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Undergraduate Research Symposium

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1. Characterization of Recombinant Human Hair Keratin Biomaterials

Erik Akbar*, Christina Kim, Jennifer McCord
Nanoscience

Keratin biomaterials show potential for use in medical applications due to their inherent biocompatibility, natural self-assembly, and controllable porosity in a bulk material. However, the extraction of natural keratins from sources such as wool, feathers, or hair require extensive processing conditions which leads to the production of undesirable by-products. Naturally sourced keratins also lack consistency as their protein sequences may be varied from source to source. Recombinant keratins can bypass these issues by providing a reliable protein sequence with every expression. This method also allows for the synthesis of individual keratin precursors such as K-31 and K-81 which would otherwise be confounded by competing proteins such as melanin. The goal of this project was to construct biomaterials using both keratin precursor proteins and K-31/K-81 oligomers. Currently, the objective is to develop keratin hydrogels, films and scaffolds and characterize the materials to better understand the unique effects imparted by the recombinant keratin in comparison to natural keratins.

E. Coli cells were used to express the protein, and were grown to an optical density of around 0.6 before the beginning of protein synthesis. Once the proteins were extracted, they were purified using a Ni-NDA column to remove any excess products. The proteins were identified through SDS page, and upon confirmation, K-31 and K-81 were dialyzed out of elution buffer. A hybrid group was also created by mixing K-31 and K-81, and all three proteins were lyophilized. This semester has been focused on synthesizing thin films by using 1,1,1,3,3,3-hexafluro-2-propanol (HFP) as a solvent. HFP would act as a crosslinker allowing the keratin proteins to self-assemble into higher order structures. The lyophilized proteins were dissolved in HFP at a concentration of 40 mg/mL. Glycerol was also added to the samples at a concentration of 17% w/volume to act as a plasticizer. Films were successfully developed, but were too fragile to continue testing. Further films are being developed with larger amounts of protein to increase the thickness of the film. Next semester will see the creation of stronger films allowing us to scrutinize the materials via tensile testing, solubility testing, and TEM imaging. Using recombinant proteins, keratin can be used as a reliable source of biomaterials for novel devices that facilitate cellular repair, assist in drug deliver, or provide structural support to bones and organs.

Contribution from the Amanda Morris group.

2. Incorporation of Corrole and Porphyrin Based Ligands into Metal-Organic Frameworks

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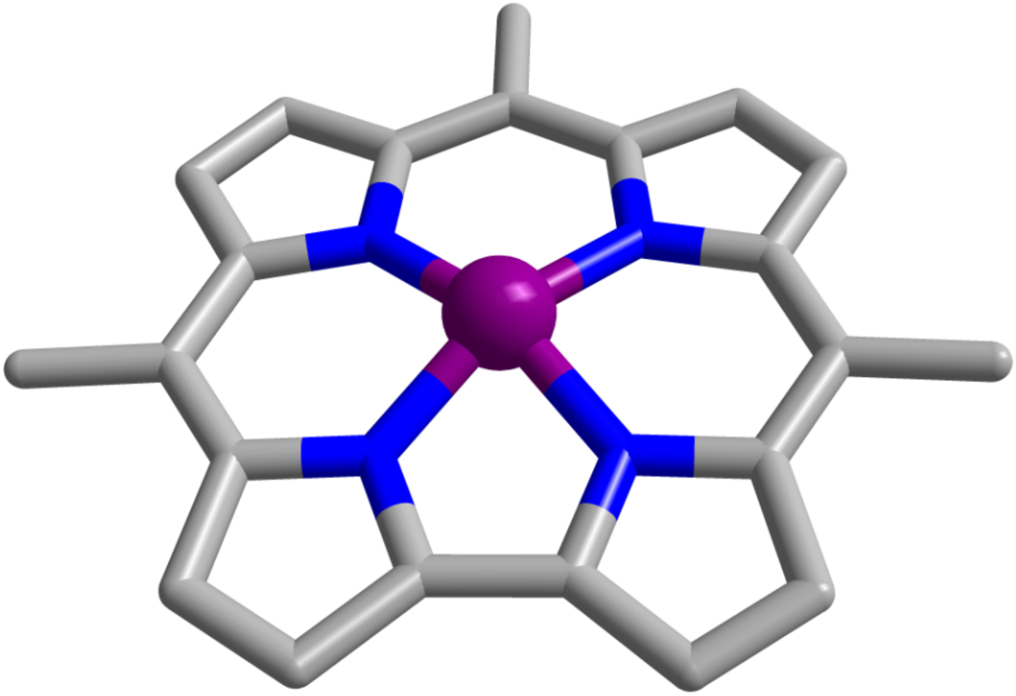

Metal-organic frameworks (MOFs) are multidimensional structures comprised of metal nodes connected by organic ligands forming highly ordered multidimensional arrays. These materials were investigated for a wide variety of applications including electrocatalysis and solar cell, among others. Corrole is a nitrogen based macrocycle that is known to form complexes with a variety of metals, and has intrinsic catalytic properties that are dependent on the metal center and the substituents around the corrole core.[1] The goal of this study is to design and synthesize a Zr based MOF using either porphyrin or corrole based ligands to generate novel MOF structures and test their properties. Of particular interest is electrocatalytic activity of corroles towards oxygen and carbon dioxide reduction, as well as water oxidation. First, the corrole functionalized with benzoate groups capable of coordinating to Zr was synthesized using a standard condensation reaction between pyrrole and an aldehyde and its purity confirmed by ^{1}H NMR spectroscopy and mass spectrometry. In the next step, a synthesis of MOFs was attempted using the free base ligand, and its linear analogue from which several powders were obtained. Powder X-ray diffraction (PXRD) analysis revealed that these powders had poor crystallinity and therefore their structure could not be determined at this stage. Known porphyrin MOFs were synthesized using a variety of modulators. The crystallinity of these MOFs was confirmed using PXRD. Future work includes further optimization of the MOF synthesis with the goal of obtaining crystalline materials that could be used for structure elucidation. Testing the electrocatalytic and light absorption capability of porphyrin based MOFs and how they differ depending on which modulator is used is also of interest. Furthermore, different metals will be incorporated inside the corrole core which will then be used to synthesize electrocatalytically active MOFs.

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Contribution from the Matson group.

3. Investigation of H_2S Release from *N*-thiocarboxyanhydrides

Blake E. Askenas, Chad R. Powell, and John B. Matson
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Carbonyl sulfide (COS) is a gas that may play important roles in mammalian and bacterial biology, but its study is limited by a lack of suitable donor molecules. We report here the use of N-thiocarboxyanhydrides (NTAs) as COS donors that release the gas in a sustained manner under biologically relevant conditions with innocuous peptide byproducts. Carbonic anhydrase (CA), an enzyme ubiquitous in mammals, converts COS into H_2S. H_2S is a known gaseous signalling molecule, which exhibits therapeutic potential in its own right. The release of H_2S from the small molecule NTA was analysed over a pH range from 6-8 and in the presence of a variety of biologically relevant nucleophiles to better understand the therapeutic applications of NTAs.

Contribution from the Schulz group.

4. Functionalization of fabric substrate for increased doxorubicin (DOX) capture

Madison I. Bardot*, Ophelia Wadsworth and Michael D. Schulz, PhD

Liver cancer is the third leading cause of cancer mortality in the United States.[1] The most common treatment is chemotherapy, such as administering doxorubicin hydrochloride (DOX) via transarterial chemoembolization (TACE).[2] DOX preferentially binds to guanine in DNA and inhibits replication, affecting both cancerous and healthy cells.[3] To prevent DOX systemic circulation and reduce side effects, this research seeks to develop a filter device that will be deployed downstream from the tumor to capture residual DOX, isolating its presence in the hepatic tumor. Cotton fabric was coated with two types of silanes (GDPTMS and ICPTMS), which served as DNA linking molecules. Herring and salmon DNA were utilized separately to react with the surface functional groups then the samples were immersed in DOX solution to assess binding capability. Scanning electron microscopy (SEM) verified the presence of DNA on the samples although the layer was not uniform. Fluorescence spectroscopy determined that GDPTMS showed the most DOX capture after 1 minute, 94.8%, while ICPTMS showed the greatest overall DOX capture of 97.3% after 12 minutes. Unfunctionalized samples were also examined to assess the impact of silane and DNA on performance and determine if fabric pretreatment by the manufacturer enhances or hinders DOX capture. After 1 minute, the prewashed fabric demonstrated 1.5% better performance than the unwashed sample (13.5% and 12%, respectively). Likewise after 12 minutes, the prewashed sample captured 58.1% of DOX while the unwashed sample captured 55.6%. The differences are too small to conclude that fabric pretreatment by the manufacturer significantly affected performance. Future work consists of functionalizing fabric surface with various silanes to enhance DNA binding, which is expected to increase DOX capture significantly. Other sources of DNA will also be explored to determine if the sequence plays a role in DOX affinity. Additionally, silanes will be directly applied to cotton surface with the goal of enhancing reactivity between the surface and silane.

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Contribution from the Yee group

5. Synthesis of new TCNE Analogs as Building Blocks of Molecule-Based Magnets

Ericka L. Bruske*, Christopher L. Houser, and Gordon T. Yee
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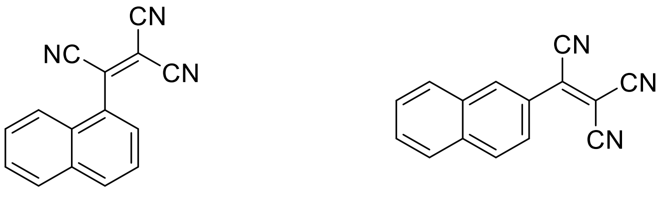
Molecule based magnets contain a well-defined spin and exhibit a slow relaxation when spin-aligned by external magnetic fields.[1] The discovery of the first room temperature molecule-based magnet vanadium tetracyanoethylene $V(TCNE)_2^{\cdot -}\cdot CH_2Cl_2$ in 1991 prompts our current research on tunable derivatives of the single-electron acceptor TCNE.[2] A newly designed candidate for use in a manganese-based magnet is bis(2,2,2-trifluoroethyl) 2,3-dicyanofumarate (Figure 1). This semester, the precursor 2,2,2-trifluoroethyl-2-cyanoacetate has been successfully synthesized; however, the yield must be improved before the precursor can be incorporated into the oxidative dimerization (Figure 1). In addition, both 1-naphthyl tricyanoethylene and 2-naphthyl tricyanoethylene have shown to be a successful candidates as the vanadium-based magnets give an ordering temperature of 120 K and 135 K, respectively (Figure 2).

2,2,2-trifluoroethyl-2-cyanoacetate bis(2,2,2-trifluoroethyl) 2,3-dicyanofumarate

Figure 1 The figure above displays the dimerized product bis(2,2,2-trifluoroethyl) 2,3-dicyanofumarate and the precursor 2,2,2-trifluoroethyl-2-cyanoacetate.



1-Naphthyl Tricyanoethylene 2-Naphthyl Tricyanoethylene

Figure 2 The figure above shows the naphthyl tricyanoethylene ligand that was successfully incorporated into a vanadium-based magnet..

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Contribution from the Tim Long group.

6. Thermal Characterization of a Series of Liquid Crystalline Co-Polyesters of 3,4’-bibenzoate and 3,3’-bibenzoate and Kinked Monomer

Jay Danziger[*], Timothy E. Long[1,2], and Charles S. Carfagna, Jr.[2]
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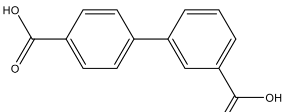
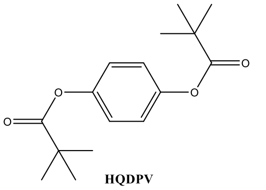
2. Macromolecules Innovations Institute, Virginia Tech, Blacksburg, VA

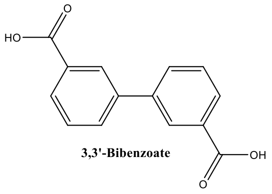
In this project, a complete thermal characterization of a series of four liquid crystalline co-polyesters, two each of 3,3’-bibenzoate and 3,4’-bibenzoate with kinked isomers of hydroquinone dipivalate (HQDPV) and resorcinol dipivalate (RSDPV) was performed to determine if the thermal properties pertaining to heat flow, expansion, and degradation were effected by variation of either monomer. Analytical techniques including: thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), gas phase Fourier-transform infrared spectroscopy (TGA-IR), and thermomechanical analysis (TMA) were used to probe the thermal character of the co-polyesters. Thermal degradation ($T_{d5\%}$) of materials containing 3,4’-bibenzoate monomer exhibited higher thermal stability (HQDPV-370 °C and RSDPV-204 °C) vs. the 3,3’-bibenzoate containing co-polyesters (HQDPV-114 °C and RSDPV-95 °C), with this trend continuing in the glass transition (T_g) temperatures as well with 3,4’-bibenzoate (HQDPV-180 °C and RSDPV-169 °C) and 3,3’bibenzoate containing co-polyesters (HQDPV-164 °C and RSDPV-146 °C). Coefficients of linear thermal expansion (CLTE) values obtained from thermomechanical analysis determined that co-polyesters containing HQDPV exhibited higher expansion values when compared to RSDPV containing co-polyesters regardless of which bibenzoate monomer was used, with 3,4’-bibenzoate containing co-polyesters exhibiting slightly higher expansion character when compared to co-polyesters containing 3,3’-bibenzoate. Based on the findings of this study is was determined that drastic differences in thermal degradation behaviour exists between co-polyesters containing RSDPV vs. HQDPV, with HQDPV containing co-polyesters exhibiting a higher T_g value that is consistent with RSDPV being more kinked, with this trend continuing in the CLTE expansion data which was surprising considering the higher free volume of RSDPV vs. HQDPV.



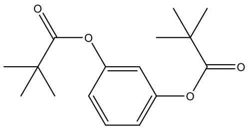
3,4'-Bibenzoate



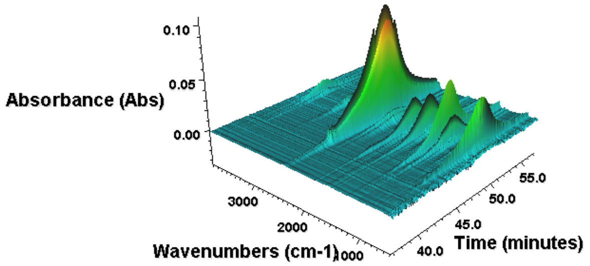
HQDPV



3,3'-Bibenzoate



RSDPV

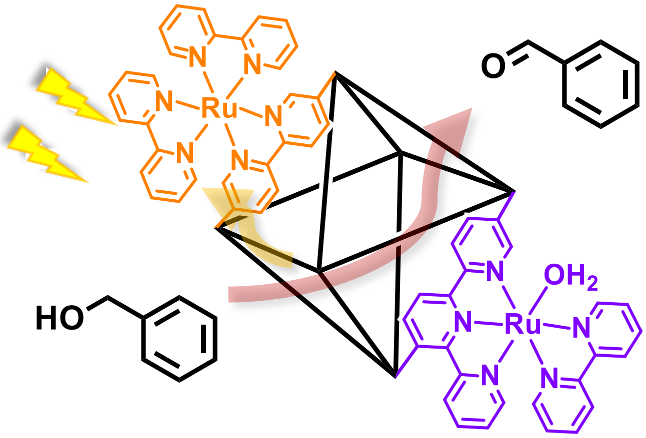


Contribution from the Amanda Morris group.

7. Photo Oxidation of Alcohol by Mixed Linker Metal-organic Framework

Dylan C. Davis, Shaoyang Lin and Dr. Amanda J. Morris
Department of Chemistry, Virginia Polytechnic Institute and State University Blacksburg, Virginia, 24061, United States

Due to the advent of global warming, energy sources that result in environmental disruption have fallen out of favour with many. Finding a reusable source of energy that is simultaneously cost effect has become the forefront of many research communities. To harness this light energy photosensitizer $[Ru^{II}(bpy)_2(dcbpy)]^{2+}$ is excited in the MOF by photons. The electron acceptor $[Co(NH_3)_5Cl]Cl_2$ removes an electron from the excited $[Ru^{II}(bpy)_2(dcbpy)]^{*2+}$. The Catalyst $[Ru^{II}(tpy)_2(dcbpy)OH_2]^{2+}$ will then be oxidized by the oxidized photo sensitizers to its higher oxidation state, $[Ru^{IV}(dcbpy)(bpy)O]^{2+}$, which can oxidize the benzyl alcohol to benzaldehyde.



Currently, We have synthesized two ligands, $[Ru(tpy)(dcbpy)OH_2]^{2+}$ and $[Ru(bpy)_2(dcbpy)]^{2+}$, through coordination reactions. These two ligands were incorporated into UiO-67 MOF via *in situ* doping method. These MOFs were then characterized by PXRD, Diffuse reflectance spectroscopy, and SEM. The MOFs were grown on TiO_2/FTO substrate and tested for photoelectrochemical oxidation of benzyl alcohol with Xe lamp as light source.

Meanwhile, another MOF used CoOOH as a catalyst was synthesized to oxidize water under a Xe lamp rather than benzyl alcohol. The Cobalt catalyst was introduced to the MOF by using on an DCBPY-UiO-67/TiO2/FTO slide under acidic conditions (pH around 3). In the future we will incorporate $[Ru(bpy)_2(dcbpy)]^{2+}$ into the MOF via post synthetic modification to bring the photo sensitizer and catalyst closer to one another.

Contribution from the Dorn group.

8. $Er_2@C_{79}N$: Discovery of a New Stable Metallofullerene for Potential Magnetic and Electro-Optical Applications

Paul Faust*[a], Kyle M. Kirkpatrick[a], James Duchamp[a] and Harry C. Dorn[a]

[a] *Virginia Tech Department of Chemistry*

A new endohedral metallofullerene (EMF), $Er_2@C_{79}N$ was identified as an impurity in a commercially available sample using spectroscopic and chromatographic techniques previously documented.[1] Erbium has been utilized as a doping agent for erbium-doped optical fiber amplifiers, which are used as high gain amplifiers for signal transmission.[2] The highly stable metallofullerene $Gd_2@C_{79}N$ with a magnetic spin state of S= 15/2 had been previously reported by the Dorn group and has been shown to be a dynamic nuclear polarization (DNP) agent with a large magnetic exchange coupling.[3] In contrast to the previously reported gadolinium, the erbium species has a higher observed magnetic moment than gadolinium and the 4f orbitals of Er^{3+} are anisotropic whereas Gd^{3+} is isotropic. Er^{3+} is also close to the observed magnetic moment of Tb^{3+} compounds.[4] While both the erbium and terbium metallofullerenes are anisotropic and $Tb_2@C_{79}N$ has been previously reported.[5] However, the anisotropy of the 4f electron density of Er^{3+} is prolate thus plane localizing the ligand electron density, whereas, the Tb^{3+} 4f electron density is oblate. This provides an opportunity to define the differences in magnetic properties between oblate and prolate species 4f orbital fields.[5] $Tb_2@C_{79}N$ displays single molecule magnet characteristics and as such, $Er_2@C_{79}N$ is also expected to exhibit these characteristics but given their directionality, it may hold different magnetic properties. **Figure 1** shows the HPLC trace for the commercial sample, the $Er_2@C_{79}N$ was found in the peak at 38.9 minutes, and was separated from the sample utilizing a previously described separation process.[1] Mass Spectrometry was used to verify the $Er_2@C_{79}N$ system was in the collected sample.

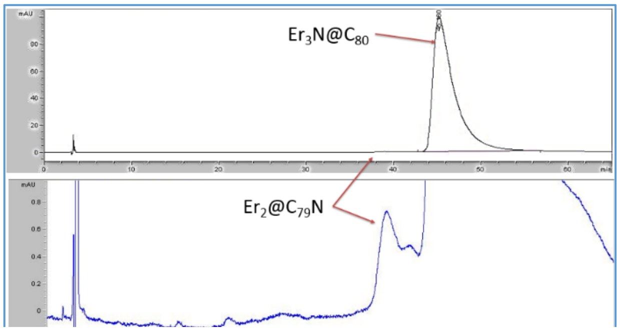


Figure 3.HPLC Trace of sample full spectrum, Er3N@C80 at 45.2 min, Er3N@C80 at 38.9 min HPLC specifications: PBB column (4.6 mm I.D. x 250 mm); λ = 390 nm; flow rate 1.0 mL/min; toluene as eluent; 25 °C; 100 µL injections

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Contribution from the Grove group.

9. Characterization of recombinant cellulose-binding protein

V. Grey Fritz*, Jennifer P. McCord and Dr. Tijana Z. Grove
Virginia Tech Chemistry Department

Lignocellulosic biomass is an inexpensive and abundant resource that has potential to be used in the production of biofuels.[1] However, the conversion from lignocellulose to glucose requires a pre-treatment step which creates compounds that inhibit the binding of enzymes which are responsible for the saccharification of lignocellulose.[1] Therefore, researchers are trying to develop helper proteins which will protect the cellulases from the inhibitory compounds.[1] Carbohydrate-binding modules (CBMs) are small domains found in carbohydrate-active enzymes which attach the catalytic domains of these enzymes to the carbohydrates, generally in order to break down carbohydrates into glucose.[1] Our goal is to create a recombinant CBM protein to be used as an additive that is more stable, and has a better binding constant than has been previously reported in the literature in order to be more effective at enhancing the production of glucose from lignocellulose. This semester, I conducted protein expression and purification for the proteins, rCBM-1WW, rCBM-1WY, rCBM-1YW, and rCBM-1YY. I optimized the protein expression and purification protocols to see what yielded the most concentrated protein. To further purify our proteins, we used FPLC. We used circular dichroism (CD) to gain insight into the secondary structure of each protein. After we discover the secondary structures for the protein, we want focus on characterizing the protein binding to cellulose.

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Contribution from the John Morris group.

10. Ozone Degradation of Zirconium based Metal-Organic Frameworks

Emerald M. Greene*, Tyler G. Grissom, Pavel Usoy, Amanda J. Morris, and John R. Morris
Virginia Tech, Department of Chemistry

Metal-organic frameworks (MOFs) are highly porous materials which have been used in a wide variety of applications including filtration of hazardous materials, gas storage, and energy conversion. The zirconium-based UiO-series MOFs are touted as having excellent thermal and chemical stability, however little is known about their long-term stability when used in atmospheric conditions. The objective of this work was to probe the effect that ozone exposure, which is present in the atmosphere, has on the zirconium-based MOFs: UiO-66, UiO-66-NH_2, and UiO-67. Four separate techniques: infrared spectroscopy (IR), x-ray photoelectron spectroscopy (XPS), attenuated total reflectance infrared spectroscopy (ATR-IR), and powder x-ray diffraction (PXRD) were used to analyze possible changes in the MOF structures following exposure to high concentrations of ozone. *In situ* FTIR monitoring of ozone exposure to UiO-66 resulted in an increase in IR absorbance in the lower wavenumber region, which we attribute to the loss of crystallinity of the MOF structure due to degradation of the organic linkers. XPS results of the ozone-exposed UiO-66 showed significant changes in the carbon and oxygen profiles of the MOF, which further verifies that changes to the chemical nature of the organic linkers occurred. ATR-IR spectra of pre- and post-ozone exposed UiO-66, UiO-66-NH_2, and UiO-67 provide further evidence of organic linker degradation. Finally, PXRD results confirm a total loss of crystallinity of all three MOFs following ozone exposure. Overall, this work reveals that exposure to high levels of ozone has a drastic effect on the stability of the zirconium-based MOFs.

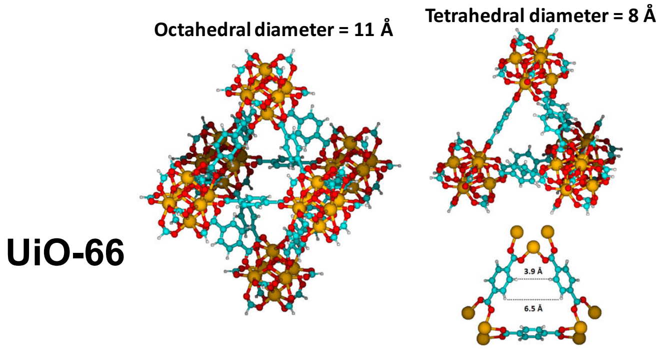
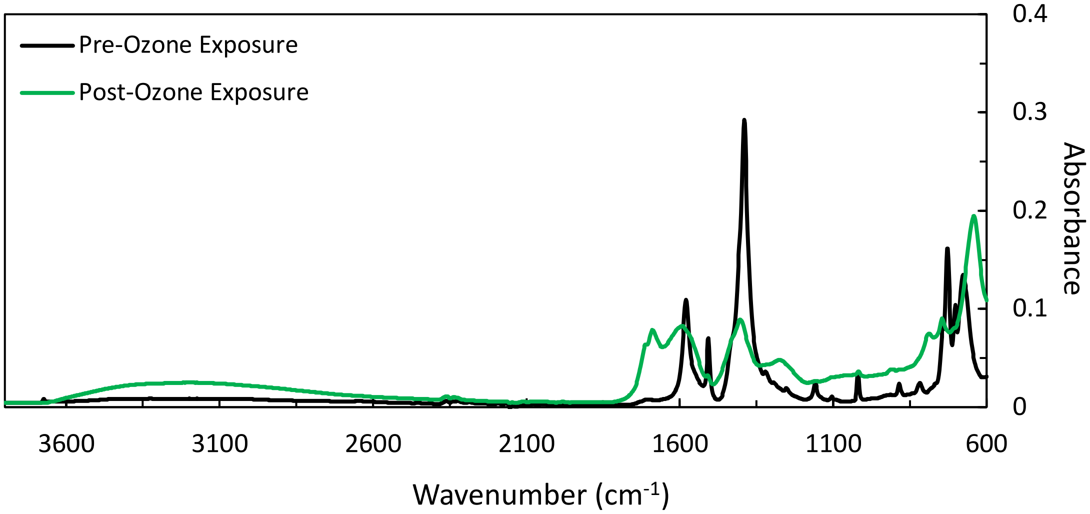


Figure Credit:
Diego Troya



Contribution from the Amanda Morris group

11. A Comparative Study of Two Isostructural Catalysts for the Fixation of CO_2

Edward E. Jensen*, Amanda J. Morris, Jie Zhu
Virginia Tech, Department of Chemistry

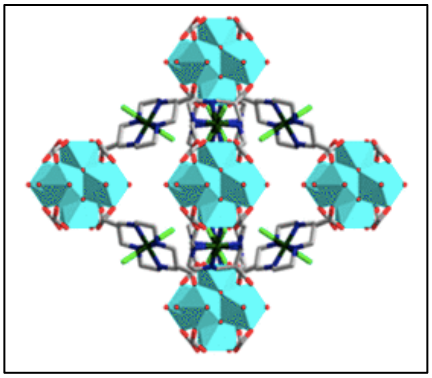


Figure 1. An illustration of the crystal structure of VPI-100

In the past decades, the atmospheric level of CO_2 has been increased significantly mainly due to the consumption of fossil fuels. Investigations of porous materials such as zeolites, covalent-organic frameworks (COFs), microporous organic polymers, and metal-organic frameworks (MOFs) in carbon capture and storage/sequestration (CCS) is one of the most attractive research topics to reduce carbon emissions. Among those, MOFs have been considering as one of the most promising next-generation material for CO_2 capture. In this work, we synthesized and characterized two isostructural hafnium-based robust MOFs as Hf-VPI-100(Cu) and Hf-VPI-100(Ni). Both frameworks demonstrated high CO_2 uptake. Comparison between CO_2 uptake capacity of absorbance has been made between Hf-VPI-100 and VPI-100. In order to better understand the interaction between the CO_2 with the frame, in situ PXRD experiments have been performed under CO_2 from 1 bar to 20 bar. The frameworks maintained their structural integrity under CO_2 atmosphere and two new peaks have been observed due to the change of electron density in the pores as the CO_2 go in the framework. The PXRD data indicated there are open metal sites in the Hf-VPI-100 MOFs and could act as potential catalytic centers for CO_2 chemical fixations.

Contribution from the Schulz Group

12. Synthesis of a Galili antigen epitope for treatment of *Clostridium difficile* Bacterial Infections

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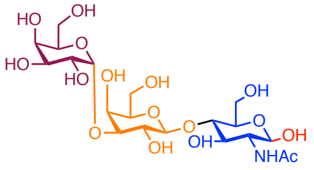
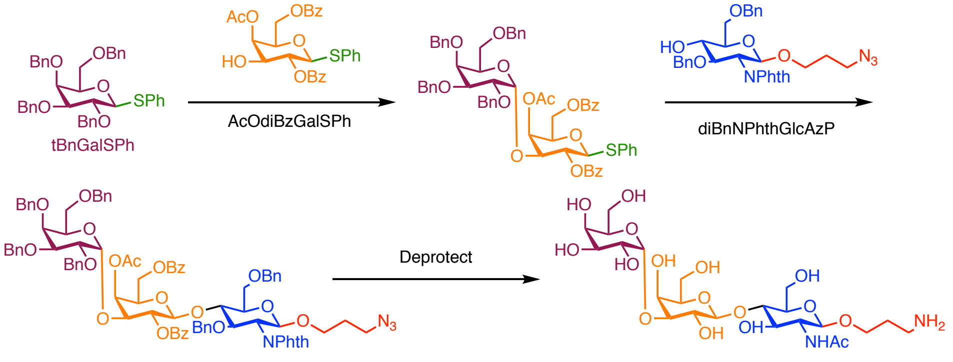
Clostridium difficile (*C. diff.*) is an anaerobic, gram-postive bacteria that colonizes in the large intestines and causes severe gastrointestinal distress and disease by producing two toxins: enterotoxin (toxin A) and cytotoxin (toxin B). *C. diff.* bacterium form spores that cause heat, acid, and alcohol resistance which allows them to survive under extreme conditions and spread rapidly. Worldwide, the rate and severity of *Clostridium difficile* (*C. diff.*) bacterial infections is increasing, with an estimated 453,000 yearly infections (64% in medical settings) occurring in North America alone.[1]

Although *C. diff.* bacteria are resistant to the most common forms of treatment (*e.g.* antibiotics), α-Gal, a natural trisaccharide expressed by intestinal bacteria, binds to toxins A and B to facilitate their removal from the body. However, while α-Gal is abundant in healthy individuals, the majority of those afflicted with *C. diff.* are immunocompromised, and therefore do not express α-Gal in quantities sufficient enough to sequester the toxins.[2] Our aim is to prepare an α-Gal epitope, append it to a polymer, and evaluate that as a treatment for *C. diff.* Herein, we carry out the synthesis of an azidopropyl functionalized α-Gal derivative through a series of protection and deprotection steps to generate each of the monosaccharides, followed by their stereospecific coupling.[3]



α-Gal



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Contribution from the Dorn group.

13. $M_2@C_{79}N$: A Stable Metallofullerene Radical Nanomaterial for Novel Electronic and Magnetic Applications

Kyle M. Kirkpatrick*[a], Paul Faust[a], Xiaoyang Liu[a], Yanlong Li[b], Cocoa Wang[c], Chenggang Tao[b], Alexey Popov[d], James Duchamp[a] and Harry C. Dorn[a]

[a] *Virginia Tech Department of Chemistry*
[b] *Virginia Tech Department of Physics*
[c] *National High Magnetic Field Laboratory (MagLab)*
[d] *IFW Dresden*

The Dorn group has previously reported a class of very stable radical containing metallofullerenes, $M_2@C_{79}N$ (M = Y, Gd, Tb).[1] The molecule features a one electron bond centred between the two metals. The fullerene cage provides a unique environment for rare interactions between the radical and two metals.

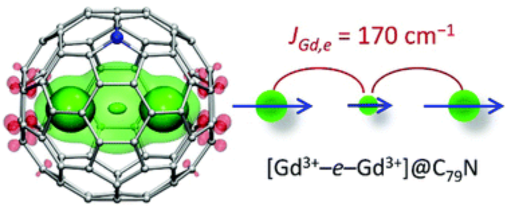

Figure 1. *Exchange coupling in $Gd_2@C_{79}N$*

The $M_2@C_{79}N$ class shows potential as single molecule magnets (SMMs) and in quantum computing. SMMs can potentially increase the memory storage density from 30 GB/cm^2 to 30 TB/cm^2. Quantum computing relies on the principles of superposition and entanglement to increase computing power.

We have shown $Gd_2@C_{79}N$ to be a next generation agent in Dynamic Nuclear Polarization (DNP).[2] In collaboration with Dr. Alexey Popov (IFW Dresden), magnetic measurements of $Gd_2@C_{79}N$ and $Tb_2@C_{79}N$ were completed to determine the exchange couplings (J) and relaxation dynamics.[3] Due to differences in electronic anisotropy, $Gd_2@C_{79}N$ is not a single molecule magnet (SMM), but $Tb_2@C_{79}N$ is in fact a SMM. To supplement this study, in collaboration with Dr. Chenggang Tao of VT Physics, STM images of $Gd_2@C_{79}N$ on a graphene sheet were obtained. An EPR spin site transfer experiment between $M_2@C_{79}N$ and TMPD is currently underway to study the charge transfer process. All of these studies are crucial in any potential commercial application of metallofullerene based electronic systems.

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Contribution from the Merola Group

14. N-alkylation of aminoquinolines: Oxidative catalysis with an Ir(III) complex

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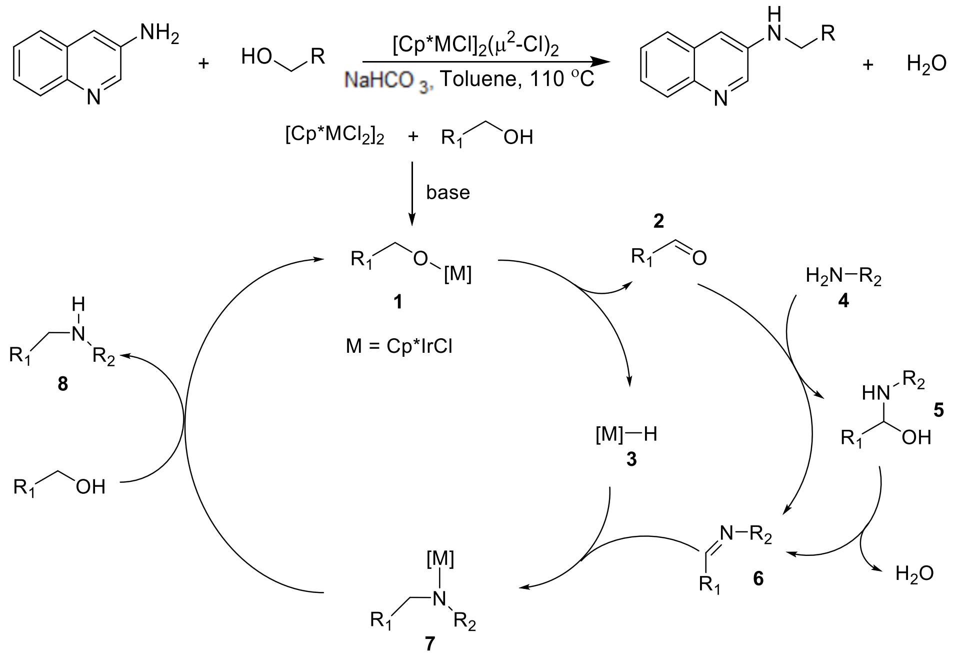
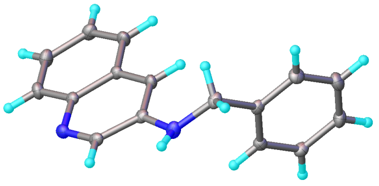
The present work describes the design and synthesis of a catalytic system for the alkylation of aminoquinolines with alcohols. The alkylated aminoquinolines were synthesized in toluene at 110°C and separated via column chromatography. The resulting product was recrystallized from dichloromethane and hexanes. The reaction to synthesize the alkylated derivatives was optimized to determine which set of conditions would produce the highest yield. The optimization was performed by altering the alcohol or diol, base, and mol % catalyst. Below depicts the catalytic cycle of this reaction.

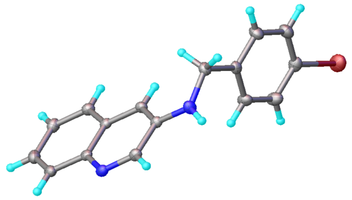


The aminoquinolines were characterized by nuclear magnetic resonance (NMR) spectroscopy, and high-resolution mass spectrometry (HRMS). Two of the formed aminoquinoline derivatives have been studied using X-ray crystallography. Below, the crystal structures obtained are displayed.

This catalytic reaction is highly preferred to the use of alkyl halides for N-alkylation since the more environmentally friendly alcohols are used in place of alkyl halides and the by-product of water does not pose the disposal problems of metal halides created in the conventional process.



*N*benzylquinolin-3-amine



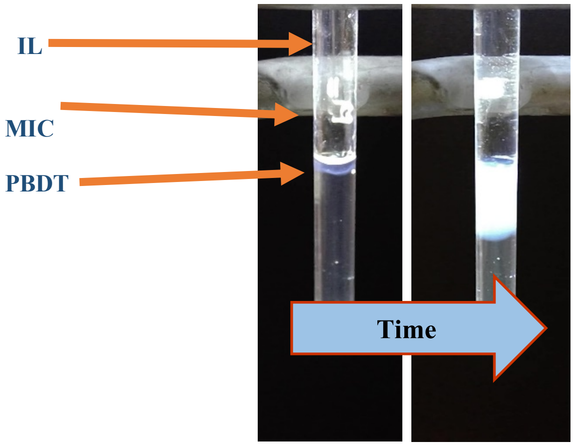
N-(4-bromobenzyl)quinolin-3-amine

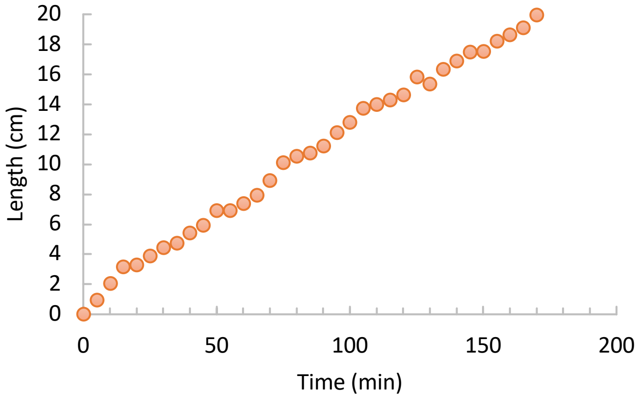
Contribution from the Madsen Group

15. Formation Kinetics and Mechanistic Modeling of Stiff and Non-Flammable Ion Conductors

Elliott D. Kunkel, Curt J. Zanelotti, Sarah E. Wollman, Eli Jelesko, Louis A. Madsen*

A new material called a molecular ionic composite (MIC) has been created in our lab with a rigid-rod polyanion, poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT), and an ionic liquid (IL), [C$_2$mim$^+$][TfO$^-$]. MICs exhibit the following properties: high ionic conductivity (up to 8 mS·cm^{-1}), tunable elastic modulus (3 MPa–3 GPa), and thermal stability up to 300C, making these MICs promising candidates for replacing volatile and flammable liquid electrolytes in rechargeable batteries.[1] The MIC is formed through an ion exchange process as IL exchanges with water in the aqueous PBDT solution. The solid MIC self-assembly process occurs downward into the PBDT solution. The interface between the growing MIC and the PBDT solution can be visually tracked because the MIC fluoresces blue (and strongly scatters light) when irradiated with white light. We created an automated program incorporating a stationary camra to measure this formation through tracking the change in fluorescence of the entire sample over time. Previously collected kinetics of formation data showed two distinct rate of formations while the MIC formed. There was an initial fast formation rate followed by a slower constant formation rate. Looking back at these formation kinetics, we found that the initial fast formation rate was caused by the IL forming nonhomogeneous sections within the MIC. The following slower constant formation rate was the formation of homogenous MIC. To approach this problem, we created an initial small portion of MIC by using 1 drop of IL. Once this initial portion was created we added the rest of the IL to the top of the small portion of MIC. We found the formation of this MIC to have a steady linear growth rate similar to the slower constant formation rate from before. We are working to to fit this new kinetics data to a mathematical model to predict what the formation rate of samples as a function of PBDT concentrations, IL concentrations, and IL molecular structures.





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Contribution from the Amanda Morris group.

16. Transition Metal Redox Mediators for Quantum Dot Sensitized Solar Cells

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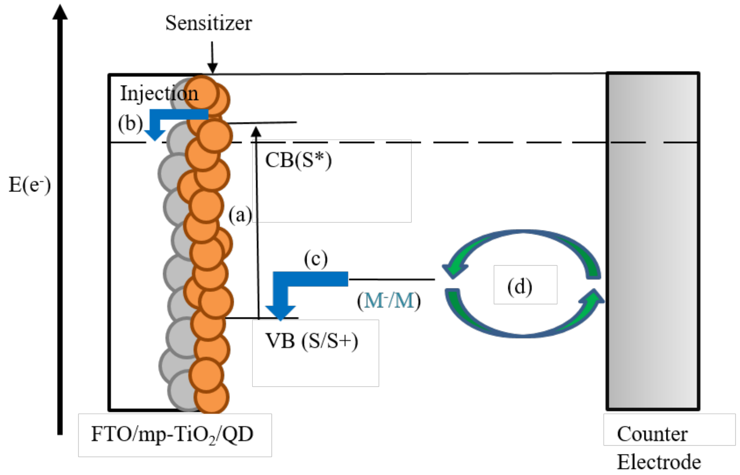
Department of Chemistry, Virginia Polytechnic Institute and State University
Blacksburg, Virginia, 24061, United States

As the ramifications of global warming become evident, research interest in cost effective renewable energy sources has increased. Solar energy shows promise with its high energy efficiency and power density. Polycrystalline silicon, perovskite, and dye-sensitized solar cells form the majority of current devices; however, they exhibit limited maximum thermodynamic efficiencies.[1] Quantum Dot Sensitized Solar Cells (QDSSCs) possess a maximum theoretical efficiency of 42%, far greater than its predecessors. However, this efficiency has yet to be achieved due to the prevalence of various loss mechanisms within the cell. One of the main loss mechanisms is through the recombination of excited electrons and the redox mediator inside the cell.



Traditionally, sulfide/polysulfide (S^{2-}/S_x^{2-}) has been used as a redox mediator in these devices. While a popular choice due to its high current densities, polysulfide undergoes rampant recombination at the working electrode.[1] This project focuses on utilizing alternative redox mediators based on the manganese(II) (bis(hydrotrispyrazolyl)borate) [$MnTp_2$] class of metal complexes. These complexes have higher redox potentials than S^{2-}/S_x^{2-} and undergo charge induced spin-crossover reducing the rate of recombination.[1] However, $MnTp_2$ complexes express poor solubility in common solar cell solvents creating a mass transport limitations in the cell. Five complexes were synthesised this semester: $MnTp_2^{4\text{-ethyl}}$, $MnTp_2^{4\text{-butyl}}$, $MnTp_2^{4\text{-hexyl}}$, and $MnTp_2^{4\text{-isopropyl}}$. These complexes were determined to be viable redox mediators by cyclic voltammetry. Structural characterization was performed using mass spectroscopy and ^1H NMR. The solubility of these complexes was determined experimentally. Solar cell efficiencies were determined via the current-voltage relationship under illumination, and electron lifetimes were analyzed through open circuit voltage decay (OCVD). Charge transfer induced spin crossover was proven via 1H NMR. Rate of electron transfer between the Quantum Dot and metal complex by Stern-Volmer Quenching. We believe the addition of these alkyl chains to the pyrazole rings will interrupt crystal packing forces making these complexes more soluble and our cells more efficient.

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Contribution from the Amanda Morris group.

17. Electrochemiluminescence of Ru Doped Metal-Organic Frameworks

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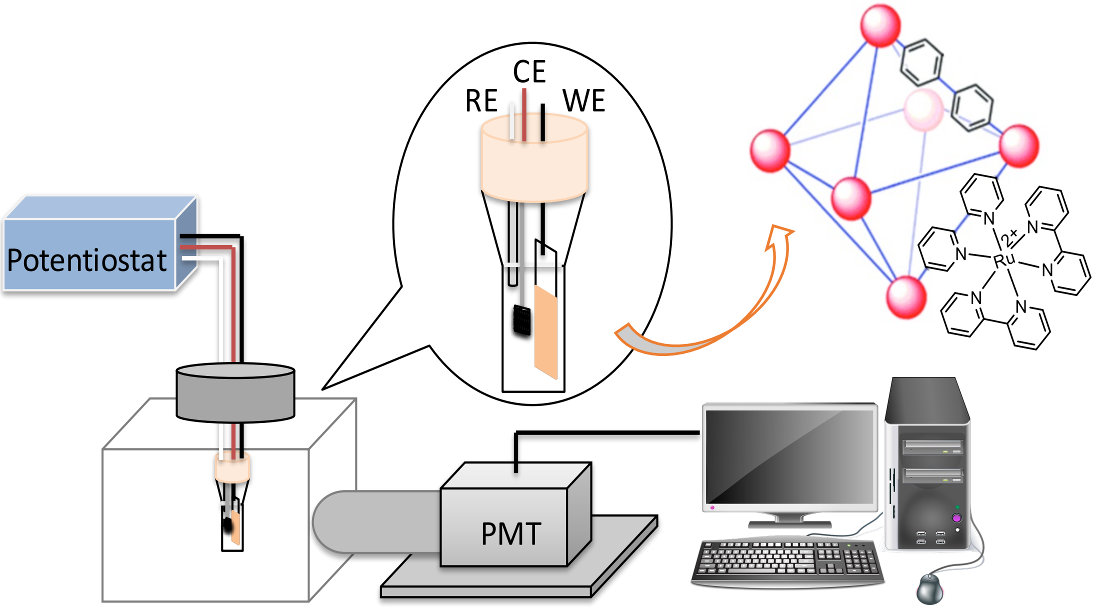
Department of Chemistry, Virginia Polytechnic Institute and State University
Blacksburg, Virginia, 24061, United States

Metal-organic frameworks (MOFs) are multidimensional crystalline coordination networks made up of organic ligands attached to metal nodes. Their characteristics, including large surface area and high porosity, have made them an ideal template material for electrochemiluminescence (ECL), a highly sensitive technique that can be used for clinical screening of various antigens and analytes.[1]

The goal of this study is to synthesize a zirconium-based MOF doped with $[Ru(bpy)_2(dcbpy)]^{2+}$ (dcbpy = 5,5'-dicarboxy-2,2'-bipyridine), as novel solid-state ECL detectors. The RuDCBPY-UiO-67 thin films were solvothermally prepared on conducting fluorine-doped tin oxide (FTO) glass slides and characterized by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). The redox pair of Ru^{2+}/Ru^{3+} was well observed in the electrochemistry study, and a stable ECL response has been observed. This work validates the strategy of using thin films for electrochemiluminescence, and suggests a promising approach for the fabrication of solid-state ECL detectors. Future work includes varying Ru loading systematically to study its effect on ECL performance.



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Contribution from the Amanda Morris group.

18. Insights into Hf-VPI-100 for CO_2 Adsorption and Chemical Fixation

Yered P. Machain*, Jie Zhu and Amanda J. Morris
Department of Chemistry, Virginia Tech, Blacksburg, VA 24061-0212

Since the industrial revolution, the burning of fossil fuels has led to a significant increase in atmospheric carbon dioxide concentrations. In an effort to reduce CO_2 emissions and recycle some of this atmospheric CO_2, CO_2 sequestration and chemical fixation has become an attractive research topic that has led researchers to investigate materials with significant CO_2 adsorption and chemical transformation properties. Metal-organic frameworks (MOFs) are promising hybrid materials that contain these desired properties. These MOFs have a high internal surface area, high chemical and structural tunability, high affinity for CO_2, and are dense with accessible catalytic sites. Because of this, MOFs can act as excellent catalysts for the cycloaddition reaction between CO_2 and epoxides. This atom economic reaction produces cyclic carbonates, which are valuable for a number of different reactions and industries. In this work, we synthesized and characterized two isostructural hafnium-based robust MOFs as Hf-VPI-100 (Cu) and Hf-VPI-100 (Ni). Both frameworks demonstrate high CO_2 uptake and catalytic efficiency for the cycloaddition of CO_2 to an epoxide. This reaction is performed in a parr reactor as this allows for the safe addition of CO_2 while keeping atmospheric air out of the system. Our previously mentioned MOF acts as the acid catalyst, while tetrabutylammonium bromide is used as the co-catalyst. The epoxides epichlorohydrin and 1,2-epoxybutane were the primary epoxides used in this research. Hf-VPI-100 MOFs have established high catalytic efficiency (up to 95% conversion yield) under mild catalytic reaction conditions (90 °C and 1.5 bars CO_2 for 6 hours). Kinetic studies were conducted to identify the reaction rate using NMR. Moreover, Hf-VPI-100 MOFs are also easy to recycle and reuse without losing the excellent catalytic performance.

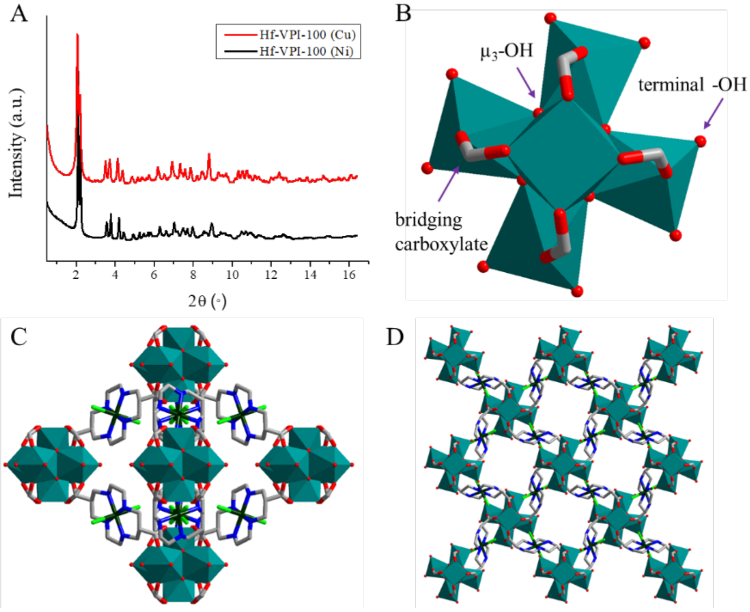

Figure 1. (A) PXRD patterns of as-synthesized Hf-VPI-100 MOFs collected at room temperature. (B) Polyhedral drawing of the Hf_6 cluster as view down from c axis. (C) Schematic structure of Hf-VPI-100 (Ni). (D) Packing diagram viewed down from c axis. Color scheme: Hf, light blue; C, grey; O, red; N, blue, Ni, dark green; Cl, green.

Contribution from the Kingston group.

19. Isolation and Structure Elucidation of Bioactive Compounds from *Stenosolen heterophyllus*

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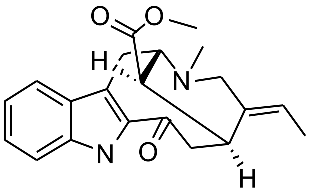
Department of Chemistry and the Virginia Tech Center for Drug Discovery, Virginia Tech, Blacksburg, Virginia 24061

Two known alkaloids, vobasine **1** and vobasine N-oxide **2**,[1] were isolated from the ethanol extract of *Stenosolen heterophyllus*. Purification and isolation were conducted using Sephadex LH-20 and C_{18} reversed-phase HPLC. The structure of the compounds were determined by analysis of NMR data and comparison with literature data. Vobasine N-oxide **2** was found to have weak antiplasmodial activity, with an IC_{50} value of about 27 μM.



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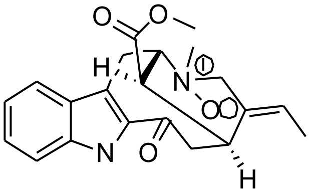

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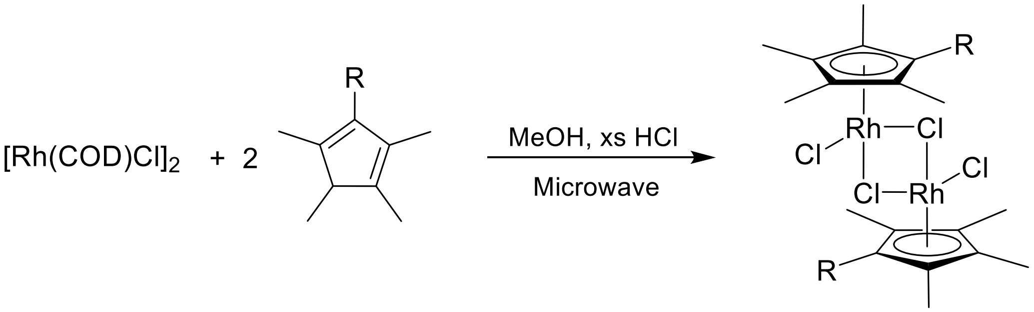
Contribution from the Merola group.

20. Synthesis and Characterization of Rhodium Cp^{*R} N-Heterocyclic Carbene Complexes

Justin S. Martinez*, Chad M. Bernier, and Joseph S. Merola
Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061

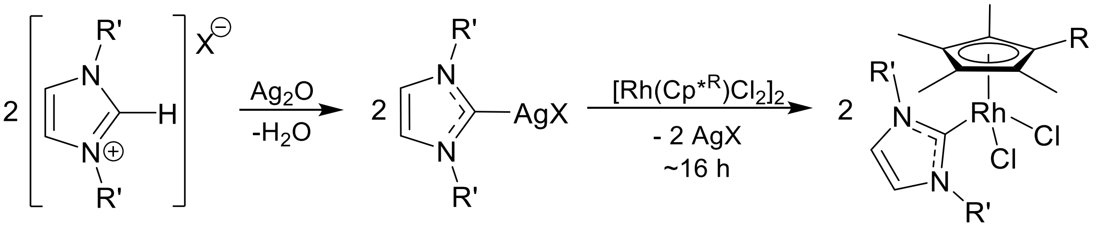
The Merola group has been investigating the effect of asymmetrically penta-substituted cyclopentadienyl ligands (Cp^{*R}) on the chemistry of noble metal complexes of rhodium and iridium. Rhodium Cp^{*R} complexes of this type are synthesized as shown below (Scheme 1).

Scheme 1. Synthesis of $[Rh(Cp^{*R})Cl_2]_2$ dimers.



This project focuses on the synthesis of rhodium N-heterocyclic carbene (NHC) complexes of the form Rh(Cp^{*R})(NHC)Cl_2 (Scheme 2). Over the last few decades NHCs have been popularized as ligands for transition metal complexes due to their relative inertness and ease of synthesis and functionalization. Several novel rhodium piano stool complexes were synthesized with a variety of Cp^{*R} and NHC ligands.

Scheme 2. Synthesis of Rh(Cp^{*R})(NHC)Cl_2 piano stool complexes.



These products were characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and X-ray crystallography, when possible (Figure 1).

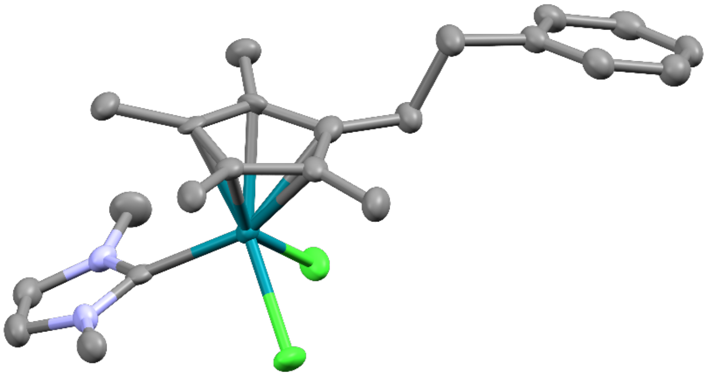


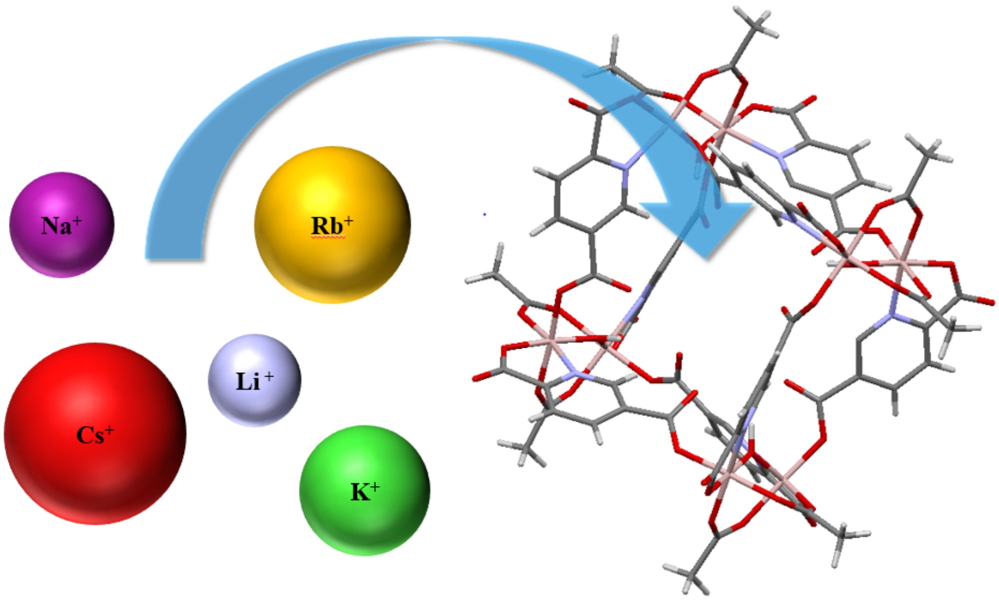
Figure 4. Thermal Ellipsoid Plot of Rh(Cp$^{*(CH_2)_2Ph}$)(IMe)Cl_2

Contribution from the Amanda Morris group.

21. Host-Guest Encapsulation of Alkali Metals by Al-pdc-AA Cages

Ann Marie May*, Pavel Usov and Amanda Morris
Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061

Since the discovery of crown ethers, a new field of alkali metal host-guest interactions has developed to improve modern medicinal and environmental practices, such as ^{137}Cs capture from nuclear runoff. In this study, Cs^+ and other alkali metals bind to a porous Al supramolecular cage, Al-pdc-AA. Al-pdc-AA consisting of pyridine-2,5-dicarboxylic acid organic ligands and dimeric Al-aceto nodes. Chemical characterization was conducted using ^{1}H NMR, ^{13}C NMR, single crystal X-ray diffraction (SXRD), and thermogravimetric analysis. Titration studies utilizing ^{1}H NMR were conducted to characterize the binding of various alkali metals to the Al cage. Larger cations, such as Cs^+, bind most strongly, as shown by the decrease in the chemical shifts of the ^{1}H NMR spectra. From these spectra, binding affinities are explored for the Al-pdc-AA cage. Future work will include the synthesis of analogous Al supramolecular cages, solid-state absorption of gases, such as CO_2, and isothermal calorimetry.



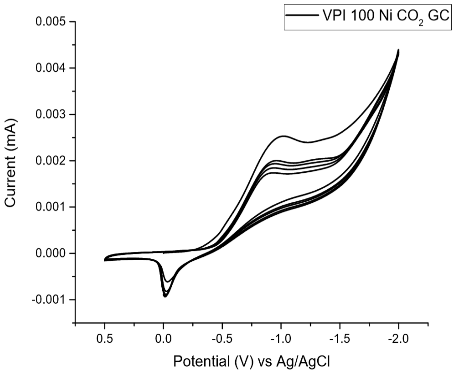
Contribution from the Amanda Morris group.

22. CO_2 Reduction through Ni-cyclam based Thin Film MOF

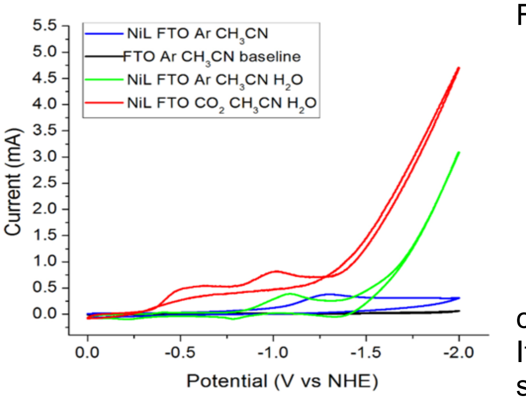
Michael McHale, Jie Zhu and Amanda Morris
Virginia Polytechnic Institute

Metal Organic Frameworks (MOFs) show great promise as catalytic agents because of their large surface area, high concentration of active centres, and tunable pore size. Specifically, some MOFs have served as efficient catalysts for CO_2 reduction[1]. In this experiment, a zirconium based MOF VPI-100 (Ni) was prepared and tested for electrocatalytic CO_2 reduction. Cyclic voltammetry (CV) experiments have been performed and catalytic current for CO_2 has been observed with VPI-100 (Ni) MOF thin films under CO_2. This MOF was chosen because of its molecular catalyst [Ni-cyclam]$^{2+}$ has been used as a building block and its framework has demonstrated high CO_2 uptake capacity.

The MOF thin films were assembled on either FTO or glassy carbon electrodes. To adhere the MOF to the GC slide, the MOF was either synthesized in a solvothermal method or drop casted onto the slide. Drop casting the MOF directly onto the GC slide led to the formation of thick film without appreciably driving catalytic activity towards CO_2 reduction. Solvothermal synthesis resulted in a uniform thin film which covered part of the slide. CV showed Ni (II) to Ni(I) reduction peak around -1V and catalytic currents have been observed.



The FTO slides were formed via a one pot solvothermal method onto the FTO slide. Nice uniform MOF thin films coated the surface of the FTO slide homogenously. CV clearly showed two reduction peaks -.5 to -1 V (relative to the reference electrode). It is also clear from this graph that the overall amount of current increased (increasing by about .5 mA). This was most likely caused by catalytic activity in the MOF.



Overall this experiment showed how VPI-100 Ni can be used to reduce CO_2 while producing current. It also appears as if FTO provides a better bonding site than GC, but more tests need to be made to draw a firm conclusion.

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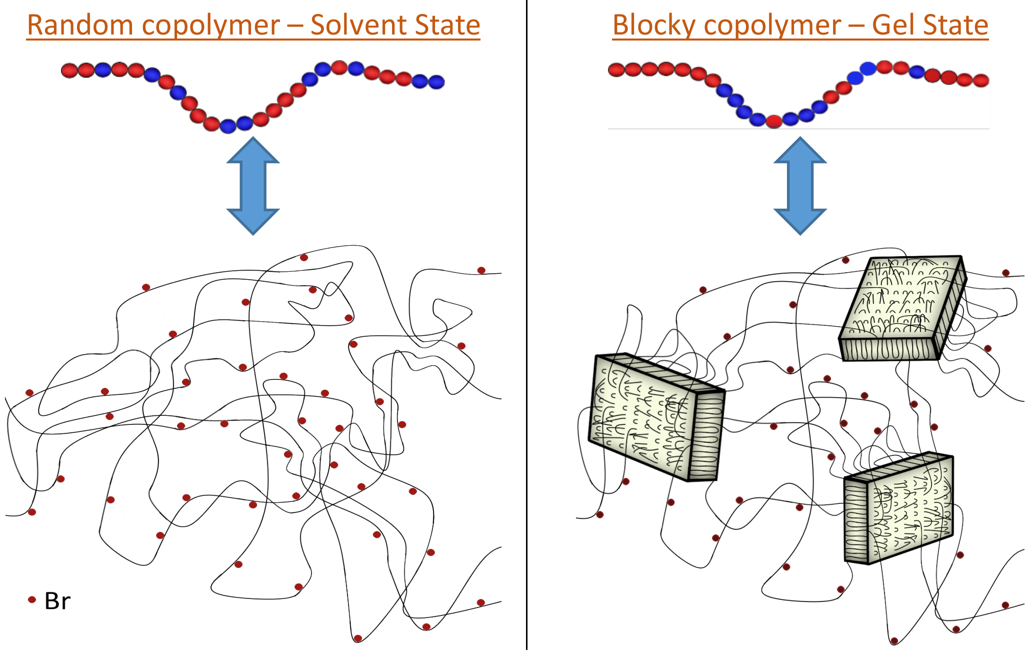
Contribution from the Moore group.

23. Tuning the Blockiness of Brominated Syndiotactic Polystyrene Copolymers via Post-Polymerization Modification in the Gel State

Peter M. Moberg*, Kristen M. Felice and Robert B. Moore
Virginia Tech, Macromolecules Innovation Institute, Department of Chemistry

Block copolymers (BCPs) are a unique class of polymer composed of two or more monomers arranged in discrete block segments. BCPs have enhanced mechanical and physical properties compared to their random copolymer analogues because of micro-phase separation between blocks. The technological applicability of BCPs, for example as membrane materials in fuel cells, desalination, and water purification, is promising; however, the direct synthesis of BCPs is inherently challenging, limiting the scope of their commercial application. Recently, the Moore research group developed a method to prepare block-like copolymers via post-polymerization modification (PPM) carried out in the gel state. Gels are 3-dimensional networks composed of crystalline domains linked together by amorphous domains. Traditionally, PPM methods are carried out by dissolving a homopolymer in solution, which exposes the entire chain to the reagents and produces a random copolymer, consequently losing all the sought-after properties of a block copolymers. In contrast, during PPM in the gel state, functionalizing reagent is excluded from the crystalline domains and reacts with the amorphous domains, thus creating a 'blocky' copolymer. This blocky copolymer can be visualized as segments of unreacted monomers and segments of randomly functionalized monomers. This work demonstrates that the blockiness of the polymer chains can be adjusted by changing the solvent used to create the gel network. Syndiotactic polystyrene (sPS) is a semicrystalline polymer that gels in a broad range of solvents, resulting in different gel morphologies. The bromination of sPS was investigated in two gelation solvents, chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4). Blocky copolymers prepared from these solvents demonstrate different thermal properties and crystallization kinetics at similar degrees of bromination, attributed to the differences in their sPS gel morphologies. Gel-state bromination is a facile approach to achieve commercially viable blocky derivatives of sPS or any other semicrystalline polymer that forms a gel.



Contribution from the Amanda Morris group.

24. A Study of Ion Pairing between Halides and Ru(bpy)$_2$(dcbpy) within a UiO-67 Metal-Organic Framework

Jennifer M. Neuhard*, Bradley J. Gibbons, and Amanda J. Morris

Ion pairing is a fascinating and functional phenomenon with a wide variety of uses in both synthesis and ‘real world’ application.[1] Contact ion pairs in particular indicate significant potential for use in electron transfer studies and improvement in solar cell light harvesting efficiency due to enabling outer-sphere charge transfers when bonded to transition metals.[1] In this study, we utilize steady-state emission spectroscopy to analyze the ion pairing between the halides chloride and iodine, and photoactive ruthenium bis (2,2’-bipyridine) (5,5’-dicarboxy-2,2’-bipyridine) (Ru(bpy)$_2$(dcbpy)) loaded in to the zirconium-based metal-organic framework (MOF), UiO-67 (Fig.1).

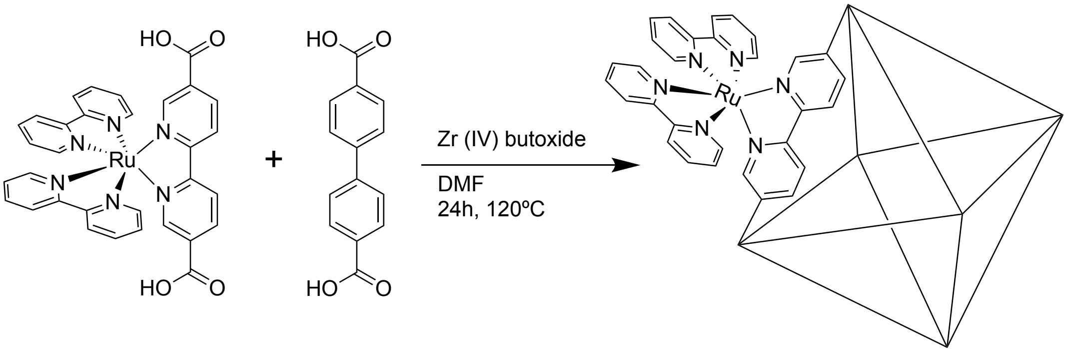


Figure 1. Synthesis of Ru(bpy)$_2$(dcbpy)-doped UiO-67

The ruthenium compound is immobilized within the MOF pore by using the functionalized bipyridyl group as an organic linker within the framework. The UiO-67 structure was chosen due to its thermal and chemical stability, and previous ruthenium-loaded analogues.[2] Such an environment allows for the comparison between relatively static ion pairs and those in solution. Consistent effects in both environments would indicate the potential use of ion pairings for improved solar harvesting capabilities of solar cells.[1]

To confirm the success of the MOF synthesis PXRD was used to characterize the ruthenium-loaded UiO-67 (Ru-UiO-67). This synthesis was adapted to use zirconium (IV) butoxide as the zirconium precursor in place of the original zirconium (IV) chloride (ZrCl$_4$) to prevent premature ion pairing. The steady state emission of Ru-UiO-67 was analyzed before and after the addition of a halide salt (tetrabutyl ammonium chloride, tetrabutyl ammonium iodide, and lithium chloride, respectively) to observe any shift in emission spectra.

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Contribution from the Merola group.

25. Oxidative Lactonization of Diols: Catalysis with Iridium(III) Complexes

Billy Owen*, Loren Brown, Joseph S. Merola
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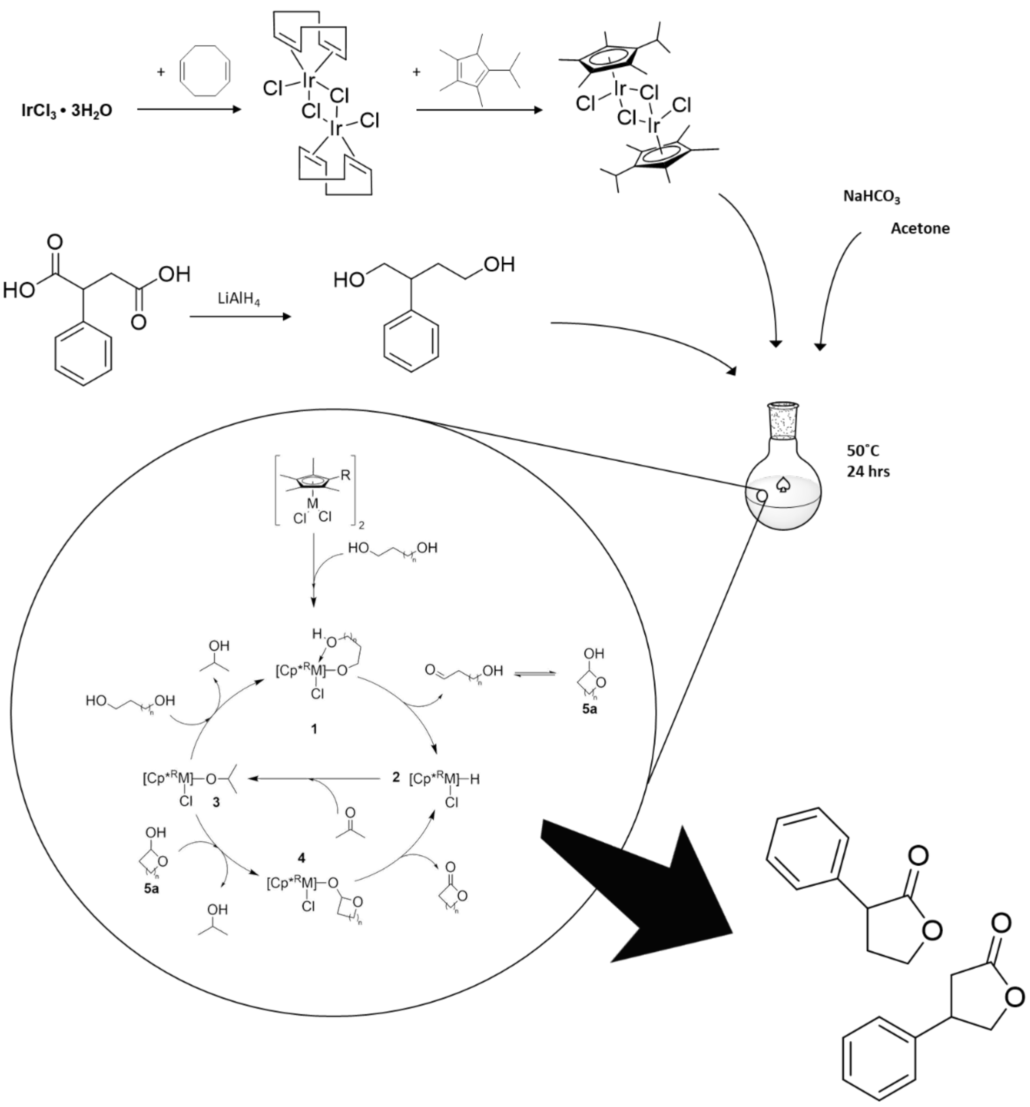
Lactones have many uses in industry including flavouring agents, fragrances, polyesters, and pharmaceuticals. The goal of this research is the use of iridium and rhodium piano stool complexes as more practical catalysts for the formation of lactones from diols. Our method, which includes synthesis of both the catalyst and the substrate, allows for simple production of many varieties of lactone under mild conditions with relatively inexpensive reagents. In this study, we have optimized the catalyst, base, solvent, and reaction conditions, as well as investigated the lactonization of many "unusual" diols including those with heteroatoms and aromatic rings. The ability to easily form such a variety of lactones harbours great potential for the improvement of industrial lactone syntheses across the board.

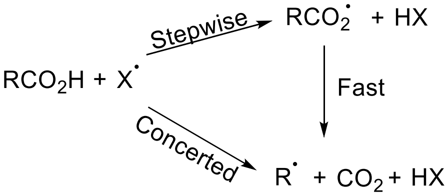


Contribution from the Tanko group.

26. Mechanism of H-atom Abstraction from Carboxylic Acids

Aditya S. Ponukumati*, Mark D. Paradzinsky and J. M. Tanko
Department of Chemistry, Virginia Tech

Historically, hydrogen atom abstraction from the hydroxy group of carboxylic acids was believed to proceed through a stepwise mechanism, with a hydrogen atom abstraction step preceding the decarboxylation step.[1] However, recent theoretical work by Denisov suggests an unprecedented concerted pathway, whereby the hydrogen atom transfer and decarboxylation occur simultaneously.[2]



For a concerted mechanism, the rate of abstraction is expected to increase with increasing radical (R•) stability, whereas for a stepwise mechanism it is not expected to vary at all.

Previous work in our group has used the reaction of cumyloxyl radical and several carboxylic acids to determine abstraction rate constants. However, some of the rate constants were too low to measure because they were obscured by a competing β-scission process and thus below the dynamic range afforded by these methods. For acids where it was possible to measure a rate constant, the results suggested a concerted mechanism, though more examples are needed to substantiate this conclusion.

In hopes of boosting H-atom abstraction rate constants above the current detection limit, cumyloxyl radical was replaced with the highly reactive hydroxyl radical (HO•). Hydroxyl radials were generated via the photolysis of 2-mercaptopyridine-N-oxide using a 355 nm laser pulse.[3] Because the concentration of HO• cannot be monitored by UV/Vis, a small amount of *trans*-stilbene (t-SB) was added to the solution as a spectroscopic probe. The t-SB adduct generated from the reaction of t-SB and HO• was monitored at 392 nm.[4] The kinetics of the hydroxyl radical can be extracted from the resulting transient trace.

The majority of our resources were dedicated toward optimizing the parameters needed to utilize the probe technique. As a result, the studies to observe the kinetic behavior of HO• have not yet been conducted.

Further, the rate of H-atom abstraction may also be obtained by competition experiments. Our group will also utilize GC-MS to determine the proportionality constants between the rates of hydrogen abstraction from pairs of carboxylic acids.

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Contribution from the Grove group.

27. Growth of anisotropic silver nanoparticles on biological surfaces.

Timothy S. Pressler*, Ethan Boeding*,Yunhua Li
Advisor: Dr. Tijana Grove

Chemical sensors, smart textiles, photovoltaics, photo-, and electro-catalysts rely on nanostructures that are supported by the substrate. While in recent years researchers have made great advances in synthesis of plasmonic nanostructures, integration of nanoparticles with functional substrates remains a challenge. The direct synthesis of plasmonic nanoparticles on the biopolymeric surfaces can, in principle, provide a scalable, cost-effective, and high throughput strategy for the synthesis of plasmonic biocomposite materials with unique physical and chemical properties. Recently, our lab has shown that immobilization of gold nanospheres and nanostars onto a protein membrane derived from avian egg-shell resulted in robust catalyst[1]. Inspired by the advances in nanoparticle synthesis at the liquid-substrate interface, we have integrated substrate-based techniques with colloidal chemistry for in situ growth of plasmonic nanoparticles in microporous biopolymeric membranes. This strategy takes advantage of seed-mediated solution protocols in which seeds direct noble metal nanostructure formation. However, we first create a substrate-bound template by immobilizing the colloidal seed onto the surface of protein fibers. Growth of nanocrystals then proceeds at the liquid-protein interface within confines of the micron-sized membrane pore. Herein, we quantitatively study the effects of pH of the pretreatment buffer, incubation time and age of the seeds on seed-immobilization efficiency. To that end we carefully designed the series of experiments in which silver seed was immobilized onto egg shell membrane. The pretreatment buffer with pH range from 2 to 12 was applied. The incubation was monitored for 20 hours. Seed age was also tested from 1 day, 3 days, 1 week, and 1 month old. The loading of the seed was characterized measuring total silver content using ICP-AES. The data showed the best seed immobilization conditions were with a pH 4 pretreatment buffer and 12-hour incubation of the ESM. Going forward, monitoring the nanoparticle growth on the ESM will provide more insight on this process and how it can be improved. Since seed-immobilization step is crucial for our overall synthetic strategy, better understanding of the immobilization step will allow us to tune the properties of the final product.

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DOI:10.1039/c7nj01908d

Contribution from the Lin group.

28. Reusing biomass for battery anode materials.

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Department of Chemistry, Virginia Tech, Blacksburg, Virginia, 24060

Since the lithium and sodium secondary batteries came to the world, research of anode materials is always a key point. As current, many anode materials has been tested and used on lab or commercial batteries including same metals with cathode, graphitic carbon, Tin etc. However, in order to maximize the value, total cost of materials should be focus on. Carbon anodes still the dominated material in the world.

For limiting the total cost, reusing biomass such as food waste, which is the most common relatively zero-cost biomass in daily life, should be a good idea in this case. Food waste, which has high carbon content, can be carbonized in oxygen negative calcining process.

My current study is focusing on finding the best way calcining raw food waste materials, making electrodes with carbonized product, assembled electrodes to coin cells under same condition and testing performance of each one. Pineapple, grape and grain wastes have been used in my study. XRD, SEM, Raman spectroscopy and Batteries testing system were used in investigating materials ‘structure, carbon content and performance data.

Contribution from the Moore group.

29. Processing-Morphology-Property Relationships of New Multi-Acid Sidechain Perfluorinated Ionomers

Robert L. Smith*, Christina M. Orsino and Robert B. Moore
Virginia Tech Department of Chemistry, Moore Research Group, Macromolecules Innovation Institute, and Institute for Critical Technology and Applied Science

The 3M developed perfluoroimide acid (PFIA) and perfluorosulfonic acid (PFSA) ionomers are used as proton-exchange membranes in hydrogen fuel cells. In this project, our objective is to both qualitatively and quantitatively investigate the effects of sidechain structure and various casting parameters on the morphology and properties observed in PFIA and PFSA membranes. A controlled method of casting the polymer dispersions and post-casting thermal annealing protocols are used for both the PFIA and PFSA as a means to prepare samples for characterization with dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS). We have used partial neutralization of the acidic sites with different counterions as a method to systematically control the strength of the ionic interactions between sidechains, which governs morphological development. The analysis conducted on PFIA and PFSA may result in a greater understanding of the overall structure and that of the functionalized sidechains under different conditions. The data obtained is in furtherance of the goal to increase fuel cell membrane durability and proton conductivity that will ultimately result in a more efficient proton exchange membrane hydrogen fuel cell system.

Contribution from the Amanda Morris group.

30. Synthesis of Charged Derivatives of $MnTp_2$ for use in Quantum Dot Sensitized Solar Cells.

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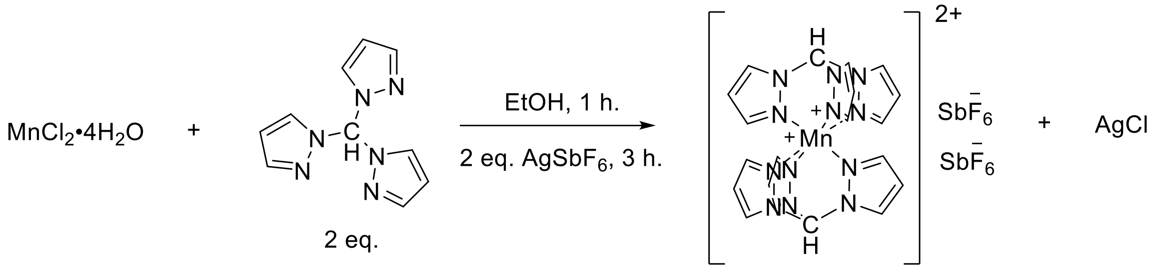
Blacksburg, Virginia, 24061, United States

Cost efficient renewable energy is a major concern for nations around the globe. The environmental impact from emissions generated by non-renewable energy sources must be limited to stymie the progress of climate change. To combat this, the realization of solar energy as a viable alternative fuel source has gained momentum over the last decade. Solar energy, remains an attractive option as it is the only energy source capable of supporting the whole of humanity without supplementation from additional sources. While crystalline silicon solar cells are currently leading the field, Quantum Dot Solar Cells (QDSSCs) are a potential alternative with a theoretical efficiency of 42% (10% above that of silicon cells). However, QDSSCs have yet to achieve landmark efficiencies comparable with other devices. One main source for efficiency losses arises from the limitations of the redox electrolyte used in QDSSCs. These electrolytes are responsible for carrying charge from the working electrode to the counter electrode and back again. They also dictate the maximum possible voltage the cell is capable of producing. Unfortunately, the efficiency of the cell is limited because the electrolytes often undergo electronic recombination at the site of the working electrode, thus reducing the current that is produced by the cell. In recent work, the Morris group has developed an alternative redox electrolyte based on the manganese(II) (bis(hydrotrispyrazolyl)borate) [$MnTp_2$] redox shuttle. This electrolyte is capable of reducing recombination within the device through Charge Transfer-Induced Spin Crossover (CTISC). While the electron lifetime in devices prepared with this electrolyte were found to possess a two-fold improvement over more common transition metal-based redox shuttles $(Co(Bpy)^{3+/2+}$, $MnTp_2$ is not without its drawbacks. Solubility remains a key concern of this electrolyte, which leads to mass transport losses within the cell. In this work, a charged analogue of $MnTp_2$ was prepared using the neutral hydrotris(pyrazolyl)methane [tpm] ligand in place of hydrotris(pyrazolyl)borate. By synthesizing a charged analogue of $MnTp_2$ the solubility of the metal complex can be controlled through utilization of the SbF_6^- anion. While this metal complex displayed enhanced solubility in acetonitrile, the electrochemical performance of such complexes is not suitable for use in QDSSCs, and is the subject of continued research.



Contribution from the Tim Long group.

31. Urea as a Monomer for the Design of Poly(dimethyl siloxane)-Containing Polyureas as Antifouling Coatings and Elastomeric Sealants

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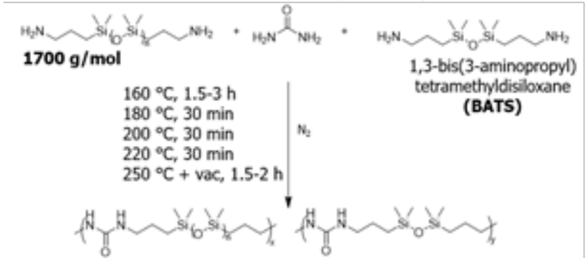
Department of Biological Sciences, Virginia Tech, Blacksburg, VA 24061
Department of Chemistry, Macromolecules Innovation Institute, Virginia Tech, Blacksburg, VA 24061

Alternative methods to produce isocyanate-free polyurethanes and polyureas are gaining popularity due to health and safety concerns surrounding isocyanates[1]. In-situ generated isocyanic acid yields urea linkages in the absence of isocyanate reagents, while products maintain the properties of polyureas made with isocyanates. This bio-based reaction creates an inherently safer and industrially relevant process with a wide array of applications. Melt polymerization of oligomeric or monomeric diamines in the presence of urea proceeds in the absence of solvent or catalyst, only requiring heat[2, 3] and form optically clear, freestanding, elastomeric films at room temperature.

Melt polymerization afforded polyureas from diamines and urea. Stoichiometric excess of diamine ensured desired 1,3-dialkylurea linkages while the formation of side products was avoided. These poly(dimethylsiloxane)- (PDMS-) based elastomers enabled a wide service window, limited only by elastomer flow temperature and potential PDMS melting for crystallizable systems. Melt polymerization in the presence of PDMS oligomers leveraged the low glass transition temperature (T_g) and nonpolarity of PDMS, enabling highly phase-separated thermoplastic elastomers isolated directly from the melt. Melt homogeneity was ensured in the beginning stages of the reaction, while higher temperatures and transureaization under vacuum drove the reaction to high molecular weight. Polymerization in the presence of short-chain diamines yielded multiblock copolymers while improving mechanical properties. Synthesis of PDMS-based elastomers with the addition of a PDMS-soluble 1,3-bis(3-aminopropyl)tetramethyldisiloxane (BATS) chain extender facilitated homogeneity in the melt and enabled a novel family of high molecular weight, linear polyurea copolymers.



Thermomechanical analysis and differential scanning calorimetry measured mechanical properties and glass transitions as a function of temperature. Tensile testing determined mechanical properties of the freestanding films. Adhesion to these silicone polyureas will also be probed with a variety of techniques and is relevant to their applications in biomaterials, microfluidics, or antifouling coatings.

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Contribution from the Matson group.

32. H_2S Releasing Hydrogels: Peptide-based Materials for Therapeutic Signaling Gas Delivery

Samantha E. Seymour*, Yun Qian and John B. Matson
Department of Biological Sciences, Macromolecules Innovative Institute, and Department of Chemistry

Hydrogen Sulfide, H_2S, is typically known as a toxic, foul-smelling gas, but it is also a key signaling molecule in enzymatic reactions vital in mammalian biology. When controlled, this gasotransmitter has a vast therapeutic potential in regenerative medicine, such as promoting wound healing by stimulating angiogenesis. Self-assembling aromatic peptides have already been designed that form a gel upon charge screening and can slowly release H_2S over a period of time[1]. The molecular structures of these known aromatic peptides can be manipulated to create shorter peptide sequences that can change the properties of the gel and alter the delivery of the H_2S. Aromatic dipeptides with the structure SATO-FBA-FE and SATO-FBA-YE (Figure 1) were designed and both formed a hydrogel. They were also able to undergo shear thinning and recover with slightly lower moduli, making them able to be injected into the body (Figure 2). Methylene Blue was also performed to measure the release rate of the hydrogen sulfide and the half-life of SATO-FBA-FE was found to be 23.6 minutes, while the half-life of SATO-FBA-YE was found to be 21.9 minutes. Transmission Electron Micrographs are included below showing the formation of nanofibers for each of the samples (Figure 3). The newly created peptide may be useful in localized signaling gas delivery for a variety of diseases and conditions.

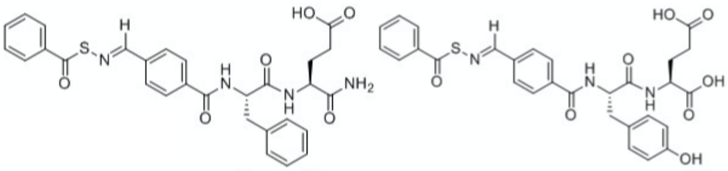

Figure 5. Chemical Structures of SATO-FBA-FE and SATO-FBA-YE

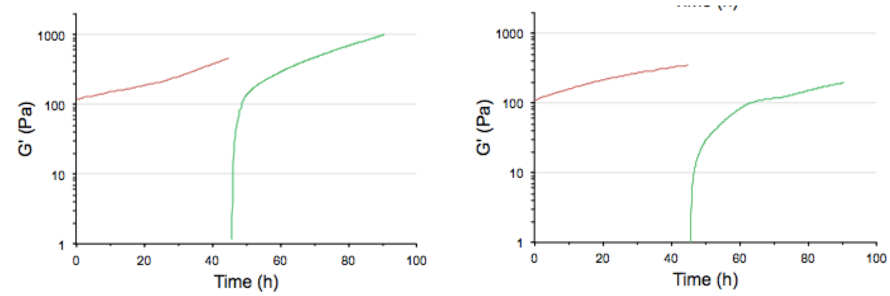

Figure 6. Shear-thinning data contributing to the ability for the dipeptide to be injected. Left: SATO-FE. Right: SATO-YE

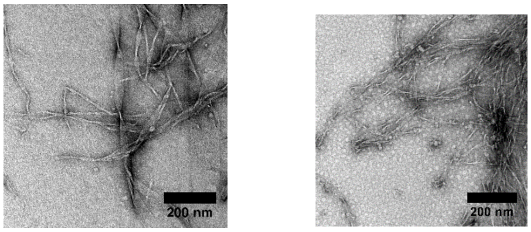

Figure 7. TEM images for SATO-FBA-FE and SATO-FBA-YE

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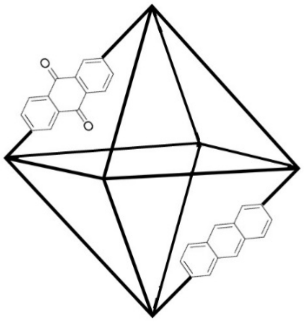
Contribution from Amanda Morris Group.

33. Synthesis and Characterization of Anthraquinone-Anthracene Mixed Metal Organic Frameworks

Connor C. Slamowitz*, Jennifer M. Rowe, Paula J. Celis-Salazar, Pavel M. Usov and Amanda J. Morris
Department of Chemistry, Virginia Tech

An artificial photosynthetic assembly can utilize metal-organic frameworks (MOFs) in order to facilitate the transport of electrons. A MOF is a coordination of metal ions connected by organic ligands to create a crystalline structure. From previous work, the Morris Group has concluded that the 2,6-Zr-AC-MOF, which utilizes 2,6 anthracene (2,6-ADCA) as an organic ligand, is an effective light absorber[1]. Additionally, 2,6-Zr-AQ-MOF, utilizing 2,6 anthraquinone (2,6-ADCQ), is an effective material to transport electrons[2]. The 2,6-ADCA ligand and the 2,6-ADCQ ligand were combined using previous methodology[1,2] of the AMorris Group to create a 2,6 ADCA/ADCQ mixed MOF with molar ratios of 1:1. Theoretically, the mixed MOF will create a photoinduced electron transfer, with the 2,6-ADCA ligand acting as the electron donor, and the 2,6-ADCQ ligand acting as the electron acceptor. This reaction will initiate a proton-coupled electron transfer to reduce the anthraquinone into hydroquinone. Future work with this mixed MOF will determine the lifetime of the excited states using steady state fluorescence and time-resolved emissions as a function of molar ratio.



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Contribution from the Santos group.

34. Structure-Activity Relationship Studies of PF-543 Derived Inhibitors of Sphingosine Kinase

Gregory M. Traversa*, Hao Li and Webster L. Santos
Department of Chemistry

Sphingosine Kinase 1 (SphK1) and Sphingosine Kinase 2 (SphK2) are enzymes responsible for the phosphorylation of the substrate lipid sphingosine (Sph) into sphingosine-1-phosphate (S1P). S1P promotes cell growth, survival, proliferation, inflammation, and migration.[1] In contradiction, Sph and its metabolic precursor, ceramide, promote apoptosis. Correspondingly, increases in S1P concentrations has been linked to diseases such as cancer, fibrosis, and sickle cell disease.[2] Inhibition of S1P production is therefore theorized as a promising strategy for treatment of inflammatory diseases as well as cancer.

The crystal structure of SphK1 indicates that the enzyme binding pocket contains a J-shaped hydrophobic passage with a pocket deep within the binding site suited for a polar head group.[3] A compound (PF-543) synthesized and characterized by Schnute *et al.* exhibited a prominent level of activity and selectivity for the inhibition of SphK1 over SphK2 with an IC_{50} of 2 nM and 100-fold selectivity for SphK1.[2] Using this as a reference point, a scaffold has been conceived with similar characteristics such as an *R*-prolinol head group and 1,3- substitution of the phenyl ring for different tail groups, shown in **Fig. 1**.
The benefits of using this scaffold include the final products sharing a common intermediate, allowing for bulk production of starting material for the final reactions needed for product. The scaffold also allows for rapid addition of a variety of tail groups since in the intermediate the 3-position is halogenated. Results have yet to be obtained regarding the biological activity of any analogues.

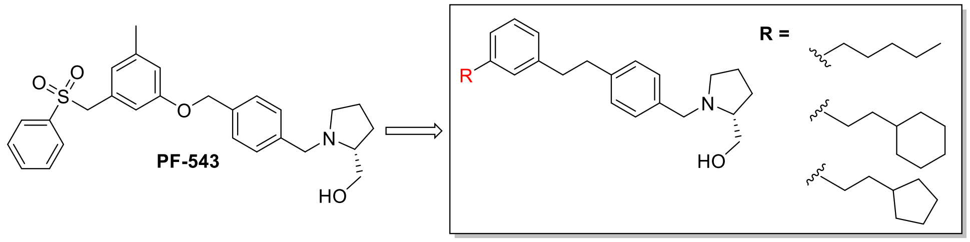

Figure 8. Designed scaffold derived from hit compound **PF-543**.

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WITHDRAWN

35. Synthesis of 4-bromophenyltricyanotheylene: A Building Block for a Molecule-Based Magnet

Isabella M. Ulate*, Christopher L. Houser and Gordon T. Yee
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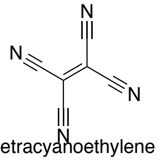
After the first discovery of a room-temperature molecule-based magnet in 1991[1], there has been an interest in synthesizing additional networks of transition metal cations and organic radical anions. The interest is largely owed to unprecedented properties of this material. One feature is that because it consists of an organic molecule, tetracyanoethylene (Figure 1) radical anion, as a building block, structurally and electronically related molecules can be synthesized and employed to change the magnetic ordering temperature, T_c, of the network. [2] From this, we can deduce the factors that determine T_c.

Figure 1. Tetracyanoethylene molecule



This semester's project was to complete the synthesis of a molecule related to tetracyanoethylene that uses a halogen-substituted phenyl ring as the new part of the structure. These compounds have been previously made by the group using chlorine and fluorine substituted phenyl rings. This synthesis focuses on bromine substituted phenyl rings. The hope is that the bromine substituent will affect the network's magnetic properties in a positive way. This new molecule will be reacted with vanadium hexacarbonyl ($V(CO)_6$) to give a new magnetically ordered material. The magnetic ordering temperature and other properties will be measured using the superconducting quantum interference device (SQUID).4-bromophenyltricyanoethylene was synthesized using 4-bromobenzaldehyde and malononitrile as starting materials (Figure 2).

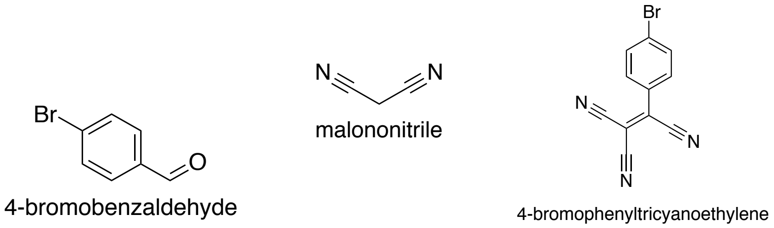


Figure 2. Shown above are the starting materials 4-bromobenzaldehyde and malononitrile as well as the final product 4-bromophenyltricyanoethylene of this synthesis.

Going forward, the project will involve making the 2-bromo and 4-bromo derivatives, along with creating derivatives substituted in multiple places with bromine groups. After evaluating the ordering temperatures, we should be able to see relationships between magnetic ordering temperatures and substituent placement and size.

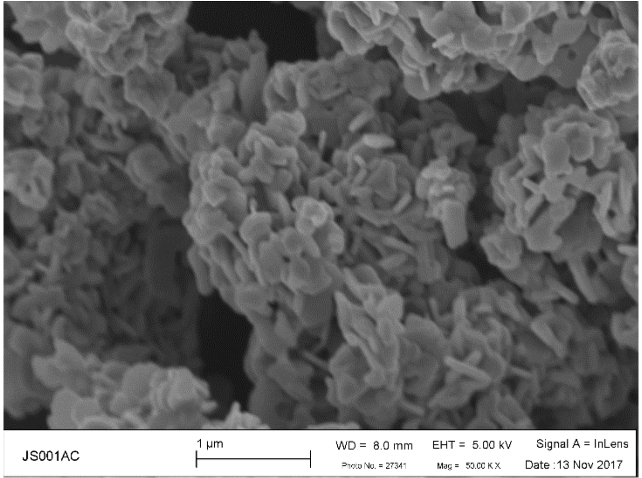
1. Amshumali, M.; Harvey, M. D.; Yee, G. T., Room temperature and near-room temperature coordination polymer magnets. *Synthetic Metals* **2014,** *188*, 53-56.
2. Harvey, M. D.; Crawford, T. D.; Yee, G. T., Room-temperature and near-room-temperature molecule-based magnets. *Inorganic chemistry* **2008,** *47* (13), 5649-5655.

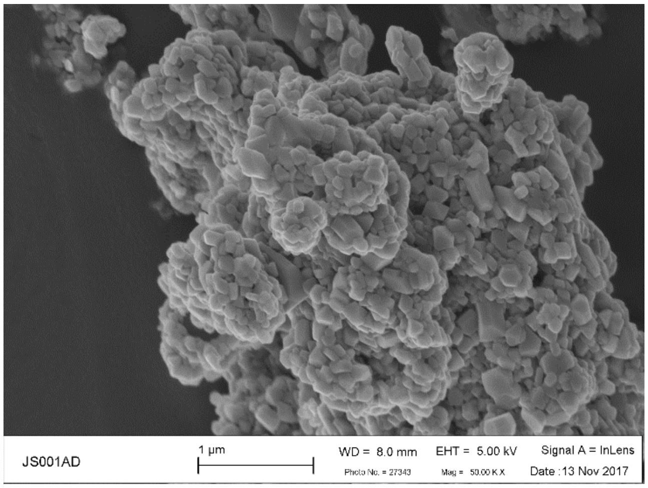
Contribution from the Lin group.

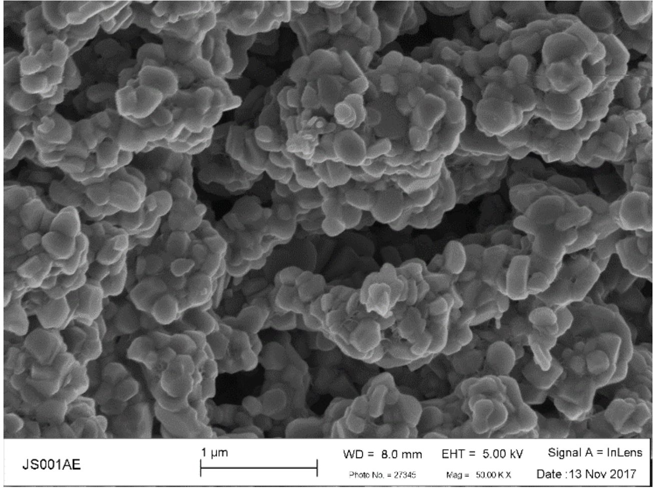
36. Controlling the Morphology of Layered Oxide Cathode Materials for Improved Lithium Ion Batteries

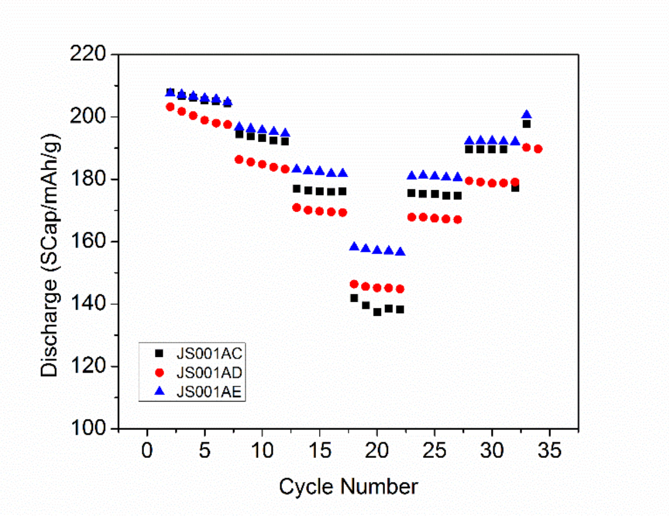
Julia K. Walsh*, Ben Zydlewski, James Steiner and Feng Lin
Virginia Tech Nanoscience

Nickel- rich layered cathode materials in lithium- ion batteries have been of high interest in electrochemical energy storage research. Herein, we have investigated the optimum conditions for synthesizing spherical Nickel Manganese Cobalt Oxide micron- sized particles by varying the ammonium hydroxide concentration in a co-precipitation synthesis method. Different ratios of NaOH/NH3 alter the morphology and the electrochemical performance of NMC cathode materials. Spherical morphology holds many advantages such as increasing the packing density and energy density, along with increasing the contact area of the powder with the electrolyte. We began by synthesizing our 811 NMC cathode precursors at different ratios of NaOH/NH3. After drying the powders, we calcined with lithium hydroxide and prepared the samples for Scanning Electron Microscopy (SEM). SEM showed spherical morphology for the ratios of 2, 1.4, and 1, therefore we focused on these samples. Electrochemical performance testing of rate change capacity and at 50 cycles showed that at a 1:1 ratio of NaOH//NH3 held the most capacity retention and high rate performance with a discharge capacity of 192.1 mAh g^{-1}.









Contribution from the Matson group

37. Synthesis of Amphiphilic Tapered Bottlebrush Block Copolymers

Jordan Watts*, Mohammed Alaboalirat, and John Matson

Traditional bottlebrush block copolymers are macromolecules composed of a linear polymer backbone with two different types of polymeric side chains that each have the same molecular weight. Tapered bottlebrush block copolymers are composed of two different types of polymeric side chains with increasing molecular weights. Bottlebrush block copolymers have been shown to exhibit self-assembly behavior and therefore a bottlebrush block copolymer with amphiphilic properties could have the potential to be used in applications in a way that current surfactants are used.[1] This poster will discuss the synthesis of amphiphilic bottlebrush block copolymers using the grafting-through method with a poly(norbornene) backbone and side chain blocks of hydrophobic polystyrene and hydrophilic poly(4-acryloylmorpholine). Polystyrene is synthesized by atom-transfer radical polymerization (ATRP) using an initiator that contains a norbornene group. Similarly, poly(4-acryloylmorpholine) is synthesized by photoiniferter polymerization using a chain transfer agent that contains a norbornene group. Next, the block copolymers can be added to the backbone by sequential ring-opening metathesis polymerization (ROMP).

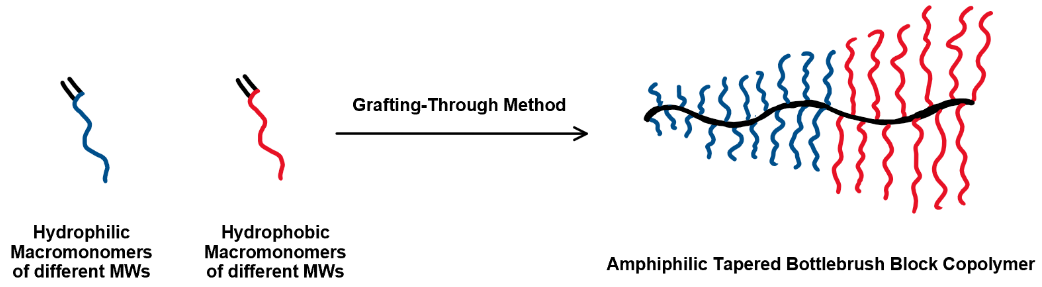


Illustration of an Amphiphilic Tapered Bottlebrush Block Copolymer put together by the grafting-through method

1. Sveinbjörnsson, Benjamin R., Raymond A. Weitekamp, Garret M. Miyake, Yan Xia, Harry A. Atwater, and Robert H. Grubbs. *Proceedings of the National Academy of Sciences of the United States of America* **2012**, 36, 14332-4336.

Contribution from the Schulz group.

38. Elucidating Polymer Structure and its Impact on Antiviral Properties

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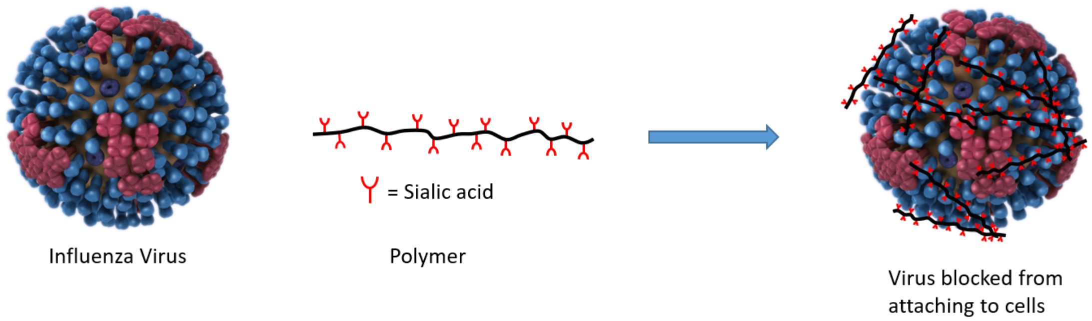
Viruses can infect a cell by attaching to the receptors on the membrane of the cell and inserting its DNA or RNA. Polymers with sialic acid attached can be used to inhibit the binding of a virus, specifically influenza, to the cell and prevent this transfer.



In this research, RAFT polymerization of pentafluorophenyl acrylate (PFPA) using 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) as the chain transfer agent was used to synthesize a series of polymers with controlled polymer chain lengths. A sialic acid derivative is being synthesized with an amine group, which will then be added to these PFPA polymers via post-polymerization functionalization. These materials will be used to elucidate the impact of polymer molecular weight on the ability of a polymer to inhibit virus attachment to the cell. Different amounts of DDMAT and the PFPA monomer were polymerized under UV light for 24 hours to create chain polymers of various lengths. In the first two polymerizations, we have targeted molecular weights of 45000 g/mol and 96000 g/mol.

Contribution from the Santos group.

39. Synthesis and Reactivity Studies of Novel Difluoroboron Compounds

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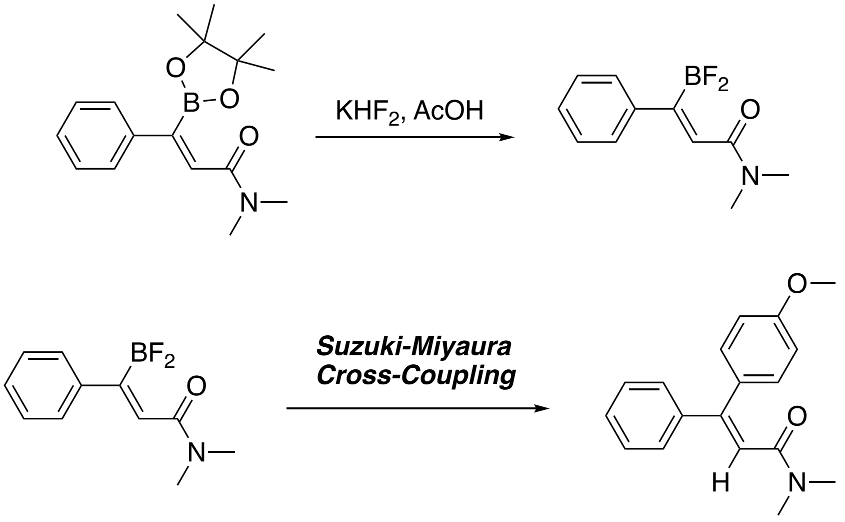
The versatile reactivity of organoboron compounds highlights their importance in organic synthesis. Notably, the Suzuki-Miyaura cross-coupling reaction allows for the efficient formation of carbon-carbon bonds.[1] Recently, we have developed the facile synthesis of novel difluoroboryl compounds displaying unique stability and reactivity.[2] We aim to demonstrate the applicability of our difluoroborates as intermediates in organic synthesis. Through optimization of reaction conditions, we will demonstrate the versatility of difluoroborates as substrates for Suzuki-Miyaura cross-coupling.



References:

1. Miyaura, N., Suzuki, A., Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chemical Reviews* **1995,** *95* (7), 2457-2483.

2. Unpublished work.

Contribution from the Lin group.

40. Synthesis and Characterization of Nickel Manganese Cobalt Oxide Cathode Materials for Use in High Energy Lithium Ion Batteries

Benjamin Z. Zydlewski*, Julia Walsh, James Steiner, and Feng Lin
The Lin Research Group at Virginia Tech

Our research focuses on synthesizing and testing various $Li(Ni_xMn_yCo_z)O_2$ (NMC) materials where $x + y + z = 1$. The goal is to effectively control the electronic configurations of transition metal 3d orbitals and oxygen 2p orbitals to enable safer and higher energy density lithium ion batteries. Current research focuses on NMC synthesized with 80% nickel, 10% manganese, and 10% cobalt. This material showed the best performance, so research moved to improving its capacity retention through doping with other metals such as titanium. These materials were synthesized using a co-precipitation technique to form NMC hydroxide precursors from sulfate salts. This material was then calcined after being mixed with nanosized lithium hydroxide. The calcined materials were then fabricated into electrodes and assembled into coin cell batteries against a lithium anode. Coin cells are tested through charge-discharge cycles to determine the specific capacity of the material as well as the capacity retention over a long period of cycling. Figure 1 shows the discharge capacity of 811 NMC and titanium-doped 811 NMC over a period of 1000 cycles. The second graph is the X-ray absorption near edge structure (XANES) of nickel in titanium-doped 811 NMC. X-ray absorption spectroscopy (XAS) is a technique that utilizes high energy synchrotron X-rays to promote low energy s and p electrons up to d orbitals. The technique offers insight into the oxidation states and local coordination of atoms based on the absorption spectra. Each element absorbs at different energies, allowing specific elements to be analyzed. This technique was used to understand how the oxidation states of the metals in NMC materials change during cycling.

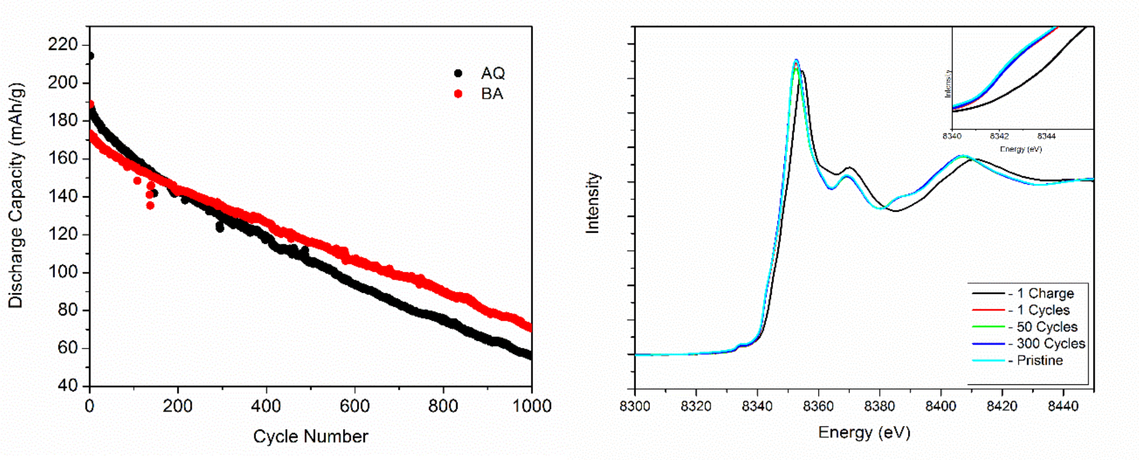


Figure 9. a) Discharge capacity vs cycling number. AQ represents pure 811 NMC and BA represents titanium-doped 811 NMC. b) XANES spectra of samples of titanium- doped 811 NMC with varying amounts of charge or cycling.

Contribution from the Merola group.

41. Synthesis of Iridium Indenyl Phosphines with Catalytic Potential

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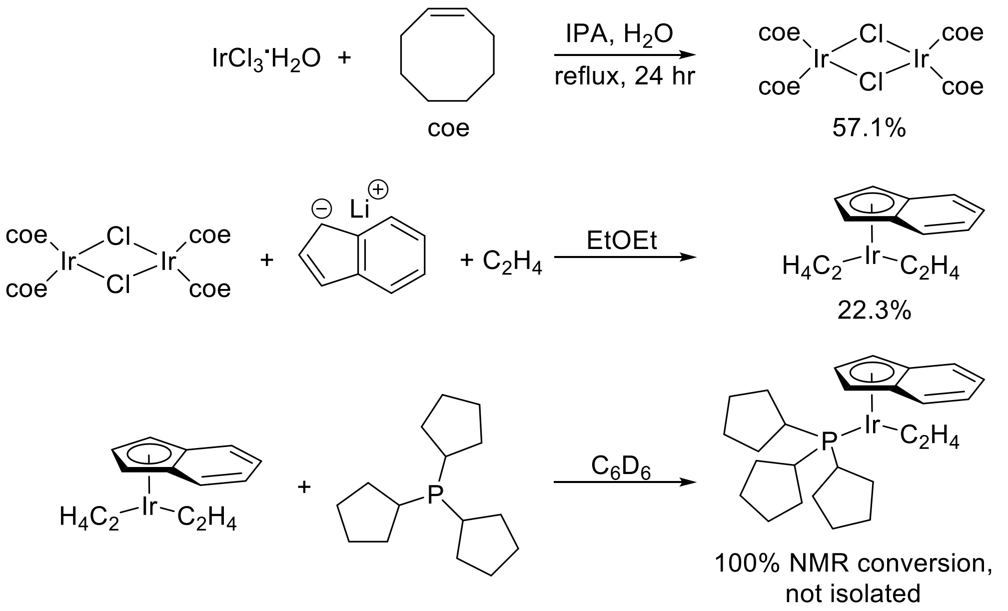
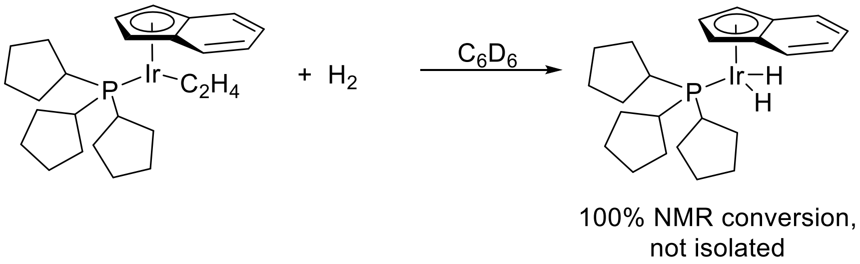
Iridium indenyl phosphine complexes of the form (η^5-indenyl)Ir(C_2H_4)(PR_3) were synthesized to study their reactivity as a testament to the indenyl effect. All complexes began with the precursor iridium indene bisethylene (η^5-indene)Ir(C_2H_4)$_2$, generated from iridium trichloride, before reaction with one equivalent of the phosphine of interest. Reaction completion was seen only when PR_3 was tricyclopentylphosphine and was confirmed by NMR spectroscopy (Scheme 1).

Scheme 3. Synthetic route to (indenyl)Ir(C2H4)PR3



Following the synthesis of (η^5-indenyl)Ir(C_2H_4)(PR_3), H_2 was oxidatively added to form the dihydride (η^5-indenyl)Ir(H_2)(PR_3) (Scheme 2).

Scheme 4. H_2 activation by (η^5-indenyl)Ir(C_2H_4)(PR_3)



Subsequent reaction with phenylacetylene led to the hydrogenation product styrene, indicating that (η^5-indenyl)Ir(H_2)(PR_3) is a fairly reactive species. Additional studies to test the catalytic potential of (η^5-indenyl)Ir(C_2H_4)(PR_3) for vinyl ester formation are underway.

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A special thanks to Susan Saxe for her great job in printing the posters.

Dr. Maggie Bump and the members of the Chemistry Club are acknowledged for their efforts in setting up the atrium, the easels and the lunch for this event.

Thanks go to the faculty members who open their labs and give their time to mentor the undergraduate researchers. Other lab members, especially the graduate students who also help with the mentoring, are acknowledged as well.

And a HUGE acknowledgment goes out to our undergraduate researchers, both those presenting in this symposium, and those who could not. They play a large role in the research mission of the university and their contributions should not go overlooked.