



Physical & Environmental Sciences
UNIVERSITY OF TORONTO
SCARBOROUGH

DIRECTED RESEARCH IN CHEMISTRY

CHMD90/91

RESEARCH PROJECTS BOOKLET

2016 Fall – 2017 Winter

[CHMD90Y3](#) & [CHMD91H3](#) (Fall 2016 - Winter 2017)
DIRECTED RESEARCH IN CHEMISTRY

Course Coordinators: Prof. Artur Izmaylov and Prof. Frank Wania

Admittance requirements:

- A Cumulative Grade Point Average of at least **2.3**. Students who do not meet this requirement are encouraged to enroll in [CHMD92H3](#) instead.
- Completion of at least 15 full credits
- Completion of at least 1.0 full credits of C-level CHM courses containing a lab component (i.e. CHMC16H3, CHMC31Y3, CHMC41H3 or CHMC42H3, CHMC47H3, BIOC23H3)

Plan of action for students planning to register in [CHMD90Y3](#) or [CHMD91H3](#)

1. Look through the projects listed below.
2. **Find a research supervisor** who will take you to do a project of your choice (to expedite the process send to your prospective advisor your unofficial transcript along with the letter of intent).
3. Obtain the D90/91 form from the registrar's office and fill the first page with your supervisor.
4. Come to Prof. Izmaylov or Prof. Wania for the signature and bring your unofficial transcript. You **MUST** have your supervisor signature and the project title at this step.
5. Obtain DPES Chair's signature.
6. Return the yellow slip to Prof. Izmaylov [you can ask a departmental program assistant Annie Kostadinova to leave the yellow slip in Prof. Izmaylov's mail box], the white slip to the registrar's office and keep the pink one to yourself

Note, it will be impossible to enroll without finding the research supervisor, thus this search is crucial. You could diversify your search by initiate conversations with more than one faculty members offering projects.

Course description:

These courses involve participation in an original research project under the direction of a faculty supervisor. Approximately 260 hours of work are expected in [CHMD90Y3](#) and 130 hours in [CHMD91H3](#). Topics will be selected in conference with the course coordinator who will provide project descriptions from potential faculty supervisors. Progress will be monitored through periodic consultation with the faculty supervisor as well as the submission of written reports. The final results of the project will be presented in a written thesis as well as an oral and/or poster presentation at the end of the term.

Prerequisite: Permission of a course coordinator.

Exclusion: Students may take either [CHMD90Y3](#) or [CHMD91H3](#) but not both. Note that [CHMD92H3](#) is an exclusion to both [CHMD90Y3](#) and [CHMD91H3](#).

EVALUATION FOR CHMD90:

Submission deadline for the mid-term progress reports: You will be submitting your mid-term reports to your supervisors in **the second week of January 2017**.

Mid-term progress presentation or report 10% (Supervisor will communicate this mark to the course manager by **the end of the second week of January 2017**)

Submission deadline for the draft thesis reports: You will be submitting your draft thesis reports to your supervisors by **April 3rd, 2017**.

Final report is due April 14th, 2017. Find two readers among faculty or postdoctoral fellows. (Grade contribution 80%: 30% Supervisor, 1st reader: 25%, 2nd reader: 25%)

Final oral presentation 10% (Tentative date: **April 21st, 2017**)

EVALUATION FOR CHMD91:

Submission deadline for the mid-term progress reports: You will be submitting your mid-term reports to your supervisors in **the third week of October 2016**.

Mid-term progress presentation or report 10% (Supervisor will communicate this mark to the course manager by **the end of the third week of October 2016**)

Submission deadline for the draft thesis reports: You will be submitting your draft thesis reports to your supervisors by **November 25th, 2016**.

Final report is due December 2nd, 2016. Find two readers among faculty or postdoctoral fellows. (Grade contribution 80%: 30% Supervisor, 1st reader: 25%, 2nd reader: 25%)

Final oral presentation 10% (Tentative date: **December 9th, 2016**)

Guidelines regarding the thesis reports: The thesis reports should be prepared in max. 20 pages, single-spaced using Times New Roman font-12 including the following sections:

1. **Title page** with the title of your project, your name and number, your supervisor(s) name, the course code, and the date of submission. **(1-page)**
2. **Table of Contents (1-page)**
3. **Abbreviations (if necessary, 1-page)**
4. **Introduction (max. 3 pages)**
5. **Experimental** with subsections such as reagents and chemicals, instruments, and procedure.
6. **Results and Discussion**
7. **Conclusions**
8. **Acknowledgments**
9. **References (max. 2 pages)** References should be prepared using the *Journal of American Chemical Society* guidelines.

Appendix can be attached to your thesis report with unlimited page numbers displaying raw experimental results such as MS, NMR, and IR data.

Safety courses

Laboratory Safety course: Winter Term dates for the UTSC course will be announced on the following link:
<http://www.ehs.utoronto.ca/Training/training.htm#ChemicalSafety>
(You should give a copy of your certificate to your supervisor)

Biosafety course: Please, consult with your supervisor whether a Biosafety Certificate is required for your project. The course dates can be found from the following link:
<http://www.ehs.utoronto.ca/services/biosafety/training.htm>
(You should give a copy of your certificate to your supervisor)

WHMIS certification submission deadline: Fri, 9 September 2016
(Please, see the instructions on the following page. After finishing the online training successfully, you should give/email a copy of your certificate to your supervisor) Online WHMIS course page:
<http://www.ehs.utoronto.ca/Training/Learning.htm#WHMIS>

Instructions on Accessing the Online WHMIS Training

Here are the directions so that employees and students can easily access the Online WHMIS training.

1. Go to the University of Toronto home page.
2. Click on the "Portal" link.
3. Click on the "Log in to the Portal" picture.
4. Enter your UTORid, and password.
5. Click on the "Community" tab in the top right hand corner.
6. Click on "Environmental Health and Safety" in the "Organization Catalog".
7. Find Organization ID "EHS 005" with the Organization Name "WHMIS". Click on the down arrow next to "EHS 005", select "Enroll" then follow the prompts.
8. Click "submit" on the first screen and then "OK" on the second.
9. You should be at a page titled "Getting Started".
10. Click on the blue "Course Content" button on the top left hand side, and you

should see "Course Presentation" in the main window. Click on the link and the presentation should start. If you get a "File Access Error", then click on the "logout" icon at the top of the screen and close your browser. Log back in to the Portal, and you should see the course title on your "My Page" tab under "My Organizations Plus". Click on the name of the course to return to "Getting Started" and start this step (9.) again. The "My Page" is the page that shows up when one first logs onto the portal.

11. When you have finished the course presentation, then you can do the quiz.

Notes

1. Within the presentations themselves, you can go back a slide by clicking on the rewind symbol, and you can also navigate by clicking on the slide names that appear under the "Outline" tab on the right hand side, or by clicking on the thumbnails found under the "Thumb" tab.

2. It is not necessary to do all of the presentation or quiz at once. The presentation will appear on your "My Page" tab under "My Organizations Plus". The "My Page" is the page that shows up, when one first logs onto the portal.

***Note: Please, consult your supervisor about the attached NSERC Consent Form on the next page.**



Appendix D (Form 100) Consent to Provide Limited Personal Information About Highly Qualified Personnel (HQP) to NSERC

NSERC applicants are required to describe their contributions to the training or supervision of highly qualified personnel (HQP) by providing certain details about the individuals they have trained or supervised during the six years prior to their current application. HQP information must be entered on the Personal Data Form (Form 100). This information includes the trainee's name, type of HQP training (e.g., undergraduate, master's, technical etc.) and status (completed, in-progress, incomplete), years supervised or co-supervised, title of the project or thesis, and the individual's present position.

Based on the federal *Privacy Act* rules governing the collection of personal information, applicants are asked to obtain consent from the individuals they have supervised before providing personal data about them to NSERC. In seeking this consent, the NSERC applicant must inform these individuals what data will be supplied, and assure them that it will only be used by NSERC for the purpose of assessing the applicant's contribution to HQP training. To reduce seeking consent for multiple applications, applicants will only need to seek consent one time for a six-year period. If the trainee provides consent by e-mail, the response must include confirmation that they have read and agree to the text of the consent form.

When consent cannot be obtained, applicants are asked to not provide names, or other combinations of data, that would identify those supervised. However, they may still provide the type of HQP training and status, years supervised or co-supervised, a general description of the project or thesis, and a general indication of the individual's present position if known.

An example of entering HQP information on Form 100 (with and without consent):

Name	Type of HQP Training and Status	Years Supervised or Co-supervised	Title of Project or Thesis	Present Position
Consent Received from Marie Roy				
Roy, Marie	Undergraduate (Completed)	Supervised 1994 - 1997	Isotope geochemistry in petroleum engineering	V-P (Research), Earth Analytics Inc., Calgary, Alberta
Consent Not Obtained from Marie Roy				
(name withheld)	Undergraduate (Completed)	Supervised 1994 - 1997	Isotope geochemistry	research executive in petroleum industry - western Canada

Consent Form

Name of Trainee	
Applicant Information	
Name	
Department Physical & Environmental Sciences (Scarboror	Postsecondary Institution Toronto
I hereby allow the above-named applicant to include limited personal data about me in grant applications submitted for consideration to NSERC for the next six years. This limited data will only include my name, type of HQP training and status, years supervised or co-supervised, title of the project or thesis and, to the best of the applicant's knowledge, my position title and company or organization at the time the application is submitted. I understand that NSERC will protect this data in accordance with the <i>Privacy Act</i> , and that it will only be used in processes that assess the applicant's contributions to the training of highly qualified personnel (HQP), including confidential peer review.	
_____ Trainee's signature	_____ Date
Note: This form must be retained by the applicant and made available to NSERC upon request.	

Project #1

Supervisor: J. DONALDSON

Co-supervisor (if any):

Office: SW 632A

Sub-discipline: Phys / Environ Chem

Laboratory: TRACES

Course code: CHM D90/91

e-mail: jdonalds@utsc.utoronto.ca

of students: 1

Web:

CAN WE MEASURE HYDROGEN BONDING TO SOLVENT USING RAMAN SPECTROSCOPY?

Abstract

Dissolved halide anions are known to perturb the intensities and shapes of the bands in the Raman spectra of water (both the OH stretching and the HOH bending modes) and some alcohols. As well, there have been some studies that have measured new, low-energy vibrations in the spectra of aqueous halide solutions; these have been assigned to hydrogen bonding between the anion and the solvating water molecules. This project will investigate the influence of a suite of dissolved anions on the Raman spectra of small alcohols, acetone, DMSO and mixtures of these with water, to look for trends in hydrogen bonding as a function of anion and cation identity. The experimental results will be analysed using simple models for vibrational spectra, and perhaps using quantum chemical methods.

- Learning outcomes. Students will gain experience in a (directed) independent research project whose outcome is not known beforehand. Specific experience will be gained in using modern Raman spectrometers and the analysis of spectroscopic data and the accurate and careful preparation of solutions.
- Required training certificates. Students will need to be trained in the use of the instrument and have access to TRACES.
- Our expectations from student. The student will meet weekly with the supervisor, discuss results and devise an updated plan for work. Student will prepare the appropriate solutions, measure their Raman spectra, save the results and create appropriate plots and analyses. The student will prepare (with some editorial guidance from the supervisor) a final report.

References for further reading

Hidaka et al., *J. Solution Chem.* **2003**, 32, 239-251.

Rull, *Pure Appl. Chem.*, **2002**, 74, 1859–1870.

Heisler et al., *J. Phys. Chem. B* **2011**, 115, 1863–1873

Project #2

Supervisor: J. DONALDSON

Co-supervisor (if any):

Office: SW 632A

Sub-discipline: Phys / Environ Chem

Laboratory: TRACES

Course code: CHM D90/91

e-mail: jdonalds@utsc.utoronto.ca

of students: 1

CAN WE TRACK OXIDATION OF DOM SPECTROSCOPICALLY?

Abstract

Dissolved organic matter (DOM), generally formed from biogenic material, is pretty ubiquitous in natural fresh and salt water systems. Such compounds, when they absorb solar radiation, can produce oxidizing species, such as OH and singlet oxygen, in solution. Although there are many different compounds involved, and thus spectral characteristics, there is often a distinctive region in the excitation – emission spectral maps that is assigned to common DOM chromophores. A recent report has shown that the spectral map of DOM exposed to photogenerated OH oxidant shows differences from the parent map. The purpose of this study is to explore and try to quantify this effect, to determine whether there is a way to infer oxidative lifetime (that is, how long the DOM has been exposed to oxidants) through excitation – emission maps.

- Learning outcomes. Students will gain experience in a (directed) independent research project whose outcome is not known beforehand. Specific experience will be gained in using modern Raman spectrometers and the analysis of spectroscopic data and the accurate and careful preparation of solutions.
- Required training certificates. Students will need to be trained in the use of the instrument and have access to TRACES.
- Our expectations from student. The student will meet weekly with the supervisor, discuss results and devise an updated plan for work. Student will prepare the appropriate solutions, measure their excitation and emission spectra, save the results and create appropriate plots (the excitation – emission maps) and analyses. The student will prepare (with some editorial guidance from the supervisor) a final report.

References for further reading

Jee et al., *Water Sci. Technol.* **2010**, 65, 340 – 346.

Project #3

Supervisor: Alen Hadzovic

Co-supervisor (if any):

Office: EV564

Sub-discipline: Inorganic Chemistry

Laboratory: EV216

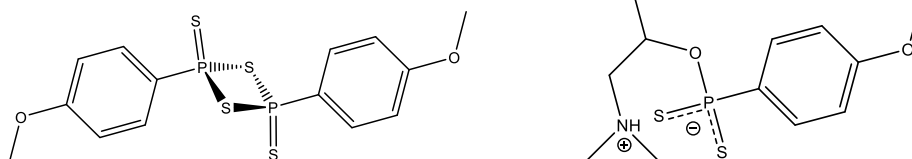
Course code: CHMD90Y/91H

e-mail: ahadzovic@utsc.utoronto.ca

of students: 1

Coordination Chemistry of Ligands Derived from Lawesson Reagent

The goal of this project is synthesis and characterization of new ligands and their complexes derived from Lawesson reagent (left structure). One such ligand (right structure) has been recently synthesized and fully characterized [1].



The project has two major parts: (1) synthesis of new similar ligands to the one shown above using different nucleophiles able to cleave Lawesson reagent (here is also important to confirm the reproducibility of procedures reported in [1] for recent ligands) and (2) synthesis and characterization of metal complexes of these ligands. The coordination chemistry will focus on late, first row transition metals (Ni, and Cu in particular). If the complex synthesis is successful, their reactivity will be further explored.

- Learning outcomes: better understanding of structural and coordination chemistry, practical experience in advanced synthetic techniques (such as oxygen-free environments), advanced IR, NMR and X-ray techniques.
- Required training certificates: relevant training on analytical instruments (IR, UV-Vis and NMR) will be provided before the actual work can start
- Our expectations from students: to work in the laboratory environment respecting all safety procedures and requirements, to be able to work under minimal supervision when dealing with basic synthetic and analytic procedures, to regularly inform the supervisor on the project progress, be versatile in literature search, be an excellent team-player.

References:

[1] This is a continuation of Li, S., Hadzovic A., CHMD90Y3 results, 2015-16.

Project #4

Supervisor: Alen Hadzovic

Co-supervisor (if any):

Office: Ev564

Sub-discipline: Inorganic Chemistry

Laboratory: EV216

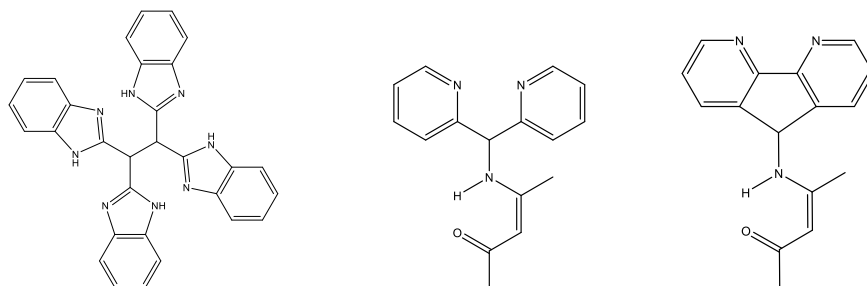
Course code: CHMD90Y/91H

e-mail: ahadzovic@utsc.utoronto.ca

of students: up to 2

Multimetallic complexes – Proof of concept exploratory research

This project focuses on the design, synthesis, characterization and coordination chemistry of ligands capable of bonding to more than one metal center. Two possible target ligand structures are:



Different substituents on C5 backbone on two ligands on the right are going to be explored. Preferably, the ligands would be able to bind two different metals with a minimum number of synthetic steps. These are hoped to become scaffolds for larger, polymeric structures. The project would encompass a preliminary exploration of these possibilities.

- Learning outcomes: better understanding of structural and coordination chemistry, practical experience in advanced synthetic techniques (such as oxygen-free environments), advanced IR, NMR and X-ray techniques.
- Required training certificates: relevant training on analytical instruments (IR, UV-Vis and NMR) will be provided before the actual work can start
- Our expectations from students: to work in the laboratory environment respecting all safety procedures and requirements, to be able to work under minimal supervision when dealing with basic synthetic and analytic procedures, to regularly inform the supervisor on the project progress, be versatile in literature search, be an excellent team-player.

Project #5

Supervisor: Alen Hadzovic

Co-supervisor (if any):

Office: EV564

Sub-discipline: Inorganic Chemistry

Laboratory: EV216

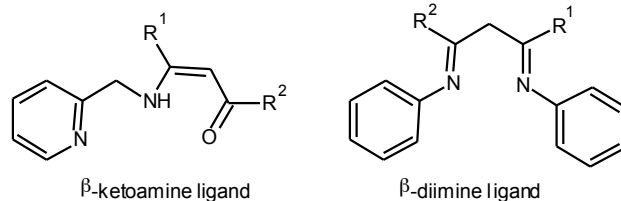
Course code: CHMD90Y/91H

e-mail: ahadzovic@utsc.utoronto.ca

of students: up to 2

β -ketoamine/ β -diimine complexes of heavier transition metals

This project focuses on the synthesis, characterization and reactivity of heavier transition metals Ru, Mo, and Re containing β -ketoamine or β -diimine ligands (see structures below) [1]. Of particular interest are complexes that also contain hydride and carbonyl ligands (for Ru), oxido (O^{2-}) (for Mo and Re) and nitrido (N^{3-}) ligands (for Re) [2].



The desired complexes would contain metals in intermediate oxidation states: II and III for Ru, IV or V for Mo and V and VI for Re. In each case these would form a series of novel compounds that have little or no precedent in the literature. Consequently, the synthetic routes and careful characterization are of primary importance.

- Learning outcomes: better understanding of structural and coordination chemistry, practical experience in advanced synthetic techniques (such as oxygen-free environments), advanced IR, NMR and X-ray techniques.
- Required training certificates: relevant training on analytical instruments (IR, UV-Vis and NMR) will be provided before the actual work can start
- Our expectations from students: to work in the laboratory environment respecting all safety procedures and requirements, to be able to work under minimal supervision when dealing with basic synthetic and analytic procedures, to regularly inform the supervisor on the project progress, be versatile in literature search, be an excellent team-player.

References:

[1] Guan, K., Hadzovic, A. CHMD90Y3 results, 2012-13.

[2] Re part is continuing on Liu, H., Hadzovic, A. CHMD90Y3 results, 2014-15; and Mo is based on Indart, C., Hadzovic A. CHMD90Y3 results, 2012-13

Project #6

Supervisor: Alen Hadzovic

Co-supervisor (if any):

Office: EV564

Sub-discipline: Inorganic Chemistry

Laboratory: EV216

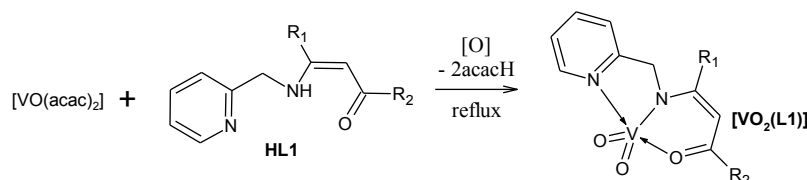
Course code: CHMD90Y/91H

e-mail: ahadzovic@utsc.utoronto.ca

of students: 1

Oxidovanadium (IV) and (V) complexes with β -ketoamine ligands

The focus of this project is synthesis and characterization of dioxidovanadium complexes containing β -ketoamine ligands such as HL1. The V(V) complex $[\text{VO}_2(\text{L1})]$ with $\text{R}_1 = \text{R}_2 = \text{CH}_3$ has been synthesized and characterized [1], and some reactivity has been explored [2].



Of particular interest now are: (1) synthesis of $[\text{VO}_2(\text{L1})]$ with unsymetric HL1 backbone (i.e. $\text{R}_1 \neq \text{R}_2$); (2) synthesis and characterization of analogous V(IV) complexes (with VO^{2+} oxido core) and (3) further exploring their reactivity. The interest in these reactions lie primarily in exploring the chemistry of the pentacoordinated oxovanadium(V) complexes which are frequently encountered in medicinal applications. [3]

- Learning outcomes: better understanding of structural and coordination chemistry, practical experience in advanced synthetic techniques (such as oxygen-free environments), advanced IR, NMR and X-ray techniques.
- Required training certificates: relevant training on analytical instruments (IR, UV-Vis and NMR) will be provided before the actual work can start
- Our expectations from students: to work in the laboratory environment respecting all safety procedures and requirements, to be able to work under minimal supervision when dealing with basic synthetic and analytic procedures, to regularly inform the supervisor on the project progress, be versatile in literature search, be an excellent team-player.

References:

[1] Guan, T., Hadzovic, A. CHMD90Y3 project 2012-13.

[2] Doner, J., Hadzovic, A. CHMD90Y3 project 2014-14

[2] See for example, Tracey, A.S. et al. "Vanadium: Chemistry, biochemistry, pharmacology, and practical applications." Boca Raton, Fla.: CRC Press, 2007.

Project #7

Supervisor: **Artur Izmaylov**

Office: **SW638**

Laboratory: **SW638**

e-mail: artur.izmaylov@utoronto.ca

Web: <http://www.uts.utoronto.ca/~aizmaylov/>

Co-supervisor: **N/A**

Sub-discipline: **Theoretical/Computational**

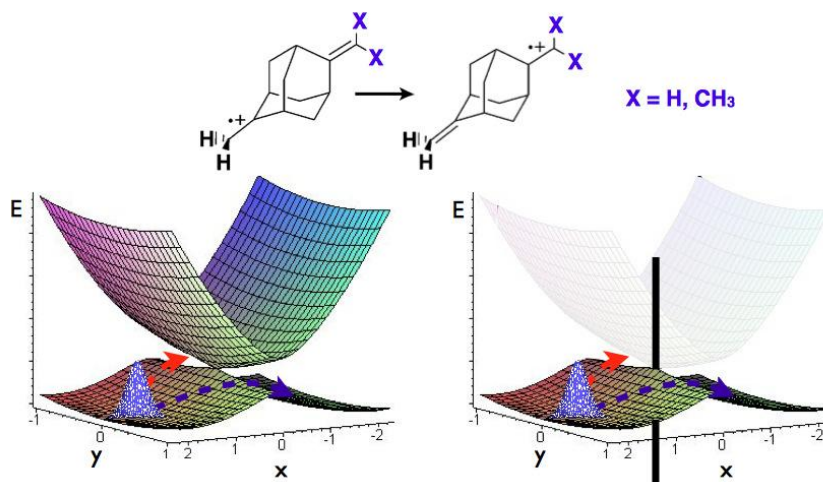
Course code: **CHMD90/91**

of students: **1**

GEOMETRICAL PHASE EFFECTS IN MOLECULAR CHARGE TRANSPORT

Usual physical properties of molecules (e.g., electronic spectra, vibrational frequencies, NMR shifts) are defined by details of potential energy surfaces (PESs). Surprisingly, there also exist measurable properties that appearing because of global geometry of PES rather than its details. The difference between global geometry and local details can be illustrated considering simple geometric objects like torus and sphere: they are very similar if we focus on their small parts but have very different overall shape. In this project we will investigate geometrical phase effects originating in some charge transfer reactions because of nontrivial intersection geometry of donor / acceptor PESs.

- A student working on this project will gain experience in modeling quantum chemistry.
- This project requires basic knowledge of physical chemistry and calculus. Programming experience is preferable but not crucial.
- Student is expected to present the research results in weekly group meetings



References:

- [1] C. A. Mead and D. G. Truhlar, **J. Chem. Phys.** **70**, 2284 (1979)
- [2] A. Shapere and F. Wilczek, **Geometric Phases in Physics** (1989)

Project #8

Supervisor: **Artur Izmaylov**

Co-supervisor: **N/A**

Office: **SW638**

Sub-discipline: **Theoretical/Computational**

Laboratory: **SW638**

Course code: **CHMD90/91**

e-mail: artur.izmaylov@utoronto.ca

of students: **1**

Web: <http://www.uts.utoronto.ca/~aizmaylov/>

FIRST STEP IN VISION: QUANTUM DYNAMICS STUDY

The first step in vision process regulated by the rhodopsin protein involves photo-induced dynamics that starts with the retinal chromophore isomerization from the 11-cis to the all-trans form. Two electronic states are involved in this photochemical process, and therefore, it is necessary to go beyond the Born-Oppenheimer approximation to build an adequate model of this process. Recently, more accurate potential electronic surfaces (PESs) have become available, and in this project we will build correlations between topography of PESs and the photochemical yield: the ratio between the 11-cis and all-trans forms. To build such correlation we will simulate quantum dynamics starting with a minimal but adequate model of two electronic surfaces and two nuclear coordinates. Future extensions of this work will investigate adding more nuclear degrees of freedom, and differences in dynamics stimulated by coherent (laser) and incoherent (sun) light sources.

- A student working on this project will gain experience in quantum mechanical modeling of biological processes using methods of quantum dynamics.
- This project requires basic knowledge of physical chemistry and calculus. Programming experience is preferable but not crucial.
- Student is expected to present the research results in weekly group meetings

References:

[1] I. Schapiro et al., **J. Am. Chem. Soc.** **133**, 3354 (2011)

Project #9

Supervisor: **Artur Izmaylov**

Office: **SW638**

Laboratory: **SW638**

e-mail: artur.izmaylov@utoronto.ca

Web: <http://www.utoronto.ca/~aizmaylov>

Co-supervisor: **N/A**

Sub-discipline: **Theoretical/Computational**

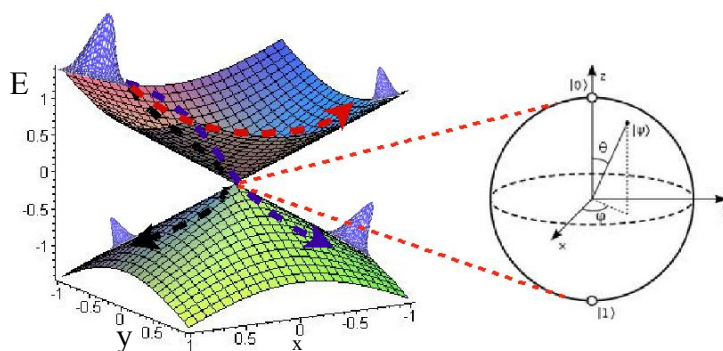
Course code: **CHMD90/91**

of students: **1**

CLASSICAL SPIN FOR PHOTOCHEMICAL REACTIONS

Molecules are very small objects and their behavior is naturally described by quantum mechanics. Quantum mechanics is a more general and more complex theory than the normal, so-called classical mechanics that describes behavior of large objects (e.g., cars and baseballs). Thus, classical mechanics should follow from quantum mechanics when we consider bigger objects. In many chemical reactions involving rearrangement of nuclear fragments that are heavier than hydrogen atom, simple classical description is satisfactory and complex quantum mechanics can be avoided. However, there are many cases, especially in photochemistry, when nuclear motion is not confined to only one potential electronic surface, in other words, the Born-Oppenheimer approximation breaks down, and classical description stops working. Is there a way to avoid complexity of quantum mechanics for such situations? In this project we will employ physical construction of classical spin to represent classically reaction dynamics beyond the Born-Oppenheimer approximation.

- A student working on this project will gain better understanding of quantum-classical correspondence and experience in modeling techniques.
- This project requires basic knowledge of physical chemistry and calculus. Programming experience is preferable but not crucial.
- Student is expected to present the research results in weekly group meetings



References:

- [1] A. Atland and B. Simons, **Condensed Matter Field Theory** (2010)
- [2] V. Krishna, **J. Chem. Phys.** **126**, 134107 (2007)

Project #10

Supervisor: **Artur Izmaylov**

Co-advisor: **Xiao-an Zhang**

Office: **SW638**
Theoretical/Computational

Sub-discipline:

Laboratory: **SW638**

Course code: **CHMD90/91**

e-mail: artur.izmaylov@utoronto.ca

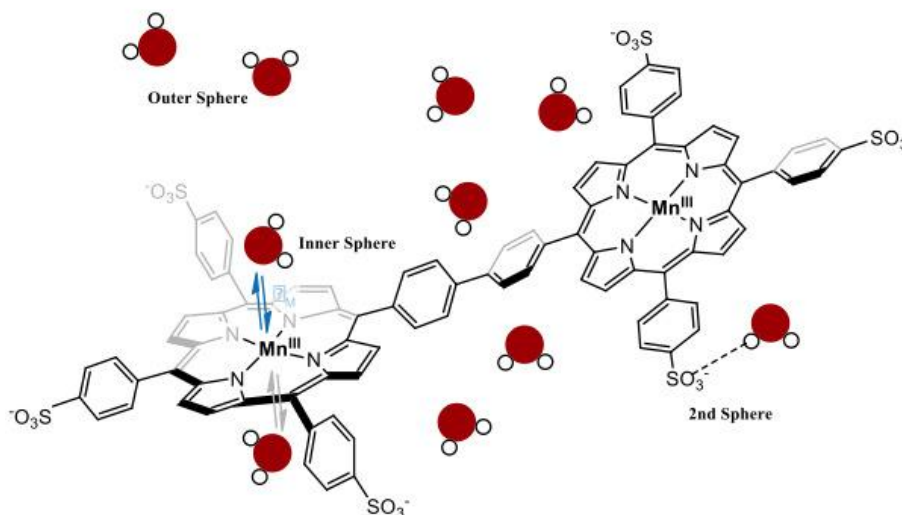
of students: **1**

Web: <http://www.utoronto.ca/~aizmaylov/>

COMPUTATIONALLY GUIDED SEARCH FOR NEW CONTRAST AGENTS IN MAGNETIC RESONANCE IMAGING

The goal of this project is to develop necessary tools for computationally guided design of new safer contrast agents in magnetic resonance imaging (MRI). The MRI technique is one of the most widely used diagnostic techniques in modern medicine. It has a great spatial resolution but limited sensitivity of its probe. To improve MRI sensitivity various contrast agents have been developed. Currently, the most widely used agents are based on Gd compounds that are not free from side effects. In order to develop safer and more sensitive contrast agents we will develop structure activity relations for perspective class of Mn-based porphyrin complexes using electronic structure calculations.

- A student working on this project will gain experience in implementing spin related properties in electronic structure software.
- This project requires basic knowledge of physical chemistry, calculus, and programming experience.
- Student is expected to present the research results in weekly group meetings.



References:

[1] N. Schaefle and R. Sharp, **J. Phys Chem. A** **109**, 3267 (2005)

Project #13

Supervisor: Bernie Kraatz

Co-supervisors:

Office: ESCB 5th floor

Sub-discipline: Inorganic/ Biological

Laboratory: ESCB 5th floor

Course code: CHMD90

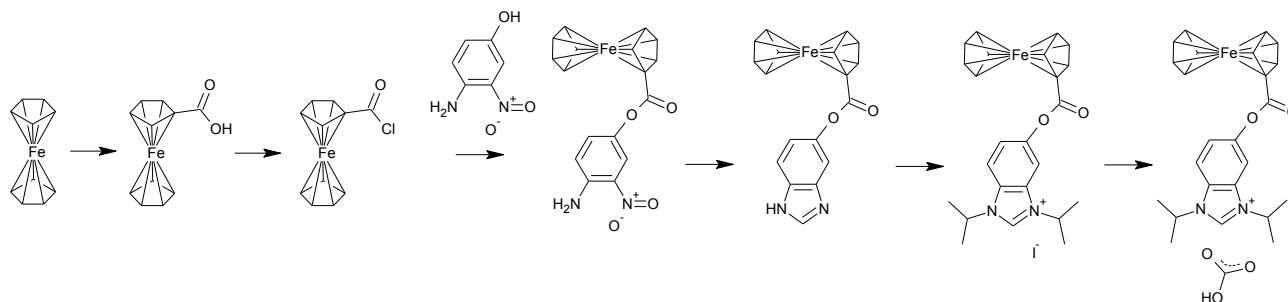
e-mail: bernie.kraatz@utoronto.ca # of students: 1

Web: <http://www.utoronto.ca/~bkraatz/>

Ferrocene-terminated benzimidazole and its derivatives

Carbenes, a class of compounds that have one of the carbon atoms in an oxidation state of two, are known to react with variety of metals forming stable self-assembled monolayers (SAMs) on surfaces. In situ carbene formation from air-stable precursors followed by a reaction with a metal surface may lead to an analogous coat formation. This organic layer covalently bound to a metal may be potentially used as a corrosion protection coat.

The ferrocene is a redox active moiety; as a result, ferrocene based building blocks have already been used successfully in fabrication of various SAMs. Analysis of cyclic voltammograms of ferrocene-terminated SAMs allows determination of the charge involved in the redox process, and thus to calculate actual surface coverage of the ferrocene units.



Ø Learning outcomes: In this project, the student will be involved in the synthesis of various ferrocene-terminated benzimidazole derivatives by solution phase methods, their isolation and characterization by spectroscopic methods (NMR, IR, MS) thus gaining invaluable experience in advanced synthetic and analytical techniques.

Ø Required training certificates WHMIS

Ø Our expectations from students: I expect students to work effectively and collaboratively with graduate students and postdoctoral fellows and fully participate in all group activities and meetings. I expect monthly written updates on progress. Weekly meetings with the supervisor will be arranged. Day-to-day interactions with Drs. Iralkii Ebralidze and Zhe She and graduate students.

Project #14

Supervisor: Bernie Kraatz

Co-supervisors:

Office: ESCB 5th floor

Sub-discipline: Inorganic/ Biological

Laboratory: ESCB 5th floor

Course code: CHMD90

e-mail: bernie.kraatz@utoronto.ca # of students: 1 -2

Web: <http://www.uts.utoronto.ca/~bkraatz/>

Development of Peptide Co-Gels

Peptide molecules can interact via hydrogen bonding and π -stacking interactions to generate materials that allow the inclusion of large quantities of solvent molecules. In these gels, peptides engage in interactions that exhibit some level of order but lack crystallinity. Our group has studied a series of stimuli-responsive gels in which the gel can react to external stimuli (see references).

This project focuses on co-gels, in which two peptide gelators can interact with each other and generate a wide range of gel properties. This project will explore issues related to co-assembly and to self-sorting. We have reported before the self-sorting behavior of a series of gels that carry a fluorescent label (see references). Here, the gel forming properties of the ferrocene-peptide conjugate Fc-CO-FFL-OMe will be probed. The investigation will involve various diastereomers of this peptide and the gel and co-gelation will be studied using a range of experimental techniques, including circular dichroism, ¹H-NMR, and IR spectroscopies. In addition, variable temperature NMR spectroscopy is ideal for the study of intermolecular H-bonding interactions. Morphologies of the gels will be studied by electron microscopy.

R. Afrasiabi, H.B. Kraatz, *Chem. Eur. J.* **2015**, *21*, 7695-7700; B. Adhikari, H.-B. Kraatz, *Chem. Commun.* **2014**, *50*, 5551-5553 and references therein.

Ø Learning outcomes: In this project, the student will be involved in the synthesis of various ferrocene-peptide derivatives by solution peptide coupling methods, their isolation by column chromatography and characterization by spectroscopic methods (CD, NMR, IR, MS) thus gaining invaluable experience in advanced synthetic and analytical techniques.

Ø Required training certificates WHMIS

Ø Our expectations from students: I expect students to work effectively and collaboratively with graduate students and postdoctoral fellows and fully participate in all group activities and meetings. I expect monthly written updates on progress. Weekly meetings with the supervisor will be arranged. Day-to-day interactions with Drs. Iralkii Ebralidze and Zhe She and graduate students.

Project #15

Supervisor: Bernie Kraatz

Co-supervisors:

Office: ESCB 5th floor

Sub-discipline: Inorganic/ Biological

Laboratory: ECSB 5th floor

Course code: CHMD90

e-mail: bernie.kraatz@utoronto.ca

of students: 1

The influence of benzimidazolium hydrogen carbonates on formation of nanostructured silver surfaces

Carbenes, molecules containing a neutral carbon atom with a valence of two and two unshared valence electrons, are known to react with variety of metal ions and metals forming stable metal complexes or self-assembled monolayers (SAMs) on metal surfaces. However anhydrous conditions and inert atmosphere are required for carbenes in their so called “free carbene” form. Alternatively air-stable carbene precursors could be utilized for the same purposes. We plan to elaborate and optimize a method for the formation of stable carbene based SAMs at ambient conditions.

This project will start with synthesis of several benzimidazolium based carbene precursors and formation of SAMs on silver surfaces. Electrochemical cycling of these SAM-covered silver surfaces in aqueous solutions will be performed to get an idea of stability of the SAMs. Further electrochemical cycling of SAM- functionalized silver surfaces in solutions of carbene precursors in organic solvents will be performed to track changes in the electrochemical response due to either disruption of the original SAM layer, or due to the formation of silver nanostructures. Since carbene precursors may form either homogeneous silver complexes or react directly with a surface of a metal cluster, electrochemical cycling may result in silver leaching from the surface followed by the formation of silver complexes in solution. Alternatively, it may result in the formation of metal clusters followed by their deposition on the surface. These clusters on silver surfaces may be potentially useful for sensing applications in biomedical sciences or pollution monitoring.

Ø Learning outcomes: Student participating in this project will be involved in the synthesis of various benzimidazole derivatives by solution phase methods, their isolation and characterization by spectroscopic methods (NMR, IR, MS) thus gaining invaluable experience in advanced synthetic and analytical techniques. In addition, the student will get valuable experience in the formation of SAMs, their characterization (XPS and e-chem stripping), and surface modification by e-chem cycling.

Ø Required training certificates: WHMIS

Ø Our expectations from students: I expect students to work effectively and collaboratively with graduate students and postdoctoral fellows and fully participate in all

group activities and meetings. I expect monthly written updates on progress. Weekly meetings with the supervisor will be arranged. Day-to-day interactions with Drs. Iralkii Ebralidze and Zhe She and graduate students.

Project #16

Supervisor: Bernie Kraatz

Co-supervisors:

Office: ESCB 5th floor

Sub-discipline: Inorganic/ Biological

Laboratory: ECSB 5th floor

Course code: CHMD90

e-mail: bernie.kraatz@utoronto.ca

of students: 1

Pathogen detection by electrochemical methods

The objective of this project is to study the electrochemical behaviour of modified surfaces and their interactions with pathogenic agents. My group has studied biosensing surfaces for a wide range of bioanalytes, including DNA. In previous studies, electrochemical studies of DNA-modified gold micro-electrodes allowed us to distinguish mismatched positions and mismatch pairs of DNA, as well as being able to distinguish between mitochondrial DNA fragments in the cytochrome C1 oxidase gene (see references).

In this study, different bio-recognition elements, such as DNA and antibody proteins, will be investigated towards detection whole bacteria and pathogen-associated molecular patterns, such as for *Escherichia coli* and *Salmonella*, which are commonly found in our lake water and in contaminated meats.

The approach will be carried out in this project is to combine surface chemistry with electrochemistry. Bio-recognition elements will be immobilized onto gold surfaces and their bindings to the targets will be monitored using Cyclic Voltammetry, Square Wave Voltammetry and Electrochemical Impedance Spectroscopy. The aim is to develop biosensors that are able to convert biological responses into sensitive quantifiable electric signals and construct calibration curves for the biological targets

Diakowski, P. M.; Kraatz, H.-B. *Chem. Commun.* **2009**, 1189; Shamsi, M. H.; Kraatz, H.-B. *Analyst* **2010**, *135*, 2280; Shamsi, M. H.; Kraatz, H. B. *Analyst* **2011**, *136*, 4724; 3107; Diakowski, P. M.; Kraatz, H. B. *Chem. Commun.* **2011**, *47*, 1431.

Ø Learning outcomes: Student will be involved in the modification of surfaces, their characterization by spectroscopic and electrochemical methods and their interactions with bioanalytes and the construction of response curves.

Ø Required training certificates: WHMIS

Ø Our expectations from students: I expect students to work effectively and collaboratively with graduate students and postdoctoral fellows and fully participate in all group activities and meetings. I expect monthly written updates on progress. Weekly meetings with the supervisor will be arranged. Day-to-day interactions with Drs. Iralkii Ebralidze and Zhe She and graduate students.

Project #17

Supervisor: Bernie Kraatz

Co-supervisors:

Office: ESCB 5th floor

Sub-discipline: Inorganic/ Biological

Laboratory: ECSB 5th floor

Course code: CHMD90

e-mail: bernie.kraatz@utoronto.ca # of students: 1

Study of metal ion interactions with peptides.

The protein Tau is responsible for microtubule stabilization in neuronal cells and their activity is regulated by kinase-catalyzed phosphorylations. Hyperphosphorylation of Tau causes catastrophic destabilization of the microtubules, followed by assembly of phosphorylated Tau into neurofibrillar tangles on the interior of the neuronal cells causing cell death. Metal ions are found to be associated with these neurofibrillary protein tangles.

This project focuses on the study of a range of metal ions (Fe^{3+} , Cu^{2+} etc) with peptide fragments of Tau. We have evaluated phosphorylations and Cu^{2+} binding to full length Tau before and studied its behavior by electrochemical and spectroscopic means (see references). This project will focus on solution studies involving Tau peptides and metal ions. The interactions will be monitored by calorimetry, which will allow the evaluation of the thermodynamics of the interaction, and by circular dichroism spectroscopy, which will allow probing structural changes as a result of the interaction.

S. Martić, M.K. Rains, H.-B. Kraatz, *Anal. Biochem.* **2013**, *442*, 130-137; S. Martić, S. Beheshti, M. K. Rains, H.-B. Kraatz, *Analyst* **2012** *137*, 2042-2046.

Ø Learning outcomes: Student will be involved in the calorimetric and CD spectroscopic studies and their evaluation and learn basic bioinorganic techniques.

Ø Required training certificates: WHMIS

Ø Our expectations from students: I expect students to work effectively and collaboratively with graduate students and postdoctoral fellows and fully participate in all group activities and meetings. I expect monthly written updates on progress. Weekly meetings with the supervisor will be arranged. Day-to-day interactions with Soha Ahmadi.

Supervisor: Lana Mikhaylichenko

Co-supervisor (if any): Kagan Kerman

Office: EV556

Sub-discipline: Organic Chemistry

Laboratory: EV225

Course code: CHMD90Y

e-mail: mikhay@utsc.utoronto.ca

of students: 1

Synthesis of New High-Swelling Hydrogels as Immobilizers of Potential Drugs for the Alzheimer and Other Diseases

The aim of this research project is to synthesize a number of high-swelling hydrogels with different viscosity and properties as immobilizers of potential drugs. Swelling agents are hydrophilic crosslinked polymers, which swell from 10 to 1,000 times their own weight when placed in an aqueous medium. Depending on their swelling properties, these materials have been exploited in developing three different classes of materials in pharmaceutical industries, i.e. swellable matrices, superdisintegrants and swelling devices. Since their development, these pharmaceutical excipients have found significant applications in drug delivery area.¹ Swelling hydrogels are also used for surface coating, production of nanomaterials and optomechanical structures.²

- Student working on this project will gain experience in preparation of different high-swelling hydrogels using co-polymers of acrylamide and methylene-*bis*-acrylamide as well as a polymer made of vinyl-pyrrolidone as one of monomers.
- This is a collaborative project with Professor Kerman's research group. Student working on this project will help to test these polymers for their swelling and immobilizing properties.
- Student is expected to present results in bi-weekly Prof. Kerman's group meetings (tentatively Friday afternoon)

References:

- [1] Omidian, H.; Park, K. Swelling agents and devices in oral drug delivery. *J. Drug. Del. Sci. Tech.* **2008**, 18 (2,) 83-93.
- [2] Thompson, M.; Cheran, L.E.; Sadeghi, S. *Sensor Technology in Neuroscience*, RSC Publishing, **2013**, p. 215.

Project #18

Joint Supervisor: **Andre Simpson** Joint Supervisor: **Xiao-an Zhang**

Office: **SY324** Sub-discipline: **Organic/Analytical/Environmental**

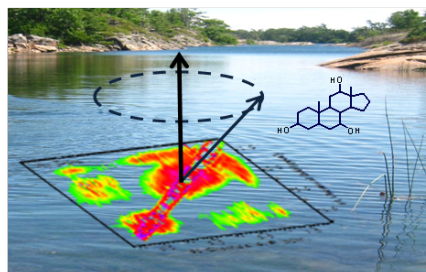
Laboratory: **SY050** Email: andre.simpson@utoronto.ca and xazhang@utsc.utoronto.ca

NMR Anion Sensors, Functional Group Capping and Mass Spectrometry: A multidisciplinary approach to address the world's most complex mixture.

Dissolved Organic Matter (DOM) is ubiquitous in all natural waters and known to play important roles in the global carbon and nitrogen cycles, the fate, transport and transformation of contaminants and nutrients and the health and biodiversity of aquatic species. DOM, however, is not just important due to its key role in environmental processes but its structural signatures themselves of immense interest. This is probably best summarized by John Hedges, arguably one of the greatest oceanographers of the modern era, he stated, "*The 10^{12} diverse organic molecules dissolved in every milliliter of seawater are the only constituents whose stored information approaches the richness needed to understand where the water has been and what has happened within it over time. The future of oceanographic research belongs in part to those who can learn to read these molecular messages.*"

Recently the A. Simpson group through hyphenation of 2D HPLC and 3D NMR has discovered the main constituents of DOM are highly oxygenation terpenoids. However, the analysis took 2 years making it impractical for routine applications. Theoretically if the material could be derivatized such that it can be dissolved in non-polar solvents, high resolution GC-MS methods should be ideal for rapid routine screening of the material. Simple derivatization is not easy as there are many acid and alcohol groups per terpenoids structure and steric hindrance may be problematic when trying to cap all of them. The Zhang group have developed a unique NMR based anion sensor. The sensor works in organic solvents and provides a simple and rapid indicator as to how many unexposed polar groups remain after derivatization.

The project will be a 50:50 collaboration between the A. Simpson and Zhang research groups. The student will attempt various derivatizations (mainly methylations) in the Zhang group and then compare the effectiveness of each approach using the NMR sensor with the A. Simpson group. Finally GC-MS analysis will be performed to assess the additional information provided by more complete derivatization of the materials.



Learning outcomes

- (1) Various organic reactions and derivatization.
- (2) Advanced NMR and NMR sensors.

(3) Gas Chromatography – Mass Spectrometry Analysis.

Required Training: WHMIS

Our expectation from students: Hard working, open minded student, with interests in more than one area of chemistry. It is highly likely the work will lead to a scientific publication, we expect the student to be highly involved and lead this process.

Project #19

Supervisor: **Myrna Simpson**

Co-supervisor (if any): N/A

Office: **SY322**

Sub-discipline: **Environmental Chemistry**

Laboratory: **SY315, Environmental NMR Centre**

Course code: **CHMD90**

e-mail: myrna.simpson@utoronto.ca

of students: **1**

Web: <http://www.utsc.utoronto.ca/~msimpson>

MOLECULAR FINGERPRINTS OF SOIL ORGANIC MATTER WITH ENVIRONMENTAL CHANGE

Two times the amount of carbon is stored in soil as compared to the atmosphere. The vast majority of this carbon is in the form of soil organic matter, which is a complex mixture of plant-, microbial- and anthropogenically-derived, compounds at varying stages of decomposition. Soil organic matter is both a source and sink of atmospheric CO₂ and plays a critical role in carbon and nitrogen biogeochemistry. Ecologists hypothesize that soil has a limit with respect to carbon sequestration (referred to as carbon saturation) and believe that soil can only house a fixed amount of carbon. This hypothesis has several implications for management practices, which aim to increase carbon sequestration in soil. To test this further, we will examine the composition of soil organic matter in samples from a long-term detrital inputs and removals treatment (DIRT) experiment (after 20 years of manipulation) conducted at the Harvard Forest, MA and the Bousson Forest, PA. The student will employ innovative mass spectrometry and nuclear magnetic resonance methods to investigate the fate of soil organic matter with DIRT. The DIRT experiment involves varying the degree of plant material inputs into soil to determine the extent of carbon sequestration. Through this work, we will directly examine if specific components of organic matter are sequestered more so than others. It will also provide molecular-level insight into the ramifications of increasing plant inputs and the role in carbon sequestration. This project is also being carried out with various researchers in the United States who are also examining other ecological variations such as: dissolved organic matter fluxes, respiration, microbial ecology and plant ecology

References: Simpson, M. J. and A. J. Simpson. 2012. The chemical ecology of soil organic matter molecular constituents. *Journal of Chemical Ecology* 38:768–784

Recommended courses: CHMC11 & CHMC16

Project #20

Supervisor: **Myrna Simpson**

Co-supervisor (if any): N/A

Office: **SY322**

Sub-discipline: **Environmental Chemistry**

Laboratory: **SY315, Environmental NMR Centre**

Course code: **CHMD90**

e-mail: myrna.simpson@utoronto.ca

of students: **1**

Web: <http://www.uts.utoronto.ca/~msimpson>

ISOLATION AND ELUCIDATION OF NOVEL NATURAL PRODUCTS FROM ENVIRONMENTAL SAMPLES

Soil organic matter contains two-thirds of the terrestrial carbon storage in the world and more than twice as much carbon as the atmosphere. Soil organic matter is vital for microbial, plant and animal life because it retains essential nutrients and water and is critical for maintaining soil fertility and long-term agricultural sustainability. Soil organic matter acts as both a source and a sink for atmospheric CO₂ and plays an important role in the regulation of global climate change and is also a major sink for environmental pollutants. Despite all of these critical functions, soil organic matter and other components of naturally occurring organic matter are “molecularly uncharacterized”. This is due to the complex, biological, chemical, and physical nature of soil organic matter. Soil organic matter, which is a collection of plant and microbial products at various stages of decomposition, is chemically heterogeneous and considered to be the most complex mixture on earth, therefore confounding studies on its structure and reactivity in the environment. Recent advances in the application of sophisticated analytical tools such as nuclear magnetic resonance (NMR) spectroscopy and high-resolution mass spectrometry (MS) have improved the fundamental understanding of soil organic matter structure. However, there are still a number of unidentified compounds that have yet to be elucidated. This project will focus on the isolation of novel compounds from soil organic matter and their structural elucidation using MS and NMR techniques. Preparative gas chromatography and liquid chromatography methods will be developed and tested for isolating unknown soil organic matter compounds. After isolation and purification, these compounds will be analyzed using high resolution MS and advanced NMR methods (one- and two-dimensional NMR) which will help ascertain the structure of these compounds. This research will yield new compounds that can be used to track soil organic matter sources and degradation processes in the environment.

Recommended courses: CHMC11 & CHMC16

Project #21

Supervisor:	Xiao-an Zhang	Co-supervisor (if any):	N/A
Office:	SW511	Sub-discipline:	Organic & Biological Chemistry
Lab:	SW332	Course code:	CHMD90
e-mail:	xazhang@utsc.utoronto.ca	# of students:	1~2
Web:	http://www.utsc.utoronto.ca/~xazhang/		

DEVELOPMENT OF Gd-FREE HIGH RELAXIVITY MRI CONTRAST AGENT

Magnetic resonance imaging (MRI) is a powerful and versatile biomedical imaging modality that is increasingly applied for clinical diagnosis, owing to its noninvasiveness, high resolution, deep penetration and capability of 3-dimensional real-time scans. Conventional MRI relies on the ^1H -NMR signal of water, the most abundant molecule *in vivo*. MRI contrast agent (CA) is a new class of pharmaceuticals that can improve contrast and sensitivity of MRI. Current FDA-approved clinical MRI CAs are predominantly based on low-molecular-weight Gd(III)-complexes, which can enhance the MRI contrast via shortening the longitudinal relaxation time (T_1) of water proton. These Gd T_1 agents, however, typically exhibit relatively low relaxivity (the efficiency of relaxation enhancement), in particular at high magnetic field. Grams-quantities of Gd-agents are required *in vivo* in order to obtain satisfactory imaging effect. Higher dose is unavoidably associated with higher risk of side effects. Recently, several Gd CAs have been implicated in nephrogenic systemic fibrosis (NSF), a severe side effect related to Gd toxicity in patients with renal dysfunction. Therefore, safer and more efficient MRI CAs are highly desirable. This D90 project will be part of our research program in developing next generation MRI T_1 CAs with high relaxivity and low toxicity. The primary goal is to design, synthesize and characterize novel Gd-free agents.

Learning outcomes

- Students will receive hands-on trainings on advanced organic and inorganic synthesis, and are expected to do chemical synthesis independently after training;
- Students will receive trainings on how to use modern spectroscopy techniques, including NMR, ESI-MS, UV-vis, etc to characterize the synthetic intermediates and final product;
- Students will learn background knowledge on MRI contrast agents and explore theory about relaxivity.
- Students are expected to present their research results in group meetings.

Required training certificates

(1) WHMIS training; (2) Chemical Safety Training; Our expectations from students...

- (1) Successfully completed CHMC41 or 42; (2) Previous experience in organic synthesis is preferred.

References: [1] Merbach, A. E.; Tóth, É., *The chemistry of contrast agents in medical magnetic resonance imaging*. Wiley: Chichester ; New York, 2001 [2] Zhang, X.-a.; Lovejoy, K. S.; Jasanoff, A.; Lippard, S. J, *Proc. Natl. Acad. Sci. USA* 2007, 104 (26), 10780.

Project #22

Supervisor:	Xiao-an Zhang	Co-supervisor (if any):	N/A
Office:	SW511	Sub-discipline:	Organic & Biological Chemistry
Lab:	SW332	Course code:	CHMD90
e-mail:	xazhang@utsc.utoronto.ca	# of students:	1~2
Web:	http://www.utsc.utoronto.ca/~xazhang/		

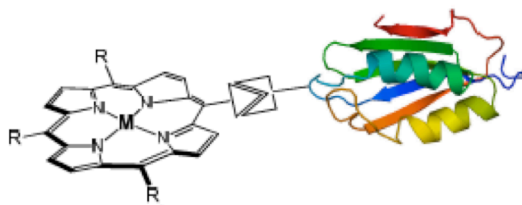
DESIGN AND SYNTHESIS OF MRI CONTRAST AGENT FOR COVALENT PROTEIN LABELING

Molecular imaging probes, including fluorophores, radioactive tracers, or magnetic resonance imaging (MRI) contrast agents (CAs) that can be selectively attached to specific bio-macromolecules, such as proteins, are powerful and versatile research tools for molecular biology as well as for medical diagnosis. These biomedical imaging probes can be used to label and track the selected protein targets inside the biological system to provide their distribution kinetics and functional information. On the other hand, certain proteins, such as antibody, can be used as a cargo to deliver imaging probes to specific sites, such as surface of tumor cells.

This project aims to develop novel MRI contrast agents based on water-soluble porphyrins for protein labeling. MRI is one of the major medical imaging modalities that is increasingly used for clinical diagnosis. The immediate goal of current project is to establish a synthetic strategy with reasonable yield and to structurally characterize the final product.

Learning outcomes

- Students will be systematically trained on organic and inorganic synthesis, in particular on porphyrin synthesis;
- Students will receive hands-on trainings on how to use modern spectroscopy techniques, including NMR, ESI-MS, UV-vis, etc to characterize the synthetic intermediates and final product;
- Students will learn background knowledge on MRI contrast agents, molecular imaging and molecular design.
- Student is expected to present the research results in group meetings.
- Required training certificates: (1) WHMIS training; (2) Chemical Safety Training; Our expectations from students...
- Successfully completed CHMC41 or 42; (2) Previous experience in organic synthesis is preferred.



References: [1] Merbach, A. E.; Tóth, É., *The chemistry of contrast agents in medical magnetic resonance imaging*. Wiley: Chichester ; New York, 2001 [2] Zhang, X.-a.; Lovejoy, K. S.; Jasanoff, A.; Lippard, S. J, *Proc. Natl. Acad. Sci. USA* 2007, 104 (26), 10780.

Project #23

Supervisor: Ronald Soong

Co-supervisor (if any): Andre Simpson

Office: SY324 Sub-discipline: Analytical/Biological

Laboratory: SY050

Course code: CHMD90

e-mail: ronald.soong@utoronto.ca

of students: 1

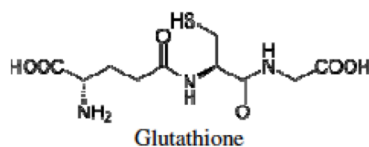
Web: <http://www.utoronto.ca/~asimpson/>

¹⁹F TAGGING OF THIOLS AS AN APPROACH FOR THE NMR DETECTION AND QUANTIFICATION OF GLUTATHIONE AND ITS DERIVATIVES IN BIOFLUIDS

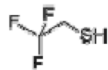
Glutathione and its derivatives are important biomarkers in the measurement of oxidative stress in an organism. Therefore, significant amount of work has been done for the detection and qualification of glutathiones in various biofluids, such as blood, urine and tissue extracts. Nuclear Magnetic Resonance (NMR) NMR spectroscopy is one of the most powerful tools for studying metabolite fluxes in intact biofluids. However, for most complex biological fluids the ¹H NMR resonances of glutathiones are often indistinguishable from other metabolites due to severe spectral overlap. However, the thiol (SH) group can be activated to form disulfide bonds, allowing us to add NMR observable ¹⁹F tag for detection. ¹⁹F tag offers several advantages, including 100% natural abundance and highly sensitive to its chemical environment. The goal of this D90 project is to investigate various strategies in incorporating different ¹⁹F tag through disulfide bond linkage in standard Glutathiones and in biological tissue extracts.

Learning outcomes :

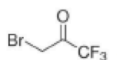
- Hands-on-experience and training with state-of-art NMR spectroscopy. Experience with the derivatization of biological molecules. Experience in metabolomics (one of the most powerful approaches to understand biological response).
- Required training certificates : WHMIS
- Our expectations from students. Hard working, open minded student, with interests in more than one area of chemistry. Ambition to publish results in a top international journal.



Possible ¹⁹F Tag



2,2,2-Trifluoroethanethiol



3-bromo-1,1,1-trifluoroacetone

References

Potapenko, D.I. et al. *Magn. Reson. Chem.*, **43** (2005) 902–909

Loewen, M.C. et. al. *Proc. Natl. Acad. Sci. USA*, **98** (2001) 4888–4892.

Project #24

Supervisor: F. WANIA

Co-supervisor (if any):

Office: SY 364

Sub-discipline: Environ Chem

Laboratory: SY370

Course code: CHM D90/91

e-mail: frank.wania@utoronto.ca

of students: 1

Predicting Phase Partitioning Equilibria of the Oxidation Products of Volatile Organic Compounds Involved in Secondary Organic Aerosol Formation

In order to understand the growth of organic particles in the atmosphere and the yield of secondary organic aerosol (SOA) formation, it is necessary to know the equilibrium partition coefficients between aerosol and gas phase at different temperatures for a large number of atmospheric oxidation products. Experimental values for these partition coefficients are missing for most of the chemicals involved in SOA formation, because many of them have not even been synthesized. In fact, many of their physico-chemical properties are missing and need to be predicted with methods of variable complexity and sophistication. Examples are the poly-parameter linear free energy relationship (ppLFER) approach, the SPARC (SPARC Performs Automated Reasoning in Chemistry) software, and the CONductor like Screening MOdel for Realistic Solvents (COSMO-RS). The project involves the identification of the relevant oxidation products, the conversion of their molecular structure into a format that can be read by computer programs, the prediction of partitioning properties and their illustration and interpretation.

- Learning outcomes. Students will gain experience in a (directed) independent research project whose outcome is not known beforehand. Specific experience will be gained in using chemical property prediction software.
- This project requires basic knowledge of physical chemistry.
- Our expectations from student. The student will meet weekly with the supervisor, discuss results and devise an updated plan for work. The student will prepare (with some editorial guidance from the supervisor) a final report.

References:

Hallquist, M., et al.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009