

## Undergraduate Research Symposium May 17, 2013 Mary Gates Hall

### Online Proceedings

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#### POSTER SESSION 2

Balcony, Easel 92

12:45 PM to 2:15 PM

##### **Organic Photovoltaic Efficiency: Fluorine Integration for Band-Gap Manipulation**

*Rylan John Kautz, Senior, Mat Sci & Engr: Nanosci & Moleculr Engr*

*Mentor: Christine Luscombe, Materials Science & Engineering*

*Mentor: Pinyi Yang*

Organic Photovoltaics (OPVs) provide a potentially cheap and clean option to harvest energy from the largest source of energy available - the sun - however they are still fairly inefficient when compared to inorganic photovoltaics. Attaching fluorine to the polymer backbone has been shown as an effective way to increase the open circuit voltage (Voc) and power conversion efficiency of the devices by lowering the highest occupied molecular orbital of the polymer. However, the impacts of fluorine attachments on the other properties of active layer, like morphology under different processing conditions and electrical properties, have not been fully studied. Knowing this information will help the future designs and processing of donor-acceptor polymers for OPV application. In this project, three structurally identical polymers, with zero, one, and two fluorine attachments (named P0F, P1F, and P2F) were studied. The morphological impact of fluorine attachments are studied by varying the ratio of PCBM (a widely used and promising acceptor) and these three polymers as well as the solvents used when processing through atomic force microscope (AFM). Hole features were found on the surface of the thin film. The density of and depth of the holes were found to correlate to the number of fluorine attachments and processing condition respectively. Future works are being done to investigate the reasoning behind the device efficiency with the attachment of fluorine and differentiating whether this is due to these physical morphologies or bandgap manipulation being the primary contributor to a higher efficiency. The influence of fluorine on the dielectric constant of the thin film and operation of OPVs will also be studied.

#### POSTER SESSION 2

MGH 241, Easel 138

12:45 PM to 2:15 PM

##### **Simple Method for Removal of Residual Catalyst From Pi-Conjugated Polymers by Suzuki Coupling and Kumada Coupling**

*Christopher Bruce (Chris) Montgomery, Senior, Mat Sci & Engr: Nanosci & Moleculr Engr*

*Mentor: Christine Luscombe, Materials Science & Engineering*

*Mentor: Ken Okamoto, MSE*

Organic electronics is a growing area of research that investigates the properties and applications of conjugated polymers and conductive small molecules. Devices made from organic electronic materials can be flexible, inexpensive to process, and have lower weight compared to inorganic devices. Prominent synthetic techniques for conjugated polymers, including the Suzuki reaction, Heck reaction, and Kumada coupling, utilize a palladium or nickel complex as the catalyst. When the reaction completes, organometallic molecules and metal nanoparticles remain stuck in the polymer, decreasing the efficiency of resulting devices by acting as charge trappers or photo quenchers. The potential commercial success of organic electronics is highly dependent on their efficiency, and so the impurities need to be removed. A palladium-catalyzed model Suzuki coupling reaction of bromobenzene and phenylboronic acid was analyzed by <sup>31</sup>P-NMR both before and after the post-synthetic addition of thiuram disulfide (TMTD). Pd(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> dibromide was present in the solution prior to the post-synthetic disulfide addition, but not after. When TMTD or diphenyl disulfide were added directly to metal catalyst in chloroform, the resulting product precipitated out; the solubility of the product was different from the reactants. The change in solubility indicates that disulfide molecules can behave as metal scavenger for residual palladium or nickel catalyst. In order to restore the performance of organic polymers, scavenger molecules are used post-synthesis. This additional step isolates palladium or nickel atoms and changes their solubility, allowing them to be separated from the polymer. The performance of disulfide-based metal scavengers added to catalyst-metal-contaminated conjugated polymers is discussed.

## POSTER SESSION 2

Balcony, Easel 93

12:45 PM to 2:15 PM

### Synthesis of CdSe Nanotetrapods for Applications in Hybrid Organic-Inorganic Photovoltaics

*Ila Kuntum, Junior, Materials Science & Engineering*

*Mentor: Christine Luscombe, Materials Science & Engineering*

*Mentor: Katherine Mazzio, Materials Science and Engineering*

Solar energy is arguably the most promising source of renewable energy because it is thought to be both the cleanest and most abundant source. There are several types of solar cells including organic, inorganic, and hybrid organic-inorganic solar cells. While inorganic solar cells have high efficiencies, good charge carrier mobilities, and relatively long charge carrier times, their expensive production and materials competition with the microelectronics industry has kept their prices high. Organic solar cells are solution processable, applicable to flexible substrates, and have the promise of being relatively cheap to produce. However, their relatively low charge carrier mobilities and short exciton diffusion lengths prevent them from being used as an alternative to inorganic solar cells. Hybrid organic-inorganic solar cells have been introduced as a substitute to both organic and inorganic solar cells in order to overcome the short-comings of each. Inorganic semiconductors are used in hybrid photovoltaics as the acceptor in the solar cell due to the ease of changing the size and shape, and therefore the bandgap, of these semiconductors, which allows them to contribute to the photocurrent of the cell while enhancing the conductivity. This project addresses the synthesis of cadmium selenide (CdSe) nanotetrapods, which may facilitate control of direction of electron motion in the active layer of the cell. The reaction time, growth temperature, ligand type, and monomer concentration were used to control the synthesis, and the effects of each variable on the size and shape of the tetrapods were studied via transmission electron microscopy (TEM).

## POSTER SESSION 2

Balcony, Easel 91

12:45 PM to 2:15 PM

### Heterocycle Synthesis through a C-H Activation Cascade Reaction

*Jeremy Benson (Jeremy) Housekeeper, Senior, Chemistry*

*Mary Gates Scholar*

*Mentor: Christine Luscombe, Materials Science & Engineering*

*Mentor: Ken Okamoto, MSE*

Until recently, little research has been done on C-S bond formation in transition-metal catalyzed transformations compared to other carbon-heteroatom bonds such as C-N, C-O, and C-P. As sulfur-based coupling partners (thiol and disulfide for example) tend to poison transition-metal catalysts, development of C-S bond formation has been slow. However, a recent nickel-catalyzed system shed new light on this difficult transformation. In this context, C-H functionalization is a sustainable and straightforward approach to sulfur-containing heteroaromatic production. C-H activation is a process whereby a carbon-hydrogen bond is cleaved, thereby allowing the exposed carbon atom to form new bonds. Thus, in order to expand the above research of C-S bond formation toward development of short synthesis for fused thiophene systems, focus was placed on a palladium catalyzed cascade-type reaction system. C-H activation reactions can and have been manipulated to work in a cascade-type fashion. By combining cascade-type methodology with the reduced environmental impact of C-H activation, these fused thiophenes can be synthesized cleanly and efficiently. The test substrates in this work are O,O-diethyl S-phenyl phosphorothioate and 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane. Both substrates were chosen because they contain sulfur, thereby aiding the C-H activation process. By effecting a C-H activation with a palladium catalyst at one of the ortho carbons of the phenyl ring with the boronic ester of the thiophene, the first C-C bond will be formed. In the time immediately after this first transformation, the now-changed palladium complex is able to insert into the S-P bond of the phenyl-based compound. This step sets up the second reaction, whereby the phosphorothioate directing group is cleaved along the S-P bond and the resulting thiol is coupled to a carbon atom to close the ring. This molecule is known as benzo[b]thieno[2,3-d]thiophene.

## POSTER SESSION 2

MGH 241, Easel 139

12:45 PM to 2:15 PM

### Controlling the Morphology of Poly(3-hexylthiophene) Nanowires for Improvement of Organic Photovoltaic Device Efficiency

*Thivanka Kaushal Samaranayake, Senior, Mat Sci & Engr:*

*Nanosci & Moleculr Engr*

*Mentor: Christine Luscombe, Materials Science & Engineering*

In this study, we attempt to gain a better understanding of how poly(3-hexylthiophene) (P3HT) nanowires self assemble in solution. P3HT is used as the primary p-type donor in conjunction with phenyl-C61-butyric acid methyl ester (PCBM) in bulk heterojunction polymer solar cells. During self assembly, individual P3HT chains begin to kink after about 40 monomer units into an S-like shape. These S-shaped

chains interact with one another via pi-pi interactions and form nanowires with widths typically between 20 and 70 nm and heights between 3 and 5 nm. In an attempt to improve device efficiency, we would like to exhibit greater control over the size of the nanowires. Controlling the morphology of the nanowires would allow us to improve the efficiency of the device. Thus, we demonstrate a method to create self-assembled nanowires from 12.5, 16, and 28 kDa molecular weight P3HT. P3HT solutions were made with a concentration of 1 mg of polymer to 2 mL of solvent (anisole and chloroform in a 4:1 ratio). These solutions were then heated at 80C and thoroughly mixed for 16 h. After mixing, the solution is removed from heat and allowed to self-assemble for several days. Finally, the solution is then spin coated onto a silicon dioxide coated silica substrate. The samples were analyzed using atomic force microscopy to provide detailed information about the surface coverage, width, and height of the nanowires.

higher prevalence of fetal microchimerism in patients with triple negative breast cancer compared to control or luminal participants consistent with the original hypothesis. Additional samples will be tested. Fetal microchimerism testing may represent a novel non-invasive method to identify women with poor prognosis breast cancers.

## POSTER SESSION 3

Commons East, Easel 78

2:30 PM to 4:00 PM

### **Breast Cancer Pathologic Subtype and Fetal Microchimerism**

*David Mahoney, Senior, Biology (Molecular, Cellular & Developmental), Biochemistry*

*Mentor: VK Gadi, Medicine*

*Mentor: Christine Luu, Clinical Research Division*

Recent studies demonstrate that certain reproductive factors such as parity (defined as the number of completed pregnancies) are disparately associated with various pathologic subtypes of breast cancer. One factor, fetal microchimerism - the term for persistent child-origin cells in a woman's circulation and tissues long after delivery - is generally deficient in women with unselected breast cancer and suggests a protective role. Here, we are testing the hypothesis that high-grade triple negative breast cancer (positive association with parity) will be distinctly associated with fetal microchimerism compared to low-grade luminal breast cancer (inversely associated with parity). Buffy coat specimens (n=450) were obtained from breast cancer patients and control participants aged 18-44 from the REACH project (Fred Hutchinson Cancer Research Center, PI Christopher Li). Using quantitative polymerase chain reaction, DNA extracts from these specimens were tested for the presence and concentration of Y chromosome sequence DYS14, a marker of male fetal microchimerism. In an interim analysis from the first 87 specimens, 33% (9/27) of women who developed luminal breast cancer tested positively for the presence of DYS14, as did 33% (10/30) of healthy controls. 47% (14/30) of women who developed triple negative breast cancer tested positively for the presence of DYS14. Preliminary results demonstrate a