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### Research Internships in Science and Engineering

Research Interns in Science and Engineering (RISE)

Summer 2009 - Student Projects

Student Major/School	Mentor	Faculty Sponsor	Department	Student Project
<a href="#"><u>Elisa Aguilar</u></a> Chemical Engineering San José State University	Jennifer Getz	Patrick Daugherty	Department of Chemical Engineering	TESTING THE BINDING AFFINITY OF THROMBIN TO PEPTIDES
<a href="#"><u>Randi-Jo Brown</u></a> Forensic Science Pennsylvania State University	Anh Vu	Frederick Dahlquist	Department of Chemistry and Biochemistry	CHEMOTAXIS: A COMPARISON OF KINASE ACTIVITY BETWEEN RECEPTOR & NON-RECEPTOR REACTIONS
<a href="#"><u>Nicole Carroll</u></a> Mathematics University of California, Santa Barbara	Hugh O'Neill	Philip Lubin	Physics Department	INFRARED AND MILLIMETER CORRELATION OF MOLECULAR EMISSIONS IN THE ATMOSPHERE
<a href="#"><u>David Garcia</u></a> Chemistry California State University Humboldt	April Sawvel	Galen Stucky	Department of Chemistry and Biochemistry	SELF-ASSEMBLY OF THROMBIN-LOADED MICROPARTICLES VIA COMPLEX COACERVATION
<a href="#"><u>Abby Goldman</u></a> Physics Mount Holyoke College	Brent Melot	Ram Seshadri	Materials	STRUCTURE-PROPERTY RELATIONS IN CoSeO <sub>4</sub> , A ONE DIMENSIONAL MAGNETIC MATERIAL
<a href="#"><u>Blanca P. Moreno Hernandez</u></a> Chemistry University of	Katie Feldman & Jasmine	Craig J. Hawker	Department of Chemistry and Biochemistry	PEG-POLYELECTROLYTE HYBRID COPOLYMERS

California Los Angeles	Hunt			
<b><u>Brandon Krull</u></b> Chemistry, Biotechnology California State Polytechnic University, Pomona	Luis M. Campos	Craig Hawker	Materials Research Laboratory	SYNTHESIS OF FUNCTIONALIZED DENDRIMERS VIA THIOL-ENE CLICK CHEMISTRY TO AID IN SELF-ASSEMBLY OF PEPTIDE AMPHIPHILES
<b><u>David Lavelle</u></b> Mechanical Engineering Cal Poly San Luis Obispo	Noah Philips	Anthony Evans	Materials	MECHANICS OF SOIL BLASTS AND THEIR EFFECTS ON MATERIAL BEHAVIOR
<b><u>Bernice McLaurin</u></b> Chemistry Jackson State University	Joanna Deek	Cyrus R. Safinya	Department of Cellular, Molecular and Developmental Biology	SALT DEPENDENCE OF NEUROFILAMENT GEL PHASE BEHAVIOR
<b><u>Nicole Ricapito</u></b> Chemical Engineering Rensselaer Polytechnic Institute	Andrew Dittmore	Omar Saleh	Materials	INVESTIGATING ATTACHMENT STRATEGIES FOR SINGLE BIOMOLECULE MANIPULATION
<b><u>Christen M. Robinson</u></b> Chemical Engineering Jackson State University	Isaac Riisness	Michael J. Gordon	Chemical Engineering Department	LIGHTS, CAMERA, ACTION! MOLECULAR SURFACE IMAGING VIA ENHANCED LIGHT-MATTER INTERACTIONS
<b><u>Jason Ross</u></b> Physics University of California Berkeley	Nidhi Nidhi	Umesh Mishra	Electrical and Computer Engineering	IMPROVED TRANSCONDUCTANCE LINEARITY OF GaN/AlGaN HEMTs
<b><u>Rachel Schoepner</u></b> Materials Engineering California Polytechnic San Luis Obispo	JJ Cowart	Michael Chabinc	Materials	MODULATION OF CONJUGATED POLYMER CONDUCTIVITY WITH MOLECULAR DOPANTS
<b><u>Alison Schultz</u></b>			Materials	KETENES IN MATERIALS

Chemistry University of Rhode Island	Frank Leibfarth	Craig J. Hawker	Research Laboratory	SCIENCE: EXPANDING THE LIBRARY OF FUNCTIONAL POLYMERS
<a href="#"><u>Sara A. Turner</u></a> Department of Chemistry Williams College	Zeric Hulvey	Anthony K. Cheetham	Materials Research Laboratory	SYNTHESIS AND CHARACTERIZATION OF FLUORINATED HYBRID INORGANIC-ORGANIC MATERIALS FOR H <sub>2</sub> STORAGE
<a href="#"><u>Willie Wesley</u></a> Chemistry Jackson State University	Brent Melot	Ram Seshadri	Department of Chemistry and Biochemistry	MAGNETIC AND DIELECTRIC PROPERTIES OF Co <sub>1</sub> - XZnXCr <sub>2</sub> O <sub>4</sub>

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### Elisa's Project Page - RISE Summer 2009



Intern: Elisa Aguilar, Chemical Engineering, San José State University

Mentor: Jennifer Getz

Faculty Supervisor: Patrick Daugherty

Department: Department of Chemical Engineering

Thrombin is a coagulation protein that plays a central role in blood clotting diseases such as myocardial infarction, stroke, acute coronary syndromes, atrial fibrillation, and venous thromboembolism. Currently, small molecule therapeutics are used to treat these diseases but have serious side effects. A safer alternative is peptide-driven therapies, however they can only be delivered intravenously. Although peptides are more appealing than small molecules due to their high specificity, high affinity and low toxicity, peptides have shown to be unstable under physiological conditions. This limitation can be overcome through the use of a stable peptide scaffold. In this project, the peptide scaffold Kalata B1 (KB1) was chosen as it retains its structure regardless of the addition of proteases, high temperatures and chemical denaturants. Various scaffold constructs were evaluated to see how less rigid structures would affect the binding affinity of thrombin to peptides. Bacterial surface display methods developed by the Daugherty lab were used to engineer desired peptide constructs on the cell surface of *E. Coli* [1]. Flow Cytometry was then used to measure the fluorescence emitted which is directly correlated to the binding affinity of thrombin. It was found that KB1 had the highest affinity compared to unconstrained linear and single-disulfide constrained loop like structures which resulted in a much lower affinity for thrombin. With this information we hope to provide more knowledge in the development of a stable scaffold that can prevent peptides from proteolytic degradation.

[1] Rice, [J.J.], & Daugherty, [P.S.] Directed Evolution of a Biterminal Bacterial Display Scaffold Enhances the Display of Diverse Peptides. *Protein Engineering, Design and Selection*, 21, [435-442].

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### Randi-Jo's Project Page - RISE Summer 2009



Intern: Randi-Jo Brown, Forensic Science,  
Pennsylvania State University  
Mentor: Anh Vu  
Faculty Supervisor: Frederick Dahlquist  
Department: Department of Chemistry and  
Biochemistry

#### CHEMOTAXIS: A COMPARISON OF KINASE ACTIVITY BETWEEN RECEPTOR & NON-RECEPTOR REACTIONS

Chemotaxis is an occurrence in which organisms regulate their movement in accordance to chemicals existing in their environment. In chemotactic bacteria, the proteins CheA, CheW, and a receptor join together to form a ternary complex, which along with CheY, is responsible for directing flagellar movement by controlling the kinase activity of CheA. In order to test the regulation of the ternary complex, CheA/CheY phosphorylation assay was necessary. Phosphorylation is a reaction in which a phosphate group is added to a protein, resulting in the activation or deactivation of present enzymes, namely CheA. It was hypothesized that using a wild type receptor, TM14, should result in a faster phosphorylation rate than no receptor at all, and that the wild type would illustrate a faster rate than the use of a mutant receptor known to disrupt the binding of this complex. We investigated the phosphorylation rates using phosphorylation assay for four different reactions: no receptor, TM14 wild type receptor, TM102 mutant receptor, and TM98 mutant receptor. Growth and purification of CheA, CheY, CheW, and the receptors was conducted using a french press, dialysis, ion-exchange chromatography, Ni-NTA affinity chromatography, size exclusion chromatography, and SDS-PAGE gels. The resulting data after performing phosphorylation assay refuted our hypothesis in that the mutant receptor, TM102, possessed the fastest rate of phosphorylation, rather than the wild type receptor.

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### Nicole's Project Page - RISE Summer 2009



Intern: Nicole Carroll, Mathematics, University of California, Santa Barbara  
 Mentor: Hugh O'Neill  
 Faculty Supervisor: Philip Lubin  
 Department: INFRARED AND MILLIMETER  
 CORRELATION OF MOLECULAR EMISSIONS IN THE  
 ATMOSPHERE

#### CHEMOTAXIS: A COMPARISON OF KINASE ACTIVITY BETWEEN RECEPTOR & NON-RECEPTOR REACTIONS

Atmospheric water vapor poses a significant problem in studying incoming infrared and microwave radiation. Water vapor absorbs and emits light strongly in both of these wavelengths, and so it interferes with our observations of incoming radiation. Unlike most atmospheric gases that absorb infrared light, water vapor is not uniform, but varies in time and space. By continuously photographing the sky at the visible and infrared wavelengths, we can construct an atmospheric model of water vapor. Using this model and image processing software, we are able to reduce the water vapor interference from the infrared data. Further, we can use these results to determine if there is a correlation between the effects of water vapor in the infrared and the microwave bands. If there is such a correlation, we will ultimately use the infrared band real-time data to correct ground-based telescopes that study radiation in the millimeter wavelength bands. In particular, this correlation can be used to help study radiation from the Cosmic Microwave Background, which will provide information on the early universe. An accurate atmospheric model of water vapor fluctuations could also have applications for research on the greenhouse effect and global warming.

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### David's Project Page - RISE Summer 2009



Intern: David Garcia, Chemistry, California State University Humboldt  
 Mentor: April Sawvel  
 Faculty Supervisor: Galen Stucky  
 Department: Department of Chemistry and Biochemistry

#### SELF-ASSEMBLY OF THROMBIN-LOADED MICROPARTICLES VIA COMPLEX COACERVATION

Uncontrolled hemorrhage continues to be the leading cause of battlefield mortality and the second leading cause of death in civilian traumas. There is currently no effective method for treating internal hemorrhage. Synthesis of a microparticle carrier for the coagulation enzyme Thrombin via complex coacervation is a novel approach to this problem. Complex coacervation is the self-assembly process formed of two oppositely charged polyelectrolytes in solution; this study involves the poly-amino acids poly-L-aspartate (PLD) and pentyllysine (LYS). Optimizing the number and size of coacervates formed is essential to forming appropriate microparticles; these properties will directly influence the thrombin-loading capacity and biocompatibility of the microparticles. We aim to find the optimal polyelectrolyte concentrations, pH and ionic strength solution conditions for coacervate formation within the PLD/LYS system. Coacervate size was determined by visual inspection, image analysis with the ImageJ software, and dynamic light scattering (DLS). The dependence of coacervate formation on pH and ionic strength was investigated with  $\zeta$ -potential measurements from a Zeta-Sizer Nano. It was found that the size of the coacervates decreases and the number of coacervates formed increases as LYS concentration is lowered (with PLD held constant); together with isoelectric point curves for both PLD and LYS this information will allow us to fine-tune microparticle properties for the ideal combination of size and number of coacervates formed.

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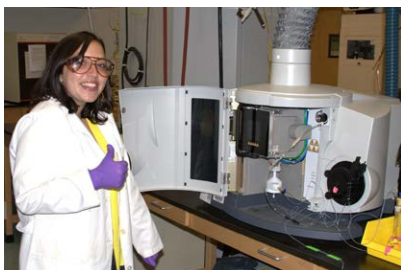
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### Abby's Project Page - RISE Summer 2009



Intern: Abby Goldman, Physics, Mount Holyoke College

Mentor: Brent Melot

Faculty Supervisor: Ram Seshadri

Department: Materials

#### STRUCTURE-PROPERTY RELATIONS IN $\text{CoSeO}_4$ , A ONE DIMENSIONAL MAGNETIC MATERIAL

One dimensional magnetic materials demonstrate interesting magnetic ordering because of the competition between nearest and next-nearest neighbor interactions. This competition can lead to a coupling between the spins and crystal lattice or of the spins and electric potential. We investigate the magnetic ordering of  $\text{CoSeO}_4$ , which contains chains of octahedral  $\text{Co}^{2+}$  connected by  $\text{SeO}_4$  molecules. The sample is prepared through solution routes and its purity is confirmed by x-ray diffraction. Preliminary measurements of the magnetic susceptibility indicate a weak ferromagnetic ordering. In addition, large magnetic fields can overcome the spin-orbit coupling and cause the spins to realign with the field. From the high temperature susceptibility data, we extract an effective magnetic moment of  $4.37\mu_B$  and a Curie-Weiss temperature of  $-35\text{K}$ , indicating a dominant antiferromagnetic ordering. We also perform heat capacity measurements to understand the change in entropy as the material orders. We will compare these heat capacity measurements to those of  $\text{ZnSeO}_4$ , a non-magnetic analogue to subtract off the lattice contributions to the specific heat and isolate the magnetic component. Finally, we plan to use neutron diffraction experiments to determine the magnetic structure of the material.

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### Blanca's Project Page - RISE Summer 2009



Intern: Blanca P. Moreno Hernandez, Chemistry,  
University of California Los Angeles  
Mentor: Katie Feldman & Jasmine Hunt  
Faculty Supervisor: Craig J. Hawker  
Department: Department of Chemistry and  
Biochemistry

#### PEG-POLYELECTROLYTE HYBRID COPOLYMERS

Polyelectrolytes copolymers are soluble in water, responsive to the environment, thermodynamically stable, and have important applications in drug delivery and underwater adhesives. These properties can be exploited to form "smart" hydrogels in which the crosslinks are discrete domains of supramolecular ionic interactions, known as complex coacervates. Cationic dimethylaminoethyl methacrylate (DMAEMA) homopolymers and ABA acrylic acid-poly(ethylene glycol) (PEG) triblock copolymers (with anionic end blocks and a neutral, hydrophilic middle block) were synthesized by ATRP and blended to form these structures. The anionic blocks formed complex coacervates with DMAEMA and the PEG served as a stabilizing block, prohibiting the growth of the complex coacervate droplets to macroscopic sizes. Results were confirmed by  $^1\text{H}$  NMR, Dynamic Light Scattering (DLS), and Gel Permeation Chromatography (GPC).

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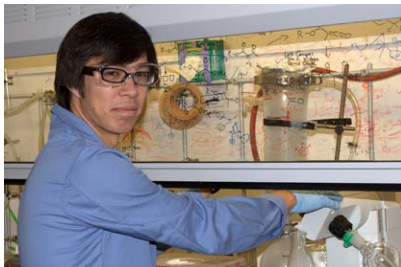
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### Brandon's Project Page - RISE Summer 2009



Intern: Brandon Krull, Chemistry, Biotechnology,  
California State Polytechnic University, Pomona  
Mentor: Luis M. Campos  
Faculty Supervisor: Craig J. Hawker  
Department: Materials Research Laboratory

#### SYNTHESIS OF FUNCTIONALIZED DENDRIMERS VIA THIOL-ENE CLICK CHEMISTRY TO AID IN SELF-ASSEMBLY OF PEPTIDE AMPHIPHILES

Biological nanoparticles have been of considerable interest as gene delivery vectors because of their high target specificity and lack of toxicity. Peptide amphiphiles, which can ideally form said spherical nanoparticles, are currently being explored because of their tendency to self-assemble but preferentially form undesired tubular structures. Dendrimers functionalized with terminal aliphatic groups are optimal candidates to act as globular templates to mediate this self-assembly into a spherical, rather than tubular, framework. Previous work within the Hawker group has shown thiol-ene chemistry, a novel type of "click" chemistry, to be highly efficient and robust, requiring ambient, solventless conditions as well as basic purification techniques. Thiol-ene click chemistry is an ideal replacement for other metal-mediated click techniques because of its benign nature, especially in biological applications. Dendrimers up to third generation have been synthesized and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR as well as gel permeation chromatography, yielding indices of polydispersity of near unity. Here we present recent advances in the divergent synthesis of various functionalized dendrimers based on the high efficacy of thiol-ene click chemistry.

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### David's Project Page - RISE Summer 2009



Intern: David Lavelle, Mechanical Engineering, Cal Poly San Luis Obispo  
 Mentor: Noah Philips  
 Faculty Supervisor: Anthony Evans  
 Department: Materials

#### MECHANICS OF SOIL BLASTS AND THEIR EFFECTS ON MATERIAL BEHAVIOR

There is great potential for further understanding of the mechanics of soil blasts generated by buried explosive charges and the behavior of materials under these impacts. This understanding could lead to breakthroughs in blast mitigation technology. This research, funded by the Office of Naval Research, aims to provide knowledge on the mechanics of soil blasts and material behavior under these impacts. We achieved this goal by accelerating soil-like projectiles into monolithic metal plates and then analyzing the impacts. A gas gun was used to accelerate the projectiles into the plates secured to the gun's end. Infra-red sensors were used to measure projectile velocity and a high speed camera to record the impact. We found that the onset of plate failure occurs at projectile momentums of  $4N*s$  for all clamp ring area to projectile area ratios tested. For all tests, two distinct failures were observed; tensile failure along the circumferential edge of the projectile and tensile failure along the inner circumferential edge of the clamp ring. Smaller area ratios increase the possibility of the latter, while increased momentum the former. However, failure along the circumferential edge of the projectile has been observed at a low range of momentums for an area ratio of 1.73.

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### Bernice's Project Page - RISE Summer 2009



Intern: Bernice McLaurin, Chemistry, Jackson State University

Mentor: Joanna Deek

Faculty Supervisor: Cyrus R. Safinya

Department: Department of Cellular, Molecular and Developmental Biology

#### SALT DEPENDENCE OF NEUROFILAMENT GEL PHASE BEHAVIOR

Neurofilament proteins (NFs) are believed to be involved in the maintenance of neuronal cell function and structure, and are present within the cytoskeleton of neuronal cells. The accumulation of NFs in the neuronal cell axons of the diseased cells inhibit transportation of particles through the axon; this eventually results in neuronal cell death. NFs self-assemble to form the extended filament with 10nm diameter and are classified into 3 subunits: NF-Low, NF-Medium, and NF-High, this is dependent by the relative length of their tail domains and have corresponding molecular weights of 63kDa, 105kDa, and 125kDa. By studying the NF network assembly and interactions the electrostatic attraction or repulsion between NFs is able to be altered using various salt concentrations. Increased monovalent and divalent salt concentrations in the reassembly buffer, in addition to sidearm interactions, have been implicated in more extensive longitudinal growth of the filaments. Crude protein containing NFs must be separated starting from subunits isolated using anion exchange. NF Phase behavior is characterized by optical microscopy, Transmission Electron Microscope, and Small X-ray Scattering. NF-Medium and NF-High behave differently due to variant inherent charge. By using a charged system, salts allow us to probe their interactions and total effective charge.

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### Nicole's Project Page - RISE Summer 2009



Intern: Nicole Ricapito, Chemical Engineering,  
Rensselaer Polytechnic Institute  
Mentor: Andrew Dittmore  
Faculty Supervisor: Omar Saleh  
Department: Materials

#### INVESTIGATING ATTACHMENT STRATEGIES FOR SINGLE BIOMOLECULE MANIPULATION

Single molecule manipulation has a wide range of applications in biophysics and materials science such as the study of polymers or motor proteins. One manipulation technique utilizes magnetic tweezers, an apparatus that records the motion of a molecule while applying magnetic forces. This technique requires tethering a single molecule to both a magnetic bead and a solid support. One of the most commonly used attachment strategies for DNA involves modifying a DNA strand with digoxigenin (DIG) and coating a surface with the DIG antibody. Although this linkage has proven useful in many experiments, it cannot withstand high forces. The goal of this research is to discover alternative attachment strategies that will enable the application of greater forces to a molecule without severing the tether. Three new chemistries are being tested which include i) formation of a peptide bond through the reaction of a carboxylic acid and an amine, ii) an epoxide/amine reaction, and iii) an amine/thiol crosslinker. These reactions form covalent bonds, which are known to be very strong and are thus the ideal method of molecule immobilization when using magnetic tweezers at high force. Preliminary results show that the peptide bond is not viable as an attachment strategy while reactions ii and iii require further investigation.

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### Christen's Project Page - RISE Summer 2009



Intern: Christen M. Robinson, Chemical Engineering,  
Jackson State University

Mentor: Isaac Riisness

Faculty Supervisor: Michael J. Gordon

Department: Chemical Engineering Department

#### LIGHTS, CAMERA, ACTION! MOLECULAR SURFACE IMAGING VIA ENHANCED LIGHT-MATTER INTERACTIONS

Scanning probe microscopy (SPM) is an efficient technique for surface characterization on the nanoscale. By using one form of STM, scanning tunneling microscopy (STM), one is able to surpass the wavelength diffraction limit and clearly image surfaces on the atomic level. Raman spectroscopy is a technique used for the unique detection for molecules' rotational, vibrational, and other low frequency modes via light scattering. The ultimate goal of this project is to develop a hybrid SPM system that can topographically and chemically image surfaces with nanoscale spatial resolution. The instrument simultaneously applies atomic force microscopy (AFM) and STM with near field optical examination, using electrochemically etched tips to amplify the Raman signal from the surface for SPM. The tips are probed across the fabricated surface, where powerful electromagnetic fields are created, ultimately allocating surface chemical imaging through near-field vibrational [Raman] spectroscopy. For the STM-Raman conjunction, glass slides are coated with gold and have thiol-linkers attached, where STM imaging using Au, W, and Ag tips allow for the surface imaging. The slides are then struck by laser light for molecular excitation, thus allowing detection of the linkers groups, allowing nanoscale detection and imaging via unique chemical signaling. In this work, techniques are currently being developed for higher image resolution and STM tip fabrication processes.

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### Jason's Project Page - RISE Summer 2009

Intern: Jason Ross, Physics, University of California Berkeley

Mentor: Nidhi Nidhi

Faculty Supervisor: Umesh Mishra

Department: Electrical and Computer Engineering

#### IMPROVED TRANSCONDUCTANCE LINEARITY OF GaN/AlGaN HEMTs

The use of Gallium Nitride (GaN) as a semiconductor in transistors has for many reasons become a promising area of research. It has a comparably large band-gap of 3.4 eV (Silicon has 1.1 eV) resulting in high breakdown voltages and the ability to manage extreme temperatures. Utilizing polarization effects, N-Polar high-electron mobility transistors (HEMTs) can be made by growing GaN on top of AlGaN without the intentional doping needed in similar devices made from other semiconductors. In all, GaN HEMTs promise to outperform and replace the current high power and high frequency transistor technology. However, one obstacle in the way of this goal is the drop off of the transconductance  $g_m$  for high channel currents. The  $g_m$  defines the amplification capability of a transistor, and so it is desired to have a relatively constant value for a large range of currents to avoid distortion of large signals. In Ga-Polar devices, where AlGaN is grown on top of GaN, it has been found that this nonlinearity/drop-off is directly related to increase in the differential access resistance  $r_s$  with drain current due to the quasi-saturation of electron velocity in the source region of the channel at electric fields higher than 10kV/cm[1]. With this knowledge, N-Polar HEMTs were measured and the intrinsic  $g_m$  was found to be more linear than the extrinsic indicating that the increasing  $r_s$  is indeed causing the nonlinearity in this case as well. In response, HEMTs with self-aligned gate designs were fabricated, which bring source and drain contacts as close to the gate as possible by regrowing highly n-doped InGaN for ohmic contacts as opposed to the traditional annealing of various metals. This design reduces the contact resistance and sheet resistance, the main components of  $r_s$ , even for high current levels. Measurements have shown that these devices have improved linearity over a larger range of current.

[1] T. Palacios, S. Rajan, A. Chakraborty, S. Heikman, S. Keller, S. P. DenBaars, and U. K. Mishra, "Influence of the Dynamic Access Resistance in the  $g_m$  and  $f_T$  Linearity of AlGaIn/GaN HEMTs," IEEE Trans. Electron Devices, vol. 52, no.10, pp. 2117–2123, Oct. 2005.

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### Rachel's Project Page - RISE Summer 2009



Intern: Rachel Schoeppner, Materials Engineering,  
 California Polytechnic San Luis Obispo  
 Mentor: JJ Cowart  
 Faculty Supervisor: Michael Chabiny  
 Department: Materials

#### MODULATION OF CONJUGATED POLYMER CONDUCTIVITY WITH MOLECULAR DOPANTS

In the field of organic electronics, conducting polymers offer the potential for new lines of flexible, light weight and cost effective products. Ideally, these polymers should be tunable to optimize conductivity while maintaining durability so that they can be used in a wide variety of devices. Extrinsic doping, adding specific molecules to the polymer, is one way to modulate the conductivity and band gap of these polymers. In this study, PBTTT was doped with F4TCNQ with a range of weight ratios to identify a dopant concentration that leads to uniform, aggregate free films. The doped films' conductivity was calculated utilizing a 2 probe method. Doped films of 5% F4TCNQ: PBTTT were successfully coated and a conductivity of  $1.15E-01$  S/cm was calculated. Extrinsic doping successfully increased the conductivity by 104 compared to the pristine polymer. Additionally, the UV-vis absorption spectrum was measured to determine the dopant-polymer interactions. The UV-vis spectrum showed an increase in the ratio of F4TCNQ to polymer peak as the dopant concentration increased, as well as the emergence of two near-IR interaction peaks related to the increase in dopant ratio. The films were then annealed at key polymer transition temperatures ranging from 100°C to 240°C and retested. With increased annealing temperatures, the F4TCNQ peak and charge transfer peaks dropped and the polymer peak increased this could be due to thermal degradation of the dopant. Future work will focus on changing the extrinsic dopants as a means of controlled modulation of the conductivity and band gap.

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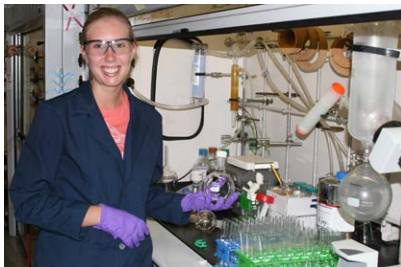
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### Alison's Project Page - RISE Summer 2009

Intern: Alison Schultz, Chemistry, University of Rhode  
Island

Mentor: Frank Leibfarth

Faculty Supervisor: Craig J. Hawker

Department: Materials Research Laboratory

#### KETENES IN MATERIALS SCIENCE: EXPANDING THE LIBRARY OF FUNCTIONAL POLYMERS

A common factor in materials science research is the need for control of functional groups and the demand for these functional groups to perform multiple roles such as crosslinking, light harvesting, detection, etc. In addition to these issues, practical utility demands that functional groups be incorporated via robust, high yielding chemistry. To meet these demands, we have developed a new method that introduces the versatile reactivity of ketenes to polymer chemistry. In this report, we present the synthesis of three new molecules and the investigation of their corresponding chemical applications to polymer chemistry. The molecules of study, which both form ketenes upon thermolysis, include a 1,3-dioxane-4-one derivative as well as an olefin- and norbornene-Meldrum's acid. Our results indicate that the former compound offers a potential in the area of fast and efficient condensation type polymerization, and the latter two in the area of copolymerization with polyethylene. Through these investigations we further expand the versatile and highly useful nature of ketenes in materials science.

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**Sara's Project Page - RISE Summer 2009**

Intern: Sara A. Turner, Department of Chemistry,  
Williams College

Mentor: Zeric Hulvey

Faculty Supervisor: Anthony K. Cheetham

Department: Materials Research Laboratory

**SYNTHESIS AND CHARACTERIZATION OF FLUORINATED HYBRID INORGANIC-ORGANIC MATERIALS FOR H<sub>2</sub> STORAGE**

Hybrid inorganic-organic materials, which are metal-based networks held together by organic ligands, are a class of materials which display an impressive array of applications. Recently the most exciting developments in the field of hybrid materials have focused on the gas storage properties of porous hybrids, specifically in the area of hydrogen storage. The open pores of some hybrid materials seem promising for hydrogen adsorption and storage, but these interactions are too weak to store a reasonable amount of H<sub>2</sub> at viable conditions. Our research involves incorporating perfluorinated ligands into hybrid structures with the intent of increasing the electrostatic interactions between the hybrid surfaces and the hydrogen molecule. Few such fluorinated hybrid structures have been synthesized and reported in the literature. Our main emphasis is in investigating how the fluorinated ligands incorporate themselves into the structure. We have only successfully incorporated perfluorinated ligands into hybrid structures when non-fluorinated (usually nitrogen-based) ligands are also present. Our current research centers around the use of 1,2-Bis(4-Pyridyl)ethane and 1,2-Bis(4-Pyridyl)propane as supporting nitrogen ligands in fluorinated materials synthesis.

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### Willie's Project Page - RISE Summer 2009



Intern: Willie Wesley, Chemistry, Jackson State University

Mentor: Brent Melot

Faculty Supervisor: Ram Seshadri

Department: Department of Chemistry and Biochemistry

#### MAGNETIC AND DIELECTRIC PROPERTIES OF $\text{Co}_{1-x}\text{Zn}_x\text{Cr}_2\text{O}_4$

$\text{ZnCr}_2\text{O}_4$  and  $\text{CoCr}_2\text{O}_4$  are two well studied magnetic spinel complex oxide systems. The spinel structure consists of the formula  $\text{AB}_2\text{O}_4$ . Both the A and B sites are coordinated by oxygen with the A site being tetrahedral and the B site octahedral.  $\text{CoCr}_2\text{O}_4$  has been found to exhibit Neel ferrimagnetic characteristic along with commensurate, incommensurate, and non collinear magnetic ordering [1]. Further studies of  $\text{CoCr}_2\text{O}_4$  have been carried out to investigate the spinel's polar behavior. Research has also found magneto-dielectric anomalies exhibited by the  $\text{CoCr}_2\text{O}_4$  system. Anomalies such as long-range ferrimagnetic ordering below a  $T_c = 94\text{K}$  and a phase transition at  $T_s = 27\text{K}$ , which was attributed to the beginning of long-range spiral magnetic ordering, have also been discovered in this system [2]. Unlike its more magnetically active counterpart,  $\text{CoCr}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$  is antiferromagnetically frustrated. The non-magnetic  $d_{10}$  Zn cation, which occupies the A site, accounts for this frustration. In this research we examined changes or connections of the dielectric constant and magnetic properties of the  $\text{CoCr}_2\text{O}_4$  system with the addition of Zn to the spinel structure. Previous studies by our group have revealed a shift from ferromagnetic and conical ground states to an antiferromagnetically frustrated system with the addition of Zn to the  $\text{CoCr}_2\text{O}_4$  spinel. Solid solutions in the system  $\text{Co}_{1-x}\text{Zn}_x\text{Cr}_2\text{O}_4$  were prepared at  $x = 0.2, 0.4, 0.45, 0.5, 0.55, 0.6, 0.8, \text{ and } 1.0$  and the effect on its magnetism and dielectric constant will be measured. Magneto-dielectric lattice coupling anomalies are being studied to gain a better understanding of the system.

[1] Melot B et al 2009 J. Phys.: Condens. Matter 21 216007 (7pp) [2] Melot B Phys. Rev. B 74, 024413 (2006)

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