DEPARTMENT OF
Chemistry
VIRGINIA TECH

A University Exemplary Department.
Three Years in a Row!

Undergraduate Research Symposium

November 30, 2018

Hahn Hall South Atrium

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 Allen Group (Biochemistry and Vet Med)

6. Determining the Immunological Effect of Irreversible Electroporation on Pancreatic Cancer

Contribution from the Dorn Group

10. Isolation of $M_2@C_{79}N$ with Toluene through PBB column

Contributions from the Grove Group

1. Characterization of Recombinant Human Hair Keratin Biomaterials

5. Growth of anisotropic silver nanoparticles on biological surfaces

11. Characterization of recombinant cellulose-binding protein

Contributions from the Lin Group

15. Synthesis of Low Cobalt and Cobalt Free Layered Oxides for Cathodes in Lithium Ion Batteries

19. Comparison of Electrochemical Performance Between Enriched Na-ion Layered Oxide Cathode Material and Li-ion Single-Metal-Based Oxide Cathode Material

29. Amorphous and Semicrystalline Carbon Materials from Biomass for Use in Batteries

35. Selective Doping of Cobalt-Free Cathode Materials for Lithium Ion Batteries

36. Compositional Design of Inorganic Oxide Nanoparticles in Ionic Liquid Gel Polymer Electrolytes (ILGPE) for Solid-State Lithium Metal Batteries

Contributions from the Long Group

14. Vat Photopolymerization of Biodegradable PLGA-based Tissue Scaffolds

16. Structure-Property Relationship on Polyester and Polyimide CTE

Contributions from the Madsen Group

17. Kinetics of Formation of Molecular Ionic Composites for Advanced Battery Electrolytes

Contributions from the Matson Group

13. Small Molecules and Peptides for Delivery of Hydrogen Sulfide

28. Bottlebrush Polymer Synthesis by Ring-Opening Metathesis Polymerization: Anchor Group Importance

34. A Persulfide Releasing Small Molecule Prodrug Specific to Alkaline Phosphatase

Contributions from the Moore Group

31. Blocky bromination of syndiotactic polystyrene via post-polymerization functionalization in the powder state, a control study

Contributions from the Amanda Morris Group

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

4. Chemical Warfare Decomposition via MOFs

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

18. Optimization of Charge Transfer Processes in Photovoltaics

20. Electrochemiluminescence of Covalent Organic Frameworks (COFs)

23. Radioactive Waste Disposal: Cesium Capture by Aluminum-Based Supramolecular Cage

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

27. Synthesis and Modification of a Metal Organic Framework for Controllable Drug Delivery

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

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

Contributions from the John Morris Group

12. Atmospheric Stability of Zirconium Based Metal-Organic Frameworks

Contributions from the Santos Group

32. Structure-Activity Relationship Study of FTY720-P Derived Inhibitors of Spinster Homolog 2

Contributions from the Schulz Group

3. Synthesis of nucleobase containing monomers for chemotherapy capture

9. Functionalization of cotton fabric for enhanced sequestration of Doxorubicin chemotherapy agent

22. Synthesis of a Galili antigen epitope for treatment of *C. diff.* bacterial infections

Contributions from the Smyth Group (VT Carilion Research Institute)

26. Investigating differences in pRb binding affinity between MAdV1 and MAdV3 E1A using surface plasmon resonance (SPR)

Contributions from the Troya Group

21. Computational investigation of through-space ^{19}F-^{19}F nuclear spin coupling in fluxional molecules

Contributions from the Yee Group

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

25. Synthesis of TCNE Analogues for Use in Ferrimagnetic Molecular Magnets

33. Synthesis of 2- and 4 - bromophenyltricyanotheylenethe: A Building Block for a Molecule-Based Magnet

1. **Contribution from the Tijana Grove group.**

Characterization of Recombinant Human Hair Keratin Biomaterials

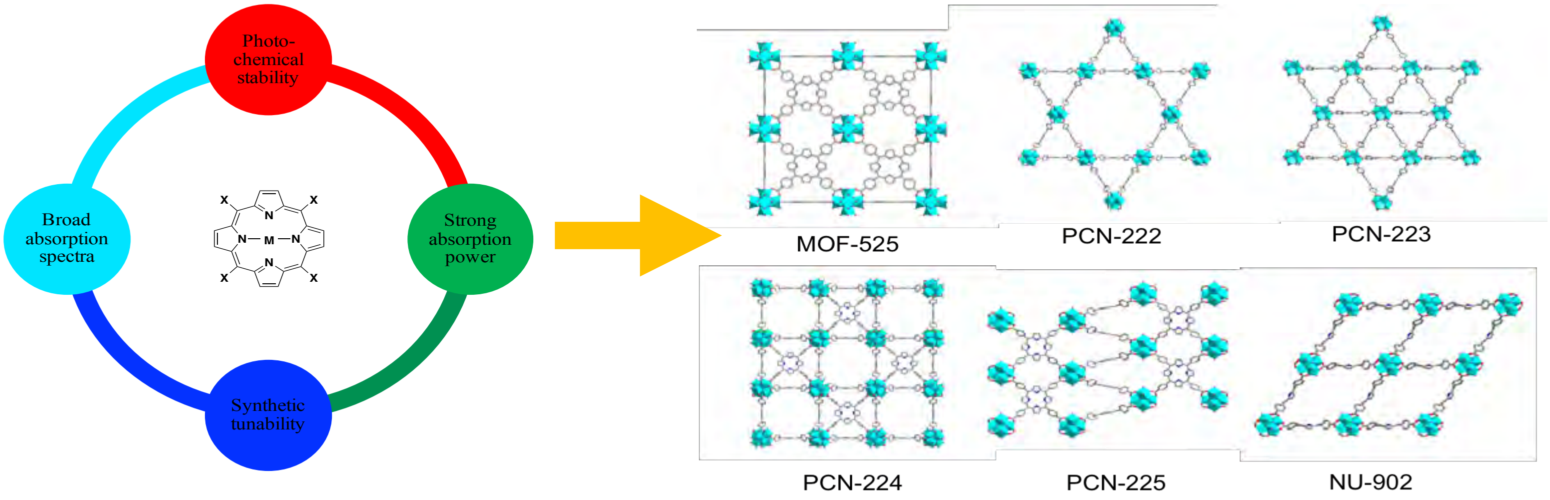
Erik Akbar*, Christina Kim, Jennifer McCord
Nanoscience

Keratin biomaterials show potential for use in medical applications due to their inherent biocompatibility, 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. Recombinant keratins can bypass these issues by providing a reliable protein sequence with every expression. The goal of this project was to construct and characterize biomaterials using both keratin precursor proteins and K-31/K-81 oligomers grown recombinantly in E. Coli. 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.

2. Contribution from the Amanda Morris group.

Synthesis and Analysis of Porphyrin Based Zr-Metal Organic Frameworks

James A. Alatis*, Shaunak M. Shaikh, Amanda J. Morris
Department of Chemistry, Virginia Polytechnic Institute and State University
Blacksburg, Virginia, 24061, United States



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. Tetracarboxyphenylporphyrin (TCPP) 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 porphyrin core.[1] The goal of this study is to synthesize and analyse Zr based MOFs using TCPC, and analyse the effects of synthesis conditions, most notably modulator, on the phase of MOF that is formed. Of particular interest is the use of the TCPP MOFs for light harvesting agents in dye sensitized solar cells. 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 minuets. The vials were heated at 120^0C for 16 hours and then isolated using 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. Future work includes testing the fluorescence quenching abilities of PCN-223 in various pH ranges, at various temperatures, and the effects of external quenchers on the fluorescence of the MOF.

1) I. Aviv, Z. Gross, *Chem.Commun*. **2007**, *20*, 1987-1999

3. Contribution from the Michael Schulz group.

Synthesis of nucleobase containing monomers for chemotherapy capture

Ash Lee Manley*, William Vaughn*, Madison Bardot, Ophelia Wadsworth and Michael Schulz
Department of Chemistry, Virginia Tech.

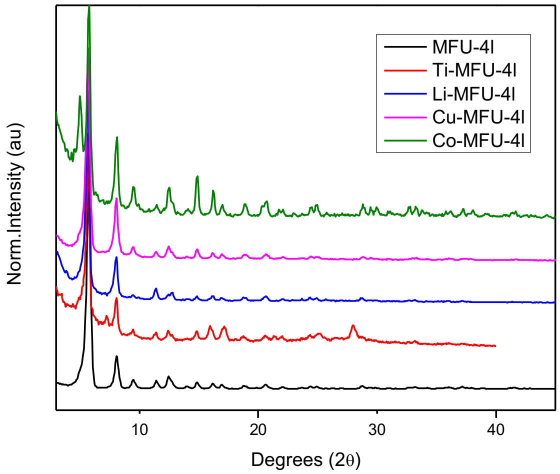
Liver cancer is the third leading cause of cancer mortality in the United States. A common treatment of liver cancer involves introducing chemotherapy and embolization materials directly into the tumor. This treatment, trans arterial chemoembolization (TACE), enables an increased chemotherapy dosage to the tumor, however healthy cells are still affected. Doxorubicin (DOX) binds to DNA, thereby inhibiting replication and effecting both tumor and healthy cells. To reduce the side effects of DOX, a drug capture device could be produced that binds to excess DOX after it exits the tumor but before it enters circulation. Previous work in the group has shown that DNA captures DOX when bound to a cellulose surface; however, depurination reactions may cause the DNA to leach from the surface. In this research, nucleobase containing monomers were successfully synthesized for polymerization into nucleobase containing polymers for DOX capture. ^{1}H NMR spectroscopy confirms the successful synthesis of N-(3-bromopropyl) acrylamide for monomer synthesis. ^{1}H NMR also confirms the successful synthesis of 3-(adenine-9-yl)propyl acrylamide, the adenine containing monomer, and 3-benzoyl thymine. Scanning electron microscope (SEM) imaging reveals successful attachment of 2-bromoisobuturyl bromide onto cellulose surfaces. Future experiments will focus on the polymerization of nucleobase containing monomers, and on the attachment of these polymers to a device for chemotherapy capture.

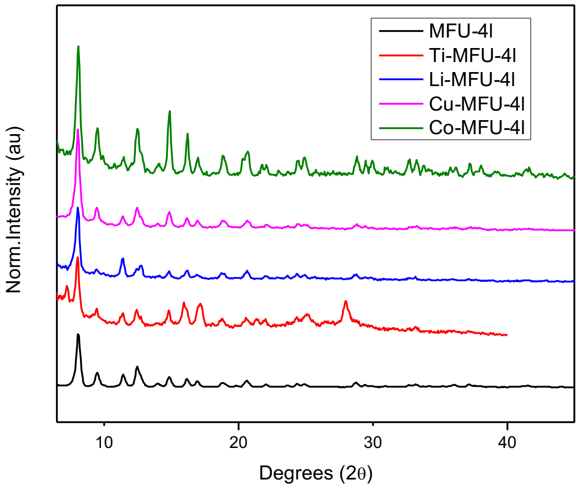
4. Contribution from the Amanda Morris group

Chemical Warfare Decomposition via MOFs

Emily L. Askew, Daniel R. Cairnie, Amanda J. Morris*

We have been working with a metal organic frame structure called MFU-4l in order to decompose chemical warfare agents. MFU-4l is a scorpionate type MOF made of Zn-Cl clusters. The Zn binds to electrophile groups like those in chemical warfare agents and decomposes them. MFU-4l is capable of many versatile cation exchanges: Cu, Ti, Li, Co, and a ligand exchange with NO_3. We synthesized each of these compounds. These cations change the chemical and physical properties of MFU-4l and effects how it decomposes the CWAs. With each cation exchange we run a PXRD and NMRs to test the integrity of the structure compared to the original MFU-4l. The stability of each compound in water was also tested.





5. Contribution from the Tijana Grove group.

Growth of anisotropic silver nanoparticles on biological surfaces.

Ethan Boeding*[1], Timothy S. Pressler[1], Yunhua Li[2], Dr. Tijana Z. Grove[2]
[1] Nanoscience
[2] Department of Chemistry

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.

1. Li, Y., Geng, X., Leng, W., Vikesland, P.J., & Grove, T.Z. (2017) Gold nanospheres and gold nanostars immobilized onto thiolated eggshell membranes as highly robust and recyclable catalysts. *New J. Chem.,* 2017, 41, 9406
DOI:10.1039/c7nj01908d

6. Contribution from the Irving Allen group.

Determining the Immunological Effect of Irreversible Electroporation on Pancreatic Cancer

Jenna T. Colturi*, Rebecca M. Brock, Veronica M. Ringel-Scaia, Natalie White, Kristin Eden, Sheryl Coutermarsh-Ott, Robert, Melvin F. Lorenzo, Navid Manuchehrabadi, Rafael V. Davalos, and Irving C. Allen
Virginia Tech Department of Biochemistry, Virginia-Maryland College of Veterinary Medicine

The five year survival rate for pancreatic cancer is low at 8%. Due to its internal nature, it is often times not detected until late stages. Treatment for pancreatic cancer is limited as the pancreas is nestled into a complex location. Surgery is rarely a reliable option, and chemotherapy often acts simply as a palliative measure. There is no highly effective cure currently available.

Irreversible Electroporation (IRE) is a non-thermal ablative technique. IRE applies short, high-voltage pulses to targeted tissue in order to permeabilize cell-membranes, causing cell death. IRE has proven to be promising in clinical trials in the U.S. and abroad for pancreatic cancer patients.

Here, we aim to study IRE in a biological context to observe the safety of it in both cancerous and healthy tissue. We are observing the immunologic response in multiple models, including both *in vivo* and *ex vivo* models.

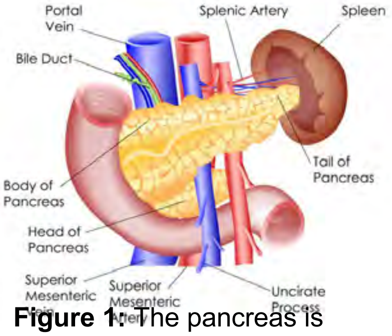
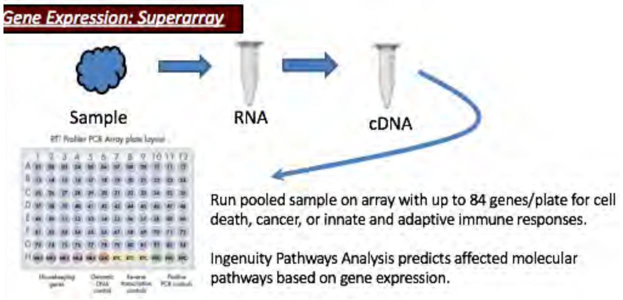


Figure 1: The pancreas is nestled within a complex mix of key organs, veins, and arteries.

We hypothesize that cancerous tissue is more susceptible to IRE, and that IRE promotes a pro-inflammatory microenvironment. This allows cancer-killing immune cells to invade and reduce tumor growth and metastatic potential, improving survival outcomes.

To test this hypothesis, we utilized both *in vivo* and *ex vivo* models. Human Pancreatic Ductal Adenocarcinoma (PDAC) Patient Derived Xenograft (PDX) tissues and porcine liver, brain, and pancreas from *ex vivo* models were treated with IRE at varying electrical fields. *In vivo,* C57Bl/6J mice were injected subcutaneously in the flank with murine Pan02 cells suspended in Matrigel or Matrigel control. Mice were treated at day 7 with IRE at 1500-200v/cm for 100 pulses.



Run pooled sample on array with up to 84 genes/plate for cell death, cancer, or innate and adaptive immune responses.

Ingenuity Pathways Analysis predicts affected molecular pathways based on gene expression.

mRNA post-IRE was subjected to Qiagen RT2 Profiler array for gene expression and assessed with Ingenuity Pathway Analysis. An increase in pro-inflammatory cytokines was also observed. Tumor growth for treated mice was also reduced, and top genes in Human PDAC PDX tissues show necrosis as a top toxicity pathway. Together, these results show that the tumor microenvironment has been modulated. We anticipate that this non-thermal tumor ablative technology will improve conventional treatment strategies.

7. Contribution from the Yee group.

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

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

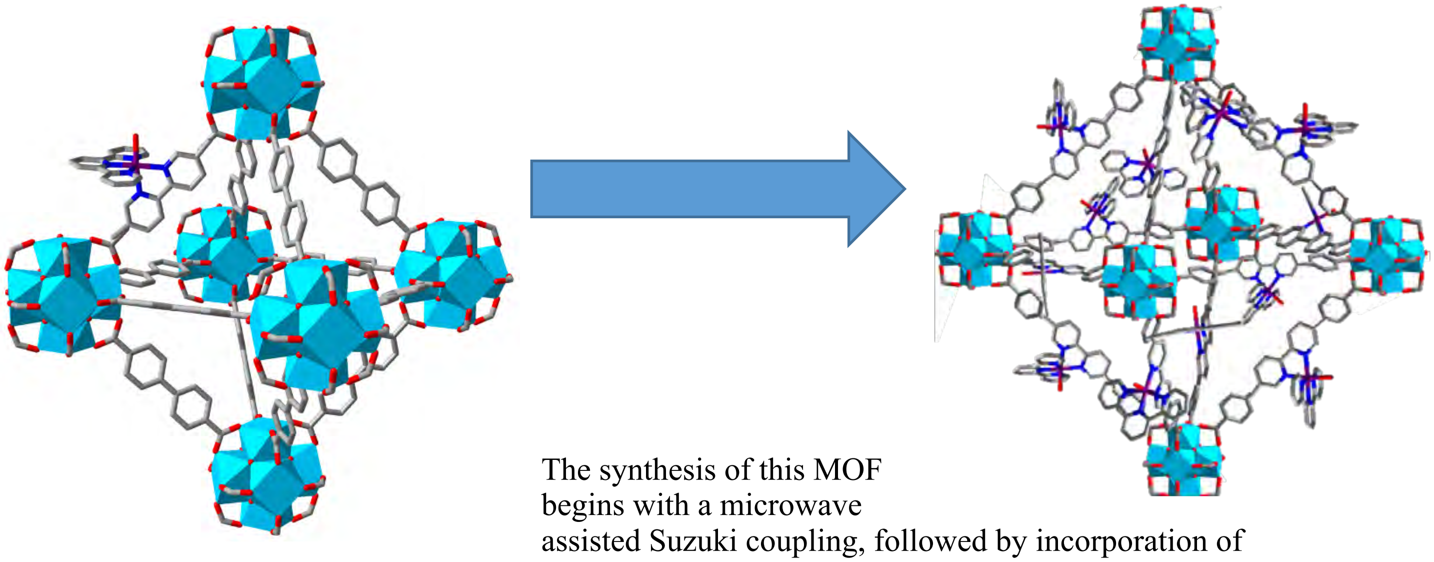
This investigation uses density functional theory to computationally analyse various methyl-substituted phenyl tricyanoethylene (PTCE) molecules, shown below, which have been used to synthesize molecule-based magnets when reduced and reacted with hexacarbonylvanadium(0). Methyl groups are weakly electron 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

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

Dylan C. Davis, Bradley Gibbons and 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. This lab has investigated metal organic frame works, subsequently know as MOFs, as a mode of transferring light energy into usable electrical energy. Specifically, this sub-group has been looking into a unique MOF with a large linker to allow for more catalyst to be incorporated into the MOF.



The synthesis of this MOF begins with a microwave assisted Suzuki coupling, followed by incorporation of the Ru(tpy) catalysed into the long back bone with perchloric acid. Finally, the long backbone is coordinated to the zirconium nodes creating the MOF. However, the ratio of Zirconium to Ruthenium catalyst continues to skew towards Zirconium 7:1 respectively. The ratio should be 1:1 indicating a serious issue with the MOF. Several possible issues have been proposed; the Ruthenium catalyst disassociates during synthesis; the storage of MOF in water could be causing the catalyst to disassociate; or the MOF that is being synthesized may just be defective and missing whole linkers. To alleviate these possible issues a mixed ligand MOF may be a potential solution. The mixed ligand would increase the overall stability of the MOF and would lead to more catalyst in the MOF as more linkers would stay coordinated with the MOF. Another solution would be to add to the catalyst post synthetically to prevent the catalyst from disassociating during synthesis.

Future work includes incorporating a semiconductor with the MOF to lower the potential required for water oxidation. The initial attempts at this has shown that Tungsten Trioxide acting as a semiconductor has increased oxygen production potential

9. Contribution from the Michael Schulz group.

Functionalization of cotton fabric for enhanced sequestration of Doxorubicin chemotherapy agent

Landon Dehart*, Simran Kala*, 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.[1] The most common method of treatment is transarterial chemoembolization (TACE) with doxorubicin (DOX) chemotherapy agent.[2] DOX intercalates between DNA base pairs to inhibit replication, resulting in apoptosis of 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 extraneous DOX, isolating the medication to the tumor cells. The DOX capture capability of cotton was first assessed by immersing plain cotton in DOX solution at 37˚C for 12 minutes. Aliquots were collected at varied time intervals and DOX concentrations were determined via fluorescence spectroscopy. After 1 minute the cotton fabric captured 12% DOX and 56% after 12 minutes. Cotton fabric was then coated with herring DNA and although energy dispersive x-ray spectroscopy (EDS) did not detect evidence of DNA on the surface, DOX capture at 1 minute was 14% and 73% at 12 minutes. Finally, the cotton surface was functionalized via chemical vapor deposition of three types of silanes (GDPTMS, ICPTMS and APTES) serving as DNA linking molecules. Herring DNA was used to react with the silane functional groups before the samples were immersed in DOX solution to assess binding capability. EDS verified the presence of DNA on the samples functionalized with ICPTMS only, although the layer was not uniform. Fluorescence spectroscopy showed that APTES samples exhibited the most DOX capture after 1 minute while ICPTMS samples exhibited the best DOX capture after 12 minutes. All samples functionalized with silanes and DNA showed an average of 65% greater DOX capture than DNA-coated and plain cotton fabric. To further assess the substrates' viability for DOX capture application, DOX capture will be determined in phosphate buffered solution and blood serum. Additionally, various silanes will be used to enhance reactivity with DNA and enhance DOX capture.

1. Wáng, Y.-X. J.; De Baere, T.; Idée, J.-M.; Ballet, S., Transcatheter embolization therapy in liver cancer: an update of clinical evidences. *Chinese Journal of Cancer Research* **2015,** *27* (2), 96-121.
2. Retrieved from: https://www.cancer.org/cancer/liver-cancer/treating/chemotherapy.html, (accessed Apr 9, 2018)
3. Chen, X.; Zhou, L.; Wang, J.; Jiang, G.; Cheng, H.; Pei, R., The Study of the Interaction between Doxorubicin and Single-Stranded DNA. *ChemistrySelect* **2016,** *1* (13), 3823-3828.

10. Contribution from the Harry Dorn group.

Isolation of $M_2@C_{79}N$ 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 current work being done on the characterization of the $Tb_2@C_{79}N$ in the Dorn group, this work focused on the separation and isolation of $M_2@C_{79}N$ and $M_3N@C_{80}$. $Tb_2@C_{79}N$ 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. The HPLC traces for 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.[1] Mass Spectrometry was used to verify the $M_2@C_{79}N$ system was in the collected sample.

References

1. Fu, W.; Zhang, J.; Fuhrer, T.; Champion, H.; Furukawa, K.; Kato, T.; Mahaney, J. E.; Burke, B. G.; Williams, K. A.; Walker, K.; Dixon, C.; Ge, J.; Shu, C.; Harich, K.; Dorn, H. C. *Journal of the American Chemical Society* **2011**, *133*, 9741.
2. Wang, X.; McKay, J. E.; Lama, B.; van Tol, J.; Li, T.; Kirkpatrick, K.; Gan, Z.; Hill, S.; Long, J. R.; Dorn, H. C., Gadolinium based endohedral metallofullerene Gd2@C79N as a relaxation boosting agent for dissolution DNP at high fields. *Chemical Communications* **2018,** *54* (19), 2425-2428.

11. Contribution from the Tijana Grove group.

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.

12. Contribution from the John Morris group.

Atmospheric Stability of Zirconium Based Metal-Organic Frameworks

Emerald M. Greene*, Tyler G. Grissom, 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. While UiO-series MOFs have shown excellent stability in solution and in a wide range of thermal conditions, their long-term stability under atmospheric conditions is unknown. The objective of this work was to probe the effect that several common atmospheric contaminants, ozone (O_3), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2), had on two zirconium-based MOFs with different pore topologies: UiO-66 and NU-1000. Both transmission and attenuated total reflectance (ATR) infrared spectroscopy (FTIR) were employed to observe possible changes in the MOF structures upon exposure to high concentrations of O_3, SO_2, and NO_2. In situ FTIR monitoring of ozone exposure to UiO-66 and NU-1000 revealed that the MOF structures degraded based on the loss of organic linker vibrational modes and a simultaneous formation of bands attributed to carbonyl species. ATR-IR spectra of UiO-66 and NU-1000 exposed to concentrations of O_3, SO_2, and NO_2 provide further evidence of carbonyl-based species formation at the expense of the aromatic linkers. While SO_2 exposure had little effect on the structure of both UiO-66 and NU-1000, NO_2 appeared to react with both MOFs to form amide-based species and nitro-containing groups. Overall, UiO-66 and NU-1000 were degraded when exposed to high concentrations of O_3 and NO_2, but are not effected by high concentrations of SO_2. These findings suggest that long-term use of UiO-66 and NU-1000 under atmospheric conditions may slowly result in a breakdown of both materials, potentially reducing their efficacy as ambient-condition use materials.

UiO-66

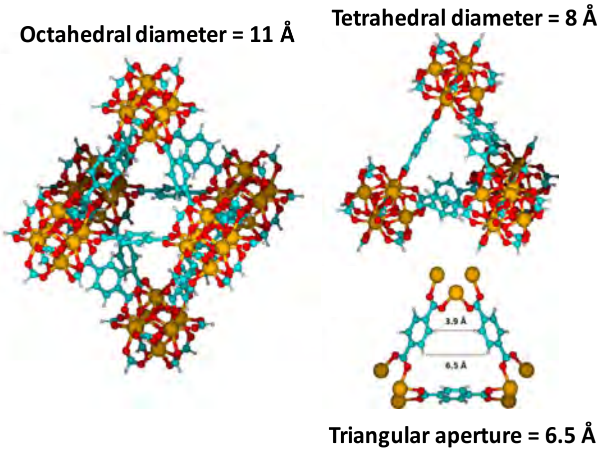


Figure Credit: Diego Troya

NU-1000

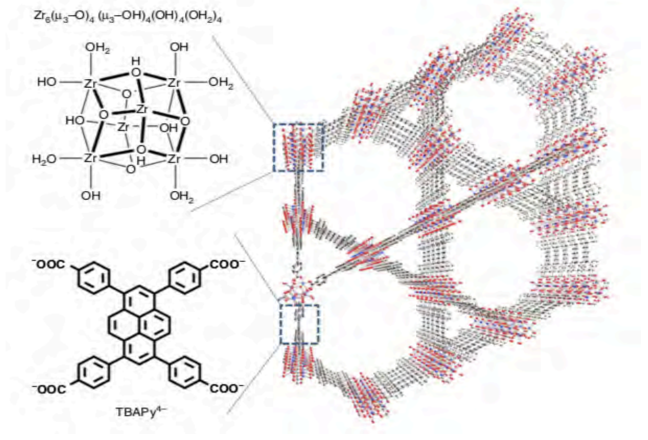
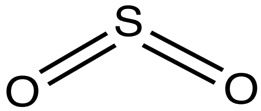
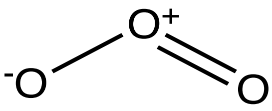


Figure Credit: Reference 2 on poster

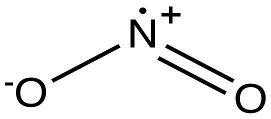
Sulfur Dioxide



Ozone



Nitrogen Dioxide

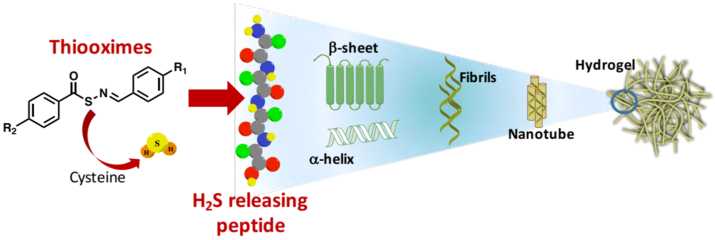


13. Contribution from the John Matson group.

Small Molecules and Peptides for Delivery of Hydrogen Sulfide

Jared Grimm*, Kuljeet Kaur, John B. Matson.
Department of Chemistry, Virginia Tech

Throughout this semester, we focused on developing and synthesizing small molecules that can be used to release hydrogen sulfide. H_2S releasing small molecules, also known as H_2S-donors, were coupled onto several self-assembling peptides that were fabricated separately via solid phase peptide synthesis technique. This project involved several techniques, including manual peptide synthesis, purification by high performance liquid chromatography (HPLC) and manual column chromatography, and analysis by mass spectrometry and NMR. Finally, peptide hydrogels were formed and the H_2S-release trends from the various hydrogels were evaluated.



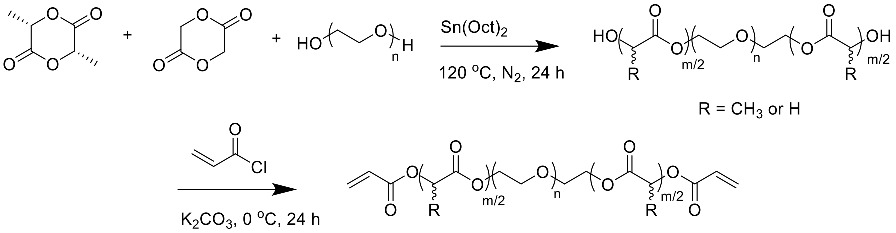
14. Contribution from the Timothy Long group.

Vat Photopolymerization of Biodegradable PLGA-based Tissue Scaffolds

Aleena M. Gula*, Emily M. Wilts, Corey Davis and Timothy E. Long
Department of Chemistry, Macromolecules Innovation Institute, Virginia Tech

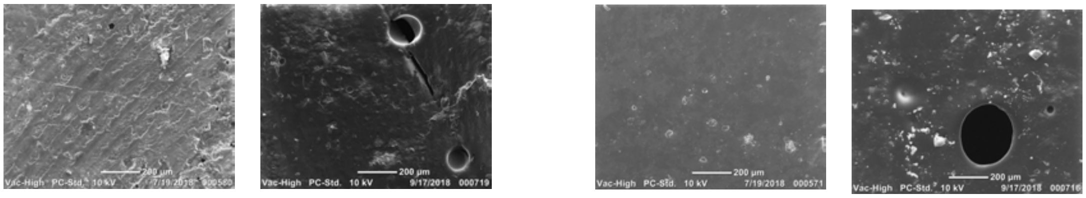
There is a demand for new methods to regenerate damaged tissue and tissue scaffolds are a promising means to promote growth of new tissue. Poly(lactic-co-glycolic acid) (PLGA) based copolymers are commonly used to create tissue scaffolds due to their biocompatibility. Vat photopolymerization, a 3D printing technique, can build tissue scaffolds by polymerizing liquid photoactive precursors with a UV light. In this research, ring-opening polymerization yielded six PLGA-based oligomers with differing ratios of lactide to glycolide to facilitate gradient degradation rates.

Scheme 1. Schematic of ring-opening polymerization to form a PLGA diol and subsequent acrylation to form a crosslinkable oligomer.



Photorheology was utilized to conclude if the synthesized PLGA-based oligomers were suitable for 3D printing. Photorheology revealed the proper irradiation time for each layer, if the materials are strong enough for printing and if the materials have a proper viscosity for printing. By examining the crossover point of the loss and storage modulus obtained from photorheology data, it was determined that the irradiation time for each layer should be between 5 and 8 seconds to ensure each layer is a solid before the next one is built. It is estimated that a strength of 10^5 pascals is strong enough to survive the recoating process during printing. Data from photorheology indicates the strength of each copolymer system surpasses the minimal strength necessary for printing. Each 3D printer has the capability of printing liquids within a specific range. By analysing the viscosities of each oligomer, it was determined the 100:0 and 75:25 oligomers are printable with Bumblebee, a printer the Williams group developed. A degradation study of five different PLGA-based polymers revealed decreasing T_g and decreasing $T_{d,5\%}$ each week analysed. SEM images depict surface and internal degradation. The polymers containing a higher percentage of lactide degraded at a slower rate.

Figure 1. Week 0 and week 8 SEM images of 60:40 and 100:0 lactide to glycolide polymers



60:40 week 0 60:40 week 8 100:0 week 0 100:0 week 8

Initial cell studies demonstrated cell viability greater than 80% for polymers containing 60 percent lactide and greater. Further cell studies are necessary to understand how these polymer systems would react in the body.

15. Contribution from the Feng Lin group.

Synthesis of Low Cobalt and Cobalt Free Layered Oxides for Cathodes in Lithium Ion Batteries

Troy K. Gustke*, Linqin Mu, Benjamin Z. Zydlewski, Feng Lin
Virginia Tech Chemistry Department

With lithium-ion batteries reaching maximum theoretical capacity, post $LiCoO_2$ batteries show good promise to fulfil the demands of the future technology market. $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) materials are one of the most attractive cathodes due to its high capacity and output voltage. However, NMCs contain cobalt which is toxic, expensive, and non-sustainable. Thus, the lithium ion battery field calls for developing low-Co/Co-free layered cathode materials, e.g., LiNiO2. We propose to synthesize one type of LiNiO2 cathode material that can deliver excellent electrochemical performance. With dopant utilization or synthesis designing, we will tune synthesis parameters (temperature, pH, and LiOH content) to obtain final cathode materials. Finally, by comparing the electrochemical performance of the cells containing these cathode materials, we will understand which parameter is the most important for low-Co and Co-free cathode materials.

16. Contribution from the Timothy Long group.

Structure-Property Relationship on Polyester and Polyimide CTE

Jonathan D. Hostetler*, Ryan J. Mondschein, Timothey E. Long
Department of Chemistry, Macromolecules Innovation Institute (MII), Virginia Tech, Blacksburg, Virginia, 24060

Many plastic products in use today need to work properly through a wide range of temperatures. These ranges could be as extreme as a seal on a spaceship to something as simple as the daily changes a water bottle will go through. The use of thermoplastics, such as polyesters and polyimides, in these applications allow the plastic to retain its properties throughout the temperature range. This includes the product dimensions, one of the most important specifications for commercial products. The change in the product dimensions as a function of a change in temperature is expressed as the linear coefficient of thermal expansion (CTE). This value indicates how much a polymer expands per °C per m of the original length of the polymer. Ultem™, frequently used as a fastener in high precision applications like the medical and aircraft industries, requires a high level of control of the product dimensions. This makes knowing the CTE value of this polymer critical for applications across large temperature ranges.

First, a thermomechanical analyzer (TMA) with different geometries measured the CTE values of a standard polyester (poly(ethylene terephthalate) (PET)). Analysis of the CTE values with the different setups determined the optimal setup for thin films. Testing verified a CTE value for PET of $9.19 \pm 0.78 *10^{-5}$ m/m/°C. This compared favourably with the literature value of $9.10 *10^{-5}$ m/m/°C. Therefore, testing of 24 mm thin films heated at 3 °C/min determined the CTE for research samples.

Using the previously determined testing setup, the influence of regiochemistry on bibenzoate CTE is tested. Increasing the mol % of 4,4'-bibenzoate repeat units in a copolymer with 3,4'-bibenzoate repeat units increased the CTE. The *para* substitution allowed for the chains to more easily slide past each other in relation to the *meta* substitution. The CTE value of a commercial polyetherimide (PEI), Ultem™, with varying degrees of branching, is also tested to determine the topology's effect on CTE. Analysis of Ultem revealed a CTE of $5.65 \pm 0.84 *10^{-5}$ m/m/°C, which is consistent with the literature value for Ultem of $5.59 *10^{-5}$ m/m/°C. The increase in branching caused a stepwise increase in the CTE value, to a value of approximately $7.00 * 10^{-5}$ m/m/°C for each branched sample.

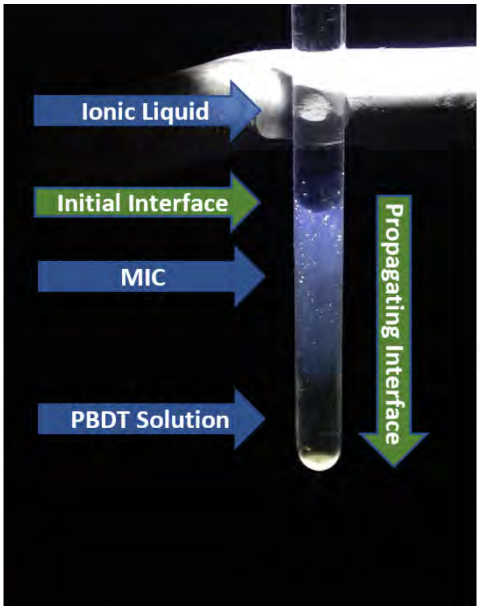
Tension

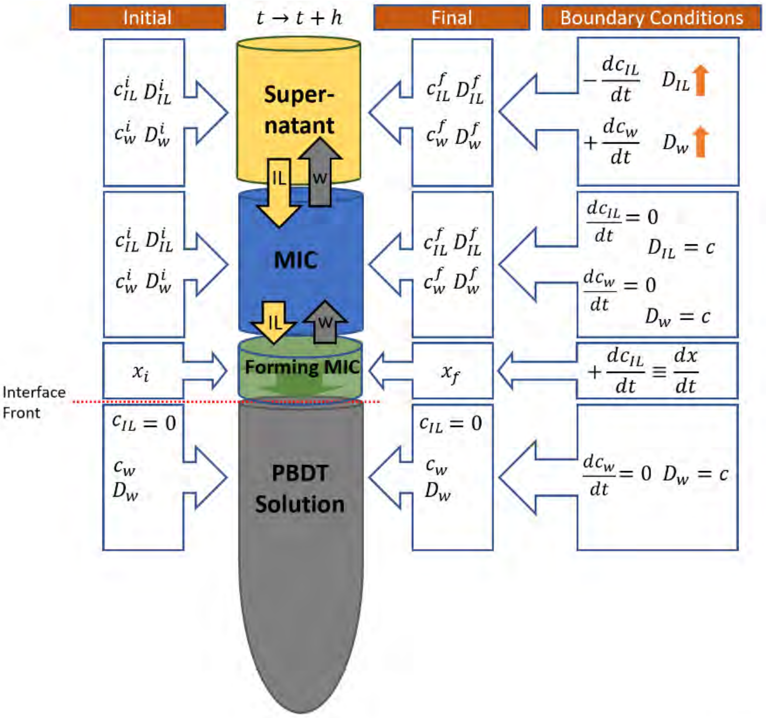
17. Contribution from the Louis Madsen group.

Kinetics of Formation of Molecular Ionic Composites for Advanced Battery Electrolytes

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

We have created a new solid electrolyte material called a molecular ionic composite (MIC) that combines a rigid-rod double helical polyanion, poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT), with an ionic liquid (IL), [C2mim$^+$][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 300°C, making MICs promising candidates for replacing volatile and flammable liquid electrolytes in rechargeable batteries. The solid MIC forms through an ion exchange process as IL infiltrates into the aqueous PBDT solution and water diffuses into a supernatant phase. We can track the interface between the growing MIC and the PBDT solution because the MIC appears iridescent blue when irradiated with white light. We created an automated program incorporating a stationary camera to measure this formation by tracking the iridescence over time. Thus, we can gather the rate of growth and use it to understand the formation mechanism and kinetics of the system. Formation of the downward propagating interface follows a linear dependence with time, leading us to believe the mechanism is dominated by the MIC self-assembly kinetics and not diffusion of the IL. We will discuss detailed measurements of diffusion coefficients and compositions in all three phases (all by NMR) involved in this process, as well as factors involved in the kinetics.



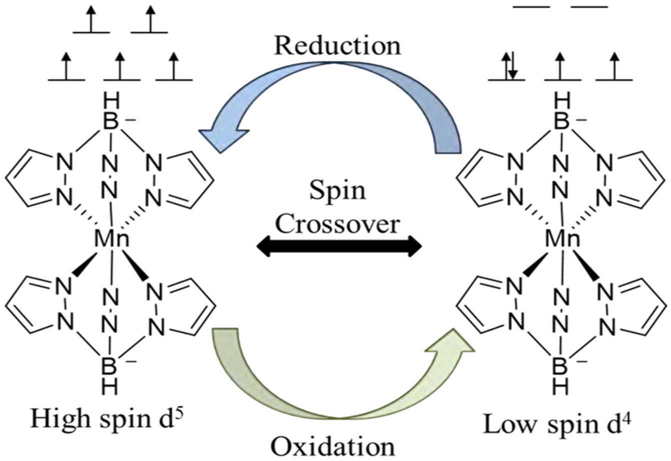


18. Contribution from the Amanda Morris group.

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 the oxidized $MnTp_2$ complex concentration in TAS. This semester two ruthenium complexes were synthesized, $Ru(bpy)_2dcbpyCl_2$ and $Ru(bpy)_2dcbpy(PF_6)_2$. Quenching of Ru Complexes by $MnTp_2$ was determined by reductive emission quenching and UV-Vis spectroscopy. Preliminary TAS measurements were conducted on both Ru Complex solutions, Ru complex doped TiO_2, and Ru complex doped ZrO_2.

1. Kessinger, M. C.; Langlois, R.; Roof, J.; Shaikh, S. M.; Tanko, J. M.; Morris, A. J., Improving the Efficiency of the Mn2+/3+ Couple in Quantum Dot Solar Cells: The Role of Spin Crossover. *The Journal of Physical Chemistry C* **2018,** *122* (25), 14135-14149.

19. Contribution from the Feng Lin group.

Comparison of Electrochemical Performance Between Enriched Na-ion Layered Oxide Cathode Material and Li-ion Single-Metal-Based Oxide Cathode Material

Hao Li*, Muhammad M. Rahman and Feng Lin

Energy consumption is increasing dramatically in this century, leading to the depletion of fossil fuels and severe environmental pollutions. Many renewable and clean energies that are under demand start growing. To integrate these various energies into a large grid scale, researchable battery, an inexpensive, efficient, and environmental-friendly electrical energy storage system, drives innumerable exciting research. Among these rechargeable battery designs, lithium (Li)-ion batteries (LIBs) have been successfully commercialized for potable electronics and electric vehicles since 1991. However, the shortage of Li resource has been concerned for future sustainable development. Compared with Li, sodium (Na) resource has rich natural abundance in the earth and versatile distribution in worldwide, causing to a low price of sodium-based raw material. Therefore, rechargeable sodium-ion batteries (SIBs) with the similar working principles of LIBs is the alterative choice to significantly reduce the cost and environmental burden.

Because cathode materials are essential component to determine the energy density and cost, numerous components have been investigated. Among these candidates, layered oxide transition metal is a promising category. Due to different intercalation electrochemistry, SIBs (Na_XTMO_2) can incorporate versatile transition metals from Ti to Cu, resulting in the potential cheap cathode materials. Conversely, most LIBs face constrained choices of transition metal that are only from Ni, Co, and Mn. Consequently, our undergraduate research investigated that how does the versatility of transition metals affect the electrochemical performance between SIBs cathode material (that incorporates enriched transition metal) and LIBs cathode material (that only includes nickel).

Therefore, $Na_{0.75}Ni_{0.125}Co_{0.125}Cu_{0.125}Fe_{0.125}Mn_{0.5}O_2$ and single-metal-based oxides $LiNiO_2$ were selected for this topic. Both materials were synthesized by co-precipitation method. First, two materials were characterized by SEM to scan the surface morphology. Then, these materials were tested by XRD to determine the material type: $Na_{0.75}Ni_{0.125}Co_{0.125}Cu_{0.125}Fe_{0.125}Mn_{0.5}O_2$ is a mixed P2 and P3 type material and $LiNiO_2$ is a O3 type material. Finally, both materials' performances were evaluated by cycling at C/10, 1C, and 5C. $Na_{0.75}Ni_{0.125}Co_{0.125}Cu_{0.125}Fe_{0.125}Mn_{0.5}O_2$ exhibited zero capacity fading after 50 cycles at C/10, 100 cycles at 1C, and 200 cycles at 5C. However, $LiNiO_2$ materials from six batches displayed unstable performance due to the off-stoichiometry material and irreversible phase change. Further new methods need to be adopted to enhance this material's performance.

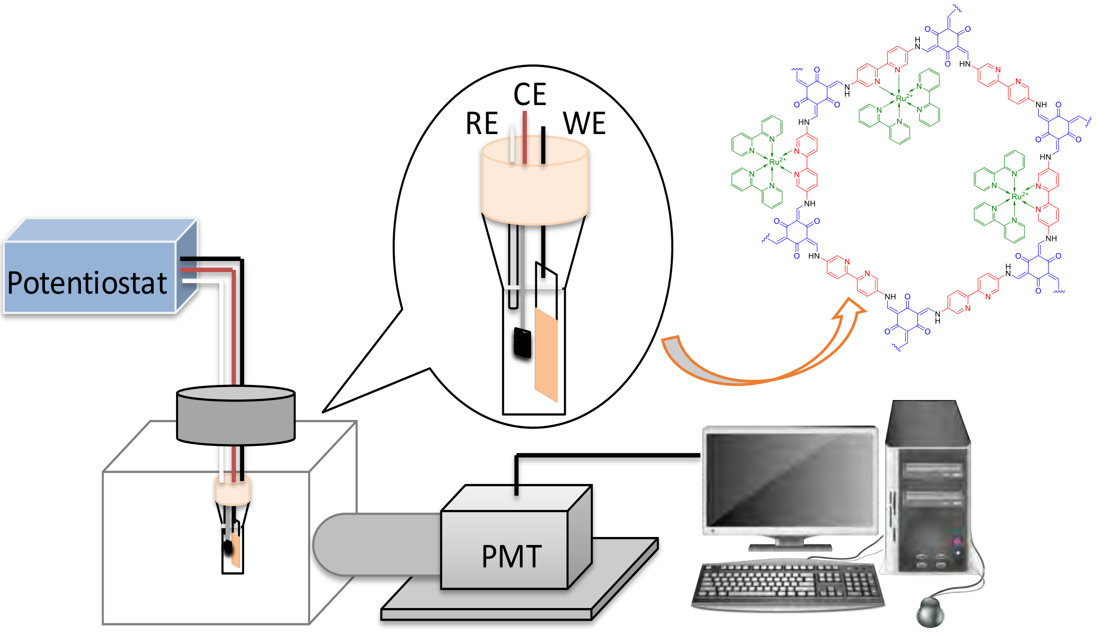
In conclusion, SIBs involving versatile transition metal oxides ($Na_{0.75}Ni_{0.125}Co_{0.125}Cu_{0.125}Fe_{0.125}Mn_{0.5}O_2$) demonstrate a more stable and efficient performance than the single-metal-based oxides LIBs ($LiNiO_2$) with a low cost.

20. Contribution from the Amanda Morris group.

Electrochemiluminescence of Covalent Organic Frameworks (COFs)

Quentin R. Loague*, Meng Cai and Amanda J. Morris
Department of Chemistry, Virginia Polytechnic Institute and State University
Blacksburg, Virginia, 24061, United States

Covalent organic frameworks (COFs) are multidimensional organic solids with repeating structures linked together by strong covalent bonds. Their characteristics, including large surface area and pore size, make them an ideal template material for electrochemiluminescence (ECL), a highly sensitive technique that can be used for clinical screening of various antigens and analytes. Advantages of COFs over analogous metal-organic framework materials includes stability in aqueous solutions, charge transfer via π-stacking, and the ability to synthesize thinner films. This study aims to synthesize Ru doped TpBpy COF, named TpBpy-Ru, to serve as a novel solid-state ECL detector. The Ru-doped COF has been prepared solvothermally, post-synthetically, and via interfacial crystallization. The COF powders have been characterized via powder X-ray diffraction (PXRD). Future work includes the synthesis of COF thin films and characterization via PXRD, SEM, and UV-Vis spectroscopy. Future electrochemical studies will be conducted on COF films to study their efficiency for ECL.

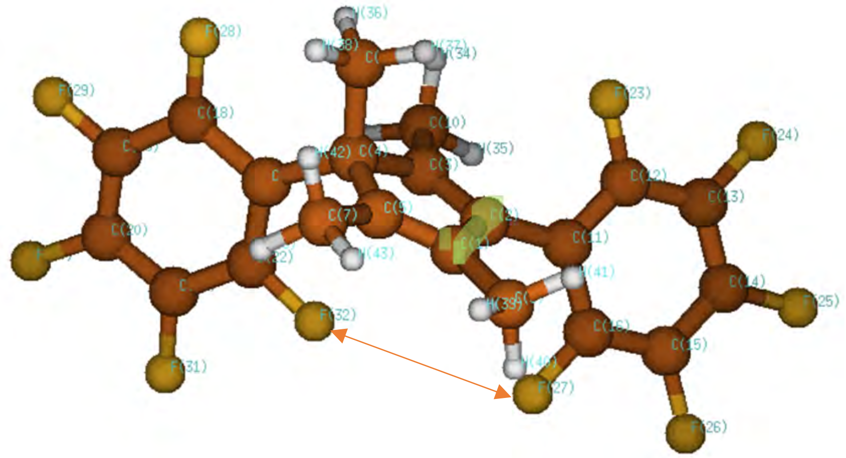


21. Contribution from the Diego Troya group.

Computational investigation of through-space ^{19}F-^{19}F nuclear spin coupling in fluxional molecules

W. Andy Lowe* and Dr. Diego Troya

Spin-spin coupling plays a key role in molecular structural determination using nuclear magnetic resonance (NMR) spectroscopy. While it is common to observe spin coupling between nuclei within three to four bonds, a compound synthesized in the lab of Dr. Deck showed ^{19}F-^{19}F coupling between atoms that are nine bonds apart (see below). Such finding suggests that the two fluorine atoms are coupling through space as opposed to through bonds, which challenges our current understanding of nuclear spin coupling. To shed light on the purported through-space coupling, we have augmented the NMR data using electronic structure calculations based on density functional theory. The vast conformational space of the fluxional molecule was characterized in detail via potential energy surface scans. Spin-spin coupling constants were calculated for 81 molecular geometries that capture the range of dynamic motion of the compound at room temperature. The coupling constants were averaged according to a Boltzmann distribution to provide a thermal coupling constant that can be compared with experiment. The calculations reveal an exponential dependence of the through-space coupling constant with the internuclear distance, suggests solvent treatment might be important in reproducing the experimental measurements quantitatively. The presence of through-space nuclear spin coupling can be used in the future to clarify the conformational space of large molecules in which intramolecular interactions might place NMR-active nuclei in close spatial proximity with each other, even if they are not within the covalent bonding range typically detected in NMR.



22. Contribution from the Michael Schulz group.

Synthesis of a Galili antigen epitope for treatment of *C. diff.* bacterial infections

Colleen Malley*, Brady Hallɣ, Michael Schulzɣ*
**Department of Materials Science and Engineering,ɣMacromolecules Innovation Institute,ɣ*Department of Chemistry*

Clostridium difficile (C. diff.) is a type of anaerobic, spore producing bacteria that it is ubiquitous in nature[1]. An image of the bacteria is located below in *Figure One*. While it is ubiquitous in nature, it can be incredibly dangerous when vulnerable populations are exposed to it[1]. Approximately 500,000 cases occur in the United States annually, with over 64% of cases originating in healthcare settings[1]. While *C. diff.* infections are a widespread problem, antibiotic resistance and problems with other common treatments makes treatment incredibly difficult[1]. The poster will outline the synthesis of a galili antigen epitope which will be appended onto a polymer in order to provide a new treatment for *C. diff* infections. This treatment has the potential to be incredibly beneficial because unlike traditional antibiotics, it will not elicit an immune response or cause antibiotic resistance. This is true because the galili antigen epitope has the ability to bind to the the toxins produced by *C. diff* instead of working to destroy the bacteria itself[2].

Background, synthetic route, advantages treatment, preliminary results, and future steps in treatment development will be included as part of the poster presentation. The structure of the galili antigen epitope is featured in *Figure Two* below.

Figure One: C. Diff.
Retrieved from wpmedia.o.canada.com

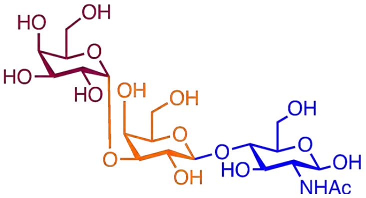


Figure Two: Galili Antigen Epitope

Sources

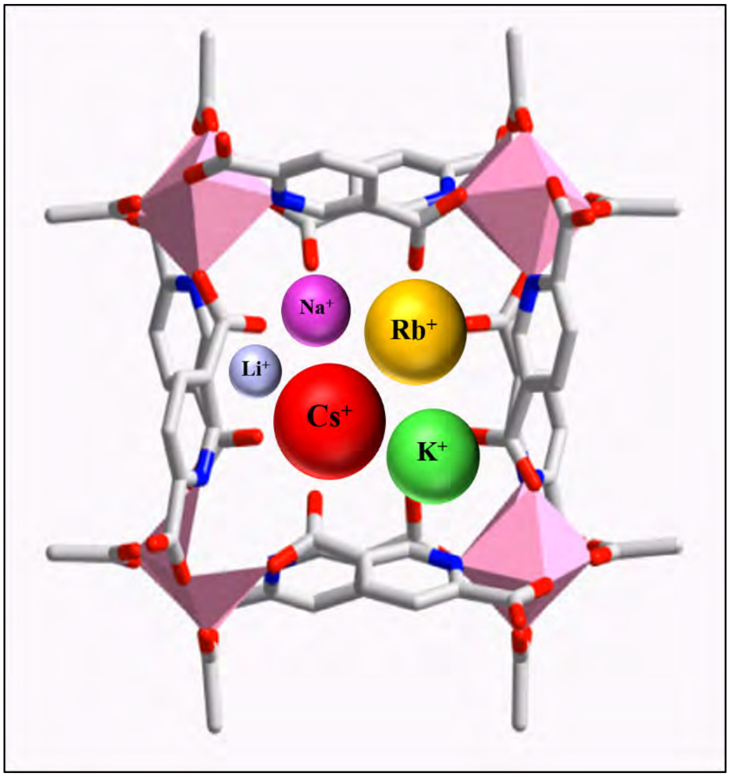
[1] Lessa, F. C; Mu, Y.; Bamberg, W.; et. al. Burden of *Clostridium difficile* infection in the United States*. New Engl. J. Med*. **2015,** 372, 825-834
[2] Macher, B. A.; Galili, U. The Galα1,3Galβ1,3GlcNAc-R(α-Gal) epitope: A Carbohydrate of Unique Evolution And Clinical Relevance. Biochim. Biophys. Acta **2008**,1780, 75-88.

23. Contribution from the Amanda Morris Group

Radioactive Waste Disposal: Cesium Capture by Aluminum-Based Supramolecular Cage

Ann Marie May*, Pavel Usov, Hannah Valentino, 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 environmental practices, such as ^{137}Cs capture from nuclear runoff. ^{137}Cs is a toxic, radioactive metal that poses harm to humans, aquatic life, and the environment. In this study, Cs^+ and other alkali metals bind to a porous Al-based supramolecular cage, Al-pdc-AA, for use in radioactive metal extractions from nuclear waste streams. Al-pdc-AA consists of pyridine-2,5-dicarboxylic acid organic ligands and dimeric Al-aceto nodes. Chemical characterization was conducted using ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, single crystal X-ray diffraction (SXRD), thermogravimetric analysis, and isothermal calorimetry (ITC). Titration studies utilizing ^{1}H NMR and ITC were conducted to characterize the binding of various alkali metals to the Al-based 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 were explored for the Al-pdc-AA cage. Preliminary findings show that the Al-based cage binds Cs in a 2:3 ratio. Future work will include the complex modelling of titrant binding, synthesis of analogous Al supramolecular cages and solid-state absorption of gases, such as nitrogen and carbon dioxide.



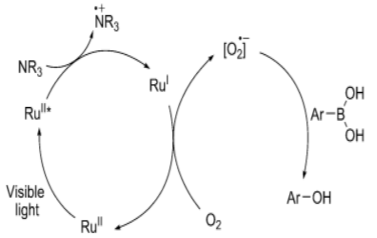
24. Contribution from the Amanda Morris Group

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

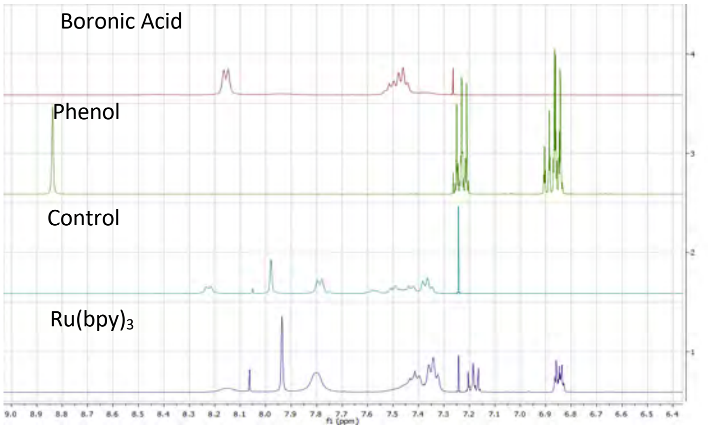
Michael McHale, Bradley Gibbons
Virginia Tech

Photocatalysis is an exciting field in chemical synthesis, as it promises green and sustainable reactions. This is a major goal of society, as current chemical synthesis can have adverse environmental effects[1]. Ruthenium based photocatalysis is already being explored as a potential solution to this issue. Many reactions have already been developed with this method[2], but oxidative reactions are particularly interesting. These reactions can use atmospheric oxygen as part of the catalysis, which further promotes sustainable reactions. However, the ruthenium catalyst is essentially lost in solution once used, which is wasteful. Ruthenium based MOFs provide a possible solution to this, as they can be recovered post reaction. They also provide a high concentration of active centres, and the tuneable pore size could provide greater percent yield.

The proposed mechanism is as follows. Under visible light radiation, ruthenium becomes excited and is then reduced by an amine in solution. It then donates a single electron to atmospheric oxygen, which then rearranges with the aryl boronic acid to produce a phenol product.



All reactions were conducted with 4-methoxyphenylboronic acid, triethylamine, and DMF under visible light radiation overnight. Four solutions were tested by NMR. One was the aryl boronic in DMF, one was the proposed phenol compound, one a reaction with all compounds except for the Ruthenium MOF (called control), and one was a reaction with catalysed with UiO-67. As shown by peaks around 6.85 and 7.25 ppm in the Ruthenium catalysed reaction, a product was formed that can reasonably be explained by peaks found in the pure phenol NMR. Notice how these peaks do not appear in the NMR of the boronic acid nor do the appear in the control. This indicated that the reaction was indeed catalysed by Ruthenium.



This experiment shows that this reaction can indeed be catalysed by a Ruthenium doped MOF. Further research should focus on characterizing yields with different MOF pore sizes. Other reaction should be test different reactions and their efficiency.

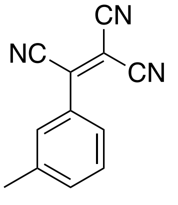
1. Poliakoff, M., Fitzpatrick, J.M., Farren, T.R., & Anastas, P.T. (2002) Green chemistry: science and politics of change. Science 297:807-810.
2. Zou, Y. , Chen, J. , Liu, X. , Lu, L. , Davis, R. L., Jørgensen, K. A. and Xiao, W. (2012), Highly Efficient Aerobic Oxidative Hydroxylation of Arylboronic Acids: Photoredox Catalysis Using Visible Light. Angew. Chem. Int. Ed., 51: 784-788. doi:10.1002/anie.20110702

25. Contribution from the Gordon Yee group.

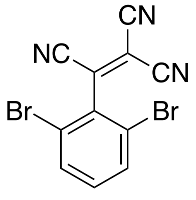
Synthesis of TCNE Analogues for Use in Ferrimagnetic Molecular Magnets

Steven D. Miller*, Christopher L. Houser, Gordon T. Yee
Virginia Tech, Department of Chemistry, Blacksburg, VA 24061 stevendm@vt.edu

Neutral vanadium can form a ferrimagnetic molecular magnet by reducing a small, organic molecule, such as tetracyanoethylene (TCNE).[1] The resulting building blocks combine to form a coordination network in which TCNE radicals bridge S = 3/2 V^{2+} cations. The spins on the organic bridge align antiferromagnetically to the spins on the metal ion to form a ferrimagnetically ordered solid. The Curie temperature, T_c, of the magnet can be manipulated by altering the organic molecule, referred to as the acceptor. From previous studies done on fluorinated phenyltricyanoethylene (PTCE) derivatives, a correlation between electron withdrawing groups, and therefore easier reduction, and higher T_c was identified.[2] This understanding is challenged by the observed T_c for PTCE compounds without electron withdrawing substituents.



(1)



(2)

Figure 1: Structures of 2-(3-methylphenyl)-1,1,2-tricyanoethylene **(1)** and 2-(2,6-dibromophenyl)-1,1,2-tricyanoethylene **(2)**

In this study, the compounds presented in **Figure 1** were synthesized from the corresponding benzaldehydes, 3-methylbenzaldehyde for **(1)** and 2,6-dibromobenzaldehyde for **(2)**. The $V[PTCE]_2 \bullet x(CH_2Cl_2)$ was then synthesized by reacting the acceptor molecules with $V(CO)_6$ in DCM under N_2. T_c for $V[3\text{-MePTCE}]_2 \bullet x(CH_2Cl_2)$ was found to be 200 K while the T_c for $V[2,6\text{-DBPTCE}]_2 \bullet x(CH_2Cl_2)$ was found to be 260 K. Compared to the base PTCE compound which orders at 215 K, the previous electronic understanding predicts significantly lower ordering temperatures than those observed for the electron donating methyl group and the weakly electronegative bromine groups.[2] This discrepancy can be rationalized by the steric effects of the substitutions disrupting the planar geometry, reducing conjugation of the acceptor molecules and increasing spin density on the nitrogen atoms.

1. Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. A Room Temperature Molecular/Organic-Based Magnet *Science* **1991**, *252*, 1415–1417. **DOI**: 10.1126/science.252.5011.1415
2. Harvey, M. D.; Crawford, T. D.; Yee, G. T. Room Temperature and Near-Room Temperature Molecule-Based Magnets *Inorg. Chem*. **2008**, *47*, 5649-5655. DOI**:** 10.1021/ic702359g

26. Contribution from the James Smyth group.

Investigating differences in pRb binding affinity between MAdV1 and MAdV3 E1A using surface plasmon resonance (SPR)

Douglas W. Murray III[1*], James W. Smyth[1,2]
[1]*Virginia Tech Carilion Research Institute and School of Medicine, Roanoke, Virginia, USA*
[2]*Virginia Polytechnic Institute and State University, Department of Biological Sciences, Blacksburg, Virginia, USA*

Adenoviruses are non-enveloped dsDNA viruses that cause a variety of human pathologies ranging from mild respiratory infections to severe conditions such as viral myocarditis. In order to enable replication of the viral DNA genome during infection, Adenovirus must uncouple cell cycle regulation, forcing the host cell into S-phase. Adenovirus early region 1A (E1A) is the first region of the viral genome to be expressed during infection. The E1A proteins facilitate subsequent viral gene expression while targeting cellular cell cycle checkpoint proteins such as the retinoblastoma protein (pRb) in order to enable S-phase entry. Though pRb normally exerts wide control over host cell gene expression through interactions with the E2F transcription factors, E1A bound pRb is inhibited. Mouse Adenovirus 1 (MAdV1) is a common model for studying adenovirus and can be isolated from lungs, kidneys, and ganglia cells of infected mice. A recently isolated virus, referred to as Mouse Adenovirus 3 (MAdV3) was reported to have cardiotropic characteristics.[1] Interestingly, the region of least conservation between MAdV1 and MAdV3 genomes is E1A[1], leading us to hypothesize that altered pRb interaction may influence tissue tropism. MAdV1 and MAdV3 E1A pRb binding motifs were amplified and cloned into the pGEX-6P-2 plasmid for expression and *in vitro* purification. Similarly, the sequence of pRb known to interact with E1A will be cloned and purified. We will then employ surface plasmon resonance (SPR), to measure the binding affinities of MAdV1 and MAdV3 E1A to pRb. This work will provide valuable insight into the role of cell-cycle perturbation in serotype-specific adenoviral disease progression.

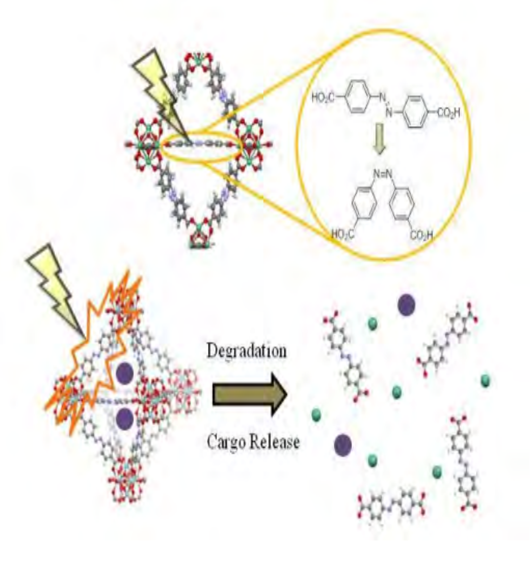
1. Klempa, B.; Krüger, D. H.; Auste, B.; Stanko, M.; Krawczyk, A.; Nickel, K. F.; Überla, K.; Stang, A., A Novel Cardiotropic Murine Adenovirus Representing a Distinct Species of Mastadenoviruses. *Journal of Virology* **2009,** *83* (11), 5749.

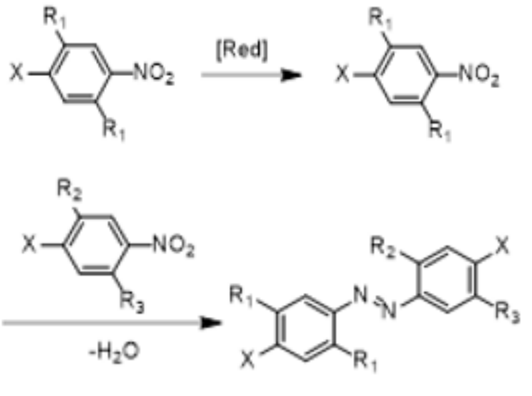
27. Contribution from the Amanda Morris group.

Synthesis and Modification of a Metal Organic Framework for Controllable Drug Delivery

Joshua J Novak*, Hannah D. Cornell, Amanda J. Morris
Virginia Tech Chemistry Department

A Metal Organic Framework (MOF) is the product of inorganic metallic nodes connected by organic linkers to form a cage-like compound. Along with being synthetically tunable and porous, these frameworks offer high versatility and can thus, uptake very complex molecular compounds into their pore space. In biomedical applications, this results in the ability to have an extremely high drug loading capacity.[1] Through the incorporation of a photo-isomerizable linker (azobenzene) into the backbone of the metal organic framework, we generated a material (UiO-AZB) that is photo-degradable.[2] Thus, when these linkers are exposed to light, isomerization results in a release of drug cargo. The MOF were characterized using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and surface area analysis. Additionally, the rate of degradation was determined in simulated cerebrospinal fluid (HEPES buffer). Cell studies were carried out and the drug-carrier conjugate was effective at initiating apoptosis upon irradiation. Importantly, the cells remain viable in the presence of loaded but unirradiated carriers. However, azobenzene absorbs around 394nm which is outside of the range of the therapeutic window of 650nm. Therefore, we have moved into synthesizing an analog of azobenzene with attachments of strong electron donating groups onto the benzene ring to shift the absorbance to the desired range.





$X = CO_2H$; $R_1 = Cl, F, NO_2, CN$; $R_2 = NH_2$; $R_3 = NHCH_3$

1. Della Rocca, J.; Liu, D.; Lin, W., Nanoscale Metal–Organic Frameworks for Biomedical Imaging and Drug Delivery. *Accounts of Chemical Research* **2011,** *44* (10), 957-968.
2. Brown, S. B.; Brown, E. A.; Walker, I. The present and future role of photodynamic therapy in cancer treatment. *The Lancet Oncology*, *5*, 497.

28. Contribution from the John Matson group.

Bottlebrush Polymer Synthesis by Ring-Opening Metathesis Polymerization: Anchor Group Importance

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

Bottlebrush polymers are of significant importance due to the unique architecture and physical properties that are a result of polymer topology. An important characteristic is the ability to undergo synthesis by means of ring-opening metathesis polymerization (ROMP) on macromonomers. Our group is interested in comparing the effect of different catalysts on the kinetics of ROMP, as well as the significance of the anchor group. To accomplish this task, we prepared a variety of different anchor groups to be tested through ROMP reactions. The significance of the anchor group on the polymerizable norbornene is important as it contains the double bonds that are opened during ROMP. Experimental and computational studies have illustrated that the rate differences of ROMP are more likely due to the steric hindrances and electronic repulsion of the anchor group rather than other factors. The catalysts being compared are $C_{43}H_{72}Cl_2P_2Ru$ (Grubbs' first-generation catalyst) and $C_{46}H_{65}Cl_2N_2PRu$ (Grubbs' third generation catalyst). The catalysts are being used to help distinguish important trends within the anchor groups effect on ROMP. To fully optimize the control of the kinetics, a ratio of catalyst to solvent has been determined based on the anchor groups. As well, the set time points are determined by the previous paper on Grubbs' third generation catalyst as well as the previous data recorded on the anchor groups. The trials were repeated several times to hopefully create a consistent average based on the kinetics of the reaction.

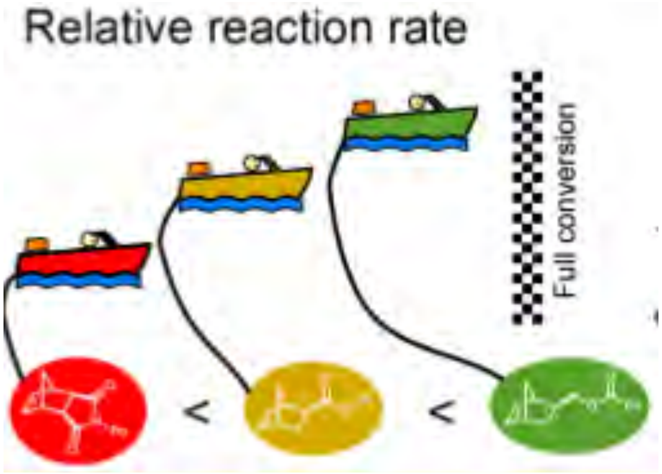


Figure 1: Comparison of anchor groups to the relative reaction rate of ROMP

29. Contribution from Feng Lin group.

Amorphous and Semicrystalline Carbon Materials from Biomass for Use in Batteries

Qingping Hou1*, Linqin Mu2, Yiming Feng3, Haibo Huang3, Feng Lin2

1. Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia, 24060
2. Department of Chemistry, Virginia Tech, Blacksburg, Virginia, 24060
3. Department of Food Science and Technology, Virginia Tech, Blacksburg, Virginia, 24060

With the severe shortage of crude oil resources and ever-growing energy consumption, there has been an increasing and urgent demand for exploring cost-effective, green and sustainable energy storage systems. Lithium ion batteries have attracted more and more attention as the most efficient, emerging energy storage dev ices that are also environmentally friendly. It is well-known that carbon based anode materials have been holding a predominant position and are widely employed for electrode materials, due to their low-cost, high electronic conductivity and excellent cycle stability. Graphite have been explored to be one of the best carbon materials for electrode materials due to their excellent electronic conductivity. However, they suffered from fixed maximum capacity of Li6C structure. Amorphous and semi crystalline hard carbon materials can offer both pseudocapacitive and intercalation properties, which will potentially increase the anode practical capacity..

Biomass composition is different in each biomass material. Usually, cellulose, hemicellulose, and lignin are the three basic components of biomass. Influences of different composition biomass on the derived hard carbonaceous materials were performed in this poster. In this research, brew, Grape pomace and Walnut Shell biomass were used as raw material for carbon anode first stage synthesis. The structure of carbon materials is depend on the carbonization temperature of biomass. Usually, the extremely high temperature treatment forces changing of carbonization structure. In this research, temperatures at 1000℃, 1200℃ and 1400℃ were tested on every material. XRD, SEM, Raman spectroscopy and batteries electrochemistry testing system were used in investigating materials' structure, carbonization types and electrochemical performance data.

Biomass Type	**Cellulose**	**Hemicellulose**	**Lignin**	**Protein**	**Majority Composition**
Brew Grain	17.2%	17.4%	11.3%	22.9%	None
Grape Pomace	12.41%	10.78%	54%	11.7%	Lignin
Walnut Shell	46%	24%	25%	1%	Cellulose

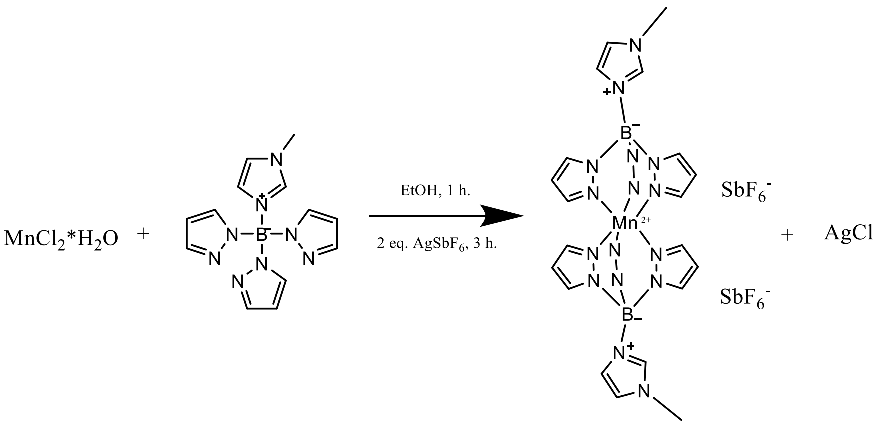
Table 1. Biomass Material Composition Table

30. Contribution from the Amanda Morris group.

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. Utilizing a zwitterionic ligand preserved the presence of the borate anion allowing a charged M-complex to be synthesised with similar electronic properties to that of the parent $MnTp_2$ complex while maintaining a positive formal charge on the coordination complex. This allows the solubility of the complex to be controlled through the identity of the anion.

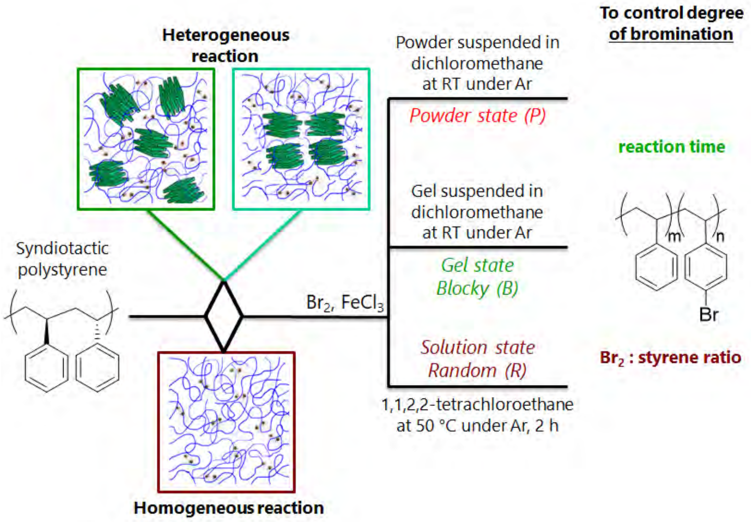


31. Contribution from the Robert Moore group.

Blocky bromination of syndiotactic polystyrene via post-polymerization functionalization in the powder state, a control study

Helen T. Tran*, Kristen F. Noble and Robert B. Moore
Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

The Moore group is interested in preparing copolymers with blocky (i.e., non-random) microstructures using a post-polymerization functionalization method carried out in the gel state. Previously, we have prepared highly brominated blocky copolymers of syndiotactic polystyrene (sPS-co-sPS-Br) with up to 32 mol% *p*-bromostyrene units using this method. In the gel network, the accessibility of the brominating reagent is limited to the monomer units in the amorphous domains because these domains are swollen with solvent. We hypothesized that a gel network is essential for producing blocky copolymers with a high Br-content. To test this hypothesis, the current work is focused on the bromination of sPS powder prepared by dissolving sPS pellets in 1,1,2,2-tetrachloroethane (TCE), precipitating in methanol, washing by Soxhlet extraction in hot methanol, drying under vacuum, and mechanically grinding with a mortar and pestle. In the powder state, the amorphous and crystalline domains are collapsed because the solvent has been removed from the amorphous component. Therefore, bromination is expected to occur only at the surface of the particles. A series of sPS-co-sPS-Br copolymers with varying Br-content were prepared from an sPS powder using the same method used for gel-state bromination. In order to analyze the properties of both the gel and powder samples, NMR spectroscopy was used to investigate the degree of bromination and copolymer microstructure, X-ray diffraction was used to probe the sPS homopolymer powder morphology, and differential scanning calorimetry was used to assess the copolymer thermal properties. In the powder state, Br-content was limited to 12 mol% *p*-bromostyrene units which supports the hypothesis. The broader impact of this research is that it demonstrates that the state of the homopolymer (i.e, powder-, gel-, or solution-state) may be used to tailor the copolymer microstructure, which may be useful in designing new transport membranes, shape memory materials, and for nanopatterning technologies.



Schematic representation of the preparation of sPS-co-sPS-Br in the powder, gel, and solution states. Image prepared by Kristen Noble.

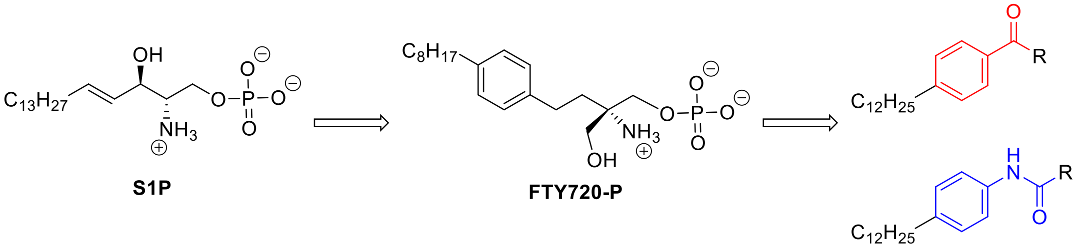
32. Contribution from the Webster Santos group.

Structure-Activity Relationship Study of FTY720-P Derived Inhibitors of Spinster Homolog 2

Gregory M. Traversa* and Webster L. Santos
Department of Chemistry, Virginia Tech, Blacksburg, VA 24061

Spinster homolog 2 (Spns2) is a member of the major facilitator superfamily of transmembrane proteins and has been shown to mediate the transport of sphingosine-1-phosphate (S1P) across the cell membrane in humans.[1] S1P is a sphingolipid signalling molecule formed in the intracellular environment through the phosphorylation of the lipid sphingosine by sphingosine kinase 1 (SphK1) and sphingosine kinase 2 (SphK2). S1P promotes cell growth, survival, proliferation, inflammation, and migration; and regulates vascular and immune systems through agonism of five G protein-coupled receptors ($S1P_{1-5}$) on the extracellular side of the cell membrane.[2] Correspondingly, elevated levels of S1P has been linked to diseases such as cancer, fibrosis, and sickle cell disease.[3] With this evidence making the transport of S1P a therapeutic target of interest, the inhibition of Spns2 through small molecule intervention proves promising and is the basis for this structure-activity relationship study.

The immunomodulating agent FTY720 is a prodrug that must first be phosphorylated to the active compound FTY720-P by SphK2. FTY720-P is a compound similar in structure to S1P and is a high-affinity agonist for the $S1P_{1,3-5}$ receptors.[1] The transport of FTY720-P across the cell membrane has also been shown to be mediated by Spns2, making the structure of FTY720-P the foundation for the potential inhibitors synthesized in this study.[1] The compounds developed can be classified into two main categories based upon whether the scaffold of the structure contains a benzoyl or benzyl carboxamide group, and vary within the categories from one another based upon the amino acid head group.



(1) Hisano, Y.; Kobayashi, N.; Kawahara, A.; Yamaguchi, A.; Nishi, T. The Sphingosine 1-Phosphate Transporter, SPNS2, Functions as a Transporter of the Phosphorylated Form of the Immunomodulating Agent FTY720. *J. Biol. Chem.* **2011**, *286* (3), 1758–1766.
(2) Santos, W. L.; Lynch, K. R. Drugging Sphingosine Kinases. *ACS Chem. Biol.* **2015**, *10* (1), 225—233.
(3) Schnute, M. E.; McReynolds, M. D.; Carroll, J.; Chrencik, J.; Highkin, M. K.; Iyanar, K.; Jerome, G.; Rains, J. W.; Saabye, M.; Scholten, J. A.; et al. Discovery of a Potent and Selective Sphingosine Kinase 1 Inhibitor through the Molecular Combination of Chemotype-Distinct Screening Hits. *J. Med. Chem.* **2017**, *60* (6), 2562–2572.

33. Contribution from the Gordon Yee group.

Synthesis of 2- and 4 - bromophenyltricyanotheylenethe: A Building Block for a Molecule-Based Magnet

Isabella M. Ulate*, 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 the variety of applications these compounds have in electronic devices that use magnets as part of their electronics. A tetracyanoethylene (TCNE) analogue is intriguing because as the analogue structure changes, the structure of the vanadium complex could change, possibly improving the magnetic ordering temperature.[2] This semester's project was to complete the synthesis of a tricyanoethylene derivative that used a halide 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 larger size of the bromine substituent will affect the vanadium complex's magnetic character in a positive way. Magnetic properties will be measured using the superconducting quantum interference device (SQUID) and have its magnetic ordering temperature measured. The TCNE derivatives 2- and 4-bromophenyltricyanoethylene (BPTCNE) were synthesized using 2- and 4-bromobenzaldehyde respectively and malononitrile as starting materials (Figure 1).

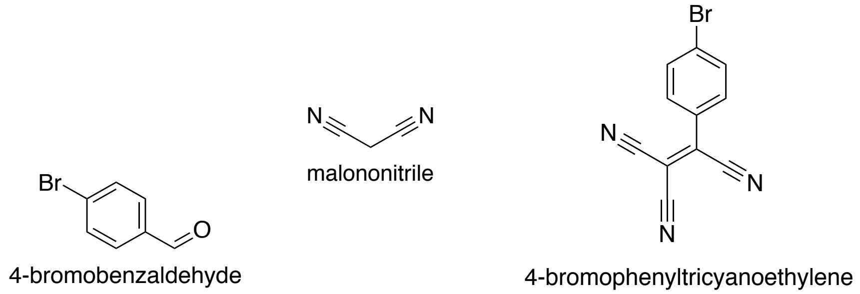


Figure 1. Shown above are the starting materials 4-bromobenzaldehyde and malononitrile as well as the final product 4-BPTCNE of this synthesis. The synthesis of 2- BPTCNE is performed using the 2-bromobenzaldehyde.

The 4-BPTCNE synthesis was successful with a 69% yield, and the 2-BPTCNE synthesis resulted in an 82 % yield. The ordering temperature of the compounds when it complexed to vanadium as in V(2- and 4- BTCNE)$_2\cdot x$CH$_2$Cl$_2$ was 220 K and 100 K respectively. Going forward, the project will involve making the 3-bromo derivative, along with creating derivatives substituted in multiple places with bromine groups. After evaluating the ordering temperatures of all the variously substituted compounds, we should be able to see relationships between magnetic ordering temperatures and substituent placement and size when considering the previously synthesized fluorophenyl and chlorophenyl analogs.

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.

34. Contribution from the John Matson group.

A Persulfide Releasing Small Molecule Prodrug Specific to Alkaline Phosphatase

Ethan Winckler
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. Particularly in systems where alkaline phosphatase (ALP) is overexpressed or upregulated, such as in osteosarcomas.[1] Currently, there are no small molecule persulfide-donor compounds that are selective toward alkaline phosphatase, which would enable the study of persulfides under these conditions. The goal of this project is to synthesize a persulfide releasing prodrug, termed PDP-NAC, which would respond specifically to alkaline phosphatase. The synthesis of the molecule was achieved in six steps, where each reaction included a synthesis, a work-up to separate and dry products, and a silica-gel purification step to isolate the desired product. 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 PDP-NAC in the presence of ALP will be studied by both NMR and mass spectrometry to better understand the timescale of persulfide release under biologically relevant conditions. Once the kinetics of persulfide release is better understood in vitro studies will ensue. This molecule will allow for biologists to better isolate the role that persulfides play in ALP overexpressed systems.

Referenes
(1) Bramer, J. A. M.; Abudu, A. A.; Tillman, R. M.; Carter, S. R.; Sumathi, V. P.; Grimer, R. J. *Eur. J. Cancer* 2005, *41* (18), 2846–2852.

Ethan W. Winckler*, Kearsley M. Dillon, Chadwick R. Powell and John B. Matson

35. Contribution from the Feng Lin group.

Selective Doping of Cobalt-Free Cathode Materials for Lithium Ion Batteries

Benjamin Z. Zydlewski*, Troy Gustke, Linqin Mu, and Feng Lin
The Lin Research Group at Virginia Tech

Our research focuses on synthesizing new lithium metal oxides that can be employed as cathode materials in lithium ion batteries. Previous research focused on $Li(Ni_xMn_yCo_z)O_2$ (NMC) materials where $x + y + z = 1$. Our research focused on moving towards a much higher nickel content in the NMC materials, due to the increased capacity it offers. Though, the increasing nickel content lead to more capacity fading most likely caused by structural changes in the material throughout cycling. The focus on increased nickel content was also due to the appeal of limiting the amount of cobalt used, due to its high cost and toxicity. This pushed our research towards a completely cobalt free material. Pure $LiNiO_2$ has poor capacity retention due to changes in the crystal structure that impede lithium intercalation, so metal dopants were used to try to stabilize the layered material to increase its cycle life, while maintaining the high capacity associated with high nickel content. Titanium doping was initially used because of the similar ionic size of the Ti^{4+} ion to the Ni^{2+} cation, which would allow the titanium to occupy the same sites in the layered structure of the material. Magnesium was also doped into the material, with the Mg^{2+} cation also having a similar atomic radius to that of nickel cations. Both the titanium and the magnesium are able to occupy the nickel sites in the crystal structure, but neither of them are electrochemically active within the operating voltage window. This allows them to stabilize the crystal structure as the nickel is oxidized and reduced during cycling. Multiple materials were synthesized but the one that showed the best electrochemical performance was $LiNi_{0.96}Mg_xTi_yO_2$. In addition to electrochemical testing, x-ray absorption spectroscopy was conducted to track changes in the oxidation state of nickel throughout different stages of cycling. TEM and SEM images were also taken of the material.

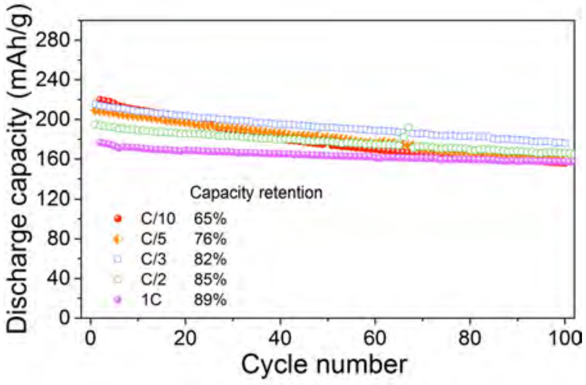


Figure 1. Discharge capacity vs cycle number of $LiNi_{0.96}Mg_xTi_yO_2$ against lithium metal at various c-rates.

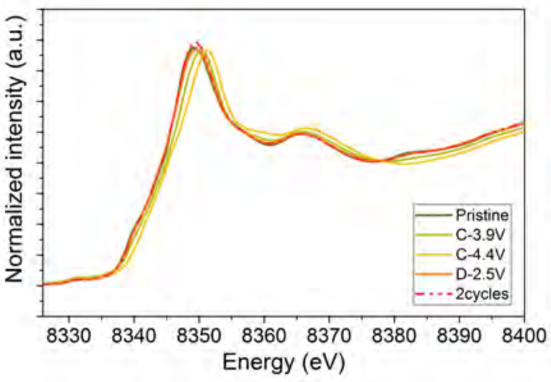


Figure 2. Nickel K-edge X-ray absorption spectra of $LiNi_{0.96}Mg_xTi_yO_2$ at various states of charge.

36. Contribution from the Feng Lin group.

Compositional Design of Inorganic Oxide Nanoparticles in Ionic Liquid Gel Polymer Electrolytes (ILGPE) for Solid-State Lithium Metal Batteries

Dr. Feng Lin, Xiaona Pan and Nasar Maung*
Virginia Tech, Department of Chemistry, College of Science - Nanoscience

Driven by the apparent drawbacks of the lithium ion battery, researchers are looking towards the safer and potentially viable solid state battery for use in the technology of the future. As such, we discuss the importance and viability of the gel polymer electrolyte as an alternative to the currently used organic liquid electrolytes. Our efforts to synthesize and characterize a range of nanofiller-polymer composite electrolytes for use in solid state batteries are displayed. The composite electrolyte consists of room-temperature ionic liquid (N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide), inorganic oxide nanoparticles, poly(vinylidene fluoride-hexafluoropropylene) polymer, and lithium bis(trifluoromethanesulfonyl)imide salt. The inorganic oxide nanoparticles include SiO2, Al2O3, NiO, MgO, CeO2, Bi2O3, TiO2, zeolites, etc. The underlying hypothesis is that adding inorganic oxide nanoparticles can reduce the crystallinity of the polymer and alter the lithium diffusion pathways in the polymer electrolyte as seen in Figure 1.

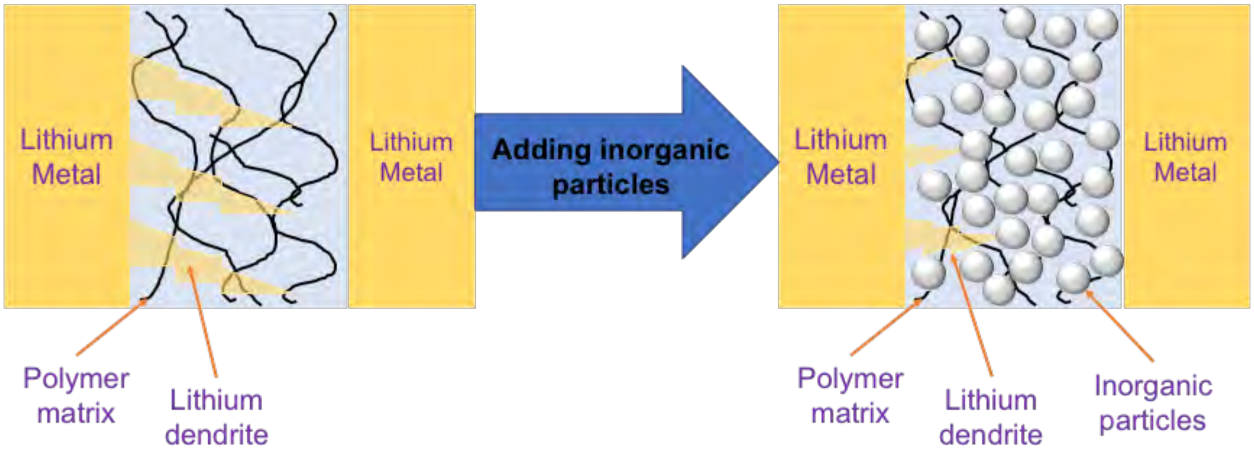


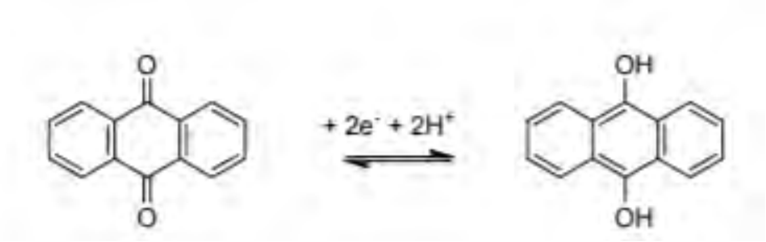
Figure 1. Comparison between standard Gel Polymer Electrolyte and Proposed Composite Polymer Electrolyte

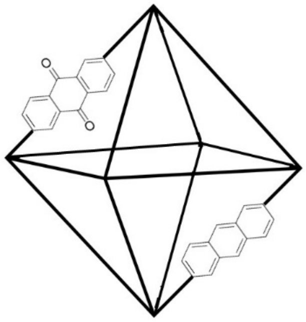
37. Contribution from Amanda Morris Group.

Synthesis and Characterization of Anthraquinone-Anthracene Mixed Metal Organic Frameworks

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

An artificial photosynthetic assembly can utilize metal-organic frameworks (MOFs) in order to both absorb light energy into electrical energy and facilitate the transport of photoelectrons. 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. Additionally, 2,6-Zr-AQ-MOF, utilizing 2,6 anthraquinone (2,6-ADCQ), is an effective material to transport electrons. The 2,6-ADCA ligand and the 2,6-ADCQ ligand were combined using previous methodology 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, a process which can ultimately be used for capacitor devices within artificial photosynthetic assemblies.





1. Rowe, J. M.; Soderststrom, E. M.; Zhu, J.; Usov, P. M.; Morris, A. J., Synthesis, Characterization, and luminescent properties of two new Zr(IV) metal-organic frameworks based on anthracene derivatives. *Canadian Journal of Chemistry* **2017,** 00 (0000), 1-6.

2. Celis-Salazar, P. J.; Epley, C. C.; Ahrenholtz, S. R.; Maza, W. A.; Usov, P. M.; Morris, A. J., Proton-Coupled Electron Transport in Anthraquinone-Based Zirconium Metal–Organic Frameworks. *Inorganic Chemistry* **2017,** *56* (22), 13741-13747.

ACKNOWLEDGMENTS

The support of the Department of Chemistry and its commitment to undergraduate research is gratefully acknowledged including the printing of the posters and sponsoring lunch.

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.