

The New Haven Local Section of the American Chemical Society Presents

The Second Annual Undergraduate Research Symposium

Saturday, April 29, 2017

Hosted by
University of New Haven
Department of Chemistry



Symposium Schedule

8:15 - 9:00	Registration Bartels Hall
9:00 - 9:10	Welcome and introductions Gehring Hall
9:10 - 10:00	Keynote speaker Gehring Hall
10:00 - 10:15	Break
10:15 - 11:40	Oral presentations Gehring Hall
11:40 - 1:15	Poster presentations and lunch Bartels Hall
1:15 - 1:30	Awards ceremony Bartels Hall
1:30	Symposium close

Keynote Speaker

Professor Tim Newhouse

(Yale University)

Mechanistically-Defined Methods for Synthesis of Neuroactive Small Molecules

The synthesis of neurologically active small molecules could enable the study of normal cognitive processes and neurological dysfunction. This talk will describe investigations on the development of palladium-catalyzed dehydrogenation reactions of carbonyl compounds that may empower the synthesis of neurologically active natural products.



Biography:

Tim received his B.A. in Chemistry from Colby College (2005) in Waterville, ME, where he was mentored by Prof. Dasan M. Thamattoor. After moving to La Jolla, CA, he completed his Ph.D. at The Scripps Research Institute with Prof. Phil S. Baran (2010). During his time at Scripps, he also worked in the laboratories of Prof. Donna G. Blackmond. He then returned to the east coast for postdoctoral studies with Prof. E.J. Corey at Harvard University. In 2013, he began his independent career as an Assistant Professor at Yale University in the Department of Chemistry and the Interdepartmental Neuroscience Program.

Corporate Sponsors

We would like to thank all our sponsors for their generous donations :
sponsorship of our symposium

Gaussian, Wallingford



Connecticut Space Grant Consortium



**Connecticut Space
Grant Consortium**

Bristol Myers Squibb, Wallingford



Perkin Elmer, Shelton



Boehringer Ingelheim, Ridgefield



Accustandard, New Haven



King Industries, Waterbury



Unilever, Trumbull



Oral Presentations

Time	Authors	Advisor	Academic Institution
10:15 – 10:35	Jason Buck <i>Computational Analysis of the Disubstitution of Tetraborylated Diene Derivatives</i>	Ericka Barnes	Southern CT State University
10:35 – 10:55	Aubrey Winiarski <i>Experimental and Theoretical Study of Aqueous Surfactant Systems of Interest in Enhanced Oil Recovery (EOR)</i>	Arthur Gow	University of New Haven
10:55 – 11:15	Mario Luis <i>Synthesis and Antimicrobial Evaluation of Tetramic Acid Derivatives</i>	Adiel Coca	Southern CT State University
11:15 – 11:35	Allyson Ho <i>Calcium Sensing Ability of PTH(1-34)</i>	Kelly Culhane and Elsa Yan	Yale University

Poster Presentations

Number	Presenter	Advisor	Academic Institution
1	Christopher Ellithorpe <i>Biochar: A Sustainable Fuel Source</i>	Amanda Simson	University of New Haven
2	Alex Posillico <i>Cyclic voltammetric studies of singly-bridged lanthanum polyoxometalates in the presence of potassium and its comparison to similar lanthanide-bridged systems</i>	James Kirby	Quinnipiac University
3	Abdulaziz Alghannam <i>Sol-Gel Synthesis of Molybdenum Oxide, and the Study of its Properties Using X-Ray Diffraction Techniques</i>	Nancy Savage	University of New Haven
4	Julia Harrison <i>Nucleophilic Additions to N-Sulfinyl Imino Esters</i>	Todd Ryder	Southern Connecticut State University
5	Yumi Koga <i>Toward re-purposing the ribosome to incorporate backbone-modified monomers into proteins: Alternate use of puromycin analogues to screen mutant ribosomes</i>	Alanna Schepartz	Yale University

(continued next page)

Poster Presentations (cont)

Number	Presenter	Advisor	Academic Institution
6	Lela Jackson	Vincent Breslin	Southern Connecticut State University
	<i>Mercury Sorption in Chondrus crispus (Stackhouse 1797) In Long Island Sound</i>		
7	Peter Wang	Matthew Simon	Yale University
	<i>Expansion of the RNA chemical probing toolkit with carbodiimide chemistry</i>		
8	Ahmed Barasheed, Shane Fisher and Amanda McKnight	Dequan Xiao	University of New Haven
	<i>Kinetics of Designed Catalysts for Converting Biomass to Liquid Fuels in Aqueous Solvent</i>		
9	Marianna Lang	Dequan Xiao	University of New Haven
	<i>Substitution Group Effect on the Inhibition of Ubiquitin C-Terminal Hydrolases for Parkinson's Disease Study: Synthesis and Computational Analysis</i>		

Abstracts: Oral Presentations

Presentation #1

Computational Analysis of the Disubstitution of Tetraborylated Diene Derivatives

Jason Buck (Southern Connecticut State University)
Advisor: Ericka Barnes

Suzuki coupling is an important reaction used in organic and organometallic synthesis, characterized as a coupling reaction between boronic acid and an organohalide catalyzed by a palladium (0) complex. Suzuki coupling can be used to synthesize a wide array of styrene and conjugated olefin derivatives, and has proven to be versatile and effective in the development of new pharmaceutical drugs.

The multiple-step synthesis of tetraaryldiene derivatives via Suzuki coupling with a palladium (0) catalyst is underway at SCSU. The coupling reaction between 1 and 2 has been shown to yield two products that are consistent with a double Suzuki coupling reaction, namely, tetramethyl 4,4',4'',4'''-((1Z,3Z)-buta-1,3-diene-1,2,3,4-tetra-yl)tetrabenzoate (**3**) or tetramethyl 4,4',4'',4'''-((1Z,3Z)-buta-1,3-diene-1,1,4,4-tetra-yl)tetrabenzoate (**4**) (see structures on next page). Computational quantum chemistry calculations in this study seek to elucidate the mechanism behind the activation of the C–B bonds in dimethyl 4,4'-((1Z,3Z)-1,2,3,4-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-diene-1,4-diyl)dibenzoate (**1**), and to determine the major product of the reaction.

Presentation #2

Experimental and Theoretical Study of Aqueous Surfactant Systems of Interest in Enhanced Oil Recovery (EOR)

Aubrey Winiarski (University of New Haven)
Advisor: Arthur Gow

Conventional modeling approaches for surfactant-oil-water systems in the “surfactant flooding” enhanced oil recovery (EOR) technique involve empirical correlations that require considerable experimental data and are not predictable for new systems [1]. Conversely, a straightforward molecular thermodynamic approach has been successfully used to describe the phase behavior of a variety of self-assembled systems including pure and mixed nonionic/ionic micelles and vesicles [2-4]. The ideal EOR formulations are surfactant-oil-salt water-alcohol mixtures that form microemulsions (Winsor type III systems), which have ultralow interfacial tension allowing them to penetrate deep into reservoir capillaries [1]. This talk reports the findings of 1) an experimental phase behavior study of a four-component surfactant-oil-water-alcohol system, and 2) development and application of a molecular thermodynamic model to predict the structure and phase behavior of simple aqueous nonionic surfactant mixtures. Specifically, a series of mixtures of sodium dodecyl sulfate (SDS), n-octane, water and 1-pentanol were systematically prepared and visually inspected for Winsor type I to type IV phase behavior. Various compositional paths to form the most desirable Winsor type III systems are documented. Furthermore, the Blankshtein molecular thermodynamic model of micellization and phase behavior in aqueous nonionic surfactant systems was modified using a new expression for the free energy of interaction between formed micellar species in solution. Several examples of the model’s predictive ability for micelle structural and bulk aqueous solution properties of surfactants from the polyoxyethylene glycol monoether and glucoside families are given. The ultimate goal is to extend this model/approach to obtain a predictive approach for the complex multicomponent systems encountered in EOR.

Presentation #3

Synthesis and Antimicrobial Evaluation of Tetramic Acid Derivatives

Mario Luis (Southern Connecticut State University)
Advisor: Adiel Coca

The purpose of this research was to synthesize several protected tetramic acids substituted with different ring structures at C-3 in order to determine the antibacterial activity of these compounds against a panel of bacteria and viruses. Several different types of carboxylic acids were coupled to three types of tetramic acid derivatives using N,N'-dicyclohexylcarbodiimide.

Presentation #4

Calcium Sensing Ability of PTH(1-34)

Allyson Ho (Yale University)

Advisor: Kelly Culhane and Elsa Yan

G-protein coupled receptors (GPCRs) are important drug targets because of their involvement in physiological processes. The parathyroid hormone 1 receptor (PTH1R) is a family B GPCR that is involved in maintaining Ca^{2+} homeostasis, and bone remodeling. Binding of a truncated parathyroid hormone, PTH(1-34) to PTH1R has been shown to be sensitive to high concentrations of calcium, suggesting a cooperative binding model. Residues D251, E252, and E258 were identified on the first extracellular loop of PTH1R as important for calcium binding, and confirmed by computational modeling. This was tested by raising stable cell lines containing these point mutations, and optimizing for receptor expression using Western blots. Ligand binding affinity and efficacy of PTH(1-34) for each mutation was measured using fluorescence anisotropy and cell-based cyclic AMP assays. These studies will uncover new pathways in PTH(1-34) hormone signaling in bones.

Abstracts: Poster Presentations

Poster #1

Biochar: A Sustainable Fuel Source

Christopher Ellithorpe (University of New Haven)
Advisor: Amanda Simson

Through fast pyrolysis in an inert environment biomass or biowaste is converted to a high energy density char; biochar. The pyrolysis process can produce a char with 20% of the weight and 80% of the energy content of the feedstock. This biochar can then be converted to synthesis gas via the Boudouard Reaction ($C + CO_2 \rightarrow CO$) to be used in a Solid Oxide Fuel Cell. For this study, our goal was to create biochar out of different residues from *Quercus velutina* (Eastern Black Oak) and analyze them for their carbon/hydrogen ratio, decrease in mass percent, and their reactivity with CO_2 . The biomass was pyrolyzed at $600^\circ C$ for 20 minutes. The char was then pulverized and loaded into an alumina crucible for thermogravimetric and gas chromatography analysis. The data has shown the biochar reacted with the CO_2 between $700-900^\circ C$ with an average C/H ratio of 3:1 and an 80% decrease in mass. Various methods were investigated to lower this reaction temperature further to the operating range of a Solid Oxide Fuel Cell. The addition of potentially catalytically active metals (FeAc, MnAc) was also investigated. The addition of Iron effectively lowered the reaction temperature to $850^\circ C$ which is within the operating range. While more experimentation is required, the production of biochar to be used as a fuel source seems to have a promising future.

Poster #2

Cyclic voltammetric studies of singly-bridged lanthanum polyoxometalates in the presence of potassium and its comparison to similar lanthanide-bridged systems

Alex Posillico (Quinnipiac University)
Advisors: James Kirby

Ever since its identification by Peacock and Weakley (1971), there have been several studies on $\text{Ln}(\alpha\text{-P2W17O61})_2$, where the lanthanide ion bridges two $(\alpha\text{-P2W17O61})_{10}$ -moieties. The purpose of this investigation is to study the cyclic voltammetric properties of a singly-bridged polyoxometalate complex using lanthanum as the lanthanide bridge. Data will be presented showing unique features in the redox properties for the complex ion. Through pH studies it is confirmed that $\text{pH} = 4.7$ is ideal for cyclic voltammetry of the lanthanum complex. A study on the effect that changing potassium ion concentration has on cyclic voltammetry will be presented as well as a comparison to other lanthanide bridged species.

Poster #3

Sol-Gel Synthesis of Molybdenum Oxide, and the Study of its Properties Using X-Ray Diffraction Techniques

Abdulaziz Alghannam (University of New Haven)
Advisor: Nancy Savage

Molybdenum oxide is a transition metal oxide, which has attracted interest for its potential application in the fields of chemical catalysis and sensing. As a result, previous works have explored different methods to synthesize different morphologies and phases of molybdenum oxide. This work describes a sol-gel method of synthesis that utilizes the inorganic source MoCl_5 and incorporates the surfactant P-123 as a templating agent. The synthesis was conducted with two different molar amounts of the MoCl_5 precursor. The resulting product was analyzed by x-ray diffraction following heat treatments at 150° , 250° , 350° , and 450°C . Preliminary data indicate that the as-synthesized material is mostly amorphous, increasing in crystallinity as the heat treatment temperature increases. The grain size also increases as a function of temperature. The results of Small Angle X-ray Scattering measurements will also be presented, giving particle and pore sizes of the materials with temperature.

Poster #4

Nucleophilic Additions to N-Sulfinyl Imino Esters

Julia Harrison (Southern Connecticut State University)

Advisor: Todd Ryder

Amino acids are widely encountered in a variety of biological contexts. There are a total of twenty naturally occurring amino acids that are used as building blocks for proteins and serve in a variety of other roles, such as signaling. In addition to naturally occurring molecules, synthetic amino acids are also used as pharmaceuticals. Of particular interest are α -amino acids. These molecules have an amine and a carboxylic acid group attached to the same carbon, along with a hydrogen atom and a variety of R-groups. This creates a stereocenter. Naturally occurring α -amino acids are also biosynthetic precursors for a variety of other important biomolecules. A subset of α -amino acids has a second R-group at the α -carbon in place of the hydrogen atom. These α,α -disubstituted amino acids also have a variety of interesting biological properties. For example, α,α -disubstituted amino acid boronates such as α -piperidine have developed as arginase inhibitors with potential use as anti-cancer agents. Despite their relatively simple structures, amino acids present significant synthetic challenges, specifically the selective installation of a stereocenter to obtain the desired compound. We are investigating organometallic additions to optically active N-sulfinylketiminoesters generated through the use of the Ellman sulfinamide auxiliary. The resulting compounds can then undergo deprotection to become stereospecific α,α -disubstituted amino acids.

Poster #5

Toward re-purposing the ribosome to incorporate backbone-modified monomers into proteins: Alternate use of puromycin analogues to screen mutant ribosomes

Yumi Koga (Yale University)

Advisor: Alanna Schepartz

Nature's capability of producing sequence-defined biopolymers, and particularly the diverse functions and architectures of proteins have inspired scientists to utilize the cell's translational machinery to produce artificial polymers. There has been great advance in the technology to incorporate non-canonical α -amino acids with side-chain modifications. However, ribosomal synthesis of proteins with altered backbones remains to be a challenge, as such task requires re-purposing of both the aminoacyl-tRNA synthetase and the ribosome. Our laboratory has investigated engineering of mutant ribosomes that incorporate non-canonical monomers such as β -amino acid into proteins, with the goal of expanding the toolbox of the translational machinery. Puromycin analogues with corresponding structures to the monomers of interest were synthesized for the purpose of screening libraries of mutant ribosomes. Previously, mutant ribosomes were evaluated by the growth inhibition of cells containing mutant ribosomes with addition of puromycin

analogues. Here, we report mass spectrometry-based analyses of in vitro translation products, using puromycin analogues tagged with a terminal alkyne and a click-chemistry based pull-down method. This method provides a more direct evidence of puromycin analogues interacting with the ribosome and thus will enable a more sensitive and accurate evaluation of mutant ribosomes.

Poster # 6

Mercury Sorption in Chondrus crispus (Stackhouse 1797) in Long Island Sound

Lela Jackson (Southern Connecticut State University)

Advisor: Vincent Breslin

Mercury is found naturally in the environment as elemental mercury (Hg) or mercury (II) sulfide (HgS). These chemical forms of mercury can be converted via anaerobic processes in sediment to monomethyl mercury (CH₃Hg) which can bioaccumulate in marine food chains. Human activity also contributes to the presence of mercury in the environment. Coal combustion and municipal wastewater discharges in industrial areas are major sources of mercury in coastal harbors. The change in coastal human population density, and associated industrial activity, from New York City to eastern Rhode Island is suspected to be responsible for contributing to a gradient of high mercury contamination to low mercury contamination from west to east Long Island Sound (LIS.) Previous studies have shown that the red alga *Chondrus crispus* is capable of absorbing monomethyl mercury through its cell membranes, thus making the species a potential bio-indicator of mercury contamination in coastal harbors. This study sampled the red alga *C. crispus* from six harbors along the Connecticut coastline and determined the mercury concentration via atomic absorption using a Milestone Direct Mercury Analyzer (DMA-80). Results of these mercury determinations were used to examine trends of mercury contamination along the northern coastline of LIS relative to the population and industrial activity surrounding each harbor. Preserved samples dating back as far as 1969 were also analyzed for trends of mercury contamination in *C. crispus* over time. This analysis showed no west to east gradient in mercury contamination, but did show a steady decrease in the concentration of mercury absorbed by the alga in this region over the last 15 years.

Poster #7

Expansion of the RNA chemical probing toolkit with carbodiimide chemistry

Peter Wang (Yale University)

Advisor: Matthew Simon

Noncoding RNAs, which carry diverse and vital functions in cells, fold into intricate conformations crucial to their functions. A powerful approach to deciphering RNA conformations, especially for RNAs that are too long or complex, is chemical probing, which employs reagents that form covalent adducts on structurally accessible regions of folded RNA. Dimethyl sulfate (DMS), a common reagent, forms adducts on the Watson-Crick face

of adenine and cytosine bases, but is unreactive towards the Watson-Crick face of guanine and uracil, implying that half of the available Watson-Crick base-pairing information is not utilized for conformational models with DMS probing. To address this limitation, we developed and characterized two carbodiimide-based reagents for probing guanine and uracil bases in RNA with high-throughput sequencing, including CMC, a previously reported carbodiimide probe, and EDC, a novel probe with smaller steric size and charge. We verified selective reactivity of both carbodiimides towards guanosine and uridine but not adenosine and cytidine nucleosides. Both carbodiimides modified RNA on individual G and U nucleobases in a conformation-, temperature-, and pH-dependent manner, characteristic of chemical probing reagents, with CMC demonstrating higher reactivity than EDC. We also observed reverse transcription termination due to carbodiimide modifications in primer extension assays. Hence, we present two promising carbodiimide-based probing reagents with nuanced reactivity profiles, which can complement current DMS probing techniques and improve future RNA conformational models.

Poster #8

Kinetics of Designed Catalysts for Converting Biomass to Liquid Fuels in Aqueous Solvent

Ahmed Barasheed, Shane Fisher and Amanda McKnight (University of New Haven)
Advisor: Dequan Xiao

In a world where global warming is prevalent and gasoline prices are constantly on the rise, finding a form of alternative energy can assist in resolving or diminishing these issues. Biofuels are an excellent form of alternative energy and is a growing topic due to their numerous advantages. Not only do they reduce the presence of global warming, but they are made from completely organic materials and help in reducing greenhouse gases, making the process healthier, safer and more sustainable and environmentally friendly. With these facts in mind and with an interest of working within the oil industry, we researched the conversion of catalytically treated biomass to biofuels using a semi-batch continuous stirred tank reactor (CSTR). Currently, copper is the catalyst known to yield the highest conversion of biofuels; however, it is expensive. In performing this research, our goal was to find an alternative composition that would maximize the conversion, while proving more cost efficient than copper. This was done by synthesizing nanoparticle catalysts of various compositions of copper, zinc and iron. The biomass (phragmites) was catalytically treated and loaded into the CSTR using water as the solvent. The reactor was then evacuated with Argon and pressurized with Hydrogen and run for 4-6 hours. The fuels produced were run through various chemical instruments, including Nuclear Magnetic Resonance (NMR), to identify the reaction products. Based on the results obtained from these aspects, we determined some issues within the research, including the phase of the product, choice of solvent and side reactions. To account for these errors, the vessel was quenched at the end of each run, and the water as a solvent was replaced with organic solvents. Our other error was within the catalysts themselves, seeing that the compositions were in need of adjustments. The solution was to reduce them in the CSTR and observe the change in configuration using the Transmission Electron Microscopy (TEM) and in composition with X-ray fluorescence (XRF). The highest conversion achieved to date is

approximately 30%. Over the course of the year, this research will be continued with the same goal in mind: maximize the conversion for this reaction. This will be done by modifying the current CSTR to allow for liquid samples to be extracted in real time during the reaction. From the extraction data, we can develop the kinetics data for the reaction and determine the ideal operating conditions of the system, which will then be used to find the optimum catalyst composition.

Poster #9

Marianna Lang (University of New Haven)
Advisor: Dequan Xiao

Substitution Group Effect on the Inhibition of Ubiquitin C-Terminal Hydrolases for Parkinson's Disease Study: Synthesis and Computational Analysis

Parkinson's disease is a neurodegenerative disorder that deteriorates motor function which can result in symptoms including tremor, stiffness, and impaired balance. A protein, Ubiquitin carboxyl-terminal hydrolase L1 (UCHL1) has been found to be related to the pathogen of Parkinson's disease and tumor progression. Recently, our group discovered that the governing interaction between UCHL1 and known inhibitors was a π - π interaction between the aromatic ring of the known inhibitors and phenylalanine. From this knowledge two inhibitors were proposed and were theoretically computed to have a higher binding interaction to UCHL1. We successfully synthesized the proposed inhibitors for protein UCHL1. From the biological test, it was found that the inhibitor bearing the electron donating group in the aromatic ring possessed a higher binding energy than that bearing the electron withdrawing group. Also, the computational study of the various analogues showed us that there is a substituent group effect that affects the binding between the inhibitor and UCHL1 protein. In our case, the general structure regarding the chlorine analogues at positions 2 and 3 yielded a lower ΔG or better binding energy while positions 3 and 5 yielded a better binding energy for amine analogues.

Thank you!

A special thanks to:

The faculty and staff at the University of New Haven Department of Chemistry for hosting this symposium on your campus

All student presenters

The wonderful student volunteers

Our judging panel:

Stephen Arpie, Absolute Standards, Inc

Dennis Jackiela, Cantor Colborn LLP

Andrea Lee, Wesleyan University

Jason Sonneberg, Gaussian, Inc

Kap-Sun Yeung, Bristol Myers Squibb

Jim Kirby

Symposium Committee:

Pier Cirillo, University of New Haven

Michaela Ford, University of New Haven

Yo Ng, University of New Haven

Max Reeve, American Chemical Society

Nancy Savage, University of New Haven

Pauline Schwartz, University of New Haven

Camille Solbrig, American Chemical Society

Dequan Xiao, University of New Haven

Nick York, University of New Haven

Sadia Younis, Southern Connecticut State University