Feeding and Powering the World 2018

"PLANNING FOR THE FUTURE"

Oxford, Mississippi
July 16 & 17, 2018
In this collaborative research program funded by the National Science Foundation under grant number OIA-1539035, the expertise of more than six research groups has been combined to address critical, multi-disciplinary challenges in the Water-Energy-Food Nexus: the production of hydrogen, the reduction of carbon dioxide to useable fuel, and the reduction of nitrogen to synthetic fertilizer. Currently, nearly all hydrogen is synthesized from non-renewable carbon sources and carbon dioxide is treated as an abundant waste. Additionally, the Haber-Bosch process for using this hydrogen to reduce nitrogen is energy intensive, which demands further fossil fuel consumption. This program has a long-range approach (1) to establish technologies to extract hydrogen efficiently and economically from water using sunlight; (2) to establish technologies that use electron/proton pairs to directly reduce carbon dioxide to usable fuels at voltages obtainable by DSC devices; (3) to establish technologies that will fix nitrogen at lower temperatures and pressures, and ultimately (4) to link these technologies with high-voltage solar cells to use electron/proton pairs derived from catalytic water splitting to directly produce molecular hydrogen fuel, reduce carbon dioxide to produce fuels and nitrogen in one cell to produce ammonia - a key component of synthetic fertilizer.

State-of-the-art photoelectrochemical (PEC) cells rely on water soluble, high-toxicity lead-based materials to produce hydrogen from water and operate at 12.3% efficiency with a tandem double-layer solar cell. Goals here include: (1) the design and demonstration of practical, low-toxicity organic materials as single-layer solar cell components in PEC devices, and (2) the demonstration of a hydrogen production efficiency nearing 15% - a commercially viable number with low-cost materials. These materials would be a dramatic step forward in the PEC field for hydrogen production. Additionally, viable carbon reduction catalysts and a low pressure, reduced-temperature process for nitrogen reduction are highly desirable technologies. The iterative evaluation of carbon dioxide and molecular nitrogen reduction catalysts is proposed through a research loop including: (1) synthesis of potential catalysts, (2) photophysical analysis, (3) electrochemical analysis, and (4) computational analysis to suggest future catalyst targets. This process will allow for a rapid evaluation of catalyst designs for high reduction activity. Ideally, these processes will be linked to facilitate the formal reduction of carbon dioxide and nitrogen with water and sunlight as inputs.

The reduction of carbon dioxide and molecular nitrogen with hydrogen are critical processes to fuel and food production. Dramatic improvements in PEC hydrogen-producing cell efficiencies with viable, non-toxic materials, as well as the low-pressure, low-temperature reduction of molecular nitrogen are desirable for practical, sustainable fertilizer synthesis. The importance of efforts improving the route to synthetic fertilizer should not be understated. As such, a key aspect to sustainable funding is public awareness and involvement of the community through outreach. The critical goal of heightening public awareness through science cafes and public service announcements directed at the K-12, community college, and university levels as well as at the general public is also a key priority.

The goal of this conference is to bring together in one location all of the faculty, students, and all other participants of this program to report achievements, develop new relationships and collaborations, teach each other new skills, and make plans for future funding opportunities.
Monday July 16

7:00 am - 8:30 am : Breakfast on Your Own
8:30 am - 9:00 am : Pick up Name Tags and Programs and Hang up Posters
9:00 am : Welcome by Prof. Gregory S. Tschumper, Chair of Chemistry & Biochemistry
9:05 am - 9:30 am : Overview of Conference Goals by Senior Personnel
9:30 am - 12:30 pm : Graduate Student Updates and Challenges
   Rebecca Adams, Schmehl, Tulane
   Venkata Adiraju, Hollis, MSU
   Shane Autry, Hammer, Ole Miss
   Dalton Burks, Papish, Alabama
   Robert Lamb, Webster, MSU
   Adithya Peddapuram, Delcamp, Ole Miss
   Pravin Shinde, Pan, Alabama
   Kallool Talukdar, Jurss, Ole Miss
12:30 pm - 4:15 pm : Lunch and Proposal Planning in Groups
4:15 pm - 4:30 pm : Break
4:30 pm – 4:45 pm : Group Photograph
4:45 pm – 6:00 pm : Poster Competition
6:00 pm - 10:00 pm : Dinner, Collaboration, Presentation Preparation, and Networking on Your Own

Tuesday July 17

7:00 am - 9:00 am : Breakfast on Your Own
9:00 am - 11:00 am : Final Proposal Presentations and Open Discussion
11:00 am : Students Dismissed
11:00 am - 4:00 pm : Senior Personnel Meeting
Feeding and Powering the World 2018: Planning for the Future

Senior Faculty at the 2015 SouthEastern Regional Meeting of the American Chemical Society (SERMACS 2015) in Memphis, Tennessee in November, 2015

Senior Faculty at the 255th National Meeting of the American Chemical Society in New Orleans, LA, March 2018
Dr. Russ Schmehl  
Tulane University  
Senior Personnel  

Dr. Charles Edwin Webster  
Mississippi State University  
Senior Personnel
Dr. James Donahue  
Tulane University  
Seed Grant Recipient, Year 2 & 3

Dr. Jonah Jurss  
University of Mississippi  
Seed Grant Recipient, Years 1 - 3

Dr. Elizabeth Papish  
University of Alabama  
Seed Grant Recipient, Years 1 - 3
STUDENT ABSTRACTS
ORAL PRESENTATIONS
Identification of the intermediates and products formed during osmium hydride protonation in acetonitrile

Rebecca Adams,1 Audrey Griffith,1 Guangchao Liang,2 Charles E. Webster,2 and Russell H. Schmehl1

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2Department of Chemistry, Mississippi State University, Starkville, MS 39762

Protonation of a series of osmium carbonyl hydride complexes has been done in acetonitrile by acids of varying strength. Intermediates have been observed by visible and infrared spectroscopy; formation of these intermediates is dependent upon both the solvent and acid strength. ESI-MS and 1H NMR have provided information to identify the intermediates that form over the course of protonation and hydrogen release. Comparison of the carbonyl stretching frequencies obtained through experimental and computational methods further supports the assignment of the species present following protonation. Protonation by triflic acid (pKa = 2.6) in acetonitrile leads to formation of a dihydrogen complex. Equilibrium between triflic acid and the hydride complex is established rapidly, and the dihydrogen complex is stable on the minutes timescale. Decomposition of the dihydrogen complex leads to formation of hydrogen and the triflate complex; the triflate ligand then slowly exchanges with solvent to form an acetonitrile complex. Both the dihydrogen and triflate complexes are light-sensitive, and formation of the acetonitrile complex is accelerated under photolysis. The use of computational data as an aid in identification of intermediates will be emphasized. The study of a metal hydride, which is an intermediate in proton reduction catalysis, has demonstrated how the choice of the proton source and solvent can influence the reactivity of a catalyst. Future investigations of additional complexes that may provide insights on catalytic mechanisms will be discussed.
State-of-the-Art Nitrogen Reduction: Haber-Bosch to Homogeneous back to Heterogeneous

Kiran Adiraju, Min Zhang, Eric Dornshuld, Robert W. Lamb, Guangchao Liang, Charles Edwin Webster, and T. Keith Hollis

Department of Chemistry, Mississippi State University, Starkville, MS 39762

From the Haber-Bosch to homogeneous catalysts for nitrogen reduction, the latest state-of-the-art catalysts will be summarized and recent results will be presented.
Spectroscopic Characterization of Newly Developed Systems and Challenges to Overcome

Shane Autry,¹ Min Zhang,² Jacqueline Gayton,¹ T. Keith Hollis,² Charles Edwin Webster,² Jared Delcamp,¹ and Nathan I. Hammer,¹

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²Department of Chemistry, Mississippi State University, Starkville, MS 39762

The Hammer lab has been focused on photocharactization of newly developed systems that can aid in feeding and powering the world. Probing the photophysics of novel transition metal containing cyclic carbenes gives insight to its potential as a catalysis and a promising bright emitter. These carbene systems show high quantum yield, long lived excited states, and photostability under constant radiation making them ideal systems for emissive displays. Red absorbing indolizine cyanine dyes have also been characterized for applications towards more efficient solar cells. We have shown that progress is being made in regards to the ability of these dyes to absorb further towards the infrared.
Update from the Webster Group

Robert W. Lamb and Charles Edwin Webster

Department of Chemistry, Mississippi State University, Starkville, MS 39762

I will be providing an update on our research involving computational investigations of photocatalysis/systems. I will also discuss some challenges that can make computational examination of such systems unexpectedly difficult.
Studies of the Reduction of Ruthenium-CNC Pincer Photocatalysts for Carbon Dioxide Reduction

Dalton B. Burks, Chance M. Boudreaux, Sanjit Das, and Elizabeth T. Papish

Department of Chemistry & Biochemistry, University of Alabama, Tuscaloosa, AL 35487

The reduction of carbon dioxide to useful products, especially fuel sources, has the potential to help alleviate the world’s energy problem. The Papish group has recently developed catalysts for photocatalytic carbon dioxide reduction based on CNC-pincers composed of N-heterocyclic carbenes and pyridinol. Two ruthenium complexes of this ligand scaffold yield high turnover numbers (TON) and selectivity to produce carbon monoxide. The ruthenium complex of the CNC-pincer with imidazolium-derived NHCs and methyl wingtips—Ru(MeCNC)—has a max TON of 250 over 40 hr. The other ruthenium complex features the CNC-pincer with benzimidazolium-derived NHCs and phenyl wingtips—Ru(PhCNC)—and has a max TON of 311 and a turnover frequency (TOF) of 143 hr⁻¹, which is a record setting TOF. The differences in the catalytic activity of these two catalysts is of interest to help determine how to design improved catalysts. Mechanistic and kinetic studies of these catalytic systems can help elucidate the reasons for the differences in the catalytic activities. Initial work has begun on this project by using a chemical reductant to reduce the catalyst and then reacting the reduced catalyst with carbon dioxide. UV-visible and IR spectroscopies have been employed to observe how the spectra of the catalysts change upon reduction and upon the subsequent reaction with carbon dioxide. Stopped-flow UV-visible spectroscopy will allow for the rate constants of the reaction of carbon dioxide with each reduced catalyst to be determined. Results on the rate constants from initial stopped-flow studies will be presented. Future stopped-flow studies will also be used to measure the rate law and activation parameters (e.g. ΔH‡ and ΔS‡) for the reaction of carbon dioxide with these catalysts and others. The rate law and activation parameters may provide insight into the mechanistic reasons for the differences in catalytic activity and may provide guidance in developing future catalysts.
Solar-to-fuel conversion using visible light directly to power homogeneous catalysts and through single and multifunction’s Dye-sensitized solar cells.

Adithya Peddapuram, Roberta R. Rodrigues, Hunter Shirley and Jared H. Delcamp

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The development of high voltage solar cells is an attractive way to use sunlight to power electrocatalysts for water oxidation, power electrocatalysts for CO₂ reduction to generate carbon-based fuels that are fossil-free, and to power consumer electronics. Through careful molecular dye engineering and redox shuttle pairing our group reported a single junction dye-sensitized solar cell (DSC), employing for the first time an iron redox mediator (Fe(bpy)₃³⁺/²⁺) in conjunction with a novel wide band gap dye (RR9). This system generates a high photovoltage of 1.42 V. To the best of our knowledge, this system is the highest photovoltage achieved by a single junction DSC device without metal oxide doping. This system utilizing RR9/Fe(bpy)₃³⁺/²⁺ redox shuttle pair in a subcell for a sequential series multijunction (SSM)-DSC system, one of the highest known three subcell photovoltage was attained for any solar-cell technology (3.34 V, > 1.0 V per subcell). Furthermore, 2,1,3-Benzothiadiazole and thienopyrroledione (TPD) π-bridges with iron based redox shuttle (Fe(bpy)₃[PB1] [ap2]) were also explored. Although all of these dyes shown photovoltages in the range of 1.20V to 1.42 V they are inherently unstable. The next generation of dyes are being developed to improve stability and photovoltage of the devices by changing the aryl ether donor currently used to weekly donating amine-based donors. To go a step further to power water oxidation and CO₂ reduction SSM-DSC systems capable of exceptionally high photovoltages ranging from 1-9-4.7 V from 2-5 subcells were developed by our group. Judicious dye selection through employing dyes that absorb the entire solar spectrum can be done to maximize photon potential energy in each region of the solar spectrum. This system was found to have a solar-to-fuel conversion efficiency of 2% for the reduction of CO₂ to CO with IrO₂ and Au₂O₃ electrocatalyst, without an external bias. Currently efforts are being made on our group to further optimize this system by carefully selecting near NIR dyes to capture more low energy photons and to minimize energy lost. In an attempt to explore photocatalytic proton reduction, our group also developed and evaluated the first known mononuclear hydrogen production photocatalyst. Our W(pyNHC)(CO)₄ catalyst was capable of converting protons to hydrogen without a co-sensitizer, significantly simplifying the total water-splitting cell assembly. An alternative electrocatalyst catalyst, Mn(bpy)(CO)₃Br, has shown remarkably low overpotentials for proton reduction and possesses a ligand framework capable of being attached to a p-type semiconductor surface, and therefore contributing to a total water-splitting system. Efforts are currently underway to prepare the surface-mounted system.
Progresses and Challenges to Overcome the Difficulties in Improving the Efficiency of Photocatalytic Solar Water Splitting

Pravin S. Shinde,1 James P. Donahue,2 Nathan I. Hammer,4 Arunava Gupta,1 and Shanlin Pan1

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We have been primarily focused on developing efficient, low-cost, and durable photoelectrodes for photoelectrochemical (PEC) water splitting to produce H2 and O2 by simple synthesis methods. For example, we recently used scanning photoelectrochemical microscopy (SPECM) technique to successfully screen cobalt doping in BiVO4 for water oxidation and screening results are validated with the bulk measurements. A Z-scheme water splitting system is formed by combining n-type Co-BiVO4/WO3 photoanode and p-type CuO/Cu2WO4 photocathode in series to generate solar fuel at no external bias. Efficiency of such system is still low and more efforts are needed for improvement. However, there are certain difficulties such as photocatalyst-substrate interface, photocatalyst heterogeneity, higher background substrate current, etc. during SPECM screening that can be overcome using scanning flow cell (SFC). SFC is a micro-electrochemical technique in which electrolyte continuously flows over the sample and can be used to study localized (photo)catalysts for their hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Additionally, we reported a stable solar water reduction performance from MoS2-protected Cu2O photocathode for H2 generation. A simple solution-based approach is used to modify and protect the surface of Cu2O with a thin conformal MoS2 layer. Although, a single MoS2 coating improves the dark current and photocurrent response of Cu2O, its long-term photostability is limited. Moreover, we noticed that certain facets of Cu2O are stable against corrosion. So, efforts need to be done to probe the crystal facets of photoelectrodes such as Cu2O and BiVO4, which are also by far the best electrode materials, to tweak their PEC and stability performance. Materials engineering in terms of nanostructured morphologies offer great promise in efficiency improvement by yielding large surface area causing multiple light scattering events and eventually improving the light absorption. Finally, we need good and non-precious HER/OER co-catalysts to efficiently separate the charge carriers to enhance efficiency.
Update from the Jurss Group

Kallol Talukdar and Jonah W. Jurss

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I will be providing an update on our research involving catalysis and discuss challenges.
STUDENT ABSTRACTS
POSTER PRESENTATIONS
Early Transition Metal CCC-NHC Pincer Complexes

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Early transition metal complexes are of interest for dinitrogen cleavage and functionalization (Nat. Chem. 2010, 2, 30-35; Science. 1997, 275, 1445-1447). Previously, the Hollis group has reported the synthesis and characterization of CCC-NHC Zr(IV), Ti(IV), and Hf(IV) pincer complexes. The reactions of these Group 4 complexes with various reducing agents are under investigation. Our latest results with the prep. and characterization of early metal low-oxidation state CCC pincer metal complexes for binding and reduction of dinitrogen will be presented.
Characterizing the Nature of Intermolecular Interactions in Dimethyl Sulfoxide: A Computational and Spectroscopic Study

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Dimethyl Sulfoxide (DMSO) is a heavily studied molecule due to its non-ideal behavior and important solvent properties. It is known that DMSO has an affinity for self-interaction in solution, but the nature of these DMSO-DMSO interactions in solution are still not fully understood. Here, density functional theory (DFT) calculations are carried out on pure liquid DMSO, DMSO in solution with water, and crystalline DMSO to study the interactions in these different environments. The theoretical spectra were compared to experimental Raman spectra.
Mycorrhizal fungi networks are essential for the nutrient uptake of higher order plant species. These fungi secrete enzymes that allow for the uptake of water, nitrogen, phosphorus, and other minerals needed by the host plant. One of the enzymes that is secreted by the fungi is laccase. This enzyme is known to oxidize para-diphenols through free radical reactions. The active site structure of laccase is made up of copper (II) histidine complexes. The most interesting part of these complexes is the bond between the nitrogen in the imidazole ring of the histidine and the copper at the center of the complex. In order to study the interactions between the copper and the nitrogen in this complex, a model was created: Cu(II)Imidazole$_4$Cl$_2$. The copper-nitrogen intramolecular interactions were studied in both solid and solution form through Ramen spectroscopy, solid form through diffuse reflectance, and in liquid form through UV-Vis spectroscopy. This data was then compared to electronic structure calculations.
Infrared inspection of the catalytic pathways of cobalt(III) oxime thiocyanate complexes in proton reduction to hydrogen; influence of free thiocyanate and acid strength

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The molecular complex [Co(III)(prdioxH)(SCN)2] is catalytically active for water reduction to hydrogen when in its reduced, Co(I), state. Cyclic voltammetry was done in acetonitrile to measure the reduction potentials, indicating that there are two reversible metal-based reductions, followed by a one-electron reduction of the ligand. Visible spectroelectrochemistry as well as cyclic voltammograms at 100 mV/s and intermediate scan rates show the first and second reductions are reversible. However, they become less reversible as the sweep rate is slowed to 10 mV/s. Infrared studies of the molecule show a peak at approximately 2100 cm⁻¹, which is attributed to the coordinated thiocyanate ligands; this frequency is also present in solutions containing the complex and weak acids. The complex begins as an isothiocyanato complex with two S-bound thiocyanate ligands which was determined from a crystal structure of the molecule. Changes in the infrared spectra are observed during reduction without protons present in a solution of acetonitrile, indicating a loss of the thiocyanate ligand and subsequent re-coordination of the thiocyanate ligand upon re-oxidation, affecting no net change. Both the infrared spectra and cyclic voltammograms are affected by the presence of stronger acids such as tosylic acid, suggesting protonation of the complex prior to reduction. Experiments in a solution of acetonitrile compared to experiments in a solution of methylene chloride suggests acetonitrile affects the reduction, possibly by coordinating to the complex. In future work, the intermediates of the first and second reductions will be explored through infrared spectroelectrochemistry with various solvents (acetonitrile, DCM), acids (TCA, TFA, Tosyllic) and the presence of free thiocyanate in solution. The poster will include information on spectroelectrochemical experiments in the presence of different proton sources as well as different solvents will be compared to gain mechanistic insight on the catalytic pathway.
New targets for ruthenium catalyzed CO$_2$ reduction

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New adoptions to the active N-heterocyclic carbene (NHC) and 4-pyridinol-derived ruthenium complexes for photocatalytic CO$_2$ reduction are underway. The current state of this catalyst is selective CO$_2$ to CO formation with 250 turnover cycles over 40h. Further development of this leading catalyst design to gain an understanding of the mechanistic needs for enhanced rate while maintaining selectivity is necessary. A new catalyst, the N,N-dimethyl amino-4-pyidyl analog, has been synthesized and characterized and another ligand, containing 4-trifluoromethylphenyl wingtips, is in the process of being synthesized. Developments to improve longevity are also underway. To achieve this goal, a complex with surface anchoring groups covalently-attached has been targeted and current synthetic progress have been outlined. These new advancements are exciting to further develop the field of selective CO$_2$ reduction.
Durable and Highly Reactive Iron-Oxo Catalyst for Hydrocarbon C-H Bond Functionalization

Lizhu Chen, Xiao-Jun Su, Jonah W. Jurss

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Petroleum and natural gas are important sources of inexpensive hydrocarbons for the chemical and pharmaceutical industries. The selective conversion of C-H bonds into new functional groups under mild conditions is therefore of considerable interest. High-valent non-heme iron-oxo catalysts have been developed as potent oxidants for the functionalization of unactivated C-H bonds. Previous studies have advanced our mechanistic understanding of these versatile intermediates, provided insight into the role of spin state on reactivity, and made strides in product selectivity and substrate scope. However, a significant limitation of synthetic non-heme iron-oxo catalysts is poor stability and low turnover numbers under the harsh oxidizing conditions required of C-H bond oxidation. Polydentate ligands used in previous systems typically utilize oxidatively-weak, aliphatic linking groups and alkyl amine donors that are susceptible to catalyst decomposition. In order to improve catalyst stability while preserving high reactivity, we have developed new catalysts employing oxidatively-rugged tetradeinate ligands comprised of robust aromatic building blocks, which provide cis-labile coordination sites at iron. Using m-chloroperbenzoic acid as the terminal oxidant, a new iron catalyst shows an alcohol-to-ketone (A/K) ratio of 6.6 for cyclohexane oxidation with conversion percentages as high as 80%. Moreover, catalysis towards adamantane oxidation shows remarkable regioselectivity (3°/2° = 48:1) favoring tertiary C-H bonds. Results indicate a molecular Fe(IV)=O intermediate is involved in the catalytic process with a characteristic absorption peak at 750 nm and a half-life of 30 min at room temperature.
Ruthenium CNC Pincer Complexes are Self-Sensitized and Highly Active Photocatalysts for Visible Light Driven Carbon Dioxide Reduction

Sanjit Das,1 Roberta Rodrigues,2 Jared H. Delcamp,2 and Elizabeth T. Papish1

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New ruthenium based catalysts have been designed for light driven carbon dioxide reduction. These catalysts are highly active, robust, and selective for the formation of carbon monoxide preferentially over other side products. This technology can be used to make solar fuels from a greenhouse gas. The ligand scaffold has proven critical for the performance of these catalysts, and must include a pi donor group (methoxy) for optimal rates and catalyst longevity. Structure function relationships in these catalysts will be described. Notably, these catalysts are effective or self-sensitized CO₂ reduction, which has been rare in the literature.
Nickel(II) Pincer Complexes Demonstrate that the Remote Substituent Controls Catalytic Carbon Dioxide Reduction

Shakeyia Davis, Dalton Burks, Robert W. Lamb, Xuan Liu, Roberta R. Rodrigues, Nalaka P. Liyanage, Yujie Sun, Charles Edwin Webster, Elizabeth T. Papish, and Jared H. Delcamp

The production of renewable fuels by the conversion of solar energy into chemical energy is a pressing challenge. Photocatalytic and electrocatalytic conversion of CO$_2$ to usable fuel precursors are two approaches to overcoming these challenges. The two-electron reduction of carbon dioxide to carbon monoxide is an appealing process because CO can be used as a commodity on an industrial scale. Many molecular CO$_2$ reduction catalysts have been reported and commonly use expensive, late-transition metals. Recently, the pyridyl-NHC ligands have gained attention in catalytic systems due to the strong donating ability of the NHC to strengthen the nucleophilicity of the transition metal center and the withdrawing ability of the pyridine ring, allowing electron storage. This promotes the catalytic activity of the complex. In this study, novel Nickel molecular catalysts, which bear a pyridyl-pincer-N-heterocyclic carbene ligand (NHC), have been studied to evaluate the effect of remote substituents on catalytic CO$_2$ reduction. The photocatalytic reduction of CO$_2$ with these complexes has been evaluated by photolyzing with a simulated solar light source.
Low Energy Raman Spectroscopic and Computational Study of Newly-Developed Boron Acid Derivatives

Austin L. Dorris, Hal Vaughan, Daniell L. Mattern, and Nathan I. Hammer

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Three unique boron acid derivatives containing a single B-C bond and either two or three B-O bonds are synthesized for the first time and are studied using Raman spectroscopy and computational chemistry. Experimental Raman spectra are obtained for each molecule with energies down to 50 cm⁻¹, a relatively unstudied energy region for boron-containing compounds (BCCs). Vibrational modes are characterized in the low energy region with special attention paid to motions involving B-O and B-C bonds. Density functional theory was used to obtain simulated spectra for comparison with the experimental data. Motions involving the B-O bonds range between 400 and 1000 cm⁻¹ and B-C modes from between 1200 to 1400 cm⁻¹, depending on the hybridization of the central boron atom. The addition of the third B-O bond changes the hybridization of the boron atom from sp² to sp³ and results in a spectral shift for peaks associated with the B-C stretching modes and new peaks corresponding to additional modes involving boron and the oxygen atoms. This study is amongst the first to characterize vibrations involving boron bonded to three oxygen atoms.
Blocking Recombinations in DSCs:
The Role of TiO₂ Particle Size, Film Thickness, and Surface Modifications

Kayla Foell, Roberta R. Rodrigues, Hammad Cheema, and Jared H. Delcamp

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High voltage dye-sensitized solar cells (DSCs) are becoming novel players in the production of various fuel precursors, such as CO and hydrogen, by powering carbon dioxide reduction, water oxidation, and proton reduction catalysts via sunlight. An important task in order to increase efficiency of DSC devices is to minimize recombination while increasing photovoltage. It has been shown that surface treatment modifications to the TiO₂ electrodes can be performed without negatively effecting fill factor (FF), short-circuit current (J_sc), and open-current photovoltage (V_oc). This can be accomplished by using larger TiO₂ nanoparticles (30 nm, P30) instead of the more commonly used TiO₂ (20 nm, P20). Enhanced photovoltage through decreasing P30 film thickness from 15 µm to 2.5 µm and through using a perfluorooctyltrimethoxysilane (PFTS) post-sensitization treatment has also proven to be an effective method to increase device performance and photovoltage. Similar enhancement of photovoltage effect was also observed with MgO/3 acid capping method. The successful increase in photovoltage was achieved by decreasing diffusion length and decreasing recombination. Based on previous studies which used HD-2-mono Ruthenium dye and Co³⁺/²⁺ electrolyte systems in combination with the PFTS post-staining treatment to yield a high efficiency of 5.4%, we expect the Ruthenium dye (B11) to produce similar results. Through the use of larger TiO₂ particles, thinner cells, and films capable of receiving surface treatment modifications, we hope to fabricate more efficient DSC devices with higher photovoltages.
Fluorescence Lifetime Studies of Donor-π Bridge-Acceptor (D-π-A) Dyes for use in Dye-Sensitized Solar Cells

Leigh Anna Hunt, Roberta R. Rodrigues, Jared H. Delcamp, and Nathan I. Hammer

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Dye-sensitized solar cells (DSCs) are a low cost and promising alternative to standard photovoltaic cells, but one major concern with DSCs is the enhancement of sensitization in the near-infrared. In order to investigate the kinetics of electron injection, fluorescence lifetime measurements were carried out for a series of dyes to evaluate electron injection efficiencies. Fluorescence lifetime studies both in solution and on TiO₂ films provide insights into evaluating the performance of dyes in DSC devices.
Photoelectrochemical Study of Carbon Modified p-type Cu$_2$O Nanoneedles and n-type TiO$_{2-x}$ Nanorods for Solar Water Splitting in Tandem Cell Configuration

Nelly Kaneza, Pravin S. Shinde, Yanxiao Ma, and Shanlin Pan

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Nanostructured photoelectrodes have high surface area and tunable optical and electrical properties that can benefit catalytic reactions such as photoelectrochemical (PEC) reactions involved in solar water splitting. PEC performance of these nanostructured photoelectrodes are usually quantified in a standard 3-electrode configuration under potential-assisted conditions because of the needed overpotentials of the two half-reactions involved in water splitting. There is a need to fully recognize their water splitting potential under unassisted conditions by designing a tandem cell to provide sufficient voltage and power output to split water. Here we present a tandem cell comprised of carbon-modified cuprous oxide (C$_{10}$/Cu$_2$O) nanoneedles and oxygen-deficient titanium dioxide (TiO$_{2-x}$) nanorods for unassisted solar water splitting. The synthesized photoelectrodes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and electrochemical impedance spectroscopy (EIS). The tandem cell performance was analyzed through the analysis of current-voltage responses in different photoelectrodes configurations. The PEC properties of the C$_{10}$/Cu$_2$O nanoneedles coupled with TiO$_{2-x}$ nanorods in a tandem configuration reached a current density of 64.7 µA cm$^{-2}$ at zero bias that can be increased with the increase in external bias. Heterojunction formed by these nanostructured electrodes in intimate contact in the absence of water exhibited 2 µA cm$^{-2}$ UV photoresponsivity at 1.5 V with promising rectifying characteristics of a diode.
Copper-Based Redox Shuttles Supported by Rigid Tetradentate Ligands for Dye Sensitized Solar Cells


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Global energy demand is predicted to double, if not triple, by mid-century. Energy consumption currently relies heavily on fossil fuels, a nonrenewable resource that will become more costly over time. An attractive alternative for accessing sustainable energy is Dye Sensitized Solar Cells (DSC), where sunlight is converted into electrical energy. In DSCs, bidentate copper redox shuttles have been reported as viable substitutes to replace the standard iodide/triiodide electrolyte, which cannot be tuned and involves a two-electron process that lowers cell efficiency. Previous work has optimized bidentate copper complexes with efficiencies slightly lower than the best efficiencies obtained with I^-/I^-3. However, copper redox shuttles are highly tunable through modifications to the ligand framework, allowing optimization and matching of electron transfer thermodynamics and kinetics with a given dye. Attempts to tune copper-based redox shuttles with bidentate donors toward more positive Cu(II/I) potentials often resulted in ligand dissociation in coordinating solvents, such as acetonitrile. Thus, we have developed a rigid tetradentate ligand platform that affords systematic tunability and a stronger chelate effect for improved stability. We present the synthesis and application of new copper redox shuttles supported by rigid tetradentate frameworks in dye-sensitized solar cells.
Theoretical Investigation on the Electronic and Steric Tuning of Catalytic H₂ Evolution by Cobalt Complexes

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Structural modifications of mononuclear cobalt complexes have provided important insights on the catalytic activities in H₂ evolution reaction. The catalytic performances of four cobalt complexes with pentadentate polypyridyl-amine ligands (1, [Co(DPA-Bpy)(H₂O)](PF₆)₃; 2, [Co(DIQ-Bpy)(H₂O)](PF₆)₃; 3, [Co(DPA-1-MPI)(H₂O)](PF₆)₃; and 4, [Co(DPA-3-MPI)(H₂O)](PF₆)₃) were investigated. Experimental results and DFT computations demonstrate that the presence of a planar conjugate bipyridyl unit and its isoquinoline derivative stabilizes the valent Co⁺ species. The incorporation of electron donating group trans to the proposed Co-H species facilitates the proton binding. H-H bond formation is proposed to occur by the heterolytic coupling of Co²⁺-H species. The overall catalytic H₂ evolution is presented as the modified electron transfer (E)—proton transfer (C)—electron transfer (E)—proton transfer (C) (mod-ECEC) pathway.
Au@Pt Nanoparticles on Transparent Electrodes for Spectroelectrochemistry Study of Methanol and Formic Acid Oxidation

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Noble metallic nanoparticles (NPs) such as Au, Ag, and Pt have interesting catalytic and optical properties which play important role in molecular sensing and alternative energy harvesting, conversion, and storage. Pt layers modified on Au surfaces were recently found to have enhanced electrocatalytic activity for methanol and formic acid oxidation. In this study, Au deposited transparent ITO electrode was further modified by Pt for spectroelectrochemistry study of methanol and formic acid oxidation. The thickness of Pt layer was precisely controlled by deposition cycles. 1, 5, 10, 20, 30 cycles of Pt deposition were performed on Au-ITO to have different Pt coverage. Enhanced catalytic activity was found for both methanol and formic acid oxidation with such structure. The oxidation current density was more than 200 times than that on Au-ITO with Au@Pt(30) sample for both methanol and formic acid. In situ dark field scattering electrochemical study of methanol oxidation in 0.1 M NaOH shows Au NPs were anodized at the potential window of methanol oxidation at lower Pt coverage. Au anodization gets weaker and was terminated with increasing Pt thicknesses. The present work provides more insights into fuel cell related study on Au-Pt core shell structure.
Excited-State Proton-Coupled Electron Transfer (ESPCET) with Ruthenium (II) Complexes with 2,2’-bipyridine-4,4’-diol (4,4’-dhbpy) Ligands

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Proton-coupled electron transfer reactions are at the center of many biological processes, including the conversion of water and CO₂ to glucose and oxygen during photosynthesis. Key to reactions that evolve fuels such as hydrogen, formic acid, oxygen and other species is the effect of redox-leveling provided by proton-coupled electron transfer. When an electron is transferred from a system with dissociable protons, the protons become more acidic, and deprotonation is thereby favored. This effectively reduces the formation of higher energy intermediate species in multi-electron transformation processes. Coupling the concept of redox leveling through PCET with light-induced processes is additionally appealing given that light can now be used to generate an excited-state species that is a more powerful reductant and acid than in the ground state, thus driving a cycle of electron/proton transfer forward without the need of thermal energy. Ruthenium polypyridyl complexes have been extensively investigated for their photophysical properties over the past several decades. Adding to the list of excited-state properties is the ability for [Ru(LL)₂(4,4’-dhbpy)]²⁺ complexes to undergo excited-state proton and electron transfer to an acceptor in solution. Upon photoexcitation, the 3MLCT for [Ru(bpy)₂(4,4’-dhbpy)]²⁺ is polarized toward the spectator bipyridine ligands, making the pKₐ of the hydroxyl protons decrease. The combination of photo-acidity and excited-state reducing strength of the complex allows it to transfer both a proton and an electron to an acceptor, such as a mono-quaternerized 4,4’-bipyridine. Of interest in proton-coupled electron transfer research are mechanisms by which ESPCET occurs, namely sequential (ETPT or PTET) or concerted. Investigated here is the mechanism by which a proton and electron are transferred to an acceptor in an aprotic solvent environment from the excited-state of [Ru(bpy)₂(4,4’-dhbpy)]²⁺. Future direction for this work involves coupling the redox leveling effect of our excited-state proton/electron donor to a catalyst system.
Raman Spectroscopic, Computational, and X-ray crystallographic investigation of Intermolecular Interactions in Trimethylamine N-oxide

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Trimethylamine N-oxide (TMAO) is well-known to affect the hydrogen bonding structure of water through the hydrophobic effect. Controlling hydrogen bond strengths and their dynamics could potentially lead to more efficient photocatalytic water splitting reactions. Here, the crystalline structures of TMAO and its perdeuterated analog (TMAO-d₉) were investigated using Raman spectroscopy, X-ray crystallography, and advanced electronic structure theory. X-ray diffraction studies confirmed that the crystal structure of TMAO and TMAO-d₉ are isomorphic and that a phase transition exists from C₂/m to P₂₁/c between 220 K and 100 K. Spectroscopic blue shifts (shifts to higher vibrational energy) were observed in both Raman Under liquid Nitrogen Spectroscopy (RUNS) and high pressure Raman spectroscopy studies. Although agreement between experimental Raman spectra and the results of electronic structure computations performed on individual TMAO molecules was very poor, very good agreement between experiment and theory was obtained when model unit cells were considered. These results yield insight into the degree of interactions between neighboring TMAO molecules in the crystalline state. Specifically, TMAO-d₉'s vibrational spectra are significantly less perturbed than those for TMAO, which suggests weaker interactions between neighboring TMAO molecules when deuterated.
Spectroscopic and Computational Study of Metformin Hydrochloride utilizing Raman Under Nitrogen Spectroscopy to Examine Lattice Structure

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The study of low energy lattice modes can reveal the weak, low energy interactions that are present in crystalline materials. Metformin Hydrochloride (MF) is one of the most widely prescribed drugs for the treatment of type 2 diabetes mellitus due to its ability to lower both basal and postprandial plasma blood glucose. Currently, two polymorphic crystal structures of MF exist, and the lattice structure of both forms has been studied extensively, as polymorphism is a major factor in active pharmaceutical ingredient determination. In this study, we use MF as a model compound for the study of lattice vibrational modes as an indicator of the presence of noncovalent interactions using Raman under Nitrogen Spectroscopy (RUNS).
New Developments in Catalytic H\textsubscript{2}-Formation by Molybdenum Sulfide Clusters

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Well defined molybdenum sulfide clusters with dithiocarbamate (S\textsubscript{2}CNR\textsubscript{2})\textsuperscript{1}, \textit{R} = Me, Et, \textsuperscript{t}Bu, Bz, 3,5-\textsuperscript{t}Bu\textsubscript{2}Bz) ligands are both homogeneous catalysts for hydrogen evolution and precursors to MoS\textsubscript{2} films by spin coating and annealing techniques. These clusters have been characterized structurally by X-ray crystallography, spectroscopically by Raman, UV-vis, and NMR spectroscopy, electrochemically by cyclic voltammetry, and computationally by DFT methods. Under photolysis, the [Mo\textsubscript{3}S\textsubscript{7}(S\textsubscript{2}CNR\textsubscript{2})\textsubscript{3}]\textsuperscript{+}\textsuperscript{+} clusters readily extrude S\textsubscript{0} from the bridging S\textsubscript{2}\textsuperscript{2}-ligands to afford clusters with an [Mo\textsubscript{3}S\textsubscript{4}]\textsuperscript{+} core. Evidence of the involvement of the [Mo\textsubscript{3}S\textsubscript{4}]\textsuperscript{+} cluster in H\textsubscript{2}-cataylsis is observed formation in the photolysis cell of the hexanuclear cluster [(R\textsubscript{2}CNS\textsubscript{2})\textsubscript{3}(μ\textsubscript{2}-S\textsubscript{2})\textsubscript{2}(μ\textsubscript{3}-S)Mo\textsubscript{3}](μ\textsubscript{3}-S\textsubscript{2})[Mo\textsubscript{3}(μ\textsubscript{2}-S)\textsubscript{3}(μ\textsubscript{3}-S)[S\textsubscript{2}CNR\textsubscript{2}]\textsubscript{3}], which is asymmetrically constituted with both Mo\textsubscript{3}S\textsubscript{7} and Mo\textsubscript{3}S\textsubscript{4} fragments. Computational work suggests the involvement of a \{Mo(H)-{μ-SH}\} intermediate in H\textsubscript{2}-formation. Continuing work will extend to isostructural dithiophosphate supported clusters, such as [Mo\textsubscript{3}S\textsubscript{7}(S\textsubscript{2}P\textsubscript{3}Bu\textsubscript{2})\textsubscript{3}]\textsuperscript{+}, for their H\textsubscript{2}-evolving ability, to the synthesis of phosphonate-functionalized dithiocarbamate ligands for immobilizing clusters onto metal oxide surfaces, and to the synthesis of well-defined heterometallic small molecule sulfides as precursors to heterometal sulfide films.
Synthesis and Characterization of Electron/Proton Acceptors from Simple Precursors

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Proton-coupled-electron transfer (PCET) is an intriguing topic in the world of alternative energy conversion research. The topic simply refers to the shift of a proton and electron in a concerted fashion. While PCET is well known in reactions of molecules in their ground electronic state, it is much less frequently observed in reactions of excited states, where electron and proton transfer must occur during the lifetime of a photoexcited reagent. Here specifically the compounds N-methyl-4,4’-dimethyl-2,2’-bipyridinium (Mdmb⁺) and N-methyl-1,10-phenanthroline (Mphen⁺), as hexafluorophosphate salts (shown below), were synthesized with the intention of learning further information regarding their ability to react with the excited state of the chromophore [Ru(bpy)₂(4,4’-dhbpy)]²⁺ (bpy = 2,2’-bipyridine; 4,4’-dhbpy = 4,4’-dihydroxy-2,2’-bipyridine). This poster will primarily focus on the synthesis and characterization of Mdmb⁺ and Mphen⁺ in particular. Based on data for the electrochemistry of Mdmb⁺, Mphen⁺ and [Ru(bpy)₂(4,4’-dhbpy)]²⁺ along with luminescence data for [Ru(bpy)₂(4,4’-dhbpy)]²⁺, it is possible to determine whether only excited state proton transfer is possible, only electron transfer is possible or whether both processes are possible in reaction with photoexcited [Ru(bpy)₂(4,4’-dhbpy)]²⁺. These photochemical processes offer insight into the dynamics of systems where excited state electron and proton transfer reactions occur. Coupling these reactions to catalysts for water or CO₂ reduction will provide needed redox leveling sought by others interested in solar fuel research.
Plasmonic Nanostructures Fabricated by Electrochemical anodization, Electrodeposition, and Sequential Self-assembling of Polyelectrolytes

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This is a collaborative work done by three Alabama high school students (Robert, Alissa, and Kayla), one international visiting student from China (Ray), and a visiting undergraduate student (Tong) with primary goal to fabricate plasmonic metal nanostructures using electrochemical and self-assembling techniques. For example, light absorption and scattering properties of silver nanoparticles can be tuned by simply controlling electrochemical anodization conditions of porous aluminum template and electrodeposition in our templating approach for nanostructure fabrication. These properties can be tuned by controlling the polyelectrolyte thickness through layer-by-layer sequential dip-coating of polyelectrolytes of PAH and PAA. These interesting plasmonic structures can potentially benefit ultrasensitive electrochemical sensing and optoelectronic devices.
A Series of Iron Redox Shuttles and Wide Band Gap Dyes Producing High Voltage DSCs Devices

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A series of Fe redox shuttles were synthesized and paired with a series of wide-band gap dyes RR8-RR10. All the redox Fe redox shuttles were able to yield functional devices with voltages on the range of 0.490 to 1.420. RR9 and RR10 were superior dyes when compared with RR8, showing the importance of surface coverage of the dye by careful design of donors to prevent recombination of electrons in TiO₂ to the oxidize redox shuttle. The aryl ether based donors of RR9 and RR10 are less stable than the most commonly use nitrogen based donors. Synthesis of less donating nitrogen donors are on the way in our group to generate more stable wide band gap dyes for high voltage applications.
Electrocatalytic CO$_2$ reduction with cis and trans conformers of a rigid dinuclear rhenium complex: Comparing the isolated monometallic and cooperative bimetallic pathways

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Anthracene-bridged dinuclear rhenium complexes are reported for electrocatalytic CO$_2$ reduction to CO. Related by hindered rotation of each Re active site to either side of the anthracene bridge, cis and trans-conformers have been isolated and characterized. Electrochemical studies reveal distinct mechanisms, whereby the cis conformer operates via cooperative bimetallic CO$_2$ activation and conversion, and the trans conformer reduces CO$_2$ through well-established single-site and bimolecular pathways analogous to Re(bpy)(CO)$_3$Cl. Higher turnover frequencies are observed for the cis conformer (35.3 s$^{-1}$) relative to the trans conformer (22.9 s$^{-1}$), with both outperforming Re(bpy)(CO)$_3$Cl (11.1 s$^{-1}$). Notably, at low applied potentials, the cis conformer does not catalyze the reductive disproportion action of carbon dioxide to CO and CO$_3^{2-}$ in contrast to the trans conformer and mononuclear catalyst, demonstrating that the orientation of active sites and structure of the dinuclear cis complex dictate an alternative catalytic pathway. Further, UV-Vis spectroelectrochemical experiments demonstrate that the anthracene-bridge prevents intramolecular formation of a deactivated Re-Re bonded dimer. Indeed, the cis conformer also avoids intermolecular Re-Re bond formation.
A Novel Homogeneous Tungsten Catalyst for the Photocatalytic production of H₂


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The photocatalytic reduction of hydrogen with a mononuclear catalyst has remained an elusive challenge for solar fuel researchers. However, a W(pyNHC-PhCF₃) complex has photocatalytic activity in the Hydrogen Evolution Reaction (HER), producing turnover numbers as high as 35 TON using sunlight in the presence of acetonitrile as solvent, triflic acid as a proton source and decamethylferrocene as a sacrificial electron donor. To the best of our knowledge this is the only mononuclear homogeneous catalyst to utilize sunlight in the HER.
Directly assembled monolayers of MoS$_2$ complexes activated on Au electrode as HER catalyst for water splitting

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Electrochemical and solar-driven water splitting is regarded as one of the most promising approaches to alternative forms of energy to produce hydrogen fuel. The production rate of such reactions are accelerated by lowering their overpotentials with the use of catalysts. The precious noble metals such as platinum are still the best electrocatalysts for the hydrogen evolution reaction (HER). However, developing a low-cost and earth-abundant catalysts with a performance comparable to that of Pt-group metals is highly desirable. Molybdenum sulfide (MoS$_2$) is one such promising candidate, which has the potential to replace precious metal catalysts for sustainable development towards hydrogen generation. MoS$_2$ is a renowned HER catalyst, known for its good ability to absorb hydrogen and the catalytic ability of its active hydrogen molecule. The enhanced catalytic performance for HER of 2-dimensional (2D) MoS$_2$ have been widely reported, however the role of monolayer MoS$_2$ is still not well elucidated in the literature. Therefore, in this work, we directed our efforts to self-assemble the monolayers of different MoS$_2$ complexes by activating them on Au-disc electrodes. To self-assemble the MoS$_2$ monolayers, the Au-disc electrode was immersed in MoS$_2$ complex precursor solution overnight and dried under nitrogen stream. The proton reduction performance of different MoS$_2$ monolayer complexes-coated Au electrodes were investigated by running polarization curves using cyclic voltammetry in 0.5 M H$_2$SO$_4$ electrolyte. The concentration of MoS$_2$ precursor derivatives and the solvents were tuned to get the optimal results. Preliminary results suggested that the proton reduction current is higher and the onset of HER is lowest for the (NH$_4$)$_2$[Mo$_3$S$_{13}$] monolayer among all the studied precursors. Further, rotating ring disk electrode (RRDE) study was performed for the monolayer of (NH$_4$)$_2$[Mo$_3$S$_{13}$] to further study its reaction kinetics. More work is underway in this direction.
Synthesis and Photophysical Characterization of Bispyridyl Hybrid Oligomers: Examining Mixed Furan-Thiophene Systems via Spectroscopic and Computational Methods

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The study of π-conjugated oligomers has garnered significant interest due to their use in organic optoelectronic devices, such as organic light-emitting diodes or organic field-effect transistors. In this study, homomeric (Py\textsubscript{r}2F\textsubscript{3} and Py\textsubscript{r}2T\textsubscript{3}) and heteromeric (Py\textsubscript{r}F\textsubscript{2}T and Py\textsubscript{r}T\textsubscript{2}F) oligomer systems consisting of furan and thiophene subunits were synthesized and characterized using UV-vis, fluorescence emission, diffuse reflectance spectroscopy, and cyclic voltammetry. Oligomers with a furan directly connected to a pyridyl moiety gave rise to the largest solution- and solid-state quantum yields and optical band gaps. Oligomers possessing a central furan subunit, on the other hand, were found to be nearly non-emissive in the solid-state, which is attributed to non-radiative decay likely caused by π-stacking interactions. Unlike the Py\textsubscript{r}2T\textsubscript{2}F hybrid oligomer, Py\textsubscript{r}2F\textsubscript{2}T not only exhibited a high solution-state quantum yield, but also the brightest solid-state emission and greatest photostability under ambient conditions. DFT computations confirm these trends indicating the largest HOMO-LUMO energy gaps and optical band gaps for Py\textsubscript{r}2F\textsubscript{3} and Py\textsubscript{r}2F\textsubscript{2}T, while that of Py\textsubscript{r}2T\textsubscript{2}F and Py\textsubscript{r}2T\textsubscript{3} are the lowest among the oligomers considered here. These results suggest that hybrid furan-thiophene oligomers could serve as viable building blocks for optoelectronic devices due to possessing the positive attributes of both individual heterocycles.
SECM for the Measuring of Heterogeneous Electron Transfer Rate Constants

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Scanning electrochemical microscopy (SECM) is a scanning probe technique that measures the local electrochemical activity of a substrate surface. The material of interest in this project is MoS$_2$, which is known to be an excellent catalyst for hydrogen evolution reaction (HER). Specifically, the edge sites are known to be the active sites for MoS$_2$ HER catalysis. This project uses a home-built SECM instrument mounted on the tip of an inverted microscope to probe MoS$_2$ thin films. The inverted microscope aids in the positioning of the microelectrode tip over the MoS$_2$ film. Furthermore, substrate-generation/tip-collection mode is used to examine the local electrochemical behavior (proton reduction) of the MoS$_2$ thin film. In this mode, the microelectrode tip is held at a potential where the H$_2$ gas produced at the MoS$_2$ surface will be oxidized back to H$. So, when H$_2$ gas is produced at the MoS$_2$ surface, current increase is observed. Another useful mode of operation is SECM feedback mode from which heterogeneous electron transfer rate constants can be calculated. In this mode, the tip is positioned over the MoS$_2$ piece of interest and slowly approached to the surface such that a feedback curve (tip current vs tip distance from substrate) can be obtained. These curves can be fitted to suitable parameters to obtain effective forward rate constants ($k^f$), which can then be used in the Butler-Volmer relationship to obtain standard electron transfer rate constants ($k^0$). Obtaining $k^0$ values for MoS$_2$ thin films for HER is what this project seeks to do.
Highly Active and Selective Cobalt Catalysts Bearing Redox-Active Bipyridyl-NHC Frameworks for Electrochemical CO₂ Reduction

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An original series of cobalt complexes bearing redox-active bipyridyl-N-heterocyclic carbene-based ligands has been developed for electrocatalytic CO₂ reduction in acetonitrile and aqueous solutions. The mechanism has been examined by electrochemical and computational methods. From controlled potential electrolyses (CPEs) in CH₃CN/2% H₂O solutions, 1-Co supported by a non-macrocyclic ligand gives a Faradaic efficiency (FE) for CO₂-to-CO conversion of 78%, while 2-Co and 3-Co supported by macrocycles afford higher selectivities for CO evolution with FEs of 92% and 97%, respectively, with the balance of charge going to H₂ production in all cases. Electrochemical experiments show that the turnover frequencies across the catalyst series, determined from the ratio of $i_{\text{cat}}/i_{\text{p}}$, increase systematically from 8.4 s⁻¹ (1-Co) to 146 s⁻¹ (3-Co). These results demonstrate that the rigidity of the ligand framework enhances catalytic activity and selectivity for CO₂ reduction over the competing H₂ evolution reaction. Catalysis was extended to water where CPEs in CO₂-saturated 0.1 M NaClO₄ and 0.1 M NaHCO₃ aqueous solutions reveal that 3-Co catalyzes CO₂ reduction to CO with a Faradiac yield of 93% at an overpotential of ~550 mV.
Synthesis and Characterization of a Novel Non-Innocent NNP-type Pincer Ligand and its First-Row Transition Metal Complexes

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Here we report the synthesis of a rigid NNP-type pincer ligand (8-(diphenylphosphanyl)-2-(pyridin-2′-yl)quinoline), and the synthesis, structure, and electrochemical properties of its first-row transition metal complexes. Given the breadth of reactivity accessible with phosphine- and diimine-based pincer ligands, we have designed a novel phosphine-substituted redox-active diimine framework to investigate its coordination chemistry with first-row metals and their reactivity. The ligand was prepared by Stille coupling of 2,8-dibromoquinoline and 2-(tributylstannyl)pyridine, and a subsequent palladium-catalyzed cross-coupling with HPPh₂. Complexes were synthesized from a variety of metal precursors with non-coordinating counter ions and characterized by ¹H, ¹³C and ³¹P NMR, HR-MS, UV/Vis, and cyclic voltammetry. Spectral information and Density Functional Theory (DFT) calculations were used to determine the structure of the complexes.
Raman Spectroscopic and Computational Study of Noncovalent Interactions between Guanidinium Chloride (Gdn-HCl), Trimethylamine N-oxide (TMAO), and Water

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TMAO and Guanidinium Chloride (Gdn-HCl) are two naturally occurring osmolytes that affect proteins. Many aquatic animals utilize TMAO to protect their cells from environmental stresses such as high temperature and high salinity. On the other hand, Gdn-HCl is found in urine as a by-product of protein metabolism. TMAO is known to stabilize and counteract the denaturing effect that Gdn-HCl has on proteins. Moreover, TMAO is known to non-covalently interact with water, which plays a crucial role in TMAO’s effectiveness as an osmolyte. Here, we use Raman Spectroscopy to describe the interactions between TMAO and Gdn-HCl in solution in order to understand how TMAO and Gdn-HCl affect the hydrogen-bonding network of water.
Excited State Proton Transfer Reactions of Ru(II) hydroxybipyridine Complexes and its Relation to Excited State Proton Coupled Electron Transfer Reactivity

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Proton coupled electron reactions are useful in processes involving transfer of more than one electron. By transferring an electron and a proton to a substrate or a catalyst, the potential required to transfer a second electron is lowered. This phenomenon is known as redox leveling. Our interest is in studying proton coupled electron transfer reactions of the excited states of molecules. To better understand this process, we need to first explore the kinetics of excited state proton transfers. The excited state to be used is a Ruthenium complex with a hydroxy bipyridine ligand and the proton acceptor (a pyridine base) will serve to quench the luminescent emission of the complex. Transient absorption spectroscopy will be used to better understand the mechanism that occurs over the lifetimes of these excited states.
Computational Studies of Chromium(III)-Imidazole Complexes

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Complexes involving chromium(III) and imidazole nitrogen atoms are naturally occurring and of much biological interest for the reduction of chromium toxicity in the environment. The metal-imidazole nitrogen bond is known to form within mycorrhizal fungi during the phytoremediation of chromium(VI) contaminated soil and in mammalian cells exposed to chromium(VI). To further characterize this bond, the vibrational frequencies and optimized geometry of $\text{[Cr(Imh)\textsubscript{6}]Cl\textsubscript{3}}$ (Imh = Imidazole) were modeled using Density Functional Theory. Future research will focus on experimentally characterizing the bonding interaction between the chromium(III) ion and the imidazole nitrogen using Raman Spectroscopy.
A Computational Investigation of 1-Hydroxyethyl Radical: Optimized Hydrated Cluster Structures, Energetics, and Vibrational Characterization

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The isoenzymatic form of microsomal cytochrome P450, CYP2E1, is involved in the formation of oxygen free radicals, specifically hydroxyethyl ether. Chronic alcohol abuse has been found to induce larger levels of CYP2E1 in the liver, thus increasing production of these harmful free radicals. Generation of the hydroxyethyl ether oxygen free radicals occurs during the metabolism of ethanol in microsomes. The hydrogen-bonding interactions of hydroxyethyl ethers with water have yet to be analyzed, and information regarding the interactions with water can be applied directly to biological systems. Here, we employ Raman spectroscopy and computational chemistry to study hydroxyethyl ether complexes in micro-solvated networks of varying complexity. Utilizing density functional theory's unrestricted B3LYP method and both the 6-31++G(d,p) and aug-cc-pVTZ basis sets, 126 total structures were found ranging from n=0-5 water clusters. Specifically, 1 (H₂O)₀ structures, 2 (H₂O)₁ structures, 3 (H₂O)₂ structures, 12 (H₂O)₃ structures, 34 (H₂O)₄ structures, and 74 (H₂O)₅ structures corresponding to local minima on the potential energy surface were found. Additional calculations were run to ensure that the lowest energy structures were in fact the lowest energy, including optimizations of the two lowest energy structures from each subset run via the M062x, wB97xD, and CCSD methods with the aug-cc-pVTZ basis set. CCSD(T) single-point calculations were run on the lowest-energy structures as well to confirm the energies discussed in this paper. The binding energies from each class of calculations were calculated and are discussed. The vibrational frequencies and shifting of the lowest-energy structures from each class (H₂O)ₙ=0-5 are presented and discussed as well. It is expected that the increasing solvation matrices will allow some of the negative charge on the radical oxygen to be delocalized into the hydrogen-bonded network formed amongst the water molecules.
Perovskite Light Emitting Electrochemical Cells based on CH$_3$NH$_3$PbI$_3$ Perovskite Films and CH$_3$NH$_3$PbCl$_{1.08}$Br$_{1.92}$ Perovskite Quantum Dots

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Various electroluminescent devices such as organic light emitting diodes (OLEDs) and light emitting electrochemical cells (LECs) have been devised to meet the lighting energy requirements. LECs have attracted significant interest due to simpler device structure, low cost, stability and low turn-on voltage. LEC is composed of a single emissive layer with the ionic polyelectrolyte sandwiched between an anode and a cathode. Recently, perovskite materials such as quantum dots, nanocrystals and thin films have shown remarkable easily modifiable optoelectronic properties. They are compatible with ionic additives allowing the formation of emissive layer as a film. In this study, CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbCl$_{1.08}$Br$_{1.92}$ light emitting electrochemical cells are devised with PEO and LiCF$_3$SO$_3$ as polyelectrolyte sandwiched between GaAs and ITO. The light was detected below 3V for both the perovskite LEC devices. To improve the charge injection, PEDOT: PSS and PCBM were used as the hole injection and electron injection layers respectively. LECs consisted of the following structures, ITO/{CH$_3$NH$_3$PbI$_3$-PEO-LiCF$_3$SO$_3$}/GaAs, ITO/PEDOT:PSS/{CH$_3$NH$_3$PbI$_3$-PEO-LiCF$_3$SO$_3$}/GaAs, ITO/PEDOT:PSS/{CH$_3$NH$_3$PbI$_3$-PEO-LiCF$_3$SO$_3$}/PCBM/GaAs, ITO/{CH$_3$NH$_3$PbCl$_{1.08}$Br$_{1.92}$-PEO-LiCF$_3$SO$_3$}/GaAs, ITO/PEDOT:PSS/{CH$_3$NH$_3$PbCl$_{1.08}$Br$_{1.92}$-PEO-LiCF$_3$SO$_3$}/GaAs, and ITO /PEDOT:PSS/{CH$_3$NH$_3$PbCl$_{1.08}$Br$_{1.92}$}/PCBM/GaAs architecture. The potential was held at 0.5V, 2.8V, 2.4V to see the change in the current and luminescence as a function of time for 400s. The future works include the formation of LEC through interdigital electrodes, Al evaporation for the formation of contacts for comparison with the GaAs contact.
The Platinum Electronic Parameter (PtEP):
A Compliment to TEP

Min Zhang,¹ Eric Van Dornshuld,¹ Jeffrey C. Bunquin,² Massimiliano Delferro,² T. Keith Hollis,¹ and Charles Edwin Webster¹

¹Department of Chemistry, Mississippi State University, Starkville, MS 39762
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Parameters and scales that provide understanding of steric and electronic effects are essential to predicting properties, and, therefore, to systematically designing new ligands. One ligand class, namely, tridentate, rigidly meridional pincer ligands, are neither conveniently nor accurately described by existing options. A scale has been developed based on $^{195}$Pt NMR chemical shift that is reflective of the total donor ability of a multi-dentate ligand in a square planar complex and that does not suffer from cis/trans stereochemical issues. An inexpensive, readily-accessible computational model for predicting the chemical shifts correlates well with the experimental data and provides a basis for predictions. This scale, Platinum Electronic Parameter (PtEP, pronounced P-tep) and defined as PtEP = $-^{195}$Pt NMR shift in CDCl₃ revealed significant deviations of CCC-NHC pincer ligands, PCP and POCOP donor abilities from predicted extrapolations using existing TEP parameters. This initial data set demonstrates the applicability and broad potential of the PtEP scale.
OUTREACH ACTIVITIES
Outreach activities take place throughout the year at different locations within Mississippi, Alabama, and Louisiana. Outreach is directed at K-12, community college, and university levels, in addition to local community outreach in the form of science cafés and public service announcements. Outreach activities are coordinated by Ms. Katie Echols.

**Women in STEM Seminars:**

This program raises student awareness of various STEM careers and the women who are successful in those fields. Women who are positive role models in STEM careers to speak at various institutions such as PUIs, HBCUs, and secondary schools. Each speaker discusses the path to her STEM career, what girls today can do to be successful in STEM fields, and opportunities available for students interested in getting involved in STEM. Three or Four seminars are conducted each year.

November 10, 2015: East Mississippi Community College (Speaker: Megan Holmes)
November 19, 2015: Itawamba Community College (Speaker: Lindsey Brown)
January 20, 2016: Tougaloo College (Speaker: Denise Cornelius)
February 27, 2017: Northwest MS Community College (Speaker: Dr. Syndey Murphy)
March 24, 2017: Columbus High School, Columbus, MS (Speaker: Ashli Brown, State Chem Lab)
March 30, 2017: Baton Rouge Community College (Speaker: Dr. Anne Robinson)
November 2, 2017: Columbus High School (Speaker: Dr. Brittney Oliver)
April 10, 2018: Itawamba Community College, Fulton, MS (Speaker: Dr. Leslie Burger)
Science Cafés:

Science Cafés increase knowledge of material science research and provide opportunities for public engagement and discussion of important research topics. Science cafés are lively events that take place in informal settings like a coffee house. They are open to everyone and include a conversation with a researcher on a particular topic. Scientists discuss current research directly related to the water-energy-food nexus and the role chemistry can play in solving the problem. At least four café's are held each year, targeting college students and adults with one café a year specifically for high school students. We work with teachers at the local high schools to promote and encourage the student’s attendance. Participants are asked to complete short surveys so data can be collected on the participants' increased knowledge on the topic.

January 21, 2016: 929 Café, Starkville, MS (Speaker: Todd French)
January 27, 2016: High Point Café, Oxford, MS (Speaker: Jared Delcamp)
April 14, 2016: Nehemiah's, Tuscaloosa, AL (Speaker: David A. Dixon)
April 26, 2016: Tulane University Lavin Bernick Center (Speaker: Russ Schmehl)
November 2, 2016: Tulane University Lavin Bernick Center (Drs. Doug Chrisey and Tom Sherry)
November 3, 2016: Starbucks Coffee, Tuscaloosa, AL (Speaker: Dr. Elizabeth Papish)
November 29, 2016: High Point Café, Oxford, MS (Speaker: Gregory Tschumper)
April 18, 2017: Starkville Coffee, Starkville, MS (Speaker: Keith Hollis)
March 5, 2018: Starbucks Coffee, Starkville, MS (Speaker: Dr. Jared Delcamp)
March 20, 2018: Fair Grinds Coffeehouse, New Orleans, LA (Speaker: Dr. Keith Hollis)
April 18, 2018: Uptown Coffee, Oxford, MS (Speaker: Dr. Davita Watkins)
Middle and High School Science Teacher Summer Workshops:

These annual workshops increase teachers’ teaching efficacy and knowledge of content related to material science and the water-energy-nexus theme. They last two weeks each summer and include 15 teachers. The location of the workshop will change annually in order to target different geographical areas. Workshops were held at Mississippi State University in 2016 and in New Orleans in 2017. Upcoming ones include Alabama in 2018 and the Mississippi Delta in 2019. Pictures from previous workshops are on the next page.
Clean Energy Harvesting:

Training and education activities closely integrated with the concept of clean energy harvesting and conversion are underway at the University of Alabama. The goal is to help improve clean energy and nanotechnology program for underrepresented minority K-12 school teachers and students in Alabama’s rural Black Belt Counties and undergraduate students by providing them with hands-on research projects and classroom education modules.
Research Experience for Undergraduates (REU) and College Teacher Program:

Undergraduate students, college teachers, and high school teachers are supported each summer to perform research in the laboratories of senior personnel. Applications are accepted on the program website. Shown below are participants from Years 1-3 in the summer program.
Feeding and Powering the World 2017 Summer Participants

Orrion Kuykendall
Kennesaw State University
Prof. Elizabeth Papish
The University of Alabama

Shelby Ruiz
Mississippi College
Prof. Keith Hollis
Mississippi State University

Jordan Wilson
University of Montevallo
Prof. Shanlin Pan
The University of Alabama

Dr. Lillian Mathews
University of Montevallo
Prof. Shanlin Pan
The University of Alabama

Dr. Divina Miranda
Baton Rouge Community College
Prof. Russ Schmehl
Tulane University

Feeding and Powering the World 2016 Summer Participants

Ian McCraw
Furman University
Prof. Edwin Webster
Mississippi State University

Son Nguyen
Xavier University
Prof. Russ Schmehl
Tulane University

Samantha McKee
University of Missouri
Prof. Elizabeth Papish
University of Alabama

Daniel Touzeau
Univ. of Alabama, Huntsville
Profs. Hammer/Delcamp
University of Mississippi

Dr. Divina Miranda
Baton Rouge Community College
Prof. Russ Schmehl
Tulane University

Dr. Kim Hamilton-Wims
Northwest Mississippi
Profs. Hammer/Delcamp
University of Mississippi


Feeding and Powering the World 2018: Planning for the Future


Methylidyne? CCC-NHC Tantalum Bis(imido) Reactivity: Protonation, Rearrangement to a
Mixed Unsymmetrical CCC-N-Heterocyclic Carbene/N-Heterocyclic Dicarbene (CCC-NHC-
DOI: 10.1016/j.ica.2017.08.050

G. Liang and C. E. Webster, “The missing agostomer in the fluxionality of
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10.1039/c8cc00266e

2017

K. M. Dreux, L. E. McNamara, J. T. Kelly, A. M. Wright, N. I. Hammer, and G. S. Tschumper,
“Probing dative and dihydrogen bonding in ammonia borane with electronic structure
computations and Raman under nitrogen spectroscopy,” Journal of Physical Chemistry A,
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 Lancaster, S. Sproules, and J. P. Donahue, “Expanding the Scope of Ligand Substitution from
[M(S₂C₂Ph₂)] (M = Ni²⁺, Pd²⁺, Pt³⁺) To Afford New Heteroleptic Dithiolene Complexes,”

P. Fontenot, B. Wang, Y. Chen, J. P. Donahue, “Structure of Tetraisobutylthiuram Disulfide,”
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Papish, “Ruthenium(II) complexes of pyridinol and N-heterocyclic carbene derived pincers as
robust catalysts for selective carbon dioxide reduction,” Chemical Communications, 53,
11217 (2017). DOI: 10.1039/c7cc05706g

Jue Wang and Shanlin Pan, “Electrodeposition of vertically standing Ag nanoplates and
nanowires on transparent conductive electrode using porous anodic aluminum oxide


2015

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The Defense Advanced Research Projects Agency (DARPA) operates on the principle that generating big rewards requires taking big risks. But how does the Agency determine what risks are worth taking?

George H. Heilmeier, a former DARPA director (1975-1977), crafted a set of questions known as the "Heilmeier Catechism" to help Agency officials think through and evaluate proposed research programs.

- What are you trying to do? Articulate your objectives using absolutely no jargon.
- How is it done today, and what are the limits of current practice?
- What is new in your approach and why do you think it will be successful?
- Who cares? If you are successful, what difference will it make?
- What are the risks?
- How much will it cost?
- How long will it take?
- What are the mid-term and final “exams” to check for success?