ABSTRACTS

Undergraduate Research in Chemistry Regional Poster Competition

114 Chemistry-Physics Building
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Department of Chemistry
University of Kentucky
Lexington, KY 40506

Author Index of Abstracts

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OVERALL SYNTHESIS OF ERGOVALINE: SYNTHESIS OF (S)-ETHYL BENZYLOXY-METHYL MALONATE ACYL CHLORIDE

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	Freshman		Sophomore		Junior	x	Senior

The experiments consist of a subset of reactions contributing to the overall synthesis of ergovaline: a biologically active mycotoxin isolated from tall fescue grasses infested with the fungus Neotyphodium lolii. The subset reported here is the 5-step synthesis of ethyl benzyloxy-methyl malonate acyl chloride from diethyl methyl malonate. The defining feature of the synthesis includes the crystallization of (R) ethyl benzyloxy-methyl malonate using the resolution agent S-α-methyl-benzyl amine and the subsequent chlorination using thionyl chloride to produce the proper stereochemical structure for the tripeptide component of ergovaline. Qualitative analysis of products carried out by silica column chromatography and thin layer chromatography. Structural analysis of products was primarily determined using NMR spectrophotometry and D.A.R.T. mass spectrometry.

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SILICON ANODE FABRICATION WITH POLYMER BINDERS FOR OPTIMIZING LITHIUM-ION BATTERY PERFORMANCE

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	Freshman		Sophomore	X	Junior		Senior

Silicon is a promising new anode material due to its high gravimetric capacity and its potential for improved battery performance. However, silicon microparticles in the anode swell to upward of 400% their original size upon battery charging. Repeated lithiation and delithiation cycles result in drastic volume fluctuations in the silicon microparticles as lithium ions enter and leave the anode. This expansion and contraction causes the microparticles to crack and fracture upon repeated charging cycles, drastically reducing the performance and capacity of the anode over time. An appropriate polymer binder for the anode of lithium-ion batteries may allow the silicon microparticles to expand and contract while maintaining connectivity and conductivity for constant battery cycling. The binder may act as a cross-linking material to connect silicon microparticles together while keeping the components flexible to reorganize upon volume fluctuations. Improving the stability of the silicon active material in battery anodes is key in extending their lifetimes to create long lasting and more powerful lithium-ion batteries. In this project, a variety of polymers were screened as binders for the fabrication of a silicon microparticle anode; these polymers included polyvinylidene fluoride, polyethylene glycol, poly(D,L-lactide-co-glycolide), and polyacrylic acid. Potential polymers were selected based on their chemical and physical properties, including electron withdrawing capabilities and solubility in organic solvents. Electrode fabrication methods were also optimized to produce uniform functional electrode materials. Ultimately, the addition of an effective polymer binder may allow for silicon to replace graphitic carbon as the anode active material in lithium-ion batteries. Developing silicon-based anodes would drastically increase the battery capacity and lifetime.

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SPONGY AND RESPONSIVE PVDF-BASED MEMBRANES FOR WATER RELATED APPLICATIONS

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The use of functionalized membranes for any number of applications is greatly increasing. It is often desired for these membranes to exhibit a high degree of functionalization so as to maximize the impact of their use. In this study, flat sheet poly(vinylidene fluoride) (PVDF) membranes are synthesized to have a thick cross section and spongy interior morphology using an immersion precipitation phase inversion technique. The result of this is a membrane with greatly increased interior surface area which allows for a high degree of membrane functionalization. The equilibrium relationship between polymer and solvent was manipulated to create a thick and spongy membrane by using dimethylformamide (DMF) as solvent and an elevated membrane casting temperature of 35 C - 40 C. The use of scanning electron microscopy (SEM) allowed for the examination of membrane morphology where a dense membrane top layer and open substructure were found. Spongy membranes were functionalized in this study using poly(acrylic acid) (PAA) and a higher degree of PAA functionalization over non-spongy membranes was found to be possible. The PAA functionalization allows for the membrane flux to be modulated by varying pH. Spongy membranes have also shown highly enhanced divalent calcium and iron ion pick up over non-spongy membranes under batch and convective flow conditions. Iron and iron oxide nanoparticles are also synthesized directly in these membranes to create advanced nano-composite systems with high nanoparticle functionalization capabilities. Membranes functionalized with iron oxide nanoparticles will be tested for their ability to degrade naphthenic acids in an application to make oil/gas industry process water more safe before discharge. Through this study, it has been shown that the synthesis of spongy PVDF membranes allows for increased functionalization allowing for tunable and high capacity performance in many applications. This project has been supported by NIH-NIEHS-SRP, and by NSF EPSCOR program.

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ELECTRON RICH PHOSPHINIMINES: CATALYSTS FOR POLYMERIZATION OF CYCLIC ESTERS

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	Freshman		Sophomore		Junior	X	Senior

The investigation and development of new phosphinimines for use as Brønsted bases in the catalytic ring opening polymerization (ROP) of cyclic esters, such as L-lactide (LA) and ε-caprolactone (CL), to produce biodegradable polymers has been investigated. The potential basicity of the synthesized phosphinimines has been evaluated via solution interactions with an alcohol using 1H and 31P NMR spectroscopy. Based on these results, we have screened our phosphinimine library as organic catalysts for the ROP of L-lactide in chlorinated solvents. Initial polymerization results show that solvent, and the structure of the alcohol initiator play an important role in these polymerization reactions. We believe our method for screening basicity based on hydrogen bonding interactions in solution can be applied to a variety of organocatalyzed reactions.

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CONTROL OF PEROVSKITE MORPHOLOGY ON FTO FOR BETTER SOLAR CELLS EFFICIENCY

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	Freshman		Sophomore	X	Junior		Senior

Improvement and growth of production of a cheap and clean energy is a great interest for our society, projections have shown great advances by solar cells. In this context, using Peroviskite, as a key component for solar cells, has increased in the past years, considering its abundance, low costs, simplicity of their processing, non-toxicity and good efficiency that has grown quickly. Although, morphology control is critical to achieve high efficient. Growth of crystalline Peroviskite films has interferences as the type of substrate, temperature, pressure and solvent. For better efficiency, the films must be smooth on the surface, reducing holes, and with high crystallinity. For this work, the use of the 3-Aminophosphonic Acid and Carboxylic Acid will direct the growth of the crystals, giving a high-quality crystalline film with a precise control over thickness. From the created samples, different morphologies by each acid are compared. This photocell has as structure FTO films coated with TiO2 by spin coat method, then the adsorption of the different acids that will lead, finally, the growth of Perovskite crystals. Images of AFM, SEM and XPS from each sample are showed and discussed in this work.

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PROBING THE REACTIVITY OF DIALKOXYBENZENE-BASED REDOX SHUTTLES IN LITHIUM ION BATTERIES

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Lithium-ion batteries have become ubiquitous with portable electronics and transportation vehicles due to their high capacity and energy density, long shelf life, and lack of memory effect. Despite this prevalence in commercial use, safety issues associated with LIBs have hindered their use in broader applications. One such issue is that of overcharge abuse, which occurs in cells connected in series. A cost effective method to combat this rise in cell voltage is to incorporate an additive directly into the electrolyte that shunt the excess current. These small organic molecules, coined redox shuttles, are subject to chemical degradation from repeated cycling as well as the demanding chemical environment within the battery. To gain a better understanding of redox shuttle reactivity within the battery we examined a functionally diverse group of dialkoxybenzene derivatives. We used bulk electrolysis and chemical reagents to simulate the battery environment and the decomposition products were characterized. Ultimately, we want to gain insight on the mechanisms of redox shuttle failure in order to synthesize next generation molecules with greater longevity and performance.

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FABRICATION AND APPLICATION OF NANOARRAYS COUPLED WITH MICROFLUIDICS FOR SINGLE MOLECULE IMAGING OF MEMBRANE RECEPTORS

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The study of single molecules in biology and chemistry provides important information about the properties of individual molecules, such as the behavior of specific receptors or ion channels within a cell. Single-molecule fluorescence spectroscopy is a method that is useful for imaging and analyzing such single-molecule properties. Nanofabricated devices such as zero-mode waveguides can be used for these applications; however, they are expensive and take a lot of time to manufacture. We will devise a cheap and relatively quick method to fabricate arrays of nanoscale holes in metallic films. Our procedure will utilize photolithography combined with microsphere lithography. The mask that will be used for photolithography has a uniform pattern of round holes that are 1 micron apart and in diameter. Once the pattern is transferred to the substrate, we will add etched, 200 nm carboxylate microspheres (beads) to the surface, remove the resist, cover the surface with a metal, and lift-off the beads. This fabrication method will create wells on the substrate that are about 200 nm in diameter but with the uniform spacing and size typically achieved with nanofabrication techniques. These wells will be coupled with microfluidics to isolate single membrane receptors in cells. The microchannels in microfluidic devices, connected to the outside by piercings of inputs and outputs, allow for isolation of single cells and the controlled delivery of reagents to these isolated areas. Once the devices are created, they will be used in biological studies. For example, the devices can be used to image and then analyze binding correlation of EGF (Epidermal growth factor) to EGFR-GFP (Epidermal growth factor receptor-green fluorescent protein) in N2a cells (mouse neuroblastoma cell line) with laser spectroscopy. Because EGFR cannot be purified outside of the cell membrane, it is necessary to transfect cells with the protein in order to image the functions of EGFR. So far, we have already seen that binding correlation occurs in 1 micron wells and some 200 nm wells.

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FLUORESCENT REPORTERS IN MEMBRANE-BOUND ION CHANNELS

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Tagging proteins of interest with fluorescent reporters is a common and reliable method of visualizing the function of a specific protein in vivo. The protein of interest in this project is ENaC, a trimeric epithelial sodium channel comprised of three subunits, α, β, and γ. ENaC is believed to play a role in cystic fibrosis, but its interaction with CFTR is not fully known. By fluorescently tagging each subunit ENaC with a red fluorescent reporter, mCherry, and co-transfecting it with a GFP-tagged CFTR, confocal fluorescent microscopy and traditional fluorescent microscopy can be performed to see if these two membrane proteins co-localize at the plasma membrane. Potentially, the roles of each specific subunit of ENaC in membrane ion transport and cystic fibrosis could be determined. In this project, the fluorescent reporter mCherry has been cloned onto the N-terminal of each subunit of ENaC. These fusion genes were cloned into a 4 T/O tetracycline induced plasmid, which were transiently transfected into T-Rex adrenal cells. Images have been taken of ENaC in cells, and a healthy cell line is being selected. This experiment could provide insightful information on the role of other membrane ion channels in cystic fibrosis, and potentially identify a new target for drugs that combat CF.

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DETECTION OF PATHOGEN-SPECIFIC DNA SEQUENCES UTILIZING ENGINEERED ZINC FINGER PROTEINS

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	Freshman		Sophomore		Junior	x	Senior

The visual detection of specific double-stranded DNA sequences possesses great potential for development of diagnostics. Zinc finger domains provide a powerful scaffold for creating custom DNA-binding proteins that recognize specific DNA sequences. We previously demonstrated a proof of concept where a ZFP array was developed to recognize specific bacterial DNA utilizing sequence-enabled reassembly of TEM-1 β-lactamase (SEER-LAC), a system consisting of two inactive fragments of β-lactamase each linked to engineered ZFPs. Here, ZFPs were engineered to recognize pathogen-specific DNA sequences encoding for shiga toxin present in E. coli O157.

The ZFP array with the SEER-LAC system provided a quantitative assay with a detection limit of 10 fmole of target DNA and high specificity to recognize specific DNA sequences. These results suggest that the ZFP array has the potential to be developed into a simple and rapid point-of-care (POC) diagnostic for the multiplexed detection of pathogens.

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ECO-FRIENDLY SYNTHESIS OF CEFTAZIDIME GOLD NANOPARTICLES AND EVALUATION OF ITS ANTIBACTERIAL ACTIVITY

William Hamilton, *Tulsi Modi, Hitesh Kumar Waghwani, Sarah Tockstein, Jason Payne, Dr. Rajalingam Dakshinamurthy*

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	Freshman		Sophomore	X	Junior		Senior

Resistance is a consequence of evolution, accelerated by human action. Antibiotic resistance, a global concern, is increasingly straining current antibiotic therapies to treat bacterial infections. There is a desperate need for innovating new antibiotic treatment courses in response to the soaring increase in cases of multi-drug resistant (MDR) bacteria, which are commonly known as “superbugs”. In this research we have tried to design an effective antibacterial agent involving gold nanoparticles (AuNPs) capped with an antibiotic (ceftazidime). By keeping the twelve principles of ‘green chemistry’ in mind an unique, single step synthesis process which is unlike conventional methods, was fabricated for making AuNPs. Using the combined reducing and capping ability of ceftazidime we were able to produce ceftazidime capped gold nanoparticles (C-AuNPs). These nanoparticles were then characterized using various analytical techniques such as TEM, TGA, SEM and UV-Vis spectroscopy to determine their morphology. Antibiotic efficiency of C-AuNPs was assessed using several antibacterial assays such as turbidimetry, spread plate method and XTT assay. A variety of bacterial strains involving both Gram-positive and Gram-negative were used for above assays. The minimum inhibition concentration (MIC) of C-AuNPs, obtained from the assays, was compared with the MIC of ceftazidime pure drug in order to evaluate the efficacy of C-AuNPs as compared to pure ceftazidime drug.

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CHARACTERIZATION OF THE REACTIVITY OF FLAVIN BOUND IN THE 'NADOX' PROTEIN SCAFFOLD

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	Freshman		Sophomore	X	Junior		Senior

The objective of the research is to elucidate mechanisms by which proteins control and modify the reactivity of bound flavins. The specific objective of this project is to characterize the reactivity of a flavin bound in the 'NADOX' protein scaffold, comparing the results obtained from 4 variants of this protein produced by single-site mutagenesis. Specifically, mutagenesis has allowed the production of not only the naturally-occurring protein (the wild-type or 'WT') but also a variant in which a conserved rigid proline is replaced by a flexible glycine (P156G), a variant in which a bulky leucine is replaced by a glycine (L158G) and a variant in which a positively charged arginine is replaced by a conditionally positive histidine (R21H). Graduate student John Hoben is measuring the reduction potentials of the flavin bound in each of these proteins. To understand the reasons for any altered reduction potentials, Karl Hempel measured the sensitivity to oxygen of each oxidized flavin by a number of kinetic assays focusing on the enzymatic properties of the 'NADOX' protein. These measurements utilized oxygen as the final electron acceptor and revealed the extent to which the amino acid substitutions affect the energetics of oxidized flavin - protein interactions. This work complements previous work done on the determination of the changes in energy upon flavin reduction to reveal how much energy is associated with redox tuning vs. how much is associated with redox-independent properties of the flavin. By comparing the values obtained for each of the protein variants, the extent to which each amino acid contributes can be determined.

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PENTACENE DERIVATIVES AS N-TYPE SEMICONDUCTORS FOR ORGANIC FIELD EFFECT TRANSISTORS

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	Freshman		Sophomore	X	Junior		Senior

Organic field-effect transistors (OFETs) are a pioneering field in the electronic device industry. Organic semiconductors are promising candidates for replacing conventional mediums used in electronic display screens, radio frequency identification (RFID) tags, and electronic device sensors.1 Currently, these transistors can be classified into two classes of semiconductors: p-type semiconductors (semiconductors that are responsible for hole transport) and n-type semiconductors (semiconductors that are responsible for electron transport).

Mobilities for conventional p-type and n-type semiconductors have reached values of 2 and 0.21 cm2/Vs respectively.2,3 Currently, pentacene derivatives are ideal molecules to create p-type semiconductors. However, unsubstituted pentacene is very unstable due to its ability to undergo Diels Alder reactions intermolecularly. But by adding alkyl silyl groups (i.e. triisopropyl silyl acetylene, tert-butyl dimethyl silyl acetylene, tributyl silyl acetylene, etc.) onto the pentacene molecule, stability is greatly improved. These silyl groups also play a vital role in solubility and overall crystal packing of the pentacene derivative; the goal is to use these substituent groups to manipulate the semiconductor to exhibit a 2-D pi-stacking motif, thus allowing the maximum transfer of electrons. Not only does this project explore how different substituents impact crystal packing, but it also examines how electron-withdrawing groups placed onto these alkyl silyl groups will affect the overall physical properties; by doing so, it is hypothesized that the LUMO of these conjugated polyaromatic hydrocarbons to be lowered. We expect this will allow us to transform pentacene molecules from a p-type semiconductor into an n-type semiconductor.

1. Marcia P.; Sean P.; Anthony J.; Kuo C.; Jackson T. Organic Field-Effect Transistors from Solution Deposited Functionalized Acenes with Mobilities as High as 1 cm2/Vs. JACS 2005, 127, 4986.
2. Llorente, Gonzalo R. Synthesis and Characterization of Solution Processable Acenes. University of Machester, 2010, 44.
3. Anthony J.; Facchetti A.; Heeney M.; Marder S.; Xiaowei Z. n-Type Organic Semiconductors in Organic Electronics. Adv. Mater. 2010, 22, 3886.

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ANALYSES OF THERMOELECTRIC FILMS FEATURING CARBON BLACK AND MULTI-WALLED CARBON NANOTUBES WITH POLYVINYLPYRROLIDONE

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	Freshman		Sophomore		Junior	X	Senior

In recent years, bulk material thermoelectric devices have presented themselves as a viable solution for capturing energy lost as waste-heat, which accounts for a significant portion of the energy being used to meet societies' needs. As with other alternative energy sources, the primary issues facing current devices are low energy conversion efficiencies and high costs of production and implementation. To account for these shortcomings, the development and subsequent testing of low cost organic molecules and conductive polymers that have experimentally significant Seebeck coefficients is of great concern in current research. In an experiment conducted by Ruben Riquelme and Camille Gomez, under the direction of Matt Weisenberger from the University of Kentucky's Center for Applied Energy Research, observations were made which suggested that thermoelectric films containing multi-walled carbon nanotubes (MWNTs) and polyvinylpyrrolidone (PVP) exhibited n-type conducting behavior and films containing carbon black (CB) and PVP exhibited p-type conducting behavior. Due to the unexpected n-type behavior of the MWNT and PVP film and the relatively low cost of the materials being used for both films, reproduction of the previously mentioned observations and the fabrication of a thermoelectric device featuring both films is of particular interest at the Center for Applied Energy Research. To test these observations, various thermoelectric films and a 5-pair thermoelectric device were constructed and then analyzed for key thermoelectric parameters.

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MOLED: A MOLECULE EDITOR ALLOWING FOR THE SPECIFICATION OF RADICALS IN SMILES

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The current state of molecule editors is incomplete. Editors are unable to display radical ions correctly, export the structure incorrectly to the simplified molecular-input line-entry system (SMILES), or both. moled was conceptualized as a replacement or supplement for molecule editors such as ChemDraw and MarvinSketch. It accomplishes two main goals. It is feature complete, allowing for the specification of radicals graphically and through SMILES strings. And it is portable, being written in javascript. The only software needed to run moled is a web browser. The moled source code is licensed under the AGPL.

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ENZYMATIC EVIDENCE FOR A REVISED CONGOCIDINE BIOSYNTHETIC PATHWAY

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Background
Naturally produced pyrrolamides, such as congocidine, are nonribosomal peptides that bind to the minor groove of DNA in a sequence specific manner, which confers anticancer activity. Considerable efforts have been made to increase this ability and overcome toxicity of pyrrolamide analogues. The majority of attempts to delineate the biosynthetic machinery for pyrrolamide assembly have been genetic methods. We discuss biochemical characterization of four essential proteins in congocidine formation: the adenylation-thiolation (A-T) di-domain Cgc18(1-610) and its MbtH-like partner SAMR0548, the AMP-binding enzyme Cgc3*, and the T domain Cgc19. We report revised substrate specificities of Cgc18(1-610) and Cgc3*, biochemical evidence of the AMP-binding activity of Cgc3*, and loading of 4-acetamidopyrrole-2-carboxylic acid onto Cgc19. Based on these biochemical studies, we suggest a revised congocidine biosynthetic pathway.

Methods
We focused on the characterization of Cgc18 and Cgc3*, enzymes dictating the identity of the amino acid-like building blocks to be incorporated into the growing natural product, and the T domain Cgc19. The enzymes were expressed in E. coli BL21 (DE3)ybdZ::aac(3)IV and were NHis6-tagged to facilitate purification via Ni2+-NTA affinity chromatography. Due to the large size of Cgc18, its DNA sequence was amplified in portions covering either the A domain or the A-T domains. Because initial attempts to express Cgc18 were unsuccessful, we cloned the gene for its MbtH-like protein partner, samr0548, into pACYCDuet-1 and co-transformed with all of our Cgc18-pET28a. The substrate specificity and kinetic parameters of the only soluble Cgc18 A-T domain (1-610) and Cgc3* were determined using ATP-[32P]PPi exchange assay. Substrate profiling of Cgc3* was performed through assay testing using commercially available and chemically synthesized pyrrole analogues. By using the phosphopantetheinyltransferase Sfp with [3H]acetyl-CoA as a co-substrate instead of CoA to facilitate counting of the radiolabeled products after protein precipitation, we confirmed the conversion of apo-Cgc19 and -Cgc18(1-610) proteins to their holo forms. Reverse-phase HPLC was utilized to investigate activity of Cgc3* and loading of the activated 4-acetamidopyrrole-2-carboxylic acid onto Cgc19.

Results & Discussion
Previous studies proposed that 4-acetamidopyrrole-2-carboxylic acid and its 4-amino analogue were the substrates for Cgc18 and that GA was the substrate for Cgc3*. The ATP-[32P]PPi exchange assay revealed that the actual substrates for Cgc18 and Cgc3* were the inverse of the proposed substrates. The Michaelis-Menten kinetic parameters (Km and kcat) further confirmed this discovery: Cgc3* displayed high catalytic efficiency against 4-acetamidopyrrole-2-carboxylic acid (kcat/Km = 2,632 ± 564 mM-1min-1). In an assay with varying concentrations of GA, Cgc18(1-610) displayed moderate catalytic efficiency (kcat/Km = 12 ± 2 mM-1min-1) compared to other amino acid-activating A domains like AspA, which activates the structurally similar L-Asp (kcat/Km = 10 mM-1min-1). HPLC data indicated that the 4- acetamidopyrrole-2-carboxylic acid pathway proceeds first via the Cgc3*-catalyzed ATP-dependent adenylation, followed by a second activation to substrate-CoA complex before loading of the CoA-activated substrate onto the apo T domain Cgc19. The discovery of the substrate promiscuity of Cgc3* towards pyrrole-like substrates is significant for future experimentation, when it may be used as a powerful catalyst for polypyrrolamide structure diversification.

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SYNTHESIS AND ELECTROPOLYMERIZATION OF ISOINDIGO-BASED MONOMERS

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We have designed and synthesized a novel set of monomers, 3a-d, that are based on the organic dye isoindigo, 1. We characterized the monomers by 1H NMR and UV/Visible spectroscopies and by mass spectrometry. Pyrrole-functionalized monomers 3c and 3d underwent oxidative electropolymerization smoothly to form films. Monomers 3a and 3b failed to polymerize. Cyclic voltammetry experiments showed that poly-3d is photoactive. We plan to use poly-3d to study electron and energy transfer processes across organic/inorganic interfaces, and eventually, to incorporate stable, photoactive polymers into solar cells.

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SYNTHESIS OF NAPROXEN AMINO ACIDS

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A benzotriazole activated naproxen compound was synthesized and verified with 1H Nuclear Magnetic Resonance (NMR). The stability of the naproxen benzotriazolide compound was tested after failed subsequent reaction. The results of the stability tests concluded a stability of about two months in the fridge. This compound was reacted with various amino acids but no viable products were recovered. A new method is currently being tested. (Convenient Synthesis of Ibuprofen and Naproxen Aminoacyl, Dipeptidoyl and Ester Derivatives. Katritzky, Jishkariani, and Narindoshvili)

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ANION SENSING USING A PLATINUM(II) COMPLEX

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As both a naturally occurring and commonly used anion, perchlorate is increasingly found in groundwater and surface water. It interferes with iodine uptake in the thyroid. The U.S. Environmental Protection Agency started the process to set a legal limit on perchlorate in drinking water under the Safe Drinking Water Act. This presentation describes an inexpensive, extraordinarily selective, rapid colorimetric and luminescence-based method for detecting perchlorate ion in water.

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EFFICIENT SYNTHESIS OF AMINES USING A SUPPORTED GOLD NANOPARTICLE CATALYST

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With the importance of amines in natural products, agrochemicals, and pharmaceuticals, the preparation of these functionalized amines has been widely investigated. However, most of the current methodologies rely on the use of homogeneous catalysts, where harsh conditions, such as high temperature and high pressure are needed, or toxic chemicals are utilized. As the field of nanotechnology matures, organic chemists are seeking easily recyclable and environmentally friendly nanosize heterogeneous catalysts. Our lab has recently reported the use of TiO2 supported nanosize gold catalyst (Au-TiO2) in the hydration of alkynes under basic conditions. As a result, the acid-sensitive functional groups that usually do not survive conventional acidic condition remained intact. Furthermore, Au-TiO2 can be reused via simple filtration or applied under flow reactor conditions with only slight loss of catalytic activity. We utilized this catalyst in the synthesis of various structurally complicated secondary and tertiary amines using easily available ketones, aldehydes, and simple primary or secondary amines under mild conditions through a process known as reductive amination. We succeeded in obtaining a wide scope of amine products in excellent yields. The reducing agent, formic acid, is believed to be dissociated on Au-TiO2, where both proton and hydride are provided to the imine intermediate from Au-TiO2 to form amine products. Good recyclability of Au-TiO2 in reductive amination is expected. In the long run, we expect that this heterogeneous, recyclable, efficient, and environmentally friendly nanoparticle gold catalyst will open new green chemistry routes in organic synthesis.

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DESIGNING A NANOFORMULATION INVOLVING GOLD NANOPARTICLES CAPPED WITH KANAMYCIN FOR POTENT ANTIBACTERIAL ACTIVITY

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Antibiotic resistance is a global issue serving as red flag and threatening numerous lives. This concern is now challenging the commercially available front line antibiotics. Hence, need for developing novel strategies are becoming necessary to combat rapidly evolving multi-drug resistant bacteria commonly called as "Superbugs". Kanamycin is an aminoglycoside antibiotic was used to cure common bacterial infections but currently, bacteria have gained resistance to the effect of kanamycin. Hence, in this study, we report a single step biofriendly method for synthesis of Kanamycin capped GNPs (Kan-GNPs) in an aqueous buffer. The Kan-GNPs were characterized using TEM, SEM-EDS, UV-Vis spectroscopy, TGA and DLS. The synthesized Kan-GNPs were tested for antibacterial activity against multiple Gram-positive (Staphylococcus epidermidis, Enterococcus durans, and Streptococcus bovis) and Gram-negative (Escherichia coli, Pseudomonas aeruginosa, and Enterobacter aerogenes) bacterial strains. This was done using in vitro antibacterial assays such as turbidimetry assay, spread plate assay, and other colorimetric methods such as XTT assay and fluorescence assay (live/dead cell viability assay). This nano-formulation was found to be effective against bacterial strains tested. Currently, Kan-GNPs are being tested against kanamycin resistant bacteria. Positive results from this study will lead to a successful platform for other commercial antibiotics to which bacteria have gained resistance against.

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EVAULATION OF AN ASSAY SYSTEM FOR MONITORING THE DISRUPTION OF AMYLOID-B PLAQUES

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	Freshman		Sophomore		Junior	X	Senior

Alzheimer's Disease (AD) is a progressive neurodegenerative disease. The pathology of the diseases is characterized by the build up of cerebral plaques formed from amyloid-β (Aβ) peptides. Amyloid-β plaques disrupt signaling neuronal pathways resulting in cell death. The toxic effect of the plaques is increased by the chelation of metal ions within the plaque. Our research focuses on the evaluation of synthetic peptide-linked metal chelators designed to disrupt the aggregation of amyloid-β plaques and remove toxic metal ions associated with the plaque. In order to evaluate the complexes, we have developed a reliable Thioflavin (ThT) assay system to monitor the aggregation of amyloid-β over time in the presence of varied concentrations of Cu2+, Zn2+, and Fe3+. The assay is designed to screen our synthetic peptide-linked metal chelator complexes and identify complexes that reduce amyloid-β plaque formation as a potential to be therapeutic treatment for Alzheimer's Disease.

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GREEN SYNTHESIS, CHARACTERIZATION OF SACCHARIDE COATED GOLD NANOPARTICLES FOR CATALYTIC APPLICATIONS

Jason Payne, *Jason Payne, Rajalingam Dakshinamurthy*

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Gold nanoparticles (AuNPs) have gained an immense interest due to their wide applications in the fields of biomedical and pharmaceutical, which is due to their unique physico-chemical properties when they are reduced to their nanoscale size range. Here, we present a novel single step bio-friendly process for synthesis of fructose (monosaccharide), sucrose (disaccharide) and raffinose (trisaccharide) capped GNPs, wherein saccharides are directly capped onto gold without the use of any secondary capping/stabilizing agent. Our study is mainly focused on the effect of various lengths of the saccharides in the formation and catalytic reduction activity of saccharide capped GNPs. Characterization of synthesized AuNPs was accomplished using various analytical characterization techniques such as TEM, SEM-EDS, FTIR, and UV-Vis spectroscopy. A 4-nitrophenol assay was used to evaluate the catalytic reduction activity of various saccharide capped AuNPs at different temperatures using UV-Vis spectrometer. Using the spectroscopic data, rate constant for three saccharide capped AuNPs was determined followed by its activation energy and exponential factor using different equations. From the kinetic data, the catalytic reduction activity for three saccharides was, in the descending order: fructose, sucrose and raffinose AuNPs respectively. This difference in the catalytic activity is believed to be due to the size of ligand on gold surface which greatly influences the surface/volume ratio.

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QUANTIFICATION OF LOCAL BONDING ENVIRONMENTS IN CESIUM SILICATE GLASSES USING SI-29 MAGIC-ANGLE FLIPPING NMR

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Cesium silicate glasses were studied using Si-29 magic-angle flipping (MAF) NMR spectroscopy. The chemical shift anisotropy parameters were extracted for each glass with a variety of Q(4) and Q(3) sites. The Q(4) site increases in width as the amount of cesium is increased. This is consistent with an increasingly disordered environment around these sites as the neighboring sites have more non-bridging oxygen atoms. Two distinct Q(3) sites are seen with very different anisotropies at the low cesium content and become more similar as cesium is added. Previous work has shown that larger anisotropies correspond to short non-bridging Si-O bond distances for Q(3) sites. Leading to a general interpretation that the large anisotropy site arises from an increasing number of coordinated cesium cations near that site. The other Q(3) site with increasing anisotropy with increasing cesium content must arise from either a smaller number of coordinating cations or a reduced local microscopic density to increase the Si-O bond length as cesium is added. This model indicates a microscopically phase separated mixture of isolated cesium cations scattered throughout the silica matrix, as well as some channels filled with clustered cesium cations. No macroscopic evidence for phase separation is seen in these glasses, however the degree of homogeneity of the melt is difficult to quantify given that samples were quenched from 1200˚C. Smaller cations such as sodium, rubidium, and potassium have ben studied in silicate glasses of similar composition with no evidence of multiple Q(3) sites, indicating that the size of the cation plays a critical role in this behavior.

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HIGHLY REGIOSELECTIVE SYNTHESIS OF Β-FLUOROAMINES VIA THE FACILE RING OPENING OF AZIRIDINES WITH HF-DMPU

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X	Freshman		Sophomore		Junior		Senior

HF-DMPU is being developed in our laboratory as a useful fluorinating reagent for both classical and metal-based transformations. We recently showcased its worth in the synthesis of mono- and di-fluorination of alkenes from the corresponding alkynes via an imido-gold catalysis. Due to the importance of the β-fluoroamine motif; which is found in numerous drug candidates, we sought to extend our application of HF-DMPU to the synthesis of the β-fluoroamines by the ring-opening of aziridines with HF-DMPU. We chose 2-methyltosylaziridine (A) for our reaction screening because previous HF-based methodologies on the tosylaziridines were sluggish and afforded low yields of β-fluoroamines and poor regio-selectivity. With our optimized condition on A, we tested the scope of our methodology on several N-tosylaziridines as well as other N-protected aziridines. Our method afforded good to excellent yields of the corresponding β-fluoroamines in very high regio-selectivity. We conclude that our protocol to β-fluoroamines from aziridines is simple, mild and economical relative to available protocols.

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SYNTHESIS OF PEPTIDE-LINKED METAL CHELATORS: A POSSIBLE TREATMENT FOR ALZHEIMER'S DISEASE

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Proteins and metals play key roles in infection and disease progression. The design and synthesis of peptide-based inhibitors and metal chelators offer potential alternative methods for disease treatment. Our research focuses on the synthesis of peptide- linked metal chelators for the treatment of Alzheimer’s Disease. These complexes disrupt the aggregation of amyloid-β, the key peptide in the formation of the characteristic neurodegenerative plaque. In addition, the peptide-chelator complexes remove toxic metal ions associated with the aggregates (including Zn2+, Cu2+, and Fe3+). Assembly of the chelator complex begins with the synthesis of an ethylenediamine backbone and the ligand binding domain. Subsequently, these two synthetic fragments are combined and linked to biologically significant peptides to form the final peptide-chelator complexes. These peptide-chelator structures provide the basis for alternative ligand synthesis in the future.

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EFFECT OF CATALYST SUPPORT ON THE DECARBOXYLATION/ DECARBONYLATION OF LIPIDS TO FUEL-LIKE HYDROCARBONS OVER NI AND NI-CU CATALYSTS

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Biofuels have attracted significant attention in recent years as a means for reducing our dependency on petroleum and curbing carbon pollution. Albeit the conversion of lipids to biodiesel represents a mature technology, the high oxygen content of biodiesel results in storage problems, engine compatibility issues and poor cold flow properties. Therefore, interest has shifted to focus on technologies capable of deoxygenating lipids to fuel-like hydrocarbons that are chemically identical to petroleum-derived fuels, which allows their use in existing infrastructure as drop-in substitutes. Additionally, these fuels are renewable and carbon neutral – the photosynthetic biomass used as feedstock removes CO2 from the atmosphere as it grows – their use resulting in reduced greenhouse gas and other emissions relative to petroleum-sourced fuels.

One method currently employed to upgrade lipids to hydrocarbons is hydrodeoxygenation, in which the feed is subjected to high temperature and hydrogen pressure in the presence of a catalyst in order to eliminate oxygen in the form of water. However, this approach has several disadvantages including the fact that the high amounts of hydrogen needed are solely available at centralized locations, dictating that the feed must be transported long distances to a processing facility, thereby reducing the economic and environmental appeal of this solution. In addition, the catalysts most commonly used are metal sulfides, which can potentially contaminate the products with sulfur, require delicate handling, and are prone to deactivation in water (a reaction product). Catalytic deoxygenation via decarbonylation/decarboxylation (deCOx) – in which oxygen is eliminated as CO and CO2, respectively – represents a better alternative, since this pathway does not require high hydrogen pressure and utilizes simpler catalysts.

Previous research has revealed that nickel-based deCOx catalysts provide comparable results to the catalysts most commonly used to achieve this transformation, namely, palladium- or platinum-based formulations (the cost of which may be prohibitive). Admittedly, Ni-based deCOx catalysts are prone to cracking and coking; however, recent results have shown that promotion with copper can curb these undesirable reactions. Indeed, recent studies indicate that a 20% Ni-5% Cu/Al2O3 catalyst provides higher selectivity to long-chain hydrocarbons and less coking than 20% Ni/Al2O3 during the conversion of lipids to diesel-like hydrocarbons via deCOx. Current work aims to determine if other metal oxide supports afford better results than alumina. Two additional oxides – namely zirconia and lanthanum-stabilized ceria – were used as supports and the resulting monometallic (Ni) and bimetallic (Ni-Cu) catalysts were tested in the conversion of triglycerides to diesel-range hydrocarbons, given that these supports have been reported by other authors to afford superior performance. Results indicate that the use of the zirconia and ceria supports leads to promising outcomes in monometallic formulations, affording high conversion and selectivity to diesel-like hydrocarbons. However, lower conversions and selectivities are observed when these supports are used in bimetallic catalysts. Efforts are underway to understand this occurrence, since the goal of this work is not only to obtain an improved deCOx catalyst, but also to gain fundamental insights on the structure-activity relationships dictating catalyst performance.

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SYNTHESIS AND ELECTROPOLYMERIZATION OF ISOINDIGO-BASED MONOMERS

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We have designed and synthesized a novel set of monomers, 3a-d, that are based on the organic dye isoindigo, 1. We characterized the monomers by 1H NMR and UV/Visible spectroscopies and by mass spectrometry. Pyrrole-functionalized monomers 3c and 3d underwent oxidative electropolymerization smoothly to form films. Monomers 3a and 3b failed to polymerize. Cyclic voltammetry experiments showed that poly-3d is photoactive. We plan to use poly-3d to study electron and energy transfer processes across organic/inorganic interfaces, and eventually, to incorporate stable, photoactive polymers into solar cells.

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GADD45 GENE EXPRESSION IN THE FIRST YEAR OF LIFE: ANALYSIS USING A RODENT MODEL

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Much is known about Growth Arrest and DNA Damage, or GADD45, gene activity in external cell sensing pathways, growth modulation, and DNA repair. Little research, however, has focused on the gerontological nature of these proteins. This study explored the epigenetics, specifically the hydroxymethylation status, of the GADD45 gene in the cerebellum region of rodents throughout the first year of life. Oxidation of carbon 5 on cytosine nucleotides was recently acknowledged as an intermediate step in the ten-eleven translocation (TET)-modulated demethylation pathway. This marker's notable presence in stem cells and neurons suggests that it may play a significant role in regulating gene expression in neuronal differentiation pathways and neuroplastic mechanisms. Nuclear DNA in cerebellum tissue from rodents of 2-12 months of age was isolated to explore the relationship between hydroxymethylation status and age. Subsequent hydroxymethylation quantitative analysis revealed a significant increase in the percentage of hydroxymethylated cytosine nucleotides (5-hmC) in 12-months-old mice compared to 2-month-old mice ($p<0.05$). Up and down regulation of GADD45 gene expression via demethylation/methylation of cytosine nucleotides has, for years, revealed the intricacy of these systems, while its precise mechanism has remained in question. Continued studies of the hydroxymethylation marker will seek to uncover the relative timing of this oxidative step and its role in neuronal gene expression and aging.

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THE EFFECTS OF TRPM8 GENE VARIANTS ON MIGRAINE

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TRPM8 is a member of the transient receptor potential cation channel family. TRPM8 is a ligand-gated ion channel that is activated by cold or menthol. When activated, the TRPM8 protein lets Na+ and Ca2+ ions enter the cell, which depolarize the cell and generate action potentials. The somatosensory cortex in the brain perceives the incoming signal as the sensation of cold. Markus Schurks' research found that heredity is an important aspect in susceptibility to migraines. About 50% of effected individuals have a first-degree relative who suffers from migraine which supports the idea that migraine risk is modulated by polymorphisms in the human genome [4]. A single nucleotide polymorphism (SNP), rs10166942, was recently found to be associated with migraine risk in three large genome-wide association studies [1-3]. People with the minor SNP allele have reduced risk of migraines. More recently, the minor SNP allele was also associated with lower sensitivity to cold. Two SNPs, rs13004520 and rs17868387, were found that are co-inherited with one another 100% in people and were in robust linkage disequilibrium with the migraine SNP. Both of these SNPs change TRPM8 amino acids (missense mutations). These mutations are predicted by poly-Phen to alter TRPM8 function. The minor and major alleles of the TRPM8 gene are being inserted to pcDNA5/FRT/TOPO, a tetracycline inducible vector, to avoid the toxicity found with long-term high TRPM8 gene expression in G418 selected AD293 cells. Using menthol or cold stimulus, the response of the two forms of the TRPM8 cells will be tested. When stimulated by cold or menthol, we hypothesize that cells with the minor allele form will require stronger stimulus to import the same Na+ and Ca2+ in response to cold or menthol. This is because people with the minor allele reported less intense cold pain. Elucidating the function of these two SNPs will thus show how we may be able to alter TRPM8 function to reduce the risk of migraine.

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DNA CONDENSATION WITH CATIONIC GOLD NANOPARTICLE

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Gene therapy offers great promise for treating genetic disorders and acquired diseases. Successful therapy requires the transport of nucleic acids into cells by delivery vehicles. For non-viral gene therapy, cationic polymers are often used for DNA delivery. A significant problem for these vectors is the high cellular toxicity inherent in the highly charged polymers. Gold colloids functionalized with amino acids have been found to provide a scaffold for effective DNA binding and protection while minimizing toxicity. Our long term aim is to develop new amino acid-functionalized gold nanoparticles optimized for DNA delivery. In this study, gold nanoparticles chemically modified with arginine (AuNP-Arg) and primary amine groups (AuNP-NH2) were used to condense DNA. Using gel electrophoresis and dynamic light scattering (DLS), we have studied the stabilities and size distribution of these DNA-nanoparticle complexes.

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HYDROTHERMAL ADDITION OF SODIUM TO A Y-MNOOH CRYSTAL LATTICE

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Hydrothermal Addition of Sodium to a γ-MnOOH Crystal Lattice

Battery technology is important in countless areas of our lives ranging from everyday handheld electronics to batteries used in aviation and aeronautics. Improving the electrochemical functions of battery components can go a long way in enhancing the function of these batteries. We have begun to study the use of various cations, such as sodium, as the charge carriers in ionic conductors because they show promise in forming nanowire structures with remarkable electrochemical properties. Currently, complicated synthesis techniques are needed to create most sodium containing nanowires. A specific drawing point for sodium cathode nanostructures is that they are relatively inexpensive to fabricate on an industrial scale and sodium is much more abundant than lithium, which is frequently used as the cation for many cathode materials1, 2.

Based on hydrothermal synthesis techniques involving the addition of other cations to the γ-MnOOH crystal3, other hydrothermal techniques have been designed to intercalate sodium cations into the manganite crystal. Sodium, however, has behaved much differently than lithium despite the similarity of the synthetic methods. Analysis techniques such as XRD, XPS, SEM imaging, and TEM/EDS imaging have been used to observe the characteristics of sodium intercalation with γ-MnOOH. These are the principle investigations involving the synthesis of NaMnO2 using hydrothermal techniques where γ-MnOOH is used as a precursor component. Further work will involve the investigation of the fabrication of cathode materials made of sodium-containing nanowires, the electrochemical performances of these products, and synthetic methods involving calcination.

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