


# ABSTRACTS

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**Undergraduate Research in  
Chemistry Regional Poster  
Competition**  
137 Chemistry-Physics Building  
April 18th, 2014  
3:00pm - 5:00pm



Department of Chemistry  
University of Kentucky  
Lexington, KY 40506



# 1

## IMPROVED STARCH DEGRADATION USING NATURAL SYSTEMS

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Starch is a vital energy molecule in plants and a key component of human diet. It also has a wide variety of uses in industry, such as biomaterials and a feedstock for biofuel production. Starch is comprised of chains of glucose molecules that intertwine to form helices, which makes the surface of starch nearly inaccessible to many enzymes.

In plants, starch is degraded in a cyclical nature that involves three main classes of enzymes: dikinases, amylases, and phosphatases. Glucan dikinases add a phosphate group to glucose units within starch and this phosphorylation promotes solubilization of the starch surface to make it more accessible to starch-degrading enzymes, the amylases. Amylases break down starch and release glucose (i.e. table sugar), but their activity is inhibited by phosphorylated glucose. Therefore, glucan phosphatases enhance amylase activity and reset the cycle by removing the starch bound phosphate.

In industry, raw plant material is degraded by milling and then treated with heat and harsh chemicals, a process that is costly and environmentally unfriendly. If the cyclic nature of plant degradation of starch can be applied to industries, the cost to degrade starch would go down significantly and the use of harsh chemicals would not be needed, making the process more environmentally friendly. We initially performed in vitro binding assays to measure the affinity of the glucan dikinases and phosphatases to glucans by incubating the enzymes with various glucans and monitoring the enzyme binding to glucans via Western blot analysis. We also utilized a gel-shift assay to measure the binding of the enzymes to glucans. We found that the glucan dikinases and phosphatases possess differing abilities to bind glucan substrates. We additionally performed a starch degradation assay to measure glucose release after the treatment of the glucan with a combination of different enzymes (amylases, dikinases and phosphatases). The results of the degradation assay show that after the addition of dikinases and phosphatases, the glucose content was significantly increased, indicating that these enzymes could be used for the industrial processing of starch.

Industrial processing of starch currently utilizes the combination of harsh acids and bases, fluctuation of temperatures, and many enzymes to generate starch feedstock. Our data suggests that we can hijack the plants native cyclical nature of phosphorylating, degrading, and dephosphorylating starch, to significantly decrease the cost of industrial degradation of starch and make the process more environmentally friendly.

# 2

## SYNTHESIS OF DINUCLEAR RUTHENIUM(II) COMPLEXES FOR IMPROVED LIGHT ACTIVATED DNA DAMAGE

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Current photodynamic therapies for cancer treatment use photosensitizing agents activated by visible to near-IR light to produce cytotoxic singlet oxygen. Unstrained Ru(II) complexes, activated with visible light, damage DNA via an oxygen-dependent pathway. Oxygen-independent, covalent modification of DNA can be obtained by using strained Ru(II) complexes. Introduction of two Ru(II) molecules could provide for more effective DNA damage, including complex interstand crosslinks. Novel homodinuclear Ru(II) complexes have been synthesized to have the same Ru(II) complex linked by an aliphatic chain, and results showed increased DNA damage by the same mechanism. Heterodimers, composed of two different linked Ru(II) complexes, would ideally provide two different types of DNA damage. The heterodimer synthesis has been optimized to provide 100% conversion at each step. These dinuclear complexes may offer a more effective route to induce DNA damage in cancer cells.

# 3

## ATMOSPHERIC REACTIONS OF CATECHOL WITH OZONE AT THE AIR-WATER INTERFACE

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Atmospheric aerosols are an important subject in environmental research due to their effects on public health and climate. The impact of aerosols on climate is poorly understood due to the many variables that control their chemistry, such as acidity, relative humidity, temperature, and chemical composition. Anthropogenic emissions contribute aromatic compound precursors to secondary organic aerosols (SOA), which can be oxidized to phenols. In order to better understand the chemical fate of phenols in SOA, the molecule of catechol is chosen to study its reactivity during atmospheric processing at high relative humidity. In this study, transmission and attenuated total reflectance Fourier transform infrared spectroscopies (ATR-FTIR) are employed to monitor in real-time the heterogeneous ozonolysis of thin films of catechol. A homemade gas-cell adapted to a ZnSe diamond ATR-accessory allowed us to expose the films to 20 mL/min ozone gas (200 ppbv–200 ppmv) at 298 K. Additional experiments were performed in a flow-trough reaction chamber to monitor the kinetics of catechol decay at 3458  $\text{cm}^{-1}$  and suggest the formation of volatile products that partition to the gas-phase.

# 4

## MUTANT STRAIN OF *M. LUTEUS* WITH A LIPOMANNAN (LM) ATTACHED TO A LIPID ANCHOR WITH ABNORMALLY LONG FATTY ACYL GROUPS

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Previous studies have shown that the major mannosylipid synthesized in *M. luteus* cells is a-D-mannosyl-(1à3)-a-D-mannosyl-(1à3)-diacylglycerol (Man<sub>2</sub>-DAG) containing a methyl branched chain C15 fatty acyl group in the 1-position and a myristoyl group in the 2-position.<sup>1</sup> Man<sub>2</sub>-DAG is formed on the cytoplasmic leaflet, and after diffusing transversely to the exterior monolayer is elongated by 46 additional mannosyl units with Man-P-undecaprenol serving as the mannosyl donor forming the membrane-associated lipomannan (LM).<sup>2</sup>

In the current study, a mutant (strain LP123) with a modest temperature-sensitive growth defect has been characterized, and shown to synthesize a mutant form of the lipid anchor containing longer, more hydrophobic methyl branched C17 fatty acyl groups. It is possible that the presence of the more hydrophobic branched chain C17 fatty acyl group, instead of the normal C15 fatty acyl group, in the lipomannan anchor is responsible for the temperature-sensitive growth defect in LP123.

### References:

- Pakkiri, L. S. and Waechter, C. J. Dimannosyldiacylglycerol serves as a lipid anchor precursor in the assembly of the membrane-associated lipomannan in *Micrococcus luteus* (2004) *Glycobiology*, 14, 1-12.
- Pakkiri, L. S., Wolucka, B. A., Lubert, E. J., and Waechter, C. J. Structural and topological studies on the assembly of the membrane-associated lipomannan in *Micrococcus luteus* (2004) *Glycobiology*, 14, 73-81.
- Lennarz, W. J. The Role of Isoleucine in the Biosynthesis of Branched-Chain Fatty Acids by *Micrococcus lysodeikticus* (1961) *Biochemical and Biophysical Research Communications*, 6, 112-116.

# 5

## SOLVENT DEVELOPMENT FOR CARBON DIOXIDE CAPTURE

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The combustion of fossil fuels generates large amounts of carbon dioxide which is released into the atmosphere. With the current power demand, the concentration of carbon dioxide in the atmosphere is causing environmental concerns with the development of global warming. With increasing environmental concerns regarding the carbon dioxide concentrations in the atmosphere, new regulations may be imposed onto power plants to reduce the levels of carbon dioxide emissions. In this case, adaptations to power plant designs may be required to capture carbon dioxide to lower emissions. In a power plant, solvent captures and transports the carbon dioxide through the absorber tower and later releases the carbon dioxide to be collected from the desorber tower. In this project, new solvents are developed to capture the generated carbon dioxide gas in order to make the process more efficient and cost effective.

Target solvents are primary and secondary amines with high pKa values, high boiling points, low viscosities, and low heat of reaction with carbon dioxide. In the absorber tower, the solvent captures carbon dioxide and forms a carbamate. The carbamate is transferred through the power plant into the desorber tower where application of heat breaks the carbamate bond, releasing carbon dioxide and the amine solvent. The amine solvent, hence regenerated, is cycled back. One of the target solvents was successfully synthesized to be used for further testing. The synthesis of remaining target solvents and their testing to determine their capturing efficiency is under progress.

# 6

## OXIDATIVE DECONSTRUCTION OF SWITCH GRASS LIGNIN

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Lignin is a cross-linked bio-polymer of several aromatic alcohols that contributes to the structural integrity of plants. As much as 30 percent of biomass is represented by lignin, meaning there is much to gain from converting this industrial waste product into a more usable form. The goal of this research is to apply a two-step oxidative method to lignin in order to derive compounds that can be used as biofuel or as feedstock chemicals. The desired outcome of this project is particularly significant with the ever-mounting environmental and sustainability concerns of continued fossil-fuel use.

Our approach consists of an initial oxidation of benzylic hydroxyl groups, which prepares the structure for oxidative cleavage of the polymer chain through Baeyer-Villiger oxidation.

In order to facilitate this approach on lignin (which is very insoluble in most traditional solvents), the first oxidation steps were carried out in ionic liquids. Many ionic liquids are more effective at dissolving lignin than traditional solvents, and are typically highly stable and have very high boiling points. These properties are conducive to a smaller total volume of solvent required, solvent recycling, and minimal air-pollution. The major ionic liquids of study were 1-butyl-3-methylimidazolium chloride and tetrabutylphosphonium chloride.

Reagents for the benzylic oxidation step that have been explored are sodium nitrate in 3-methylimidazolium hydrogen sulfate, DMSO/oxalyl chloride (Swern oxidation), H-K-OMS-2 manganese catalyst/O<sub>2</sub>, and (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO)/NaNO<sub>2</sub>/O<sub>2</sub>. Although meta-chloroperoxybenzoic acid was briefly explored for the Bayer-Villiger step, a hydrogen peroxide/formic acid mixture was the method of choice for most of the work. Using this two-step oxidation scheme, the molecular weight (as determined by GPC) of lignin is decreased, and solubility is increased. Lignin that has undergone this treatment is entirely soluble in DMSO and n-methylimidazole in concentrations as high as 100 mg per 0.6 mL, while lignin before oxidation is largely insoluble at any concentration. Although GPC could not be performed on starting lignin, it could be performed on lignin having undergone exclusively Baeyer-Villiger oxidation as well as the two-step product. The comparison of these products was the basis for mass reduction.

# 7

## USING PERMANGANATE AS A COLORIMETRIC PROBE TO UNDERSTAND RUTHENIUM DNA INTERACTIONS

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Our laboratory has particular interest in understanding the primary and secondary structure of DNA (deoxyribose nucleic acid). In particular, we are interested in the interaction of short single-stranded DNA segments exposed to a Ruthenium complex, Ru(bpy)<sub>2</sub>(dmbpy) (2). We are interested in this complex because of its potential implications as an anti-cancer agent. Using this complex, we use an identification method developed in our lab called CIENA, or Colorimetric Identification of Exposed Nucleic Acids (1). This process allows one to identify the nucleobases' interactions with Ru(bpy)<sub>2</sub>(dmbpy) in an aqueous environment by changes in solution color. Many current analytical techniques require radiolabeling, PAGE gels, high concentrations, and solid-state analysis; each taking the DNA out of its natural state and being high-cost. CIENA provides a low-cost, easy to interpret, visual image that can offer great insight to the interaction of different transition metal complexes with DNA bases. In this study, permanganate is used as a colorimetric indicator offering understanding of how Ru(bpy)<sub>2</sub>(dmbpy) interacts with monomeric and oligomeric DNA. Herein, Ru(bpy)<sub>2</sub>(dmbpy) indicates selectivity for deoxyguanosine monophosphate monomer while other monomeric DNA remains inactive (deoxyadenosine monophosphate, deoxycytidine monophosphate, and thymidine monophosphate). Further studies include Ru(bpy)<sub>2</sub>(dmbpy) reactions with oligomeric DNA.

### Works Cited

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2. Howerton, B. S., Heidary, D. K., & Glazer, E. C. (2012). Strained ruthenium complexes are potent light-activated anti-cancer agents. *J. Am. Chem. Soc.*, 134, 8324-8327.



# 8

## VAPOR-LIQUID-SOLID MECHANISM GROWTH OF METAL/METAL OXIDE CATALYZED TIN(IV) OXIDE NANOWIRES

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Localized surface plasmon resonances, or LSPR, are the collective oscillations made by external electrical fields in metallic nanoparticles. Plasmon resonances can therefore be used for multiple applications such as, sub-diffraction limited waveguiding materials (i.e. sensors, solar cells, plasmonic resonators, Li-ion conductors, etc.). A novel approach to fabricating a waveguiding material is by synthesizing one directly in the form of a heterostructured nanowire, which resembles a peapod with metal “peas” encased in a metal oxide “pod”. This has a number of advantages such as, this process is spontaneous at certain temperatures and the growth and morphology of the fabricated nanowire can be controlled. Here we will discuss the synthesis and characterization of nanowires grown using the vapor liquid solid mechanism, as a starting material for heterostructure formation and some preliminary results showing the formation of such heterostructures.

# 9

## EFFECT OF CARDIAC TROPONIN I DEGRADATION ON FORCE AND POWER OUTPUT IN HUMAN HEART FAILURE

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We have recently reported that muscle preparations from patients with heart failure have reduced force and power generation than donors with non-failing hearts. The data also showed that calcium sensitivity, or the amount of force generated for a given calcium concentration, decreased from the inner (sub-endocardial) to the outer wall (sub-epicardial) of the left ventricular free wall. This transmural pattern was disrupted in failing hearts; interestingly, the study also found that cardiac troponin-I content (cTnI) was reduced in the failing hearts. cTnI is the inhibitory part of the troponin tri-complex that binds to actin on the thin filament and inhibits myosin binding sites on actin. In the presence of calcium the troponin complex undergoes a conformational change which allows myosin to bind to actin causing muscle contraction. Previous studies have shown that loss of the C-terminus of cTnI leads to diminished contractility and lowered calcium responsiveness in transgenic mouse models (Murphy, et al., 2000). We hypothesized that the decrease in cTnI content found in our study represents the degraded form of cTnI and that degradation of cTnI may be different transmurally through the left ventricular wall of the failing samples. We are studying left ventricular tissue from failing and non-failing human hearts separated in three transmural layers: the sub-endocardium, mid-myocardium and sub-epicardium. We are using western blotting with monoclonal antibodies to probe for the presence of cTnI (4H6: targeting the amino acids 13-190 in the middle of cTnI) and its C-terminus (TnI-1: targeting exon 8 that codes the 27 C-terminal residues of human cTnI). Both the absolute and relative content of the two antibodies are being compared between the heart failure status and the transmural region using Linear Mixed Model statistical methods. If we find degraded cTnI in our failing samples it would imply that the loss of normal function in our failing samples maybe due to the proteolysis of cTnI. A malfunction in the ability to inhibit myosin head binding due to the inability of troponin I to block the myosin head interaction would lead to an eventual damage to the myocytes. This ultimately would lead to a decrease in function, as seen in the decrease in force and power output.

**REDUCING DNA INTERACTION WITH THE ADDITION OF NON-PLANAR LIGANDS**

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The future of cancer photodynamic therapy (PDT) relies on the synthesis of compounds with low toxicity in the dark and high toxicity when exposed to light. Strained ruthenium (II) polypyridyl complexes are believed to induce cell death by damaging DNA, similar to the pathway by which the chemotherapy drug cisplatin induces cell death.[1] Visible light activation leads to ligand loss and results in the Ru(II) center covalently modifying DNA; the compounds are designed to be inactive in the dark, and low toxicity in the absence of light is a desired characteristic of Ru(II) complexes. It is known that intercalation of Ru(II)-coordinated ligands into DNA may account for some level of dark toxicity. When coordinated with Ru(II), flat phenanthroline derivatives with extended, nitrogen-containing  $\pi$  systems, such as dipyrido[3,2-f:2',3'-h]-quinoxaline (dpq) can intercalate DNA base pairs. [1,2] Reduction of the intercalation activity by modification of coordinated ligands may be a viable method for decreasing dark toxicity of Ru(II) PDT agents. Dpq-ce, a non-planar cyclic ether-containing dpq derivative, was complexed with Ru(bpy)<sub>2</sub> and Ru(dmphen)<sub>2</sub> to give unstrained and strained complexes, respectively. The non-planar geometry of the dpq-ce ligand may reduce intercalation by preventing insertion of the ligand into the DNA base pair stacks.

## References

- [1] B. S. Howerton, D. K. Heidary, E. C. Glazer, *J. Am. Chem. Soc.* 2012, 134, 8324-8327.  
[2] (a) I. Greguric, J. R. Aldrich-Wright, J. G. Collins, *J. Am. Chem. Soc.* 1997, 119 (15), 3621-3622. (b) J. G. Collins, A. D. Sleeman, J. R. Aldrich-Wright, I. Greguric, T. W. Hambley, *Inorg. Chem.* 1998, 37 (13), 3133-3141. (c) J. G. Collins, J. R. Aldrich-Wright, I. D. Greguric, P. A. Pellegrini, *Inorg. Chem.* 1999, 38 (24), 5502-5509.

**DISSOCIATION OF A $\beta$  OLIGOMERS INTO MONOMER BY DHBA DETERMINED BY FLUORESCENCE CORRELATION SPECTROSCOPY (FCS)***An L. Ho, Chen Chen<sup>1</sup>, Harry LeVine III<sup>2</sup>, Jason DeRouchey<sup>1</sup>*

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The diffusible soluble oligomeric amyloid  $\beta$ -peptide (A $\beta$ ) has been identified as a major toxic agent in Alzheimer's disease (AD)<sup>1</sup>. These A $\beta$  oligomers are thus an important biomarker and potential therapeutic target. Previous work used an ELISA assay to measure A $\beta$  oligomers to identify small molecules that enhance oligomer dissociation<sup>2</sup>. In this study, we used Fluorescence Correlation Spectroscopy (FCS) to monitor diffusion of fluorescein tagged – A $\beta$ (1-42) species at the single molecule level and near physiologic concentrations. Oligomers exposed to isomers of dihydroxybenzoic acid (DHBA) active in dissociating oligomers reduced the proportion of oligomeric A $\beta$  species and increased the amount of monomer at a [DHBA]-dependent rate. Because we did not detect intermediate size oligomer species, we suggest that active, but not inactive isomers of DHBA mediate cooperative oligomer dissociation.

**SYNTHESIS OF PHOTOCLEAVABLE MOLECULES FOR SURFACE MODIFICATION**

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Exploring the properties of single molecules has a wide variety of applications in chemistry and biology. Being able to study single proteins, for example, can reveal important information regarding shape conformations, active sites, bond distances, and the like. These characteristics are useful to study as they can describe the mechanism of action of the biomolecule. Recently, single-molecule properties have been studied using nanoscale plasmonic devices[1]. If light is shone on to the surface supporting the devices, photon intensity has a tendency to aggregate in discrete locations—effectively photonic “hot-spots”. Compounds which selectively undergo photocleavage within the localized locations (i.e. “hot-spots”) can then be used as a probe to explore single-molecule properties.

In this project, compounds were developed with two major components: a chromophore which can be photocleaved to expose a reactive amine and a surface modifying group. In particular, targets were designed with two different chromophores which can serve as protecting groups for alkyl amines: coumarins and nitromethoxybenzene (NMB) derivatives. In addition, the alkyl amine is capped with either a silane or a thiol, which modify glass and gold surfaces respectively. Photocleavage is performed in the presence of a fluorescent dye containing a N-hydroxysuccinimide (NHS) ester moiety. Irradiation leads to deprotection of amine which subsequently reacts with the NHS-ester of the dye. Fluorescence spectroscopy is then used to observe where the dye has attached to the surface.

Preliminary experiments (i.e. excluding nanostructures) revealed that irradiation for one second at 405 nm resulted in 16,000 (photon) counts of fluorescence, demonstrating successful photocleavage and binding of the dye. Future work will require the incorporation of nanostructures in order to determine whether or not photocleavage can be executed selectively. In addition, systems which utilize other functionalities (e.g. a protected thiol binding to a dye possessing a maleimide moiety) are being investigated to diversify applications.

[1] Kinkhabwala, A.; Yu, Z.; Fan, S.; Avlasevich, Y.; Müllen, K.; Moerner, W.E. *Nature Photonics*, 2009, 3, 654.

## OVEREXPRESSION OF PIN1 IN APP/PS1 KNOCK-IN ALZHEIMER DISEASE

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Oxidative stress in Alzheimer disease (AD) has been found to be a major contributing factor to the pathological hallmarks, amyloid-beta plaques and neurofibrillary tangles, that precede neurodegeneration [1]. The peptidyl-prolyl cis/trans isomerase Pin1 is a crucial regulator of both amyloid precursor protein (APP) and the production of amyloid-beta through direct interaction as well as control of key kinases and phosphatases [2]. Pin1 has recently been found by our group to be both oxidatively modified and present at decreased levels in brain in various stages of AD [3]. It is thought that this decrease and damage of Pin1 leads to an increase in amyloid-beta production, and therefore, an increase in overall oxidative stress. By upregulating the gene for Pin1 in brain of human APP and presenilin 1 (PS1) double-mutant knock-in mice, a common AD mouse model, levels of oxidative stress should decrease. In order to study these effects of this genetic modification, immunochemistry is used to measure the common indices of protein and lipid oxidation, specifically protein carbonyls (PC), 3-nitro tyrosine (3-NT), and 4-hydroxy-nonenal (HNE), respectively, in brain tissue samples. Additionally, levels of key proteins related to the cellular antioxidant response system are determined by Western-blot analysis in order to provide insight into the redox state of the cell. By restoring control over the production of amyloid-beta, a better understanding into the mechanisms that contribute to the progression of AD might be achieved. This understanding, in turn, may eventually lead to more effective therapeutic methods for AD patients. Support: NIH grant to D.A.B. [AG-05119].

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3. Sultana, R., et al., Oxidative modification and down-regulation of Pin1 in Alzheimer's disease hippocampus: A redox proteomics analysis. *Neurobiology of Aging*, 2006. 27(7): p. 918-925.

**CONVERSION OF GLUCOSE TO 5-HMF VIA ALUMINUM HALF-SALEN COMPLEX CATALYSIS IN IONIC LIQUID***Benjamin McCalla, Daudi Saang'onyo, Folami Ladipo*

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A spectrum of half-salen ligands were developed as a complex with  $AlMe_3$  for the catalytic dehydration of Glucose to 5-HMF. Utilizing ionic liquid as a solvent and both an oil bath and MARS 5 microwave reactor. Our analysis of the developed catalysts had two goals; (1) to determine the nature of the group attached to nitrogen's effect on yield, conversion, and selectivity of the Glucose $\rightarrow$ 5-HMF reaction. (2) To find the effect of microwave irradiation versus conventional heating on the yield, conversion, selectivity, and reaction time for the aforementioned reaction.

## AROMATIC-AROMATIC INTERACTIONS OF COMPLEX IONS

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Aromatic compounds have the ability to stack onto each other in face-face, edge-face, or parallel positions. Tri-methyl-triazatriangulenium (1NMe<sub>3</sub>) and tri-oxa-triangulenate (2), are two molecules that have been shown to interact to form 1•2 ion pairs. Interestingly, it has been observed that 1(NMe<sub>3</sub>) is capable of 1•1 but 2 is not capable of homodimerization.

Hexabenzocoronene (3), while having similar size, aromaticity and symmetry as 1 and 2, has Lewis basicity somewhere in between that of 1 and 2. From this 1•3 was predicted to exist, forming complex solvent separated ion pairs: 1•3 + BF<sub>4</sub>. 3 is relatively insoluble in most solvents when compared to 1 and 2. It is predicted that 1•3 complexes are soluble in organic solvents, thus allowing the cation 1 be referred to as phase transfer catalysts.

We will introduce N-nHexlydioxatriangulenium because of its increased solubility properties to determine the solubility of 3 when combined with 1(NHexO<sub>2</sub>) in solution. Using NMR and UV spectrometry in different solutions, as well as soft ionization mass spectrometry to determine existence of species like 1 (NHexO<sub>2</sub>) •3. This change in solubility for 3 means that 1(NHexO<sub>2</sub>) has properties of a phase transfer catalyst for aromatic hydrocarbons.



**FUNDAMENTAL STUDIES OF DONOR-ACCEPTOR CONJUGATED POLYMERS:  
HOW BULKY SIDE CHAINS MAY INFLUENCE SOLUBILITY AND ELECTRONIC  
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Garnering the interest of those in organic and materials chemistry, organic photovoltaic devices and transistors have been subjected to vigorous research in an attempt to increase their desired electronic properties, decrease the cost of synthesis, and improve stability in air and light. In this highly competitive field, however, some groups substitute in-depth understanding for simply mimicking another's results to obtain a temporary record in carrier mobility, power conversion efficiency, etc.

The Watson group has, over the past few years, focused on obtaining a fundamental understanding of donor-acceptor conjugated polymers through one-variable manipulations—for instance, using benzodithiophene as the donor material, different length alkyl groups are attached by a secondary carbon and the polymer prepared using 1,2,4,5-tetrafluorobenzene as the acceptor.

By manipulating the length of these chains one saturated hydrocarbon at a time, one can determine the length at which the polymer becomes soluble. But this result is trivial—though a highly soluble polymer is desired, one can abstract more information from this repertoire of polymers besides solubility. For instance, because the branch is close to the polymer backbone, does its presence effect pi-stacking and thus alter electronic properties? Moreover, though alkyl groups do not directly interfere with conjugation in the backbone of the polymer, does increased steric bulk disrupt p-orbital overlap between oxygen and the aromatic carbon, retarding the electron donation from oxygen and, thus, further affecting electronic properties of the material? With a library of polymers recently synthesized, the Watson group is beginning to answer these fundamental questions.

## ABILITY OF *SHEWANELLA PUTREFACIENS* TO COUPLE MN(II) OXIDATION TO NITRATE (NO<sub>3</sub><sup>-</sup>) REDUCTION

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The nitrogen cycle is a continuous process of reduction and fixation of nitrogen to be used in soil environments and released back into the atmosphere. Nitrogen is highly demanded by plants and limits growth rates and yields when found in low concentrations. Alternatively, plant growth is also limited as nitrate concentrations rise in ground water. Through recent research under Dr. Matocha, it was determined that divalent manganese (Mn) can be reoxidized during nitrate reduction<sup>[2]</sup>. An explanation is that a known metal-reducing bacteria *Shewanella* can utilize Mn(II) as an electron donor and couple this activity to nitrate reduction<sup>[3]</sup>. The objective of this experiment is to assess whether *Shewanella* can oxidize dissolved Mn(II) and couple this to nitrate reduction under growth and non-growth conditions, using the stirred-batch method. Because such little information is known in the area of Manganese in the nitrogen cycle, the experiment had to be controlled very well. The research done thus far deals with the controls of manganese with nitrate, manganese alone, and manganese with nitrite, and the preliminary assessments of the growth patterns of *Shewanella*.

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**PIN1 IN ALZHEIMER'S DISEASE***Ngan Kim Tram, D. Allan Butterfield*

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Alzheimer's disease is a neurodegenerative disorder accompanied by loss of memory, speech, cognitive function and behavioral activities. The major neuropathological characteristics of Alzheimer disease (AD) are the abundant accumulation of intracellular neurofibrillary tangles (NFT), extracellular senile plaques and synaptic loss. The main component of senile plaques is amyloid  $\beta$ -peptide ( $A\beta$ ) derived from amyloid precursor protein (APP). Neuronal cytoskeletal components such as hyperphosphorylated tau and neurofilament proteins are the major components of NFT. Tau proteins have many important roles in intracellular tracking by maintaining the stabilization of microtubules. Hyperphosphorylation of tau protein can interrupt the intracellular transport by disassembling microtubules, which eventually causes degeneration of the neuron. The hyperphosphorylation and dephosphorylation of tau protein are associated with unbalanced kinase or phosphatase activities, which are regulated by Pin1 (peptidyl-prolyl cis/trans isomerase); therefore, Pin1 is involved in pathogenesis of AD. In hippocampus of AD subjects where memories are processed, Pin1 protein was found to be oxidatively modified and decreased activities. The reduced expression of Pin1 promotes phosphorylation of protein tau, which is responsible for NFT formation and AD progression.

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**SURFACE PASSIVATION OF GRAPHENE QUANTUM DOTS SYNTHESIZED FROM CARBON NANO-ONIONS***Michael Ware, Sin Hea Yeom, Dr. Doo Young Kim*

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Graphene quantum dots (GQDs) are a new class of carbon nano-materials with unique structural and optical properties. GQDs are gaining a lot of attention due to many attractive features including cost-effective preparation, bright and stable photoluminescence, environmental friendliness, and bio-compatibility. For our study, GQDs were prepared by the chemical oxidation of carbon nano-onions. While as-prepared GQDs showed a low fluorescence quantum yield with green color emission, GQDs showed blue-shifted emission with greatly enhanced photoluminescent properties after their surfaces were covalently linked to simple organic species like polyethylene glycols (PEGs). The focus of my research is to further examine how different synthetic and structural factors can influence the results of this surface passivation. Such factors include (i) surface passivation temperature and (ii) the content of oxidative defects present in unpassivated GQDs, and (iii) the structure of passivating organic species (e.g., either branched or linear polymer). Knowledge obtained from this study will be crucial in understanding the emission mechanism of GQDs and in designing highly versatile fluorescence probes with desirable spectral properties for many applications such as bio-imaging of cancer cells.

## OXIDATIVE STRESS ASSOCIATED WITH PIN1 IN ALZHEIMERS DISEASE

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The influence of PIN1 on measures of oxidative stress are analyzed. PIN1 is a peptidyl-prolyl cis/trans isomerase which is specific for the phosphorylated Ser/Thr-Pro motif.<sup>1</sup> The Cys113 residue located in the active site of PIN1 plays a significant role in the enzyme's isomerization capability. <sup>1</sup> One of the known functions of PIN1 is its involvement in the transcriptions process, where phosphorylation of Ser2 and Ser5 in the C terminal domain of RNA polymerase II serve as important regulatory factors allowing for the progression of transcription to occur.<sup>2</sup> PIN1 interacts with the C terminal domain of RNA polymerase II in order to prevent dephosphorylation and subsequent hindrance of the transcription process. <sup>2</sup> Another important role of PIN1 is its involvement in the DNA replication checkpoint of the cell cycle.<sup>3</sup> Abnormal activation of mitosis is linked to hyperphosphorylation of Tau, which is a key pathological marker involved in Alzheimer's disease. <sup>3</sup> As previously mentioned the Cys113 residue is essential to the isomerization capability of PIN1, but is also the site of oxidation of the enzyme to SOH, SO<sub>2</sub>H, SO<sub>3</sub>H.<sup>4</sup> The varying levels of oxidation are completely reversible, somewhat reversible, and irreversible for sulfenic, sulfinic, and sulfonic acids, respectively. PIN1 is normally found in the nucleus of neurons, however in the case where it is oxidized, such as in Alzheimer's disease brain, PIN1 is translocated to the cytoplasm and neurofibrillary tangles.<sup>5</sup>

For this specific project, mice were injected with the adeno-associated virus 2 containing the genes for either PIN1 or GFP. The mice received two injections, one in each of the temporal lobes, and the injection was performed between 24 hours and 72 hours of birth. The mice were then sacrificed at either 1, 6, 9, or 12 months of age with a total N of roughly 8 per age group. It is hypothesized that a decrease in global oxidation levels will be observed for the APP/PS1 mice with PIN1 in comparison to the GFP control. The specific oxidative stress markers that are monitored include 3-NT, 4-HNE, and protein carbonyls for each age group.

<sup>1</sup>Lu K. P. (2004) Pinning down cell signaling, cancer and Alzheimer's disease. Trends Biochem. Sci. 29, 200–209.

<sup>2</sup>Komarnitsky P., Cho E. J. and Buratowski S. (2000) Different phosphorylated forms of RNA polymerase II and associated mRNA processing factors during transcription. Genes Dev. 14, 2452–2460.

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**CELLULAR MODEL OF BRAIN DAMAGE CAUSED BY LONG-TERM ALCOHOL DEPENDENCE***Luke A. Williams, Anna R. Reynolds, and Mark A. Prendergast*

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Alcohol withdrawal is consequently associated with alcohol dependence. Periods of withdrawal oftentimes lead to increased cognitive and neurodegenerative effects in humans. The present studies assessed the role of mGluR1 and sigma-1 on the development of ethanol dependence. In these studies, rat hippocampi were exposed to ethanol (50 mM) for 3 cycles of chronic intermittent EtOH exposure (CIE). Each cycle involved 5 days of exposure, followed by a 24-hour period of withdrawal. Cytotoxicity was assessed using immunohistochemistry to label mature neurons. Thionine staining was used as a secondary source to label Nissl bodies. Subset slices were exposed to Sigma-1 receptor antagonist BD1047 (0-80  $\mu$ M) in ethanol naïve-medium or co-exposed to 3 cycles of CIE with or without mGluR1 antagonist COCCOEt (0-3  $\mu$ M). NeuN immunoreactivity and thionine staining confirmed that 3 cycles of CIE resulted in cytotoxicity in each of the examined cell layers of the hippocampal formation. The lowest concentration of BD-1047 (20  $\mu$ M) did not produce significant effects, while the higher concentrations (40 and 80  $\mu$ M) were neuroprotective in the CA1 and dentate gyrus. Co-exposure to CPCCOEt and ethanol prevented cytotoxicity in the cell layers of the hippocampal formation. These findings suggest that the sigma-1 receptor may be neuroprotective against toxicity produced by medium changes. These findings also suggest that ethanol activates the mGluR1 prior to withdrawal to promote development of ethanol dependence in vitro. Future studies should replicate these findings, and use lower concentrations of BD-1047 (20  $\mu$ M) in slices exposed to CIE to determine potential neuroprotective properties.

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