], [(TpPh,Me)Co(thiomaltolato)], and [TpPh,Me)Co(thioguaia col) - using  $^1\text{H}$  NMR relaxation measurements. Calculation of the electron correlation time for each proton was carried out, matching the measured T1, while varying the orientation of the magnetic z-axis, using a modified version of the Solomon-Bloembergen-Morgan relationships. We find that the orientation of the principal magnetic axis of the complex in solution is not correlated directly with the geometry implied by the crystal structure. The results demonstrate that the apparent orientation of the principal magnetic axis of all three complexes is highly sensitive to the presence or absence of fluxional behavior.

## C-H Bond Activation Facilitated By a Zirconium-Cobalt Heterobimetallic Complex

*Nathanael Hunter, Elizabeth Lane, Kathryn Gramigna, Christine Thomas*

The Ohio State University

Advisor: Christine Thomas

By incorporating a Lewis acidic early transition metal and an electron-rich late transition metal into a single metal complex, a polar metal-metal bond is formed. A bis(phosphinoamide) zirconium/cobalt complex has been synthesized and has been shown to be active toward a variety of bond cleavage reactions, including C-H bonds, such as the ortho-C-H bonds of pyridine derivatives and the C-H bonds of terminal alkynes. The products of these oxidative cleavage reactions have been characterized and provide insight into the reactivity of these complexes.

## **Br-mediated production of renewable biopolymer precursor from furfural and CO<sub>2</sub>**

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Advisor: Yujie Sun

Lignocellulosic biomass valorization to renewable polymer unit 2,5-furandicarboxylic acid (FDCA) is highly desirable to replace petroleum-derived terephthalate acid monomer. However, the conversion from lignocellulose to 5-hydroxymethylfurfural (HMF) as the FDCA precursor is still challenging. On the other hand, the use of CO<sub>2</sub> as a feedstock for biomass valorization is also highly attractive to reduce greenhouse gas emissions. Herein, we use the industrially produced furfural as the starting material and incorporate with CO<sub>2</sub> to synthesize FDCA. Furfural is first converted to furoic acid through a facile electrochemical oxidation step and then to ethyl 2-furoate by an esterification process. Then, in order to efficiently react with CO<sub>2</sub>, the target C-H bond in ethyl 2-furoate was brominated first and then react with CO<sub>2</sub> through a facile electrochemical carboxylation in ambient conditions to produce 2-ethyl ester-2,5-furandicarboxylic acid. The subsequent hydrolysis or esterification produce FDCA or 2,5-furandicarboxylic acid diethyl ester, respectively, which are both highly desirable feedstocks in polymer industry. Our work realizes the biomass upgrading combined with CO<sub>2</sub> utilization, and more synthesis can be promisingly anticipated.

**Fatty acid-like Pt(IV) prodrugs overcome cisplatin resistance in ovarian cancer by harnessing CD36**

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Advisor: Yaorong Zheng

This is the first study of engineering mitochondria-damaging fatty acid-like Pt(IV) prodrugs (FALPs) to harness CD36, a fatty acid translocase, to treat drug resistant ovarian cancer. Mitochondria-damaging therapeutics have been proven effective against drug resistant ovarian cancer cells, but their systematic toxicity is higher. To lower the toxicity and increase the therapeutic window, there is a need to generate mitochondria-damaging therapeutics with high specificity against ovarian cancer cells. CD36 is a transmembrane protein responsible for facilitating uptake of free fatty acids, and it is upregulated in ovarian tumors. We hereby employed Pt(IV) prodrugs that mimic the fatty acid structure and act as “Trojan horse” to exploit CD36 for ovarian cancer treatment. First, the CD36-dependent cell entry of FALPs was confirmed by graphite furnace atomic absorption spectroscopic (GFAAS) analysis using ovarian cancer cells with different levels of CD36 expression. Unlike fatty acids that fuel lipid metabolism, these FALPs induce mitochondrial damage and kill ovarian cancer cells. In particular, we found that FALPs are being activated and release cisplatin in mitochondria upon reduction by cytochrome c, and therefore, FALPs induce mitochondrial damage and eliminate chemoresistant ovarian cancer cells. Mitochondrial accumulation and activation of FALPs were attested using HPLC studies, fluorescein imaging, and GFAAS analysis. Corresponding mitochondrial damages were validated by MitoSOX and Mitostatus flow cytometric analysis. Finally, the high potency against chemoresistant ovarian cancer cells was confirmed by cell viability assays. Overall, this work demonstrates an innovative design that allows for selective activation of mitochondria-damaging Pt therapeutics at chemoresistant ovarian cancer cells.

**Modulation of LUMO/Fermi Energy Gap in Polypyridine based Metal Complexes  
for Molecular Current Rectification**

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Advisor: C. N. Verani

Molecular electronics is the concept of using molecules as the major building blocks of electronic devices. Molecules can show conductor, rectifier or insulator like behavior in electronic components. The Verani group is mainly focused on understanding electron transfer in complexes that can act as molecular rectifiers which allows directional electron mobility. Our approach is to use the Langmuir-Blodgett technique to deposit well-ordered monolayers of metallosurfactants on solid substrates and to study their molecular electronic properties. In a molecular rectifier, the Fermi energy level of the electrode should have comparable energy with the frontier molecular orbitals of the metallosurfactants under an applied bias potential. We hypothesize that asymmetric placement of the electroactive moiety will lead to molecular rectification in junctions that involve  $[M^{II}\text{-terpy}^0]$ ,  $[M^{III}\text{-terpy}^0]$  and  $[M^{III}\text{-terpy}^{-1}]$  states. This research project involves synthesis of symmetric terpyridine based Ruthenium(II), Cobalt(II) and Iron(II) complexes. Cyclic voltammetry results indicate that these complexes show metal oxidation at ca. 0.8 V vs ferrocene for symmetric Iron(II) and Ruthenium(II) species and ligand reduction peaks at -1.6 V. The difference between oxidation and reduction potentials suggest that  $[\text{Fe}(\text{terpyOC}_{18})_2](\text{PF}_6)_2$  complex can act as molecular rectifiers in junctions involving  $\text{IM}^{II}\text{-terpy}^0$  and  $\text{IM}^{III}\text{-terpy}^{-1}$  states. The Cobalt(II) complex shows two peaks at -0.1 V and -1.2 V vs ferrocene which are attributed to Co(III)/Co(II) process and Co(II)/Co(I) reduction respectively. Current-Voltage studies of symmetric  $[\text{Co}(\text{terpyOC}_{18})_2](\text{PF}_6)_2$  and  $[\text{Fe}(\text{terpyOC}_{18})_2](\text{PF}_6)_2$  shows asymmetric curves implying those can show molecular rectification behavior. However, the  $[\text{Ru}(\text{terpyOC}_{18})_2](\text{PF}_6)_2$  complex indicate a molecular insular behavior due to higher HOMO-LUMO energy gap of the molecule.

**Real-time viscosity monitoring in adhesives using luminescent Cu(I) phenanthroline molecular sensors.**

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Advisor: Alexis Dee Ostrowski

Optical probes such as  $[\text{Cu}^{(\text{I})}(\text{dmp})_2]$  ( $\text{dmp} = 2,9\text{-dimethyl-1,10-phenanthroline}$ ) have been utilized by our group in the past for sensing the viscosity of polymers. An increase in the lifetime of the excited state was correlated to greater viscosity of the polymer. This was attributed to a known Jahn-Teller distortion in the  $[\text{Cu}^{(\text{I})}(\text{dmp})_2]$  geometry from tetrahedral in the ground state to square planar in the excited state. However, monitoring the viscosity of polymers in real-time remains a challenge. This is especially critical in confined environments where traditional rheological measurements are hard to apply. In this study, we have utilized  $[\text{Cu}^{(\text{I})}(\text{diptmp})_2]$  ( $\text{diptmp} = 2,9\text{-diisopropyl-2,4,7,8-tetramethyl-1,10-phenanthroline}$ ) as an optical probe for real time sensing of viscosity in various adhesives during curing process (viscosity increases) via changes in luminescence. The emission lifetime of the triplet metal to ligand charge transfer (3MLCT) state of  $[\text{Cu}^{(\text{I})}(\text{diptmp})_2]$  in epoxy glue increased exponentially similar to viscosity values obtained from oscillatory rheology. The real-time viscosity was also monitored reversibly by emission lifetime as polymer was being swollen (viscosity and lifetime decrease) and unswollen (viscosity and lifetime increase). Monitoring emission lifetime unlike absorption lifetime in our previous study allowed us to even measure viscosity in opaque samples such as  $[\text{Cu}^{(\text{I})}(\text{diptmp})_2]$  in Gorilla Glue, which depicted the same correlation. We have also compared these lifetime changes using  $[\text{Ru}^{(\text{II})}(\text{bpy})_3]$  ( $\text{bpy} = \text{bipyridine}$ ) as a standard.  $[\text{Cu}^{(\text{I})}(\text{diptmp})_2]$  showed not only higher emission lifetime but also more ubiquity as a real-time viscosity sensor.

**Reversible photoresponse in Vanadium(V)-tartrate clusters containing a mixed-valent intermediate**

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The photochemistry of polyoxovanadates has been studied using electrochemistry, X-ray crystallography, gas chromatography, FTIR and electron paramagnetic resonance (EPR) spectroscopy. These materials show potential as photoresponsive catalysts that can operate in an aqueous environment. The photoreduction reaction of V(V) to V(IV) in the respective tartrates is presented and discussed. Additionally, it is possible to use light to switch between different oxidation states through the presence of a mixed valence [V(V)/V(IV)] intermediate species. The photoreduction reaction is most likely coupled to a proton transfer event in this system. Irradiation at 365 nm (175 mW/cm<sup>2</sup> LED source) at pH 6.5 in HEPES buffer causes solutions of V(V) tartrate to change from orange yellow through green to brownish purple, developing a characteristic three-band absorption spectrum with maxima corresponding to a V(IV) photoproduct. The crystal structures as characterized by X-ray crystallography reveals that the initial V(V) species is tetranuclear Na<sub>5</sub> [V<sub>4</sub>O<sub>8</sub>(2R,3R)-tart] ((2S,3S)-tart)•11H<sub>2</sub>O, and the final photoproduct as dinuclear Na<sub>4</sub> [(VO)<sub>2</sub>(2R,3R)-tart] ((2S,3S)-tart)•12H<sub>2</sub>O. EPR spectroscopy confirms that reduction from diamagnetic V(V) to paramagnetic V(IV) takes place, with the growth of an 8-line V(IV) hyperfine pattern over time, with the corresponding color change. This suggests that the odd electron is located on a mixed valence intermediate. Cyclic voltammetry shows the transformation from a single one-electron oxidation peak to two one-electron oxidation peaks, supporting the formation of a mixed valence species. Gas chromatography and FTIR spectroscopy showed that CO<sub>2</sub> is produced during photolysis of this system, indicating catalytic oxidation of the hydroxy acid. The process is reversible, suggesting that novel macroscopic photoresponsive effects in molecules and materials may emerge from this photochemistry.

## **Exploration of Novel Binding Modes in Pincer-Ligated N-Heterocyclic Phosphonium/Phosphido Nickel Complexes**

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Advisor: Christine M. Thomas

While N-heterocyclic carbenes (NHCs) have been well-studied ligands for transition metal complexes, their group 14 analogues, which instead incorporate a phosphorus atom in the heterocycle, remain relatively unexplored in comparison. In contrast to NHCs, N-heterocyclic phosphonium cations (NHP<sup>+</sup>s) are weak σ-donors and strong π-acceptors, leading to different reactivity, properties, and potential applications. Similar to nitrosyl ligands, NHPs are thought to interconvert between a phosphonium (NHP<sup>+</sup>) and a phosphido (NHP<sup>-</sup>) through a two-electron process, which may offer a new avenue to unique properties and coordination. Incorporation of an NHP unit into the center of a rigid chelating pincer ligand and coordination to a nickel center has yielded a (PP<sup>Cl</sup>P)Ni(PMe<sub>3</sub>) complex, which can further be treated with a reagent acting as a hydride source to afford a new dimeric nickel complex [(PP<sup>H</sup>P)NiPMe<sub>3</sub>]<sub>2</sub> in which the chloride bound to the central phosphorus is abstracted and a new P-H bond is installed. Structural characterization of this compound reveals an unprecedented structural motif in NHP coordination as the dimerization occurs through a P<sub>2</sub>N<sub>2</sub> core of the two ligands, resulting in a bridging mode that does not involve the two transition metal centers or the hydride fragment. Furthermore, an unusual μ<sup>2</sup>-H ligand bridging between the nickel center and the central phosphorus of the NHP unit is also observed in this structure. Progress toward probing the electronic nature of the P-H bond and exploration of the novel coordination of the NHP framework will be discussed.