



2014 Ohio Inorganic Weekend Poster Presentations

7-10 p.m. Friday, November 14, 2014

(Registration begins at 6:30 p.m.)

Chemistry Building Atrium

930 N. University Ave.

University of Michigan

We would like to thank the following sponsors of the 2014 Ohio Inorganic Weekend:



SIGMA-ALDRICH



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Time-Based Dependence of the Response of Vapochromic Materials

Mahmood K. Abdolmaleki,¹ M. Sadegh Riasi,² Kelsey A. Mengle³, and William B. Connick^{4*}

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Vapochromic materials that are both reversible and highly selective are attracting increased attention due to their potential use in chemical sensing applications. In particular, the development of vapochromic materials, which exhibit pronounced color changes upon exposure to volatile organic compounds (VOCs), is advantageous because these materials can be used as visual indicators for hazardous chemicals. Stacked square planar d⁸-electron metal complexes with relatively short metal-metal interactions have proven especially effective in this capacity. However, the discovery of vapochromic materials is mainly serendipitous, and predicting vapochromic properties of materials prior to synthesis seems only a distant possibility. This problem is deepened by the lack of unambiguous structural information, as well as knowledge of the energetics of the vapochromic response. To address these challenges, we seek to determine the relationships between structure, selectivity, speed of response, and sensitivity of vapochromic materials. In this presentation, we report a method for quantitatively monitoring the dynamics of the vapochromic response of vapochromic materials over time.

N-Hydroxysulfonamides RSO_2NHOH as Nitroxyl (HNO) Donors: Improved Preparation and Kinetics of HNO Generation

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Nitroxyl (HNO) is an important biomolecule whose biological chemistry is challenging to study due to its rapid dimerization. As a result, a variety of HNO donors have been developed as in situ sources of HNO, including several N-hydroxysulfonamides RSO_2NHOH (e.g. Piloty's acid ($\text{R}=\text{Ph}$), MSHA ($\text{R}=\text{Me}$)). As part of a program aimed at understanding the fundamental bioinorganic chemistry of HNO, we needed to prepare these N-hydroxysulfonamides as well as the new related HNO donor $\text{CF}_3\text{SO}_2\text{NHOH}$. Surprisingly, we found that there is a dearth of reliable and efficient approaches for the preparation of these targets. Herein, we will outline improved preparative approaches to these N-hydroxysulfonamide HNO donors. In addition, we will present detailed decomposition kinetics for HNO generation from these compounds, using aquacobalamin to quantify HNO generation.

Structural and Thermal Characterization of chlorotetrakis(*N,N'*-diethylthiourea)nickel(II) chloride, [Ni(det_u)₄Cl]Cl.

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Our laboratory recently reported the structural characterization of a solid-state spin equilibrium for a nickel(II) scorpionate complex [(Tp^{Ph,Me})NiS₂CNMe₂], where Tp^{Ph,Me} = hydrotris(3-phenyl-5-methylpyrazolyl)borate.¹ Spin crossover has attracted intense and sustained attention due to possible applications of bistable molecules in nanoscale devices, but the phenomenon is typically circumscribed to involve d⁴–d⁷ metal ions in octahedral ligand fields.² We were curious whether precedent existed for our unusual result involving tetragonal modulation of a d⁸ metal ion. In fact, several nickel(II) complexes displaying “anomalous magnetism” in the solid state have long been known, but surprisingly, structural details of the implied spin equilibria are generally lacking. Among the several candidates, our particular attention focused on “[Ni(det_u)₄Cl₂],” where det_u = *N,N'*-diethylthiourea. This complex can be readily and inexpensively synthesized in large quantities, and is known to exhibit spin crossover under ambient conditions, in response to variation of both temperature and pressure.^{3,4} We recently obtained a crystal structure of this complex, which clearly suggests key details of the spin equilibrium. The structures and electronic spectra of the limiting spin states were further modeled by DFT and TD-DFT calculations. Thermal behavior was analyzed by differential scanning calorimetry; in addition to the spin equilibrium, a low-temperature thermochromic equilibrium was also found, apparently involving a tetragonal–monoclinic lattice distortion that perturbs the equatorial ligand field. These phenomena will be discussed.

References

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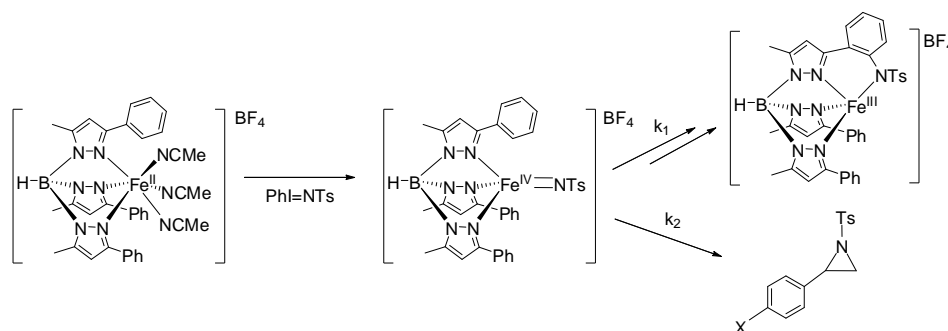
Intramolecular Amination as a Competitive Probe of Nitrene Transfer Catalysis

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Homogeneous nitrene transfer catalysis continues to emerge as viable strategy for the formation of synthetically valuable C–N bonds.¹ We recently identified half-sandwich iron(II) scorpionate complexes as highly effective catalysts for styrene aziridination using $\text{PhI}=\text{NTs}$ as a nitrene precursor.^{2,3} Although an imidoiron(IV) complex is assumed to be the reactive intermediate,⁴ kinetic and mechanistic studies are impeded by the poor solubility of the heteroatomic iodine ylide. To circumvent this difficulty, we have examined the analogous reactivity of $[(\text{Tp}^{\text{Ph,Me}})\text{Fe}(\text{NCMe})_3]$, $\text{Tp}^{\text{Ph,Me}}$ = hydrotris(3-phenyl-5-methylpyrazolyl)borate: in the absence of a viable nitrene acceptor substrate, an intense anilide–iron(III) LMCT chromophore is obtained, which arises from intramolecular amination of a pyrazole 3-phenylsubstituent. The rate of this unimolecular reaction (*i.e.*, k_1) has been used to clock to competitive rates of bimolecular nitrene transfer to *para*-substituted styrenes (*i.e.*, k_2), by determining the concentration-dependent suppression of chromophore accumulation under single turnover conditions. The resulting data enable direct comparison of the bimolecular transfer rates as a function of styrene substitution (*i.e.*, $k_{2,\text{X}}/k_1$), yielding a linear free energy correlation (*i.e.*, $k_{2,\text{X}}/k_{2,\text{H}}$). Such a Hammett correlation is consistent with the proposed mechanism, particularly with a common electrophilic intermediate lying at the branch point of unimolecular and bimolecular nitrene transfer.



References

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Synthesis and Stability of Ge/Sn Alloyed Analogue of Graphane

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With the success of the synthesis of an sp^3 -hybridized germanium graphene analogue, the prospects of an sp^3 -hybridized tin analogue have gathered great attention due to its potential as a topological insulator with dissipationless transport along its edge states. Herein, we have explored for the first time the possibility of incorporating of up to 9% of Sn into the 2D germanane lattice through the topochemical transformation of Sn-alloyed CaGe_2 Zintl phase. The 2D GeSn alloy retained the hydrogen (-H) termination of Ge while a hydroxide (-OH) ligand was observed with Sn. Diffraction studies of the material showed a lattice expansion in both the a/b and c direction consistent with the incorporation and surface ligand termination of the larger Sn atom. Raman measurements also confirmed the Sn incorporation with the shifting of the A_1 (out-of-plane) and E_2 (In-plane) phonon modes to lower wavenumbers with increasing Sn percentage. Through Sn alloying, there was a consistent change in the optical band gap of these materials as observed in the diffuse reflectance absorption measurements where a shift from 1.59 eV (GeH) to 1.38 eV ($\text{Ge}_{0.91}\text{Sn}_{0.09}\text{H}_{0.91}(\text{OH})_{0.09}$) was observed. Wavelength-dependent photocurrent measurements on single crystal devices also reflect a similar band gap shift. Lastly, it was determined that these alloys undergo surface oxidation upon exposure to ambient air ($t = 15$ days). The incorporation of Sn into the GeH lattice illustrates the possibility of this class of alloys as a platform for two-dimensional materials with tunable band gaps.

Toward Detection of Galectin-3 Using Fluorine-Labeled Thiodigalactosides

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Galectin-3 is a β -galactoside-binding protein that is overexpressed in early pancreatic cancer. This cancer has poor prognosis when diagnosed late because of a lack of effective treatments at the late stage of the disease. The survival of patients with pancreatic cancer likely can be improved by earlier detection using diagnostic imaging. However, there are no clinically approved imaging agents that selectively target biomarkers associated with early stages of pancreatic cancer development. We hypothesize that early detection of cancer will be facilitated by selectively imaging the cancer biomarker galectin-3 that is expressed in cancer but not normal cells. Further, we have taken the first steps necessary to develop a radiolabeled glycoconjugate that has high affinity and specificity to galectin-3 to enable the early detection of galectin-3 expression in tumor cells using positron emission tomography. We have designed a focused library of ten fluorinated β -thiodigalactopyranose analogs based on the structure of the carbohydrate recognition domain of galectin-3. These compounds, which vary in their aromaticity and steric bulk, will be tested for their affinity to galectin-3 using isothermal titration calorimetry and surface plasmon resonance. Our understanding of the effect of the aromaticity, steric bulk, and fluorine atoms on the structure-affinity relationship to galectin-3 will be presented. We expect that our results will take the initial steps toward improving the survival of cancer patients by advancing an imaging technique to enable earlier diagnosis of the diseases. In addition, visualization of cancer at the early stage may allow for assessment of prognosis of therapy.

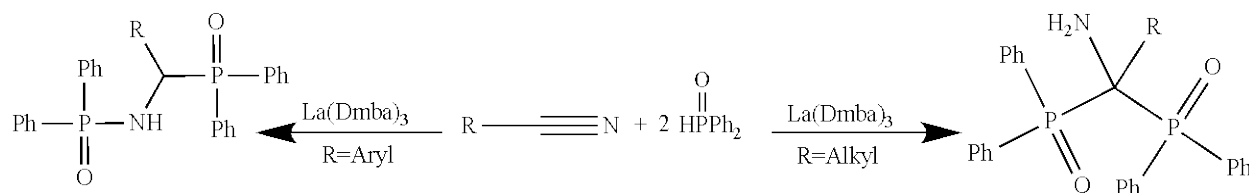
Unprecedented Double Hydrophosphinylation of Nitriles

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Hydrophosphinylation is defined as the addition of H-P(O)R_2 across an unsaturated system. Examples of this reaction are quite limited and double hydrophosphinylation is very rare. A new lanthanum-based catalyst was shown to effect the double hydrophosphinylation of common inactive nitriles. Surprisingly, this double hydrophosphinylation of nitriles yielded different regioisomeric products depending on the nature of the starting material. It was observed that 2,2 addition to the carbon of the nitrile occurred in alkyl nitriles resulting in a P-C-P product and a primary amine. However, using the same conditions with aryl nitriles gave 1,2 double hydrophosphinylation products (Scheme 1), where one diphenylphosphine oxide was added to the carbon of the nitrile and the second equivalent was added to the nitrogen resulting in a P-C-N-P product. The catalyses were conducted in minimal amounts of solvent, required little workup and gave high to moderate yields. Overall, this system proved to be highly tolerant to different functional groups making it an attractive and facile way to access new P-C-N-P and P-C-P ligands.



Scheme 1. Lanthanum catalyzed double hydrophosphinylation of nitriles

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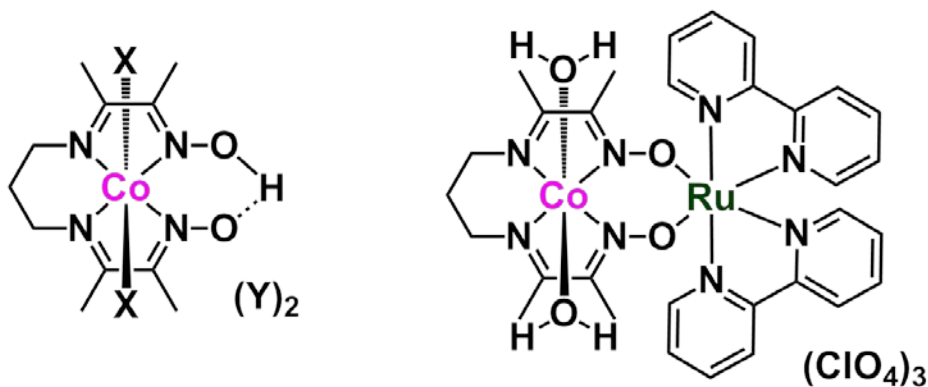
Investigation of New Ligand Architectures towards Proton and Water Reduction Catalysis by Cobalt Complexes

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The ever-increasing demand for alternative energy sources and continuous decline of fossil fuels has driven the extensive research on water splitting to generate dihydrogen. In this regard, several redox-active ligand architectures were designed to optimize and understand the redox, electronic, and catalytic properties of their respective cobalt complexes towards proton and water reduction. Ligand designs were systematically varied from a π -donating phenolate-rich $[\text{N}_2\text{O}_3]$ ligand to a π -acceptor oxime-based $[\text{N}_2\text{N}_2']$ ligand to reduce the overpotential of hydrogen generation from organic acids. Furthermore, cobalt complexes of pentadentate nitrogen-rich oxime- and pyridine-based ligands were synthesized, thus demonstrating water reduction in addition to proton reduction catalysis. Moreover, a $[\text{Ru}(\text{bpy})_2]^{2+}$ -based photosensitizer was incorporated with selected catalytic modules to generate catalytic heterobimetallic $[\text{Ru}^{\text{II}}\text{Co}^{\text{III}}]$ species.



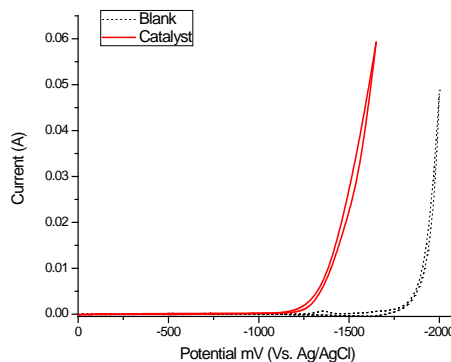
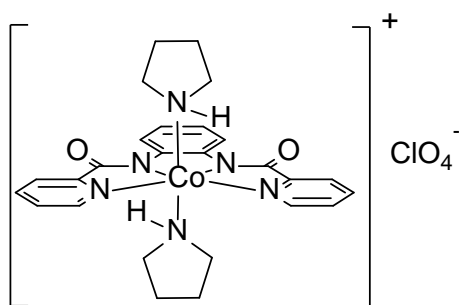
Proton and Water Reduction Electrocatalysis by Cobalt(III) Complexes based on Amido-pyridine Framework

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Dihydrogen is one of the most appealing environmentally friendly renewable energy sources. However, current methods of hydrogen production preclude any practical large scale applications, and in order to solve this problem new, and more efficient ways of producing H₂ need to be developed. Hydrogen can be catalytically generated *via* the two electron reduction of two protons. Most commonly expensive organic acids have been used as proton sources. However water is the chief readily available proton source available, as it is both ubiquitous and environmentally benign. When water is used in proton reduction the process is called water reduction. Herein we report on a new and accessible series of cobalt electrocatalysts in a redox active square planar bis-amido pyridine ligand capable of generating H₂ from neutral water at an onset overpotential of 0.5 V. Catalytic studies have revealed an inverse dependence between turn over number and catalyst concentration. This indicates that the deactivation pathway of the catalyst follows a multimetallic route. Furthermore, turnover numbers as high as 1250 within 15 minutes have been achieved. Ligand modifications in order to increase catalytic activity and lifetime of the catalyst are proposed and preliminary results are discussed.



Synthesis and Reactivity of Open Chain Bis(iminopyridine) and Macrocyclic Bis(di(imino)pyridine) Bimetallic Complexes for the Activation and Sensing of Small Molecules

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Metal complexes that react with small molecules are of interest because they may provide a key to creating lower cost and more efficient catalysts. Predesigned dinuclear systems are of special interest whenever the reaction is expected to involve a bimetallic transition state or bimetallic substrate binding. Toward this goal, we are designing and synthesizing dinucleating ligand platforms for the binding, activation, and sensing of small molecules. Two ligand platforms will be discussed: open chain bis(iminopyridine) ligands and macrocyclic bis(di(imino)pyridine) ligands linked by one or two para-xylylene bridges, accordingly. Bimetallic complexes of the open chain ligands have been shown to activate CS_2 and act as efficient sensors for the detection of oxalate. The reactivity of these complexes will be discussed. The colorimetric detection of oxalate and competition experiments with other mono- and di-carboxylates will be presented. We will also describe the synthesis and initial reactivity macrocyclic bis(di(imino)pyridine) ligands and metal complexes.

Synthesis of Low-Coordinate Bis(alkoxide) Metal Complexes and Their Reactivity in N-N Bond Formation Reactions

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We are designing low-coordinate metal complexes in bis(alkoxide) ligand environments for the activation of small molecules. Specifically we are interested in bond activation and bond formation reactions involving azide precursors, with the goal to develop new catalysts for N-N and C-N bond formation. Recently we reported the synthesis of quasi-two-coordinate complexes $M(OR)_2(THF)_2$ ($OR = OC(tBu)_2Ph$, $M = Mn, Fe, Co$) that proceeds via unusual cluster intermediates with metals possessing rare seesaw geometry. The reaction of the iron(II) precursor $Fe(OR)_2(THF)_2$ with aliphatic azides results in their reductive coupling to form the iron(III) hexazene complex $(RO)_2Fe(\mu-\kappa^2:\kappa^2-RN_6R)Fe(OR)_2$. DFT studies propose formation of an Fe-azide dimer on the route to hexazene in which each azide is monoreduced and the iron centers are oxidized to the 3+ oxidation state. The reaction of the iron(II) precursor with aromatic azides ArN_3 leads to the formation of azoarenes $ArNNAr$, with concomitant liberation of dinitrogen. The reaction is postulated to proceed through a metal-nitrene intermediate and is catalytic in both coordinating and noncoordinating solvents. Mechanistic, spectroscopic, structural, and theoretical studies will be reported.

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Low Temperature Synthesis Of Vanadium Oxides.

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Metal oxides are traditionally synthesized at high temperatures. However, low temperature synthesis is needed for production of metastable inorganic phases as well as for application in *in-situ* polymer composite synthesis. Vanadium oxides are of particular interest due to their semi conductive nature in all oxidation states. In this project vanadium oxides will be synthesized using a low temperature route, the non-hydrolytic sol-gel (NHSG) method, which involves the reaction of metal halides with organic ethers to produce a metal oxide and alkyl halide which will later be removed from the product. The goal of this project is to find low temperature synthesis conditions that can be incorporated into a polymerization reaction to make semiconducting composites.

Photoelectrochemical Properties of CH₃-Terminated p-Type GaP(111)A

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Crystalline gallium phosphide (GaP) converts light energy to energy stored in chemical bonds through photochemical reductions. GaP rapidly forms a non-passivating oxide layer when in contact with air which diminishes photocathode performance. Herein, photoelectrochemical properties were compared between native GaP surfaces and surfaces after chemical modification by chlorination/Grignard reaction sequence previously found to reduce surface oxidation, with special interest in the impact on dye sensitization for application in dye-sensitized solar cells. The effect of the modified surface on photoelectrochemical properties such as flat-band potential and sensitivity of band-edge energetics towards solution pH was explored using electrochemical impedance spectroscopy. Studies were performed to assess stability towards reductive degradation under white light illumination. Photocurrent measurements using sub-bandgap light provided insight on the number of surface states, which act as recombination centers for trapping and de-trapping of charge carriers, of the unmodified and CH₃-terminated GaP(111)A. Physisorbed Brilliant Green dye exhibited higher quantum yield measurements on CH₃-terminated GaP(111)A, which indicated less deleterious charge recombination due to surface states. Due to shift in band-edge energetics, only CH₃-terminated GaP(111)A was sensitized by several dyes with less positive HOMO levels (0.60 to 0.80 V vs Ag/AgCl). CH₃-terminated p-GaP(111)A showed less change in band edge energetics with solution pH, fewer surface states, extended stability against reductive degradation, and improved performance after dye physisorption than unmodified GaP(111)A.

Bifunctional Copper Catalysts for the Hydrogenation of Aldehydes and Ketones

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Hydrogenation of aldehydes and ketones has been achieved at room temperature using homogeneous copper catalysts supported by bis(phosphino)amine ($^R\text{PN}(\text{H})\text{P}$) ligands. Related $[\text{}^R\text{PN}(\text{H})\text{P}]\text{CuX}$ (where $\text{R} = \text{}^i\text{Pr}$, Cy, ^tBu and $\text{X} = \text{Br}$, BH_4) complexes have been synthesized and characterized by NMR, IR, and X-ray crystallography. PhCHO and $\text{PhC}(\text{O})\text{CH}_3$ are reduced to the corresponding alcohols with 80 psig H_2 pressure, 2 mol% of $[\text{}^i\text{PrPN}(\text{H})\text{P}]\text{CuBr}$, and 2.4 mol% of KO^tBu . More carbonyl group containing substrates are being investigated under the optimized reaction conditions. A $[\text{}^R\text{PN}(\text{H})\text{P}]\text{CuH}$ species has been postulated to be the active form of the catalyst in these reactions and isolation of this complex is currently being pursued.

Experimental and Theoretical Studies of Anodic Oxidation Induced Olefin Coupling Reactions Using Organo-Re(II)

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The radical cation, $[\text{ReCp}(\text{CO})_3]^+$ ($\mathbf{1}^+$, Cp = $\eta^5\text{-C}_5\text{H}_5$) has been known to initiate radical-based intermolecular carbon-carbon coupling reactions of unactivated terminal alkenes.¹ The very promising nature of the $\mathbf{1}/\mathbf{1}^+$ couple ($E_{1/2}$ value = 1.16 V vs. $\text{Fc}^{0/+}$) makes $\mathbf{1}^+$ a powerful one-electron oxidizing agent in the presence of the $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as supporting electrolyte.²⁻³ The *in situ* anodic generation of $\mathbf{1}^+$ by electrolysis at $E_{\text{app}} = 1.25$ V initiates coupling reactions between excessively added linear alkenes (1-octene, 1-hexene and 1,7-octadiene) with individual $E_{1/2}$ values exceeding 1.8 V. Electrocatalytic bulk oxidation of $\mathbf{1}$ in each case was exhausted in < 0.25 – 0.5 h, following the passage of 0.2 - 0.3 F/mol of alkene. Products from these coupling reactions were obtained in **65-73%** yields and identified by GC-MS, ^1H - and ^{13}C -NMR, HMQC data. The electron-transfer mechanisms of these reactions will be discussed based on the DFT calculations. Presented is an efficient synthetic tool of carbon-carbon coupling reactions under mild conditions and pertinent ramifications therein.

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Synthesis and Characterization of Re and Mn-based Electrocatalysts containing Diaminobenzene Ligands

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A series of compounds of the form: $[M(NN)(CO)_3X]$ (where NN = phenylenediamine, diaminotoluene or diaminobenzoic acid; M=Mn when X=Br, and M=Re when X=Cl) were synthesized. All complexes are characterized by 1H NMR, FT-IR, and HRMS. Mn(diaminotoluene)(CO)₃Br is characterized by X-ray crystallography. Preliminarily, electrocatalytic reduction of carbon dioxide to carbon monoxide is only observed for the Mn-based compounds, in the presence of an external proton source.

Manganese Carbonyl Complexes with Phosphorous Ligands: Synthesis, Characterization, and CO₂ Reduction

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Eight novel manganese complexes of the type $[\text{Mn}(\text{bpy-tBu})(\text{CO})_3\text{L}]^+$ have been prepared and characterized, where the L ligand is various phosphorous containing ligands. From a known compound $\text{Mn}(\text{bpy-tBu})(\text{CO})_3\text{Br}$, the halide is removed by precipitation. Substitution of labile intermediate (OTf bound species) by L is then achieved at very mild conditions. All complexes are characterized by ¹H NMR, FT-IR, UV/vis, Cyclic Voltammetry and HRMS. There is evidence for interesting pi-stacking interactions when L is an aryl phosphine ligand.

Europium(II) and Europium(III) as Reducing Agents and Catalysts for Organic Reactions.

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Catalysis is an important aspect of synthetic chemistry, and the lanthanides can act as catalysts in many organic reactions. Due to its Lewis acidity, redox potential, and spectroscopic properties, europium ions are attractive lanthanides to use for the catalysis of organic reactions. Europium commonly exists in two oxidation states. In the 2+ state, europium is a mild reducing agent with a redox potential that can be influenced by the addition of different ligands. In the 3+ state, europium is a relatively hard Lewis acid catalyst for the formation of new asymmetric carbon-carbon bonds. Selectively reducing certain organic functional groups would allow for shorter syntheses due to the smaller number of protection steps that would be necessary. Additionally, stereospecific reactions are of vital importance when making biologically active molecules; however, traditional asymmetric synthesis usually involves reactants that are sensitive to water. We will describe our efforts to show that the potential of europium(II) can be fine-tuned to perform selective reductions and reductive couplings. We will also describe our efforts to show that europium(III) can be used as an enantioselective catalyst for the water-tolerant Michael addition. The use of lanthanides in organic synthesis allows for the use of less organic solvent and shorter synthetic routes.

Doping Control in Germanane

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Recent research on emerging semiconductor materials has explored dimensionally-dependent phenomena, where confining a material to one or two dimensions leads to the emergence of properties not observed in the bulk material and improved electron transport properties. Germanane, a robust two-dimensional semiconductor, has piqued interest in this emerging area of study but is held back for use in conventional semiconductor devices due to poor electrical conductivity. Controlling doping in two-dimensional sp^3 germanium is an attractive route to the improvement of electronic properties. A topotactic deintercalation of both p and n doped CaGe_2 crystals to create millimeter-scale germanane crystals, using gallium or phosphorus/arsenic, respectively, as dopants. These crystals, while structurally indistinguishable from undoped germanane, exhibit a reduction of >3 orders of magnitude in measured resistance. The increase in electronic response, along with the layered structure of these doped germananes allow for integration into conventional few-layer transistors. Introducing these dopants results in the emergence of new atmospheric dependent properties, activating and deactivating dopants, which lead to the possibility of using doped germanane as a gas detector. The ability to integrate doped germanane into conventional field effect devices, along with the ability to respond to the atmosphere, make germanane an attractive material for real-world applications in the emerging research of dimensionally-dependent semiconductors.

First-Row Metal Complexes Bearing Proton-Responsive Pincer Scaffolds

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Hydrogen bonding interactions within the secondary sphere of metalloenzyme active sites are often critical to their function, however most bio-inspired organometallic complexes do not attempt to reproduce these interactions in synthetic systems. Our group has designed a ligand scaffold, based on the tridentate terpyridine framework, that contains appended functionality in the form of hydroxy and anilino variants that provides directed hydrogen bonding with metal-bound substrates. Furthermore, the functionality can serve as hydrogen bond donors or acceptors depending on protonation state. Characterization of first-row metal complexes bearing the proton-responsive ligands will be presented alongside continued work toward the stabilization and reactivity of biologically-relevant intermediates in various small molecule catalytic cycles.

Fe₂S₂ Hydrogenase-inspired Electrocatalysts

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The discovery of the iron-only Hydrogenase enzyme's Fe₂S₂ active site component has lead to the study of numerous molecular catalysts containing iron and sulfur in a butterfly structure. We seek to design an electrocatalyst in which a diiron metallocenter has appropriate electronic properties, to mimic the enzyme's catalytic ability to interconvert protons and dihydrogen.

We have synthesized (μ-XPh)₂Fe₂(CO)₆ catalysts to investigate how variations in electronic, steric, and atomic structure impact electrocatalytic activity for the reduction of protons. Variation of X amongst the chalcogens (X= S, Se, Te) has been explored spectroscopically and electrochemically. Electrocatalysis of the reduction of protons from a weak acid source are not enhanced by the use of the larger chalcogens, likely due to enhanced rate of catalyst degradation. X-ray crystallography of (μ-SePh)₂Fe₂(CO)₆ displays only the *syn* isomer. This thermodynamic product when X= Se is different to that of the previously reported sulfur analog, where the *anti*-isomer is reported as the thermodynamic product.

Additonally, a (μ-S-EDG)(μ-S-EWG)Fe₂(CO)₆ catalyst to investigate how variations in electronic structure affect catalysis, via an Electron-Donating Group (EDG) and an Electron-Withdrawing Group (EWG).

$[M(\text{dpphen})(\text{CO})_3\text{X}]$ (M=Re & Mn): Electrocatalytic reduction of CO_2 to CO without an external proton source

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$[M(\text{dpphen})(\text{CO})_3\text{X}]$ (dpphen= 4,7-Diphenyl-1,10-phenanthroline, M=Mn & X=Br (**1**), and M=Re & X=Cl(**2**)) were synthesized and their catalytic activities for CO_2 reduction to CO were studied by using electrochemical methods. Complex **1** is the first known organomanganese catalyst to catalyze the CO_2 reduction significantly ($i_c/i_p = 12.2$ at the potential of -2.5 V vs. $\text{Fc}^{+/0}$) without the help of any external proton source. Factors other than the electrocatalyst reduction potentials such as steric effects and degree of conjugation are responsible for the catalytic activities. The manganese analogue (**1**) displays larger catalytic currents than that of rhenium (**2**) which indicates the possibility of using earth abundant manganese as a substitute for expensive rhenium metal in making CO_2 reduction electrocatalysts.

Rethinking the Heterogenization of Photocathode Systems; Novel Methods for Catalyst Functionalization of Semiconductors and Applications in Photoelectrocatalysis

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Engineering solar-powered catalyst systems for fuel production is of critical importance to the advancement of the global energy economy. Heterogeneous catalyst manifolds most promising for photocatalysis are those that boast versatile and cheap, stable components. Huisgen's 1,3-dipolar cycloaddition ('click' chemistry) and π -stacking graphene adsorption systems provide a range of facile methods for electrode-surface modification and catalyst binding to build stable photocathode systems. In this work, click chemistry has been made accessible to gallium-based semiconductors for the first time by decorating the semiconductor surface with azide functionalities, opening a whole new world of versatility to semiconductor catalysis. Resilient iron-based dihydrogen production catalysts with customizable ligand systems have been prepared and functionalized with terminal alkynes, and were shown to 'click' onto the azide-functionalized GaP surfaces. X-ray photoelectron spectroscopy (XPS) confirms the presence of the triazole-tethered iron species on the surface. These systems are currently being analyzed for photocatalytic activity for H₂ production. Graphene π -stacked catalyst manifolds were demonstrated as heterogeneous electrocatalysts by adsorption of simple cobalt catalysts onto graphene-coated metal oxide surfaces. These catalysts possess impressive catalytic efficiency for dihydrogen production (TOF > 6,000 s⁻¹) at low overpotentials (~0.3 V versus platinum). Design of photocathode systems incorporating these catalysts on graphene-coated GaP is currently under way. These design methods give access to a nearly unlimited variety of substrates and catalyst systems, making graphene and 'click' manifolds the template for a solar-fueled future.

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Low Temperature Synthesis of Scandium Iron Molybdate

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$\text{ScFeMo}_3\text{O}_{12}$ was synthesized at low temperatures using the non-hydrolytic sol-gel (NHSG) method. $\text{ScFeMo}_3\text{O}_{12}$ is a member of the $\text{A}_2\text{M}_3\text{O}_{12}$ family (A=trivalent metal, M=tungsten or molybdenum) of compounds, which typically display negative thermal expansion if an orthorhombic structure is formed. Different metals in the A and M site can cause variations in expansion and phase transition behavior, and compositions with mixed trivalent cations have shown interesting properties. Negative thermal expansion is a property seen when compounds in this family adopt a certain crystal structure, which leads to particles shrinking instead of expanding upon heating. In the case of this study, two trivalent metals, scandium and iron, were used for the synthesis. The properties of the products were analyzed using scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), and powder x-ray diffraction (PXRD).

One pot in-situ synthesis of poly(3-hexylthiophene)/metal oxide composites

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Composite materials have a broad range of applications due to their diversity and tunability of properties through careful selection of components. Polymer/inorganic composites are of particular interest because they can combine the advantageous properties of the polymer matrix (lightweight, flexible, easy to process) with value-added properties imparted by the inorganic filler material, which can add mechanical strength, thermal stability or other new properties to the composite. However, the synthesis of these composites is not an easy process, and can require multiple separate synthesis and purification steps for the individual components as well as the composite. This may result in loss of material and formation of inhomogeneous composites. A one pot in-situ synthesis, where polymerization and formation of the inorganic material happen concurrently in the same reaction vessel, can prevent these issues. In this project the one pot in-situ synthesis of metal oxide/poly(3-hexylthiophene) composites is explored.

Attempts to Modulate Frontier Molecular Orbitals in Asymmetric Iron(III) Complexes for Current Rectification

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Rectifiers are devices that allow electric current to flow unidirectionally. Molecular rectification can be achieved using electron donor and electron acceptor moieties with accessible energy at the electrode|molecule|electrode junction. Our group has demonstrated molecular rectification with trisphenolate and bisphenolate iron(III) complexes,^{1,2} therefore aiming towards nanoscale rectifying devices with high current efficiency, as well as efforts towards modulating molecular frontier orbitals for a better match with the electrode Fermi levels, led to the synthesis of new series of iron(III) asymmetric metallocosurfactants. Asymmetry is achieved by incorporation of pyridine and phenolate groups to the hydrophobic core with the metal ion. Amphiphilic properties and film formation were assessed using isothermal compression and Brewster angle micrography. All the complexes showed collapse pressures ~ 45 mN/m. Langmuir Blodgett films deposited solid substrates were characterized using UV-visible, infrared reflection absorption spectroscopy (IRRAS) and AFM. Current-Voltage measurements for gold|molecule|gold junction are under investigation.

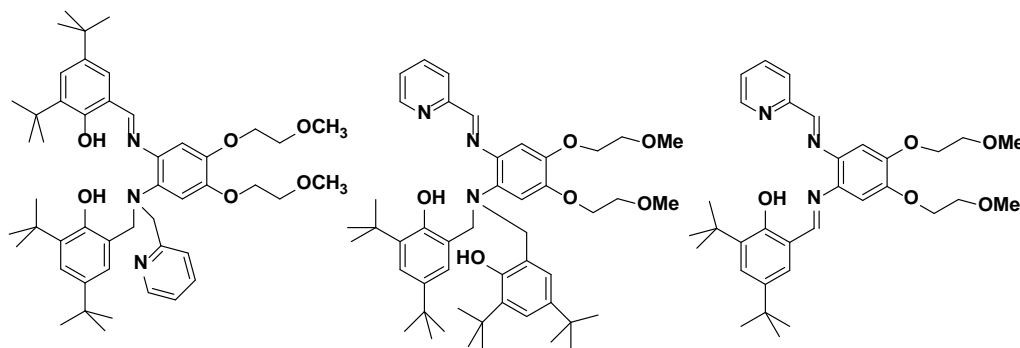


Figure 1: The asymmetric ligands for iron(III) complexes

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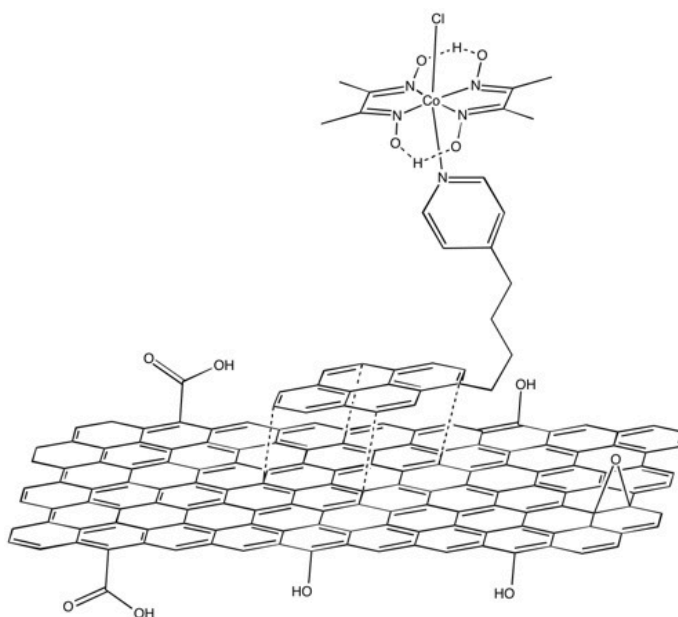
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Analysis of Pyridine-Tethered Aromatic Ligand Systems for Adsorption of Cobaloximes to Reduced Graphene Oxide

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Cobaloximes are a class of bis(dimethylglyoximate)cobalt(III) complexes that are widely known to be active dihydrogen production catalysts in neutral pH aqueous solutions. This research focuses on synthesizing cobaloxime derivatives with pyridine-tethered aromatic ligand systems to assess electrostatic adsorption on reduced graphene oxide (RGO). A relatively simple synthetic pathway has been developed to produce a wide variety of pyridine-tethered substituted aromatic ligands from commercially available reagents. A systematic approach was taken to investigate how the size, electron density, and tether length of the conjugated ring system ligated to the cobaloximes effect adsorption to the RGO surface. Cyclic voltammetry (CV) experiments were used to assess the activity and stability of the adsorbed cobaloxime species. Initial studies suggest successful electrostatic adsorption of the aromatic tethered cobaloxime compounds, and that catalytic activity of these derivatives is retained on the RGO surfaces. As RGO can be easily deposited onto a variety of substrates, the systematic analysis of various conjugated ligands and the resulting electrostatic adsorption on RGO provides guidelines for the development of other heterogeneous manifolds using a graphitic interface.



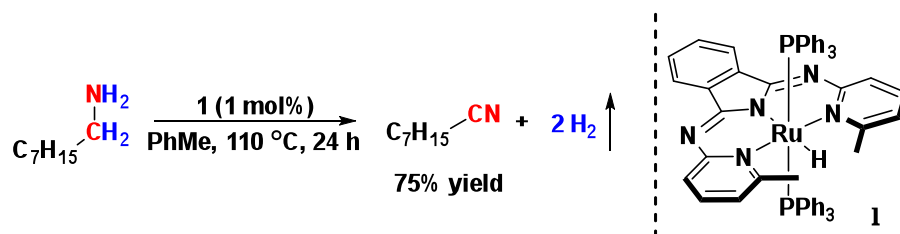
Mechanistic Insights for the Acceptorless Dehydrogenation of Primary Amines to Nitriles with Ru-[NNN] Pincer Complexes

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Acceptorless dehydrogenation reactions have received significant attention over the past several decades as benign, versatile, and atom-economical synthetic strategies.¹ We have recently reported an amide-derived *NNN*-Ru(II) hydride complex (**1**) that catalyzes the oxidant-free, acceptorless dehydrogenation of primary amines to nitriles², a transformation that has previously required exogenous oxidants, base, or hydrogen acceptors. Mechanistic investigations are currently underway to elucidate the unique reactivity of **1**. Preliminary studies suggest an inner-sphere pathway, where a single phosphine dissociation event allows coordination of amine to a Ru(II) 16 electron complex. We propose a rate-limiting dehydrogenation step occurs through deprotonation of coordinated amine by hydride, subsequently followed by fast β -hydride elimination and secondary dehydrogenation steps. Kinetic rate data and computational studies suggest a highly-ordered dehydrogenation transition state that is stabilized through hydrogen bonding effects of free amine. Additionally, the role of the *NNN*-pincer ligand is carefully examined through a systematic study of electronic and steric effects.



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Tin Sulfides Through Non-Hydrolytic Sol-Gel Synthesis

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Semiconducting sulfides have long been an area of interest to many researchers. Many modern applications require nanosized materials or powders with high surface area. Such materials can be obtained by low temperature synthesis. Our group is exploring non-hydrolytic sol gel routes to metal sulfides. In this poster, results on investigations of the tin sulfide system will be presented. The effects various solvents, sulfurizing agents, starting halides, temperature, and solution additives are studied.

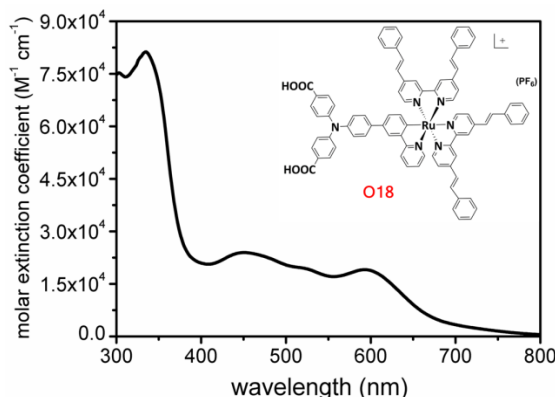
Molecular Orbital Engineering of a Panchromatic Cyclometalated Ru(II) Dye for p-type Dye-sensitized NiO Solar Cells

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Dye-sensitized mesoporous NiO has been widely investigated as photocathode in p-type dye-sensitized solar cells¹ and photosynthetic cells for water reduction². The parasitic absorption and slow hole transport process in NiO limits the use of very thin (<5 μm) films. Thus, dyes with intense and wide spectral response are highly desired. Recently, we report a panchromatic cyclometalated Ru(II) complex, denoted as O18, which shows intense metal-to-ligand charge transfer transitions in the visible to near-IR region with the absorption tail extending to 800 nm.³ The panchromatic spectra response and enhanced molar extinction coefficient ($\epsilon = 1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 593 nm in solution) of O18 are attributed to the stabilization of the lowest unoccupied molecular orbital and the increased absorption cross section via rationally extending the π -conjugated system of 2,2-bipyridyl ligands. As a result, NiO solar cells sensitized with O18 show short-circuit currents up to 3.43 mA cm^{-2} and efficiencies up to 0.104 %, which are the best among all cyclometalated-Ru(II)-sensitized p-type dye-sensitized NiO solar cells. Femtosecond transient absorption spectroscopy reveals decreased geminate recombination across the O18–NiO interface by 1 order of magnitude compared to our previous report.



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Tethered Homobimetallics for the Activation of Small Molecules

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C-H bond activation and small molecule activation are at the forefront of organometallic chemistry. Both processes allow for efficient one-step transformation of inexpensive and readily available molecules into functionalized organic compounds. Metal catalysis is required for these transformations. One specific example of metal catalyzed C-H bond activation involves formation of the metal-nitrene functionality from azides and its subsequent reaction with alkanes to form alkyl amines. Apart from C-H amination, the metal-nitrene functionality converts olefins, isocyanides, and carbon monoxide into aziridines, carbodiimides, and isocyanates, respectively. Late transition metals are particularly suited for catalytic nitrene transfer to organic substrates, as they feature reactive nitrene functionalities. Mononuclear nickel and copper complexes catalyzing C-H amination have been reported, where nitrene transfer was proposed through a bridging nitrene moiety. Thus, it may be anticipated that bimetallic precursors will facilitate nitrene transfer. In the field of small molecule activation, carbon dioxide has attracted attention, due to its low cost and detrimental effects on the environment. However, activation of carbon dioxide is difficult, due to its thermodynamic and kinetic stability, combined with the need for multi-electron reduction. Recently, the focus shifted to development of multi-metallic systems towards carbon dioxide activation. Multi-metallic systems may be advantageous to monometallic systems as they **(1)** may enable cooperative binding and activation of carbon dioxide; **(2)** are capable of providing more reducing equivalents simultaneously compared with monometallic systems. Herein, we report tethered, homobimetallic systems featuring late transition metals and their progress towards C-H amination and carbon dioxide activation.

Synthesis of a Macromolecular Lanthanide Complex for Luminescent Imaging

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Lanthanide complexes have been used in luminescent imaging due to their long luminescent lifetimes (milliseconds) as opposed to purely organic fluorophores (nanoseconds). However, lanthanide emission is generally weak due to the Laporte forbidden transitions; therefore, organic chromophores are attached to lanthanide complexes to act as antennas for energy transfer to increase efficiency through allowed transitions. Lanthanide complexes with antennas have been previously reported, but they include coordinated solvent molecules which can quench luminescence. We synthesized a new macromolecular ligand that uses 1,7-bis(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane (DO2A-*tert*-butyl ester) as a precursor with the aim of excluding quenching solvent molecules while increasing the luminescence intensity with the aid of an antenna. The precursor, DO2A-*tert*-butyl ester, is reported to take three days to synthesize, but we have reduced the time needed to synthesize DO2A-*tert*-butyl ester to less than one day by application of heating and adjustment of conditions based on pK_a considerations. Complexation of our macromolecular ligand with europium and terbium ions enables the complex to have luminescent properties. We will present these lanthanide complexes and data supporting their potential use in the field of luminescent imaging. We expect that complexes based upon our new ligand will further studies in luminescent imaging due to the expected lack of coordinated solvent.

Photophysical and Electrochemical Properties of $\text{Mn}(\text{NN})(\text{CO})_3\text{Br}$ (where NN = Substituted Phenanthroline)

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Three novel complexes of the type $\text{Mn}(\text{NN})(\text{CO})_3\text{Br}$ have been synthesized, where NN = 5-substituted-1,10-phenanthroline. The novel compounds have been characterized by ¹H-NMR, FTIR, LSV, HRMS, UV/vis and X-ray crystallography. Analogous Re(I) compounds are also presented and the photophysical and electrochemical properties are discussed. A correlation is apparent between the MLCT absorbance bands and the electrochemical reduction of both the Re and Mn series of compounds.

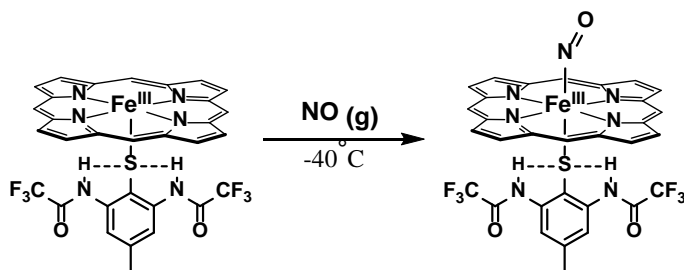
Synthesis and Spectroscopic Characterization of Ferric Heme–Thiolate Complexes as Models for Cytochrome P450nor

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Cytochrome P450s are a ubiquitous class of heme proteins which utilize a proximal thiolate ligand to catalyze challenging and complex chemical transformations. Nitric oxide (NO) is an important intracellular signaling molecule at nanomolar concentrations; however, it is toxic at high micromolar concentrations, consequently making NO production and regulation essential in biological systems. Cytochrome P450 nitric oxide reductase (Cyt P450nor), a unique class of the P450 enzymes used during anaerobic respiration by soil dwelling fungi and yeast, catalyzes the reduction of NO to nitrous oxide (N_2O) and as a result prevents the accumulation of this toxic metabolite. In the proposed mechanism of Cyt P450nor, a ferric heme binds NO to form a ferric heme-nitrosyl complex, which subsequently reacts with NADH and another equivalent of NO to close the catalytic cycle.¹ These ferric heme-nitrosyls with thiolate coordination are stable in a protein environment, but the generation of a stable model complex remains highly elusive. This is challenging due to reductive nitrosylation of the ferric heme in the presence of excess NO and the decomposition of the complex by nitrosylation of the thiolate ligand resulting in a ferrous heme-nitrosyl complex.² This work focuses on the use of a hydrogen-bonded thiolate ligand, S-2,6-di(trifluoracetyl-amino-4-methyl) thiophenol (abbreviated SR-H_2^-), to prevent these undesirable side reactions. Here, preparation of the ferric complex $[\text{Fe}(\text{TPP})(\text{SR-H}_2)]$ is presented, which is obtained by reaction of ferrous tetraphenylporphyrin, $[\text{Fe}(\text{TPP})]$, with the hydrogen bonded thiolate ligand SR-H_2^- . In addition, the reactivity of this ferric thiolate complex with NO is studied using different spectroscopic methods.



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Discovery of New Metal Clusters Entrapped Within Fullerene Cages

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Since the discovery of metallofullerenes nearly 30 years ago, little research has been conducted to expand the concept of entrapping new endohedral metals. Traditional metal clusters have focused on Group IIIB transition metals and 4f-block elements. Our goal is to venture outside of these conventions and expand the selection of which metals can or cannot be entrapped. To date, there are no endohedrals containing transition metals outside of Ti, Sc, Y, and La. In this presentation, we investigate the feasibility of encapsulating additional metals beyond the already established metal clusters. Preliminary results indicate that new metallofullerenes can successfully be produced utilizing our electric-arc, plasma reactor.

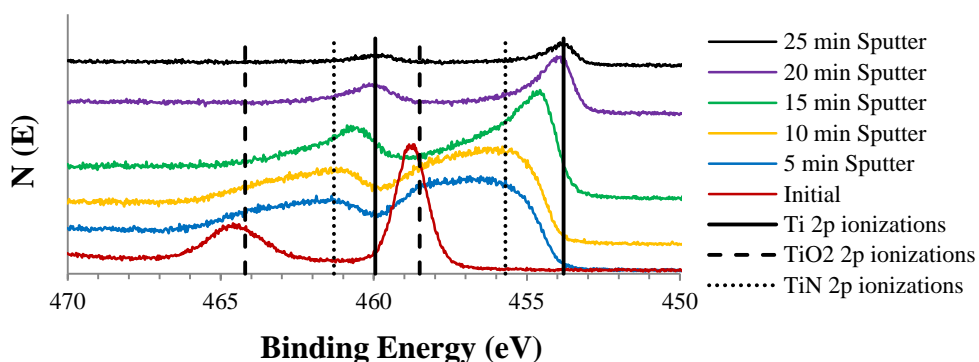
Growth of Elemental Titanium by Atomic Layer Deposition Using 1,4-Bis(trimethylsilyl)dihydropyrazine as a Coreagent

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Metal-containing thin films are employed in microelectronic, solar cell, catalytic, and battery technologies. Thermal atomic layer deposition (ALD) is the preferred technique for controlled, conformal film growth in the high aspect ratio features of nanodevices. With the exception of copper, the negative electrochemical potentials of first-row transition metal cations make the growth of these element films extremely challenging.¹ Due to the lack of strongly-reducing coreagents, the low-temperature thermal ALD of high-purity metallic films is an intractable problem for many elements, precluding their use in modern microelectronic devices. Selected bis(trimethylsilyl) six-membered ring systems were previously used as salt-free reductants for various metal chloride complexes; 1,4-Bis(trimethylsilyl)dihydropyrazine (DHP) was especially useful for this purpose.² Herein, we demonstrate the reducing power of DHP toward the growth of elemental titanium thin films by ALD. This process likely proceeds through $\text{Cl}(\text{CH}_3)_3\text{Si}$ bond formation, and a pyrazine dianionic intermediate species, facilitating the reduction of TiCl_4 to elemental titanium. A growth rate of 0.12 \AA/cycle was maintained within the $90\text{--}100^\circ\text{C}$ temperature range. Characterization by scanning electron microscopy, atomic force microscopy, and X-ray photoelectron spectroscopy suggest uniform films with low surfaces roughnesses, comprised of titanium in the zero oxidation state.



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Insights Into the Activity of a Set of Glycosylated Polyphenols and their Synthetic Derivatives Against Metal-A β Species

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Alzheimer's disease remains a growing issue for the global population, yet in depth understanding of its chemical underpinnings and the roles of metal-free and metal-associated A β (A β /metal-A β) in the disease are unclear. The development of small molecular probes to specifically target and modulate the reactivity of A β /metal-A β is essential in order to expand our understanding of their molecular mechanisms. Herein, we present three different natural product frameworks (phlorizin, verbascoside, and rutin) and their selectively acetylated derivatives (F2, VPP, and R2, respectively) for their ability to interact with and modulate the reactivity of and metal-free A β and metal [Cu(II) and Zn(II)]-A β species. We found that both verbascoside and VPP show a non-specific, though unique, ability to disrupt the aggregation of A β species as well as partially disaggregate pre-formed fibrillar aggregates. The molecular level reactivity of these compounds was further examined by 2D NMR spectroscopy and far-UV CD spectroscopy. These studies suggest that verbascoside provides a functional framework for further compound development toward a more specific and higher affinity anti-amyloidogenic probe.

Synthesis, Characterization, and Reactivity of Non-Heme Iron Nitrosyl Complexes

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As part of immune defense, macrophages in the human body produce nitric oxide (NO) in order to kill off invading pathogens. Bacteria that express flavodiiron nitric oxide reductases (FNORs) are able to detoxify the NO by reducing it to N₂O, allowing them to proliferate. Despite the importance of these enzymes in bacterial pathogenesis, the mechanism of FNORs is not currently known. Our group recently reported that upon two-electron reduction, the FNOR model complex [Fe₂(BPMP)(OPr)(NO)₂](BPh₄)₂ produces N₂O, suggesting that the enzyme could use a similar pathway to detoxify NO *in vivo*. In order to demonstrate that a diiron motif with *cis* NO moieties is required for efficient N₂O production, model complexes employing derivatives of the ligand BMPA-PhOH (*N*-(2-hydroxybenzyl)-*N,N*-bis(2-pyridylmethyl)amine) have been synthesized and characterized using UV-Visible, IR, and EPR spectroscopies as well as X-ray crystallography. These complexes can exist in solution as monomers or as phenolate-bridged dimers (shown below), depending on the substitution of the phenolate group of the ligand. In contrast to the BPMP model complex, which produces N₂O rapidly and quantitatively upon reduction, the BMPA-PhO model complexes initially disproportionate upon reduction to form a ferrous complex and a dinitrosyl iron complex (DNIC). N₂O formation occurs only slowly and in low yield.

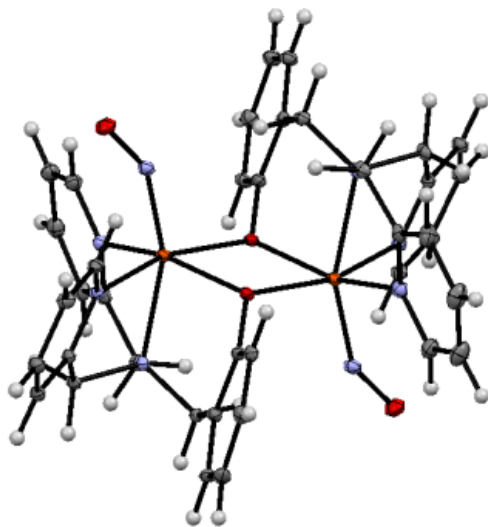


Figure 1. Crystal structure of the dimeric model complex [Fe₂(BMPA-PhO)₂(NO)₂]²⁺

Redox and Electronic Properties of $[\text{Ru}^{\text{II}}-\text{M}^{\text{III}}]$ and $[\text{Mn}^{\text{III}}(\text{bpb})\text{X}]$ Complexes as Platforms for Water Oxidation

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Significant progress has been made recently towards a sustainable and carbon-free energy economy. One promising approach is photochemical splitting of H_2O into O_2 and H_2 . Water oxidation is challenging in water splitting, where more efficient catalysts are required to lower the kinetic barrier of this process. Particularly catalysts based on earth-abundant metals such as manganese and iron are highly attractive compared to their noble metal analogues. We report the synthesis and characterization of a series of complexes $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{Fe}^{\text{III}}(\text{L}^2)]^{+2}$, $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{Mn}^{\text{III}}(\text{L}^2)]^{+2}$ and $[\text{Mn}^{\text{III}}(\text{bpb})\text{X}]$ (**figure 1**). The complexes were fully characterized by spectroscopic and spectrometric methods.

Upon reduction, $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{Fe}^{\text{III}}\text{L}^2]^{+2}$ shows four reversible reduction processes. The process at $-1.21 \text{ V}_{\text{Fc}/\text{Fc}^+}$ corresponds to the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ couple, whereas those at $-1.74 \text{ V}_{\text{Fc}/\text{Fc}^+}$ and $-2.1 \text{ V}_{\text{Fc}/\text{Fc}^+}$ are attributed to two bipyridine reductions and the one at $-2.3 \text{ V}_{\text{Fc}/\text{Fc}^+}$ involves imine reduction. Comparable reversible redox processes were observed for the two bipyridines, and imines in $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{Mn}^{\text{III}}(\text{L}^2)]^{+2}$. A quasi reversible process observed at $-0.32 \text{ V}_{\text{Fc}/\text{Fc}^+}$ is attributed to $\text{Mn}(\text{III})/\text{Mn}(\text{II})$ couple. For the $[\text{Mn}^{\text{III}}(\text{bpb})\text{X}]$, $\text{X} = \text{Cl}$, complex, a reversible process observed at $-0.46 \text{ V}_{\text{Fc}/\text{Fc}^+}$ is attributed to $\text{Mn}(\text{III})/\text{Mn}(\text{II})$ couple. A quasi reversible process observed at $0.4 \text{ V}_{\text{Fc}/\text{Fc}^+}$ is attributed to ligand-based oxidations. DFT calculations support these assignments.

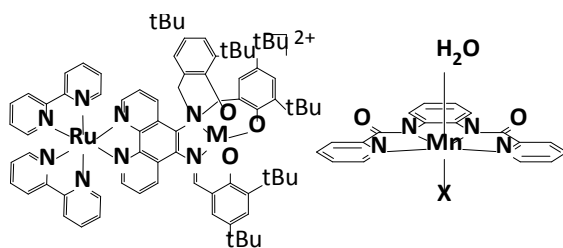


Figure 1: Isolated complexes

Key M = Manganese (Mn), Iron (Fe), X = Cl, SCN

Influence of Cryptand Structure on the Physicochemical Properties of Ln^{II} -Containing Cryptates

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The goal of this project is to study the effect of different structural features on the physicochemical properties of Ln^{II} -containing cryptates. These complexes are important because of their potential application as contrast agents (Eu^{II} -containing cryptates) at ultra-high field strengths (≥ 7 T) in magnetic resonance imaging,¹ as reducing agents, as luminescent materials, and as oxygen sensors. However, reports of the influence of cryptand-type ligands on physicochemical properties of Ln^{II} -containing complexes are limited, making improvements to Ln^{II} -containing complexes challenging. We hypothesized that changing ligand structural features including the coordinating atoms and pendant functional groups in multiple complexes would produce redundancies in these changes that would enable a systematic study. This hypothesis is based on previous studies done by our group where Eu^{II} was found to form stable complexes with soft donating ligands.² To test our hypothesis, we are synthesizing amide and amine-containing cryptand complexes with different functional groups, as well as different coordinating atoms. Tuning redox properties results in selective reducing agents for organic functional groups and tuning magnetic properties, results in potential contrast agents. kinetic stability,³ thermodynamic stability, and relaxivity are being measured for the resulting Eu^{II} -containing cryptates and the structure–property relationship will be evaluated. Here, we present the synthesis of functionalized cryptands and their measured physicochemical properties when metalated. Ultimately, we expect that this study will advance our ability to explain and quantify the influence of structural changes in cryptand-type ligands on the physicochemical properties of Ln^{II} -containing cryptates.

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Study of the Properties of Eu(II)-Containing Cryptates Relevant to Contrast Agents

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The purpose of this research is to study the influence of molecular parameters and field strength on the efficiency (relaxivity) of Eu(II)-containing cryptates as contrast agents for magnetic resonance imaging. Relaxivity is governed by several molecular parameters including rotational correlation time (τ_R). The relaxivity of Eu(II)-containing cryptates with short and long value of τ_R have been reported. To understand the boundary between these two extremes, Eu(II)-containing cryptates of intermediate τ_R values are needed. To obtain cryptates with intermediate τ_R values, we are synthesizing a biphenyl-functionalized cryptand to form host-guest adducts with β -cyclodextrin and poly- β -cyclodextrin inspired by previous work with Gd(III)-containing complexes. Here, we present the progress towards the relaxometric studies of Eu(II)-containing cryptates. We expect that these studies will lead to a complete understanding of the influence of τ_R and field strength on the relaxivity of Eu(II)-containing cryptates to design more efficient contrast agents.

Studying Water-Exchange Rates of Lanthanide Ions in Ionic Liquids Using Variable-Temperature ^{17}O -NMR Spectroscopy

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Ionic liquids have been studied serving as “green solvents” in lanthanide-catalyzed organic reactions. However, reaction rates and yields vary as a function of composition of the different ionic liquids, and the reasons for this variance are not well understood. It is important to understand the reasons when choosing and designing ionic liquids for catalysis. To better understand the effect of ionic liquids on catalysis, the association of substrates to and dissociation of substrates from lanthanide ions in ionic liquids are important. We used water as a model substrate to illustrate the measurement of the dissociation and association rates between the substrates and lanthanide ions in ionic liquids. We will present the water-exchange rate measurements of five lanthanide ions (Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , and Er^{3+}) in wet 1-ethyl-3-methylimidazolium ethylsulfate using variable-temperature ^{17}O -NMR spectroscopy. The water-exchange rates of the studied ions generally increase as a function of ionic radius. Interestingly, this trend is the inverse of what is observed in aqueous solutions. We expect this research will be a benefit to researchers choosing and designing ionic liquids as solvents in lanthanide-catalyzed reactions.

Solvent Dependent Assembly of Zinc Metallacrown Frameworks

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Since their discovery in 1989, metallacrowns have shown properties as single molecule magnets and lanthanide luminophores. However, the construction of these compounds in solution is not well understood, and any effects of solvent interactions could alter the final framework. Metallacrowns composed of zinc, lanthanides, and picolinic hydroxamic acid (picHA) offer a variety of possible structures, varying from a $\text{Zn}_5(\text{picHA})_4$ complex to a $\text{LnZn}_{16}(\text{picHA})_{16}$ complex. We have investigated the effect of solvent direction on these zinc metallacrown scaffolds, taking advantage of hard/soft interactions and the thermodynamics of various geometries. X-ray crystallography, ESI-MS and NMR spectroscopy were used to characterize these compounds.

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Epitaxial growth of large area single-crystalline few-layer MoS₂ with high space charge mobility of 192 cm² V⁻¹ s⁻¹

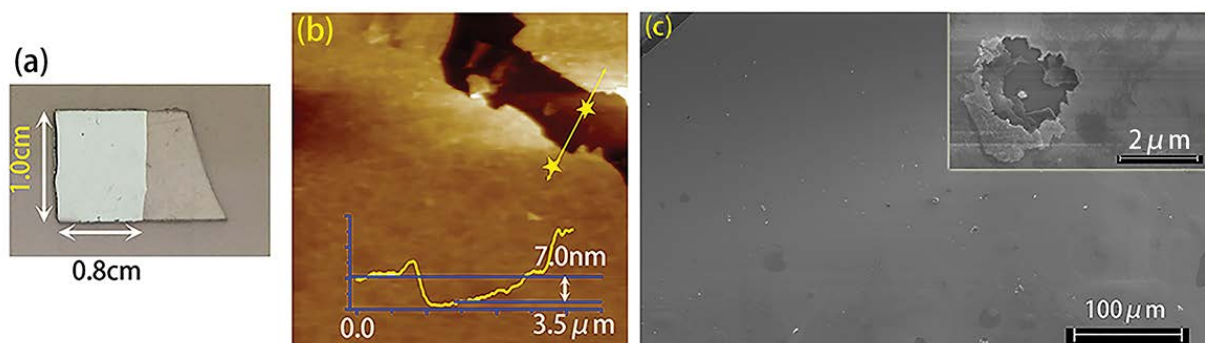
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Single crystalline few-layer MoS₂ films on (0001)-oriented sapphire with excellent structural and electrical properties over centimeter length scale were made by vapor-solid growth. High-resolution X-ray diffraction scans indicated that the films had good out-of-plane ordering and epitaxial registry. A carrier density of $\sim 2 \times 10^{11}$ cm⁻² and a room temperature mobility of 192 cm²/Vs were extracted from space-charge limited transport regime in the films. The electron mobility was found to exhibit in-plane anisotropy with a ratio of ~ 1.8 . Theoretical estimates of the temperature-dependent electron mobility including optical phonon, acoustic deformation potential and remote ionized impurity scattering were found to satisfactorily match the measured data. The synthesis approach reported here demonstrates the feasibility of device quality few-layer MoS₂ films with excellent uniformity and high quality.



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Spectroelectrochemical Determination of Conduction Band Edge in Mesoporous TiO₂ Photoanode Used in Dye-Sensitized Solar Cells

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Mesoporous wide bandgap semiconductor films have been widely studied in various solar energy conversion technologies due to their stability under sunlight and their large surface area resulting enhancement of the solar energy conversion efficiency.¹ However, the conduction band edge position (E_{CB}), arguably the most important physical parameter in these photoanode films has remained uncertain so far.² Due to the smaller dimensions (less than the depletion width) and presence of large density of trapped electrons, E_{CB} cannot be determined from Mott–Schottky analysis or from photocurrent onset potential.³ The spectroelectrochemical method, developed by Fitzmaurice *et al.*⁴ also has drawbacks like (1) absorbance of the film is scan rate (of Cyclic Voltammetry) dependent, (2) assumption of flat interface is unlikely in these nanoparticulate semiconductor electrodes, (3) extinction co-efficient (ϵ) was calculated considering the total electron concentration instead of free electrons in the Conduction Band. Moreover, it has been argued that the absorbance spectrum measured while charging the film by applying reductive potential is due to the total electron or trapped electron instead of free electrons in the CB.⁵

In our spectroelectrochemical method, we have conclusively characterized the absorption features in nanostructured TiO₂ film and E_{CB} has been determined. In addition to this, extinction co-efficient(ϵ) of the free electrons has also been determined which is also very useful parameter for various spectroelectrochemical methods being used to study charge transfer process in solar cells.⁶

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Azurin as a Protein Scaffold for the Construction of a Functional Hydrogenase Mimic

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The impending energy crisis has presented an opportunity for creative approaches towards potential solutions. Hydrogen has emerged as a leading alternative fuel candidate. Towards this end, hydrogenases, enzymes that carry out the interconversion of protons and electrons to hydrogen gas, are of great interest, as they are often suggested for potential incorporation into a fuel cell and clean generation of hydrogen. However, native hydrogenases are poorly suited for general-purpose application due to their limited stability, rapid inactivation when exposed to oxygen, complexity of their biosynthesis, and restricted potential for scalability. Thus, we seek to circumvent these issues and *accomplish chemistry similar to that performed by the [NiFe] hydrogenases by designing new functionality into a currently existing metalloprotein.*

We seek to harness the advantages of bioinorganic platforms, which include stable protein folds, well-defined coordination environments, and controlled substrate access, while overcoming the limitations of fragile, multimeric protein systems. Using the electron transfer protein azurin as a platform for protein redesign, we have shown that replacement of the native copper center with nickel produces a tunable, redox-active site. We can further modulate this potential using targeted mutations to develop an artificial enzyme capable of hydrogen production. Spectroscopic and electrochemical techniques, in conjunction with DFT calculations, were used to probe the electronic structure and assess the catalytic potential of this protein. Comparison of these features to native [NiFe] hydrogenases and functional model compounds will provide insight into the key parameters required for catalytic activity and guide future work.

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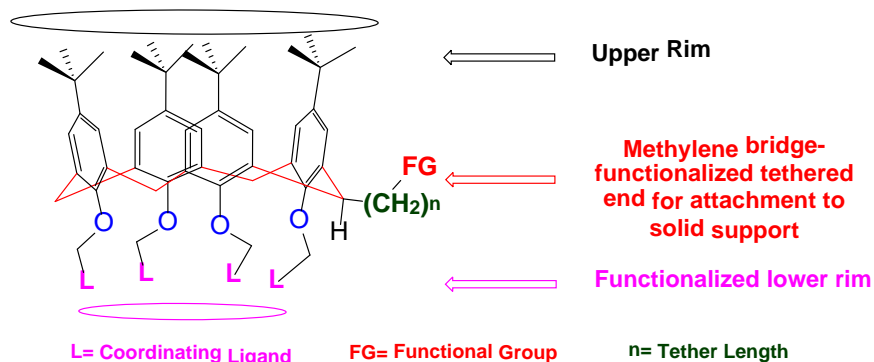
New Calix[4]arene Based Precursors For Stationary Phases Useful In Separation Of Rare Earth Metals

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The rare earth elements (REE), composed primarily of the fifteen lanthanides, find broad application in many modern devices making these elements indispensable and important to the sustainable, green world approach prevalent these days. Liquid-liquid extraction for the separation of lanthanides using a calix[4]arene scaffold with coordinating ligands on its lower rim has been studied for many years.¹ In the present work, we discuss the synthesis and characterization of new chlorine and amine terminated 2-alkyl-p-tert-butylcalix[4]arenes with phosphine oxide, ketone, ester, and CMPO based coordinating ligands incorporated on the lower rim.² These new moieties will act as useful precursors for the synthesis of functionalized stationary phases. Novel heterogeneous materials will be prepared by immobilizing the 2-functionalized amine terminated calix[4]arene derivatives on the surface of a solid support like silica and will find application in chromatographic separation of REE from a wide range of electronic wastes or slurries, subsequently helping to isolate these metals in high purity. Before immobilization onto a solid support, we have investigated the extraction efficiencies of these new calix[4]arenes for rare earth metals in liquid-liquid extraction in order to confirm that functionalization at the 2-position of the calix[4]arenes does not interfere with the extraction properties of the coordinating ligands on the lower rim.



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Separation of $B_{12}H_{10}(S(CH_3)_2)_2$ Isomers by Selective Complexation with β -Cyclodextrin

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The synthesis, separation, and characterization of the three isomers of $B_{12}H_{10}(S(CH_3)_2)_2$, **I**: 1,12- $B_{12}H_{10}(S(CH_3)_2)_2$, **P**: 1,7- $B_{12}H_{10}(S(CH_3)_2)_2$, **M**; and 1,2- $B_{12}H_{10}(S(CH_3)_2)_2$, **O**, were recently reported by Shore et al.^{1,2} Separation was achieved by use of column chromatography. In our hands when performing the preparation of **I** on a multi-gram scale it was found that chromatographic separation of the isomers was inconvenient and used large quantities of solvents. By adding a solution ($CH_3CN:H_2O$) of β -Cyclodextrin to a solution containing a mixture of the **P** and **M** isomers, it was found that all of **P**, and a small amount of **M**, was precipitated out of solution, allowing for a high yield of pure **M** to be isolated without the need for chromatography. Details of our separation scheme will be presented.

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Electron-Transfer Processes between Quantum Dots and Organic Donor/Acceptor Species: A Study of the Role of Ligand Binding Affinities

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Inorganic semiconductor nanocrystals (Quantum Dots, QDs) are a fascinating class of materials, with electronic, chemical, and optical properties that directly depend on the size and shape of the crystallites. Whereas considerable efforts have been devoted over the last thirty years to the study of the detailed photophysics of quantum dots perfectly isolated from their surroundings, much less attention has been given to phenomena involving exchange of electronic charge and energy between QDs and molecular species surrounding them. We recently initiated a broad research program aimed at designing and characterizing hybrid donor/acceptor systems based on the coupling of inorganic QDs and paramagnetic molecules, with the aim of controlling the exchange processes through spin-polarization effects. The system presented here is based on the coupling of archetypical cadmium chalcogenide nanostructures and nitroxide free radicals. Our studies show that the electron transfer rate constant is rather larger, but with an efficiency which is limited by the radical binding affinity towards the QDs surface. We investigated the role of surface binding affinity by focusing on a typical kind of organic radicals, nitronyl nitroxide (NN), which were synthesized with different anchoring group to vary their binding affinity. Exchange interactions between QDs and bound radical species were followed by CW and time-resolved photoluminescence quenching studies, and different quenching behaviors were observed. A detailed mechanism is proposed to support the observed photophysics.

Physical Variation in Lanthanide Containing DOTMA Complexes Across the Series

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There are currently many different contrast agents available magnetic resonance imaging; however, these agents are optimized for magnetic field strengths below 3 T. This project involves the synthesis, purification and crystallization of N-[1-(2, 3-dioleoyloxy)propyl]-N,N,N-trimethylammonium chloride (DOTMA) complexes with 11 trivalent lanthanide metal ions (all except Gd^{3+} , Ho^{3+} , and Pm^{3+}) and Y^{3+} . The exceptions of Gd^{3+} and Ho^{3+} from crystallization are due to their structures having already been published. Pm^{3+} was excluded due to its radioactivity, and Y^{3+} was included as a diamagnetic control group. These complexes were synthesized using a modified version of the synthesis put forth by Aime.¹ X-ray crystallography is being performed to allow us to make physical measurements of these complexes and will ideally allow us to determine the effects that the physical changes across the series have on the CEST effects these metals exhibit. We will present the X-ray crystal structures we have been able to resolve. As well as the bond measurements that we have obtained for these complexes. We expect our results to be relevant to molecular imaging using magnetic resonance imaging.

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Secondary coordination sphere interactions with a tripodal ligand derived from 2-hydroxypyridine

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Ligand-metal cooperativity has emerged as a powerful tool in the design of new inorganic complexes. Often, the ligand platform in these complexes serves to modify the electronic nature of the metal site; thereby providing a thermodynamic stabilization of otherwise reactive species. Such changes in ligand field may be achieved by aromatization/dearomatization, protonation state changes and/or tautomerization. Recently, we have initiated studies of transition metal complexes supported by a tripodal ligand (H_3thpa) derived from 2-hydroxypyridine. We have previously shown that copper-chloride complexes engage in hydrogen bonding interactions with H_3thpa and the strength of these hydrogen bonding interactions is dictated by the electronics at the metal center. Continued reaction chemistry of transition-metal complexes supported by the H_3thpa ligand will be presented with an emphasis on reactivity consequences of protonation-induced ligand field changes.

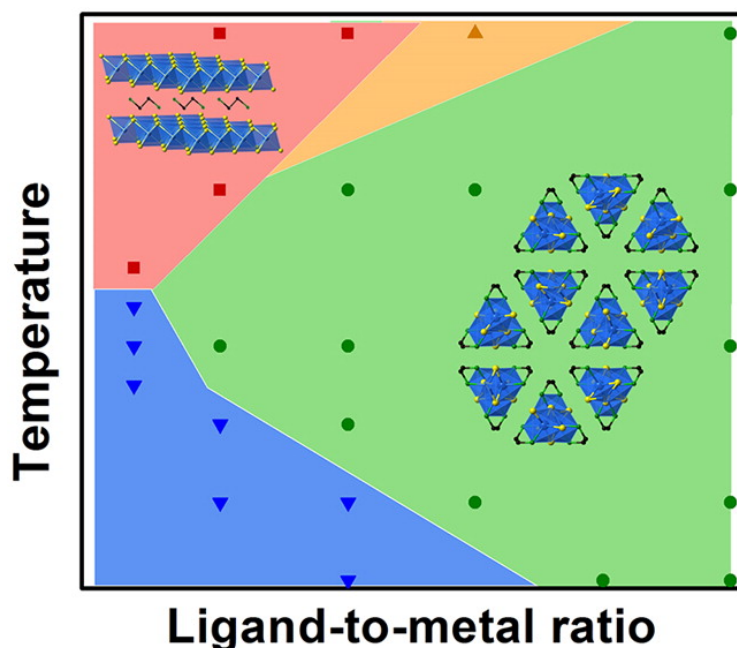
The Rational Synthesis of Dimensionally Reduced TiS_2 Phases

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Despite the fact that new dimensionally reduced hybrid organic-inorganic compounds have attracted considerable interest due to their unique optical and electronic properties, the rational synthesis of these new materials remains elusive. Here we systematically studied the relative influence of the major synthetic parameters including temperature, ligand structure and ligand to metal stoichiometry on the preparation of dimensionally reduced TiS_2 . One dimensional TiS_2 phases tend to form at high ligand to metal ratios and relatively lower temperatures, while the parent two dimensional lattices are preferred at higher temperature. The organic ligand structure dictates the temperature window at which a dimensionally reduced phase can be accessed. Although a small change in ligand structure, such as from ethylenediamine to propylenediamine, will significantly influence the stability of these phases, it will only subtly change the electronic structure. By developing a systematic understanding of the effects of various factors during the synthesis we provide a pathway to rationally create new dimensionally reduced materials.



Synthesis and Characterization of Biocompatible, Light Activated, Nitric Oxide Releasing Metallopolymers

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Metal-nitrosyl complexes are a well-known class of photoactive compounds that release nitric oxide (NO) after light irradiation. These complexes can be used for a variety of biological applications such as for vasodilation since NO is a bioregulatory agent involved in blood pressure regulation. In order to be used *in vivo*, however, these complexes have to be able to release NO upon red light activation. Unfortunately, the energy of this type of light is too low to undergo a photochemical reaction and release NO. We have created Ru-NO complexes that release NO after red (617nm) light irradiation. Furthermore, by modifying the structure of different ligands, we have created polymers that both sensitize the metal-nitrosyl complex toward the red light activation and allow for NO release in the solid state. In addition, these NO releasing metallopolymers can be used as materials for regenerable NO release since it has been shown to regenerate the NO-moiety by treatment with nitrite solution. Future work will focus on improving the efficiency of the NO release and testing *in vivo* for NO release.

Understanding Magnesium Electrolytes through Modification of Lewis Acid/Base Pairs

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Magnesium-ion batteries are still in the early stages of development. The earliest research in this post-Li battery occurred in the 1990's and early 2000's. The solution chemistry of Mg is more complex compared to lithium, making the synthesis of an electrolyte that displays both reversible Mg deposition and a wide electrochemical window a major obstacle in rechargeable Mg batteries. Currently most electrolytes are composed of highly air sensitive Grignard reagents, precluding their application in commercialized EV or HEV systems due to reactivity and flammability concerns. In an effort to improve the commercial viability of Mg-ion battery systems we are working towards the synthesis of air and moisture resistant Mg electrolytes. Starting from commercially available phenols, we have synthesized a series of non-Grignard electrolytes with various para-substituents. Controlling the electron withdrawing ability of the para-substituent has resulted in the ability to shift the anodic stability of the electrolyte by ~400 mV. The para-CF₃ substituted phenol exhibited the highest stability of 3 V vs Mg. These electrolytes also show significantly improved stability to air and moisture, with no loss in electrochemical stability after stirring for 6 hours in air. Examination of the solution speciation revealed ligand exchange occurred between the Mg and Al species creating the $\text{Mg}_2\text{-}\mu\text{Cl}_3(\text{THF})_6$ cation and aluminum phenoxide anions. By starting with the Al(OPh)₃ Lewis acid and PhMgCl Lewis base, we find the oxidative stability of the electrolyte is expanded to 5 V on both platinum and stainless steel working electrodes.

Crystal and Molecular Structures of New Metallocarboranes, Au₂₅ Gold Cluster and Metal Sensor Molecules

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In this study, we hypothesized that the Inorganic complexes readily icosahedral clusters, and it is important to understand why very different types of molecules form. It is also important to understand the relationship between their molecular and electronic structures. Two very unrelated icosahedral complexes were studied: $\text{Re}(\text{C-H})\text{B}_9\text{H}_z$ and $[\text{N}(\text{C}_8\text{H}_{18})_4][\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{C}_6\text{H}_5)_{18}]$ by X-ray crystallography and magnetic susceptibility method techniques.

Results Obtained showed that one cluster is a distorted icosahedron made of one Re atom, two C atoms and nine B atoms. The cage is empty, and the metal forms part of it and has one NO and two CO ligands attached. One of the C atoms is substituted with an O-CH₂-CH₂-O-CH₂-CH₂-I group. This cluster is an analog of the core of **2** but without the central atom occluded in the cage. The molecule is diamagnetic but has interesting properties. The other cluster is a the “spherical” Au₂₅ cage inside the $[\text{Au}_{25}(\text{SCH}_2)_n\text{C}_6\text{H}_5]^-$ anion. The core of this anion consists of a central occluded Au atom surrounded by the 12 vertices of the icosahedron. Around the 12-vertex core of Au₂₅ are the ligands Au-(SCH₂CH₂C₆H₅) in “staple” form. Reports of some analogs of Au₂₅ examined the materials via their magnetic properties, and observed abrupt phase changes, i.e. abrupt changes in electronic structure. Therefore the electronic structure of cluster **2** was also examined magnetically to search for electronic phase changes, and at the same time, the molecular structure was determined at a series of temperatures to check for molecular phase. There was no abrupt change in molecular structure.

The icosahedral core of Au₂₅, nor the “staple” shell around it produce any electronic or molecular phase changes. More measurements and theoretical work to resolve the question: are the $[\text{Au}_{25}(\text{SCH}_2)_n\text{C}_6\text{H}_5]^-$ ions very small nanoparticles or are they better considered “molecular”.

Borrowing Nature's Recipes: Heterodinuclear Metal Complexes for the Reductive Cleavage of CO₂

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Activation and utilization of the highly abundant carbon dioxide is of primary interest in modern society, due to its detrimental effects on earth's atmosphere. Transformation of CO₂ into a more reduced form to make fuel is one possible solution for this problem. However, activation of carbon dioxide is difficult, due to its thermodynamic and kinetic stability. On the other hand, nature has developed elegant systems capable of CO₂ reduction.¹ One of nature's principal transformations involving CO₂ is its reversible reductive cleavage to CO; $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$. The enzymes catalyzing these transformations are called carbon monoxide dehydrogenases (CODH).¹ Two principle systems are known: Ni-Fe CODH and Mo-Cu CODH.¹ Inspired by these systems, our goal in this project will be to apply the elaborate design of nature's frame work, bringing these metals together in a synthetic system, in order to carry out this transformation. As these enzyme-catalyzed transformations employ hetero-multimetallic centers, we will design and synthesize a bio-inspired hetero-bimetallic system that mimics the disposition and nature of the metal centers in Mo-Cu CODH.² The metal centers will be brought to proximity by a pre-designed dinucleating ligand containing two different chelating sites, separated by a rigid linker. The major reaction under investigation will be the stoichiometric and electrocatalytic reductive splitting of CO₂.

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Photoactive Cobalt (III) Based Metallopolymers

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We have designed organic-inorganic metallopolymeric hybrid materials where new material properties are due to a unique interaction between a polymer and a metal ion. Specifically, the creation of labile bonds inside a polymer material adds new mechanical properties to the material when the bonds can undergo reversible reformation by itself or upon certain stimulus¹. We are interested in using light as an external stimulus to trigger changes in mechanical properties. Our current approach is to synthesize a metallopolymer crosslinked through cobalt (III) ions. Cobalt (III) Schiff-base complexes can be reduced by a photoinduced electron transfer to cobalt (II)². Upon reduction, the cobalt center changes its initial octahedral geometry to a square planer one, and releases axial ligands. Oxidation of cobalt (II) to cobalt (III) opens axial positions for ligands to coordinate and form metal-ligand bonds. Such mechanism can be used to introduce labile bonds into a polymer material to create active sites for self-repairing features.

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Tuning Ligand vs Metal Radical Distribution: Non-Planar Reduced Nickel Complexes of Bis(aldimino)pyridine Ligands

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Bis(imino)pyridine [NNN] ligands are among the most commonly used ancillary ligands in transition metal chemistry and catalysis. The success of these ligands can be attributed to their redox non-innocence (accepting 1-3 electrons), that facilitates redox transformations at the first-row transition metal centers. The majority of the previously utilized bis(imino)pyridine ligands contain ketimine sidearms. Specifically for nickel, several groups have recently reported that reduction of bis(ketimino)pyridine-ligated nickel(II) dihalides forms invariably square-planar nickel(II) products and a ligand-based radical anion. In contrast, the chemistry of bis(aldimino)pyridines has received considerably less attention. Herein, we present evidence that replacing bis(ketimino)pyridine by an analogous bis(aldimino)pyridine has a significant effect on the electronic structure and reactivity of the resulting nickel complexes. EPR spectroscopy demonstrates a significant spin density at the metal center. DFT calculations suggest it is a Ni^I complex whose electronic structure is enabled by the electronic and steric features of the ligand's aldimine arms.

Preparation of Cooperative Four-Electron Reagents

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2nd and 3rd row transition metal complexes with d⁶- and d⁸-electron configurations have attracted considerable attention because of their potential to function as catalysts for multi-redox reactions. At the core of this reactivity are bond-making and –breaking steps coupled to two-electron changes in oxidation state of the metal center. Modulation of the underlying one-electron redox potentials may be reasonably expected to form part of a strategy for designing new catalysts or optimizing existing catalysts. However, knowledge of these redox potentials is lacking because the outer-sphere electron transfer reactions tend to be irreversible. This is related to the large reorganization accompanying the interconversion between the square planar geometry favored by the d⁸-electron configuration and the six-coordinate geometry favored by the d⁶-electron configuration. To address this problem and begin to identify the factors governing the redox cooperativity, we have designed complexes with ligand architectures that are capable of stabilizing both the geometries favored by the d⁸- and d⁶-electron configurations. These complexes undergo outer-sphere, reversible and cooperative two-electron transfer. The focus of this project is on the assessment of the interactions between two-electron redox centers in dimers. Efforts to prepare target dimers using Schiff-base ligand systems, and click chemistry will be discussed.

Crystal Structure Comparisons of *De Novo* Designed Proteins Containing Thiolate-Rich Binding Sites Modified by D-Leu in order to Control Specific Geometries of Bound Cd(II)

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Unlike other protein modification strategies, the *de Novo* design approach is much less limited in using non-coded amino acids in the primary sequence.^{1,2} Previously, we spectroscopically reported the use of D-Leu in the second coordination sphere to enforce desired coordination geometries of Cd(II)-thiolate complexes.³ Herein we present two X-ray diffraction structures of apo-(GRAND CSL12_DLL16C)₃ and apo-(GRAND CSL16CL19_DL)₃ determined to 1.40 and 1.83 Å resolution, respectively. The structures clarify a pre-organized thiolate-rich pocket, suitable to bind Cd(II) and have allowed us to understand how D-Leu manipulates the sterics around the binding pocket. We have found that the control of specific geometries depends on where D-Leu is replaced. When positioned in the twelfth layer of GRAND CSL12_DLL16C sequence, the alternative chirality of the D-Leu side chain reorients towards the metal site resulting in a small space above the coordination site, which potentially blocks the access of an exogenous water ligand. This structural detail correlates to the previous spectroscopic evidence of CdS₃ formation. On the other hand, D-Leu in the nineteenth position of GRAND CSL16CL19_DL opens a space below the metal binding site, possibly allowing for formation of the hydrated CdS₃O. Based on our knowledge, this is the first structural report of metal binding sites modified by D-amino acid ligands. Thus, a broad application of D-amino acids could be possible and may provide a powerful tool for protein design.

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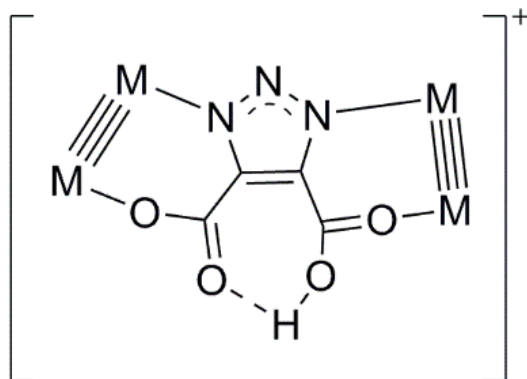
Triazole Based Dimers of Dimers as a Test Bed for Photovoltaic Devices

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The synthesis, characterization, and electrochemistry of a series metal-metal quadruply bonded species are described. The compounds being discussed are dimers of dimers which utilizes quadruply bound metal centers that are bridged by an organic ligand. The compounds of interest are of the structure $[M_2(T^iPB)_3]_2(\mu-TAD)$ where $M = Mo$ or W and T^iPB = triisopropylbenzoate and TAD = 1,2,3-triazole-4,5-dicarboxylic acid. The organic ligand TAD allows for the study of the electronic properties of the compound, and for the investigation of proton-coupled electron transfer. By monitoring the nature of the valence states of the metals within the compounds, the character of the electronic properties of these compounds can be determined. To further explore the electronic structure, density functional theory (DFT) and time dependent DFT have been utilized. Compounds similar in nature to this have been shown to have properties lending themselves to applications in renewable energy in the form of photovoltaic devices and molecular studies. This molecule will act as a test bed for future energy related materials.



Preventing the Degradation of Free Nitroxide Radicals Coupled to II-VI Semiconductor Quantum Dots

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Organic free radicals coupled to inorganic semiconductor quantum dots have been proposed to be interesting candidates for bio-sensing applications, but to this day no attention has been given to studying the long-term stability of these hybrid systems.^{1,2} Here, we assessed the stability of an inorganic/organic hybrid system consisting of CdSe and CdTe quantum dots and nitronyl nitroxide radicals (PhNN). Analysis of the long term electron paramagnetic resonance Spectroscopy (EPR) of this system shows a slow degradation of PhNN caused by Trioctylphosphin (TOP) occurring typically on the timescale of several hours. Interestingly, we found that trioctylphosphine (TOP), one of the principal ligands used to control the surface chemistry of quantum dots, is directly responsible for the degradation process. Kinetics of the degradation reaction between TOP and PhNN has thus been investigated using EPR, Nuclear Magnetic Resonance (NMR) and High Resolution Mass Spectroscopies (HRMS), which all together confirm the redox nature of the reaction between TOP and PhNN. We show that using phosphine-free quantum dots prevents degradation of PhNN radicals, and leads to perfectly stable mixtures, and are adequate candidates for any future studies involving the coupling of nitroxide radicals to inorganic quantum dots.

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Towards Spherical Arrays of Carbazole-based Push-Pull Chromophores

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Metal-Organic Polyhedra (MOPs) are robust molecular cages which self-assemble from organic linkers and metal cluster nodes. 9H-Carbazole-3,6-dicarboxylate reacts with the bimetallic copper paddlewheel to form a molecular cube with exotopic N–H groups at each corner.[1] As N-aromatic substituted carbazoles belong to a class of push-pull chromophores with strong transition dipole moments, we envision that their incorporation into 3D MOP structures can establish an intriguing spacial distribution of push-pull units. Here we demonstrate our strategy to direct solid-state arrays of organic chromophores (carbazole) within metal-organic polyhedra. Photophysical behavior of simple carbazole cubes are reported in addition to synthetic progress towards more complex functional metal-organic materials.

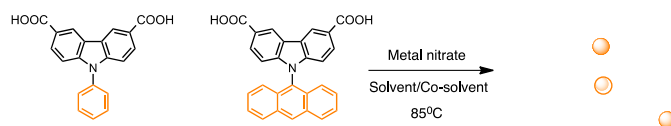


Figure 1. Synthesis of functionalized metal-organic cubes from N-aromatic substituted carbazole-3,6-dicarboxylate ligands

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Tunable photoreactivity in Iron-polysaccharide materials

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Alginate, a naturally- occurring plant polysaccharide is able to undergo photochemistry with Fe^{3+} and reduce to Fe^{2+} after light irradiation. We report that another polysaccharide, pectate, was also photoactive, reducing Fe^{3+} to Fe^{2+} after light irradiation. We have shown that quantitative comparison of the efficiencies of the photoreduction (QY) for alginate and pectate indicate that the photoreaction is more efficient in alginate than pectate. This dramatic difference in QYs from two similar polysaccharides led us to investigate the role of different functional groups on the photoreaction. The polysaccharides were modified by acetylating (Ac) and carboxomethylating (Cx) some hydroxyl groups. The QY was determined and both the Ac and Cx polysaccharides displayed lower QYs compared to the parent polysaccharides. We hypothesize that these different QYs are due to the changes in supramolecular structure and binding of Fe^{3+} with the polysaccharides.

Hydrogel beads from both polysaccharides were formed by crosslinking with Fe^{3+} . Upon irradiation of the beads, Fe^{3+} is reduced, which causes a disruption in the crosslinking and results in breaking apart of the hydrogel bead. The Stability and reactivity of the beads was tested for both alginate and pectate, and pectate beads are less reactive than alginate upon irradiation. This mirrors the QYs determined for the two polysaccharides.

Characterization of a Non-Heme $\{\text{FeN(H)O}\}^8$ Complex: Implications for the Reactivity of Iron Nitroxyl Species in Biology

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One-electron reduced non-heme ferrous nitrosyl complexes (referred to as iron nitroxyl complexes, or $\{\text{FeNO}\}^8$ in Enemark-Feltham notation) have been proposed as intermediates in bacterial nitric oxide reductases (NORs). In addition, non-heme iron enzymes may be involved in the generation and sensing of nitroxyl (NO^-/HNO) in biological systems via formation of $\{\text{FeN(H)O}\}^8$ intermediates.¹ Despite their significance, non-heme $\{\text{FeN(H)O}\}^8$ complexes have remained elusive, and little is known about their properties and reactivity. In order to model such complexes, we have synthesized the high-spin non-heme $\{\text{FeNO}\}^7$ complex $[\text{Fe}(\text{TMG}_3\text{tren})(\text{NO})](\text{OTf})_2$.² In contrast to other reported high-spin non-heme $\{\text{FeNO}\}^7$ complexes which decompose upon reduction, this species can be reduced chemically or electrochemically to generate the first stable high-spin non-heme $\{\text{FeNO}\}^8$ model complex. Whereas low-spin $\{\text{FeNO}\}^8$ complexes in hemes are diamagnetic, our data show that this complex is high-spin ($S=1$). Experimental and computational results demonstrate that the reduction is metal-centered, causing a relatively small downshift in $\nu(\text{N-O})$ and a decrease in Fe-NO covalency. Additionally, whereas the $\{\text{FeNO}\}^7$ complex is stable in the presence of acid, the $\{\text{FeNO}\}^8$ is basic and can be protonated at low temperature to form an $\{\text{FeNHO}\}^8$ compound. Taken together, these results suggest that in biological systems, reduction may serve as a method to activate stable non-heme $\{\text{FeNO}\}^7$ units towards protonation and other reactivity, for example N-N coupling in NORs.

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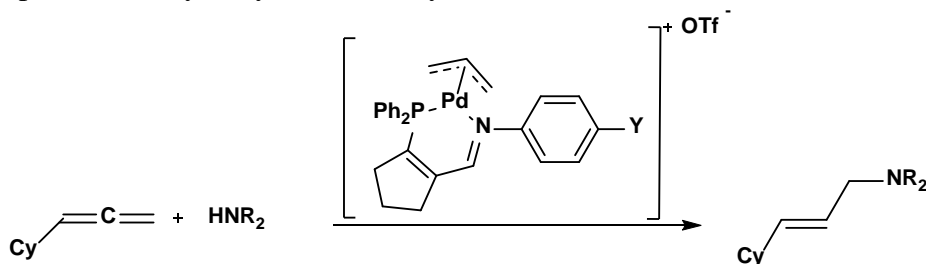
The Electronic Role of 3-Iminophosphine Ligands in Palladium-catalyzed Allene Hydroamination

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Over the past few years, our group has focused on the hydroamination of mono-substituted allenes with primary and secondary amines catalyzed by allylpalladium complexes supported by 3-iminophosphine ligands. Recently, we reported the most active catalyst known for the intermolecular hydroamination of mono-substituted allenes with anilines, which also displayed a high functional group tolerance at ambient temperature. In a recent publication, we showed the effect of various groups on phosphorus and backbone size on the catalysis.¹ However, we were unable to comment on the electronics of the imine unit on catalytic hydroamination, since only two groups were tested (tert-butyl and xylyl) and in the experiments reported, a few variables were changed simultaneously. Thus, understanding the electronic role of the imine fragment of the 3IP ligand on catalysis remained unexplored. In our current study, we have focused on the electronic effect of the imine fragment while keeping the rest of the ligand constant. Different complexes were synthesized varying only in the para substituent of the phenyl attached to the imine unit of the ligand. The catalytic activity of these complexes was examined by hydroamination of cyclohexylallene. To analyze the data obtained, we took advantage of the Hammett σ value and plotted catalytic activity versus σ , revealing an interesting trend related the the mechanism involved in the process. Based on the kinetic results and kinetic isotope effects, we have proposed a catalytic cycle for this system.



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Designing an FeS₄ Site in a *De Novo* Designed Peptide

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Sulfur-rich metal binding sites are important in a variety of metalloproteins, particularly those that utilize iron-sulfur complexes for catalysis and electron transfer. Rubredoxin, a functionally promiscuous electron transfer protein, is the simplest protein that uses a sulfur-ligated iron center (FeCys₄). The reduction potential of rubredoxin is centered around 0 mV, varying between -90mV and 40mV, depending on the species. Understanding the structure-function relationship in the active sites of metalloproteins is central to gaining insight into their chemical properties and roles in biological systems. One approach that is used to study this relationship is *de novo* protein design. This bottom-up approach involves designing a protein “from scratch” that is intended to fold into a defined three-dimensional structure. From the perspective of protein design, the creation of a rubredoxin-type tetrathiolate-coordinated iron center in a designed protein would allow for the investigation of general requirements beginning with the primary coordination sphere for electron transfer centers with reduction potentials in a physiologically relevant range as well, in the long term, allow for the design of a multi-site, multi-functional protein. Here we report the design of a peptide with a tetrathiolate metal binding motif that binds iron and cadmium. It has been characterized by UV-vis spectroscopy, ¹¹³Cd nuclear magnetic resonance spectroscopy, ^{111m}Cd perturbed angular correlation spectroscopy, Mössbauer spectroscopy, and has a reduction potential of -75mV at pH 8.5.

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Optical Properties of Bi-Icosahedral Au₂₅ and Au₂₄ Clusters: Influence of Central Gold Atom

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Temperature dependent absorption and ultrafast luminescence measurements of $[\text{Au}_{24}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_4\text{Ph})_5\text{Cl}_2]^+$ (bi-Au₂₄) were studied and compared with $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{C}_6\text{S})_5\text{Cl}_2]^{2+}$ (bi-Au₂₅). The investigations are carried out on these two clusters as they are structurally similar except for the absence of central Au atom for bi-Au₂₄. The objective of the work is to probe the influence of the central gold atom on the optical transitions and electron-phonon interactions in bi-icosahedral nanoclusters. The investigations are focused both on the electron-phonon as well as hydrogen bonding interactions of axial Cl atoms with hydrogen bonding solvents and their influence on the vibronic transitions. It was theoretically shown that the absorption at 670 nm arises due to coupling of two icosahedrons which Au₂₅ does have and Au₂₄ does not. While for Au₂₄, broad band at ~560 nm was observed which was due to the interactions of the two units (two Au₁₂ units), 415 nm shoulder and 383 nm band that is due to the electronic transitions related to the localized electronic structures of the individual 12 Au atoms in the icosahedron. All these peaks becoming sharper and blue shifted when it goes to lower temperatures and it increases the oscillator strength and also it showed a new peak around 480 nm in lower temperatures. The electron-phonon interactions were obtained from fitting the band gap data as a function of temperature. Solvent dependent absorption measurements and ultrafast luminescence measurements show the hydrogen bonding formation of clusters with alcoholic solvents.

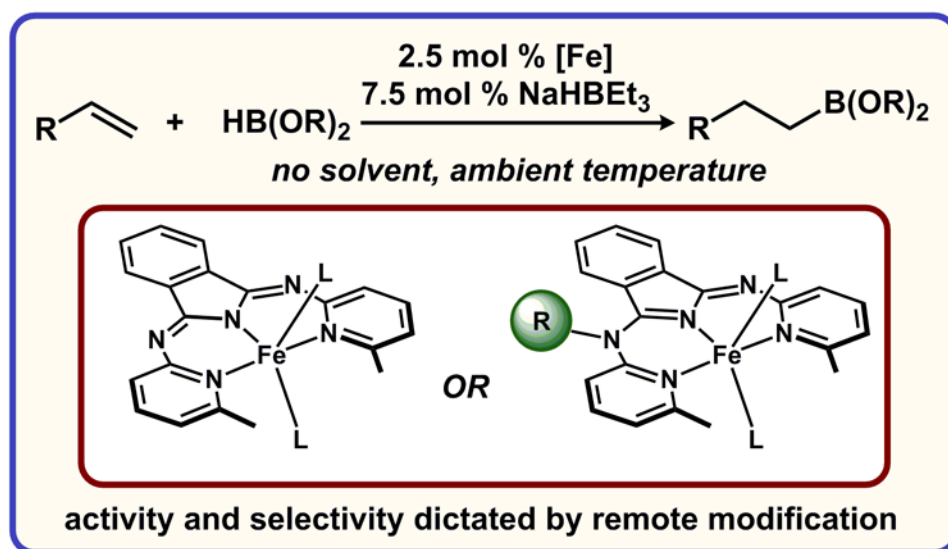
Regulation of Iron-Catalyzed Olefin Hydroboration by Ligand Modifications at a Remote Site

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An amide-derived *N,N,N*-Fe(II) complex catalyzes the hydroboration of olefins under ambient conditions. Alkylation of a remote site on the ligand backbone was used to introduce a distinct electronic environment at the metal, without rearrangement of the primary coordination sphere. The activity and regioselectivity in the catalytic hydroboration of olefins was found to be regulated by this remote modification.



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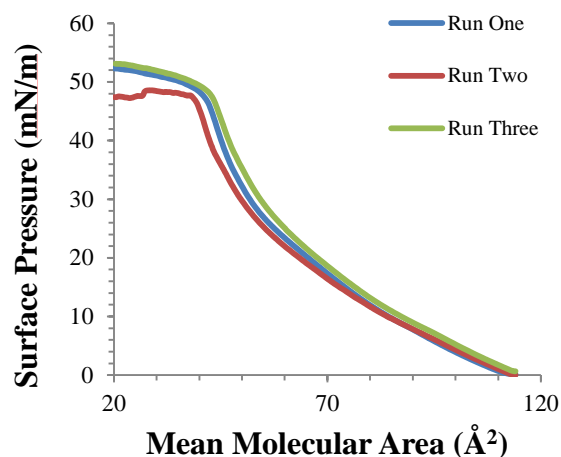
Metal-Terpyridine Complex Characterization towards Rectification Capable Devices

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There is a growing need for complexes for the development of rectifying thin-films for use in molecule-based devices. The ligand 4'-(4-(octadecyloxy)phenyl)-2,2':6',2''-terpyridine (terpy-C₁₈) was synthesized and characterized by ¹H-NMR. Complexes [Co^{II}(terpy-C₁₈)₂](ClO₄)₂ (**1**), [Fe^{III}(terpy-C₁₈)₂] (**2**), and [Cu^{II}(terpy-C₁₈)₂] (**3**) were then synthesized and characterized by ESI-mass analysis, FTIR spectroscopy and UV-visible spectroscopy. The three complexes were characterized by cyclic voltammetry to assess their redox behavior in solution. Reduction-oxidation processes were seen at -0.14 V_{Fc/Fc+} and -1.17 V_{Fc/Fc+} for complex **1**, 0.72 V_{Fc/Fc+}, -1.6 V_{Fc/Fc+} and -1.8 V_{Fc/Fc+} for complex **2** and -0.68 V_{Fc/Fc+} for complex **3**. Furthermore, Langmuir-Blodgett film formation ability has been evaluated to obtain the isotherm compression of complex **1**, which showed a collapse pressure of 46 mN/m. This information enables us to move towards device fabrication and evaluation of the complexes rectification properties.



Secondary Phosphine Oxides as Effective Ligands for Nickel-Catalyzed Carbon-Sulfur Cross-Coupling Reactions

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Carbon-sulfur cross-coupling reactions have received great attention among the synthetic community due to their importance in the synthesis of pharmaceutically active compounds that contain an aryl sulfide moiety. Air and moisture stable secondary phosphine oxides are excellent emerging preligands for transition-metal-catalyzed carbon-sulfur cross-coupling reactions. Although secondary phosphine oxides exist predominantly as the pentavalent form for the phosphorus center, they can be tautomerized to the less stable trivalent phosphinous acid. The phosphinous acid formed exhibits good coordinating capability toward transition metals. Compared to the well-known monodentate secondary phosphine oxides, bidentate secondary phosphine oxides are less explored but potentially more superior in stabilizing active catalytic species. A novel bidentate secondary phosphine oxide was therefore synthesized from the reaction between organolithium compounds and $\text{Cl}(\text{NEt}_2)\text{PPh}$ followed by hydrolysis in acidic media. This compound was fully characterized and its ligated nickel complex was demonstrated to catalyze the thiolation of iodobenzene. Optimized catalytic reaction conditions are 0.5 mol% of catalyst, 1.1 equiv. of KOH in DMF at 80 °C for 1 h. Investigation of substrate scope are in progress.

Modification of Small Heme Proteins to Produce Novel Organometallic Catalysts that Function in Water

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Small molecule transition metal complexes have proven to be effective catalysts in industrial organic synthesis, often catalyzing thousands of turnovers with high turnover rates and long catalyst lifetimes. However, these catalysts usually require expensive and environmentally-detrimental solvents to carry out these reactions. Metalloproteins contain metal centers that catalyze a variety of reactions in water, and modifying these proteins could lead to the development of “greener” organometallic catalysts. Small heme proteins in particular are good candidates for modification due to the ease with which the heme can be substituted for a modified heme or synthetic porphyrin.¹ Myoglobin has been modified by introducing ruthenium and rhodium porphyrins into the apoprotein. These artificial proteins will be characterized by a variety of spectroscopic techniques including UV-vis, CD, and resonance Raman spectroscopy. Diazo compounds will be reacted with the proteins in order to form a metal-carbene bond at the active site of modified myoglobin. Catalytic studies with these artificial proteins will focus on synthetically useful cyclopropanation reactions between a variety of carbenes and olefins. The total turnover numbers of the catalysts will be quantified by GC/MS after extraction by organic solvents. The stability of the catalysts and the possibility of recycling the catalysts after product extraction will be determined by spectroscopic methods as well. In the future, the proteins may be modified by mutating key active site residues in order to alter the stereoselectivity of the catalyst or open up the active site and allow larger diazo compounds to bind to the metal center.

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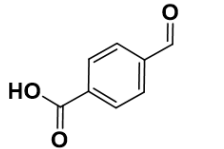
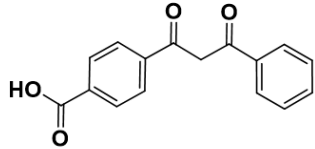
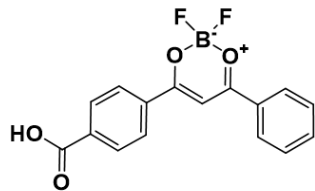
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Influencing Excited State Dynamics of Avobenzene Derivatives by Use of M₂ Quadruple Bonds

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From the reactions between Mo₂(TⁱPB)₄, where TⁱPB is 2,4,6-triisopropylbenzoate, and 2 equivalents of the acids, 4-formylbenzoic acid, HBzald, 4-(3-oxo-3-phenylpropanoyl)benzoic acid, HAvo, and 4-(2,2-difluoro-6-phenyl-2*H*-1λ³,3,2λ⁴-dioxaborinin-4-yl)benzoic acid, HAvoBF₂, the compounds *trans*-Mo₂(TⁱPB)₂(Bzald)₂, **I**, *trans*-Mo₂(TⁱPB)₂(Avo)₂, **II**, and *trans*-Mo₂(TⁱPB)₂(AvoBF₂)₂, **III**, have been isolated. Compounds **I** and **II** are red while compound **III** is blue. The new compounds have been characterized by ¹H NMR, MALDI-TOF MS, steady-state absorption and emission spectroscopies, and femtosecond, fs, and nanosecond, ns, time resolved transient absorption and infrared spectroscopies. Electronic structure calculations employing density functional theory and time-dependent density functional theory have been carried out to aid in the interpretation of these data. These compounds all have strong metal to ligand charge transfer, MLCT, transitions in the visible region of their spectra, with the S₁ states having lifetimes ~5-20 ps. The triplet states are Mo₂δδ* with microsecond lifetimes. The spectroscopic properties of **I** and **II** are similar while the planarity of the ligand in **III** greatly lowers the energy of the MLCT and enhances the intensity of the transient and emission spectra. The Mo₂ unit completely quenches the usual enol-keto isomerization of the avobenzene moiety.

| Structure | Abbreviation | Formal Name |
|---|---------------------|---|
|  | HBzald | 4-formylbenzoic acid |
|  | HAvo | 4-(3-oxo-3-phenylpropanoyl)benzoic acid |
|  | HAvoBF ₂ | 4-(2,2-difluoro-6-phenyl-2 <i>H</i> -1λ ³ ,3,2λ ⁴ -dioxaborinin-4-yl)benzoic acid |

Design of Low-Coordinate Transition Metal Alkoxides for the Activation of Small Molecules

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A typical approach for the activation of small molecules involves the design of low-coordinate metal centers in relatively low oxidation states. Toward this goal, we have decided to investigate the potential of quasi two-coordinate transition metal complexes of the form $M(OR)_2(THF)_2$ to involve in binding and activation of small molecules. This work focuses on studying the reactivity of Cr(II), Mn(II), Fe(II), and Co(II) bis(alkoxide) precursors toward [O] and [S] atom transfer, eventually targeting CO_2 and CS_2 activation. Also, we attempt to develop and investigate a new bulkier alkoxide ligand in order to synthesis a more reactive lower coordinate metal alkoxide of the form $M(OR)_2$.

Synthesis and Photolysis of a Novel Photocontrollable HNO Donor

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The development of new nitroxyl (HNO) donors has received increasing attention due to their promise for treating congestive heart failure. We are developing new HNO donors, suitable for studying the fundamental bioinorganic chemistry of HNO, which rapidly release HNO via photoactivation. Herein, we report the synthesis of a new photoactivatable HNO donor **1** based on the use of the (3-hydroxy-2-naphthalenyl)methyl (HNM) phototrigger. Mechanistic photochemical studies of **1** leading to HNO generation (along with a competing side reaction) are discussed.

