



Boston College

Graduate Student Symposium



October 10, 2011
9:00 a.m. – 5:30 p.m.
Connors Family Retreat and Conference Center
Dover, MA

Dear Friends and Colleagues:

Welcome to the 2011 Boston College Chemistry Department Graduate Student Symposium! This annual symposium provides a platform for graduate students in the department to share their exciting research accomplishments with fellow students and faculty. We have an impressive lineup of speakers and poster presenters, and we hope that you enjoy this opportunity to learn about the diverse areas of research currently ongoing in the Chemistry Department.

In addition to the poster session and student presentations, it is our pleasure to welcome Dr. Ed Jackson, a scientist at Konarka Technologies in Lowell, MA, and a Boston College graduate student alumnus. We are very grateful to Dr. Jackson for his participation in this event, and for giving us insight into his successful career path and serving as an exceptional role model for current graduate students.

Please enjoy your day at the beautiful Connors Family Retreat Center!

Sincerely,

Nick Pace, Yani Zhou, Fang Wang, (Chemistry GSA)
Professors Frank Tsung and Eranthie Weerapana



Connors Family Retreat and Conference Center

Schedule of Events:

9:00 – 9:50 a.m.

Breakfast and Poster Session
Dining Room, Estate Parlor

10:00 a.m. – 12:20 p.m.

Student Presentations
Estate Room

12:30 – 2:00 p.m.

Lunch, Poster Session, Break
Dining Room, Estate Parlor

2:15 – 4:00 p.m.

Student Presentations
Estate Room

4:00 – 4:15 p.m.

Break
Coffee and Refreshments

4:15 – 5:15 p.m.

Keynote Speaker: Dr. Ed Jackson
Estate Room

5:30 p.m.

Buses depart for Boston College

Student Poster Session

(9:00-9:50 a.m. & 1:10-2:00 p.m., Estate Parlor)

Organic and Organometallic Chemistry

Hoveyda Group:

"Enantioselective Conjugate Additions of Vinylaluminum Reagents to Acyclic Enones"

~ **Kevin McGrath**

"Mo-Catalyzed Z-Selective Cross-Metathesis of Allylic Ethers"

~ **Tyler Mann**

Scott Group:

"Pushing the Ir-catalyzed C–H Polyborylation of Aromatic Compounds to Maximum Capacity by Exploiting Reversibility"

~ **Maria Eliseeva**

"A synthetic route to tribenzocorannulene and higher analogs"

~ **Natalie Smith**

Snapper Group:

"Ruthenium catalyzed tandem reactions"

~ **Lu Xiao**

"Development of a Tandem Ru-Catalyzed Ring-Closing Metathesis/Hydroacylation Sequence"

~ **Youn Hee Nam**

Morken Group:

"Pt-Catalyzed Enantioselective 1,2-Diboration of 4,4-Disubstituted Dienes: A Route to Novel Alpha-Chiral Allylation Reagents"

~ **Grace Ferris**

"A Palladium-Catalyzed Allyl-Allyl and Allyl-Propargyl Cross-Coupling: Utilizing a Unique β , γ -Reductive Elimination to Generate 1,5-Dienes and Enynes"

~ **Mike Ardolino**

"Platinum-Catalyzed Enantioselective Formation and Functionalization of Allyl and Alkyl Boronic esters"

~ **Kai Hong and Scott Mlynarski**

Tan Group:

"Enantioselective Hydroformylation of Aniline Derivatives using a Chiral Scaffolding Ligand"

~ **Candice Joe and Tom Blaisdell**

"Scaffolding Catalysts: Highly Enantioselective Desymmetrization Reactions"

~ **Xixi Sun**

Byers Group:

"Applications of Organometallic Chemistry in: Catalytic Coupling Reactions, Novel Polymer Syntheses, and Hydrogen Storage"

~ **Jeff Byers**

Chemical Biology and Biochemistry

McLaughlin Group:

"Novel approach for specific duplex DNA recognition employing the Janus Wedge format"

~ **Ayan Pal**

"Synthesis of Ring-Expanded Fused Nucleosides"

~ **Han Yueh**

"Fused Deoxyuridine: Synthesis and Evaluation"

~ **Hongchuan Yu**

Kantrowitz Group:

"Crystallographic Snapshots of the Complete Catalytic Cycle of the Unregulated Aspartate Transcarbamoylase from *Bacillus subtilis*"

~ **Kate Harris and Greg Cockrell**

"Trapping and Structure Determination of an Intermediate in the Allosteric Transition of Aspartate Transcarbamoylase"

~ **Wenyue Guo**

Roberts Group:

"Structural Studies of Phosphatidylinositol-specific phospholipase C from *S. aureus*; an Intramolecular π -Cation Latch"

~ **Becca Goldstein**

Gao Group:

"A Facile Method to Evaluate Protein Dimerization by Split Ligands for Lanthanide Binding"

~ **Yue Zhao**

"Cofactor-free Detection of Phosphatidylserine with Cyclic Peptides Mimicking Lactadherin"

~ **Hong Zheng**

Weerapana Group:

"Activity-based Proteomic Approaches to Investigate Oxidation in Aging *C. elegans*"

~ **Julie Martell**

"Identification of Cysteine S-nitrosylation Sites Using Activity-based Proteomic Profiling"

~ **Yani Zhou**

Physical and Theoretical Chemistry

Wang Group:

"PEC Carboxylation of Aromatic Ketones from CO₂ Using Si/Si NWs Photocathode"

~ **Rui Lui**

"Comparing One- and Two-Dimensional Heteronanostructures as Si-Based Li Ion Battery Anode Materials"

~ **Jin Xie**

Tsung Group:

"Novel Nanostructures for Heterogeneous Catalysis"

~ **Brian Sneed and Maggie Sheehan**

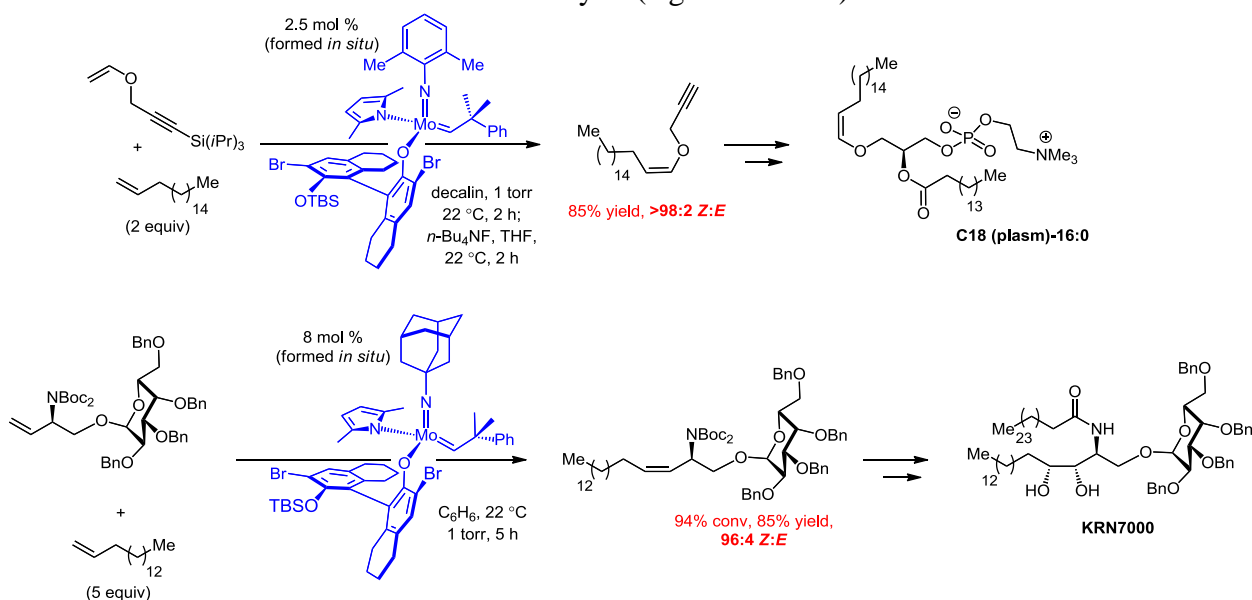
Student Lecture Abstracts, Group 1
(10:00 a.m. – 12:20 p.m., Estate Room)

Mo-Catalyzed Cross-Metathesis for Stereoselective Synthesis of Disubstituted *Z* Olefins

Robert V. O'Brien, Josep Llaveria, Simon J. Meek, Richard R. Schrock, and

Amir H. Hoveyda

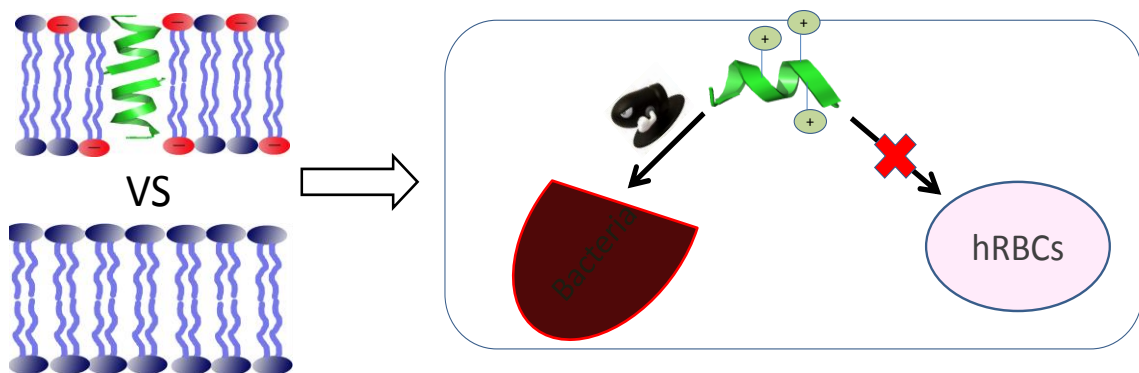
Z olefins are found in a vast number of natural products, and can be functionalized through a variety of diastereoselective transformations. Olefin cross-metathesis offers a versatile approach for synthesizing *Z* olefins, due to the ease of synthesis and wide availability of terminal olefins substrates. Commercially available metathesis catalysts, however, promote cross-metathesis that predominantly furnishes the *E*-isomer (usually as a mixture of *E* and *Z* olefins). We have developed stereogenic-at-metal Mo catalysts (bearing monodentate aryloxy and pyrrolide ligands) that promote *Z*-selective cross-metathesis of allylic amides and enol ethers efficiently (up to 97% yield) and in high selectivity (in up to >98% *Z*). In many cases the use of vacuum was found to improve both the efficiency of the reaction and the *Z* selectivity (through removal of the ethylene byproduct). The utility of this method was demonstrated in the synthesis of an enol ether anti-oxidant, plasmalogen C18 (plasm)-16:0(PC), which is implicated in Alzheimer's disease. Additionally, *Z*-selective cross-metathesis was used to synthesize the potent immunostimulant KRN7000, which was obtained through diastereoselective dihydroxylation of a *Z* allylic amide. We have extended this methodology to include vinyl(pinacolato)boron, which provides access to *Z* vinyl boronates. Vinylboronates are a versatile class of olefin substrates that can be functionalized in numerous ways (e.g. Suzuki-Miyaura cross-coupling). By combining cross-metathesis and cross-coupling, we will be able to access *Z* olefin products otherwise unattainable with our current catalysts (e.g. *Z* stilbenes).



Solubilized Gramicidin A as Potential Systemic Antibiotics

Fang Wang, Luoheng Qin, Christopher J. Pace and Jianmin Gao

The rapid development of multidrug resistance by pathogenic bacteria poses a serious threat to the society and demands new antibiotics with different mechanisms. Within the past decade, a significant amount of effort has been paid to developing membrane active peptides and their functional analogues as novel antibiotics. Gramicidin A (gA) is a fifteen-residue linear peptide with known antibiotic activity but prevented from systemic application by its poor solubility in water and high hemolytic toxicity. The peptide readily forms a trans-membrane β -helical channel to facilitate the passive diffusion of water and monovalent cations (e. g. Na^+ , K^+). Herein, we report a soluble variant of gA that displays bacterium-specific activity. This is made possible by incorporating charged residues into the C-terminal fragment of gA, where the charged species are best accommodated by the gA channel structure. The gA mutants display sub to low micromolar antibiotic potency and remarkable therapeutic indices. Given the well defined structure and active mechanism of gramicidin A, the soluble gA variants are highly promising as systemic antibiotics.

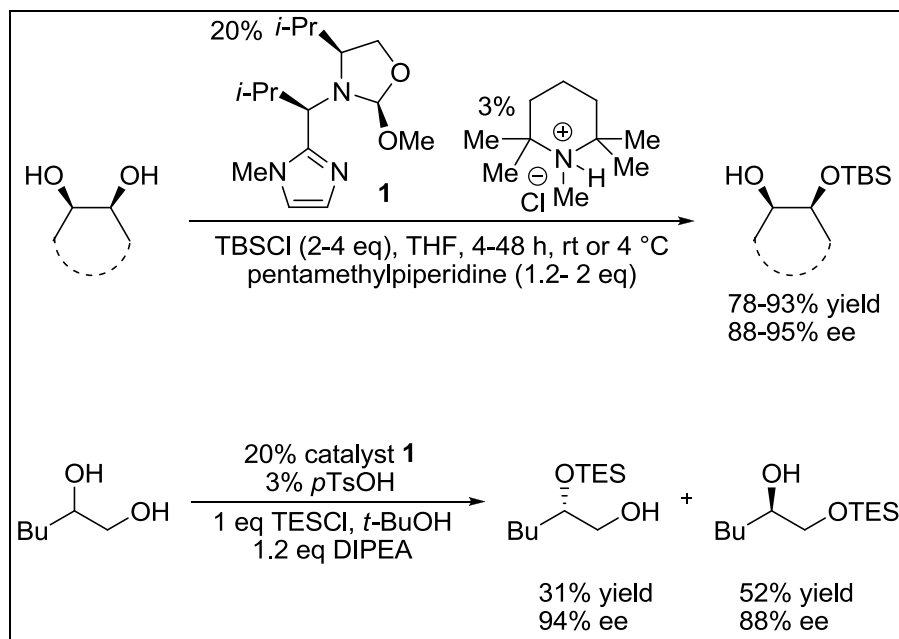


Makeover of an old antibiotic!

Stereoselective Functionalization of Diols Through Covalent Organocatalysis

Amanda Worthy and Kian L. Tan

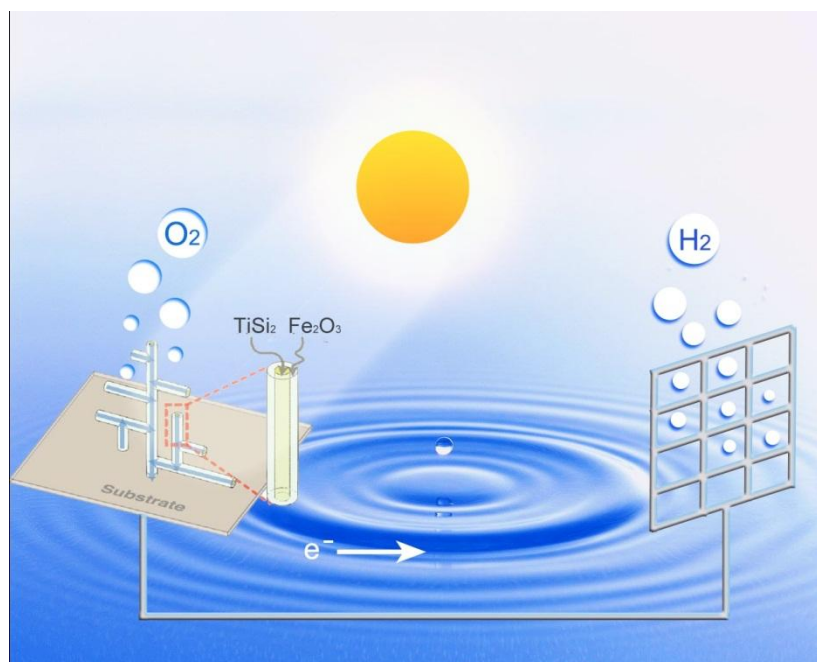
The stereoselective functionalization of diols is important because it yields synthetically useful monofunctionalized, enantioenriched products. To this end, we have developed a cheap and easy to synthesize amino alcohol-based covalent organocatalyst. This catalyst binds covalently and reversibly to one alcohol and directs functionalization of the other alcohol. We have shown this catalyst to be effective in the enantioselective desymmetrization of 1,2-diols. The substrate scope is broad with both cyclic and acyclic diols giving good yields and selectivities under mild conditions. Using the same catalyst, the parallel kinetic resolution of 1,2 diols results in good ees for both monofunctionalized, enantioenriched products. Notably, for the (S)-enantiomer of the diol, the secondary alcohol is protected over the primary. We are optimistic that this mode of catalysis will be applicable to a broad range of reactions.



Hematite-based Heteronanostructure for solar water splitting

Yongjing Lin and Dunwei Wang

The prospect of generating H_2 from H_2O using solar energy is a particularly appealing one because this technology is renewable and environmentally friendly. Among them, hematite is considered as one of the most promising candidates for solar water oxidation due to its broad absorption and good stability. Despite intense research efforts, the efficiency of utilizing hematite is still limited by its intrinsic properties such as extremely short carrier diffusion distance. In this talk, we presented a method of forming hematite-based heteronanostructure to tackle these challenges and greatly enhance its efficiency. The heteronanostructure design can improve charge collection efficiency in hematite and extend its absorption range.

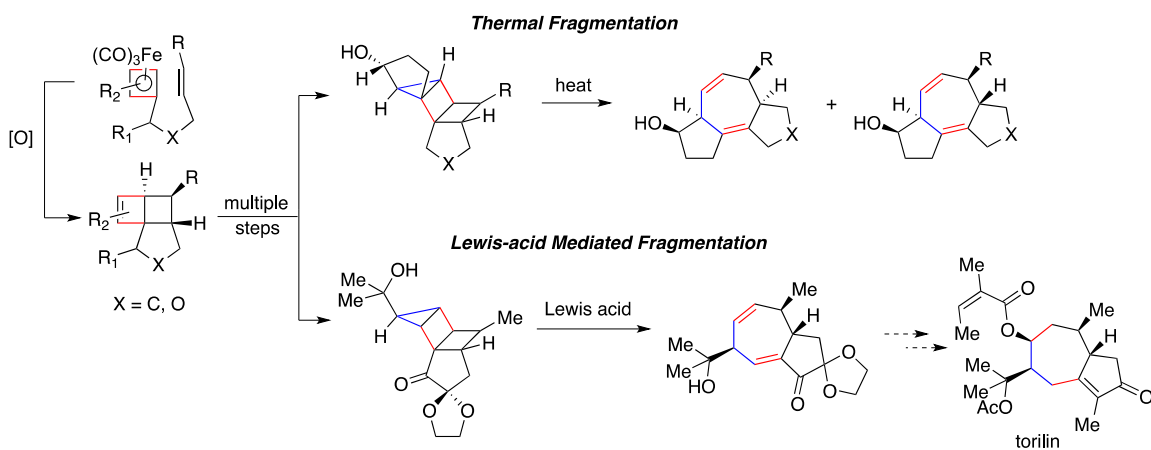


Student Lecture Abstracts, Group 2
(2:15 – 4:00 p.m., Estate Room)

Cyclobutadiene Cycloadditions: Applications toward the Syntheses of Functionalized 5-7-5 Tricyclic Ring Systems and the Guaiane Natural Product Torilin

Jing He and Marc L. Snapper

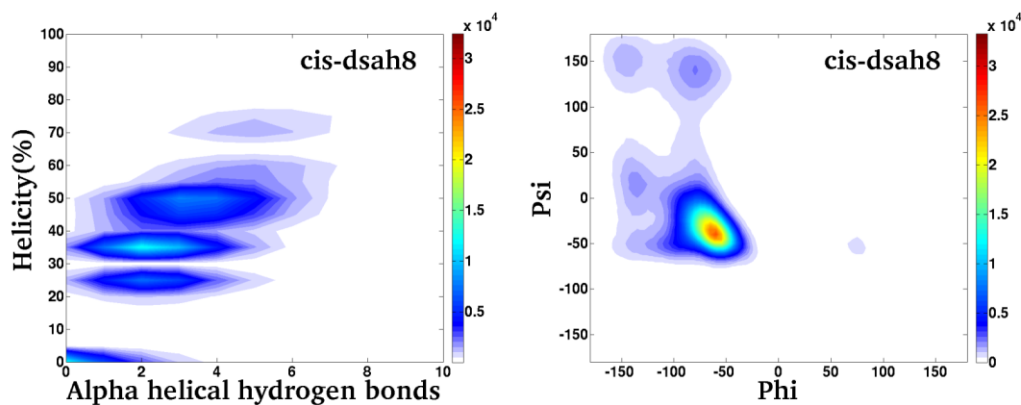
Cyclobutadiene cycloadditions provide rapid access to rigid polycyclic systems with high strain energies and unique molecular geometries. Further functionalization of these systems followed by strain-release fragmentation provides great opportunities to construct fused-medium-ring architecture. An intramolecular cyclopropanation/thermal rearrangement sequence is developed to access two different molecular frameworks of 5-7-5 tricyclic ring systems. The highly strained cyclopropyl compounds are believed to fragment through two competing pathways affording the corresponding diastereomeric products. A library of functionalized 5-7-5 tricyclic ring systems can be systematically built up from one simple starting material for potential future use in high-throughput screening. In a complementary fashion, an intermolecular cyclopropanation/Lewis acid-mediated rearrangement strategy has been previously developed to access the 5-7 bicyclic ring systems in a stereospecific manner. The application of this strategy is being studied for the synthesis of torilin, a guaiane natural product with many attractive biological activities, but with no total synthesis reported so far.



Probing the Alpha-Helical Structural Stability of Stapled p53 Peptides

Zuojun Guo, Udayan Mohanty

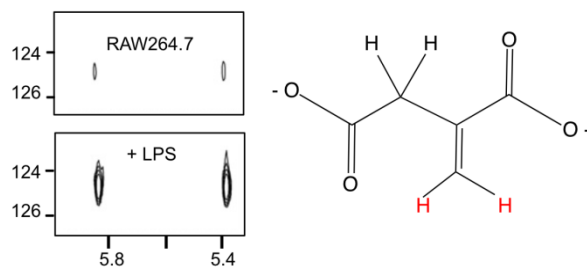
The α -helical conformation and structural stability of single and double stapled all-hydrocarbon cross-linked p53 peptides in solution and when bound to MDM2 are investigated. We determined the effects of the peptide sequence, the stereochemistry of the cross-linker, the conformation of the double bond in the alkene bridge, and the length of the bridge, on the relative stability of the α -helix structure. The conformation population distribution indicates a fully helical state and several partially folded states. The distribution of dihedral pairs of the stapled peptides in the bound state indicates a significant population around the α -helical region. Sequences over which the linker spans tend to have the highest helical occupancy. Significant helical content is observed for a double stapled p53 peptide at 575 K.



Itaconic acid is a novel mammalian metabolite induced during macrophage activation

Cheryl L. Strelko, Wenyun Lu, Fay J. Dufort, Thomas N. Seyfried, Thomas C. Chiles, Joshua D. Rabinowitz, and Mary F. Roberts.

Itaconic acid (ITA), or methylenesuccinic acid, is not generally classified as a mammalian metabolite. Using NMR-based metabolomics and ^{13}C -labeling, we have detected ITA in both macrophage-like VM-M3 and RAW 264.7 tumor cell lines as well as stimulated and unstimulated primary murine macrophages. Macrophage activation by addition of lipopolysaccharide and IFN- γ markedly increased ITA production and secretion. We were able to identify the method of biosynthesis in VM-M3 cells using the distribution of isotopologues obtained from LC-MS sample analysis. Crude cell extracts synthesize ITA via decarboxylation of cis-aconitate, indicative of a novel mammalian cis-aconitic decarboxylase activity. Our results highlight a previously unidentified biosynthetic pathway related to TCA cycle metabolism in mammalian cells and a novel metabolite that likely plays a role in macrophage-based immune response.



Keynote speaker

4:15 – 5:15pm, Estate Room

Dr. Ed Jackson
Konarka Technologies
Lowell, MA

Background:

PhD: Boston College, 2008 (Advisor: Lawrence T. Scott)

Postdoctoral Fellow: SAFC Hitech (a subdivision of Sigma Aldrich),
Sep, 2008-Oct, 2010

Scientist: SAFC Hitech, Organic Chemist, *Oct, 2010-Dec, 2010*

Scientist: Konarka Technologies, Organic Chemist,
Dec, 2010-present

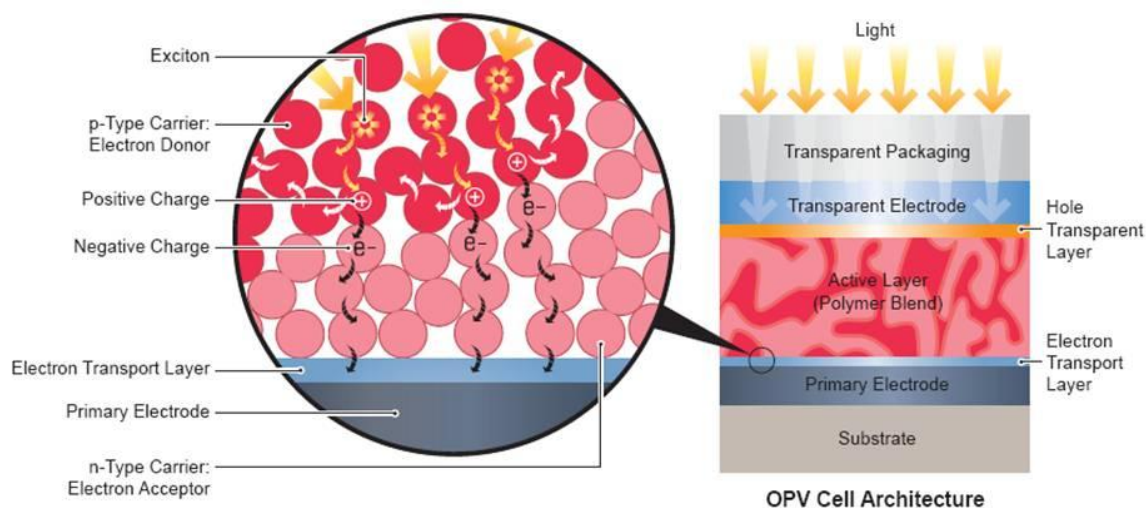
Biosketch:

Ed Jackson is currently working as a scientist at Konarka Technologies in Lowell, MA. He joined the Konarka polymer synthesis and development group on January 1st, 2011 and is using his skills as an organic chemist to support the advancement of OPV technologies. Before moving to Konarka, Ed completed an industrial posdoc at SAFC Hitech (a subdivision of Sigma Aldrich) where he delivered advanced organic targets for use in the semiconductor industry. Ed received his doctoral degree in physical organic chemistry from Boston College in 2008 under the direction of Professor Lawrence T. Scott for work including the synthesis of a carbon nanotube endcap, and received his bachelors degree in chemistry from the University of Richmond, Richmond, Virginia in 2002

Material Applications of Synthetic Organic Chemistry

---A Short Career in Perspective

There can be no progress in materials technologies incorporating organic compounds without the design and synthesis of new targets that meet increasingly stringent and challenging structural and electronic standards. In this talk we hope to share an understanding of organic photovoltaics (OPV) gained during our first year of employment at Konarka Technologies in Lowell MA. We will start by considering the current state of organic photovoltaics and the qualities that set OPV apart from other photovoltaic technologies. This macroscopic assessment will be followed by an elucidation of the OPV device structure and energy production mechanism with special emphasis on the design and synthesis of compounds incorporated into the active layer. A small amount of time will also be devoted to previous work at Boston College and postdoctoral work at SAFC Hitech in Haverhill, MA. Finally, we hope to share the benefit of our brief career experience as a secondary theme throughout the talk.





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