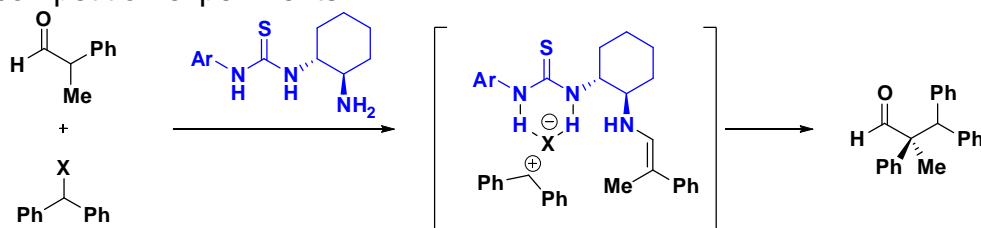
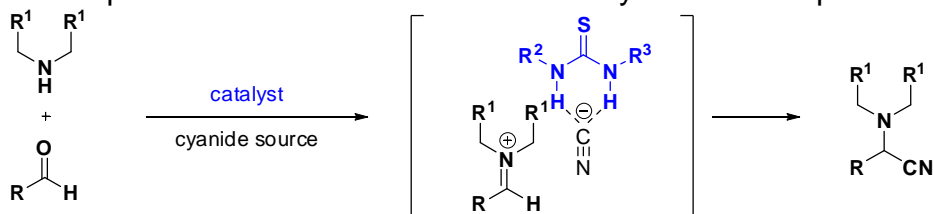


Adam Brown - Asymmetric Additions to Cationic Electrophiles Catalyzed by Dual H-Bond Donors

1. Primary aminothiurea derivatives are shown to catalyze enantioselective alkylation of  $\alpha$ -arylpropiionaldehydes with diarylbromomethane. Evidence for a stepwise,  $S_N1$  mechanism in the substitution reaction induced by anion binding to the catalyst is provided by catalyst structure-activity studies, kinetic isotope effects, linear free-energy relationship studies, and competition experiments.



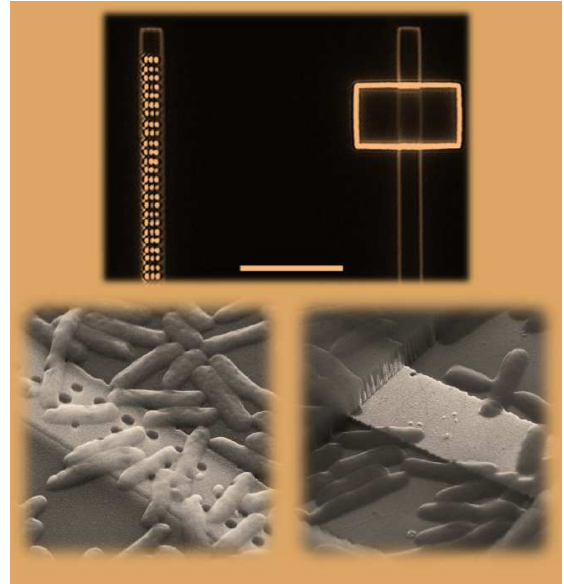
2. Thiourea derivatives that catalyze the enantioselective addition of cyanide to  $N,N$ -dialkyliminium ions have been discovered. These Strecker-type reactions provide direct access to chiral tertiary aminonitrile products.



**XiaoCheng Jiang**

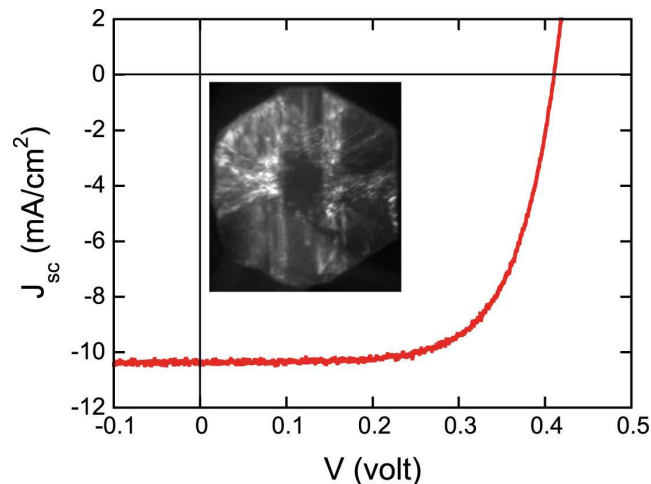
**Nanostructured Interface for Probing and Facilitating Extracellular Electron Transfer in Microbial Fuel Cells**

Microbial fuel cells (MFCs) have been the focus of substantial and growing research interest due to their potential for long-term, renewable electrical power generation via the metabolism of a broad spectrum of organic substrates. Despite efforts to date, the fundamental factors and limits determining charge transport and power extraction remain controversial and/or poorly understood. Our research is focusing on development of nanotechnology enabled platform to understand and improve electrochemical power extraction from exoelectrogenic bacteria down to the single cell level, through the rational design and defining of nanostructured cellular interface. Nanostructured electrodes, in which the presence or absence of cell contacts is physically controlled, are explored to unambiguously address the extracellular electron transfer mechanism in *S. oneidensis* and *G. sulfurreducens* cells. Moreover, we demonstrate the potential to significantly improve the power extraction using controlled synthesized inorganic nanoparticles as bridges for more efficient electron transfer at electrode/cell interface and within interconnected cell network. These results provide new insight into the intimate cell-electrode and cell-cell interaction and are expected to advance our fundamental understanding of MFCs.



**Thomas J. Kempa** - Core-shell nanowire photovoltaics and their assembly towards efficient ultra-thin solar cells.

Core-shell nanowires are a versatile platform on which to realize single standalone photovoltaic devices whose tunable electronic and optical properties can be exploited for emerging next-generation solar cell concepts. We report *in situ* synthesis of silicon core-shell nanowires with unique heteromorphic crystalline shells and well-defined diode geometries. Optimized devices yield open-circuit voltages as high as 0.50 V and fill-factors greater than 72%, even for nanowires with diameters as small as 200 nm. Notably, single nanowire devices exhibit current densities double the expectation for equivalent bulk films and 1-sun power conversion efficiencies of up to 6%. Furthermore, wavelength-dependent single nanowire photocurrent spectra reveal tunable optical resonances within the nanowires, and quantitative analyses show that absolute external quantum efficiencies approach values equal to or greater than unity. Simulations and measurements further suggest a unique approach for enhancing efficiency through assembly of designed nanowire elements. We demonstrate directed assembly and parallel interconnection of nanowires in planar geometries and vertical stacks, and show that this can yield cells with efficiencies in excess of 8%. Simulations and experiments further suggest that sub-micron thick assemblies of single nanowire elements can achieve efficiencies (> 13%) well in excess of those obtained in thin-film solar cells. Together, these results suggest a new paradigm for development of next-generation, ultra-thin solar cells.

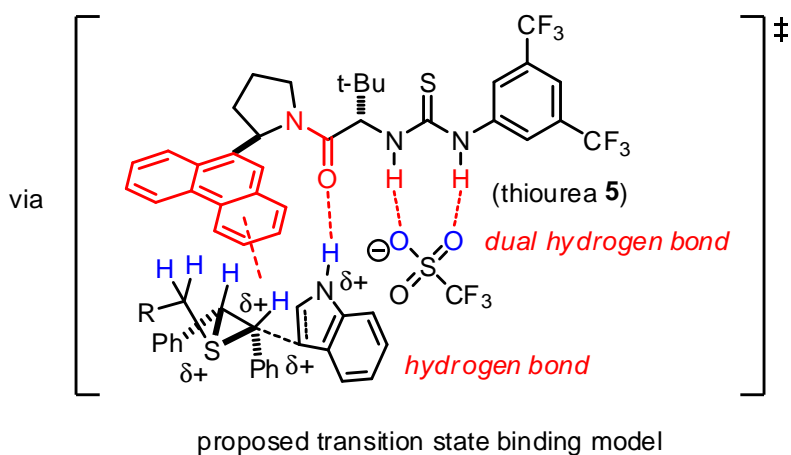
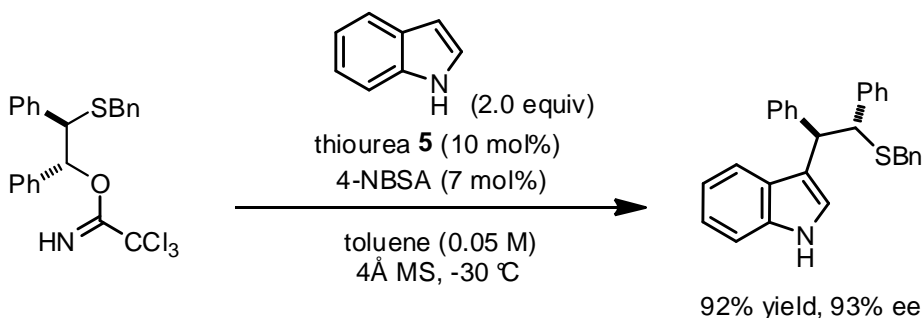


High performance single nanowire device yields  $J_{sc} > 10 \text{ mA/cm}^2$  and a  $V_{oc} = 0.42 \text{ V}$ . Inset is dark-field aberration-corrected TEM image of core-shell nanowire cross-section revealing distinct crystallographic features of the heteromorphic nanowire.

Song Lin

**Abstract:**

Arylpyrrolidine-derived multi-functional thiourea catalysts are shown to catalyze enantioselective nucleophilic opening of epi-sulfonium ions. Evidence for a transition state stabilization effect enabled by thiourea through a network of weak, non-covalent interactions (mainly anion binding, cation- and indole-involving hydrogen bonding interactions) in the rate- and selectivity- determining event is provided by experimental mechanistic investigation.



Author: Roberto Olivares-Amaya

Title: Finding Donor Polymer Materials for Bulk-Heterojunction Solar Cells One Screensaver at a Time

Abstract:

Organic photovoltaic (OPV) devices have emerged as competitors to silicon-based solar cells, currently reaching efficiencies of over 8% and offering desirable properties for manufacturing and installation. We study conjugated donor polymers for high-efficiency bulk-heterojunction photovoltaic devices with a set of molecules based on the combination of heterocyclic units. We use quantum mechanics and a distributed computing approach (<http://cleanenergy.harvard.edu>), in collaboration with IBM, to explore this vast molecular space. The distributed computing approach allows individual users around the world to contribute their idle computer time to calculate the properties of these molecules. We have used more than 2500 years of computer time to analyze more than a million candidate molecules. In order to develop the screening methods of the molecular library, we use Hückel-based physicochemical descriptors and chemoinformatics methods to probe quantitative structure-property relations of open-circuit voltage, short-circuit current density and power conversion efficiency: all important parameters in OPV materials. We will present results of the analysis of these candidates as well as connections to experimental efforts by the Bao group at Stanford University.

Vikram Pattanayak

Title: An *In Vitro* Selection to Identify Off-Target Cleavage Sites of Therapeutic Endonucleases

Abstract:

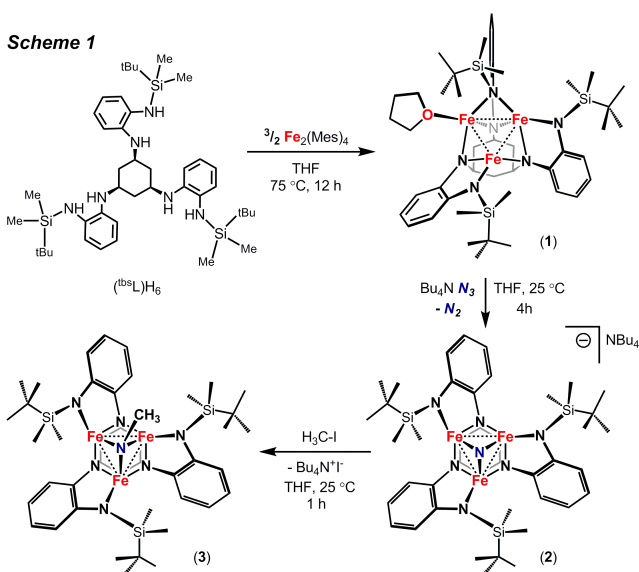
Zinc-finger nucleases are promising genome manipulation tools with potential uses in both the laboratory and the clinic. Despite recently entering clinical trials, off-target cleavage events of active ZFNs have yet to be comprehensively revealed. We developed an *in vitro* DNA cleavage selection that interrogates up to  $10^{11}$  DNA sequences in a single experiment for the ability to be cut by a ZFN. We applied this selection to reveal hundreds of thousands of DNA sequences, including some found in the human genome, that can be cleaved *in vitro* by a ZFN currently in clinical trials. In cultured human cells, we observed evidence for ZFN-mediated modification at seven of these sites. Our findings also establish a compensation model of ZFN specificity in which sites with disfavored spacer sequences or off-target base pairs in one half-site exhibit a more stringent sequence preference at the other half-site, suggesting that excess binding energy enables ZFN off-target activity.

## Synthesis, characterization, and reactivity of tri-iron clusters

Tamara Powers, G3, Betley Group

Our lab is interested in achieving small molecule activation, which requires the control of multi-electron processes. The use of metal clusters to bind and activate small molecule substrates has received increasing attention due to the expanded redox reservoir afforded by the polynuclear core. Utilizing a hexadentate ligand platform, I have synthesized a high-spin trinuclear iron complex (**1**) of the type  $(^{tbs}L)Fe_3(thf)$  ( $[^{tbs}L]^{6-} = [1,3,5-C_6H_9(NPh-o-NSi^tBuMe_2)_3]^{6-}$ ). The cluster has an asymmetric triiron core, where two of the three iron sites remain coordinatively unsaturated and have the potential to bind substrate. With this cluster I have demonstrated that, despite its asymmetry, the triiron core can cooperatively bind a wide range of substrates including halides and alkoxy groups as well as perform cooperative redox chemistry. The triiron complex  $(^{tbs}L)Fe_3(thf)$  rapidly consumes inorganic azide at ambient temperature and pressure to afford an anionic, trinuclear nitride complex (**2**)  $(^{tbs}L)Fe_3(\mu^3-N)NBu_4$ . Unlike monometallic iron nitrides which are low spin and electrophilic, the  $(^{tbs}L)Fe_3(\mu^3-N)NBu_4$  complex is high spin ( $S = 3$ ) and nucleophilic at the nitride, as demonstrated by its reaction with methyl iodide to afford a neutral  $\mu^3$ -imido complex (**3**)  $(^{tbs}L)Fe_3(\mu^3-NMe)$ . These systems could prove to serve as functional surrogates for polynuclear reaction sites found in heterogeneous catalysts (i.e. Fe(111) face in the Haber-Bosch dinitrogen reduction) or in metalloenzyme cofactors (i.e. FeMo-cofactor in nitrogenase), where it is speculated that binding, activation, and chemical break down of substrate occurs. Future work will involve study of the magnetic properties of these clusters. In addition, I am investigating the reactivity of the triiron cluster  $(^{tbs}L)Fe_3(thf)$  as well as its reduced counterpart  $[(^{tbs}L)Fe_3]^-$  toward small molecules, specifically CO, O<sub>2</sub>, NO, and N<sub>2</sub>.

Scheme 1



Yiqiao Tang:

### **Enhanced enantioselectivity in excitation of chiral molecules by superchiral light**

A molecule or larger body is chiral if it cannot be superimposed on its mirror image (enantiomer). Light may be chiral too, with circularly polarized light (CPL) as the paradigmatic example. We introduced a measure of the local degree of chiral dissymmetry in electromagnetic fields suggested the existence of optical modes more selective than circularly polarized plane waves in preferentially exciting single enantiomers in certain regions of space. By probing induced fluorescence intensity, we demonstrated experimentally an 11-fold enhancement over CPL in discrimination of the enantiomers of a biperylene derivative by precisely sculpted electromagnetic fields. This result establishes that optical chirality is a fundamental and tunable property of light, with possible applications ranging from plasmonic sensors to absolute asymmetric synthesis.

reference:

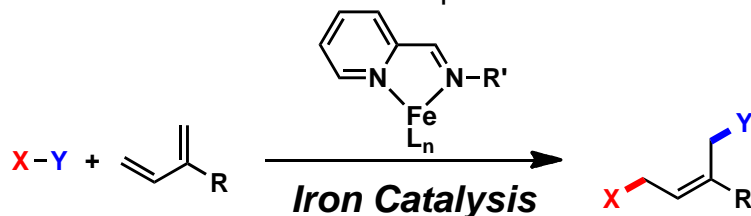
1. Yiqiao Tang, Adam E. Cohen. "Enhanced enantioselectivity in excitation of chiral molecules by superchiral light" *Science*, in press, 2011
2. Yiqiao Tang, Adam E. Cohen. "Optical chirality and its interaction with matter" *Phys. Rev. Lett.* 104, **163901**, 2010 (featured on the front cover).
3. Yiqiao Tang, Tim Cook, Adam E. Cohen. "Limits on fluorescence detected circular dichroism of single helicene molecules" *J. Phys Chem A* 113, **6213**, 2009.
4. Nan Yang, Yiqiao Tang, Adam E. Cohen. "Spectroscopy in sculpted fields" *Nano Today*, **4**, 269-279, 2009.



Jessica Wu

## Development of Iron Catalysts in Selective 1,4-Additions to 1,3-Dienes

Jessica Wu  
Ritter Group



This presentation will focus on the development of iron catalysts for the identification of new reactions for organic synthesis. The Ritter group became interested in the growing field of iron catalysis due to the wide range of reactivity iron exhibits and the untapped potential that iron has for catalyzing new synthetic transformations. The talk will discuss the use of iminopyridine-iron catalysts to effect C–C, C–B, and C–Si bond-forming reactions. We have found that iminopyridine-iron complexes catalyze regio- and stereoselective 1,4-addition reactions including addition of  $\alpha$ -olefins to 1,3-dienes, hydroboration of 1,3-dienes, and hydrosilylation of 1,3-dienes to selectively produce linear regioisomers with (*E*)-trisubstituted double bonds. The presentation will also include the development of a general iron pre-catalyst, which generates low-valent iron via reductive elimination of two aryl ligands.

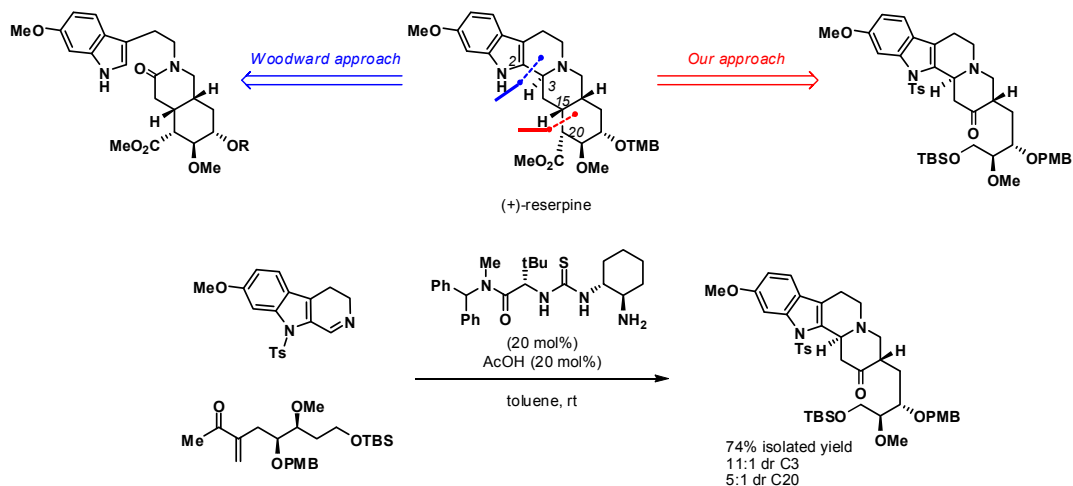
Bingjun Xu

"Gold surfaces: The chemical benchtop of oxidative coupling-reactions".

Abstract:

Metallic gold owes its centuries-old mystique and intrinsic value to its chemical inertness toward bulk compound formation. In the past decade, however, it has been discovered that the surface of gold is far from inert, and that gold can catalyze important chemical transformations – particularly with the assistance of molecular oxygen or other oxidizing agents. These processes are of particular significance because they may occur at remarkably low temperatures and pressures, suggesting the possibility of energy efficient and environmentally benign reaction conditions using metallic gold catalysts. Recently, there has been a focus on selective oxidation of alcohols to aldehydes, oxidative self-coupling of alcohols to form esters and, most recently, acylation via amine-formaldehyde coupling. A general reaction mechanism for this class of coupling-reactions is established: surface alkoxy or amide is formed via the deprotonation of the corresponding alcohol or amine by surface atomic oxygen, which can subsequently nucleophilically attack the aldehydes (formed in situ from alkoxy or introduced directly) and produce the corresponding ester or amide. The product distribution of our low-pressure experiments match remarkably well with gas phase reactions carried out in the ambient condition as well as liquid phase reactions, proves the generality of the mechanism.

Reserpine is an indole alkaloid natural product that has intrigued synthetic chemists because of its pharmacological activity and structural complexity since its isolation in 1952. Woodward's landmark total synthesis of reserpine in 1956, and all subsequently reported syntheses, employed a retrosynthetic disconnection across the C2-C3 bond. However, the installation of the C3 stereogenic center proceeded with undesired diastereoselectivity. We describe our progress towards an enantioselective total synthesis of (+)-reserpine that uses a fundamentally different approach and addresses the historically-problematic C3 stereogenic center. The target is disconnected across the C15-C20 bond. An aminothiourea-catalyzed formal aza-Diels–Alder reaction between  $\beta$ -carboline imines and enones that was developed in our group is used to generate the tetrahydro- $\beta$ -carboline core of reserpine and install the C20 and C3 stereogenic centers. An intramolecular aldol reaction installs the E-ring and the pentacyclic skeleton of reserpine. Our strategies for the final steps of the synthesis are described.



# Advanced Thin Film Materials and Metallization Processes for Microelectronics

Yeung (Billy) Au

Gordon Group

## Abstract

The packing density of microelectronic devices has increased exponentially over the past four decades. Scaling of the physical size of devices and increasing the number of metal wiring levels have achieved continuous enhancements in device performance and functionality. Copper (Cu) is

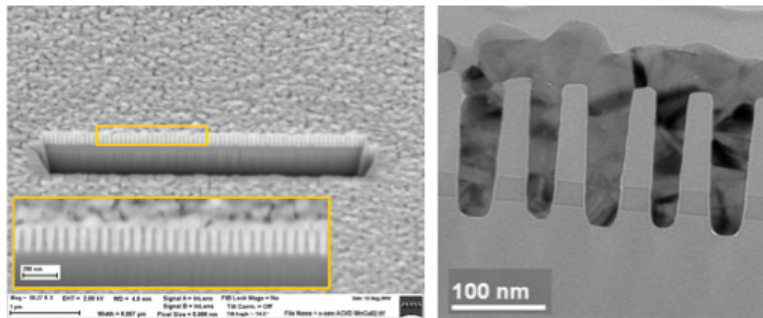


Figure 1. Cross sectional SEM (left) and TEM (right) showing complete filling of narrow trenches by iodine-catalyzed CVD of Cu

used as an interconnecting metal due to its superior electrical conductivity and resistance against electromigration, but a liner layer is needed to prevent diffusion of copper and to promote adhesion to insulators. As the packing density increases, conventional deposition techniques cause formation of voids and discontinuous films in nanoscale features. We present a process for the void-free filling of narrow trenches with copper or copper-manganese alloy by chemical vapor deposition (CVD). Conformally deposited manganese nitride film serves as an underlayer that prevents diffusion of copper and enhances the adhesion between copper and dielectric insulators. Iodine acts as a surfactant catalyst floating on the surface of the growing layer during CVD of copper or copper-manganese alloy. As the iodine concentrates near the narrowing bottoms of features, void-free, bottom-up filling of CVD of pure copper or copper-manganese alloy is achieved in trenches narrower than 30 nm with aspect ratios up to at least 5:1 (Figure 1). During post-deposition annealing, manganese in the alloy diffuses out from copper through the grain boundaries and forms a self-aligned  $MnSi_xO_y$  layer that further improves barrier properties at the copper/insulator interface (Figure 2). Presence of manganese at the interface greatly increases the strength of the bonding between copper and the insulator to prevent electromigration of copper. This metallization process facilitates the fabrication of future generations of nanoscale microelectronic devices with higher speeds and longer lifetimes.

used as an interconnecting metal due to its superior electrical conductivity and resistance against electromigration, but a liner layer is needed to prevent diffusion of copper and to promote adhesion to insulators. As the packing density increases, conventional deposition techniques cause formation of voids and discontinuous films in nanoscale features. We present a

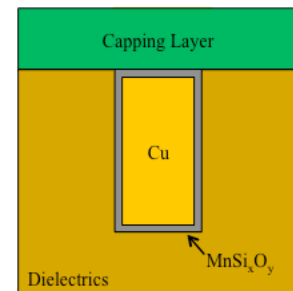


Figure 2. Schematic diagram of Cu interconnect structure after post-annealing

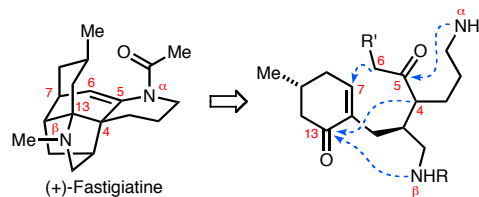
## Related Publications

“Filling Narrow Trenches by Iodine-Catalyzed CVD of Copper and Manganese on Manganese Nitride Barrier/Adhesion Layers”, Y. Au, Y. Lin and R. G. Gordon, *J. Electrochem. Soc.*, **158** (5) D248-D253 (2011)

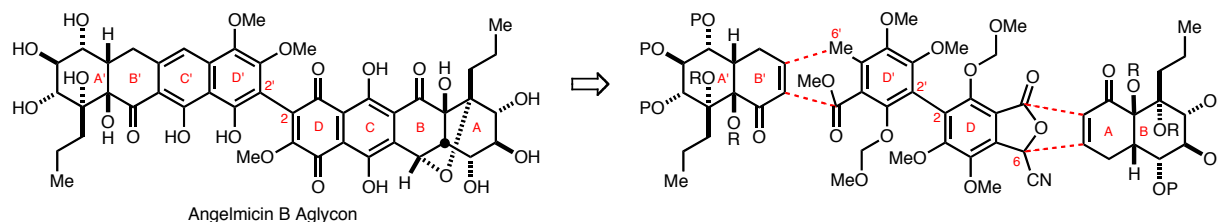
“Selective Chemical Vapor Deposition of Manganese Self-Aligned Capping Layer for Cu Interconnections in Microelectronics”, Y. Au, Y. Lin, H. Kim, E. Beh, Y. Liu and R. G. Gordon, *J. Electrochem. Soc.*, **157** (6) D341-D345 (2010)

**Brian Liou** – (1) Total Synthesis of (+)-Fastigiatine and (2) Progress Toward a Total Synthesis of Angelmicin Aglycon.

(1). The first total synthesis of the *lycopodium* alkaloid (+)-fastigiatine has been accomplished. Notable transformations include a convergent fragment coupling via a nucleophilic cyclopropane opening, a highly diastereoselective formal [3+3]-cycloaddition, and a transannular Mannich reaction to construct the strained pentacyclic core of the natural product.



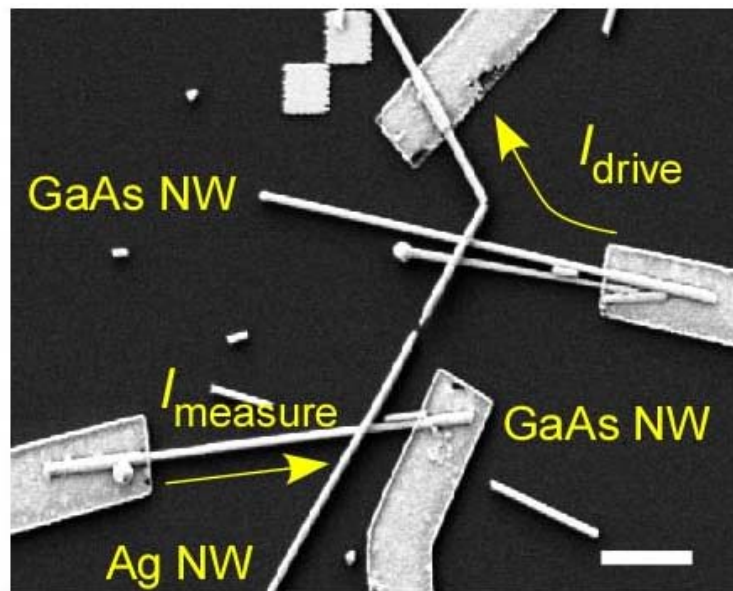
(2). Angelmicin B is an unprecedented pseudo-*C*<sub>2</sub>-symmetric polyketide that potently inhibits proliferation and induces differentiation of human leukemia tumor cells. Significant progress toward a synthesis of angelmicin B aglycon has been accomplished via a convergent strategy that features a bidirectional unsymmetric double annulation reaction and late-stage oxidative desymmetrization.



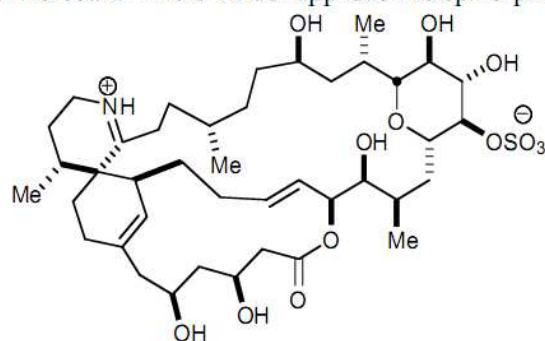
## Near-Field Generation and Detection of Surface Plasmon Polaritons on Silver Nanowires

CHUN L. YU, Park Group

Surface plasmon polaritons (SPPs) are electromagnetic waves on metal surface. Nanoscale photonic circuits based on SPPs hold great promise in confining light in sub-wavelength scale, thus shrinking the size of devices. Conventionally, SPPs are generated optically by a laser. However, an on-demand and electrically-driven SPP source is more desirable for a lot of on-chip applications. Chemically-grown silver nanowires are highly crystalline and excellent waveguides for SPPs. We demonstrate nanowire junction-based techniques for generating and detecting SPPs in the near field. For near-field SPP generation, we use a silver nanowire as both an SPP waveguide and an electrode for an electroluminescent Schottky junction. For near-field SPP detection, a photosensitive GaAs nanowire is used as a detector. Our demonstration is a step closer to a dark plasmonic circuit, which completely eliminates far-field photons and optics in signal transduction using SPPs.



**Alex Speed** - An intermolecular Diels- Alder approach to spiro-prorocentrimine



An approach towards the zwitterionic marine toxin Spiro-prorocentrimine that involves a late stage intermolecular Diels-Alder reaction is described.

Several approaches were required before the stereochemistry around the spirocycle could be correctly established. In the course of these investigations some findings were made that may allow rate enhancements in all organocatalytic reactions containing iminium ion intermediates. The stereochemistry and bond constructions around the tetrahydropyran segment of the molecule were established using transformations involving organometallic species, and this chemistry will be presented. Finally, approaches towards the end part of the synthesis strategy will be discussed.