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INDEX

This index has the posters listed by research group. The numbers correspond to the order in the abstract booklet and the number of the poster.

Contribution from the Deck Group

20. Synthetic Models of Polymer Functionalization Reactions

26. Aromatic Polymers with Pendant Ionic Functionality

Contribution from the Dorn Group

6. Isolation of $M_2@C_{79}N$ and $M_3N@C_{80}$ with Toluene through PBB column

12. Isolation of a Newly Discovered Metallofullerene —$Tb_2O@C_{74}$

Contribution from the Grove Group

30. Characterization of recombinant cellulose-binding protein

Contribution from the Kingston Group

14. Isolation and Structure Elucidation of Antiplasmodial Compounds from *Galtonia regalis*

Contributions from the Lin Group

15. Inhibition of Manganese Ion Dissolution During Charging/Discharging Process for $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ Cathode Material by Ionic Liquid Gel Polymer electrolytes

17. Electrochromic Tungsten Oxide Thin Films for Dynamic Glass Utilizing Intercalating Chemistry

Contribution from the Liu Group

22. An Evaluation of Hydrolysed PLA-*b*-PEI-*b*-PLA Films for use as Stable Separators for Lithium Metal Batteries

Contributions from the Matson Group

9. Peptide Hydrogels for H_2S Release

27.An Esterase-Triggered Small Molecule and Polymeric Persulfide Prodrug

29. Bottlebrush Polymer Synthesis by Ring-Opening Metathesis Polymerization: Importance of Anchor Group Selection

Contribution from the Merola Group

10. Iridium N-Heterocyclic Carbene (NHC) Amino Acid Complexes as Catalysts for Asymmetric Transfer Hydrogenation

Contributions from the Amanda Morris Group

1. Synthesis and Analysis of Porphyrin Based Zr-Metal Organic Frameworks

4. Development of Novel Catalytically Active Metal Organic Frameworks for Water Splitting

8. Polymer-MOF Composites for Ultra-light Weight Coatings and Reverse Osmosis Membranes

11. Optimization of Charge Transfer Processes in Photovoltaics

16. Capturing Radioactive Cesium: Alkali Metal Binding to an Aluminum-Based Supramolecular Cage

18. Photocatalyzed Aerobic Oxidative Hydroxylation of an Aryl Boronic Acid Using a Ruthenium Based Metal Organic Framework

23. Synthesis of Charged Derivatives of $MnTp_2$ for use in Dye Sensitized Solar Cells.

24. Spin-Orbit Coupling Induced Energy Transfer in UiO-67 MOFs Doped with Photoactive Transition Metal Complexes

Contributions from the Schulz Group

2. Development of a Therapeutic Polymer for *Clostridioides difficile* Infections

5. Modification of cotton fabric surface for sequestration of doxorubicin

7. Isothermal Titration Calorimetry Studies of the Binding of Metal Ions to Poly(Ethyleneimine Methyl Phosphonate)

13. Synthesis of polymers with pendant DNA bases for doxorubicin sequestration during chemotherapy treatment

19. Synthesis and characterization of poly (arylene ether sulfones) (PAES) for metal chelation

Contribution from the Tanko Group

21. Mechanism of H-atom Abstraction from Carboxylic Acids

Contributions from the Yee Group

3. Computational Analysis of Various Methyl-substituted PTCE Molecule-Based Magnet Building Blocks

25. Synthesis of n-bromophenyltricyanotheylene: A Building Block for a Molecule-Based Magnet

Contribution from the Amanda Morris group.

1.Synthesis and Analysis of Porphyrin Based Zr-Metal Organic Frameworks

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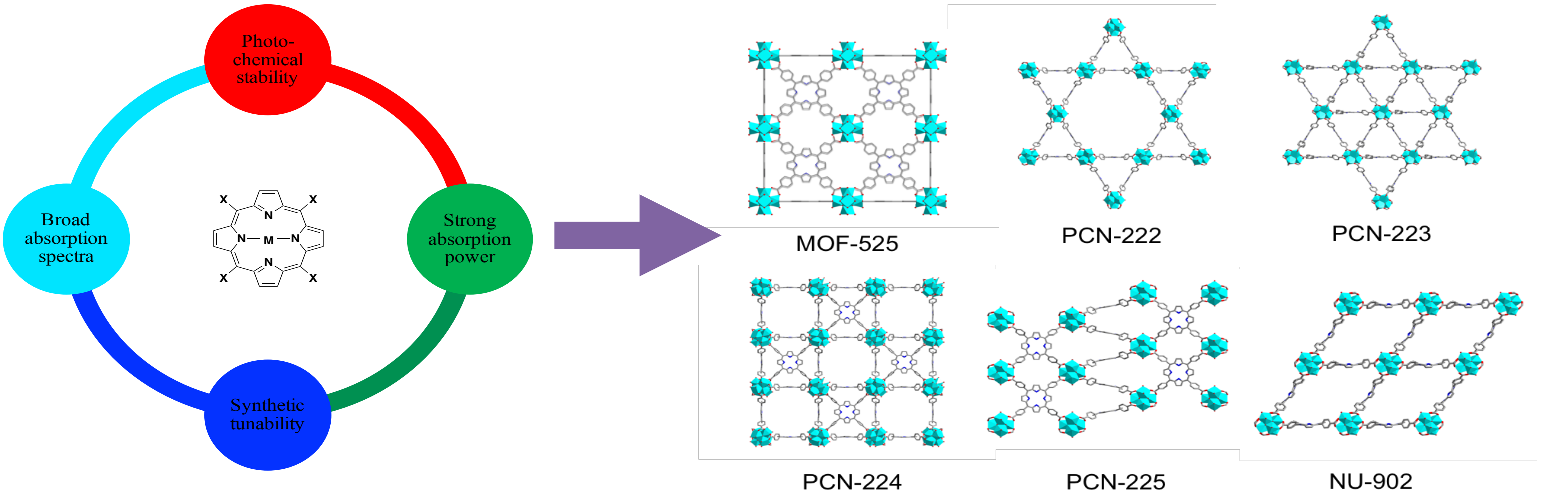

Metal-organic frameworks (MOFs) are multidimensional structures comprised of metal nodes connected by organic ligands forming highly ordered multidimensional arrays. These materials have been investigated for a wide variety of applications including electrocatalysis and light harvesting, among others. Tracarboxyphenylporphyrin (TCPP) is a nitrogen based macrocycle that is known to form complexes with a variety of metals, and in its free base and zinc metallated forms it has been studied as a substitute for chlorophyll as a light harvesting agent in artificial photosynthesis.[1] The goal of this study is to synthesize and analyse Zr node MOFs using TCPP as a linker, and analyze the effects of synthesis conditions, most notably modulator, on the phase of MOF that is formed. The self-quenching properties of PCN-223 is of particular interest. TCPP MOFs were synthesized using a one pot solvothermal reaction method. First, TCPP, $ZrCl_4$ and DMF were mixed in a 10-dram vial. Then modulator was added to the vial and it was sonicated for 15 minutes. The vials were heated at 120^0C for 16 hours, and then washed with DMF and then ethanol. Powder X-ray diffraction (PXRD) was used to determine the phase of MOF that was formed based on the type and concentration of modulator used in the synthesis. It was found that increasing the pK_a and concentration of modulator generally led to different phases of MOFs forming. This method resulted in the synthesis of PCN-222, PCN-223, and MOF-525, often a mixed phase of two of these. With pure MOFs in hand, efforts shifted to explore the ability to harness and transfer solar energy through PCN0223. PCN-223 to transfer solar energy was tested by measuring the steady-state fluorescence of the MOF under different temperatures and at different pH's. The results of this study displayed that the rate of quenching of PCN-223 is significantly higher than that of the TCPP ligand

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Contribution from the Schulz group.

2.Development of a Therapeutic Polymer for *Clostridioides difficile* Infections

Andy Brenner+ †, Brady Hall‡, Michael Schulz†
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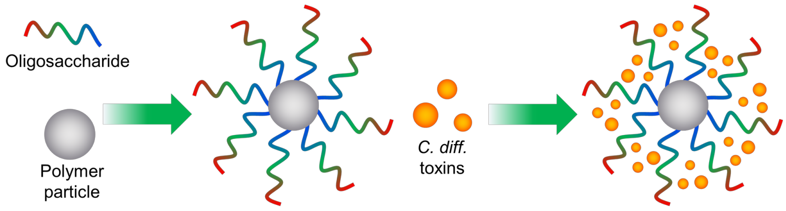
Clostridioides difficile (*C. diff.;* formerly known as *Clostridium difficile*) is a species of gram-negative bacteria that can populate the gastrointestinal (GI) tract of most mammals. Antibiotic usage in combination with other factors leads to *C. diff.* infections (CDIs), the number-one cause of healthcare-associated diarrhea. In the United States approximately 500,000 cases of CDIs were reported in 2015. Of those, approximately 20% were recurrent cases and 6% of those infected perished within 30 days.[1]

C. diff. bacteria produce an enterotoxin (toxin A) and a cytotoxin (toxin B) that adversely interact with the cells in the GI tract.[2] The current methods of treatment (*e.g.* antibiotics and probiotics) are often ineffective against antibiotic resistant strains. Herein, we outline the synthesis of a naturally-inspired polymer-based therapy for sequestering *C. diff.* toxins. By appending azide terminal oligosaccharides to an alkyne functional polymer resin, we aim to make a material capable of sequestering *C. diff.* toxins from the GI tract and thereby reduce the effect of CDIs.



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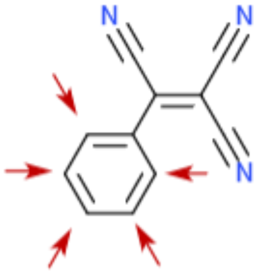
Contribution from the Yee group.

3. Computational Analysis of Various Methyl-substituted PTCE Molecule-Based Magnet Building Blocks

Ryan E. Corkill*, Diego Troya, and Gordon T. Yee

This investigation uses density functional theory to computationally analyse various methyl-substituted phenyl tricyanoethylene (PTCE) molecules, shown below, which have been used to synthesize molecule-based magnets when reduced and reacted with hexacarbonylvanadium(0). Methyl groups are weakly electron donating, making the derivatives more difficult to reduce. Unexpectedly, the magnetic ordering temperature of these materials did not correlate simply with the ease of reduction of the acceptor. Our hypothesis is that steric effects can produce a significant dihedral angle between the phenyl ring and olefin that increases the spin density on the nitrogen atoms. The molecules were optimized in their radical anionic states and spin densities determined. In addition to this, a coordinate scan of these molecules was performed in order to obtain data on their rotational barriers, which reflect the importance of non-planar geometries. The tests showed that the molecules with methyl groups substituted at the 2 and 6 locations on the phenyl ring (2,6-dimethyl PTCE, 2,4,6-trimethyl PTCE, and pentamethyl PTCE) experienced the greatest twisting about the dihedral angle. These same three molecules were also found to have the greatest Mulliken spin densities on their nitrogen atoms compared to the other molecules tested.



PTCE with arrows denoting possible methyl group locations

Contribution from the Amanda Morris group.

4.Development of Novel Catalytically Active Metal Organic Frameworks for Water Splitting

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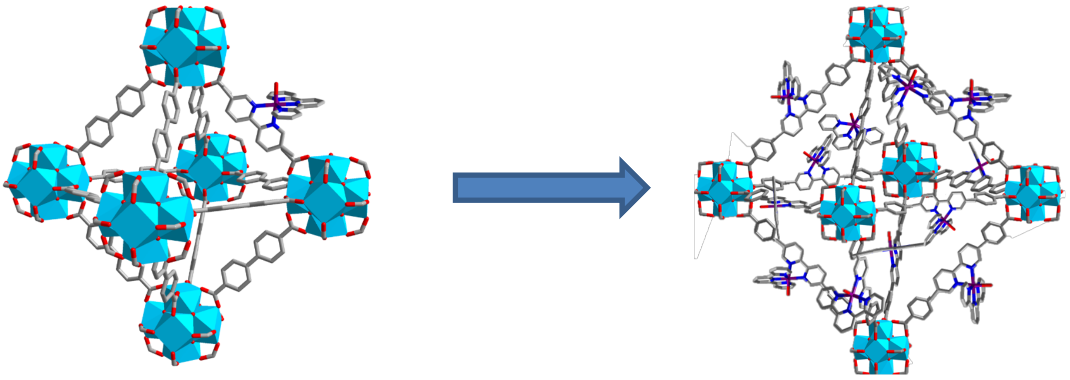
Due to the rise of global warming, energy sources that result in environmental disruption has become less popular recently. Finding a reusable source of energy that is simultaneously cost effect has become the forefront of many research communities. The Morris lab has investigated metal organic frameworks (MOFs) as a mode of transferring light energy into usable electrical energy. Specifically, previous work revealed that incorporation of a known ruthenium terpyridine catalyst into a UiO-67 backbone resulted in water oxidation chemistry with geometric rate enhancements of near a factor of 100.We hypothesize that the observed reactivity enhancement was limited by the amount of Ru catalyst that could be incorporated into the framework. As a result, we are investigating a new MOF with a large linker to allow for more catalyst to be incorporated into the MOF.



To make this MOF a Suzuki coupling is used to create our long organic backbone. The backbone is then modified to incorporate the catalytic functionality, and finally, the long backbone is coordinated to zirconium nodes creating the MOF. After MOF synthesis, ICP analysis showed the Zr:Ru ratio to be 7:1, as opposed to the expected 1:1. The difference was attributed to a highly defective MOF structure. Focus is now directed towards optimization of the ligand synthesis to allow for ideal MOF synthesis. This includes both the synthesis of the initial target MOF and a slight modification through the use of a mixed backbone MOF. The mixed backbone MOF would incorporate less of the catalyst than the initial proposed structure, but may result in greater crystallinity, if catalyst-catalyst geometric interactions are limiting MOF formation. In this approach both the extended catalyst backbone and a native quarterphenyl backbone will be mixed in various ratios to determine maximum catalysts loading.

Contribution from the Michael Schulz group.

5. Modification of cotton fabric surface for sequestration of doxorubicin

Simran Kala*, Landon Dehart, Ophelia Wadsworth and Michael Schulz
Department of Chemistry, Virginia Tech, Blacksburg, VA 24061

Liver cancer is the third leading cause of cancer mortality in the United States. A common method of treatment is transarterial chemoembolization (TACE), a procedure that injects doxorubicin (DOX) chemotherapy agent directly into the tumors while obstructing their blood supply.[1-2] In every TACE procedure, part of the chemotherapy dose leaves the liver, enters systemic circulations, and causes off-target damage.[3] DOX intercalates between DNA base pairs to inhibit replication, resulting in apoptosis of cancerous cells in the liver and healthy cells upon leaving the liver. To sequester DOX in the liver and prevent toxicity to healthy cells, this research seeks to develop a chemotherapy drug filter device that can be deployed downstream from the liver to capture any DOX before it damages healthy cells. We have focused on modifying cotton surfaces with DNA, which has a high affinity for DOX, to produce DOX-binding materials. The DOX capture capability of unmodified cotton was first assessed and then compared to cotton modified with specific silane molecules selected to link DNA to the surface. The silane molecules were adsorbed to the cotton surface via chemical vapour deposition (CVD) and a solution reaction. Herring DNA was then reacted with the electrophilic moiety of each silane to complete surface modification. Fluorescence spectroscopy was used to determine the change in DOX concentration over time after the unmodified and modified cotton samples were immersed in a DOX solution. The samples modified with silane and DNA showed better DOX capture performance than the unmodified cotton samples. Between the two methods used to adsorb silane to the cotton surface, the CVD-coated samples with DNA captured more DOX than the solution-coated samples with DNA. Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) showed evidence of DNA on the solution-coated samples, however, no DNA was detected on the CVD-coated samples. X-ray photoelectron spectroscopy (XPS), which enables increased depth analysis, will replace EDS to determine the presence of DNA on the modified cotton surfaces. In the future, DOX capture will be assessed in serum and blood to determine the viability of modified cotton surfaces as an improved filter for DOX.

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Contribution from the Dorn group.

6.Isolation of M_2@$C_{79}N$ and M_3N@C_{80} with Toluene through PBB column

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

[a] *Virginia Tech Department of Chemistry*

Previous research found M_2 endohedral metallofullerenes (EMF), identified as impurities in commercially available samples using spectroscopic and chromatographic techniques previously documented.[1] 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.[2] The previously reported lanthanide endohedral metallofullerenes have consisted of isotropic, anisotropic prolate, and anisotropic oblate species. With the recent work published on the characterization of the Tb_2@$C_{79}N$ system by the Dorn group, this work focused on the separation and isolation of M_2@$C_{79}N$ and M_3N@C_{80}. For the PYE HPLC traces of the commercial samples; M_2@$C_{79}N$ was found in the peak between 38 to 41 minutes and was separated from the sample utilizing a previously described separation process, M_3N@C_{80} was found in the peaks between 44 and 48 minutes. Mass Spectrometry was used to verify the M_2@$C_{79}N$ system was in the collected sample.

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Contribution from the Schulz group.

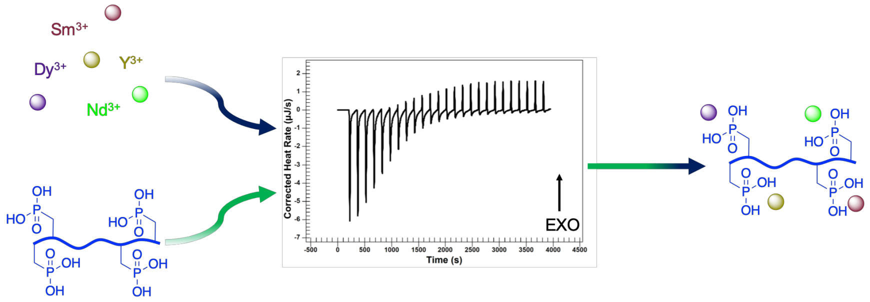
7. Isothermal Titration Calorimetry Studies of the Binding of Metal Ions to Poly(Ethyleneimine Methyl Phosphonate)

Agustin Fiorito[1*], Marianne A. Sawyer[1*], Samantha A. Winn[1], William R. Archer[1], and Michael D. Schulz[1]

[1]Department of Chemistry, Virginia Tech, Blacksburg, VA, USA 24061

In 2011, the global production of rare earth elements (REEs) was 132,000 metric tons.[1] REEs are critical components in many technologies such as magnets, hard drives, LEDs, catalytic converters, and various green technologies (e.g., wind turbines, batteries, etc.). With advances in the electronics and clean energy industries, modern society relies heavily on REEs. Extracting REEs from non-traditional sources, such as coal ash, can dramatically increase the production of REEs and satisfy this ever-increasing demand. Polymers have several advantages as sequestration materials, including relatively low cost and high affinity for target compounds. As a result, we are investigating a number of polymer-based metal-chelation materials. Specifically, we installed α-amino phosphonate chelating groups onto commercially available linear and branched polyethyleneimine (PEI).

In addition to synthesizing these new materials, we investigated the application of polymers for the selective chelation of various heavy metal ions. The effect of polymer architecture on metal chelation was examined using isothermal titration calorimetry (ITC) in order to gain insight into the thermodynamics of binding and the specific structure-metal binding relationships of these materials. ITC enables the direct measurement of the binding affinity (K_a), enthalpy changes (ΔH), and stoichiometry of the interactions between macromolecules and metal ions in solution.[2] By elucidating the thermodynamic profile of each chelating material, we have gained insight into each polymer's properties as a metal chelator.



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Contribution from the Amanda Morris group.

8. Polymer-MOF Composites for Ultra-light Weight Coatings and Reverse Osmosis Membranes

Katie M. Flint*, Brittany Bonnett and Amanda J. Morris
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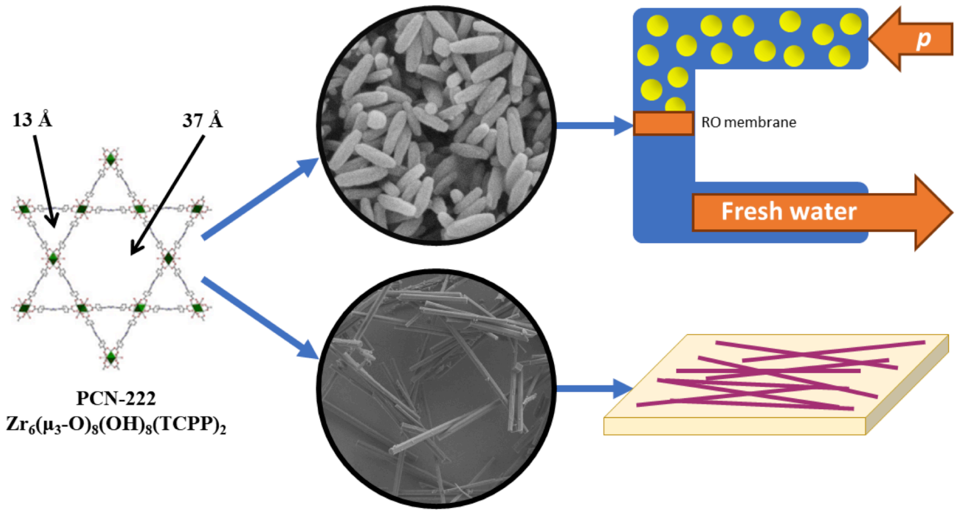
Blacksburg, Virginia, 24061, United States

Polymer nanocomposites are materials composed of nanoparticles dispersed throughout a polymer. The nanoparticles have been found to improve the electrical, thermal, and mechanical performance of the polymer. This project focuses on two polymer nanocomposites, which are lightweight coatings for vehicles and reverse osmosis membranes. The nanoparticles that we are adding to the polymers in this research are metal-organic frameworks (MOFs). MOFs are crystalline, permanently porous nanomaterials comprised of metal nodes and organic ligands. By adding MOFs to polymers to form lightweight coatings, we can decrease the energy cost of vehicles by decreasing the weight of the paint or other coatings. When added to reverse osmosis membranes, the MOFs are able to better control the size of particles allowed through the membrane. This research is focusing on two specific MOFs to solve these problems. PCN-222 is a zirconium-based porphyrinic MOF that is applied to reverse osmosis membranes, as well as to lightweight coatings. The second MOF is NH_2-MIL-53(Al), which is an Al-node MOF. This MOF is also applied to polymer nanocomposite lightweight coatings. The use and applications of the MOFs depend on their aspect ratio. We are able to control the aspect ratio by supersaturating the organic ligand in the MOF.



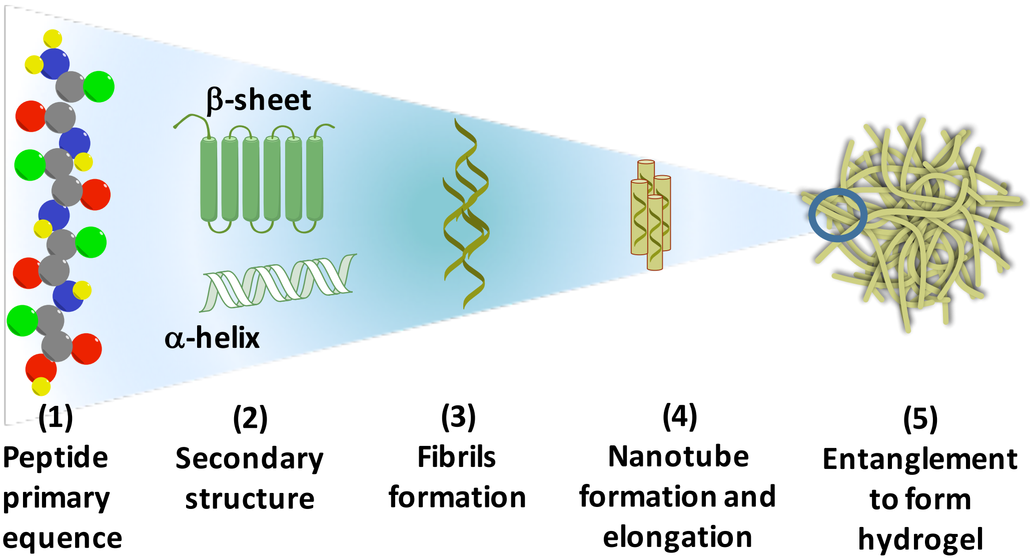
The low-aspect-ratio MOFs are used primarily for the reverse osmosis membranes and the high-aspect-ratio MOFs are used in low-density, high-strength polymer nanocomposite coatings. As an outcome of modifying and controlling the aspect ratio, our MOFs have shown promising results. Polymer nanocomposites reinforced with high-aspect ratio PCN-222 fillers have shown superior storage modulus compared to neat polymer. In addition, low-aspect ratio PCN-222 post-synthetically modified with myristic acid incorporated into a reverse osmosis membrane exhibits superior flux over control membranes.

Contribution from the Matson group.

9.Peptide Hydrogels for H_2S Release

Jared Grimm*, Kuljeet Kaur
Virginia Tech, Department of Chemistry

H_2S is a known gasotransmitter, and the localized H_2S delivery is required to maintain high local H_2S concentrations for better understanding of the therapeutic models. Throughout this semester, we focused on developing and synthesizing peptide hydrogels that can be used to release hydrogen sulfide locally. H_2S releasing small molecules, also known as H_2S-donors, were coupled onto several self-assembling aromatic peptides amphiphiles that were fabricated separately via solid phase peptide synthesis technique. The peptides were purified by high performance liquid chromatography (HPLC) and analyzed by mass spectrometry. Peptide hydrogels were formed using physical crosslinking with calcium. The H_2S-release trends from the various hydrogels were evaluated and correlated to the hydrogel's stiffness. Finally, H2S-release trends using glutathione to evaluate the kinetic mechanism of gel stiffness were observed.



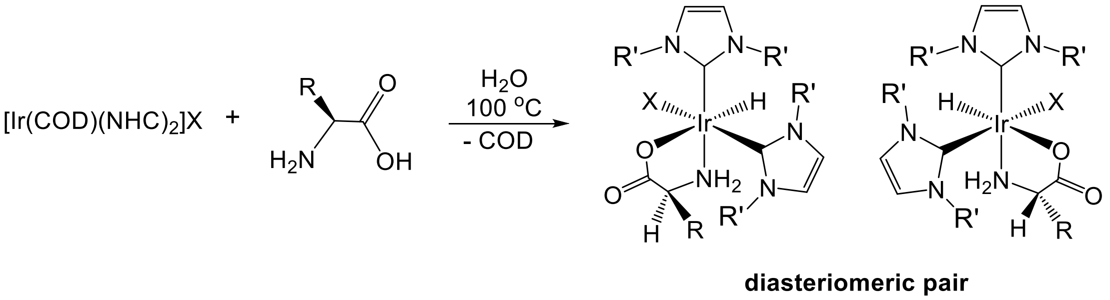
Contribution from the Merola group.

10. Iridium N-Heterocyclic Carbene (NHC) Amino Acid Complexes as Catalysts for Asymmetric Transfer Hydrogenation

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

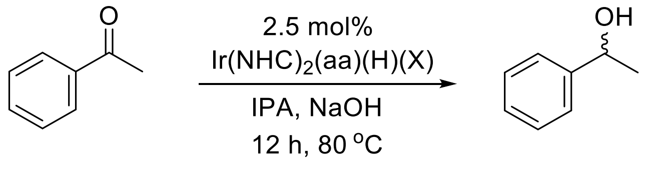
The Merola group has taken a recent interest in the chemistry of electron-rich noble metal complexes incorporating strongly σ-donating N-heterocyclic carbene (NHC) ligands. We have found that iridium(I) bis-NHC complexes undergo oxidative addition with a variety of amino acids, yielding a series of novel octahedral iridium(III) hydride complexes. Oxidative addition using a chiral amino acid results in a stereogenic metal center, leading to the formation of two diastereomers (Scheme 1). All of these complexes were characterized by NMR spectroscopy, mass spectrometry, and X-ray crystallography when possible.

Scheme 1. Synthesis of iridium(III) NHC amino acid complexes



These complexes were tested for catalytic activity in the asymmetric transfer hydrogenation (ATH) of ketones (Scheme 2). Complexes incorporating cyclic amino acids provided the highest enantioselectivity of the alcohol product. Of all the amino acid ligands used, proline gave the most promising results, with an enantiomeric excess (ee) of over 50% as determined by chiral gas chromatography.

Scheme 2. Asymmetric transfer hydrogenation of acetophenone



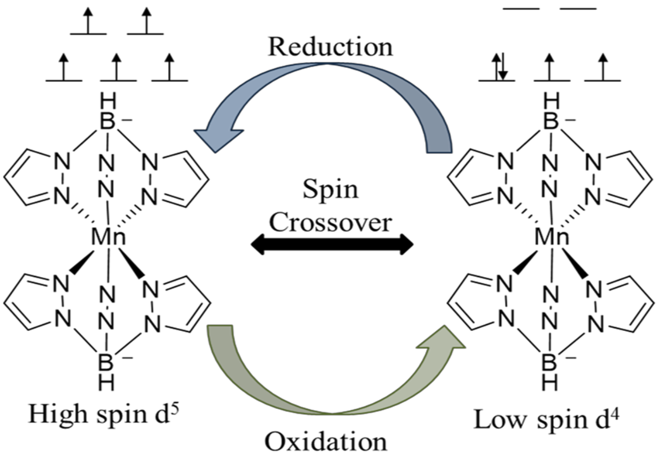
We have hypothesized that varying the NHC scaffold and R-groups may have an effect on substrate selectivity, and future studies will incorporate bulkier NHC substituents as well as chelating NHC ligands. The substrate scope will also be expanded to other aromatic and aliphatic ketones.

Contribution from the Amanda Morris group.

11.Optimization of Charge Transfer Processes in Photovoltaics

Rachael L. Langlois*, Matthew Kessinger and Amanda J. Morris
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. Increasing the efficiency of Photovoltaic devices (PVs) depends strongly on the optimization of charge transfer between the TiO_2/chromophore photoanode and a redox couple present in the electrolyte solution. In previous studies completed by this group we have proven manganese(II) (bis(hydrotrispyrazolyl)borate) [$MnTp_2$] to be an effective redox mediator in Quantum Dot Sensitized Solar Cells (QDSSCs) due to its unique donor-acceptor interactions.[1] The charge transfer kinetics of $MnTp_2$ can be directly correlated to the photovoltage and photocurrent produced by the cell. Kinetically, the redox mediator must possess a sufficient driving force for rapid reduction of the oxidized photosensitizer while also possessing slow reduction kinetics towards electronic recombination between the injected electrons in TiO_2 and the oxidized redox mediator in solution. The $MnTp_2$ complexes developed by this group are known to undergo charge transfer induced spin crossover (CTISC) which is believed to decrease the likelihood of recombination events in the cell, however the true rate constants of the donor-acceptor charge transfer event have only been estimated from electrochemical measurements thus far.



This project focuses on the use of Transient Absorption Spectroscopy (TAS) to accurately determine the kinetics of this charge transfer event. Using Ruthenium (II) tris(bipyridine) ($Ru(bpy)_3$) doped TiO_2 we are able to observe a reduction in lifetime of the ground state bleach of $Ru(bpy)_3$. This semester two ruthenium complexes were synthesized, $Ru(bpy)_2dcbpyCl_2$ and $Ru(bpy)_2dcbpy(PF_6)_2$. Preliminary TAS measurements were conducted on both Ru Complex solutions, Ru complex doped TiO_2, and Ru complex doped ZrO_2. TAS mapping was conducted on Ru complex doped TiO_2 in the presence and absence of $MnTp_2$.

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Contribution from the Dorn group.

12.Isolation of a Newly Discovered Metallofullerene —$Tb_2O@C_{74}$

Chengen Li*, James Duchamp, Rong Huang, Xiaoyang Liu and Harry C. Dorn

The idea of encapsulating metallic species in carbon cages has been one of most interesting topics in the field of metallofullerene chemistry. The metallic endohedral fullerenes exhibit various attractive material properties, for example, single molecule magnets (SMM). However, the terbium rare-earth-element-containing endohedral metallofullerenes have not been fully discovered and characterized. Recently, the Dorn group discovered a metallofullerene that encapsulates a di-terbium oxide cluster (Tb-O-TB) in a cage of C_{74} carbons, which is identified as $Tb_2O@C_{74}$.[1] A HPLC technique has been used to isolate this molecule and UV-vis spectroscopy, mass spectrometry, and X-ray diffraction techniques have been applied to reveal the detailed structure of this molecule.[1] Terbium-containing molecules are known to have a long magnetization time, making this molecule an excellent candidate for a single molecule magnet.[2]

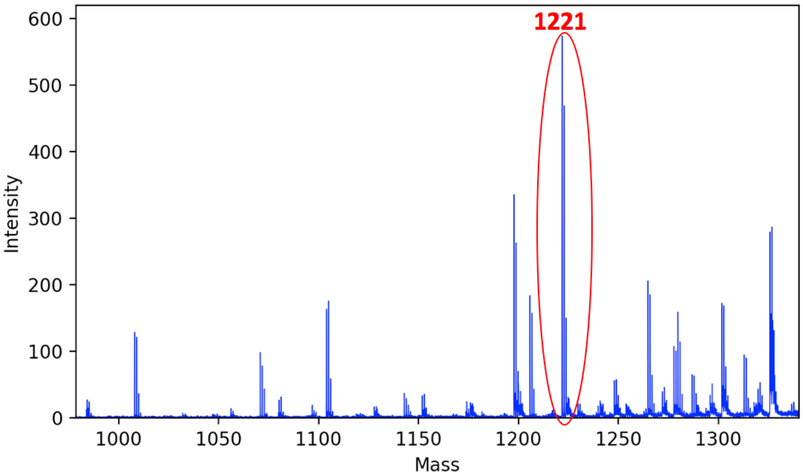

Figure 1. Mass spectrum of a mixture of metallofullerens. The peak of $Tb_2O@C_{74}$ (mass detected: 1221 m/z) is circled in red.

In the present study, I will isolate more $Tb_2O@C_{74}$ for further magnetic studies. By utilizing mass spectrometry, I have found the existence of $Tb_2O@C_{74}$ (M/z=1221) in a mixture of metallofullerenes (Figure 1). In the future study, HPLC will be further used to isolate this molecule from the mixture of metallofullerenes.

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Contribution from the Michael Schulz group.

13. Synthesis of polymers with pendant DNA bases for doxorubicin sequestration during chemotherapy treatment

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Liver cancer is the third leading cause of cancer mortality in the United States.[1] A common method of treatment is transarterial chemoembolization (TACE), a procedure that injects doxorubicin (DOX), a common chemotherapy agent, directly into a tumor.[2] DOX intercalates between DNA base pairs to inhibit replication, resulting in apoptosis. However, DOX doesn't discriminate between healthy cells and cancerous cells, causing off target toxicity, i.e., the death of healthy cells. This toxicity leads to side effects including nausea, hair loss, and organ death preventing high doses of DOX for clinical use.[3] In a typical TACE procedure about half the DOX dose passes through the liver, enters systemic circulation and causes side effects. To confine the DOX exclusively to liver and prevent toxicity to healthy cells, this research seeks to develop a chemotherapy filter device that can be deployed downstream from the liver to capture any DOX before it damages healthy tissue. We hypothesize that the interaction between DOX and nucleobases can be utilized to sequester DOX. Polymers with pendant nucleobases would be able to interact with the DOX and sequester it in the liver, thereby preventing toxicity in healthy cells. By attaching nucleobase-containing polymers to a surface, a device could be made to act as a filter for DOX leaving the liver. To this end, we have begun synthesizing polymers with pendant adenine and thymine, two nucleobases, and testing their ability to capture DOX in solution. Adenine was reacted via Michael addition to 1,4-butanediol diacrylate to produce adenine 1,4-butanediol acrylate. Fourier-Transform infrared spectroscopy (FT-IR) of the crude product confirmed the C=N, C=O, N-H and NH_2 moieties with the stretches at 1600, 1725, 3300 and 3350 cm^{-1},respectively. Proton NMR confirmed the free acrylate by the presence of three doublet of doublets peaks at 5.90, 6.12 and 6.28 ppm, respectively. Additionally, the C-N bond between both monomers was confirmed by the presence of a triplet at 4.1 ppm which represented the adjacent methylene protons to adenine. Thymine 1,4-butanediol acrylate was similarly synthesized and characterized. Both monomers will be polymerized and the resulting materials will be evaluated for DOX capture using fluorescence measurements.

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Contribution from the Kingston group.

14.Isolation and Structure Elucidation of Antiplasmodial Compounds from *Galtonia regalis*

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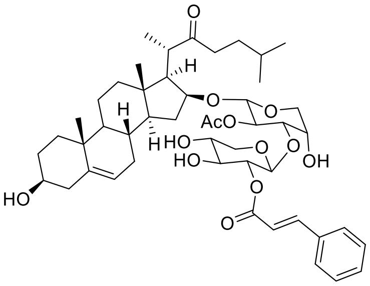
Natural products have proven to be an excellent source when considering new compounds to include in the drugs used to treat malaria.[1] This study looked to investigate the activity of *Galtonia regalis* because it appeared to have good antiplasmodial activity upon initial testing, with an IC_{50} value of << 1.25 μg/mL. Because of this good activity, three new (**1**-**3**) and two known (**4**-**5**) cholestane saponins were isolated from the dichloromethane extract of *Galtonia regalis* for further testing. Purification and isolation were conducted using Sephadex LH-20, C18 SPE and C18 reversed-phase HPLC. The structures of the isolated compounds were determined by analysis of MS, 1D, and 2D NMR data, then comparison with literature data. The known compound OSW-3 (**4**) was found to have the best antiplasmodial activity, with an IC_{50} value of about 0.95 μM.



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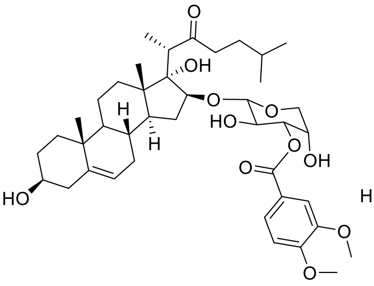

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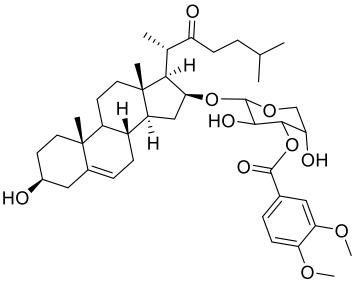

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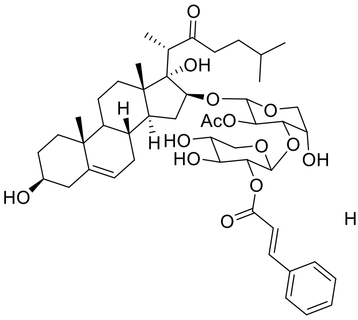

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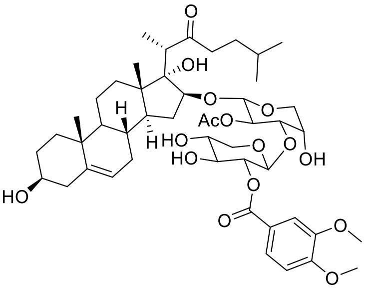

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Contribution from the Lin group.

15.Inhibition of Manganese Ion Dissolution During Charging/Discharging Process for $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ Cathode Material by Ionic Liquid Gel Polymer electrolytes

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Virginia Tech, Department of Chemistry, College of Science - Nanoscience

Research continues to improve upon the safer and potentially viable alternatives to the lithium ion battery, the commercially chosen battery that exhibits many issues, stemming from its unsafe, unstable, and expensive material. In this regard, we explore the possibility of another use of the ionic liquid gel polymer electrolyte (ILGPEs) as an inhibitor of manganese ion dissolution found in $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) cathode materials. Our efforts to characterize the effects of the ILGPEs are displayed. The ILGPEs consist of a room-temperature ionic liquid (N-methyl-N-propyl piperidinium bis(trifluoromethanesulfonyl)imide), poly(vinylidene fluoride-hexafluoropropylene) polymer, and lithium bis(trifluoromethanesulfonyl)imide salt. The cathode consists of NMC811 material, carbon black, and PVdF polymer with a mass ratio of 8/1/1. The hypothesis is that the ILGPEs can inhibit the manganese ion dissolution during the charge/discharge process while still serving as a good hybrid separator material. We also fabricated the ILGPEs-coated-NMC811 cathode to decrease the interfacial resistance of the electrolytes and electrodes, because the high interfacial resistance will cause the capacity fading and short the batteries cycle life.

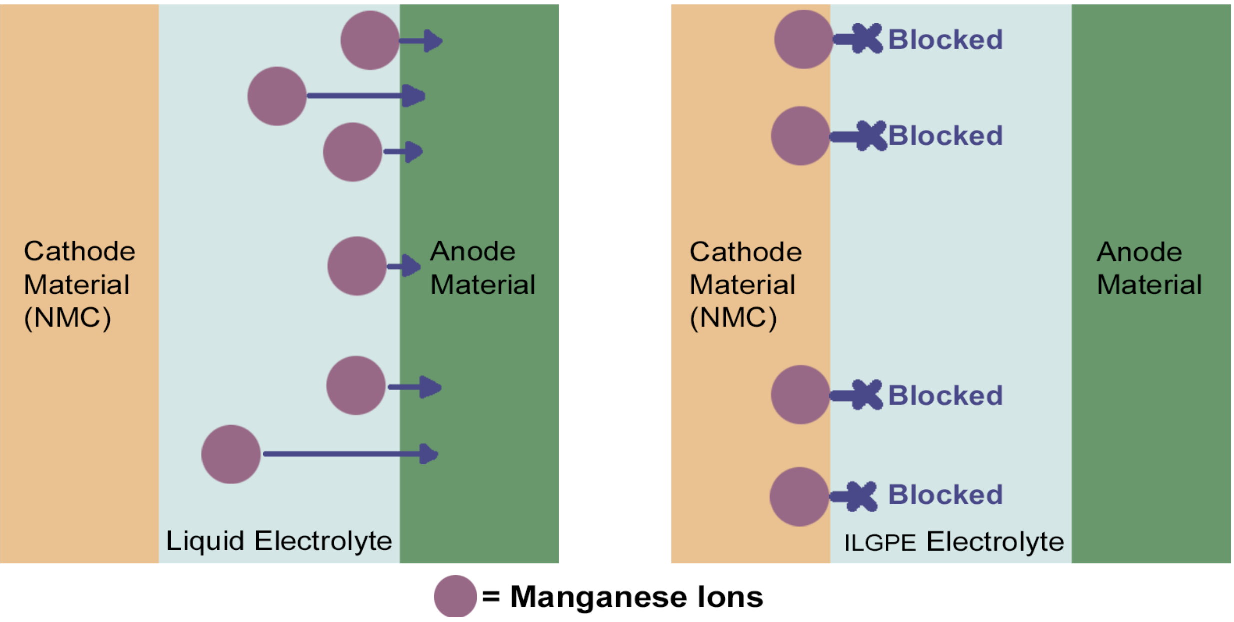

Figure 1. Comparison between NMC batteries with common Liquid Electrolyte (Left), which exhibits a migration of Manganese (Mn) Ions from the cathode to the anode, and the ionic liquid gel polymer electrolyte (Right), which could block this migration.

Contribution from the Amanda Morris group.

16. Capturing Radioactive Cesium: Alkali Metal Binding to an Aluminum-Based Supramolecular Cage

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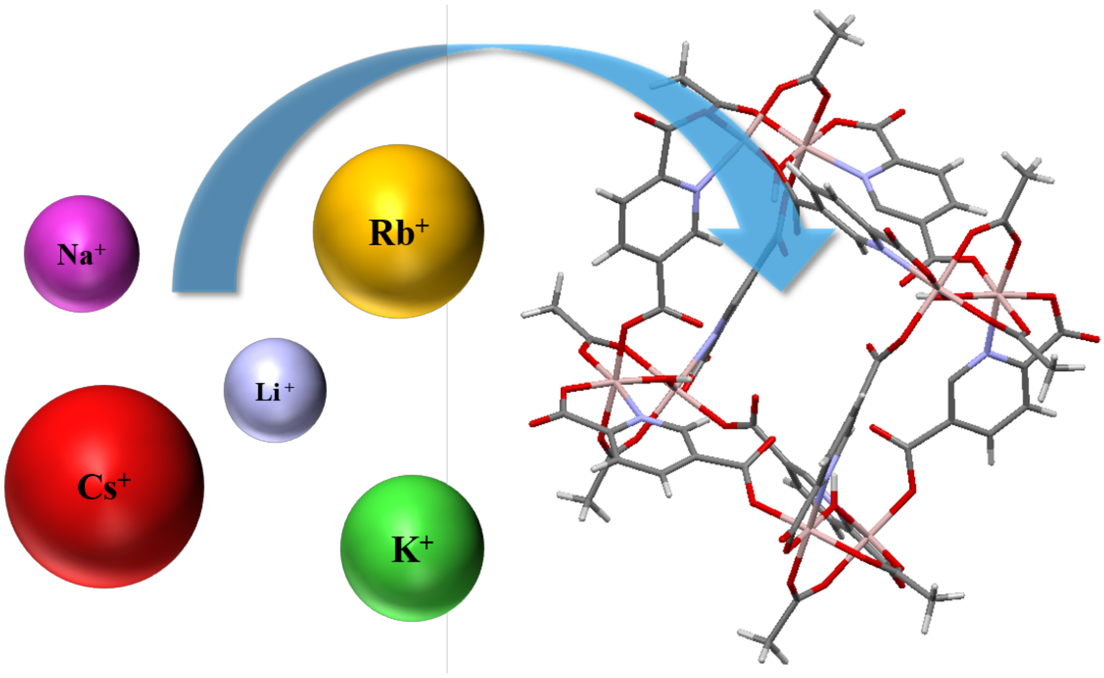
Blacksburg, VA 24061

With the decreasing supply of fossil fuels worldwide, nuclear power has gained attraction on a global scale as an alternative energy source. However, nuclear power plants come with several complications, such as radioactive waste production and adverse environmental impacts. A major radioactive by-product, ^{137}Cs, is toxic to humans, animals, and plants, especially in marine environments.[1] Binding and extracting cesium ions from high-level radioactive waste would streamline ion exchange disposal efforts and eliminate health and environmental risks.

In this study, the binding of alkali metal ions (Li^+, Na^+, K^+, Rb^+ and Cs^+), to the recently synthesized molecular cage Al-pdc-AA ($[(Al_2(OH))_4(pdc)_8(AA)_8]$, pdc = pyridine-2,5-dicarboxyllic acid, AA = acetate), was investigated. Al-pdc-AA consists of four μ_2-OH bridged Al dimers connected by pdc linkers and capped by acetate anions, forming a square. The compound was characterized using ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, single crystal X-ray diffraction (SCXRD), and thermogravimetric analysis (TGA). Titration studies with various alkali metals were performed using ^{1}H NMR spectroscopy to investigate their binding to the cage. Larger cations, such as Rb^+ and Cs^+, bind most strongly, as shown by the chemical shifts in ^{1}H NMR spectra. Similarly, isothermal titration calorimetry (ITC) was used to obtain the thermodynamics of binding associated with Rb^+ and Cs^+. Future work will include the modelling of NMR spectroscopic data to obtain binding constants, competitive binding studies, and the synthesis of analogous pyrazine-based Al cage structures.



Contribution from the Feng Lin group.

17.Electrochromic Tungsten Oxide Thin Films for Dynamic Glass Utilizing Intercalating Chemistry

Scott T. McGuigan*, Anyang Hu and Feng Lin
Chemistry Department: Virginia Tech

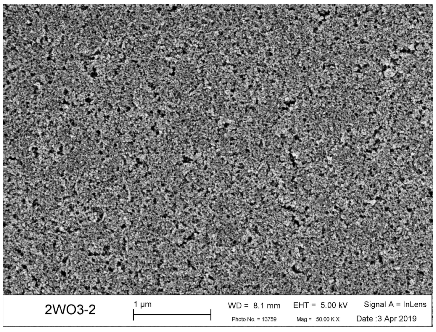


Figure 1: SEM Image of WO3 Structure

This research involves developing a thin electrochromic tungsten oxide (WO_3) film using a spray deposition technique for dynamic glass applications. In using a less expensive approach than magnetron sputtering and a more practical approach than spin-coating for large scale operations, the goal of this study is to create a cathodic oxide that is amorphous, mesoporous, and rivals the efficiency of currently used films. Dynamic glass has been explored as an energy saving application by monitoring solar light transmittance and heat absorption to reduce electricity costs associated with indoor comfort.[1] Analytical methods are used to characterize the WO_3 film's thickness, porosity, and performance. These methods include scanning electron microscopy (SEM) as in Figure 1, cyclic voltammetry (CV) as in Figure 2, chronoamperometry (CA), profilometry, and UV-Vis spectroscopy. It is critically important to measure how the electrochromic material performs in situ between the bleached and coloured states at different electrochemical parameters to deductively find optimal operating conditions. This study is leading to a better understanding of how the size of the electrochromic film and methodology used, affects the efficiency of the ion intercalation with hopes to increase the switching speed and limit degradation over time. Some consistent results are also suggesting that specific oxidation state changes are occurring at unique points during the cycling process.[2] These experimental findings can be used to further develop the cathodic material for use in combination with an ion-storage or an electrochromic anodic film, completing the electrochromic framework. Future studies may focus on altering the procedure used to create the thin films or doping of the deposition solution to enhance stability and develop more favorable colours.

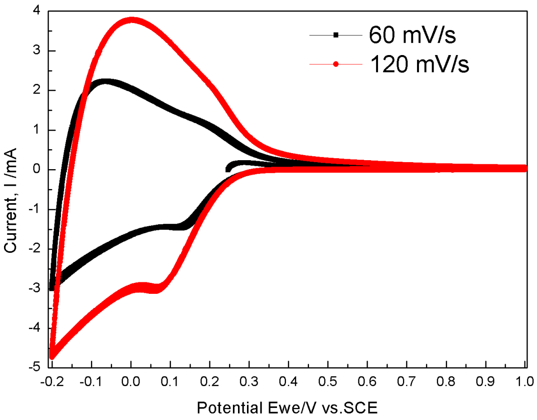


Figure 2: CV Cycles at Different Scan Rates

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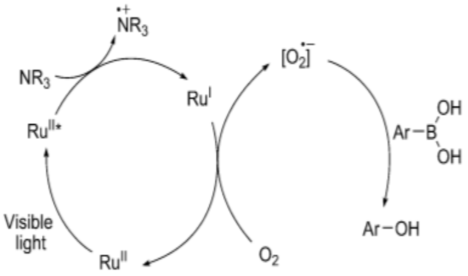
Contribution from the Amanda Morris Group

18.Photocatalyzed Aerobic Oxidative Hydroxylation of an Aryl Boronic Acid Using a Ruthenium Based Metal Organic Framework

Michael McHale, Bradley Gibbons, Amanda Morris
Virginia Tech

Photocatalysis is a promising field of green chemistry due to its energy efficient production of chemicals and limited by-products from the synthesized reactions. As environmental awareness and concern continues to rise new reaction pathways will be considered and implemented to adhere to changing the standards[1]. A typical organophotocatalysis approach involves a soluble inorganic chromophore that when irradiated transfers electrons to dissolved oxygen (or other relevant substrates) to drive relevant reactivity, i.e. oxidative hydroxylation of an aryl boronic acid (scheme right). A remaining challenge to this approach is the elimination of the complex work-up procedures involved in the recovery of chromophore post-reaction. Metal Organic Frameworks (MOFs) are one possible solution as they can be loaded with chromophores and be recovered after the reaction runs to completion. Previous reports have shown that a ruthenium-based chromophore could promote the hydroxylation of an aryl boronic acid, but this ruthenium species is difficult to recover post-reaction, limiting its reusability[2]. This report researches the possibility of using a ruthenium chromophore loaded MOF (UiO-67) to catalyze the hydroxylation of an aryl boronic acid.



The hydroxylation of 4-methoxyphenylboronoic acid was tested in ambient conditions with light irradiation. Products were then tested with H NMR. While initial tests showed that triethylamine was a successful electron donor, the basic nature of the solution degraded the MOF. As a result, other electron donors were tested for catalytic activity while maintaining MOF integrity. Future research on the subject will finish screening various electron donors for catalytic activity. One could also test various of pore sizes on the collected yield, as well as other similar reactions.

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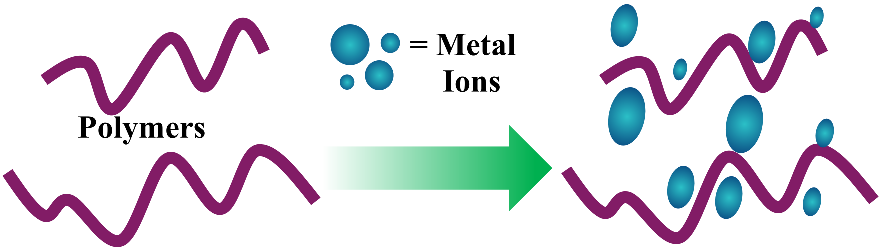
Contribution from The Schulz Group.

19. Synthesis and characterization of poly (arylene ether sulfones) (PAES) for metal chelation

Elliot B. Shelton*, Brady A. Hall and Michael D. Schulz

Metal ions, freely available in water supplies at varying concentrations, represent both a severe environmental threat and a potentially lucrative recycling opportunity. The sequestration of these ions occurs via coordination of the lone electron pairs of a chelating agent; the number of lone pair electrons available, flexibility of the structure, and overall size of the chelator factor into its ability to bind the metals.[1] The most prominent methods of metal chelation, membrane filtration and chemical precipitation, suffer from degradation due to environmental factors and produce large quantitates of waste, respectively.[2] Conversely, PAES demonstrate excellent oxidative stability, resistance to hydrolytic degradation, and recyclability.[3]

PAES-based metal chelators can be readily prepared and provide a platform to remove metal ions from solution. The stepwise preparation of these macromolecules provides a unique opportunity for tuning the physical properties (*e.g.* glass transition temperature, impact strength, and chelation propensity) over a wide range. This work focuses on the preparation of sulfonamide-based monomers using a combination of nucleophilic substitution, polycondensation, and ring-closing metathesis chemistries, which were characterized using ^{1}H, ^{13}C, ^{19}F, DEPT, COSY, and HSQCAD nuclear magnetic resonance (NMR) spectroscopy.



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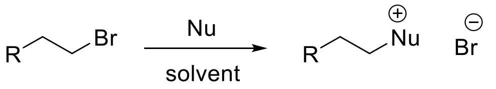
Contribution from the Deck Group.

20. Synthetic Models of Polymer Functionalization Reactions

Rudra P. Patel* and Paul A. Deck
Department of Chemical Engineering and Department of Chemistry, Virginia Tech

Ionomers are ion-containing polymers with important applications including anion exchange membranes (AEMs). The poster presentation of Andrew Williams describes some of the progress we have made in this area. The final, critical synthetic step involves nucleophilic (S_N2) reaction of an alkyl bromide that is pendant to an aromatic (ether-sulfone) polymer backbone (Scheme 1).

Scheme 1: General plan for introduction of pendant ionic functionalities.



Nu = NEt_3, PPh_3, $EtPPh_2$, Ph_2S, pyridine, DMAP

target R = aromatic polymer **model** R = $C_{10}H_{23}$

solvent = DMF (preparative), DMSO-d_6 (NMR scale)

This poster describes a series of NMR-scale reactions using a small molecule (1-bromododecane) as a model for the pendant 5-bromopentyl substituents on the polymer chain. Using model chemistry, we wanted to determine which types of nucleophilies we can use for polymer functionalization without consuming large quantities of the bromoalkyl-functionalized polymer. Model chemistry allows the reactions to be examined in closer detail because NMR spectra of polymers often have less well-resolved peaks. Also, NMR-scale reactions can be sampled for GCMS analysis, whereas polymeric species cannot.

As shown in Scheme 1, several nucleophiles were examined for reactivity. We chose DMSO-d_6 as our NMR solvent for its ability to dissolve both non-polar and ionic compounds. DMSO-d_6 also has a high boiling point, allowing us to examine these reactions at different temperatures (up to 80 °C in this study). Reactions were followed at regular time intervals using ^1H NMR spectrometry and, where appropriate, ^{31}P NMR spectrometry.

In general, we observed that the expected substitution reactions were complete after about 1 day at 60 °C. The relative reactivity of the nucleophiles was approximately DMAP > pyridine > $EtPPh_2$ > PPh_3 >> Ph_2S. (Triethylamine was examined previously by Dr. Kevin Kaurich and seems about as reactive as pyridine.)

During the course of this study, we discovered several interesting side-reactions that appear to involve the solvent (DMSO). For example, in the reactions of the two phosphine compounds, large quantities of the corresponding phosphine oxides were observed. Preliminary evidence suggests that bromide ion (a by-product of the desired substitution reaction) is catalysing the oxidation of triphenylphosphine by DMSO. Work is underway to develop a kinetic model for that autocatalytic process. Similarly, the reactions of pyridines resulted in complex NMR spectra with signals that we tentatively assigned to products of hydrolysis (RCH_2CH_2OH), oxidation (RCH_2CHO), as well as sulfur-containing species.

This poster describes our effects to characterize the mixtures formed in these interesting reactions and to determine the mechanisms leading to their formation.

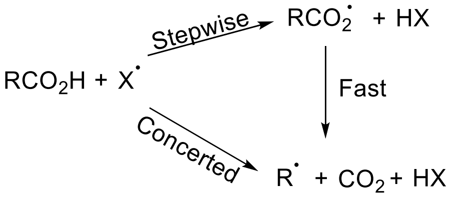
We thank Kenneth Knott for help with NMR experiments.

Contribution from the Tanko group.

21. 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 radical (R•) stability, whereas for a stepwise mechanism it is not expected to vary at all as it proceeds through an oxygen-centered radical intermediate.

Previous work in our group has used the reaction of cumyloxyl radical and several carboxylic acids to determine hydrogen abstraction rate constants. However, some of the rate constants were obscured by a competing β-scission side reaction. For acids where it <u>was</u> 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 the dynamic range of our study, cumyloxyl radical was replaced with the less reactive and more selective nitrate radical (NO_3•). Nitrate radicals lack the competing β-scission reaction while remaining spectroscopically active. We generated NO_3• by photolyzing cerium (IV) ammonium nitrate (CAN) using a 355 nm laser pulse.[3] The concentration of NO_3• was monitored at a microsecond time scale using a characteristic absorption wavelength of λ_{max} = 630 nm. The rate constant of NO_3• consumption can be extracted from the resulting transient trace, assuming pseudo first-order kinetics.

We measured rate constants for five carboxylic acids: acetic, propionic, butyric, isobutyric, and pivalic acid. As predicted, the rates of H-atom abstraction increased with radical stability. We utilized the Evans-Polanyi relationship to find the Polanyi constant ($\alpha = 0.064 \pm 0.015$), which characterizes the position of the transition state over the course of the reaction and suggests our transition state occurs early in the reaction. This is consistent with Denisov's claim and strongly suggests a concerted mechanism for this decarboxylation.[2] However further work is still needed.

To collect more data for the faster-reacting hydrocarbons and carboxylic acids, we will invest in a flow system to avoid limit the effects of CAN degradation from successive laser pulses and reagent consumption from reactivity with CAN.

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Contribution from the Guoliang Liu group.

22. An Evaluation of Hydrolysed PLA-*b*-PEI-*b*-PLA Films for use as Stable Separators for Lithium Metal Batteries

James Riet*, Dong Guo and Guoliang Liu
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Division of Nanoscience, Virginia Tech, Blacksburg, Virginia 24061, USA

Lithium metal batteries (LMBs) are more energy-dense relative to lithium ion and other batteries but have known issues with stability.[1] The most immediate obstacle facing LMBs are their tendency to form lithium dendrites that extend from the lithium metal and pierce the polymer ion-permeable separator, short-circuiting the battery (figure 1).[1] With the knowledge of the mechanical strength of polyetherimides (PEI),[2] the goal was to fabricate mesoporous PEI films that provide a barrier to halt lithium metal dendrite growth and create a battery that will be stable in the long-term.

To prepare PEI-based porous films as separators in LMBs, polylactide-*b*-polyetherimide-*b*-polylactide (PLA-*b*-PEI-*b*-PLA, also AIA) block copolymers were synthesized, cast into thin films, then hydrolyzed to create mesopores. To begin, PEI with molecular weights ranging from 12 to 30 kDa were reacted with lactide. To achieve the necessary morphology for the PEI film to halt dendrite growth,[3] the volume fractions of PLA in the copolymer were targeted at ~40%. After syntheses, the ~40% volume fractions of PLA in AIA block copolymers were confirmed with NMR and TGA. During cast into thin films, the AIA block copolymers phase-separated into microstructures with mesoscale PLA domains embedded in PEI matrix. Then the PLA domains were eliminated via hydrolysis using a phosphate buffer solution to produce the mesoporous films.[4] The produced PEI-based films were to be assembled in a Li/Li symmetric battery and subjected to a square-wave charging/discharging current. The responding voltage would be measured. The voltage over time was expected to be stable relative to the applied current, demonstrating the capability of PEI-based mesoporous separator suppressing lithium dendrites.

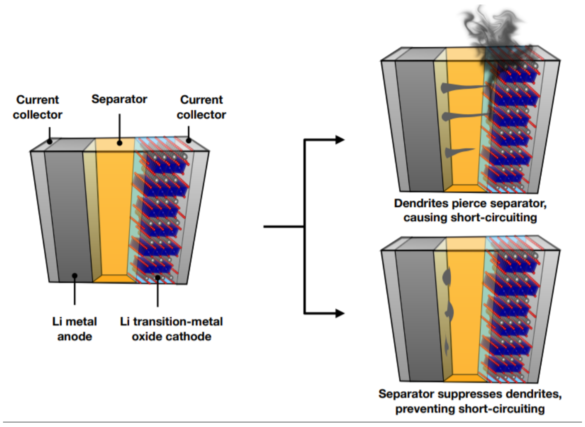

Figure 1, visualization of lithium dendrites

Hydrolysis for ten days eliminated nearly all the PLA, whereas any films that were hydrolysed for 3 or fewer days had significant PLA remaining. Previous tests with Kapton® battery separators were found to have more long-term stability relative to common commercial separators such as Celgard® made from polyethylene and polypropylene. Finally, it is hypothesized but not yet observed that the AIA with PLA of higher molecular weights will produce final PEI-based films with larger pore sizes.

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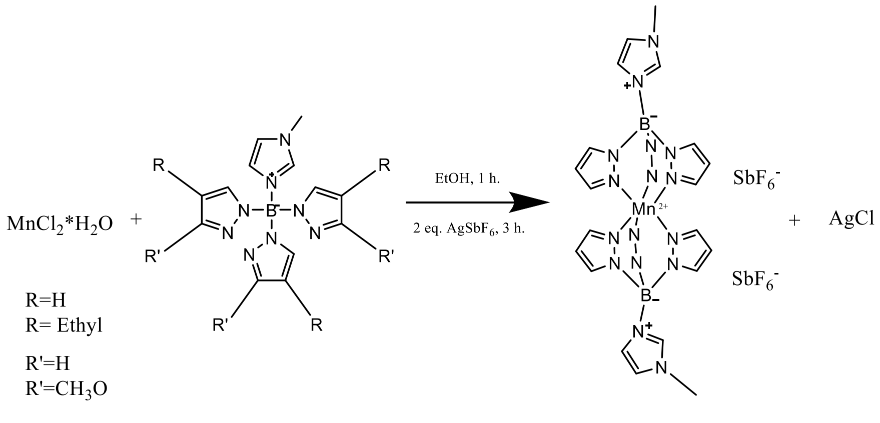
Contribution from the Amanda Morris group.

23.Synthesis of Charged Derivatives of MnTp$_2$ for use in Dye Sensitized Solar Cells.

Jonathan Roof*, Matthew Kessinger and Amanda J. Morris
Department of Chemistry, Virginia Polytechnic Institute and State University
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 thirty years. Solar energy presents 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, Dye Sensitized Solar Cells (DSSCs) are a lower-cost alternative. DSSCs are an attractive option due to the low cost associated with the materials and solution processability of thin film devices when compared to other types of solar cells. One of the most important components used in DSSCs is the redox electrolyte. The electrolyte is responsible for carrying charge from the working electrode to the counter electrode and back again. It also dictates the maximum possible voltage the cell can produce during operation. Unfortunately, the electrolyte is also the source of some of the major limitations of DSSC technology. Namely, electronic recombination at the site of the working electrode. This recombination event is currently not well understood in commercial electrolytes which utilize the iodide/triiodide redox couple (I^-/I_3^-) due to its complex redox chemistry. In recent work, the Morris group has developed an alternative redox electrolyte based on the coordination complex manganese(II) (bis(hydrotrispyrazolyl)borate) [MnTp$_2$] which is capable of undergoing charge transfer-induced spin crossover (CTISC). This phenomenon causes a change in the spin state of the coordination complex upon oxidation from high spin d^5 to low spin d^4 and the subsequent reduction back to high spin d^5. This spin reorganization instils a higher energy barrier for the recombination process, thus lowering the rate of recombination within the device. While the efficiency of devices prepared with this electrolyte were found to possess a three-fold improvement over the more common cobalt-based redox mediator (Co(Bpy)$^{3+/2+}$, MnTp$_2$ is not without its drawbacks. Solubility of the coordination complex remains a key concern, as it leads to mass transport losses within the cell. In this work, a novel redox mediator utilizing a zwitterionic ligand N-methylimidazoliumtris(pyrazolyl)borate was prepared. The complex was made soluble in acetonitrile as a SbF^{6-} salt. The complex functions as a redox mediator, but the redox potential is outside of the desirable range. Substituent groups on the pyrazole rings were modified to examine different electron donating groups. The modification of electron density in the pyrazole rings will likely shift the redox potential to more anodic potentials allowing them to be implemented into photovoltaic devices.

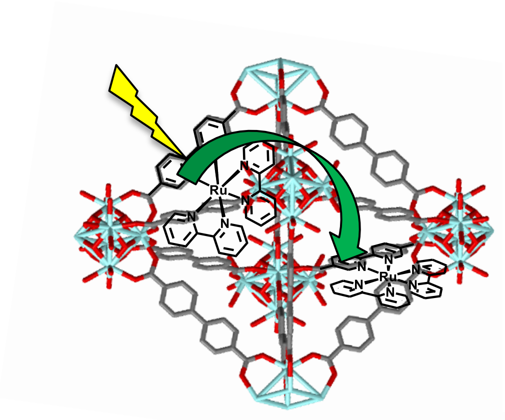


Contribution from A. Morris Group.

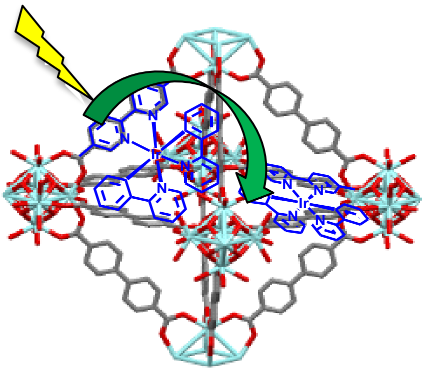
24. Spin-Orbit Coupling Induced Energy Transfer in UiO-67 MOFs Doped with Photoactive Transition Metal Complexes

Connor C. Slamowitz*, Arnab Chakraborty and Amanda J. Morris

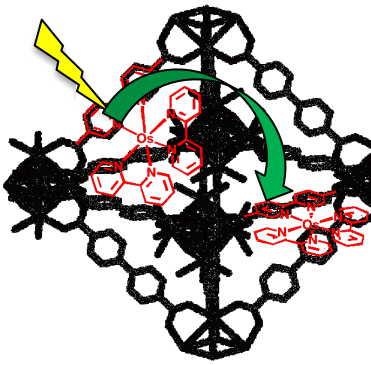
An artificial photosynthetic assembly can utilize metal-organic frameworks (MOFs) in order to both absorb light and facilitate the transport of photo-excited states for use in catalysis. In order to maximize quantum yield, the nature of the energy transport mechanisms must be fully understood. Here, we present the synthesis and photophysical investigation of Ru(II), Os(II), and Ir(III) polypyridyl complexes doped into the 3D-framework of UiO-67 MOF with zirconium nodes. MOFs were synthesized by following one-pot solvothermal synthetic protocol from previous literature. The resultant powders were structurally characterized by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). Steady-state and time-resolved spectroscopic techniques aided in exploring the photophysical behavior in the MOFs as a function of Ru(II), Os(II), or Ir(III) concentration. By studying the phosphorescent lifetime of doped UiO-67 MOF, we further explored the energy transfer process with systematic variation of MOF-incorporated chromophore as a function of spin-orbit coupling. Our recent study reveals a substantial increase of Förster energy transfer distance (R_0 = 88±12Å) in OsDCBPY doped UiO-67 MOF in comparison to our previously reported RuDCBPY doped UiO-67 MOF (R_0 = 22±5Å). Further study will reveal the energy transfer mechanisms for IrDCBPY doped MOF, confirming spin orbit coupling energy transfer for metal-ligand doped UiO-67 MOFs.



Ru(II) polypyridyl Doped UiO-67 MOF



Ir(III) polypyridyl Doped UiO-67 MOF



Os(II) polypyridyl Doped UiO-67 M

Contribution from the Yee group.

25. Synthesis of n-bromophenyltricyanotheylene: A Building Block for a Molecule-Based Magnet

Isabella M. Ulate*, Steven D. Miller*, Christopher L. Houser and Gordon T. Yee
Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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 contains 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.

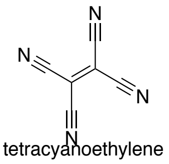


Figure 1. Tetracyanoethylene molecule

This semester's project was to complete the synthesis of molecules related to tetracyanoethylene that use 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 substituents will affect the network's magnetic properties in a positive way. These new molecules will be reacted with vanadium hexacarbonyl ($V(CO)_6$) to give new magnetically ordered materials. The magnetic ordering temperature and other properties will be measured using the superconducting quantum interference device (SQUID). For example, 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.

With the synthesis of several n-bromophenyl compounds, both mono and dibrominated, our group has successfully synthesized a sizeable catalogue of halogenated phenyl-tricyanoethylene derivatives. By comparing these compounds, the effects of size, position, and electronegativity of substituents become more apparent. Moving forwards, this information will provide insight for the design of novel molecule-based magnets.

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 Deck Group.

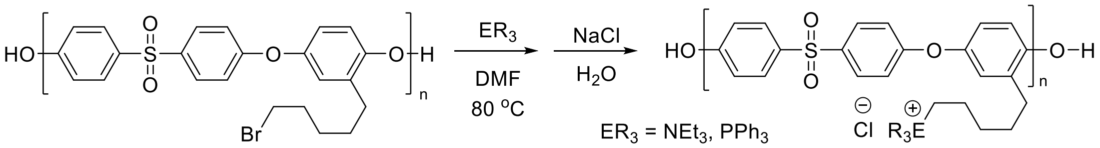
26.Aromatic Polymers with Pendant Ionic Functionality

Andrew K. Williams* and Paul A. Deck
Department of Chemistry and Macromolecules Innovation Institute, Virginia Tech

Ionomers are ion-containing polymers with many important applications such as anion exchange membranes (AEMs). AEMs are used in fuel cells and batteries, offering new and attractive options for managing energy consumption. AEMs are superior to proton exchange membranes (PEMs), which require costly noble metal catalysts and suffer from slow oxygen reaction kinetics at the cathode.

Our approach to ionomer synthesis starts with a functionalized aromatic polymer as shown in Scheme 1. The aromatic (ether-sulfone) backbone provides thermal and chemical stability, while the pendant bromoalkyl group offers an electrophilic reactive site that is easily converted to ionic functionalities by quaternization reactions.

Scheme 1: General plan for introduction of pendant ionic functionalities.



Treatment of the bromoalkyl-functionalized polymer with excess trimethylamine or triphenylphosphine required the use of DMF to maintain the solubility of the polymer throughout the reaction. In, addition, we found that the starting polymer and solvent must be scrupulously dry to avoid crosslinking the polymer through the formation of ether bonds (Williamson-type reaction). We used azeotropic distillation (Dean-Stark apparatus) to ensure complete removal of water from the reaction. After reaction at 80 °C for 30 h, we precipitated the polymer into aqueous sodium chloride, which ensured that our counter-anions would all be chloride ions. Polymers were purified by dissolving them in DMF and precipitating the DMF solutions into diethyl ether, followed by vacuum-oven-drying. Yields of the isolated polymers were about 60%. Some losses inevitably occurred in the many filtration and handling steps.

We chose the reaction conditions based on NMR-scale experiments. However we downscaled the quantity of triphenylphosphine in the preparative-scale reaction from about 10:1 to about 3:1, hoping to avoid having a large quantity of triphenylphosphine to remove later. Unfortunately, this change resulted in incomplete conversion of the bromoalkyl groups as determined by ^{1}H NMR spectrometry in DMSO-d_6 solution. This procedure requires further optimization. NMR characterization confirmed the quantitative conversion of the starting polymer using trimethylamine.

Further characterization using size-exclusion chromatography (SEC), thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) will be done on the ionomer to determine the molecular weight, the thermal stability and glass transition temperature, respectively. This data will be presented and discussed within this poster if the data is gathered in time.

We acknowledge Kevin Kaurich for preparing the bromoalkyl-functionalized polymer starting material, Dong Guo (Liu Group) for TGA and DSC data, Ryan Carrazzone (Matson Group) for SEC data, and Dr. Michael Hickner (PSU) for helpful discussions.

Contribution from the Matson group.

27.An Esterase-Triggered Small Molecule and Polymeric Persulfide Prodrug

Ethan W. Winckler*, Kearsley M. Dillon, Chadwick R. Powell and John B. Matson
Virginia Tech Department of Chemistry

Despite the growing body of evidence that small molecule persulfides (R-SSH) may play key roles in mammalian systems, the action of persulfides in various biochemical pathways within the human body remains largely unknown. In the literature it has been suggested that persulfides are critical redox mediators of biochemical pathways; however, there is a lack of tools available to biologists to study persulfide interactions in a physiologically relevant context. The goal of this project was to synthesize a persulfide releasing small molecule and polymeric prodrug, termed EDP-NAC and pEDP-NAC, respectively. These prodrugs would respond specifically to esterases that are ubiquitous in the body and will allow for the study of persulfides in biochemical pathways under normoxic conditions. The synthesis of pEDP-NAC was achieved in six steps. Notably, the last step of the synthesis of pEDP-NAC was a post-polymerization modification of pHEMA-OEGMA using EDP-NAC in a Steglich esterification reaction. Furthermore, each intermediate was fully characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Once isolated, the kinetics of persulfide release from EDP-NAC and pEDP-NAC in the presence of porcine liver esterase (PLE) were studied by both NMR and mass spectrometry to better understand the timescale of persulfide release under biologically relevant conditions. The half-life of EDP-NAC and pEDP-NAC was 1.5 hours and 35 hours, respectively. The data from the pEDP-NAC studies suggest that its release kinetics could be tunable by both varying the length of the polymer and the substituent attached to the ester, which will be studied in the future.

Contribution from the Bump-Berg group.

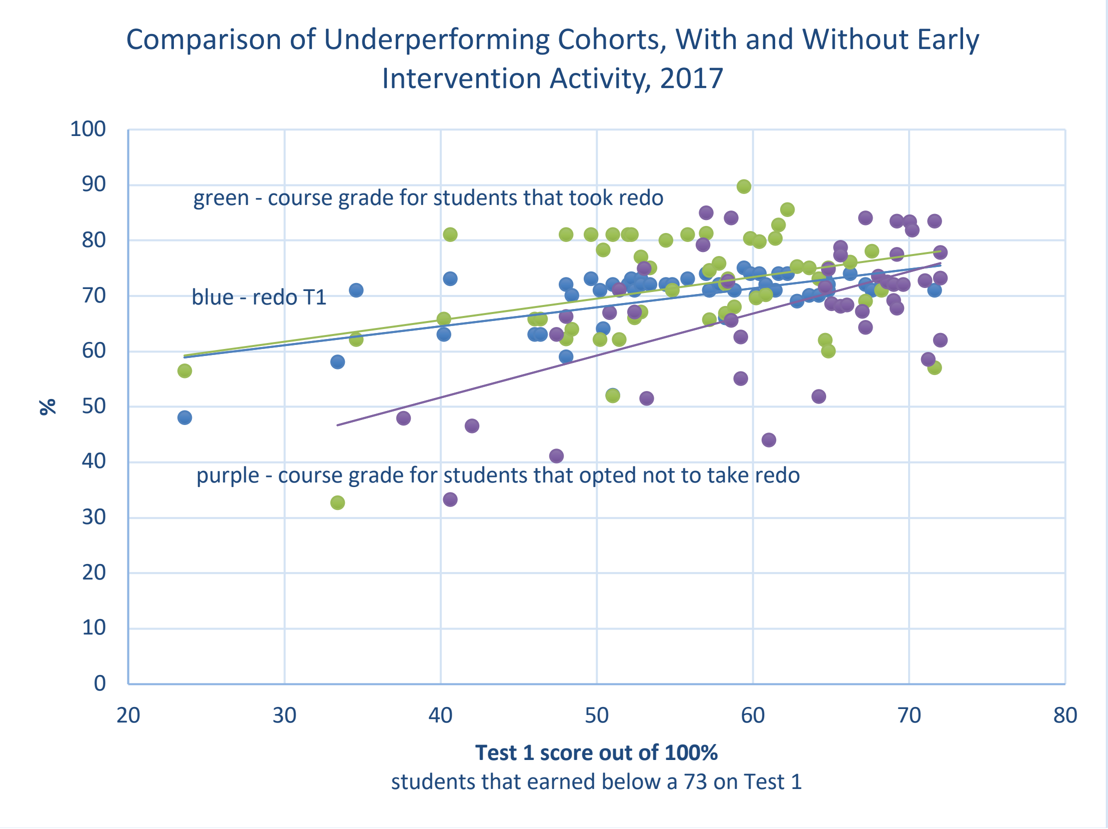
28. Analysis of Student Performance in Organic Chemistry 2535 Before and After the Use of an Early Intervention Activity

Ryan R. Adams*, Magan Matteodo*, Michael A. G. Berg, Maggie B. Bump
Department of Chemistry

The first semester of organic chemistry is notorious for its intensity and often plays a gate-keeping role for several majors as well as for professional school. The first semester frequently has a high percentage of low achievement, as measured by below average grades, failures, and withdrawals (DFW). Because the material in this course builds upon itself, it was hypothesized that students that underperform on the first test, often fail to have sufficient mastery to achieve good grades on subsequent tests. One potential solution is to use the grade on the first test as an identifier of those who are at risk of DFW grades and then use an intervention to entrench mastery of the foundational material.

First, we wished to examine the trend in under achievement over the period of 2014 to the present. Second, we wished to correlate performance on the first test to overall performance for the semester. Not surprisingly, students that earn a higher grade on Test 1 are more likely to complete the course. We then designed an intervention activity and have used that in 2017 and 2018. We found students attending 'Boot Camp' and taking another Test 1 performed better in the class (green) than students that did not (purple), and fewer students withdrew from the course.

The authors wish to acknowledge Virginia Tech Center for Excellence in Teaching and Learning for financial support of this project.



Contribution from the Matson group.

29. Bottlebrush Polymer Synthesis by Ring-Opening Metathesis Polymerization: Importance of Anchor Group Selection

Anshul R. Paripati*, Samantha J. Scannelli, and John B. Matson
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Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia 24061, United States

Bottlebrush polymers consist of a polymer backbone with polymeric side chains attached and are important due to the unique architecture and physical properties. Ring-opening metathesis polymerization (ROMP) is used to polymerize the backbone through the addition of macro-monomers. Anchor groups, which are the atoms connecting the polymer side chain to the polymerizable group, have been shown to affect the rate of polymerization. Various anchor groups were prepared, and the ROMP kinetics were investigated. The effects the anchor group has on the rate of ROMP is important because it can have various effects on the conversion from monomer to polymer. Several factors are thought to influence the propagation rate of ROMP such as steric hindrance, catalysts, and differences in electronic structure.

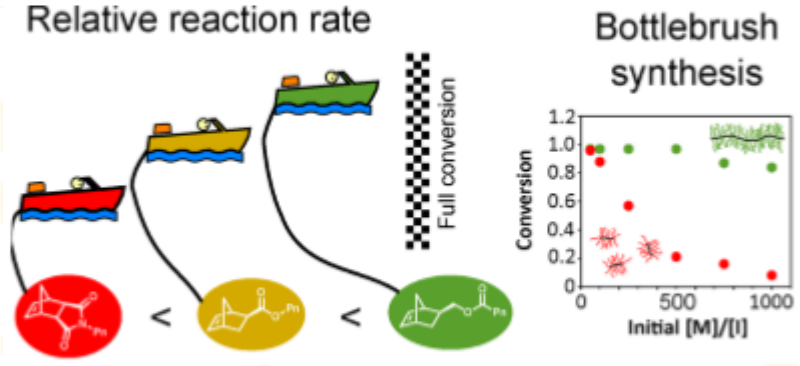

Figure 1: Comparison of anchor groups to the relative reaction rate of ROMP

Contribution from the Grove group.

30. 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. In addition, this semester I worked on cloning DNA to produce bacterial colonies with a plasmid containing a DNA sequence that encoded for our desired protein.

1. Carla Oliveira, A. R., Daniel Gomes, Joana T. Cunha, Francisco M. Gama, Lucilia Domingues, Recombinant family 3 carbohydrate-binding module as a new additive for enhanced enzymatic saccharification of whole slurry from autohydrolyzed Eucalyptus globulus wood. *Springer Nature* **2018**, 2505-2514.

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A welcome and thank you go to the members of DCAC who give of their time and talents to help out the department, including judging the posters at this symposium.

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.

Thanks for the cover art of this booklet go to Corrin Lundquist.

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.