

Department of Chemistry
The University of Western Ontario

Chemistry 4490E
Chemistry Research Projects
2008-2009

Chemistry 4490E Research Project

A Notice from the Registrar:

"Unless you have either the prerequisites for this course or written special permission from your Dean to enroll in it, you will be removed from this course and it will be deleted from your record. This decision may not be appealed. You will receive no adjustment to your fees in the event that you are dropped from a course for failing to have the necessary prerequisites."

Prerequisites: Completion of the courses required for a Major in Chemistry and registration in Specialization in Chemistry, Honours Specialization in Chemistry or Honours Specialization in Biochemistry and Chemistry. Permission of the department is required.

Course Facilitators:

Professor John F. Corrigan	ChB 16
Professor François Laguné-Laberthet	ChB 22
Professor Mark S. Workentin (coordinator)	ChB 223

Please feel free to contact any of the course facilitators about any aspect of this course.

Course Web-Page: <http://instruct.uwo.ca/chemistry/490/>

Course E-mail: instrmsw@uwo.ca

Emails **must** be from your @uwo.ca address. Please put Chem 4490 in the subject line.

About the Course:

Chemistry 4490E is regarded as the signature course in our Specialization and Honours Specialization in Chemistry and the Honours Specialization in Biochemistry and Chemistry Modules. The course provides the student with the opportunity to integrate the breadth of knowledge gained in pre-requisite courses and apply it towards a hands-on chemistry experience while doing an independent research project under the direction of a faculty member in the department. In addition to learning advanced laboratory skills and techniques needed to do research in an active chemistry research group, the course culminates with the writing of a thesis summarizing the year's work and then presenting and defending the project to a panel of faculty examiners and their peers.

Expectations:

The minimum requirements for this course are 12 hours/week throughout the 13 weeks in each term working on your research project with your assigned supervisor AND attendance with participation at the following Chem 4490E events (times to be determined):

Initiation Meetings: Attendance is REQUIRED.

Thursday September 4, 2:30 pm Rm ChB 115: Course Initiation Meeting

AND

Friday September 12, 2:00-4:00 pm. Rm ChB 115: Laboratory Safety. Attendance is REQUIRED. This special presentation is required in order to be able to work in a research laboratory.

**Additional Meetings, usually on a Friday afternoon in Room ChB 115 at 1:30 p.m.:
Dates and times will be communicated by email. Attendance is required.**

September Meeting:

“Scientific Ethics” Friday, September 26, 1:30 pm. ChB 9
Dr. Natasha Patrino, Educational Developer, Teaching Support Centre

October Meeting:

“Professionalism in Science and Chemistry”
Dr. K. M. Baines, Chair, Department of Chemistry. Friday, October 24 1;30 p.m. ChB 9

November Meeting:

“How to give a Scientific Presentation”
Dr. Mark Workentin Time TBA

Early December Meetings:

“Mid-year research Summary Presentations” Time TBA

January Meeting:

“Strategies for resumes and Job-Hunting”
Tentative Date: Friday, January 16, 2009. 1:30 p.m. ChB 9.

February Meeting:

“Employment Skills: Mock Interview”
Tuesday, February 10. Times to be scheduled and announced.

Saturday April 4, 2009: Chemistry 4490E Research Presentation Day

In addition, information sessions on “how to apply for graduate school scholarships” and “information on how/when to apply for graduate school” will be provided.

Evaluation:

Assuming that the minimum requirements above are met then the final grade for the course will be determined by the following:

Mid-year (December) Evaluation by Supervisor: 5%

The supervisor will provide a grade based on the level of active participation and research activities. This will include an evaluation of achieving the 12 hour/week over the 12 weeks participation in the laboratory and the abilities to integrate the skills learned to the project. Feedback will be provided.

Mid-year (December) Research Project Progress Presentation: 5%

Each student will present a short (5 minute max) presentation outlining the project and progress towards its goals to their peers and the course facilitators. Feedback will be provided.

Research Performance Grade 25%

The faculty project supervisor(s) will assign a grade based on the student`s research performance throughout the year.

Thesis: (2 x 20% from each of the two faculty examiners) 40%

Each student will write a formal thesis (guidelines will be provided) of their research project. (*Final day for laboratory work is March 2, 2009*) This thesis will be read and graded by two faculty members (who are not supervisors of the project). These grades will be submitted prior to the Presentation and Oral Examination.

Due date: Monday, March 30, 2009 no later than 1:00 p.m.

Research Project Presentation and Oral Examination: 25%

Each student will present a 15 minute formal oral presentation of their year`s work, and answer 20 minutes of questions from the two examiners. All faculty in attendance will provide a grade based on the quality of the presentation and the overall comprehension displayed.

Date: Saturday, April 4, 2009. Please reserve from 8:00 a.m.- 3:00 p.m. You must be present for the entire day.

Additional Administrative Notes:

Plagiarism is a serious scholastic offense and more importantly a serious breach of scientific ethics in research. Any cases of cheating or plagiarism will incur appropriate penalties, possibly including failure in the course.

Plagiarism: Students must write their laboratory reports, assignments and tests on their own and in their own words. Whenever students take an idea, or a passage from another author or student, they must acknowledge their debt both by using quotation marks where appropriate or by proper referencing such as footnotes or citations. Plagiarism is a major academic offence (see Scholastic Offence Policy in the Western Academic Calendar):

[http://www.westerncalendar.uwo.ca/western/web/2005\(new\)/ACADEMIC_RIGHTS_AND_RESPONSIBILITIES_305144.html](http://www.westerncalendar.uwo.ca/western/web/2005(new)/ACADEMIC_RIGHTS_AND_RESPONSIBILITIES_305144.html)

It is the Department of Chemistry policy that when a student undertakes a test, an examination or any other evaluation procedure, they have deemed themselves fit to do so. Claims of distress or other medical issues after the fact will not be considered as the basis of a grade appeal.

If you are unable to meet a course requirement due to illness or other serious circumstances, you must provide valid medical or other supporting documentation to the Dean's office as soon as possible and contact your instructor immediately. It is the student's responsibility to make alternative arrangements with their instructor once the accommodation has been approved and the instructor has been informed. In the event of a missed final exam (for Chem 4490 this is the thesis presentation Day), a "Recommendation of Special Examination" form must be obtained from the Dean's Office immediately. For further information please see:

<http://www.uwo.ca/univsec/handbook/appeals/medical.pdf>

A student requiring academic accommodation due to illness, should use the Student Medical Certificate when visiting an off-campus medical facility or request a Records Release Form (located in the Dean's Office) for visits to Student Health Services. The form can be found here:

https://studentservices.uwo.ca/secure/medical_document.pdf

English Language Proficiency for Assignment of Grades: Each student granted admission to Western must be proficient in spoken and written English. Students must demonstrate the ability to write clearly and correctly. Work presented in English in any subject, at any level, which shows a lack of proficiency in English and is therefore unacceptable for academic credit, will either be failed or, at the discretion of the instructor, returned to the student for revision to a literate level. To foster competence in the use of the English language within their own discipline, all instructors will take proficiency in English into account in the assignment of grades.

Chemistry 4490E 2008-2009

To achieve optimal Student-Project-Supervisor matching, all students must proceed as follows:

- 1) Review the project descriptions available this year
- 2) Take the opportunity to meet with the potential supervisors to get more information about the project. This meeting can take place at the general group meeting times that will be organized and communicated to you by the course facilitators or via direct communication with the supervisor or designate as indicated on their project description.
- 3) Indicate below your **FOUR** preferred projects. Two would be your first preferences and the next two would be your second preferences. This list of four must include at least three different supervisors (*co-supervisors excluded*).
- 4) Before Friday, September 12th at 4:00 p.m. give this form to Ms. Clara Fernandes in the Chemistry Main Office, ChB 119 or email your selections to instrmsw@uwo.ca. The selections will be announced via email sometime on Monday, September 15
- 5) After you are assigned a project you must arrange to meet your assigned supervisor immediately and no later than Wednesday, September 17. Laboratory work should start immediately. We recommend Thursday, Sept. 18.

Name: (please print): _____

Signature: _____

	Supervisor(s)	Project Number (as indicated on the project description)
First Preference A		
First Preference B		
Second Preference A		
Second Preference B		

Preliminary Guidelines for the Thesis (more details will be provided later)

The thesis must conform to these guidelines:

- The thesis will include a Title Page (example to be provided), Abstract, Table of Contents, Acknowledgements, and List of Abbreviations. These pages must be numbered in roman numerals from (i) onward (the title page does not have to show the number)
- Introduction, Results/Discussion, Experimental, Conclusions and References. **The maximum number of pages allowed for items listed in this bullet is 25 pages, including all figures, schemes and tables.** These pages must be numbered.
- Print must be in black ink and letter quality.
- Minimum 1.5 line spacing for the text.
- Acceptable fonts are Arial (11 pt), Times New Roman (12 pt), or comparable.
- Figures/schemes have to be large enough so that the text/scales are readable.
- Use white paper only, 21.5 cm x 28 cm, in portrait format.
- Set margins at a minimum of 1 cm on top, bottom and right. The left margin must be a minimum of 1.9 cm.
- Print on one-side of the paper only.
- The experimental section must be contained within the 25 page limit that describes key experiments and or representative procedures and characterization of new compounds. Occasionally, as in the case of synthetic chemistry, summarizing the characterization data for new compounds within the thesis will be difficult with the page limit. In these types of cases an appendix may be included. The thesis itself must be a self-contained document independent of the appendix. Someone reading the thesis must not be required to look at the appendix for additional information, figures, schemes etc. in order to understand the results/discussion presented. The purpose of the appendix is to provide interested readers with more details to critically evaluate the completeness of the work. The function is similar to supporting information provided in many scientific journals.

Additional Notes on Appendix:

1. The appendix may only contain supporting experimental details and characterization information. There can be no additional discussion of results. Typical information may include: experimental details, melting points, R_f values, summaries of IR, NMR or other spectroscopic data, combustion analysis, mass spectrometry data summaries, X-ray data and tables. It may also include computer programs or other lengthy information.
2. Raw data, such as spectra, may be included where warranted. (consult your supervisor)
3. The appendix is not intended to make it look like someone as done more work and it can not be used to expand the thesis beyond the allowed page limit except as indicated above.

Professor K.M. Baines

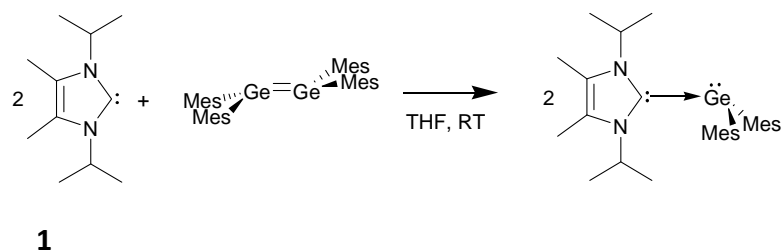
ChB 120A

kbaines2@uwo.ca

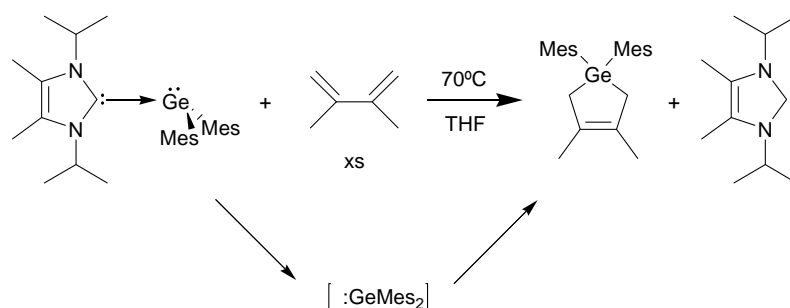
<http://publish.uwo.ca/~kbaines2/index.html>

Kinetic Investigation of the Reaction of a Base-Stabilized Germylene with 2,3-Dimethylbutadiene

Germylenes ($R_2Ge:$), the germanium analog of divalent carbenes, are one of the most important reactive intermediates in organogermanium chemistry. Recently (see Baines *et al. Organometallics*, **2007**, *26*, 4109) we have synthesized a rare example of a base-stabilized diorganogermylene (**1**) by reaction of a stable *N*-heterocyclic carbene with a stable digermene (Mes=2,4,6-trimethylphenyl).



Upon heating, complex **1** reacts with 2,3-dimethylbutadiene to replace the carbene and to give the germacyclopentene. The mechanism of this reaction is unknown. Does the diene react directly with **1** to give the products or does complex **1** release the free germylene which undergoes reaction with the diene?



In this project, the mechanism of this reaction will be investigated. The kinetics of the reaction will be monitored by NMR spectroscopy and/or UV-VIS spectroscopy in an attempt to distinguish between the two pathways.

Professor K. M. Baines

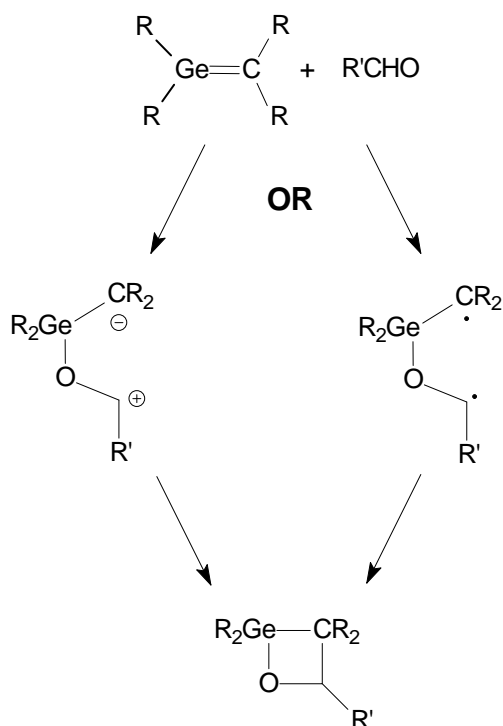
ChB 120A

kbaines2@uwo.ca

<http://publish.uwo.ca/~kbaines2/index.html>

PROBING THE MECHANISM OF THE ADDITION OF ALDEHYDES TO GERMENES

Although the cycloaddition reactions of aldehydes to unsaturated carbon compounds are fairly well understood, the mechanism of the addition of aldehydes to germenes ($R_2Ge=CR_2$) is not. We have recently developed a mechanistic probe for the investigation of the cycloaddition reactions of aldehydes and have successfully applied it to the study of the mechanism of the addition of aldehydes to silenes ($R_2Si=CR_2$) (see Milnes and Baines, *Organometallics*, **2007**, 26, 2392). This project will involve examination of the addition of the probe to $Mes_2Ge=CR_2$ (Mes=2,4,6-trimethylphenyl; R_2 =fluorenylidene), a known, stable germene.



The student involved with this project will become familiar with inert gas/vacuum line and modern chromatographic techniques as well as with modern analytical methods including mass spectrometry, IR and especially NMR spectroscopy.

Professor John F. Corrigan

ChB 16

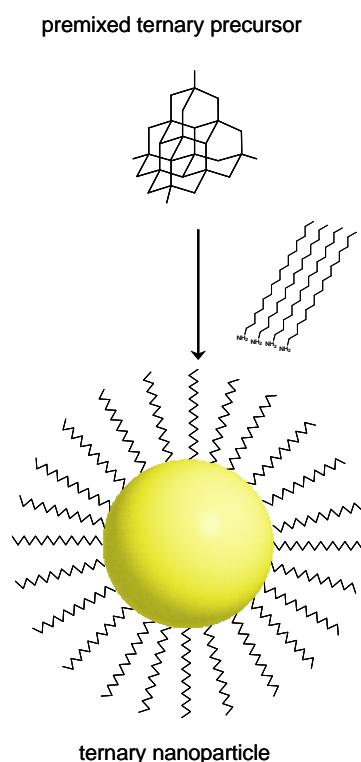
jfcorrigan@uwo.ca

publish.uwo.ca/~jfcorrigan

Preparation of Magnetic Semiconductor Nanoparticles: Lyothermal Synthesis from A Single Source Precursor

Direct band gap semiconductors such as the 12-16 materials CdSe and CdTe are now routinely prepared on the nanometre scale. These systems are of current widespread interest due to potential applications in LED displays and photovoltaic and photoelectrochemical devices due to their size-dependent photophysical properties. Recently, we have reported that the ternary (three component) molecular nanoclusters $[Zn_xCd_{10-x}Se_4(SePh)_{12}(PnPr_3)_4]$ can be used as single-source precursors for the synthesis of high-quality hexagonal $Zn_xCd_{1-x}Se$ nanocrystals (scheme).[1] The tellurium clusters $[Zn_xCd_{10-x}Te_4(TePh)_{12}(PnPr_3)_4]$ are equally convenient precursors for the synthesis cubic $Zn_xCd_{1-x}E$ nanoparticles. The thermolysis of the cluster molecules in hexadecylamine provided an efficient system in which the metal-ion stoichiometry of the nanoclusters is retained in the nanocrystalline products, whilst also affording control of particle size (2-5 nm)

The development of syntheses that would allow production of *paramagnetic* ion-doped nanoparticles is important for future applications of these materials in magnetic devices. Recently, our collaborators at the Institute for Nanotechnology (Germany) have developed methods to produce the mixed metal complex $[Cd_4Mn_6Se_4(SePh)_{12}(PR_3)_4]$ in high yield. In this Chem 4490E project, you will develop the chemistry of the molecular precursor for the preparation of high quality magnetic semiconductor nanoparticles. You will learn the techniques of inert atmosphere synthesis, powder X-ray diffraction and UV-Vis absorption and emission spectroscopies.



[1] M. W. DeGroot, H. Rösner, J. F. Corrigan, *Chem. - A Eur. J.*, **2006**, *12*, 1547-1554 *Control of Metal-Ion Composition in the Synthesis of Ternary II-II'-VI Nanoparticles by Using a Mixed-Metal Cluster Precursor Approach*

Professor John F. Corrigan

ChB 16

jfcorrig@uwo.ca

publish.uwo.ca/~jfcorrig

Professor Lars Konermann

B&G 2016

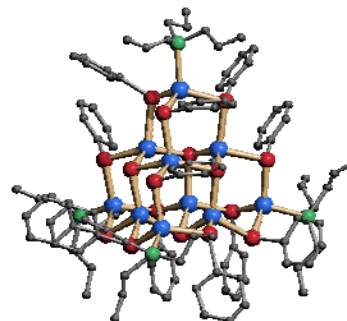
konerman@uwo.ca

<http://publish.uwo.ca/~konerman/>

An Investigation of Ternary Zn-Cd-E (E = Se, Te) Nanoclusters via Electrospray Ionization Mass Spectrometry

Direct band gap semiconductors such as the 12-16 materials CdSe and CdTe are now routinely prepared on the nanometre scale. These systems are of current widespread interest due to potential applications in LED displays and photovoltaic and photoelectrochemical devices due to their size-dependent photophysical properties.

Included in this arena of chemistry is a series of structurally characterized nanoclusters $[M_{10}(\mu_3-E)_4(\mu-EPh)_{12}(PR_3)_4]$ $M = Zn, Cd, Hg$ (illustrated). This structure consists of four fused adamantane cages and thus represents a small piece of the sphalerite lattice. Work in our laboratories [1] has recently illustrated that it is possible to prepare, as single crystals, ternary 12-12'-16 nanoclusters such as $[Zn_2Cd_8(\mu_3-E)_4(\mu-EPh)_{12}(PR_3)_4]$ ($E = Se, Te$). Chemical, photophysical and structural analysis of these crystals confirms the presence of both Zn(II) and Cd(II) centres in the crystals. What cannot be readily confirmed however is whether these mixed-metal nanoclusters exist exclusively as "Zn₂Cd₈" or whether the metals are present in a statistical distribution e.g. Zn₁Cd₉ → Zn₉Cd₁ molecules in the crystal.



Electrospray Ionization Mass Spectrometry (ESI-MS) represents a method that can unambiguously determine the atomic composition of these systems. In this Chem. 490 project, you will prepare the neutral nanoclusters $[Zn_2Cd_8(\mu_3-E)_4(\mu-EPh)_{12}(PR_3)_4]$ and chemically convert them to a charged species via ligand exchange reactions, specifically replacing PR_3 at the apical sites with PhE^- . Solutions of the charged clusters will then be examined via ESI-MS to determine the nature of the Zn/Cd metal ion distribution.

A student working on this project will learn advanced inorganic synthesis techniques and analysis of solutions via ESI-MS.

[1] M. W. Degroot, N. J. Taylor and J. F. Corrigan, *Inorg. Chem.*, **2005**, *44*, 5447-5458. *Controlled Synthesis of Ternary II-II'-VI Nanoclusters and the Effects of Metal Ion Distribution on their Spectral Properties.*

Professor John F. Corrigan

ChB 16

jfcorrigan@uwo.ca

publish.uwo.ca/~jfcorrigan

Professor Mark S. Workentin

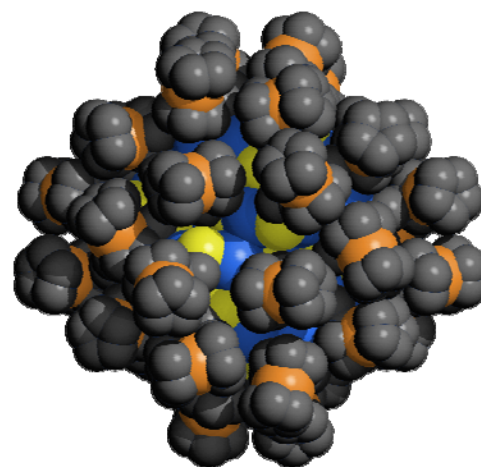
ChB 223

mworkent@uwo.ca

publish.uwo.ca/~mworkent

Developing the Solution Chemistry of the Fully Ferrocenated Nanocluster $Ag_{48}S_6(SCH_2Fc)_{36}$

The incorporation of multiple di(η^5 -cyclopentadienyl)iron fragments onto well defined molecular architectures is being pursued for the potential applications of such frameworks (by exploiting the Fe(II)/Fe(III) redox couple) in areas encompassing electro-catalysis, anion recognition and the preparation of specialty electrodes. We have shown recently that with a suitably designed ferrocenyl reagent ($FcCH_2SSiMe_3$; Fc = ferrocenyl), it is possible to use a monodisperse Ag_2S architecture for the formation of ferrocenyl passivated semiconductor nanoclusters. We have recently reported [1] the high yield preparation of structurally characterized $[Ag_{48}(\mu_4-S)_6(\mu_{2/3}-SCH_2Fc)_{36}]$. In this nanocluster, 36 ferrocenyl units form a closely packed shell on the surface of a $Ag_{48}S_{42}$ core (illustrated; Ag = blue, S = yellow, C = grey and Fe = orange) with overall molecular dimensions of $\sim 3.0 \times 3.0 \times 2.2 \text{ nm}^3$.



The high yield preparation of such an unprecedented complex allows for the development of its surface chemistry. In this Chem 4490 project, you will develop the solution chemistry of this novel nanocluster: you will probe the substitution of the thiolate ligands on the surface via NMR methods and examine the electrochemistry of the Fe(II) sites on the surface of this and related frameworks. This will include cyclic voltammetry, constant potential electrolysis and chemical oxidation methods.

A student working on this project will learn the techniques of advanced inorganic synthesis, NMR spectroscopy and electrochemistry.

[1] S. Ahmar, D. G. MacDonald, N. Vijayaratnam, J. F. Corrigan, submitted. *A Nanoscopic 3-D Polyferrocenyl Assembly: Preparation of the Structurally Characterized Triacotakaihexa(ferrocenylmethylthiolate) $[Ag_{48}(\mu_4-S)_6(\mu_{2/3}-SCH_2Fc)_{36}]$*

Professor Elizabeth Gillies

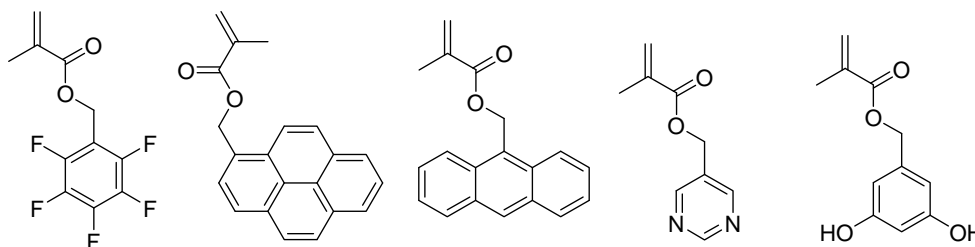
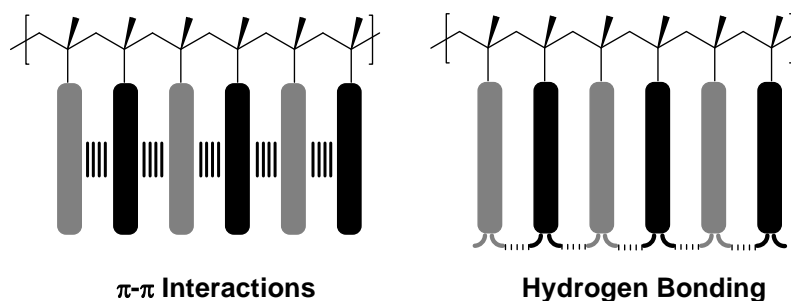
Chemistry 219A

egillie@uwo.ca

<http://publish.uwo.ca/%7Eegillie/index.html>

Alternating Vinyl Copolymers Via Non-Covalent Interactions

Alternating copolymers consist of two monomers which repeat in a regular fashion, (A-B)_n. In general, the formation of alternating copolymers is governed by the electronic properties of the monomers and follows basic mechanistic organic chemistry principles. This project will investigate the possible use of non-covalent interactions, π -stacking or hydrogen bonding, for the generation of alternating vinyl copolymers (see below). Examples of possible methacrylate based monomer are also shown. Modern synthetic polymer methods including atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) will be used for the polymerization reactions. These were chosen due to the increased control and narrow polydispersity as compared to classical radical polymerizations. These polymerization reactions have also shown great compatibility with a wide range of functional groups and can be carried out at a wide range of temperatures.



Professor Elizabeth Gillies

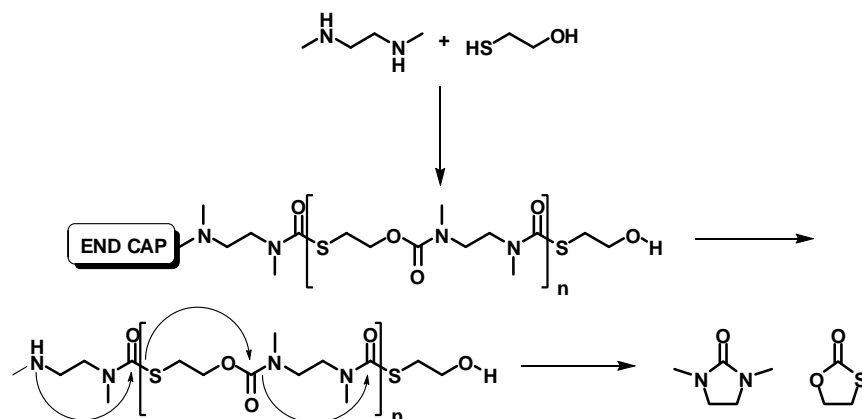
ChB 219a

egillie@uwo.ca

<http://publish.uwo.ca/~egillie/>

Cascade Biodegradable Polymers

Cascade biodegradable polymers are a unique class of polymers comprising a polymer backbone and an end cap. While the end cap is attached, the polymer is stable. However, removal of the end cap results in a cascade end-to-end depolymerization resulting in small molecules (shown below). Compared to conventional biodegradable polymers which degrade via random scission of the backbone, this class of polymers offer a much more controlled degradation, as depolymerization is dependent on a single cleavage event, the conditions of which can be varied to suit many biological applications.



This project will focus on the synthesis of a polymer composed of 2-mercaptoethanol and N,N'-dimethylethylenediamine, both of which have been reported to spontaneously cyclize under physiological conditions.^{1,2} Upon completion of the synthesis, degradation studies will be carried out, both on the polymer itself as well as on the monomeric unit. If time allows, various end caps will also be synthesized and incorporated into the polymer, and their degradation properties will be investigated.

1. Meyer, Y., *et al.* *Org. Lett.* 2008, 10, 1517-1520

2. Haba, K. *et al.* *Angew. Chem., Int. Ed.* 2005, 44, 716-720

Professor J. Peter Guthrie

ChB 222

peter.guthrie@uwo.ca

www.uwo.ca/chem/people/faculty/guthrie.htm

Ester aminolysis studied using No Barrier Theory

Ester aminolysis (conversion of an ester to an amide) is a reaction which is thermodynamically favored yet often difficult, unless the ester is very reactive. This project will examine the mechanism of the reaction and try to clarify the reasons for the difficulty in carrying out the transformation. Rate constants for both attack by amine and for expulsion of alkoxide will be calculated by the methods of No Barrier Theory.

No Barrier Theory is a method being developed in my lab for predicting rates of chemical reactions. Reactions can be analyzed into a few simple processes, for each of which the energy is a quadratic function of a suitable reaction coordinate. By calculating the energies of the "corner species" the entire energy surface can be interpolated, and the energy of the saddle point, the transition state, can be found. The experimental equilibrium constant is used to give the product relative to starting point, and molecular orbital theory is used to calculate the distortion energies leading to the "corner species".

Professor J. Peter Guthrie

ChB 222

peter.guthrie@uwo.ca

www.uwo.ca/chem/people/faculty/guthrie.htm

Hypochlorite chlorination studied using No Barrier Theory

Chlorination of aldehydes and ketones in basic solution involves reaction of the enolate with hypochlorite ion with some contribution from hypochlorous acid. The reaction with hypochlorite ion is comparatively slow despite an enormous thermodynamic driving force. This project will examine the origins of this kinetic barrier to the reaction, by calculating rate constants by the methods of No Barrier Theory.

No Barrier Theory is a method being developed in my lab for predicting rates of chemical reactions. Reactions can be analyzed into a few simple processes, for each of which the energy is a quadratic function of a suitable reaction coordinate. By calculating the energies of the "corner species" the entire energy surface can be interpolated, and the energy of the saddle point, the transition state, can be found. The experimental equilibrium constant is used to give the product relative to starting point, and molecular orbital theory is used to calculate the distortion energies leading to the "corner species".

Professor J. Peter Guthrie

ChB 222

peter.guthrie@uwo.ca

www.uwo.ca/chem/people/faculty/guthrie.htm

Electrophilic aromatic substitution studied using No Barrier Theory

Electrophilic aromatic substitution is a common synthetic reaction, and the rate is extremely sensitive to substituent effects. Nitration is one of the most extensively studied reactions of this class. This project has two goals: The first is to see if current computational methods will allow calculation of the equilibrium constant for formation of the benzenium from an arene and nitronium ion. The hardest part of this calculation is to get the solvation energy, and for these benzenium ions this should be relatively straightforward. The second goal is to calculate rates for formation of the benzenium ions by the methods of No Barrier Theory, using these calculated equilibrium constants..

No Barrier Theory is a method being developed in my lab for predicting rates of chemical reactions. Reactions can be analyzed into a few simple processes, for each of which the energy is a quadratic function of a suitable reaction coordinate. By calculating the energies of the "corner species" the entire energy surface can be interpolated, and the energy of the saddle point, the transition state, can be found. The experimental equilibrium constant is used to give the product relative to starting point, and molecular orbital theory is used to calculate the distortion energies leading to the "corner species".

Professor Yining Huang

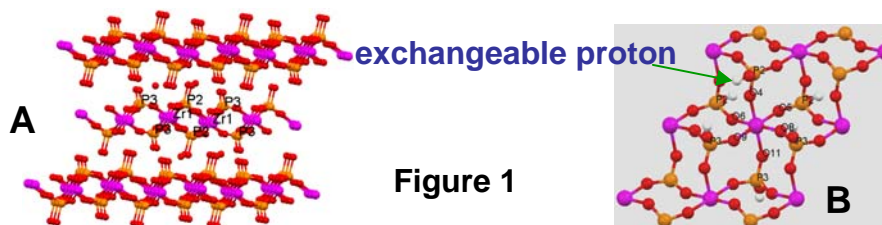
ChB-17

yhuang@uwo.ca

<http://www.uwo.ca/chem/people/faculty/huang.htm>

Project Title Characterization of Layered zirconium Phosphates by Solid-state Zr-91 NMR Spectroscopy

Layered zirconium phosphates have many important applications in the areas of ion exchange, intercalation, catalysis, sorption, and protonic conductors. The most important layered zirconium phosphate is α -Zr(HPO₄)₂·H₂O (α -ZrP). A particular important property of α -ZrP is its ion-exchange capability. The structure of α -ZrP is illustrated in Figure 1A. Each layer contains a single sheet of octahedral Zr atoms. Each Zr atom is octahedrally coordinated to 6 oxygen atoms belonging to six PO₄ tetrahedra with each P atom tetrahedrally coordinated to three oxygens shared with three different ZrO₆ octahedra and to one hydroxyl oxygen. The proton in the hydroxyl group can be exchanged with cations (Figure 1B). The local structures around the Zr need to be characterized because they often determine the properties of the material. Solid-state NMR spectroscopy is one of the most important techniques for characterizing solid materials. However, Zr-91 ($I = 5/2$) is quadrupolar nucleus with a large quadrupole moment, leading to broad signals. It also has as a low natural abundance and low gyromagnetic ratio, resulting in low sensitivity.



Recently we have characterized α -ZrP and its Na⁺ exchanged phases by solid-state Zr-91 NMR [1]. In this project, we will extend the study to include Zn²⁺, Mg²⁺ and Ba²⁺ -exchanged ZrPs by Zr-91 NMR. You will first learn to prepare parent α -ZrP and its ion-exchanged derivatives and then evaluate the effect of different cations on the local environments of Zr centers by acquiring and analyzing Zr-91 NMR spectra. Theoretical calculations may be performed to assist in understanding the experimental results. Through this project you will learn chemistry of layered metal phosphates and the practical skills and basic theoretical background of solid-state NMR.

[1] Z. Yan, C. W. Kirby, Y. Huang, *Journal of Physical Chemistry C* 112 (2008) 8575–8586.

Professor Robert Hudson

Lab 209, Office 226

robert.hudson@uwo.ca

http://publish.uwo.ca/~rhhudson

Nucleobase-Modified PNA via the Huisgen 2+3 Dipolar Cycloaddition

The Huisgen dipolar cycloaddition between terminal alkynes and azides is a useful reaction because of its ease and reliability. The product of the reaction is a disubstituted triazole (Fig. 1).

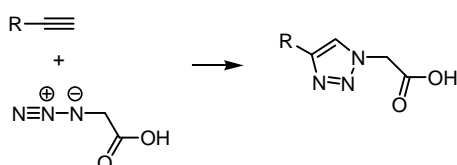


Figure 1. The Huisgen reaction between azidoacetic acid and an alkyne produces a triazolylacetic acid.

Peptide nucleic acid (PNA) is an analog of DNA which amongst other uses is employed as a hybridization probe against both DNA and RNA. Modifications to the nucleobase portion can increase the binding affinity for complementary nucleic acids or be used to introduce reporter groups such as fluorophores. We have recently developed good methods for the synthesis of the "PNA backbone" that when combined with the base acetic acid derivatives will produce PNA monomers suitable for oligomerization, Fig. 2. For this project, a small variety of alkynes bearing interesting functionality will be used to make nucleobase analogs for eventual incorporation into PNA oligomers and investigation of their binding properties.

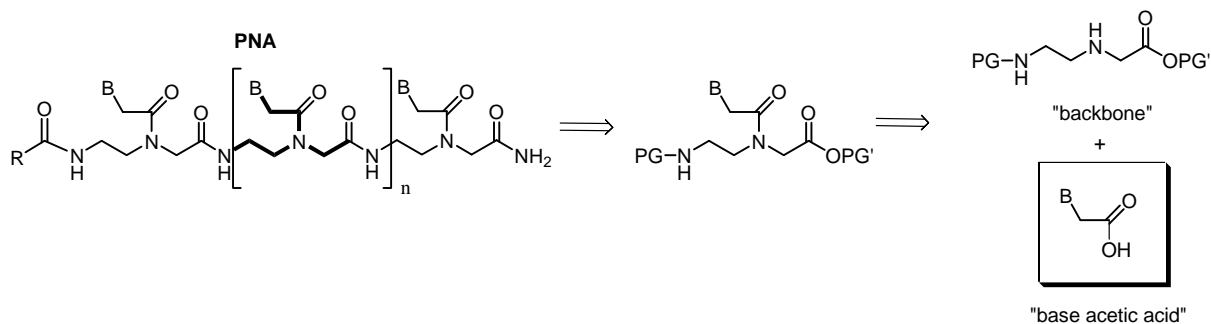


Figure 2. Nucleobase acetic acid analogs produced by the Huisgen reaction for incorporation into PNA. PG, PG' = protecting group. B = nucleobase or surrogate.

NOTE: Professor is away from Sept. 3-15. Please contact David Dodd ddodd@uwo.ca for information about this project.

Professor Nathan Jones

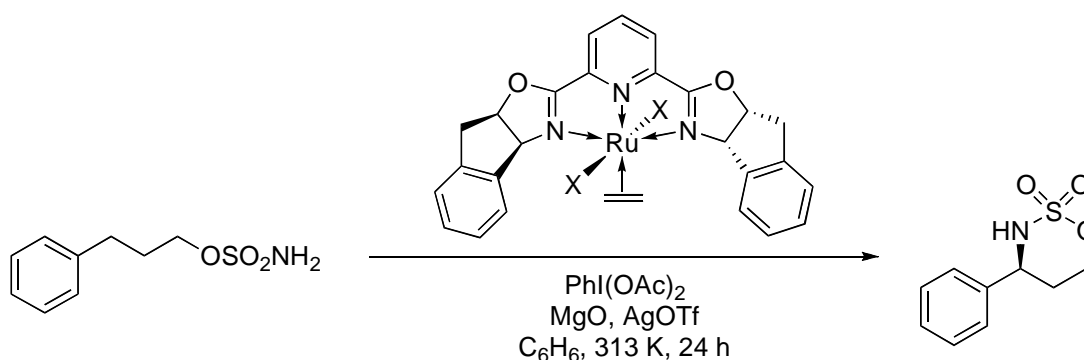
B&G 2024

njones26@uwo.ca

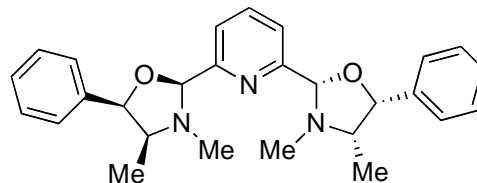
<http://organometallic.ca>

Enantioselective C–H bond activation by chiral ruthenium complexes

General methods for enantioselective aminations (C–H → C–NHR) are in high demand. A recent report by Blakey and coworkers¹ describes the use of Ru(II) complexes of pyridylbis(oxazoline) (“pybox”) ligands as catalysts in the intramolecular asymmetric reaction shown below.



We have recently developed a family of chiral ligands based on the oxazolidine ring, which is the fully saturated version of the oxazoline.² Our structural studies show that the oxazolidine is much more sterically demanding than the oxazoline. It may therefore confer considerable advantage when used in asymmetric catalytic applications. The objective of this project is to make and characterize Ru(II) complexes of oxazolidine-based ligands like the one shown at below, and to compare them against the analogous pybox complexes in asymmetric amination reactions. This project will entail synthetic inorganic and organic chemistry, and kinetic and mechanistic analysis. Extensive use will be made of multinuclear NMR spectroscopy and gas chromatography-mass spectrometry.



- (1) Milczek, E.; Boudet, N.; Blakey, S. *Angew. Chem. Int. Ed.* **2008**, *47*, in press. DOI : 10.1002/anie.200801445.
- (2) Cardile, S. A.; Jennings, M. C.; Jones, N. D. *Dalton Trans.* **2006**, 4672–4678.

Professor Nathan Jones

B&G 2024

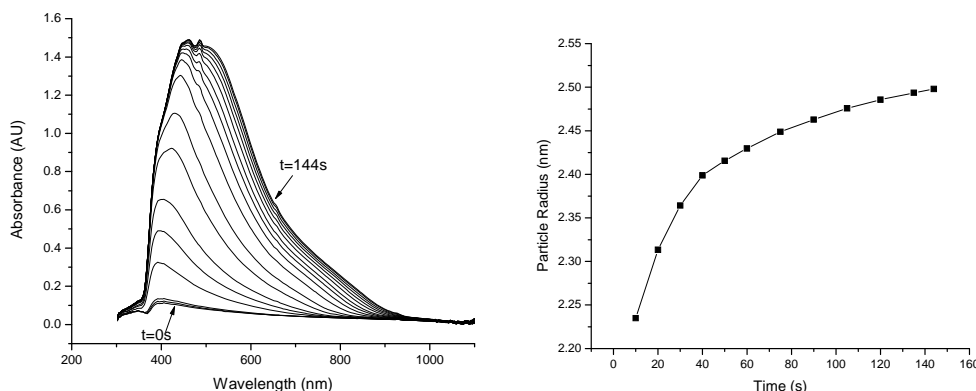
njones26@uwo.ca

<http://organometallic.ca>

Water-soluble cadmium sulfide nanocrystals

Over the last decade, solution-grown nanoparticles of semi-conducting materials, or “quantum dots,” (QD) have seen wide-ranging application in opto-electronic devices and imaging. They tend to be very brightly fluorescent, and their chief advantage over organic dyes is that their properties are size-dependent and therefore amenable to tuning. For example, the emission wavelength (colour) may be made shorter (more blue) by making the QD smaller.

We have recently been interested in water-soluble QD for bioimaging applications.¹ Among these are thiolate-capped lead sulfide (PbS) nanoparticles whose synthesis and solution behaviour we have studied extensively, both over long (min – h) and short (s) timescales. Shown below are the evolution of the absorption spectra of PbS nanoparticle solutions studied by stopped-flow spectrophotometry, and the variation in particle radius over the same timespan.



The aim of this project will be to control the size and shape of water-soluble, thiolate-capped cadmium sulfide (CdS) nanoparticles,² and to study their growth. Extensive use will be made of stopped-flow spectrophotometry, dynamic light scattering and transmission electron microscopy.

(1) Cornacchio, A. L. P.; Jones, N. D. *J. Mater. Chem.* **2006**, *16*, 1171-1177.

(2) Martinez-Castanon, G. A.; Sanchez-Loredo, M. G.; Martinez-Mendoza, J. R.; Ruiz, F. *Adv. Tech. Mater. Mater. Proc.* **2005**, *7*, 171-174.

Professor Michael A. Kerr

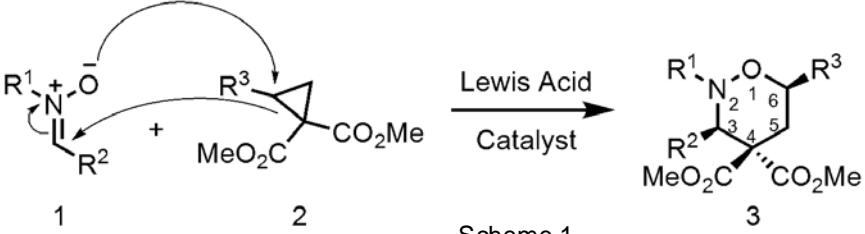
ChB 219

makerr@uwo.ca

<http://publish.uwo.ca/~makerr/index.htm>

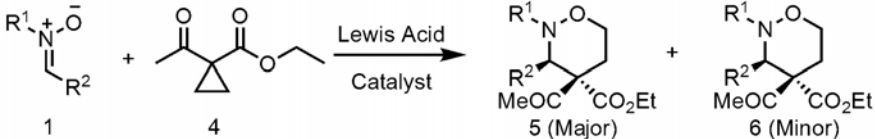
Diastereoselectivity in the homo 3+2 dipolar cycloaddition

Recently we discovered a fundamentally new chemical transformation. In it, a nitron **1** (the dipole) reacts with an activated cyclopropane **2** (the dipolarophile) to form a heterocyclic compound known as a tetrahydro-1,2-oxazine **3** (Scheme 1). The systematic investigation of this new reaction is an important theme in our laboratory.



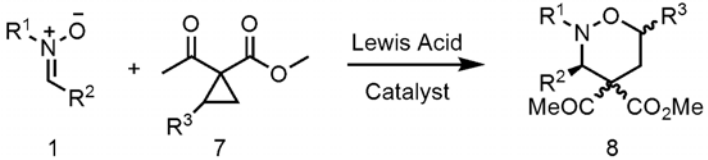
Scheme 1

More recently we have shown that cyclopropanes such as **4** also react to produce tetrahydro-1,2-oxazines such as **5** with moderate to good diastereoselectivities (Scheme 2).



Scheme 2

It is our wish to further probe the synthetic aspects of this reaction. The goal of this project is twofold. First, we wish to continue and complete the investigation started using cyclopropane **4**. Secondly, we want to investigate the diastereoselectivity of this reaction when carried out with a cyclopropane such as **7** which possesses two different electron withdrawing groups on the cyclopropane and further substitution at the 2-position (Scheme 3). Specifically the student will prepare and react **7** with a series of nitrones and determine the diastereomeric nature of the products **8**.



Scheme 3

The student will be exposed to a wide variety of experimental techniques common in an advanced synthetic laboratory and will be responsible for the synthesis, isolation, purification, and full spectroscopic (NMR, MS, IR) characterization of both the reaction substrates and products.

Professor Michael A. Kerr

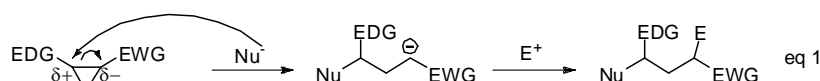
ChB 219

makerr@uwo.ca

http://publish.uwo.ca/~makerr/index.htm

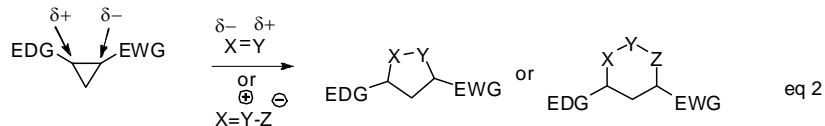
Boronic acid catalyzed activation of donor-acceptor cyclopropanes

Cyclopropanes bearing an electron donating group and an electron withdrawing group on adjacent carbons are known as donor-acceptor cyclopropanes. Because of the nature of the

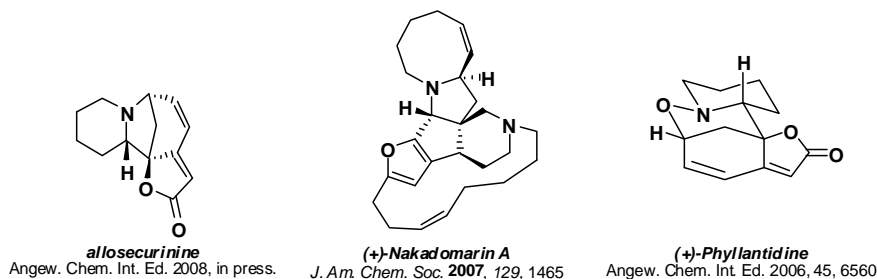


EDG = electron donating group
EWG = electron withdrawing group

Nu⁻ = nucleophile
E⁺ = electrophile

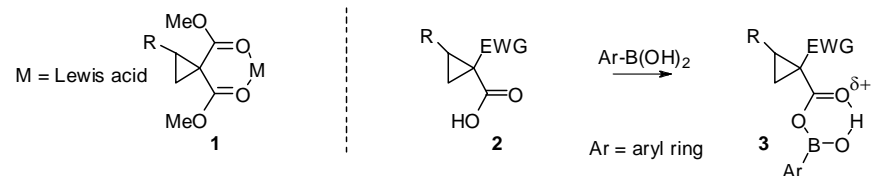


substituents, the cyclopropane sigma bond is polarized and weakened. Nucleophiles may react at the site which is more cationic in nature releasing a stable anion which in turn can react with an electrophile (eq 1). In many cases this dipolar nature can be exploited via reaction with another dipolar reactant resulting in the formation of a cyclic product (eq 2).



Reactions such as those shown above have been used by us group to prepare complex, bioactive natural products such as allosecurinine, nakadomarin A, and phyllantidine.

Typically the cyclopropane must be activated by complexation of the electron withdrawing groups with a Lewis acid,



amplifying their electron withdrawing nature. It has been shown that boronic acids form mixed anhydrides with carboxylic acids making the carbonyl group “super electron withdrawing” via hydrogen bonding. It is our hypothesis that this can be used to activate cyclopropanes such as **2** in an alternative fashion to Lewis acid catalysis by forming a reactive species **3**. We will then screen some of our known reactions for success using this method of activation.

The student will be exposed to a variety of experimental techniques common in an advanced synthetic laboratory and will be responsible for the synthesis, isolation, purification, and full (NMR, MS, IR) characterization of both the reaction substrates and products.

Professor Lars Konermann

B&G 2016

konerman@uwo.ca

<http://publish.uwo.ca/~konerman>

Mapping the Structure of Proteins by Hydroxyl Radical Labelling and Mass Spectrometry

The general topic of this research project is the "protein folding problem", i.e., the question how and why proteins fold from a random coil structure to their highly ordered native state. Because this native state represents the biologically active conformation, protein folding is incredibly important from a biological point of view. Misfolding and aggregation can have fatal consequences, leading to debilitating disorders such as Alzheimer's or Parkinson's. Despite many years of research, the principles by which proteins fold remain poorly understood. One particular challenge is that folding occurs very rapidly, within milliseconds to seconds. This short time scale precludes the application of traditional high resolution methods such as NMR and X-ray crystallography.

In this 4490 project we will use hydroxyl radicals ($\cdot\text{OH}$) for the covalent labelling of proteins during folding. An excimer laser will be used for radical production from H_2O_2 . The interaction of $\cdot\text{OH}$ with proteins leads to oxidative modifications at solvent-exposed amino acid side chains within a few microseconds. Importantly, folded regions are protected from $\cdot\text{OH}$ attack. Using HPLC, peptide mapping and mass spectrometry we can determine the locations of labelled sites within the protein. These data allow tracking the conformational changes during folding. One specific aim of this project will be to investigate how external factors such as protein concentration and solvent additives affect the labelling level. Different "reporter molecules" will be tested as a means to normalize data recorded under different experimental conditions.

References:

L. Konermann, X. Tong, and Y. Pan *J. Mass Spectrom.* **43**, 1021-1036 (2008).

X. Tong, J. C. Wren, and L. Konermann *Anal. Chem.* **80**, 2222-2231 (2008).

Professor Bernie Kraatz

ChB 18

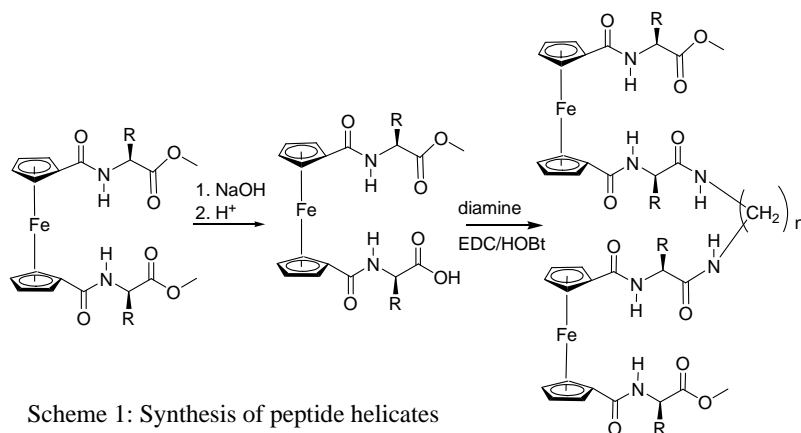
hkraatz@usask.ca

publish.uwo.ca/~hkraatz

Ferrocene-Peptide Conjugates: Towards Extended β -Helical Structures

The design of structurally well-defined peptide motifs has been an active area of research aimed at gaining a deeper understanding of biochemical processes to generate molecules with potential biological or biomaterials applications. Using non-proteinogenic amino acids or molecular scaffolds, some peptide foldamers can be designed to adopt the structure of an α -helix or a β -sheet. In our research, we exploit ferrocene as a molecular scaffold and have shown that peptide conjugates can be designed to adopt a variety of secondary and tertiary structures. These peptide conjugates are accessible via peptide coupling which allows attachment of a peptide directly to the cyclopentadienyl rings of the ferrocene via an amide bond.

The objective of this research is to exploit ferrocene dicarboxylic acid as a scaffold for the synthesis of a series of supramolecular peptide structures (Scheme 1). The synthesis proceeds from a 1,1'-disubstituted ferrocene conjugate which has the C-terminal side of the amino acid protected as a methyl ester. Such compounds are well known for their ability to adopt a rigid secondary structural motif and are stable under a variety of conditions. Deprotection of one of the methyl esters by stoichiometric amounts of base provides a free acid which is coupled to a series of alkyldiamines.



Scheme 1: Synthesis of peptide helicates

In this project, two design parameters will be changed: a) the amino acid residue attached to the ferrocene group will be changed in order to probe the influence of the sidechain residue and b) the diamine spacer linking two 1,1'-ferrocene peptide conjugates will be changed in order to probe the influence of the alkyl spacer on the

ability of the peptides to interact. The student will have the opportunity be involved in solution peptide synthesis and will be responsible for the synthesis, isolation and purification of all ferrocene-peptide conjugates and their spectroscopic characterizations (NMR, IR, MS).

Professor Bernie Kraatz

ChB 18

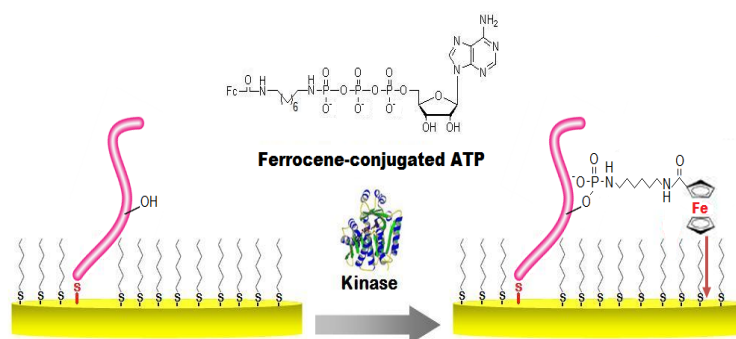
hkraatz@usask.ca

publish.uwo.ca/~hkraatz

Electrochemical detection of kinase-catalyzed phosphorylation using ferrocene-conjugated ATP

Protein phosphorylation is a universal regulatory mechanism that plays a critical role in the transmission of signals controlling a diverse array of cellular functions including cell growth, survival differentiation and metabolism. During protein phosphorylation, a phosphoryl group from ATP is transferred to specific serine, threonine, or tyrosine residue of a protein. As a result of this modifications, the function or localization of the protein may change, which in some cases may lead to the formation of the oncoproteins. Abnormal protein phosphorylation is a cause of major diseases, including cancer, diabetes and chronic inflammatory diseases.

Analytical methods to quantify protein kinase activity are critical for understanding their role in the diagnosis and therapy of these diseases. Methods for the measurement of protein kinase activity include the use of fluorescence and radioactive labels. Simple and cost-effective methods that can be readily adapted for multiplexed kinase detection are desirable to enable kinase activity profiling for diagnostic applications and to accelerate the *in vitro* elucidation of cellular signal transduction pathways.



Towards this effect, we used the electro-active adenosine-5'-[γ -ferrocene] triphosphate (Fc-ATP) to introduce the ferrocene redox label to a target peptide as shown in Scheme 1.

Briefly, a substrate peptide is immobilized covalently on a gold electrode surface. The kinase-catalyzed

reaction transfers a γ -phosphate-Fc group to the serine/threonine or tyrosine residue of a target peptide. The Fc group attached to the peptide is electrochemically observed and quantified by cyclic voltammetry (CV) and/or square wave voltammetry. To extend this work, we seek to validate the utility of this method for protein kinases that are part of the MAP kinase pathway and will investigate the effect of a series of kinase inhibitors.

Professor François Lagugné-Labarthe

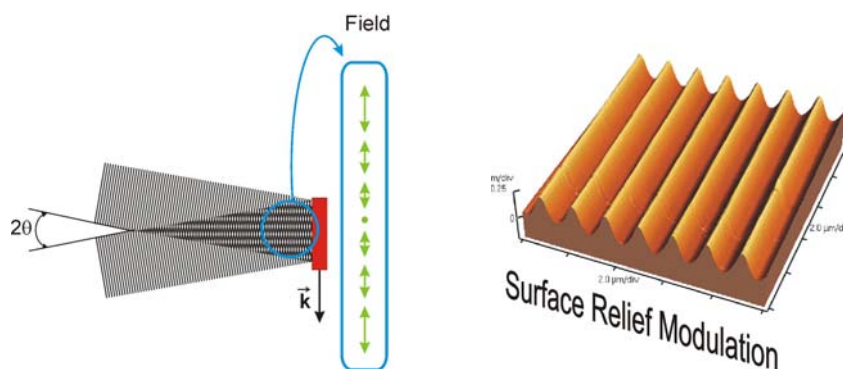
ChB 22

flagugne@uwo.ca

www.uwo.ca/chem/people/faculty/lagugne.htm

Fabrication of holographic gratings and localization of field enhancement around gold structures.

Azobenzene containing polymeric systems have been a subject of intensive research in the last few years in the areas of photofunctional applications such as diffraction optics. Using advanced optical methods such as holography, it is possible to deform periodically the surface of the polymer thin film reaching a sinusoidal shape of the surface with an amplitude of a few hundreds of nm with a very good control of the amplitude and the spacing.



Interference pattern and field modulation resulting from the interference of two coherent lasers. Resulting surface relief diffraction grating as observed by atomic force microscopy.

This project focus on (i) the fabrication and recording of holographic gratings with different polymer surface (iii) the characterization of such gratings using optical methods and atomic force microscopy (diffraction efficiency, surface relief amplitude), (iii) evaluate the enhancement of the electromagnetic field when such films are decorated with gold structures. The presence of such gold structures should enhance the dynamic, and the diffraction efficiency of such gratings. Holography will involve the use of visible continuous wave laser (green Ar⁺ and Red He-Ne) to record the simple hologram (interference pattern) onto the thin film and probe it simultaneously to measure in real-time the diffraction efficiency.

A student working on this project would learn to make polymer thin films, align and use lasers of different wavelengths, learn optical techniques and atomic force microscopy to fully characterize thin films.

Professor François Lagugné-Labarthe

ChB 22

flagugne@uwo.ca

www.uwo.ca/chem/people/faculty/lagugne.htm

Keith Griffiths

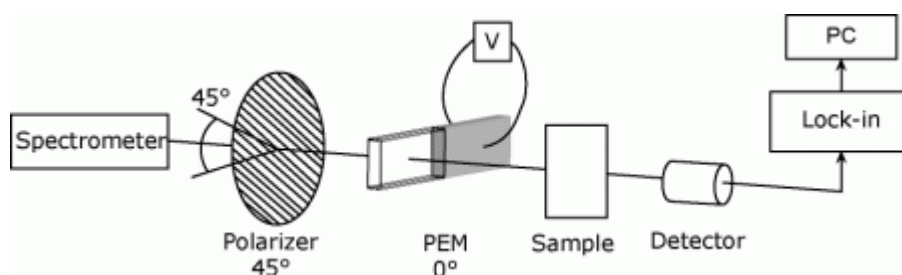
ChB 126

griff@uwo.ca

www.uwo.ca/chem/people/faculty/griffiths.htm

Development of Linear and Circular Dichroism in the Mid-infrared range by Polarization modulation Spectroscopy

This experimental project involves the instrumental development of linear and circular vibrational dichroism. Infrared absorption spectroscopy (IR) is the principal tool available for the study of molecular vibrations giving an “image” of the system at a molecular level. In an infrared spectrometer, the infrared light can be polarized at high frequencies (typically 50 kHz) between two polarizations using a photoelastic modulator. The light can for example be switched between two linear orthogonal directions, i.e. // and \perp , giving information about the linear anisotropy of a molecule deposited onto a surface, a sheared polymer thin film, or a single layer at the air-water interface.



In this project, we will (i) set up a full polarization modulation apparatus to probe oriented thin films of polymers. This will involve optical alignment in the mid-infrared range and setting up an electronics chain such as lock-in amplifier and bandpass filters. (ii) once the setup is working, we will study photo-oriented thin films of photosensitive polymers and rubbed polymer surfaces such as Teflon surfaces. More specifically, we will evaluate rubbed Teflon surfaces for the alignment of smaller guest molecules (iii) we will also make use of this setup for vibrational circular dichroism measurements probing the chirality of molecules at a vibrational level. This last approach is quite challenging due to the weak signal of VCD, but of tremendous interest to probe chiral molecules providing complementary informations to standard circular dichroism methods in the UV-Vis spectral range.

Professor R. H. Lipson

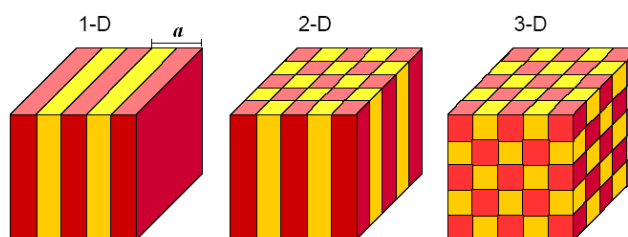
ChB 1A

rlipson@uwo.ca

<http://publish.uwo.ca/%7Erlipson/>

New Materials for Direct Fabrication of Photonic Crystals

A photonic crystal (PC) is defined as a dielectric medium with an index of refraction periodicity on the order of the wavelength of light being localized. As shown in the figure below they can be made in one-, two- or three dimensions. The length scale “a” is the periodicity.



When constructed correctly, PCs can act as perfect mirrors at wavelengths on the order of the periodicity itself. They have been proposed as critical components in applications ranging from waveguides, to lasers, to sensors. There are two main challenges associated with making PCs. The first is achieving periodicities that allow them to operate in the visible region of the spectrum (a on the order of 100s of nm). The second is that the index of refraction contrast of the dielectric medium must be very high. The most popular approach to making photonic crystals is to make air holes ($n = 1$) in silicon ($n > 3$). However this is a complex multistep process that requires a nanofabrication lab and tools worth millions of dollars (although Western has the facilities).

The Lipson group is exploring more “chemical” routes that allow PCs to be made in one step. This involves devising syntheses for materials that have very high dielectric constants and can be processed easily on the bench in a lab. In this project, a student will study the fabrication of Hafnium oxide (HfO) thin films. HfO has an extraordinarily high dielectric constant and as a result is often used in semiconductor chips as transistor gates. Surprisingly, it has not been studied extensively with PC applications in mind. We propose to use sol-gel methods to fabricate thin films of this material. We will attempt to increase the viscosity of the precursor solutions by adding polyvinyl pyrrolidone (PVP). In this way two-dimensional PCs can be fabricated by simple spin-coating, heating, and contact lithography.

An interested student will not only optimize the synthesis conditions but will use a variety of analytical tools to characterize the films including Scanning Electron Microscopy (for imaging), ellipsometry (for thickness measurements), and powder X-ray Diffraction (for crystal structures).

Professor R. H. Lipson

ChB 1A

rlipson@uwo.ca

<http://publish.uwo.ca/%7Erlipson/>

No matrix for MALDI mass spectrometry?

Matrix-Assisted Laser Desorption/Ionization (MALDI) mass spectrometry (MS) is an established technique where a laser beam illuminates a solid solution of matrix compound (usually a light absorbing low molecular weight organic molecule) doped with an analyte (usually a high molecular weight biomolecule). Upon irradiation a plume of material is rapidly vaporized where chemical reactions take place such as protonation or deprotonation yield cations or anions, respectively. These generated ions can be detected in a mass spectrometer.

Most matrixes used commercially operate using either ultraviolet lasers or infrared lasers. However, there are advantages to using visible lasers. First, these sources are cheaper, and most biomolecules do not absorb in the visible which reduces possible fragmentation. Conventional wisdom indicates however that visible-MALDI simply doesn't work. However, our group has shown that it does, and that it does quite well provided a good matrix can be found.

Our group is working with MDS Analytical Technologies a leading mass spectrometer manufacturer in Toronto on various aspects of MALDI MS including the use of vacuum ultraviolet (VUV lasers) for post-ionization of neutrals to increase the detection sensitivity, the viability of doing MALDI in the visible using visible absorbing matrix compounds, and the use of using porous silicon (p-Si) as a substrate for matrixless MALDI.

In this project a student will explore examine the use of p-Si as a substrate for matrixless MALDI. Although p-Si has been studied by others before, the experiments were almost always involved fixed wavelength ultraviolet lasers. Yet, p-Si has a band gap of only 1.1 eV which lies in the infrared. Our lab has tunable lasers which can allow the wavelength dependence of p-Si to be assessed and compared for the first time using infrared, visible and ultraviolet photons.

An interested student will learn about mass spectrometers and lasers, and contribute to work which may have commercial implications.

Professor Len Luyt

A4-817, London Regional Cancer Program

lluyt@uwo.ca

<http://publish.uwo.ca/~lluyt/>**Note: I am available for discussing the project only Sept 4 or 5, as I am out of town Sept 8-18.****Otherwise contact Ms. Jen Hickey (jlhickey@uwo.ca) to discuss the project during the week of Sept 8.****Control of Isomer Formation for Histidine-Re(CO)₃ Complexes**

Technetium(I) and rhenium(I) tricarbonyl complexes are being incorporated into biologically relevant compounds for medical imaging or therapy. One reported approach to including the organometallic species within the structure of a targeting peptide is through the addition of a terminal histidine. This can be accomplished in a manner such that three coordination sites are available. However, upon coordination the resultant complex forms as a mixture of diastereomers. Diastereomeric mixtures are not desirable for pharmaceutical products as single isomer products tend to simplify the regulatory process. A recent example of a cyclic RGD peptide developed in our lab with a histidine chelator is shown in Figure 1 and forms as a mixture of two isomers.

We have recently investigated the possibility of creating single isomer histidine-Re(CO)₃ chelation complexes (Figure 2). It appears that forming a bulky tertiary amine for the α -amine of histidine results in preferential formation of a single diastereomer. This project will explore the ability to control isomer formation by varying the structure of histidine chelators and determining the effect on the ratio of diastereomers formed. The student will learn solid-phase and solution-phase synthesis and will characterize the products using mass spectrometry, NMR and possibly X-ray crystallography.

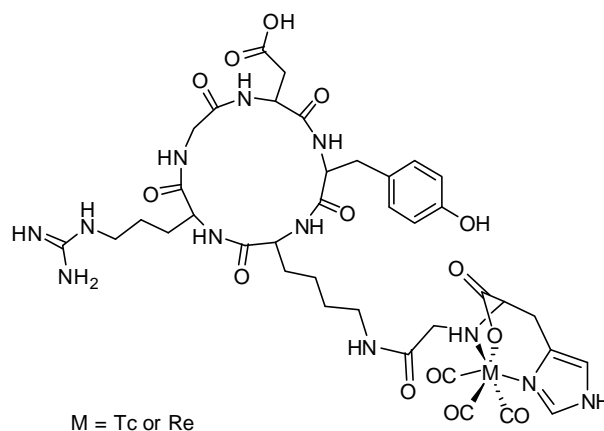


Figure 1. Cyclic RGD pentapeptide containing a tridentate histidine.

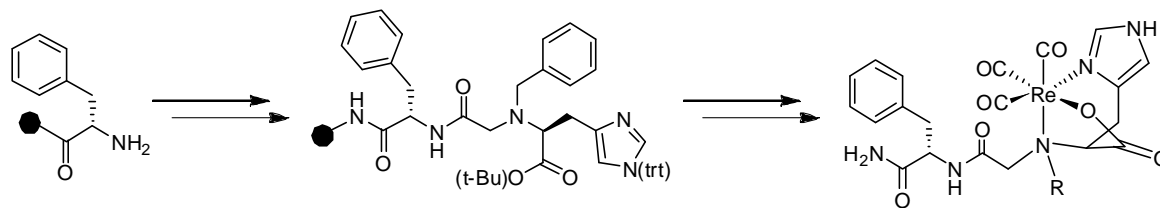


Figure 2. Model histidine-Re(CO)₃ system to explore diastereomer formation.

Professor Ron R. Martin

ChB 23

rrhm@uwo.ca

Professor Peter Norton

ChB 063

prnorton@uwo.ca

The role of Zn in Human cementum

Zn is enriched in human cementum (the calcified substance covering the root of a tooth) but its role remains unclear. This project will seek to establish a possible link between organically bound Zn and the hardness of the cementum system using micro-indentation techniques.

Professor Brian L. Pagenkopf

B&G 2008

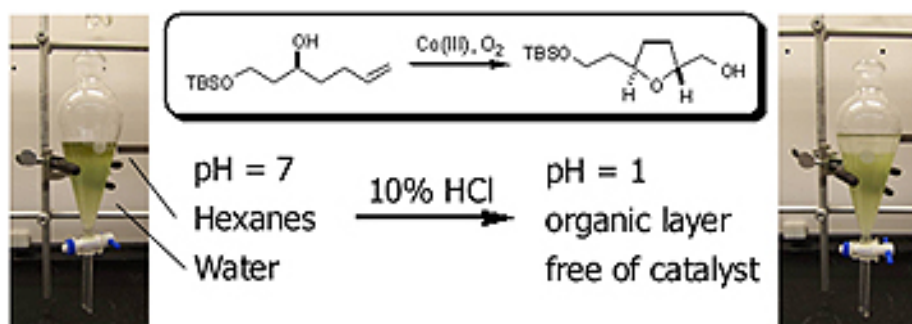
bpagenko@uwo.ca

Publish.uwo.ca/~bpagenko/

Water Soluble Cobalt Catalyst for Mukaiyama Oxidation

The Mukaiyama oxidation provides a highly efficient route to trans-THF rings by oxidative cyclization of the corresponding pentenol derivative.¹ Recently this procedure has emerged as a powerful tool in synthesis, and we have used this reaction in the total synthesis of two natural products, aplysallene and bullatacin.² A significant drawback of the Mukaiyama oxidation is the difficulties associated with removing the catalyst from the THF product. The materials are often too large for distillation, and column chromatography is complicated by catalyst decomposition.

Recently, a water soluble cobalt catalyst has been synthesized in our laboratory, which upon treatment with acid will enter the aqueous layer during an extraction, leaving only the desired trans-THF product in the organic layer. This eliminates a column chromatography step, making the Mukaiyama oxidation a much more scalable and industrial friendly reaction.



Goal: The student undertaking this project will synthesize a variety of pentenol derivatives and compare the yields using the water soluble cobalt catalyst to those using the standard catalysts. Time permitting; attempts will be made at synthesizing a cobalt catalyst that is water soluble at neutral pH.

1. Inoki, S.; Kato, K.; Takai, T.; Isayama, S.; Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1989**, *18*, 515-518.

2. See group website.

Professor Brian L. Pagenkopf

B&G 2008

bpagenko@uwo.ca

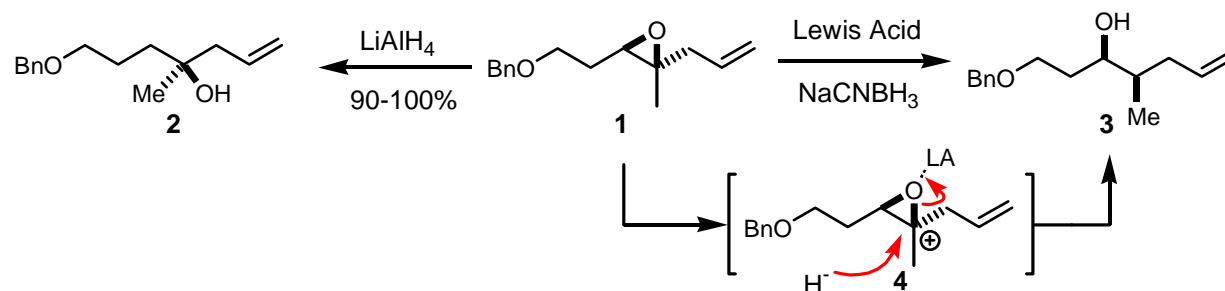
Publish.uwo.ca/~bpagenko/

Regio- and Stereo-Selective Reductive Epoxide Opening

Typically, nucleophilic attack with hard nucleophiles (such as hydrides) on tri-substituted epoxides takes place at the sterically more accessible carbon to give **2**. However, it was shown 25 years ago by Hutchins that upon activation of an epoxide with a Lewis acid ($\text{BF}_3 \cdot \text{OEt}_2$) it was possible to promote hydride attack at the more hindered carbon to give **3**.¹ This hydride attack took place in an $\text{S}_\text{N}2$ fashion to result in a single diastereomer.

Upon application of Hutchin's procedure in our lab, we found that there were several competing side reactions, presumably due to the Lewis acid opening the epoxide to give a relatively stable tertiary carbocation intermediate.

We have succeeded in attenuating the strength of the Lewis acid by replacing fluorine with OBn, a less electronegative group. Repeating the reaction using our weaker Lewis acid resulted in a substantial improvement, providing only the desired **3** in a 7:1 dr. These promising initial results have not yet been optimized.



Goal: The student undertaking this project will synthesise a variety of difluoro-alkoxy Lewis acids and test different solvent systems and reaction conditions to optimize the procedure with a model substrate. The modified Lewis acids will be tested against Hutchins original procedure. Time Permitting: other tertiary epoxides will be made and the student will test the generality and scope of the procedure.

1- Hutchins, R. O.; Taffer, I. M.; Burgoyne, W. J. *Org. Chem.* **1981**, *46*, 5214-5215.

Professor Brian L. Pagenkopf

B&G 2008

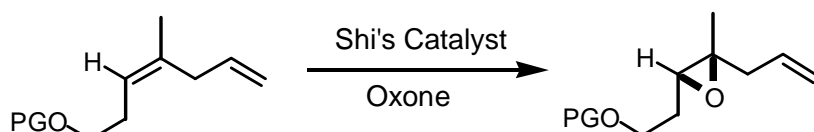
bpagenko@uwo.ca

Publish.uwo.ca/~bpagenko/

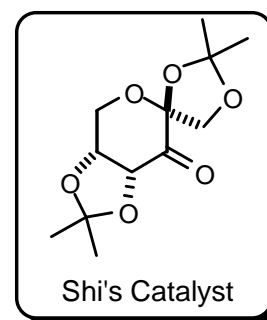
Studying a Subtle Electronic Effect of the Shi Epoxidation

The Shi catalyst is a fructose derived substrate, which in the presence of oxone (a persulfate salt) will stereoselectively epoxidize olefins. This represents one of the most powerful asymmetric epoxidation catalysts available because it is the most effective way to epoxidize non-activated trisubstituted olefins. The rate of Shi epoxidation is proportional to the electron-richness of the olefin, so tri-substituted olefins can be selectively epoxidized in the presence of di- or mono- substituted olefins.

In our labs, an attempt was made to selectively epoxidize a tri-substituted olefin over a mono-substituted olefin. Normally the selectivity would be 100% for the tri-substituted olefin. However, in this case the tri-substituted olefin was a bis-homoallylic alcohol, which decreased its electron density, resulting in competitive epoxidation of the mono-substituted olefin. Initial studies have shown that varying the protecting group on the alcohol influences the ratio of products by changing the electronic nature of the tri-substituted olefin.



PG = TBS - 63% mono, 23% di, 16% SM



Goal: The student undertaking this project will test the Shi epoxidation on the model substrate with a wide variety of protecting groups, and attempt to quantify the electronic effect on the outcome of the reaction. Time Permitting: epoxides will be reductively opened in collaboration with the previous project "Regio- and Stereo-Selective Reductive Epoxide Opening".

Professor Brian L. Pagenkopf

B&G 2008

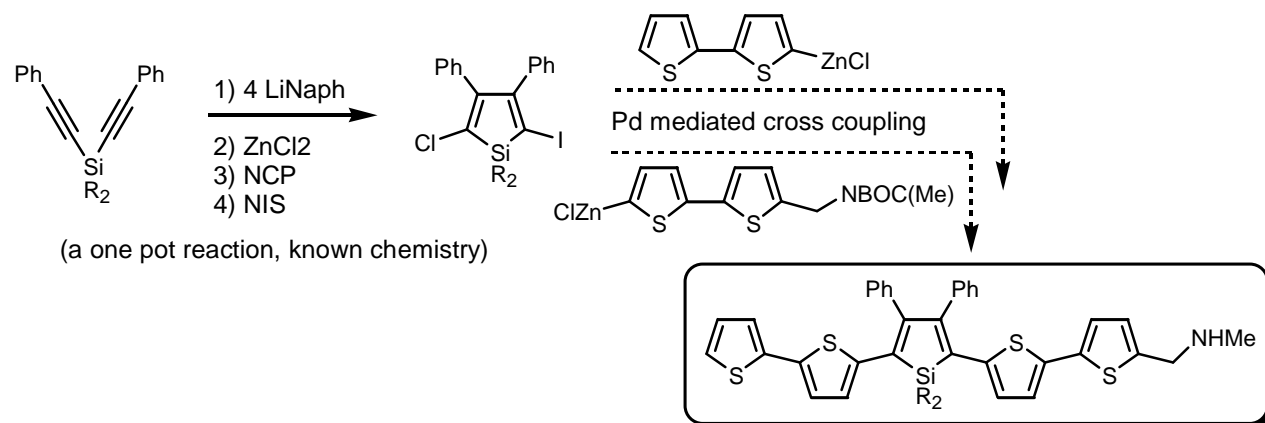
bpagenko@uwo.ca

Publish.uwo.ca/~bpagenko/

Dissymmetric Siloles as Potential Fluorophores for Analytical Biomedical Applications

Siloles are a silicon analog of cyclopentadiene. The silicon atom greatly lowers the LUMO thereby giving these molecules some very interesting properties. Siloles have interesting fluorescent properties, have potential in Photovoltaic systems, have been used as the active layer in Organic Light Emitting Diodes.

We, in collaboration with the Ding group, recently discovered that thiophene containing silole chromophores show impressive Electrogenenerated Chemiluminescence (ECL). ECL, when coupled with biological probes, is a remarkably powerful method for the detection of trace materials in biological samples, and is used extensively in hospitals world wide to help diagnose disease. In simple laboratory experiments the ECL from our thiophene silole hybrids is much more efficient than the currently used commercial Ru(bipy) fluorophores.



Goal: The point of this project is to synthesize in the lab a suitably functionalized dissymmetric silole. While in principle the synthesis is really short, the presence of a somewhat chemically sensitive silole can complicate what might otherwise be straightforward transformations. If successful, and if time permits, the dissymmetric silole will be tested in the Ding group for its ECL response, and given to the Hudson group for attachment to a biological probe.

Professor Paul J. Ragogna

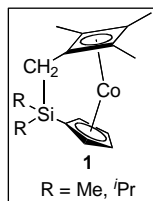
B&GS 2026

pragogna@uwo.ca

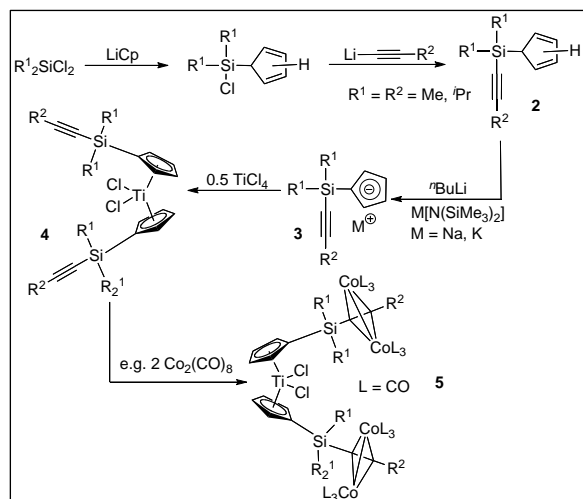
http://publish.uwo.ca/~pragogna

New Ligands for Early – Late Bimetallic Complexes

BACKGROUND: An ongoing project in our group has centred on developing new synthetic routes to strained, bridged cobaltocenes that feature both cyclopentadiene and cyclobutadiene rings. These species are members of a general class of compounds called [2]metalloarenophanes and for cobalt only two complexes have been reported (**1**). In an attempt to expand on the potential routes to these compounds, we have developed a ligand (**2**) that can potentially be installed on a cobalt centre, where further transformations should yield the target [1]cobaltoarenophane. However, this ligand should be useful for the development of early, late and early/late mixed metal systems as it bears a Cp and an alkyne functionality.



PROPOSED RESEARCH: Your target goals for the project will likely be composed of the following:



1 – The synthesis of substituted dialkylsilanes featuring both cyclopentadienyl and alkyne functionalities (**2**).

2 – To deprotonate the substituted silane to give the corresponding group 1 metal salts (**3**).

3 – Using simple salt metathesis to produce a titanocene dichloride derivative (**4**)

4 – Synthesize early/late bimetallic species by introducing a late metal such as Ni, Co or Mo to the pendant alkyne (**5**).

SIGNIFICANCE: Your efforts in this area will be important in developing our understanding of this ligand system and its future applications in

generating other important organometallic species featuring one or multiple metals.

SKILLS AND EXPERTISE: Students who take on this project will gain expertise in the synthesis and characterization of inorganic and organic compounds. Specifically, they will become proficient in the manipulation of air sensitive compounds using inert atmosphere Schlenk line and glove box techniques. Multinuclear NMR (^1H , ^{13}C , ^{29}Si), IR and X-ray crystallography will be central for the compound characterization and in this context, students can expect to be exposed to all of these methods.

NOTE – Any Chem 490 student who joins the Ragogna Group will be required to have a full draft of the introduction to their final report by December 15th and an up to date experimental section by February 15th.

Professor Paul J. Ragogna

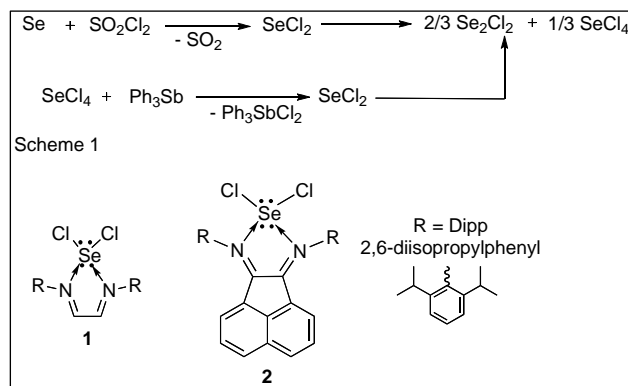
B&GS 2026

pragogna@uwo.ca

http://publish.uwo.ca/~pragogna

“Bottleable” SeX_2 –Delivery of a Highly Reactive Molecule

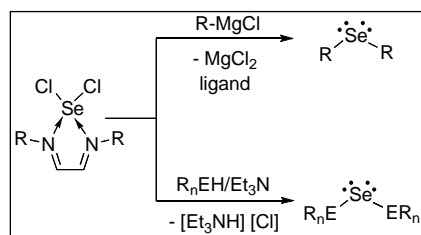
BACKGROUND: The heavier ($n \geq 3$) chalcogen dihalides are unstable species that decompose rapidly at room temperature (Scheme 1).



Although molecules such as ChX_2 can be synthesized ($\text{Ch} = \text{S}, \text{Se}; \text{X} = \text{Cl}, \text{Br}$), the synthetic routes are considered onerous, the products must be used *in situ* and within a short period of time (approx. 30 to 60 min.). Given the immense potential utility of ChX_2 as a reagent, our group has successfully been able to sequester SeX_2 fragments within an N,N' chelate by employing a variety of diazabutadiene ligand systems (e.g. **1**, **2**).

Preliminary work suggests that these molecules are excellent storage vessels for SeX_2 and can release the chalcogen dihalide in a stoichiometric fashion.

PROPOSED RESEARCH: Your target goals for this project will be composed of the following:



1. Utilize derivatives of **1** or **2** in a unique and facile route to synthesize a variety of known dialkyl/arylselenides to set identify potential problems with the methodology (Scheme 2).
2. Extend the methodology to generate molecules featuring E-Se-E connectivity, where E is another main group element (e.g. Si, Ge, Sn, N, P).

SIGNIFICANCE: Your efforts on this project would provide a breakthrough into a new area of chalcogen chemistry. Stabilized SeX_2 that can be used in further transformations will undoubtedly expand the synthetic organic/inorganic “toolbox”.

SKILLS AND EXPERTISE: Students who take on this project will gain experience in the synthesis and characterization of inorganic (and some organic) compounds. Specifically, they will become proficient in the manipulation of air sensitive materials using inert atmosphere Schlenk line and glovebox techniques. Multinuclear NMR (^1H , ^{13}C , ^{77}Se and ^{125}Te), IR and X-ray crystallography will be central to this project and in this context, students can expect to be exposed to all of these characterization techniques.

NOTE – Any Chem 490 student who joins the Ragogna Group will be required to have a full draft of the introduction to their final report by December 15th and an up to date experimental section by February 15th.

Professor Oleg Semnikhin

ChB 067

osemenik@uwo.ca

<http://www.uwo.ca/chem/people/faculty/semnikhin.htm>

Interfacial processes in organic solar cells

Development of new technologies that would enable us to use solar power instead of burning fossil fuels is a major present-day scientific problem. However, the technologies developed so far for harvesting the solar energy are quite inefficient. For instance, the most efficient present-day solar cells use silicon as an active material; however, according to some estimates, a silicon solar cell should work 5 to 7 years just to recoup the energy used in its production.

Therefore, it is extremely important to find ways to improve the efficiencies of solar cells in order to make them a viable economic alternative to fossil fuels. A major source of losses in solar cells are losses at the interfaces between the active semiconductor material and metal contacts, which are necessary to collect the energy produced by the cell. The chemical and physical nature of the processes occurring at the contacts is not well understood; however, it is known that one way to boost the efficiency is to introduce certain intermediate interfacial layers of nanometre thicknesses. For organic solar cells, where the active material is an organic semiconductor, such layers could be LiF or TiO₂. However, little is known how these compounds interact with organic materials and what is the reason for their positive effect.

In this project, the student will study the processes occurring at the interface between organic photovoltaic material based on electroactive polymer polybithiophene, and metal contacts, with and without interfacial sublayers such as LiF or TiO₂. The techniques to be used are electrochemical polymerization of the active material, vacuum evaporation or chemical deposition of the sublayers, vacuum magnetron sputtering of the metal contacts, electrochemical and photoelectrochemical characterization of the prepared devices, atomic force microscopic characterization of the deposited layers on the nanoscale.

Professor Oleg Semnikhin

ChB 067

osemenik@uwo.ca

<http://www.uwo.ca/chem/people/faculty/semnikhin.htm>

Polymer Batteries Revisited

Rapidly rising fuel prices, even if they eased a little recently, have resulted in an increased demand for new technologies to improve the fuel efficiency of motor vehicles. One such technology is hybrid vehicles, either classical or “plug-in”. In both cases, a significant portion of the vehicle power comes from electrical batteries that are installed on board. However, the existing types of batteries are not very well suited for automotive applications: they take long time to charge, may have memory effect, have a limited service life, may be explosion-prone, some are difficult to recycle. Also, advanced batteries such as lithium cells are very expensive. And, lastly, all existing batteries are heavy, which is a very important consideration for automotive applications.

At present, the best solution seems to be lithium ions batteries, the technology essentially borrowed from electronic industry. However, strong candidates for the next generation electrical energy storage for automotive applications are organic electroactive materials such as conducting polymers. They are extremely lightweight as compared to all metal based inorganic batteries, should not be difficult to recycle, are not explosion-prone, do not contain toxic or hazardous metals and ions, and could be quite inexpensive. There have been some attempts in 1990s to develop new polymer batteries; however, the oil was cheap then and the interest in this area has gradually diminished. Now it is time to revisit the polymer batteries as a potentially groundbreaking technology for new generation of hybrid vehicles.

In this project, the student will make a series of polymer batteries and study their characteristics. Electrochemical polymerization and electrochemical characterization techniques will be used extensively, as well as surface analytical techniques and atomic force microscopy (AFM). Various conducting polymer materials as well as battery designs will be used.

Professor T.K. Sham

ChB 030a

tsham@uwo.ca

<http://publish.uwo.ca/~tsham>

The influence of capping ligands on the optical and electronic properties of Au nanoparticles

Au nanoparticles differ from their bulk counterparts and exhibit interesting size dependent catalytic, optical and electronic properties. For instance, the energy band of the Au d electrons narrows with decreasing particle size (approx. as $1/R^2$, where R represents the particle's radius) and ultimately becomes a non-conductor nanoparticle with a band gap. This is a quantum confinement effect as the radii of the nanoparticles becomes smaller than the exciton radius in the nanoparticle (exciton is an hydrogen atom like electron hole pair in which the electron and hole can recombine leading to luminescence). This is demonstrated by a size dependent blue shift of the UV-Vis absorption and optical emission features in these systems. Using colloidal chemistry methods, nano Au particles with diameters of 1 - 100 nm can be synthesized to contain a high degree of crystallinity and narrow size distribution. These nanoparticles are passivated by capping ligands and hence the question arises as to how these ligands modify the electronic structure of the nanoparticle. The aim of the project will be to investigate the size and ligand dependence of the electronic structure and optical emission in different Au nanoparticle systems. To study the influence of the surrounding ligands (citrate, triphenylphosphine and alkanethiol) both ligand stabilized nanoparticles and ligand-free Au nanoparticles (formed by thermal evaporation on SiO₂, Si, TiO₂ and Al₂O₃ substrates) will be synthesized at varying sizes and examined. In order to probe the local chemical environment of the atoms in the clusters as well as the interaction of the ligand with atoms on the clusters surface X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) will be employed. Particularly, inner-shell X-ray absorption fine structures (XAFS) is a useful XAS technique as atomic core levels are highly localized and reflect the local properties of the material. The method is therefore sensitive to the local chemical environment of each atom type and enables investigation of the geometric and electronic structure of nanoparticles as a function of size. Conventional characterization techniques such as Scanning electron microscopy and Transmission electron microscopy will also be employed.

In this project you will be working closely with Michael Murphy in sample preparation and characterization. Michael is an experienced graduate student in my research group. You will prepare several samples in each category with varying parameters, either size or capping ligand. You will also prepare bare Au nanoparticles on different substrates by evaporation or electrodeless deposition. These materials will be examined with X-ray Powder Diffraction (XRD), UV-visible, Photoluminescence (PL), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Selected samples will be investigated at the synchrotron with X-ray absorption spectroscopy. We will meet regularly to discuss the progress.

T.-K. Sham, P.-S.G. Kim, P. Zhang, *Solid State Comm.* (2006) **138**, 553-557.

C. Nowak, *et al.*, *J. Chem. Phys.* (2001) **114**, 489-494.

Professor Yang Song

ChB 066, Ext 86310

yang.song@uwo.ca<http://publish.uwo.ca/~ysong56/>**Professor Yining Huang**

ChB 17, Ext 86384

yhuang@uwo.ca

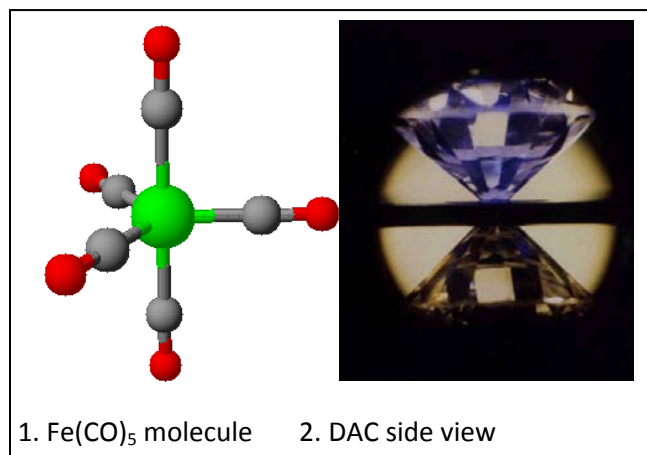
High pressure studies of metal carbonyls by vibrational spectroscopy

In this project, you will study the pressure effects on some fundamental metal carbonyls, primarily iron pentacarbonyl $[\text{Fe}(\text{CO})_5]$. Transitional metal-carbonyl complexes have attracted considerable attention as catalysis in many reactions. Their crystal structures, molecular geometries and bonding patterns exhibit sensitive response to pressures. Previous study on the $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, $\text{Ru}_3(\text{CO})_{12}$, and $\text{Fe}_2(\text{CO})_9$ [1], etc., had yielded rich observations on pressure-induced transformations. However, the iron

pentacarbonyl has never been studied under high pressures before and may exhibit very intriguing pressure behaviours. For example, $\text{Fe}(\text{CO})_5$ (object 1 in above picture) adopts a bi-pyramid geometry with five indistinguishable carbonyl groups at ambient conditions because of pseudo-rotation, but under high pressures, equatorial and axial carbonyls are expected to respond differently to compression. The study of pressure effect will greatly enhance our understanding of the structure-property relations and will aid the design of novel metal carbonyl compound.

The device to generate high pressures is called diamond anvil cell (DAC) as shown in the above picture (object 2, zoomed by 1,000 times from real object under an optical microscope). Samples loaded into a DAC will be examined by Raman spectroscopy and Fourier transform infrared (FTIR) micro-spectroscopy using the state-of-the-art optical systems in the Song lab. Therefore, student taking this project will obtain hand-on trainings on high pressure techniques and will develop analytical skills by using the modern laboratory instruments. To start the projects, you are expected to perform extensive literature review. Finally, critical data analysis and drafting of scientific articles are essential components of this project.

Reference: [1] M. Safa, Z. Dong, Y. Song and Y. Huang, "Examining the structural changes in $\text{Fe}_2(\text{CO})_9$ under high external pressures by Raman spectroscopy", *Can. J. Chem.*, **85**, 866 (2007) [Special Issue: Dedicated to Professor G.M. Bancroft].

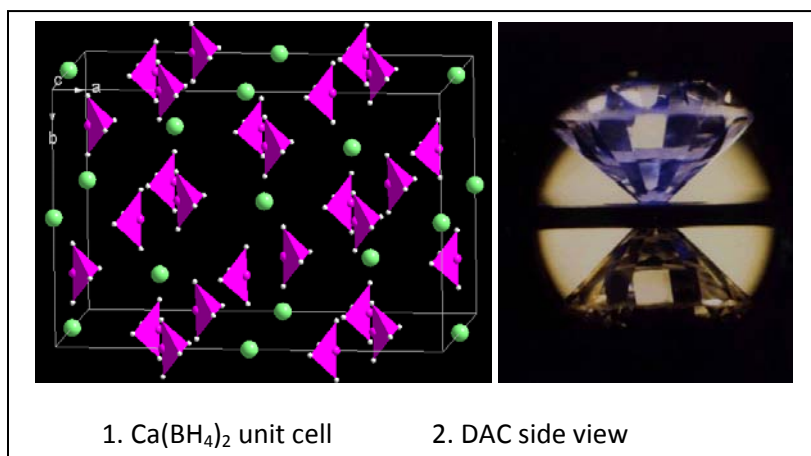


Professor Yang Song

ChB 066, Ext 86310

yang.song@uwo.ca<http://publish.uwo.ca/~ysong56/>**Exploration and characterization of hydrogen storage materials**

As clean and almost perfect fuel, hydrogen poses a big challenge particularly with respect to its storage. Discovery of suitable hydrogen storage (HS) materials, therefore, is of fundamental importance for the development of the next generation clean fuels, and could potentially revolutionize the automobile industry.



Recently, development of novel HS materials under high pressures has demonstrated strong promises. Metal hydrides, for example, are specific combinations of metallic alloys that absorb hydrogen like a sponge under high pressures and then desorb hydrogen later. Calcium borohydride [$\text{Ca}(\text{BH}_4)_2$], a recently commercially available hydride, exhibits high hydrogen stoichiometry, but has not been tested for the capacity as how much hydrogen it can take and release with pressure treatment. As the first step, in this project you will study the how structure of this compound (as shown in the above figure) changes under high pressures using vibrational spectroscopy. The understanding of the high pressure structures and stabilities of this hydride is critical for us to evaluate its hydrogen storage potentials.

The device to generate high pressures is called diamond anvil cell (DAC) as shown in the above picture (object 2, zoomed by 1,000 times from real object under an optical microscope). Samples loaded into a DAC will be examined by Raman spectroscopy and Fourier transform infrared (FTIR) micro-spectroscopy using the state-of-the-art optical systems in the Song lab. Therefore, student taking this project will obtain hand-on trainings on high pressure techniques and will develop analytical skills by using the modern laboratory instruments. To start the projects, you are expected to perform extensive literature review. Finally, critical data analysis and drafting of scientific articles are essential components of this project.

Professor Viktor N. Staroverov

ChB 20

vstarove@uwo.ca

<http://publish.uwo.ca/~vstarove>**Professor Kim M. Baines**

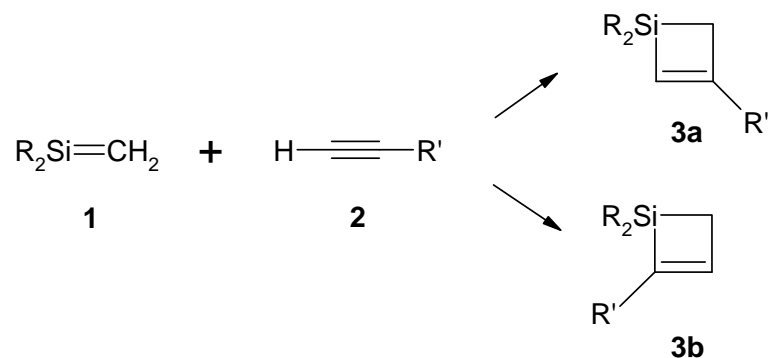
ChB 120A

kbaines2@uwo.ca

<http://publish.uwo.ca/~kbaines2>

Computational Study of the Cycloaddition of Alkynes to Silenes

The addition of silenes to asymmetric alkynes is a facile, nearly quantitative reaction producing substituted silacyclobutenes:



This process is highly regioselective: Depending on the nature of substituents R and R', it yields either **3a** or **3b**, but not both, which makes it very useful for synthetic purposes. Unfortunately, very little is known about the mechanism of this cycloaddition reaction and the factors that govern its regioselectivity. What makes the problem particularly intriguing is that the observed product is often not the one you would expect based on the polarity of the Si=C bond and inductive effects of the alkyne substituent.

In this project, we will use a popular quantum-chemistry program called GAUSSIAN to gain insight into the mechanism of this reaction and thus to answer the question: Given substituents R and R', is the product **3a** or **3b**? While working on this project, you will learn how to use the GAUSSIAN program in a LINUX environment, map out reaction pathways, construct energetic profiles of chemical reactions, locate and identify intermediates and transition states on a potential energy surface, and to characterize electronic and structural properties of transient chemical species.

Professor Viktor N. Staroverov

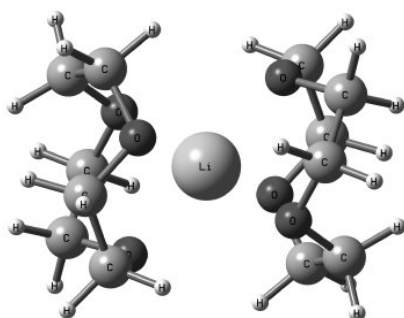
ChB 20

vstarove@uwo.ca

<http://publish.uwo.ca/~vstarove>

Electronic Structure of Alkali Metal Complexes

Crown ethers are well known for their ability to bind alkali metal ions. Less known is their property to form complexes with *neutral* alkali metal atoms. A typical example of such supramolecules is the sandwich complex of Li and 9-crown-3:



$$f_{\text{ELF}} = \frac{1}{1 + \chi^2}$$

$$\chi = \frac{\tau - \tau_W}{\tau_{\text{unif}}}$$

$$\tau_W = \frac{1}{8} \frac{|\nabla \rho|^2}{\rho}, \quad \tau_{\text{unif}} = \frac{3}{10} (3\pi^3)^{2/3} \rho^{5/3}$$

This invites the following question: Does the Li atom in the $\text{Li}(\text{9-crown-3})_2$ complex remain neutral or does it exist as a Li^+ cation after the valence electron has moved to some other part of the molecule? The prevailing opinion is that the alkali atom is indeed ionized, but it is uncertain whether the loose electron is smeared over the crown-ether frame or is pushed outside of it. The answer to this question has important implications for the chemistry of electrides.

In this *computational* project, we will find out the whereabouts of the alkali metal's detached electron in two crown-ether complexes, $\text{Li}(\text{9-crown-3})_2$ and $\text{Na}(\text{12-crown-4})_2$, by building upon our earlier studies of these molecules. While working on this project, you will learn how to use the GAUSSIAN program in a LINUX environment, calculate molecular geometries, visualize GAUSSIAN output, and analyze electron distributions in a molecule using a variety of theoretical techniques including molecular orbital isosurface plots, natural atomic population analysis, and electron localization functions (ELF).

Professor Martin Stillman

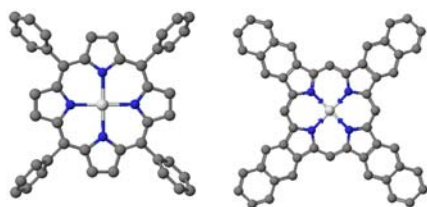
ChB 064

martin.stillman@uwo.ca

stillmangroup.ca

How does low symmetry change the electronic structure of highly symmetric porphyrin rings?

While fairly symmetric porphyrin rings (Figs LHS) are common in nature, all life on the planet depends on the really distorted chlorophyll (Fig RHS). Why go to bother of adding all that extra chemistry to distort a rather neat ring? It is much easier to make symmetric molecules. The experimental evidence



is that the electronic structure in the distorted chlorophyll is much better at converting solar energy into electrical energy – hence green plants! In this project, we will examine a series of synthetic low-symmetry porphyrins made

by our collaborators in Prague (sadly, no visit is planned during the project).

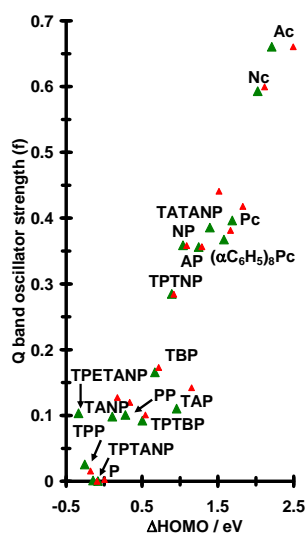
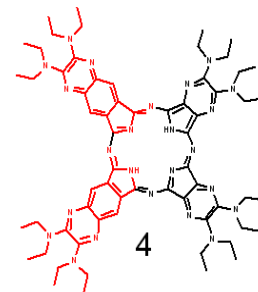
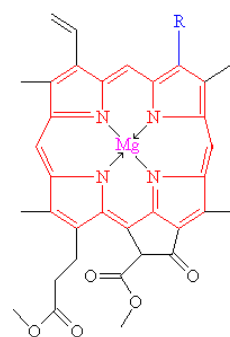
The project involves measuring the absorption, emission and magnetic circular dichroism (MCD) of a series of low-symmetry porphyrin compounds

(one is on the RHS) sent to us this summer, then calculating the predicted spectra. How close are we to predicting the electronic spectra (UV-visible absorption)

of these compounds? We have previously published trends (Fig LHS*) of typical properties – we want to add these new data to those trends. If we can understand

the electronic properties of these low symmetry porphyrins, perhaps we can understand how chlorophyll supports life on the planet and predict the properties of ‘designer’ porphyrins not yet made. For more details check

the board outside Dr Stillman’s office. Please note: Dr Stillman will be speaking at a conference in Italy 15 -19th September. Please meet with Dr Stillman before 12th Sept. for more information. *This is a very detailed paper but – like all trends – needs new data: Mack, J., Asano, Y., Kobayashi, N. and Stillman, M. J. (2005) J. Am. Chem. Soc. 127, 17697.



Professor Martin Stillman

ChB 064

martin.stillman@uwo.ca

stillmangroup.ca

Experimental proof of a new theoretical result – overturning 50 years' of interpretation.

The porphyrins are at the core of Nature's photochemistry and electrochemistry (all life on the planet depends on the operation of chlorophyll). Similarly, all mammalian life depends on the oxygen binding of the iron porphyrin in hemoglobin. There is also an extremely active synthetic chemistry of the porphyrins as researchers attempt to make more and more exotic molecules to act in many different ways, from solar collectors, to flat-screen dyes, to antitumor drugs. Not surprisingly then, considering all this exciting chemistry, every type of spectroscopy has been used to study porphyrins – the goal is an accurate description of the electronic structure of these vitally important molecules that predicts the chemistry. Sounds like with so many molecules this should have been done decades ago, but no! Our group has specifically made both measurements and calculations to try and develop trends so that we can understand the natural molecules' chemistry, and design new molecules by computer, calculate the electronic structure and predict the electronic-structure-based properties. So, what's the problem? Well, these calculations are calibrated – or confirmed – by experimental data and a recent calculation by Prof. Tom Ziegler at Calgary has thrown into doubt the usual interpretation of the data. The aim of this project is to measure absorption and magnetic circular dichroism spectra of target porphyrin molecules (ones that Ziegler's theory applies to) and either 1) confirm that his group's calculations are right or 2) confirm the rest of the world is right. The project will use molecules out of the drawer or bought and some made simply, followed by careful measurements of MCD spectra. A great project if you liked spectroscopy, like the idea of solving problems, and like the idea of discussing your results* one on one with the top theoretician in the country next May at CanBIC-2009 (canbic.ca). For more details check the board outside Dr Stillman's office. Please note: Dr Stillman will be speaking at a conference in Italy 15 -19th September. Please meet with Dr Stillman before 12th Sept. for more information. *You'll be right whatever you measure as the data are always correct!



Professor Martin Stillman

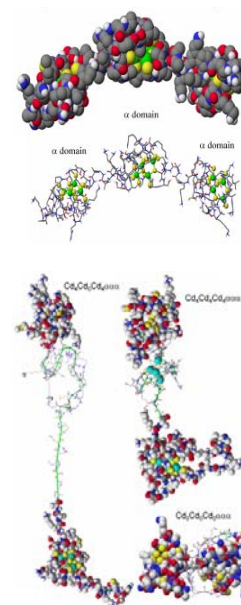
Room number: ChB 064

e-mail address: martin.stillman@uwo.ca

Web address: stillmangroup.ca

Exploring the metal binding of a novel protein

The protein metallothionein (MT) binds all the group 11 and 12 metals. Metallothioneins are characterized by the presence of numerous Scys-x-Scys and Scys-Scys motifs in the sequence. Thiols are perfect metal binding ligands. Nature uses this protein to control metal concentrations (especially Zn and Cu), because metallothioneins are such superb metal chelators. Metallothioneins bind metals into clusters of 3, 4 (see RHS), or 6 metals; one can think of these metal-thiolate clusters as being shrink-wrapped by the peptide. However, it occurred to us that the use of chains of a number of these metal-thiolate domains offers the possibility of chemically tuneable electrochemical or photochemical surface modifiers and as nanomachinery with nanomechanical properties. (Notice the change in size between 0, 8, and 12 Cd bound –RHS-lower.) In this work, the metal binding properties of the α -rhMT1a assembled into a chain of two and three concatenated domains, biological 'necklaces', will be studied by spectrometric techniques (emission, absorption, circular dichroism and mass spectrometry). Interactions within the structures will be modelled using molecular dynamics (MM3). These chains can be metallated with 8 or 12 Cd(II) to the 22, and 33 cysteinyl sulfurs in the α -rhMT1a, and $\alpha\alpha$ -rhMT1a proteins, respectively. This project will introduce you to straightforward molecular biology in making the protein, use of spectroscopy to follow metallation reactions (especially, the powerful electrospray mass spectrometry method). The molecular modelling (MM3) does not require a theoretical background as all the output is graphical. This is a bioinorganic project with a biotechnological focus – can we find novel applications for this special protein system? For more details check the board outside Dr Stillman's office. Please note: Dr Stillman will be speaking at a conference in Italy 15 -19th September. Please meet with Dr Stillman before 12th Sept. for more information.



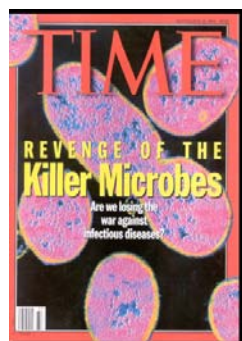
Professor Martin Stillman

ChB 064

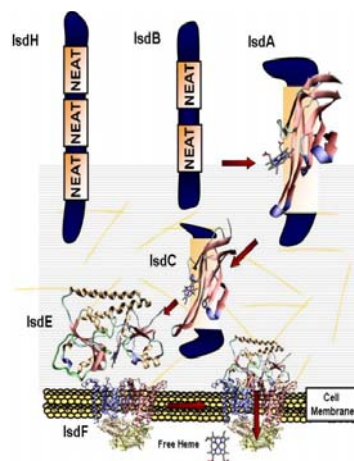
martin.stillman@uwo.ca

stillmangroup.ca

Understanding the key to healthy bacteria: Successful iron scavenging in humans.



The pathogenic bacteria *Staphylococcus aureus* in mammals extract their critically important iron requirement from the host environment. A recent hypothesis suggests that the iron porphyrin known as heme (used for oxygen binding in haemoglobin) is scavenged by a protein located on the cell wall (named Isd) and that this protein passes the heme along a chain of several (Isd) proteins (H to B to A to C to E finally across F that is located in the cell membrane – see the diagram) that eventually traps the iron inside the cell. This project involves study of the bioinorganic chemistry* of this system by probing how specific the heme scavenging is to answer the questions: Can the first protein in the chain ‘grab’ any porphyrin (see other projects for examples)? Does the metal in the porphyrin have to be iron (could it be zinc, or cobalt, etc.)? Does the protein ‘know’ that the iron is present. These are all vitally important questions that will help establish the mechanism for this chemistry. (As an aside, MRSA – Google it – is killing 1000’s Canadians each year.) Luckily, there are very good spectroscopic probes that we can use. The experiments will include measuring spectroscopic data for the model protein myoglobin. ESI-mass spectrometry will be used to determine the porphyrin and heme binding. Once we have established the porphyrin specificity, experiments will be carried out to see if information can be obtained about the handover of the porphyrin from the first protein to the next using these techniques with intensities monitored as a function of time. This project will provide an insight into the wonderful chemistry of large structures that bridge biology and chemistry in the cell. (See “Passage of heme-iron across the envelope of *Staphylococcus aureus*.” *Science*. 2003 299:906-9). It would be helpful to have taken biochemistry courses but not essential. *Bioinorganic chemistry focuses on the inorganic chemistry of biology. See the links on our web site for more details. For more details check the board outside Dr Stillman’s office. Please note: Dr Stillman will be speaking at a conference in Italy 15 -19th September. Please meet with Dr Stillman before 12th Sept. for more information.



Professor James Wisner

ChB 215

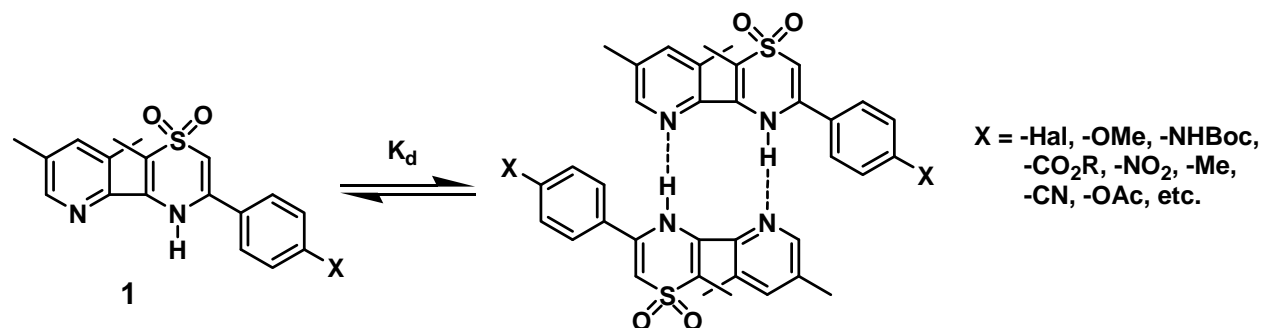
jwisner@uwo.ca

<http://publish.uwo.ca/~jwisner/>

Derivatization of a Self-complementary Molecule for Attachment to a Monomer/Polymer Backbone

Hydrogen bonding interactions between two molecules can be very specific when they are designed in a complementary manner. The classic and most widely recognized example of this phenomenon is the association of two single strands of DNA to form a double helix as a result, in part, of hydrogen bond complementarity between specific nucleobases (A-T and C-G). We have designed and synthesized an entirely synthetic system of oligomers composed of pyridine and 1,4-thiazine-1,1-dioxide heterocycles that associate in a complementary manner to form double helical complexes in a similar fashion.¹ Part of our group is currently engaged in attaching these subunits to monomeric or polymeric backbones to form *supramolecular* polymers. The reversible non-covalent interactions between the appended subunits yield materials with properties that are uniquely dependent on external stimuli (such as temperature and solvent) in contrast to traditional polymers.

The goal of your project will be to synthesize one of the simplest self-complementary subunits (X; shown below) with various functional groups attached at the *para*-position of the terminal phenyl ring. The result will be a series of molecules that may be further appended to existing monomer or polymer structures using these groups. In addition, these changes in molecular structure will be correlated against the magnitude of self-complexation the molecules display (e.g. when R = H the molecules dimerize with a constant $K_d = 400 \text{ M}^{-1}$ in CDCl_3).



The student working on this project will obtain experience in organic synthesis, purification, and structural analysis using NMR, MS, possible exposure to single crystal X-ray diffraction (depending on whether single crystals can be obtained of any of the synthesized compounds) and spectroscopic techniques such as UV-vis and fluorescence.

1. Li, J.; Wisner, J. A.; Jennings, M. C. *Org. Lett.* **2007**, *9*, 3267-69.

Professor James Wisner

ChB 215

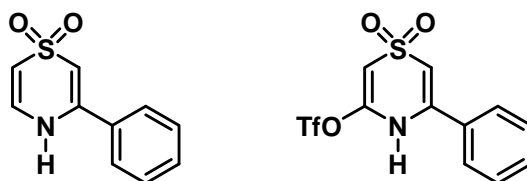
jwisner@uwo.ca

<http://publish.uwo.ca/~jwisner/>

Synthesis of 1,4-Thiazine-1,1-Dioxide Derivatives for Transition Metal Coupling Reactions

Hydrogen bonding interactions between two molecules can be very specific when they are designed in a complementary manner. The classic and most widely recognized example of this phenomenon is the association of two single strands of DNA to form a double helix as a result, in part, of hydrogen bond complementarity between specific nucleobases (A-T and C-G). We have designed and synthesized an entirely synthetic system of oligomers composed of pyridine and 1,4-thiazine-1,1-dioxide heterocycles that associate in a complementary manner to form double helical complexes in a similar fashion.¹ The synthetic route we have developed to synthesize these oligomers is highly facile. However, it would be very advantageous if smaller subunits could be coupled to one another (forming longer oligomers) or to other covalent scaffolds using modern transition metal catalysis in a single high yield step.

The goal of your project will be to synthesize the two 1,4-thiazine-1,1-dioxide derivatives pictured below. These two molecules will then be used as model substrates in transition metal catalyzed C-C bond forming reactions such as Heck, Suzuki, Stille, Sonogashira, etc. with particular attention to reaction optimization. Once developed, the transformation(s) will be applied to the synthesis of longer oligomeric species using the reaction conditions you have developed.



The student working on this project will obtain experience in modern organic synthesis, purification, and structural analysis using a variety of techniques.

1. Li, J.; Wisner, J. A.; Jennings, M. C. *Org. Lett.* **2007**, *9*, 3267-69.

Professor Mark S. Workentin

ChB 223; Laboratory ChB 203

mworkent@uwo.ca

publish.uwo.ca/~mworkent

Professor Yang Song

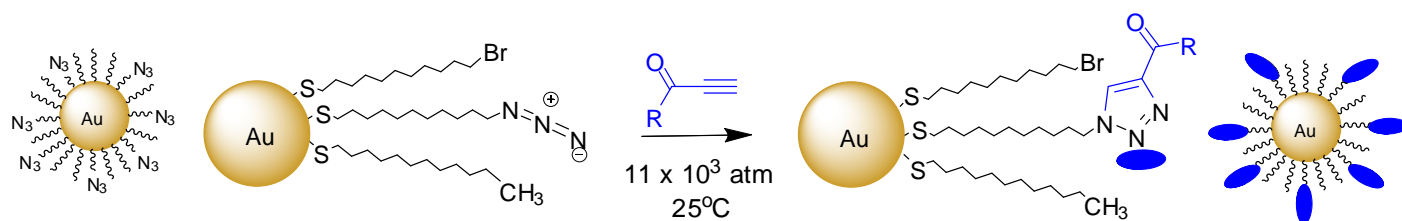
ChB 066

Yang.song@uwo.ca

http://publish.uwo.ca/~ysong56/

Spectroscopy and Kinetics of Hyperbaric Dipolar Cycloaddition Reactions on Monolayer-Protected Nanoparticles

The Workentin group utilizes photochemical and thermal reactions of organic substrates as monolayers on protected metal nanoparticles (MPN) to probe how reactivity is affected in these environments. The broader physical organic understanding gained about the reactivity of the probes on the MPN has led to the design and synthesis of substrates that permit the building of new architectures and assemblies in these materials. For example, because of the unique environment of the monolayer on these nanoparticles some cycloaddition reactions, such as the Diels-Alder reaction and dipolar cycloadditions like the reaction between an azide and alkyne are sluggish or impractical for their modification. We have discovered that the use of high pressures can be used to accelerate these reactions to the point that they can be utilized for the effective modification for materials application.¹⁻³ After preparing and characterizing suitable organic substrates and the desired nanoparticles in the Workentin laboratory the project will use the state-of-the-art facilities in Professor Song's laboratory to study the spectroscopy of systems under extreme pressure conditions. Specifically, the project involves examining a number of the high-pressure induced dipolar cycloaddition reactions of specific organic modified particles (like the one shown below) using a diamond anvil cell high pressure apparatus (see a description on other projects with Dr. Song) and a new FTIR microspectroscopy system. This will allow us to follow the course of the reactions and lead us to understand more clearly the factors that control the reactivity and the kinetics of these types of reactions on these particles under high pressure conditions.



A student working on this project will gain a broad research experience and will have the opportunity to do some preparative organic chemistry (synthesis) and product characterizations using standard organic analytical methods (NMR, Uv-vis and IR spectroscopies), prepare and characterize organic modified nanoparticles, obtain hands-on training on high pressure techniques and will develop analytical skills by using the modern spectroscopic techniques.

References: (1) J. Zhu, M. Ganton, M. A. Kerr, M. S. Workentin* *J. Am. Chem. Soc.* **2007**, 129, 4904-4905
 (2) Jun Zhu, Brandon Lines, Michael Ganton, Michael Kerr and Mark S. Workentin* *J. Org. Chem.* **2008**, 73, 1099-1105
 (3) Hossein Ismaili, Abdolhamid Alizadeh, Mark S. Workentin. *Submitted to Can. J. Chem.*

Professor Mark S. Workentin

ChB 223; Laboratory ChB 203

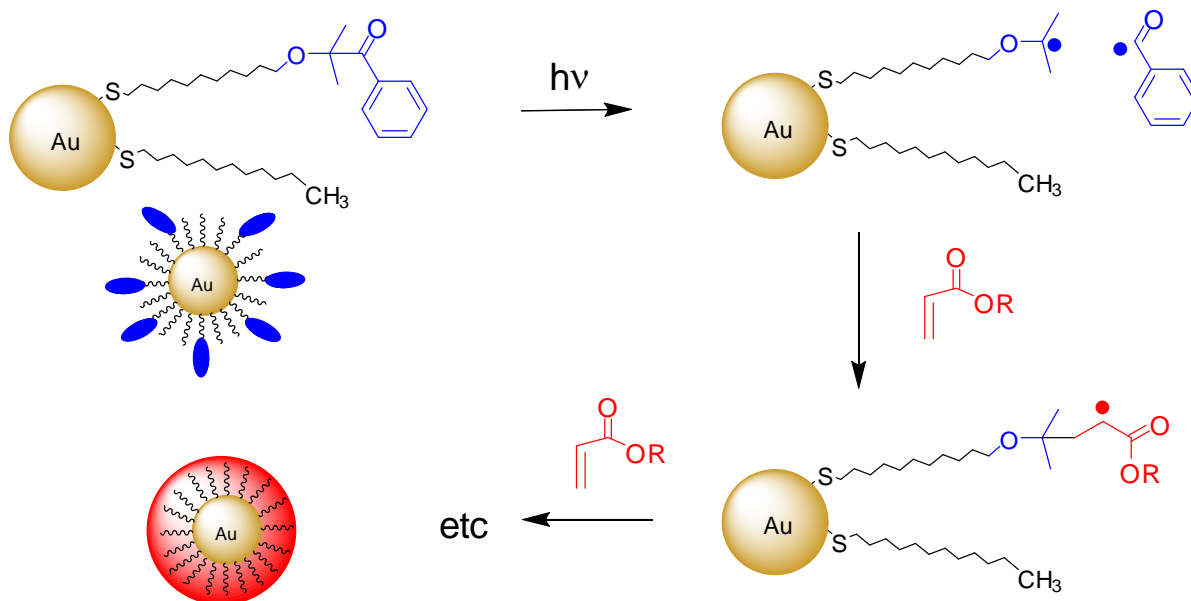
mworkent@uwo.ca

publish.uwo.ca/~mworkent

Photoinitiated Radical Reactions on Monolayer-Protected Gold Nanoparticles

The Workentin group utilizes photochemical and thermal reactions of organic substrates as monolayers on protected metal nanoparticles (MPN) to probe how reactivity is affected in these environments. The broader physical organic understanding gained about the reactivity of the probes on the MPN has led to the design and synthesis of substrates that permit the building of new architectures and assemblies in these materials.

In this project you will prepare an MPNs modified with interfacial groups that are commonly used photoinitiators in free radical polymerization reactions (see MPN-1 below as an example). Upon absorption of UV-light these functionalities will undergo photolysis to generate a benzoyl and a ketyl-type radical. The latter reacts with monomers to initiate a polymerization on the MPN. The resulting polymer modified MPNs will be characterized using a number of different monomers.



A student working on this project will gain a broad research experience and will have the opportunity to do some preparative organic chemistry (synthesis) and product characterizations using standard organic analytical methods (NMR, Uv-vis and IR spectroscopies), prepare and characterize organic modified nanoparticles, develop skills in organic photochemistry.

References: (1) Arnold J. Kell, Abdolhamid Alizadeh, Li Yang, Mark S. Workentin *Langmuir* 2005, 21(21); 9741-9746. (2) Arnold J. Kell, Robert L. Donkers and Mark S. Workentin *Langmuir*, 2005, 21 (2), 735 -742.

Professor J. Clara Wren

Professor David W. Shoesmith

ChB 019

jcwren@uwo.ca

http://publish.uwo.ca/~jcwren/

ChB 214

dwshoesm@uwo.ca

http://publish.uwo.ca/~ecsweb/

ELECTROCHEMISTRY OF STEEL CORROSION

Understanding the factors that can affect the corrosion of steel pipes or containers is an important concern for nuclear power plants. Corrosion involves metal oxidation and dissolution, and, hence, its kinetics depends on the aqueous redox condition and the physical and chemical nature of surface oxide formed during corrosion. Nuclear plant environment include the added challenge of fields of ionizing radiation that can affect the redox conditions in solution. To develop a fundamental understanding of radiation induced corrosion, the kinetics of steel corrosion in aggressive and dynamic redox conditions that simulate radiolytic environments are being studied. We are particularly interested in the chemical composition and phase structure of surface oxide film as a function of electrochemical and corrosion potential, and their effects on corrosion kinetics, Figure 1. In this project, the kinetics of oxide film formation and conversion on steel will be studied as a function of temperature, using various electrochemical analysis techniques, such as cyclic voltammetry, linear polarization and electrochemical impedance spectroscopy. The electrochemical study will be complimented by ex-situ Scanning Electron Cycle Microscopy and Raman spectroscopy.

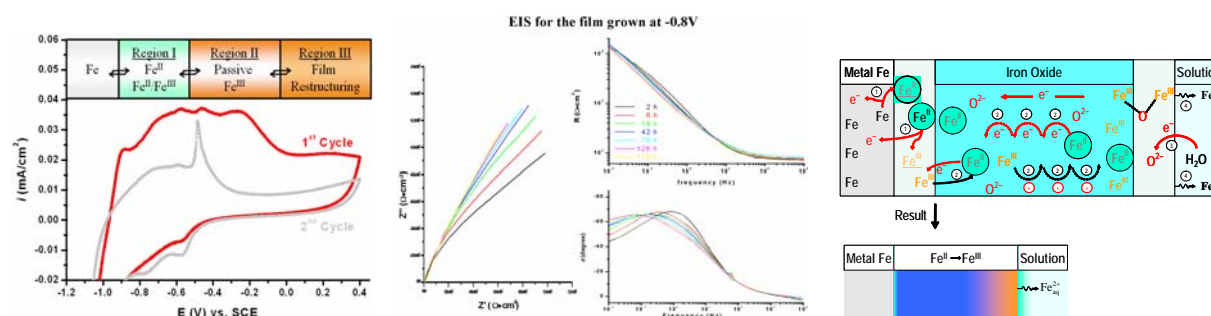


Figure 1: Some results from an electrochemical study of carbon steel corrosion at room temperature.

Professor J. Clara Wren

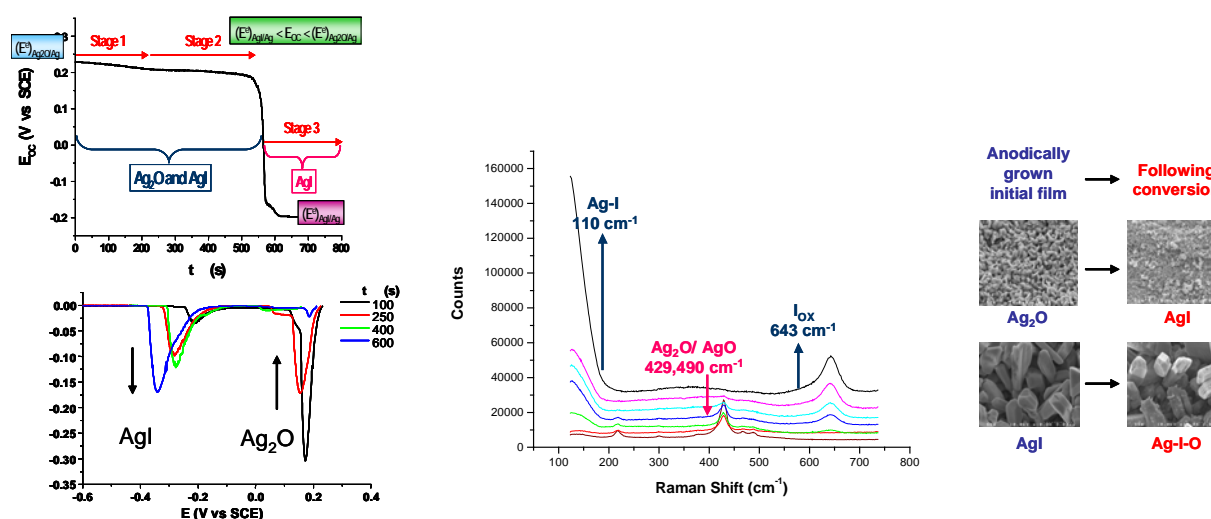
Chem 019

jcwren@uwo.ca

http://publish.uwo.ca/~jcwren/

SURFACE OXIDE – HALIDE CONVERSION ON Ag AND Cu

The rate of aqueous corrosion or dissolutive loss of materials depends on the physical and chemical nature of surface film, which can be significantly altered in the presence of chemically and/or electrochemically reactive anions (e.g., I^- and S^{2-}). The order of film formation (oxide vs halide) and the film growth and conversion mechanism will vary, depending on the metal and anion species involved and the system redox condition. By controlling these parameters, it may be possible to switch from a highly insoluble to a soluble state, or vice versa. Such a technology can be of a great value to the nuclear medicine community which needs to manage and control the delivery of tracer levels of radioiodines as diagnostic agents. The research objective is to establish the mechanism and kinetics of oxide/halide film growth and conversion, figure below. The metals and anions being studied include silver and copper, and Group 6 (O^{2-} , S^{2-}) and 7 (Cl^- , Br^- , and I^-) anions. Electrochemical techniques, such as cyclic voltammetry, potentiostatic control, and cathodic stripping, are used to control initial film thickness and composition, and follow the conversion kinetics. The electrochemical study is augmented by surface analyses, such as scanning electron microscopy and in-situ Raman spectroscopy.



Professor J. Clara Wren

ChB 019

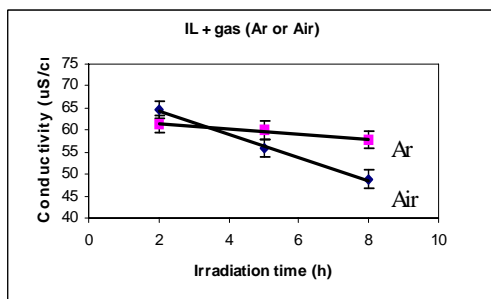
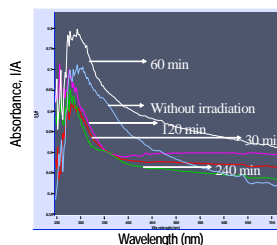
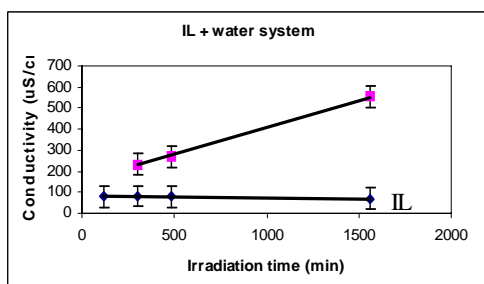
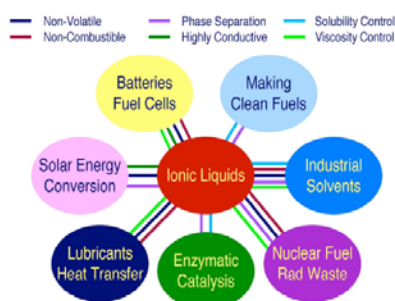
jcwren@uwo.ca

<http://publish.uwo.ca/~jcwren/>

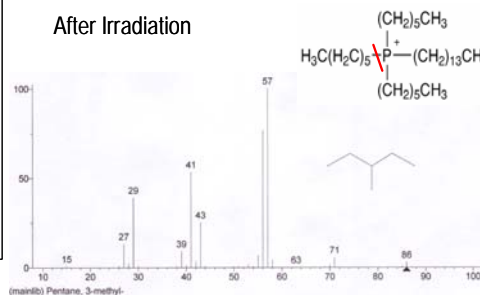
EFFECT OF RADIATION ON INTERFACIAL STABILITY AND TRANSFER OF IONIC LIQUIDS

Room temperature ionic liquids (ILs), made up of distinct ion pairs ("salts"), possess remarkable properties, which make them ideal materials for various applications. Ionic liquids have already replaced volatile, hydrocarbon solvents in some industrial processes, and are being considered for use in separation technologies for inherently safe processing of nuclear fuel and radioactive waste. For the nuclear applications it is important to understand how unusual environment, in particular, radiation, will affect the physical and chemical properties of ILs which determine separation efficiency. The objective of the research is to investigate the radiation stability of ILs, and the effect of radiation on *gas - IL* and *aqueous - IL* interfacial stability and transfer processes. Ionic liquid in contact with water or gas will be irradiated in a ^{60}Co γ -cell. The conductivity of IL and water, and chemical speciation will be determined as a function of irradiation time, using an AC impedance method for conductivity, UV-Vis spec. for aqueous speciation and GC/MSD/TCD/ECD for gaseous speciation.

Featured in the President's FY 2005 Budget Request to Congress
(DOE/Science/Basic Energy Sciences/Chemical Sciences, Geosciences, and Biosciences)



After Irradiation



Professor Ken Yeung

MSB 374

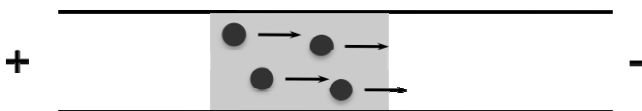
kyeung@uwo.ca

<http://publish.uwo.ca/~kyeung/>

Nanoliter-volume protein sample purification with capillary electrophoresis

Tris buffered saline (TBS) and phosphate buffered saline (PBS) are commonly used in washing biological samples and solubilizing proteins. However, these buffers are not compatible with protein analysis by mass spectrometry (MS). Purification by dialysis or solid-phase extraction is therefore performed, but they require relative large sample volume (micro- to milliliters).

Capillary electrophoresis (CE), a separation technique, will be used in this project to develop a nanoliter volume protein purification methodology. The original protein sample will be introduced into the capillary, and positioned in between sections of MS-compatible buffers. The idea is to selectively extract the protein molecules out of the original background using an applied electric field.



Subsequent to purification by CE, the protein molecules are deposited on a target plate for analysis with matrix-assisted laser desorption/ionization (MALDI) MS.

The following references are examples of other nanoliter-volume protein sample preparation methods developed using CE and MALDI MS in my group.

“Nanoliter-Volume Protein Enrichment, Tryptic Digestion, and Partial Separation based on Isoelectric Points for MALDI-MS”, Chandra A. Nesbitt, Kristina Jurcic and Ken K.-C. Yeung. *Electrophoresis*, Vol. 28, pages 466 - 474 (2008).

“An Integrated Procedure of Selective Injection, Sample Stacking and Fractionation of Phosphopeptides for MALDI MS Analysis”, Haixia Zhang, Graeme K. Hunter, Harvey A. Goldberg, Gilles A. Lajoie and Ken K.-C. Yeung. *Analytica Chimica Acta* Vol. 581, pages 268-280 (2007).

Professor Ken Yeung

MSB 374

kyeung@uwo.ca

<http://publish.uwo.ca/~kyeung/>**Analysis of Bio-char for pesticidal activity**

Pyrolysis, or thermal cracking in the absence of oxygen, is being investigated as a technology in transforming low-value plant residues into sources of fuels and valuable chemicals. The student in this project will join a multi-disciplinary research team, comprised of the chemical engineering and chemistry departments, the Institute for Chemicals and Fuels from Alternative Resources (ICFAR)¹ and Agriculture and Agric-Food Canada (AAFC)², to study the value of the pyrolysis products from various plant residues.

In general, pyrolysis produces matters in all three phases of gas, liquid and solid. All previous studies focused on the gases and liquids, and chemicals with pesticidal properties had been identified in the liquid phase. In this work, the objective is the analysis the solid phase (bio-char) of the pyrolysis products, particularly in looking for any pesticidal activities. Extraction with aqueous, as well as organic solvents will be performed on the bio-char, to solubilize the potentially active chemicals. The extracted fractions will then be tested for inhibition activities on a variety of insects, bacteria and fungi (at AAFC). Gas-chromatography mass spectrometry will be used identify the composition of the active fractions.

1. Professors Cedric Briens and Franco Burruti, <http://www.eng.uwo.ca/icfar/>
2. Drs. Ian Scott and Kenneth Conn

Supervisor: Leo Lau

Room number: G1, WSC

e-mail address: llau22@uwo.ca

Web address: www.uwo.ca/ssw

Co-supervisor H.Y. Nie

Room number G1, WSC

e-mail address: hnie@uwo.ca

Web address: www.uwo.ca/ssw

Chemistry with a tiny hammer: cross-linking polymer precursors for the fabrication of novel ultrathin membrane with specific functional applications

A new synthetic approach for the formation of ultrathin molecular films with customizable properties has recently been invented by Lau and coworkers [see, e.g., J. Amer. Chem. Soc. 126(2004)12336; Chem. Comm. 29(2006)3124; and Chem. Euro. J. 13(2007)3187]. In this approach, C-H bonds of organic precursor molecules condensed on a substrate are cleaved by hitting the “H”s of the molecules with a beam of “**H**” projectiles having an adequate kinetic energy. The simple kinematics nature that **H**--X collision is only effective in energy transfer when X is H as other atoms are much heavier than H. Hence, the tiny hammer of 5-10eV **H** does no harm to the target molecule except “chiselling” hydrogen away to create a carbon radical. The subsequent recombination of carbon radicals gives a cross-linked molecular thin film, with virtually no other changes of the chemical functionalities of the precursor molecules. Since the cross-linking reactions are mainly driven by kinematics, the traditional reliance on chemical additives and catalysts are lifted. In 2007, a production prototype chemical reactor was constructed at Western to prepare for the research and development of practical industrial applications of this “chemistry with a tiny hammer” approach. This R&D program has indeed been launched in 2008 by a multidisciplinary team of researchers from Western and LANXESS Inc. (Sarnia), with funding from LANXESS, OCE and NSERC. The program now has 10 students and 5 PDFs making new precursor molecules and “hammering” them onto various polymer substrates for the development of industrially relevant applications.

The proposed 4490 project is an extension of this R&D program, with the objective of “hammering” precursor molecules to novel ultrathin membranes with specific functional applications. Two students can be accommodated and be trained to synthesize the membranes with the “hammering” approach, characterize their microstructural and chemical properties with SEM, AFM and XPS, and test their functional performance with a model device. The students will interact with the researchers of the Western and LANXESS joint team.

Supervisor: Leo Lau

Room number: G1, WSC

e-mail address: llau22@uwo.ca

Web address: www.uwo.ca/ssw

Co-supervisor: Sridhar Ramamurthy

Room number G1, WSC

e-mail address sramamur@uwo.ca

Web address www.uwo.ca/ssw

Oxidation of steam generator tubing under primary side water chemistry

Steam generator (SG) tubing is used as heat exchangers to transfer heat from the primary side of the nuclear reactor to its secondary side. In service, they are susceptible to a phenomenon known as stress corrosion cracking (SCC) which occurs when a susceptible material under stress (residual or external) is exposed to an aggressive environment. This results in the failure of SG tubing and causes nuclear reactor shutdown and leads to expensive tubing repair/replacement process.

In this study, stressed Alloy 600 (75%Ni, 15%Cr and 10%Fe) and Alloy 800 (40%Ni, 20%Cr and 40%Fe) SG tubing samples will be exposed to primary water chemistry (steam/H₂ atmosphere at ~ 480 °C) for various periods. Characteristics of the oxide layer formed on these specimens as a function of the exposure time will be investigated using a number of advanced analytical techniques available at Surface Science Western. It is expected that Alloy 600 SG tubing samples will be more susceptible to SCC compared to Alloy 800 SG tubing samples. Hence, the objective of this study is to determine the role of alloy composition and the exposure conditions in influencing the development of oxide layer, its morphology and chemical composition and its relative susceptibility to SCC. Working on this project will also lead to networking opportunities with personnel from Ontario's nuclear industry.

Professor David Shoosmith

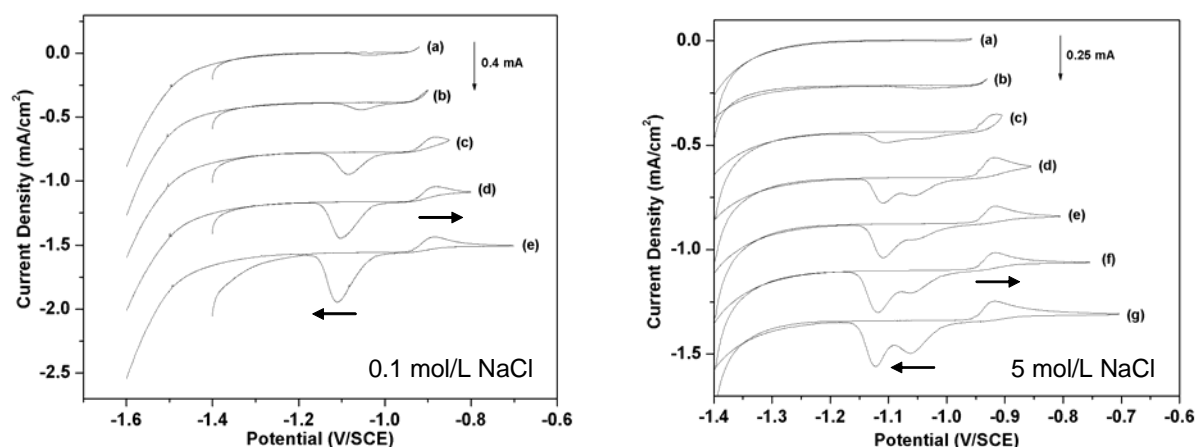
ChB 214

dwshoesm@uwo.ca

<http://publish.uwo.ca/~ecsweb/>

The Electrochemical Kinetics of Sulphide Film Formation on Copper

Our primary interest is in the formation of sulphide films on copper (Cu_2S , $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{1.75}\text{S}$), a possible degradation mechanism for copper nuclear waste containers. As illustrated in the figure, anodic film formation ($\text{Cu} \rightarrow \text{Cu}_x\text{S}$) on the forward potential (negative to positive) scan leads to either a single or dual reduction process, observed on the reverse scan, depending on the anodic limit and the $[\text{Cl}^-]$. These differences will be determined by the mechanism and kinetics of film formation, involving either solid state defect transport, solution-mediated dissolution/film deposition, and/or stress-driven recrystallization.



The mechanism and kinetics of this process will be investigated using a range of electrochemical and analytical techniques. The conductive and structural properties of films grown under potential control and open circuit conditions will be investigated by electrochemical impedance spectroscopy. The film morphologies will be examined by SEM, and the porosities investigated using cross sections prepared with a focussed ion beam. Film compositions will be determined using X-ray diffractometry and energy dispersive X-ray analysis.

Professor David Shoemith

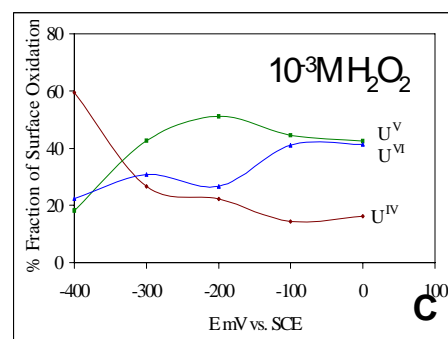
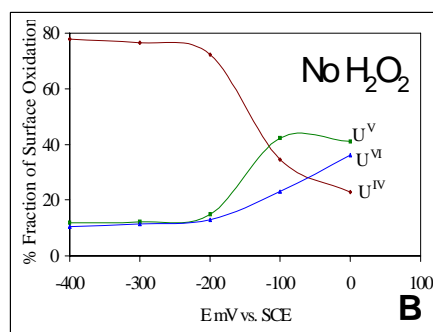
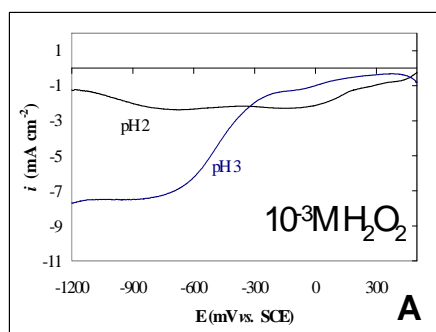
ChB 214

dwshoesm@uwo.ca

<http://publish.uwo.ca/~ecsweb/>

Electrochemical Kinetics of Reactions between Uranium Dioxide and Hydrogen Peroxide

The oxidative dissolution of UO_2 is the key reaction leading to the release of radioactive species from used nuclear fuel under waste disposal conditions. Oxidation is driven by H_2O_2 , the primary oxidant produced by the radiolytic decomposition of water. The mechanism of this reaction is complicated, and the kinetics very dependent on a balance of electrochemical and chemical reactions which change the composition of the UO_2 surface. For instance, Figure A shows the sensitivity to pH of the H_2O_2 reduction current as a function of applied electrochemical potential, and Figures B and C show how H_2O_2 changes the composition of the surface (as determined by X-ray Photoelectron spectroscopy (XPS) on electrochemically treated surfaces at pH = 2).



The mechanism and kinetics of this reaction will be investigated electrochemically using rotating disk electrodes to control diffusive transport. Changes in surface structure will be studied by scanning electron microscopy and in surface composition by XPS. The bulk structural properties of the UO_2 will be characterized by Raman spectroscopy. The primary goal will be to elucidate the effects of pH and solution anions (e.g. Cl^- , SO_4^{2-}) on the kinetics.

Professor Styliani Consta

ChB 071

styliani.constas@gmail.com

<http://www.theory.chem.uwo.ca/>**Molecular simulations of charged droplets containing macroions**

Charged liquid droplets composed of water molecules and ions are abundant in the atmosphere and constitute the environment where many atmospheric chemical reactions take place. The charge of the droplets is due to excess charge arising by the presence of ions. In analytical chemistry such droplets play a crucial role in electrospray mass spectrometry. We study these systems by molecular simulations and we have developed techniques that allow us to estimate the quasi-equilibrium structures of the systems as well as the dynamics of their break-down due to the excess charge and the reactions that may take place. Our current research is in the fragmentation of these systems in the presence of macroions such as charge polypeptides. The student involved in the project will use our software to simulate charged polypeptides in the droplets and characterize their quasi-equilibrium states, and the energetics and entropic effects involved in the fragmentation of the droplets. Computer programming skills are helpful for the project but not required. These skills can be developed in the course of the project.

1. Consta, S; Mainer, KR; Novak, W. 2003. Fragmentation mechanisms of aqueous clusters charged with ions. *JOURNAL OF CHEMICAL PHYSICS* 119 (19): 10125-10132.
2. Consta, S. 2002. Fragmentation reactions of charged aqueous clusters. *JOURNAL OF MOLECULAR STRUCTURE-THEOCHEM* 591: 131-140.
3. Ichiki, K; Consta, S. 2006. Disintegration mechanisms of charged aqueous nanodroplets studied by simulations and analytical models. *JOURNAL OF PHYSICAL CHEMISTRY B* 110 (39): 19168-19175.

Professor Styliani Conostas

ChB 071

styliani.constas@gmail.com

<http://www.theory.chem.uwo.ca/>**Molecular simulations of diffusion in zeolites**

Zeolites are micro-porous materials often used as catalysts. They have numerous applications in petrochemical industry, agriculture, medicine to name few. Molecular simulations will be used to study the diffusion of benzene and toluene through the zeolite channels. The model for the zeolite is a silicate matrix with intersecting channels in which the diffusion of various substances take place. The zeolite atomic sites and the benzene and toluene molecules are modelled by empirical force fields. The simulations will be performed with software that will be made available to the student and the use of combination of Molecular Dynamics and Monte Carlo techniques. The diffusion of aromatic compounds in zeolites has been studied for many years by several research groups. The novel aspect of these simulations is the application of techniques developed in our group for the study of the dynamics of diffusion. Computer programming skills are helpful for the project but not required. The skills can be developed in the course of the project.

Professor Zhifeng Ding

ChB 016

zfding@uwo.ca

<http://publish.uwo.ca/~zfding/>

Investigating Zircalloys Using Scanning Electrochemical Microscopy

Scanning electrochemical microscopy (SECM) is a type of scanning probe microscopy. Topographical and surface reactivity images are generated through the conversion of a current obtained from an ultramicroelectrode (UME) tip. This tip is scanned over a sample surface which is submerged in a solution containing a redox agent and electrolyte. A positive Faradaic potential is applied to the tip causing the redox agent to become oxidized at the tip. At regions of higher reactivity, the oxidized agent gains electrons from the sample surface and gets reduced; thus, producing a greater current at the UME tip. At regions of lower reactivity, the oxidized agent gains less electrons (or in the case of a pure insulating substrate it gains none) and produces a small current at the UME. This current gathered at the tip is converted into a 3D plot via computer. Thus, the topography and/or the reactivity of a sample surface can be observed in an image.

In recent years it has been shown that titanium alloy grains and boundaries could be investigated using SECM. Regions of higher reactivity were shown to correspond to imperfect oxide formation on the grain boundaries. Due to the accumulation of impurities and defects at the boundaries, the oxide over these sights was defective, allowing for electrons to pass. Regions of lower reactivity were shown to correspond to the more uniform oxide formed on the grains of the metal where the underlying metal had a higher purity and less defects. Thus, the surface microstructure of the titanium sample could be determined using SECM.

Zirconium metals, like titanium, are self passivating. Due to their ability to form and regenerate oxides on their surface, zirconium is a good candidate metal for use in areas where corrosion is not wanted. Since bare zirconium metal is very reactive, when it comes into contact with oxygen it forms an oxide layer on its exposed surface. Thus, if the oxide is ever punctured through, the exposed bare metal will reform its oxide, once again protecting itself from corrosion. Along with its resistance to corrosion, zirconium's low neutron absorption makes it a great candidate metal for the use in the nuclear industry.

In this 4490 project we would like to characterize some important zircalloys and hopefully determine their surface microstructure using the same SECM technique as was used for the titanium samples. Through this project the student will be familiar with the scanning electrochemical microscopy technique and analytical instrumentation.

Professor Zhifeng Ding

ChB 016

zfding@uwo.ca

<http://publish.uwo.ca/~zfding/>**Electrogenerated chemiluminescence of polymers**

Electrochemistry is to study the relationship between chemical reactions and the electric work. In this 4490 project, electric work is employed to generate radical cations and anions of some luminescent polymers, which react in the vicinity of the working electrode and promote the polymers to excited states. The excited states go back to the ground states and photons (the smallest unit of a light) are released. This process is called electrogenerated chemiluminescence (ECL).

In our lab, ECL can be generated by simply applying a voltage to an electrochemical cell containing the polymers. Two areas where ECL is really beginning to make an impact are biology and light-emitting diode (LED) technology. Indeed, LEDs are those little colored lights you see in electronic equipment, household appliances, toys, on signs, on vehicles, and many other places. Red, yellow, green ones are the most common, since they have been around the longest. Other colors, like turquoise, blue, pure-green and white are much newer, so you may not see many of them yet. But you will see in this 4490 project.

Our luminescent polymers can be dissolved in dichloromethane and produce quite bright emission. They may be useful in LEDs.

We propose to characterize the polymers by using UV-vis spectroscopy, luminescence spectroscopy as well as electrochemistry. Light emission will be monitored by our ECL set-up. Through this project, the student will be familiar with modern electrochemistry, spectroscopic methods and analytical instrumentation. Most importantly, the student will learn the electrochemical arts to tune the ECL of the polymers.