ABSTRACTS

Undergraduate Research in Chemistry Regional Poster Competition

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

Author Index of Abstracts

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TOWARDS THE DETERMINATION OF THE MECHANISM OF PD(PPH3)4-CATALYZED HYDROGENATION OF ALKYNYL ALDEHYDES WITH BU3SNH

Maxwell Ain / Chemistry, University of Kentucky (Senior)
Shubhankar Dutta / Chemistry, University of Kentucky
Dr. Robert Grossman / Chemistry, University of Kentucky

The goal of this research project is to study the unexpected hydrogenation of certain electron deficient alkynes when allowed to react with Bu3SnH under Pd catalysis in order to find the scope and a mechanism for the reaction. This reaction is useful in a proposed synthesis of 7-epi-clusianone. The work towards synthesis of 7-epi-clusianone is being performed by Shubhankar Dutta.

Clusianones are polycyclic polyprenylated acyl phloroglucinols (PPAPs) that are believed to have medicinal significance. It was the study of synthesizing the particular 7-epi-clusianone that led to the concern of the lack of understanding of this specific mechanism of reaction. The reaction of an alkynyl aldehyde with tributyltin hydride (Bu3SnH) catalyzed by tetrakis(triphenylphosphine)palladium Pd(PPh3)4 was expected to give a stannane product by a carbometalation mechanism in which Pd bonds with Sn first, then to the alkynyl carbon before undergoing reductive elimination.

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MULTIDIMENSIONAL MASS SPECTROMETRY OF POLYGLYCEROL

Tyler Arntz / Chemistry, University of Akron (Junior)
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Chrys Wesdemiotis / Chemistry, University of Akron

Polyglycerol is an industrial polymer that is widely used as an intermediate for the production of emulsifiers. It has been available since the early 1900's, however little research has been done on the structure. Industrial grade polyglycerol was obtained from Lubrizol and analyzed by matrix assisted laser desorption/ionization and electrospray mass spectrometry. Upon analysis, three distributions were present, two of which display degrees of water loss. Ion mobility spectrometry was coupled with mass spectrometry to separate the polyglycerol by charge and structure. From the ion mobility data, collisional cross sections were calculated. Ongoing theoretical modeling aims at determining the product architecture and likely points for branching. Overall this study will contribute information that can be used to improve the manufacturing of polyglycerol and polyglycerol derivatives.

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DETERMINING TOTAL OXIDATIVE STRESS IN BRAIN OF THE MCGILL-R-THY1-APP TRANSGENE RAT MODEL OF ALZHEIMERS DISEASE

Grant Austin / Chemistry, University of Kentucky (Senior)
David Allen Butterfield / Chemistry, University of Kentucky

Alzheimers disease (AD) is a neurodegenerative disorder affecting millions of Americans. AD is characterized by amyloid plaque and neurofibrillary tangle pathology caused by oxidative stress. The goal in AD research in the coming years therefore will be to understand the pathology of AD better on a biochemical level and to do this new and more accurate animal models is a necessity. The McGill-R-Thy1- APP transgene rat is a new promising AD animal model that could be used to make significant strides in AD research. This rat model uses the hAPP751 gene with Indiana and Swedish mutations and under the influence of the Thy 1.2 promoter to induce amyloid pathology and increase oxidative stress. Oxidative stress is the process of reactive oxygen species oxidizing biomolecules causing them to change their structure. Reactive oxygen eventually leads to covalent additions of 4 -hydroxy-2-nonenal (HNE), 3-nitrotyrosine (3-NT), and carbonyls to proteins leading to conformational changes and dysfunction. These oxidative stress biomarkers can be measured using the slot blot technique with an immunochemical development procedure. The McGill rat model has already been shown to follow many of the hallmark pathological pathways of AD and the next step is to determine whether the cellular oxidative stress pathology is also the same as human AD. The purpose of this project was to determine whether the total oxidative stress was significantly increased in this rat model and therefore pave the way for future proteomic studies on this model. There were four sets of rats used in this study: a control, a control with lithium treatment, a transgene, and a transgene with lithium treatment. The lithium treatment is designed to reduce oxidative stress. The results of this project show that the transgene rat with no treatment showed an increase in oxidative stress for HNE and 3-NT biomarkers and the transgene rat with lithium treatment showed a recovery from the oxidative stress increase seen in the normal transgene rat.

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PROPERTIES OF SOFT METAL CHELATING AGENT, B9

Michael Baker / Chemistry, University of Kentucky (Senior)

Mercury has a strong presence in many water bodies from chemical spills, or presence in fish. It is naturally transported to oceans and lakes via watershed runoff, and through the direct deposit of atmospheric mercury. The FDA states that coal-burning power plants are the largest human-caused source of mercury emissions into the air, accounting for more than 50% of all domestic human-caused mercury emissions. Even in small quantities, metals such as mercury and arsenic are toxic to humans.

The N,N’-Bis(2-mercaptoethyl)isophthalamide (Trade names: BDTH2 or B9) molecule forms strong metal-sulfur bonds, with a specific value of the bond formed with Mercury being around 200 kJ/mol, which, for comparison is roughly equal to that of a Br-Br bond. This bond strength leads to a coumpound that is insoluble in a wide variety of solvents at various pH and temperature conditions. This research is important for the advancement of environmental chemistry, as B9 has been observed to successfully chelate Cd, Pb, Hg, and As, showing potential for water and soil treatment.

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INHIBITION OF ACRB EXPRESSION BY ANTISENSE KNOCKDOWN AS A MECHANISM FOR REDUCTION OF DRUG RESISTANCE IN E. COLI

Michael Bale / Chemistry, University of Kentucky (Senior)
Wei Lu / Chemistry, University of Kentucky
Yinan Wei / Chemistry, University of Kentucky

Drug resistance presents a major obstacle in treating bacterial diseases. An appealing therapeutic strategy to combat resistance is to inhibit systems which confer resistance, such as efflux systems. In this study, we monitored the effects of six antisense (AT) RNA constructs on translation of ArcB—an efflux system component in E. coli. Parent AT constructs (1-3) were created based on the sequences of the beginning, middle, and end of the gene. From AT1, three truncated daughter constructs (1a -1c), were created to assess the effect of AT length on knockdown. Western blot analyses indicated AT1 and AT1c treatments exhibited decreased ArcB expression. Knockdown effects of AT1 and AT1c were characterized by susceptibility assay against three antibiotics: tetraphenylphosphonium, novobiocin, and erythromycin. Susceptibility to novobiocin was unaffected, while both AT1 and AT1c had a modest effect on Ery and TPP susceptibility. These results suggest that antisense knockdown may provide a mechanism to sensitize a pathogen toward certain antibiotics and may enable the ability to determine a relative concentration of AcrB to confer a drug resistance phenotype.

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SYNTHESIS OF PENICILLIN-G DERIVATIVES TO COMBAT ANTIBIOTIC RESISTANCE

Kevin Burridge / Chemistry, Thomas More College (Senior)

Many strains of bacteria are now gaining resistance to various antibiotics. One common resistance is to β-lactam antibiotics, such as penicillin-G, a foundational member in the world of antibiotics. Certain triazole compounds have had success in overcoming β-lactam resistances. Presented here is the production of a triazole-derivatized version of Penicillin-G. The superior pathway first created a 1,2,3-triazole via the CuAAC "click" reaction with 50% pure crystal yield. Then, this product was added to Penicillin-G via a specialized Steglich Esterification with an 82% yield of moderately pure product. This was characterized by modern instrumentation (NMR and DEP-MS). An alternate pathway was attempted but was ultimately unsuccessful.

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PHENOTHIAZINE DERIVATIVES FOR NON-AQUEOUS REDOX FLOW BATTERIES

Steven Chapman / Chemistry, University of Kentucky (Senior)
Matthew Casselman / Chemistry, University of Kentucky
Aman Kaur / Chemistry, University of Kentucky
Susan Odom / Chemistry, University of Kentucky

Renewable energy sources are often intermittent due to their methods of generation (i.e. wind, sunlight); thus, there are times when energy needs are not met by supply. One potential solution is to store the excess energy and to draw upon that stored energy when demand increases beyond supply. Redox flow batteries (RFBs) are candidates for large scale energy storage due to their ease of scalability. RFBs are only limited in capacity by the size of their reservoirs, as energy is stored in liquid electrolytes. Current state-of-the-art vanadium RFBs suffer from limited operating voltage due to the electrochemical voltage window of water (ca. 1.5 V). Next generation non-aqueous RFBs operate at higher voltages (3 V or more), but are limited in lifetime and energy density. This project examines the use of two novel phenothiazine derivatives as the non-aqueous electro-active species for RFBs. These two new derivatives were synthesized and screened for the electrochemical performance and lifetime. They exhibit enhanced stability and solubility, which may lead to a higher energy content and longer lived batteries.

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ORDERED CONFORMATIONS IN BIS-(AMINO ACID) DERIVATIVES OF RHENIUM PENTA-CARBONYL CHLORIDE AND NICOTINIC ACID

Fouad Choueiry / Chemistry, University of Akron (Senior)
Fouad Choueiry / Chemistry, University of Akron
Abed Hasheminassab / Chemistry, University of Akron
Christopher Ziegler / Chemistry, University of Akron

An amino acid derivative of nicotinic acid (NA) was synthesized and bound to an organometallic fragment. L-Valine was conjugated to nicotinic acid via the formation of an amide bond, and two equivalents were bound to a Re(CO)3 center. NMR and X-ray diffraction techniques were used to characterize both the free ligand and the resultant metal complex. Hydrogen bonding between the valine groups was observed in the solid state.

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SYNTHESIS AND IN VITRO ANTI-TUMOR STUDIES OF BIS IMIDAZOLIUM SALTS WITH ALKYL CHAIN LINKERS AND NAPHTHYLMETHYL SUBSTITUENTS

Steven Crabtree / Chemistry, University of Akron (Senior)
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Cancer is the second leading cause of death in the United States; therefore, finding novel chemotherapeutics to treat these diseases is vital. Bis imidazolium salts, with alkyl chain linkers ranging from methylene to dodecyl, were synthesized with naphthylmethyl substituents at the N1 and N1' positions for a structure-activity relationship (SAR) study. All compounds were characterized by 1H and 13C NMR spectroscopy. The cationic portion of 2 as the PF6 salt, 3, 4, and 5 were also characterized by single-crystal X-ray crystallography.

Compounds 1-8, 10, and 12 were tested for their in vitro anti-cancer activity against four NSCLC cell lines via the MTT assay (NCI–H460, NCI–H1975, HCC827, and A549). Compounds 10 and 12 which contained the decyl and dodecyl chains, respectively, had IC50 values of < 1 μM (NCI-H460), < 1 μM (A549), 2 μM (NCI-H1975), and 7 μM (HCC827) and < 1 μM (NCI-H460), < 1 μM (A549), < 1 μM (NCI-H1975), and 4 μM (HCC827), respectively. The results of the MTT assays showed that activity increased as the length of the alkyl linker increased; the bis imidazolium salts with longer chains, compounds 6-8, 10, and 12, had IC50 values comparable to cisplatin.

The National Cancer Institute's (NCI) Developmental Therapeutics Program (DTP) also tested compounds 1-8, 10, and 12 with its 60 human cancer cell line panel in the one-dose assay (10 μM). Results from the one-dose assay are growth percentages relative to control cells; a negative growth percentage means the compound was lethal leaving fewer cells alive at the end of the assay than were alive at the beginning. These results corroborated the SAR findings of our lab that activity increased with the longer chain alkyls, compounds 6-8, 10, and 12, linking the imidazole rings, with compound 12 being the most active having lethality against all of the NSCLC lines examined and lethality against nearly all cell lines tested.

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SILVER NANOWIRE SURFACE MODIFICATION EFFECTS ON DISPERSABILITY, FILM MORPHOLOGY, AND ELECTRICAL CONDUCTIVITY

Cameron Day / Chemistry, University of Kentucky (Senior)
Kenneth Graham / Chemistry, University of Kentucky
Zhiming Liang / Chemistry, University of Kentucky

The need for alternative energy sources in the world today is clearly evident with rising energy costs and continual conflict in resource rich countries, not to mention the debilitating effects on the environment. The most common transparent conductor used today in both solar cells and light emitting displays is indium tin oxide (ITO), which is both brittle and expensive. That is why conductive metal nanowires such as silver, are a potentially important next step in solar cell research. However, previous studies have shown that AgNWs have the tendency to form nonhomogenous blend films with polymers. Recent experiments have shown that surface modification of AgNWs has led to improved morphological and electrical properties. The approach taken in our research is to synthesize and functionalize AgNWs with certain modifiers, blend them in a single step with high performance organic semiconductors and characterize the dispersability, morphology and conductivity of the thin films produced. In the work presented we successfully altered the work function of the AgNWs and manipulated the overall conductivity of the electrode. The ionic, carboxylic acid derivative, and alcohol modifiers blended with PCBM and gave work functions that varied by as much as 0.5 eV.

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LASER-ASSISTED SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF GADOLINIUM NANOPARTICLES

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Dong-Sheng Yang / Chemistry, University of Kentucky

Gadolinium (Gd) nanoparticles were prepared by Nd:YAG second-harmonic (532 nm) ablation of a Gd pellet in deionized water. Chemical compositions, optical properties, and structures of the resultant particles were investigated with an array of spectroscopic and microscopic techniques. These techniques include transmission electron microscopy, energy-dispersive x-ray spectroscopy, ultraviolet-visible and infrared absorption, and fluorescence spectroscopy. The transmission electron microscopic measurements show that the metal particles are in two distinctive structural forms: nanotubes and clusters. The absorption spectroscopic measurements indicate the presence of Gd3+ and Gd2+, presumably in the forms of Gd2O3, GdO, or Gd(OH)2,3. The fluorescence measurements show both excitation—wavelength dependent and independent emissions. This work represents the first detailed characterization and fabrication of gadolinium nanoparticles by laser ablation synthesis in an aqueous solution.

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SYNTHESIS OF INFRARED-ABSORBING, ACENE-DERIVED DYES FOR USE IN BIOMEDICAL IMAGING

Walker deVerges / Chemistry, University of Kentucky (Senior)
John Anthony / Chemistry, University of Kentucky

Light in the near-infrared region is of particular use in biomedical imaging due to biological tissues' near transparency in the NIR range and a lack of resulting fluorescence from the body’s intrinsic fluorophores, thus lowering background noise. For this purpose, near-infrared-absorbing, acene-derived dyes are being investigated due to their low cytotoxicity and their chemical and photostability. These dyes will ideally absorb in the 650-900 nm range thus avoiding the fluorescence of intrinsic fluorophores. This presentation will address the synthesis of some such dyes and their optical capabilities.

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DESIGN AND SYNTHESIS OF DIKETOPYRROLOPYRROLE- AND ISOINDIGO-BASED DYE-ROTAXANES

John Dietz / School of Sciences, Indiana University Kokomo (Senior)
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Though they show considerable promise as biological imaging agents and components of organic electronic devices, only a handful of dye-rotaxanes have been described in the literature. Compounds 1 and 2 incorporate, respectively, diketopyrrolopyrrole (DPP) and isoindigo (iI) chromophores. We plan to test 1 and 2 as templates for the synthesis of new dye-rotaxanes such as 3 and 4. Computational modeling (PM3) suggests that 1 and 2 will facilitate the self-assembly of amide-based macrocycles in clipping reactions. We anticipate that 3 and 4 will have significantly different photophysical properties than their corresponding templates. A water soluble version of 4 could potentially function as a bio-imaging agent. Ultimately, we plan to synthesize and test responsive rotaxanes that exhibit on-to-off fluorescence in the presence of an enzymatic triggers.

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PHOTODEGRADATION OF BETA-CAROTENE IN THE PRESENCE OF PRIMARY, SECONDARY AND TERTIARY ORGANIC RADICALS

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Amber Johnson / Chemistry, University of Dayton
Katelyn Arnold / Pharmacy, University of North Carolina, Chapel Hill
Sarah Dubay / Biomedical Sciences, Case–Western Reserve University
Robert Poston / Chemistry, University of Dayton
Mark Masthay / Chemistry, University of Dayton

β–carotene (βC; C40H56) is an orange, conjugated hydrocarbon which acts as an antioxidant in the hydrophobic interior of human cell membranes. Upon exposure to ultraviolet light, βC photodegrades into a diverse mixture of photoproducts—some of which are immune suppressive—via an unknown mechanism. Solutions of βC dissolved in neat n–hexane, 0.1M and 0.01M 2,3–dimethylbutane [DMB] in n–hexane, and 0.01 M 2,2,3,3–tetramethylbutane [TMB] in n–hexane were accordingly irradiated with the broadband (BB; unfiltered, with a wavelength range covering actinic wavelengths λactinic > 190 nm) output of a 100 W Hg arc lamp to help characterize the potential roles of solvent–derived 1°, 2° and 3° alkyl radicals in the photodegradation. The rates of photodegradation R(X) in these solutions followed the trend R(DMB) + n–hexane > R(neat n–hexane) > R(TMB + n–hexane), suggesting that R(2°) > R(1°) > R(3°). The rate laws were first order in [βC] in the DMB + n–hexane solutions (both 1° [propyl] and 2° [isopropyl] radicals present) but zeroth order in [βC] in neat n–hexane (1° [propyl] radicals present) and
TMB + n–hexane (3° [t–butyl] radicals present). In contrast, solid βC is photostable under ambient atmospheric conditions; solvent radicals are thus clearly implicated in the photodegradation.

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SOLUTION SYNTHESIS OF CESIUM LEAD HALIDE PEROVSKITE NANOSTRUCTURES: PROMISING MATERIALS FOR OPTOELECTRONIC APPLICATIONS

John Dunlap / Chemistry, University of Kentucky (Senior)
Kenneth Graham / Chemistry, University of Kentucky

Mixed-halide perovskite semiconducting materials have emerged as effective materials for many optoelectronic applications including solar cells, light emitting diodes, and lasers, due to their favorable material and chemical properties. While hybrid organometal methyl ammonium lead halide perovskites are being heavily researched in solar applications, their inorganic analogues have received much less attention. Inorganic cesium lead halide perovskites are of great interest due to their tunable band gap, electrical conductivity, and their high thermal stability with respect to their hybrid counterparts. Nanoparticles are of particular interest for these applications, as their properties may be altered so as to improve device performance over that of bulk-phase crystals, and may be incorporated with organics for composite materials. Monocrystalline nanowires (NW) and nanocrystals (NC) lend themselves to superior optoelectronic and semi-conductive properties in comparison to bulk crystals. In this work, the synthesis of cesium lead bromide NWs and NCs are investigated, with emphasis on morphology control and tunability of their optoelectronic properties through substitution of the halide component.

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COMPUTATIONAL PRE-SCREENING OF ORGANIC MATERIALS FOR ENERGY-STORAGE SYSTEMS

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Lithium-ion batteries (LIBs) are a preferred power source for portable electronics, while redox flow batteries (RFBs) present an opportunity for large-scale stationary energy storage. Materials optimization has brought about substantial improvements in both systems, but there remain limitations to the efficiency and safety of these devices. LIBs suffer from overcharge – a harmful condition which limits battery lifetimes and can lead to increased internal pressure and thermal runaway, thence to smoking and/or fire. The aqueous, all-vanadium RFB system is the most advanced yet under consideration, but the voltage window is limited and components are often extremely corrosive. Organic aromatic compounds may constitute a solution to both of the above limitations – as redox shuttles to protect against overcharge in LIBs and as electrolyte materials in non-aqueous RFBs. This research utilizes computational and experimental pre-screening/design techniques to identify promising compounds for use in LIBs and RFBs, thereby reducing the amount of time (and money) lost in synthesizing and cycling incompatible compounds. It furthermore encompasses the synthesis and incorporation of said compounds into battery systems to determine the validity of the aforementioned pre-screening techniques, as well as the performance of each compound in real-life systems.

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REGULATION OF THE ESTROGEN RECEPTOR BY CATECHIN POLYPHENOLS FROM GREEN TEA

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Ross Weatherman / Chemistry and Biochemistry, Rose-Hulman Institute of Technology

It has long been suggested that green tea could aid in preventing breast cancer. Green tea is rich in catechin polyphenols that have been associated with bioactive properties, including anti-proliferative effects on antiestrogen resistant breast cancer cells. There is currently no consensus mechanism for how catechins work. Proposed mechanisms include both estrogen receptor dependent and independent pathways. Studies in this laboratory conclude that green tea catechin polyphenols, particularly catechin gallates, exhibit weak estrogenic effects on estrogen receptor(ER)-mediated transcription. The catechins tested were (-)-Epicatechin gallate, (-)-Gallocatechin gallate, (-)-Epigallocatechin, and (-)-Gallocatechin. This research determined the antiestrogen strength of these catechins relative to prominent antiestrogens, and tested them in antiestrogen sensitive and resistant cell lines to determine catechin polyphenol behavior as agonistic or antagonistic. This was accomplished via fluorescence polarization (FP) binding assay and luciferase assay. FP binding assay results showed that catechins demonstrate successful binding to ER at high concentration doses, but they are weaker than prominent antiestrogens. Catechin polyphenols were tested with regard to ERα and ERβ in order to compare effectiveness between receptor forms. The luciferase assay data demonstrated that catechins are able to stimulate ER-mediated transcription, but at levels lower than those observed with estradiol. However, the extent of catechin ER-mediated transcription activation does not seem to correlate with binding affinity. This suggests a more complicated mechanism for further study. Additional experimentation could also dissect whether these catechin polyphenols, particularly the catechin gallates, are low potency full agonists or high potency partial agonists.

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FORMULATION AND CHARACTERIZATION OF RUBRENE AND PENTACENE -DERIVED IN SILICO POLYMORPHS VIA DENSITY FUNCTIONAL THEORY

Tristan Finn / Chemistry, University of Kentucky (Senior)
Karol Jarolimek / Chemistry, University of Kentucky
Chad Risko / Chemistry, University of Kentucky

From isolated molecules to their solid state counterparts, developing an understanding of molecular structure-function relationships has been a long withstanding effort in the material science community. Centered on the need to engineer π-conjugated molecules into electronically useful crystalline materials, we report the results of a series of density functional theory (DFT) investigations on rubrene—a tetraphenyl-substituted tetracene—and trialkylsilylethynyl-substituted pentacene derivatives to determine how simple chemical substitutions produce highly impactful changes in solid-state packing and electronic characteristics. Of particular interest to this study's approach are the variations seen in lattice and cohesive energies after chemical substitution. By exploring the differences in these properties among experimentally determined crystal structures as well as in silico polymorphs, we develop a picture of how molecular design impacts the non-covalent interactions that determine the thermodynamically favorable solid-state packing arrangements and, in turn, the materials-scale electronic properties. The underlying physicochemical relationships derived from these investigations will provide the insight required to precisely design molecular materials for new generations of electronic and photonic applications.

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SINGLE MOLECULE IMAGING OF LIGAND AND MEMBRANE RECEPTOR INTERACTIONS THROUGH THE USE OF FLUORESCENT MICROSCOPY AND ZMWS

Emily Furnish / Chemistry, University of Kentucky (Senior)
Elliott Martin / Chemistry, University of Kentucky
Ning Ge / Engineering, University of Kentucky

The study of single molecule fluorescence in biology and chemistry provides important information about the properties of individual biomolecules, such as the behavior of specific receptors or ion channels within a cell. Single-molecule fluorescence spectroscopy is an effective method for imaging and analyzing such single-molecule properties. Nanofabricated devices such as zero-mode waveguides coupled with microfluidics can be used to study specific interactions at the single-molecule level. In my research, electron-beam (e-beam) lithography and photolithography were implemented to create membranes with evenly spaced 200 micron wells on a silicon nitride substrate. These membranes were coupled with microfluidics to isolate single membrane receptors in cells. The microchannels in microfluidic devices allow for isolation of single cells and the controlled delivery of reagents to these isolated areas. The devices were then used to image and then analyze individual binding events 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 only a small volume of cells could be added to the ZMW, a cell line was generated to help ensure 100% expression of EGFR in cells. Cells expressing EGFR-GFP were added to the devices and excited at 488 nm. Once fluorescent cells were found sitting in the wells of the ZMW membrane, EGF-Alexa 647, which is excited at 640 nm and emits around 680 nm, was delivered to the devices so that binding events could be observed in real time. This allowed us to visualize single protein-ligand interactions. The results of this study could be applied to other areas of research, such as pharmaceuticals, in order to observe how receptors and proteins interact and are affected at the single molecule level through drug delivery.

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CHEMICAL-INDUCED CYTOTOXICITY IN PC-12 CELLS

Jonathan Gardner / Chemistry, University of Kentucky (Senior)
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Jenna Vanrooyen / Physiology, University of Kentucky
Samir Patel / Physiology, University of Kentucky
Alexander Rabchevsky / Physiology, University of Kentucky

Spinal cord injury results in increased intracellular calcium, reactive oxygen species production (ROS), and ATP depletion which are associated with mitochondrial dysfunction. Our overall hypothesis is that these secondary cascades may be attenuated by directly transplanting healthy exogenous mitochondria in to the injured spinal cord. However, in parallel to assessing the therapeutic potential of mitochondria transplantations in vivo, a more mechanistic approach is to study the cellular environment after toxic injury in vitro, with or without mitochondrial supplementation. Accordingly, the present study focused on standardizing techniques to reproducibly insult cells derived from rat pheochromocytoma (PC12) which are commonly used due to their high proliferation rate and neuronal-like phenotypes. Methods were focused on consistently targeting cell death rates of ~40% after the designated duration of insult to evoke a sufficient injury effect while leaving a large pool of salvageable cells. We hypothesized that with each type of insult we would see dose-response effects on cell death, and that this baseline level of attrition could be attenuated by mitochondrial supplementation. PC12 cells were incubated with one of four different insults at empirical concentrations. 1) Calcium ionophore A23187 results in an increase of membrane permeability to calcium which is taken into the mitochondrial matrix- of which excessive levels will cause mitochondrial bursting. 2) Hydrogen peroxide (H2O2) simulates ROS production which induce oxidative stress by oxidation of proteins, lipids and nucleic acids in the cell. 3) Oligomycin causes depletion of cellular ATP from the arrest of ATP synthase by blocking the F0 subunit. 4) Paraquat causes an increase in ROS production through electron transfer interference in the electron transport chain creating mitochondria-derived ROS production. Each of these insults ultimately initiates apoptotic or necrotic cell death pathways. Multiple concentrations of each insult were applied for incubation times of 1 hr for oligomycin and paraquat or 12, 18, or 24 hrs for Ca2+ ionophore and H2O2, after which time cell death was immediately calculated. Results showed a dose-response effect of Ca2+ ionophore and H2O2 insults to induce cell death in the 24 hr groups. Alternatively, no concentrations tested in vitro resulted in remarkable paraquat- or oligomycin-induced cell death. In summary, cells incubated in 6uM Ca2+ ionophore resulted in 28% cell death, the closest to our target of 40% of any trial. This study lays the groundwork for future studies aimed at measuring differences in cell death following chemically-induced cytotoxicity. Further studies aim to directly assess mitochondrial function of cells after injury, notably with or without supplementation.

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SYNTHESIS OF [2,3-B]SELENOPHENE PYRROLE

Daniel Gilani / Chemistry, Belmont University (Senior)

Protein structure has primarily been studied using X-ray crystallography and NMR, and heavy metal amino acid analogs have been useful probes in the elucidation of three-dimensional structures by mutliwavelength anomalous diffraction (MAD) techniques. L-tryptophan and L-methionine were identified as ideal amino acid targets for heavy metal attachment because of their low abundance and limited structural and catalytic roles. The synthesis of selenium containing analogs of L-tryptophan has previously been demonstrated by the Paulmier/Philips method, and the potential uses of a selenium-containing tryptophan analog have also been demonstrated with β-seleno[3,2-b]pyrrole-L-alanine ([3,2-b]SeTrp). The synthesis of the selenophene pyrrole is a key step in the production of SeTrp. However, the Paulmier/Philips method requires several manipulations of selenophene, resulting in an inefficient process with a low yield of Se labeled pyrroles. Instead, an alternative synthesis of selenophene is investigated in this proposed scheme to produce [2,3-b]selenophene pyrrole. In this alternative synthesis, the selenophene is attached to a pyrrole prior to the enzymatic coupling of a serine side chain, which should produce [2,3-b]selenophene pyrrole in higher yields than previously reported.

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CESIUM LEAD BROMIDE NANOWIRES AND THEIR APPLICATIONS TO THERMOELECTRIC DEVICES

Christopher Hayden / Chemistry, University of Kentucky (Senior)
Kenneth Graham / Chemistry, University of Kentucky

ABSTRACT: Considering the current energy landscape, the world saw almost a twenty times increase in the use of fossil fuels during the twentieth century, and these fuels have been shown to negatively effect our environment.1 These adverse effects have prompted the scientific community to research alternative forms of energy. Thermoelectric devices convert heat energy into electrical power utilizing the Seebeck effect.2 By utilizing devices of this nature, the overall energy efficiency of a power plant or automobile can be increased. The efficiency of a thermoelectric material directly depends upon a dimensionless figure of merit, . In this equation, S represents the Seebeck coefficient, represents the electrical conductivity of the material, T is the absolute temperature, and represents the thermal conductivity of the material.2 Inorganic nanowires blended with organic materials are emerging as promising candidates for use in thermoelectric devices. In this project, cesium lead bromide nanowires were synthesized, and the nanowires were blended with a conjugated organic polymer in order to analyze the film's thermoelectric properties and the polymer's effect on nanowire film morphology. The ratio of nanowires to polymer was varied, and the study set out to investigate how this would affect film morphology and the Seebeck coefficient. This project concluded that by changing the ratio of nanowires within the organic polymer, a change in the Seebeck coefficient can be observed, and through optical microscopy, the nanowires were seen to disperse better throughout the film as the concentration of nanowires increased. Films were also doped with $FeCl_3$ in order to optimize the Seebeck coefficient and sheet resistivity.

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USING CONJUGATED AROMATIC MOLECULES FOR BIOIMAGING

Ashley Heighton / Chemistry, University of Kentucky (Senior)
John Anthony / Chemistry, University of Kentucky
Devin Granger / Chemistry, University of Kentucky

My research has been focused on the synthesis of a molecule to be used for optoacoustic imaging to enable high-resolution optical imaging beyond that of optical microscopy. It has been proposed that quenched fluorescence-dye nanoparticles to be an alternative to typical metal nanoparticles for near-infrared optoacoustic signal generation (1). Most of my work thus far has been on the synthesis of diFluorene-ADT and attempts at recrystallizing it with different solvent solutions. UV-Vis and fluoresce microscopy were utilized to compare diFluorene-ADT to a known molecule, diPhenyl-ADT. I plan to discuss the synthesis of diFluorene-ADT and the microscopy comparison to diPhenyl-ADT.

References

(1) Nunes, A.; Pansare, V. J.; Beziere, N.; Ntoukas, A. K.; Reber, J.; Bruzek, M.; Anthony, J.; Prud'homme, R. K.; Ntziachristos, V. Quenched Hexacene Optoacoustic Nanoparticles.

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PRODUCING REACTIVE INTERMEDIATES VIA PHOTODRIVEN ELECTRON TRANSFER

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Flavoenzymes are essential to all forms of life and make up a large portion of genomes, e.g. 0.25% Homo sapiens and 1.8% Escherichia coli. Flavoproteins are proteins that contain a flavin that may be covalently or non-covalently bound. Flavins are redox-active prosthetic groups; flavin adenine dinucleotide (FAD) or flavin mononucleotide (FMN), which are Vitamin B2 derivatives. The flavoprotein name reflects the fact that flavoenzymes are an intense yellow color because the flavin absorbs blue light. Understanding the mechanism by which flavin cofactors are photoexcited and transfer electrons is essential in harnessing flavoproteins for organic electronic applications, e.g. functionalized electrodes. After the initial photoexcitation of flavin, the fluorescence lifetime can be anywhere from 1 femtosecond to 100 nanoseconds until the excited state is quenched by electron transfer. Therefore, femtosecond transient absorption spectroscopy (TAS) was needed to study these extremely short lived excited states. To optimize the yield of electron transfer intermediates, a donor was needed to supply an electron to the vacancy that was formed by exciting the initial flavin group. With this electron hole filled, the flavin adopted an excited semiquinone state. We used fluorescence quenching to measure the efficiency of electron transfer to photoexcited flavins and screened an array of candidate electron donors to identify those with optimal efficiency and favorable dissociation constants. We learned temperature and pH have a significant effect on fluorescence emission intensity in our systems of study. With a reliable way to produce flavin semiquinone, TAS can be utilized to understand the formation and decay of the semiquinone state.

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DIOXYALKYLENE PEEK POLYMERS CONTAINING VANILLIN SUBUNITS

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Vanillin has many interesting properties and is frequently used as a building block in organic synthesis. Poly(ether ether ketone)s (PEEK) have been known to exhibit thermal stability, solvent resistance, and excellent mechanical properties. A series of dioxyalkylene based monomers containing vanillin subunits were generated via a three-step process, 1) a Williamson ether synthesis, 2) a Grignard reaction with p-bromofluorobenzene, and 3) a Jones oxidation. The monomer was then polymerized in an A2B2 Nucleophilic aromatic substitution (NAS) polymerization with Bisphenol-A. The polymers exhibited thermal stability with 5% weight loss occurring at about 390 °C and Tg occurring around 100 °C.

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SYNTHESIS OF ROD-SHAPED, SPHERICAL, AND CUBIC ZINC SULFIDE NANOCRYSTALS FOR ENERGY CONVERSION APPLICATIONS

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It is an inescapable truth that energy is needed to maintain the stability of life. Combustion of fossil fuels generates environmentally harmful by-products, and because demand for energy continues to grow, fossil fuels will no longer be sustainable as primary sources of energy. Solar energy is a very abundant form of energy, but is not currently absorbed nor converted to useable energy with 100% efficiency. New materials are needed to effectively convert, store, and use the energy in sunlight. This work focusses on the synthesis of lead-doped zinc sulfide nanocrystals (PbxZn1-xS NCs) to generate hydrogen gas using (and therefore storing) solar energy. When sunlight is absorbed by the NCs, the energy in sunlight generates high energy electrons in the NCs. When the NCs come in contact with hydrogen ions in water (H+), two excited electrons from NCs form a chemical bond between two H+ to yield hydrogen gas. In this way, energy in the form of sunlight is converted into chemical energy practically packaged as a storable fuel. While ZnS NCs do not absorb much sunlight, introducing Pb dopant ions into the ZnS crystal lattice alters the optical properties of the NCs such that more sunlight is absorbed by the resulting doped crystals. We hypothesize that changing the shape and size of the ZnS NCs may enable Pb doping which will enhance the NCs' absorbance of sunlight. If realized these nanostructures will influence the design of future synthesis of nanocrystals to be used for the generation of solar fuel.

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DETERMINATION OF FISH-GELATIN RISK THRESHOLD:APPLICATION ON ALLERGENIC RISK

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Determination of fish-gelatin risk threshold: Application on allergenic risk
Youjin Hwang, Dr. Robert Lodder
Abstract

The number of patients with allergies has dramatically increased in recent years. An allergy is an overreaction caused by the immune system when the allergen, which can be any substance from outside the body such as pollen, enters the body. Immunoglobulin E (IgE), produced by B cells induces mast cells to release histamine. These histamines lead to several different symptoms, such as vasodilation. The study of allergies has been quite active for a decade. Likewise, studies about the threshold amount of allergens, or determining No-observed-adverse-effect level (NOAEL) is part of the allergy studies for determining exposure risk. This experiment was based on a paper by Hansen.2 In the paper written by Hansen, Skin Prick Test (SPT), Histamine Release test (HR), and Double-Blind Placebo-Controlled Food Challenge (DBPCFC) were done to determine the Lowest-observed-adverse-effect level (LOAEL). The LOAEL of fish gelatin was calculated as 3.61g with 90% confidence and 1/30 patients were truly sensitive to fish gelatin. However, 3 g would be an unrealistically large accidental contamination in a foodstuff, where cross contamination is more likely to occur in microgram or milligram quantities. To calculate a more realistic risk threshold with regard to fish gelatin exposure, a statistical software package, MATLAB, was used in conjunction with the Weibull distribution method. The experiment concluded that 10mg of fish gelatin would be unlikely to cause an allergic reaction in even one person in a population the size of the United States.

Keywords
Allergy-1, IgE-2, Fish gelatin-3, Matlab-4, Weibull distribution-5

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KINETIC AND MECHANISTIC STUDIES OF A MANGANESE(V)-OXO CORROLE

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There is significant interest in the catalytic activity of metallocorroles owing to their structural similarities to metalloporphyrins. In this study, 5,10,15-tripentafluorophenyl corrole (H3TPFC) and its manganese(III) complex [MnIII(TPFC)] were successfully synthesized according to literature-reported methods. The manganese(III) precursor was oxidized by two different oxygen sources to a manganese(V)-oxo complex [MnV(TPFC)O]. The kinetics of its oxygen atom transfer reactions were investigated under pseudo-first-order reaction conditions. Our studies indicate that MnV(TPFC)O reacts via two pathways depending significantly upon the solvent. We assert that MnV(TPFC)O undergoes disproportionation in acetonitrile, generating a putative manganese(VI)-oxo species that acts as the true oxidant. In dichloromethane, MnV(TPFC) oxidizes the substrate directly.

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UNDERSTANDING ION BINDING AFFINITY AND SELECTIVITY IN BETA-PARVALBUMIN USING MOLECULAR DYNAMICS AND MEAN SPHERE APPROXIMATION

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Parvalbumin (PV) is a globular calcium-binding protein expressed primarily in skeletal muscle and secondarily in neuronal tissue. Our computational studies of the beta PV isoform seek to quantify thermodynamic drivers of high affinity and selective calcium (Ca2+) binding at the EF structural motifs. Specifically, we have employed molecular dynamics (MD) simulations and Mean Sphere Approximation (MSA) theory to quantify the structural and thermodynamic factors favoring Ca2+-binding relative to other common intracellular electrolytes in both EF-hands. Our MD simulations provide the coordination geometry and the density of metal-chelating oxygens within the EF-hand scaffolds for both calcium and magnesium. These structural data inform the MSA model, from which the free energy, chemical potential, within the metal binding site are predicted. This approach provides a thermodynamic basis for ion affinity and selectivity in beta-PV over a broad range of electrolyte compositions and concentrations that would be difficult to ascertain by MD alone. These computations offer the potential to predict key thermodynamics quantities across a wide range of PV sequence homologs and Ca2+-binding proteins.

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A NOVEL DUAL FUNCTIONAL TAG FOR PROTEIN PURIFICATION AND MODIFICATION

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Yinan Wei / Chemistry, University of Kentcuky

Proteins are naturally occurring biopolymers that have evolved to perform all kinds of functions in living cells. Researchers are making tremendous progress in the last couple of decades in exploiting the natural function of proteins by introducing them into artificial systems. The immobilization of proteins is usually the first step to their applications in biotechnology that include a broad range of areas such as catalysis, biosensing, and material development. Ideal immobilization method should be highly effective and site specific, while at the same time does not denature the target protein. This study seeks to develop a new tag-based method for site specific protein labeling and immobilization. A dual function tag, which can be used for both protein purification and immobilization, was designed and tested. The tag is composed of 4 Met and 6 His residues: HMHMHMHMHH. Using sfGFP as the model system, we demonstrated that when added to the C-terminus, the tag can facilitate purification via the metal affinity chromatography method (similar as in the well-established Histag), while the abundance of Met enables the metabolic incorporation of the unnatural amino acid azidohomoalnine (AHA), which could be subsequently labeled using the well-developed click chemistry method.

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CONDENSATION OF DNA BY PROTAMINE AT VARYING CONCENTRATIONS

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The nature of DNA condensation and packaging is an important function in living organisms. DNA condensation is the process in which a polycation packages a cell's genetic material into a form that allows protection, transportation, and storage of the DNA. The subject of our work is understanding the condensation of DNA by the protein protamine. Protamine is a highly basic protein used to package DNA in sperm chromatin. Specifically, we are interested in the effects of underprotamination on the packaging of DNA. Using gel electrophoresis, UV-Vis spectroscopy, and small-angle X-ray experiments we have examined the DNA packaging for varying nitrogen to phosphate (N/P) charge ratios. UV-Vis and gel electrophoresis show that significant DNA condensation can still occur at N/P ratios less than one. SAXS allows us to follow the interaxial DNA spacings as a function of N/P ratios. We show that underprotamination plays a significant role in the resulting final packaged state in the DNA condensate.

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DETERMINATION OF THE ACTIVATION ENERGY OF THE RATE-LIMITING STEP OF THE FENTON REACTION

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The Fenton reaction is commonly used to remove polycyclic aromatic hydrocarbons from waste water streams. In this reaction, hydrogen peroxide and ferrous ions are thought to produce a highly reactive hydroxyl radical intermediate. However, the identity of the intermediate and the mechanism for this reaction are under dispute. In this research, the rate of the Fenton reaction was studied under pseudo first-order conditions by allowing the reaction intermediate to convert benzoic acid to hydroxy-benzoic acid and following the concentration of the product using fluorescence spectroscopy. The rate constant for this reaction was studied under pseudo first-order conditions at temperatures between 3°C and 25°C allowing for the determination of an Arrhenius activation energy of 38.8 kJ/mol.

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LOLINE ALKALOIDS: SYNTHESIS OF EXO-1-ACETAMIDOPYRROLIZIDINE AND EXO-1-ACETAMIDOINDOLIZIDINE

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Lolines are insecticides produced by endophytic fungi of grasses. Exo-1-aminopyrrolizidine (AP) and exo-1-acetamidopyrrolizidine (AcAP) are intermediates in the biosynthetic pathway leading to the loline alkaloids. The published synthetic route to these compounds includes a Raney nickel reduction of the ketoxime 1-oximinopyrrolizidine to AP, but this reaction proceeds in very low yield. Our laboratory recently discovered that nickel boride is a more productive reagent for this conversion. Looking to test the promiscuity of lolO, an enzyme in the biosynthetic pathway that acts on AcAP, a homolog of AcAP called exo-1-actamidoindolizidine was produced from the reduction of the ketoxime 1-oximinoindolizidine with nickel boride.

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VISIBILE LIGHT GENERATION OF HIGH-VALENT PORPHYRIN IRON-OXO INTERMEDIATES

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Tse-Hong Chen / Chemistry, WKU
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High-valent porphyrin iron–oxo intermediates play central roles as active oxidants in enzymatic and synthetic catalytic oxidations. In this presentation, a new photochemical method to generate high-valent iron–oxo model will be presented. As controlled by the electronic nature of porphyrin ligands, iron (IV)–oxo porphyrin radical cations (compound I model) and iron (IV)–oxo porphyrin derivatives (compound II model) were produced, respectively, by visible light irradiation of the corresponding iron (III) bromate complexes. These observations indicate that the photochemical reactions involve a heterolytic cleavage of O–Br in precursors to give a putative iron (V)–oxo intermediate, which might relax to compound I through electron transfer from electron rich porphyrin to the iron or undergo rapid comproportionation reaction with residual iron (III) to afford the compound II derivative.

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PALLADIUM-CATALYZED SYNTHESIS OF ANTHRACENE AND PENTACENE DERIVATIVES AS ORGANIC SEMICONDUCTOR CANDIDATES

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John Anthony / Chemistry, University of Kentucky
Marcia Payne / Chemistry, University of Kentucky
Jenny Washbourne / Chemistry, University of Kentucky
Matt Bruzek / Chemistry, University of Kentucky

Experiments consisted of reactions to synthesize two different target molecules as possible candidates for organic semiconductors: 2,3-tricyclopentylsilylacetylene-5,6,7,8-tetrafluoroanthracene-1,4-dione and a pentacene derivative with dimethylpropylsilylacetylene substituents. The synthesis of 2,3-tricyclopentylsilylacetylene-5,6,7,8-tetrafluoroanthracene-1,4-dione was attempted using a palladium catalyzed Sonagashira coupling reaction with 2,3-dibromo-5,6,7,89-tetrafluoranthracene-1,4-dione and tricyclopentylsilyl acetylene. A reaction scheme for a pentacene derivative with dimethylpropylsilylacetylene substituents was proposed and explored.

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STUDIES ON SPE-GC-MS FOR ISOLATION, IDENTIFICATION AND QUANTITATION OF ALKALOIDS IN FROG SKIN

Allyson Morris / Chemistry, Indiana State University (Senior)
Richard Fitch / Chemistry, Indiana State University

Dendrobatid poison frogs are well-known for their bright coloration and toxicity. Arthropods that make up these frogs' diet are the principal source of toxic compounds, typically alkaloids. We typically analyze these by gas chromatography-mass spectrometry (GC-MS) in electron impact (EI) and chemical ionization (CI) modes. In many species of poison frogs, inter-individual variation has been observed and some studies have correlated color with toxicity. Concomitant with this we sought a method which would allow high throughput analysis of many samples of individual frog secretions. In this study, we have focused on improving the alkaloid extraction and GC-MS methods for these compounds using solid phase extraction (SPE). SPE is a potential replacement for the current liquid-liquid extraction (LLE) method and can easily be multiplexed with 96-well plates, thus improving throughput. We examined cation exchange SPE as a promising alternative to acid-base LLE partitioning. Fifteen commercially available amines were chosen for their structural variation including primary, secondary and tertiary as well as diamines and amino alcohols. These amines were chosen for their structural diversity and similar polarity to frog alkaloids. We also studied the effects of split and splitless injection in GC-MS. We have found that surged splitless injection appears to be a superior method for increasing sensitivity. We determined that while cation exchange holds promise, issues with sorbent capacity/breakthrough, irreversible adsorption of polar amines (particularly H-bond donors) are significant. Careful selection of phase (strong vs weak cation exchange, silica vs polymeric support) and solvents (loading/wash/elution/additives) are critical for obtaining useful recoveries across structural classes. Our results to date will be presented.

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IDENTIFICATION OF COMPOUNDS WITHIN BOURBON USING GCMS

Benjamin Munson / Chemistry, University of Kentucky (Junior)

Bourbon whiskey is an important cultural icon within Kentucky, and the United States at large. While there are already several inquiries into the compounds that make up whiskey at large, Bourbon whiskey itself is often used at most as a comparison drink. As such, specific analysis into Bourbon whiskey by itself is a potential field to be considered. This is a proposal into the analysis of Bourbon whiskey by identifying the compounds that comprise and contribute to its flavor, and what compounds remain consistent and what varies among different brands, using gas chromatography mass spectrometry to identify various compounds and their corresponding peaks in a chromatagram of Bourbon.

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NOVEL RUTHENIUM-BASED COMPOUNDS AS A POTENTIAL CHEMOTHERAPEUTIC

Leona Nease / Chemistry, University of Kentucky (Junior)
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Edith Glazer / Chemistry, University of Kentucky

Cancer is currently the second leading cause of death worldwide, with over 1.6 million people diagnosed this year in the US alone. A large majority of current treatment regimens include platinum-based drugs such as cisplatin, carboplatin and oxaliplatin. Unfortunately, there are several drawbacks to this class of compounds such as lack of potency, systemic toxicity, neurotoxicity and the tumors' ability to build resistance to the drugs. In an effort to solve these issues, we are exploring a new class of metal-based compounds where ruthenium(II) is used to coordinate derivatives of quinolone ligands, creating a three-dimensional structure to serve as a potential chemotherapeutic agent. Hydroxyquinoline compounds have been shown to have a wide variety of anti-cancer mechanisms, including inhibiting protein kinases, telomerase, and many more pathways. When coordinated to ruthenium, these ligands have been shown to produce a dramatic increase in cell cytotoxicity. For example, in the HL60 leukemic cell line, the EC50 value of a particular ligand improved from 4.09 for the ligand alone to 0.054 for the coordinated compound: a 75-fold change. Through western blotting, we observed a dose-dependent decrease in caspase-3, PARP, and phospho-AKT, and an increase in phospho-H2AX, which all points towards a cell death mechanism of apoptosis. Contrary to platinum-based compounds, the change in cellular level of these proteins was observed without any cell cycle arrest. We will continue research to determine the exact target and cellular mechanism of the compounds. We also hope to determine a structure-activity relationship of these ruthenium(II) complexes in order to improve compound potency.

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ANALYSIS OF THE MECHANISM BEHIND BIOLOGICAL DESULFURIZATION OF PETROLEUM

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Biodesulfurization is the process by which sulfur compounds are removed from petroleum through biological means. It is an alternative to conventional hydrodesulfurization since biodesulfurization can remove heterocyclic organo-sulfur compounds such as dibenzothiophene. The commercialization of biodesulfurization relies upon biocatalytic activity improvements. To understand the process behind biocatalytic activity, we will investigate 2'-hydroxybiphenyl-2-sulfinate (DszB), which catalyzes the rate-limiting step of the biodesulfurization of dibenzothiophene. Recent literature on the structure of DszB has indicated that kinetic limitations are a result of substrate specificity and competitive inhibition by the product and compounds found in petroleum. We hypothesize that substrate specificity and enzyme inhibition are critically linked to active site dynamics and chemical composition. The catalytic mechanism will be analyzed using quantum mechanical calculations to determine the energy barrier and catalytic cycle rate. This will allow us to complete a mechanistic description of substrate specificity.

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FABRICATION OF METAL OXIDE NANOWIRE-THIN FILM COMPOSITES

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Yao-Jen Chang / Chemistry, University of Kentucky
Bethany Hudak / Chemistry, University of Kentucky
Beth Guiton / Chemistry, University of Kentucky

Photolithographic, top-down, fabrication has been the industry standard for semiconductor device production for decades. However, there is optimism for more efficient bottom-up approaches. Our work involves the chemical vapor deposition of metal oxide nanowires with the ultimate goal of producing a thin film-nanowire composite. The concept of this device is a thin film of one metal oxide with nanowires of another metal oxide embedded axially within the thin film. It is hypothesized that such an arrangement would produce interesting electronic properties compared to standalone thin films or nanowires. If complementary oxides are used (n-type with p-type), the result is potentially akin to rectifying junctions used in silicon chips.

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SYNTHESIS OF IRON CONTAINING NANO-STRUCTURES

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Lei Yu / Chemistry, University of Kentucky
Honore Djieutedjeu / Chemistry, University of Kentucky
Beth Guiton / Chemistry, University of Kentucky

Magnetic nano-structures are interesting because they can exhibit a wide range of extraordinary properties, such as induced magnetization in noble metals and low dimensional magnetism. Additionally, in the past decade one dimensional single crystalline nano-structures have become a burgeoning area of research due to their potential application to nano devices. Hence, an enormous effort has been made to further understand the magnetic and electronic properties of nano-structures. Here we report a low temperature synthesis of one-dimensional single crystalline nano-rods with controllable and homogenous size distribution, from a number of magnetic, iron-containing oxide compositions.

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AQUEOUS PHASE SYNTHESIS OF TRANSITION METAL NANOPARTICLES

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Thulitha Abeywickrama / Chemistry, Western Kentucky University
Hemali Rathnayake / Chemistry, Western Kentucky University

Here we propose a method for an economically feasible and environmentally friendly method for the reduction of metal salts to elemental metal nanostructures. Metal nanoparticles and nanopowders have commonly been synthesized using heat, capping agents, and the highly toxic reducing agent, hydrazine. Although this procedure has proven effective, our method utilizes the milder reducing agent, sodium borohydride (NaBH4), and is run at room temperature in the aqueous phase without capping agents. This novel procedure has been used for transition metals like copper, iron, nickel and zinc. Analysis by Energy-dispersive X-ray Spectroscopy (EDS) confirmed reduction, with some unexpected metal oxide production, which has since been minimized by running the reaction under argon. The nanostructures' morphology was analyzed via Transmission and Scanning Electron Microscopes (TEM and SEM). This analysis confirmed particle formation, with some aggregation shown from nickel and iron. These nanostructures will be tested for their conductivity and will have future application as metal-organic hybrid semiconducting nanocomposites for use in thin film organic-based solar cells.

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LIGAND EXCHANGE OF AN ENZYME-MIMIC SCHIFF BASE COPPER(II) COMPLEX

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Sarah Williams / Chemistry and Physics, Belmont University
Jeanette Krauss / Chemistry, University of Cincinnati
Justin Stace / Chemistry and Physics, Belmont University

The synthesis, purification and characterization of a Copper(II) Schiff-base complex is presented. The [CuLN4](ClO4)2 complex (LN4 = N,N'-bis-(1-pyridin-2-yl-ethylidene)-propane-1,3-diamine) is highly soluble in acetonitrile, and moderately soluble in water, and exhibit Beer's Law behavior. The compound is unreactive in the presence of strong oxidizing agents, but does react slowly with oxalic acid. The reactivity of the complexes in aqueous solvent in the presence of oxalic acid is investigated. Rapid mixing of various concentrations of [CuLN4](ClO4)2 and oxalic acid monitored by UV-visible spectroscopy suggest an overall second order rate law. At greater time resolution, however, there is underlying complexity, suggesting a two step mechanism upon further analysis. The reaction seems to be unaffected by exposure to the atmosphere. The solid produced is found to be copper (II) oxalate, and various mechanisms are investigated with their respective plausibilities discussed.

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RING OPENING POLYMERIZATION OF SIX MEMBERED CYCLIC CARBONATES USING BIMETALLIC CATALYSTS

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Stephanie Poland / Chemistry and Biochemistry, Rose-Hulman Institute of Technology

Due to the numerous applications of polytrimethylene carbonate (polyTMC), especially in the medical field, devising an effective and cost effective method for the synthesis of polyTMC is an important area of research. In this study, two previously reported bimetallic zinc and magnesium catalysts were synthesized used for the catalytic ring opening polymerization of trimethylene carbonate (TMC). Primarily, the effect of temperature on catalyst activity was examined, with a maximum conversion via isolation of purified polymer of about 67% at 90^{o}C using the bimetallic magnesium catalyst. In addition to studying the temperature effect, the polymerizations were performed both with and without solvent in order to assess the prospect of implementing a more environmentally-friendly neat polymerization. Recent results regarding the ring-opening polymerization of 2,2-dimethoxy-1,3-dioxane, a TMC analogue derived from dihydroxyacetone, will also be discussed.

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INVESTIGATING NANOCERIA AS A POTENTIAL THERAPEUTIC AGENT

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Robert Yokel / Chemistry, University of Kentucky
Danielle Lee / College of Pharmacy, University of Kentucky
Aaron Swomley / Chemistry, University of Kentucky
D. Allan Butterfield / Chemistry, University of Kentucky

Oxidative stress is a condition of which arises when free radical production exceeds biochemical means of scavenging these free radicals. The presence of oxidative stress is a characteristic of neurodegenerative disorders. Nanoscale ceria exhibits specific redox activity, which has the potential to cause antioxidant and anti-inflammatory activity in certain organisms that could reverse or modulate this oxidative stress. However, the literature is conflicted on the suitability of nanoceria as a therapeutic agent, and there is no clear conclusion as to the specific effects nanoceria has on biological systems under varying conditions. Our group has recently discovered that nanoceria causes oxidative stress in brain up to a month after administration to rats. The nanoceria not only persists, but over long time periods undergoes size and morphological changes in the rat to a chemical species with antioxidant properties, suggesting biotransformation to a beneficial form. The research presented shows my preliminary studies in which LPS has been used to induce oxidative stress and antioxidant defense system responses in rat, so that we can determine an appropriate nanoceria pretreatment dose and time.

Support: 1 R01GM109195 from NIH

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POLYBOROSILOXANE BINDER FOR SILICON BATTERY ANODES IN LITHIUM-ION BATTERIES

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Susan Odom / Chemistry, University of Kentucky
Yang-Tse Cheng / Department of Chemical and Materials Engineering, University of Kentucky
Matthew Casselman / Chemistry, University of Kentucky

Harnessing silicon (Si) as the anode material in lithium-ion batteries offers the possibility of a nearly ten-fold capacity increase over traditional graphite anodes. However, the 300% volume expansion and contraction upon charging and discharging hinders its practical use due to a significant loss in capacity with cycling. Unique geometric arrangements of Si particles, as well as modifications of polymer binder, have resulted in advances in capacity retention over time, but many modifications are cost-prohibitive for producing a commercially viable electrode. Our strategy to minimize the loss in capacity retention of this high-capacity anode material involves the utilization of a viscoelastic cross-linked polysiloxane polymer binders. This presentation will discuss the mechanical properties and cycling characteristics of the electrodes prepared with this binder and comparable polymers. A highlight of our progress is a retention of charge capacity over >100 cycles. In addition to the retention of capacity, we highlight the low cost and simple synthesis of this polymer binder.

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SYNTHESIS AND CHARACTERIZATION OF MOLECULAR DYADS AND THEIR CORE-SHELL NANO PARTICLES

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Wendy Loomis / Chemistry, Western Kentucky University
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Small molecules have several advantages making them promising materials for organic electronics such as: monodispersity, high charge carrier mobility, and relatively simple synthesis with reproducibility. Here, we described three molecular dyad systems derived from fused arenes such as anthracene, pyrene and thiophene. These three novel molecular systems, 1,2-Benzene-di-(anthracene-9-yl-methyl-carboxylate), Anthracene-9-yl-methyl-5-bromo-thiophene-2-carboxylate, and 1,2-Benzene-di-(pyrene-9-yl-methyl-carboxylate), were prepared using Steglich esterification. The molecular structure and functional groups were confirmed by 1H-NMR and FTIR spectroscopies. The photophysical properties of the products were also evaluated in solution and in thin films. A simple solvent aggregation method, followed by UV cross-linking with a derivative of perylenediimide silane core -shell nanoparticles, was used to prepare the particles with the size range of 50 nm to 200 nm. Morphologies of these particles were analyzed using transmission electron microscopy. The method developed here will aid in making water-dispersible nano ink since they can disperse in water.

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OXIDIZED SOLID STATE RHENIUM THIOLATE AS A HIGHLY SPECIFIC ETHYLENE GAS SENSOR

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In plants, ethylene is an important plant hormone that is involved in many different areas of phenotypic expression and regulation. In that, ethylene is primarily the culprit responsible for the ripening of fruit. The mechanism of this biosynthetic pathway has been explored in depth over the last decade or so, and has been repeatedly shown to be a result of a disulfide bridge formed between the two carbons of ethylene and two protruding sulfur groups that extend out from the ETR-1 (ethylene response sensor-1), which is comprised of two adjacent histidine-kinase receptors. The Zamborini Research Group reports here a new, cost-effective, and portable ethylene sensor that utilizes a Rhenium-Thiolate complex, that has been spray coated on the surface of a Quartz-Crystal, which mimics the active sites of the ESR-1 subfamily of transmembrane, ethylene-binding, proteins in plants. Through use of a Quartz-Crystal Microbalance, we can measure the amount of ethylene present in a gas sample with high specificity and high accuracy. Not only will this sensor selectively bind ethylene, but it will bind reversibly as well. Currently, the lowest detectable concentration of ethylene we have observed is around 1% with no maximum detection level, however, work is being done to create a sensor with the goal of sensing in the ppm and ppb levels.

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CHARACTERIZATION OF THE FORMATION OF PROTEIN CORONAS ON NANOPARTICLES BY FLUORESCENCE CORRELATION SPECTROSCOPY (FCS)

Leslie Uche / Chemistry, University of Kentucky (Senior)
Xiaolu Zhang / Chemistry, University of Kentucky
Jason DeRouchey / Chemistry, University of Kentucky

Characterization of the formation of protein coronas on nanoparticles by fluorescence correlation spectroscopy (FCS)

Leslie Uche, Xiaolu Zhang, Jason DeRouchey

Abstract

Due to the high surface area of nanoparticles, once exposed to biological media they quickly become covered in biological molecules such as proteins or lipids. It is thought that the corona is the most important factor determining the nanoparticle's biocompatibility and in vivo fate. Here we have used fluorescence correlation spectroscopy (FCS), a non-invasive, single-molecule analysis technique, to characterize the adsorption of fluorescently labeled human transferrin and bovine serum albumin onto nanoparticles using the model system of 50nm polystyrene beads. FCS allows us to quantitatively examine the formation of the corona by examining the fraction of bound and unbound fluorescently labeled proteins. We observe that for Polystyrene (PS), multi-layered coronas are formed for both albumin and transferrin. We also used FCS to follow the kinetics of the corona formation as a function of buffer pH and added salt. Our results suggest that the thickness of protein corona, the assembly rate of protein-NP complex and the protein binding affinities on PS beads are dependent on the properties of proteins as well as the local physicochemical properties.

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INHIBITION OF THE PRODUCTION OF GLUCOCORTICOID IN RESPONSE TO EARLY LIFE STRESS AND ITS EFFECT ON METABOLIC GENE EXPRESSION.

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Clinical studies show a positive correlation between early life stress (ELS) and the development of cardiovascular disease and type 2 diabetes. Previous studies performed in the Loria Lab have indicated that female WKY rats that were exposed to the early life stressor of maternal separation (MatSep) showed an exaggerated body weight gain in response to high fat diet (HFD) when compared to control rats. When these rats were treated with the glucocorticoid synthesis inhibitor metyrapone before daily exposure to maternal separation, it was observed that this treatment abolished the diet induced obesity and glucose intolerance later in life. The aim of this study was to analyze gene expression in adipose tissues of key metabolic enzymes that might contribute to the exaggerated obesity of female rats exposed to MatSep. We exposed WKY female rats to MatSep (3 hr/day) during the first two weeks of life (day 2 to 14). In a separate group of pups, Metyrapone was administered prior to daily MatSep (MTP, 50 g/kg, postnatal day 2-14). Non-disturbed littermates were used as controls. The MatSep and control rats were then fed either a high fat diet (60% kcal from fat) or a low fat diet (10% kcal from fat) upon weaning for 12 weeks. Glucose tolerance tests were performed in week 9. Adipose tissues were collected from the sacrificed rats and mRNA from these tissues was extracted. To do so the technique of polymer chain reaction (PCR) was used to determine levels of gene expression of five distinct genes associated with metabolism. The first gene selected, GAPDH, which is expressed constitutively in most tissues and then used as housekeeping gene to normalize expression data. Levels of expression of PGC-1a, a key coactivator that regulates mitochondrial biosynthesis and function, was not significantly different between MatSep and control in all treatments. Levels of GLUT4, an insulin regulated glucose transporter in adipose tissue, was not changed between groups as well. Levels of expression for insulin receptors in gonadal adipose tissue were found to be down regulated in MatSep fed a HFD when compared to control rats (0.55±0.074 vs. 1.04±0.113 2-ddCt, $p<0.05$). Interestingly, MTP treatment reverted this effect. The last gene whose expression was measured was angiotensinogen (AGT) which is the precursor of a peptide hormone that causes vasoconstriction and elevated blood pressure and obesity. It was found that levels of expression were upregulated in HFD MatSep rats (2.56±0.360 vs. 1.14±0.364 2-ddCt, $p<0.05$) and MTP treatment blunted this effect (0.38±0.098 vs. 1.05±0.143 2-ddCt, $p<0.05$). The differences in gene expression in fat tissue from rats exposed to stress during postnatal life help to explain how these female rats develop exaggerated obesity and metabolic dysfunction.

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SYNTHESIS OF DITHIOLS USED FOR HEAVY METAL ION CAPTURE

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Heavy metals such as arsenic, mercury, lead and cadmium are all known for their dangers to human health. This presentation will give notice to the synthesis of a dithiol compound called N, N'-bis(2-mercaptoethyl) isophthalamide; also known as BDTH2 or B9. It will also give synthesis details on a B9 derivative, called AB9 or Acid-B9. These compound use their soft dithiol groups to bond with soft acids such as mercury, cadmium, and arsenic (III) to a certain degree. What makes AB9 different is that it has two additional carboxylic acid groups; these groups act as additional reaction sites as well as hard bases to bond with vanadium (V), arsenic (V), and lead (II). In total this presentation will primarily focus on the capture of lead (II) and vanadium (V) with AB9, health concerns related to arsenic, and potential capture of arsenic (III) with B9.

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EXPOSURE TO STRESS-INDUCED GLUCOCORTICOIDS DURING EARLY LIFE EXAGGERATES HEPATIC GLUCONEOGENIC GENE EXPRESSION IN FEMALE RATS

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Exposure to stress-induced glucocorticoids during early life exaggerates
hepatic gluconeogenic gene expression in female rats.

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Studies in humans and animal models have shown a positive correlation between early life stress (ELS) and the development of Cardio Metabolic disease later in life, but few have addressed the sex-specific disparities. Previously, we have shown that maternal separation (MatSep), a model of ELS in rodents, does not change body weight, glucose tolerance or renal function in male rats fed a HFD for 20 weeks following weaning. Therefore, the goal of this study was to determine whether female rats exposed to MatSep display increased susceptibility to develop cardiometabolic disease in response to a HFD challenge. MatSep was performed in WKY rats by separation (3 hr/day) from the dam during the first two weeks of life (day 2 to 14). Non-disturbed littermates were used as controls. MatSep and control rats (n=6-8) were placed on a HFD (60% kcal from fat) upon weaning for 12 weeks. At week 9, an oral glucose tolerance test (OGTT) was performed and 3 days before the end of the study, rats were placed in metabolic cages for urine collection. MatSep exaggerated body weight gain (253±3.9 vs. 234±2.75 g, $p<0.05$), gonadal fat pad (6.4±0.6 vs. 4.1±0.3 g, $p<0.05$) and subcutaneous fat pad weights (2.1±0.1 vs. 1.59±0.12 g, $p<0.05$). Oral glucose tolerance test was impaired in MatSep rats compared to control rats (25776±339 vs. 22491±982 A.U., $p<0.05$). In a parallel study, we performed a postnatal treatment with metyrapone, (MTP, 50g/kg, postnatal day 2-14 s.c.) prior to the daily maternal separation using rat pups, in order to determine whether the inhibition of the stress-induced corticosterone release will play a role in our model. Notably, we found that this treatment abolished the diet-induced obesity and glucose intolerance in female rats ($p<0.05$), indicating that the attenuation of the stress-induced corticosterone in early in life prevent the exaggerated obesity-related metabolic derangements in a rat model of ELS. In this study we looked at the expression of hepatic 11β HSD1, an indicator of local glucocorticoid generation, and PEPCK, PC, and G6Pase genes, which are important in gluconeogenic pathways. We did not find significant differences in the expression of 11β HSD1, PEPCK, and PC genes; however, there was a significant upregulation in G6Pase in MatSep female rats fed a HF diet compared to the control (1.04±0.34 vs. 2.37±1.01 2-ddCt, $p<0.05$). This upregulation was blunted by MTP treatment (1.26±0.29 vs. 1.18±0.77 2-ddCt). Taken together, these data indicate that MatSep enhances HFD-induced obesity, glucose intolerance and alterations in genes regulating gluconeogenesis, which are primed by early exposure to glucocorticoids. Glucocorticoids could be a potential therapeutic target in early life stress-induced cardiometabolic disease.