Physical & Environmental Sciences
UNIVERSITY OF TORONTO
SCARBOROUGH

DIRECTED RESEARCH IN CHEMISTRY

CHMD90/91

Research Projects Booklet

2019 Fall – 2020 Winter

CHMD90Y3 & CHMD91H3
DIRECTED RESEARCH IN CHEMISTRY

***Course Coordinator*: Prof. Xiao-an Zhang**

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, your CV along with the letter of intent).
3. Request the course on ACORN and contact the course Coordinator (listed in the timetable as the instructor) to inform of your intent to take the course. Your status will be INT. You will not be officially enrolled until you complete the remaining steps (below)
4. Obtain the D90/91 Supervised Study form, which is available online at https://www.utsc.utoronto.ca/registrar/supervised-study-form or at the Office of the Registrar (Highland Hall, Main Floor).
5. Meet with your Supervisor and obtain their signature on a 'Supervised Study form'. Make sure the course code, supervisor name, title of the project are **clearly** printed on the form as this information will appear on your transcript. Your supervisor will also complete information regarding the grading structure of the project.
6. Collect the two required signatures under the Physical and Environmental Sciences section. The Department Chair or the Associate Chair Undergraduate can sign under the 'Chair' section; the course coordinator, Prof. Xiao-an Zhang (xazhang@utsc.utoronto.ca) or Chemistry Discipline Representative Dr. Effie Sauer (esauer@utsc.utoronto.ca) can sign under the 'Secretary' section.
7. Once the above steps are complete, please submit the form to the Assistant to the Chair (Room EV241). The completed forms will be collected and forwarded to the Registrar's Office to process enrolment. Once finalized, your course status on ACORN from interim (INT) to approved (APP). Students are advised to complete this process early so that the required forms can be submitted and processed by the last day to add courses for the session.

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 draft thesis reports: You will be submitting your draft thesis reports to your supervisors by **April 3, 2020**.

Final report is due April 10, 2020. Find two readers among faculty or postdoctoral fellows. (Grade contribution 80%: 30% Supervisor, 1st reader: 25%, 2nd reader: 25%)

Final oral or poster (TBD) presentation 20% (Tentative date: **April 17, 2020**)

EVALUATION FOR CHMD91:

Submission deadline for the draft thesis reports: You will be submitting your draft thesis reports to your supervisors by **November 29, 2019**.

Final report is due December 6, 2019. Find two readers among faculty or postdoctoral fellows. (Grade contribution 80%: 30% Supervisor, 1st reader: 25%, 2nd reader: 25%)

Final oral presentation 20% (Tentative date: **December 13, 2019**)

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, September 13, 2019 (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.**

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	Postsecondary Institution

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 *Privacy Act*, 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: **EV568** **Sub-discipline: Inorganic Chemistry**

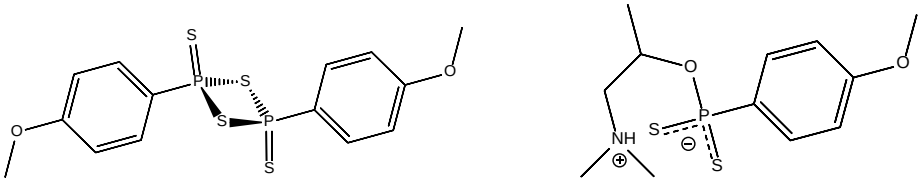
Laboratory: **EV216** **Course code: CHMD90Y/91H**

e-mail: **ahadzovic@utsc.utoronto.ca** **# of students: 1**

Web:

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 synthetized 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 and Malhotra, H., Hadzovic, A. CHMD90Y3 results 2018-19.

Project #4

Supervisor: **Alen Hadzovic** **Co-supervisor (if any):**

Office: **EV568** **Sub-discipline: Inorganic Chemistry**

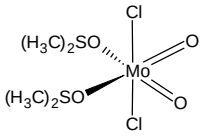
Laboratory: **EV216** **Course code: CHMD90Y3**

e-mail: **ahadzovic@utsc.utoronto.ca** **# of students: 1**

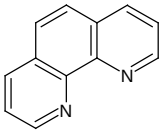
Web:

Dioxidomolybednum(VI) complexes with pyridyl-donor ligands

The aim of this project is to explore the synthetic utility and potential application of reactions between *trans,cis,cis*-[$MoCl_2O_2(dmso\text{-}\kappa O)_2$] (**1**) as Mo(IV) starting material and 1,10-phenantroline (**2**) and 2,2'-dipyridylketone (**3**) as pyridyl-type donor ligands. [1]



1



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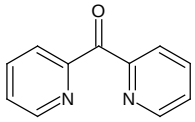


3

Of particular interest now are: (1) influence of solvent choice on the outcome of reaction *trans,cis,cis*-[$MoCl_2O_2(dmso)_2$] with 1,10-phenantroline, (2) exploring the conversion of 2,2'-dipyridylketone to diol upon coordination to Mo(IV) fragment as potential synthetic route to functionalized tridentate ligands and (3) lability of chlorido ligands in complexes formed in above reactions with aim of further functionalization.

- Learning outcomes: better understanding of structural and coordination chemistry, practical experience in advanced synthetic techniques, advanced IR, NMR and X-ray techniques, development of scientific writing skills.
- 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] Shan, Chen, Hadzovic, A. PSCB90H3 project summer 2019.

Project #5

Supervisor: **Alen Hadzovic** **Co-supervisor (if any):**

Office: **EV568** **Sub-discipline: Inorganic Chemistry**

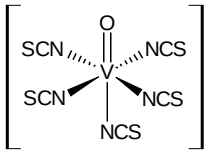
Laboratory: **EV216** **Course code: CHMD90Y/91H**

e-mail: **ahadzovic@utsc.utoronto.ca** **# of students: 1**

Web:

Oxidovanadium(IV) complexes with thiocyanate

The anion $[VO(NCS\text{-}\kappa N)_5]^{3-}$ (**1**) has been reported more than 50 years ago. [1] After the initial publication, the spectroscopic characterization (IR and UV-Vis) of the anion followed. However, our recent results (notably elemental analysis and single crystal X-ray analysis) indicate that this anion is very elusive species and is prone to loss of NCS^- ligand trans to oxido group. This observation questions validity of all published characterization and reactivity of this anion. The solid-state of the anion **1** has not been reported, unsurprisingly.



1

The project goals are: (1) structurally characterize **1**, (2) explore the stability of the complex anion in non-donor and donor solvents, (3) determine the influence of couterion on the stability, solubility and synthesis of **1** and (4) explore the usefulness of the anion in the synthesis of more complex materials relying on ambidentate character of thiocyanate ligands.

- Learning outcomes: better understanding of structural and coordination chemistry, practical experience in advanced synthetic techniques, advanced IR, NMR and X-ray techniques, development of scientific writing skills.
- 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] Selbin, J., Holmes, L.H. *J. Inorg. Nucl. Chem.* (1962) 24, 1111.

Project #6

Supervisor: **Alen Hadzovic** **Co-supervisor (if any):**

Office: **EV568** **Sub-discipline: Inorganic Chemistry**

Laboratory: **EV216** **Course code: CHMD91H**

e-mail: **ahadzovic@utsc.utoronto.ca** **# of students: 3 (or more)**

Web:

Technical analysis of museum objects

Please note: *This is a CHMD91H project and will be offered in Winter 2020 semester only! The number of student positions available will be determined on a later date.*

Technical art history (TAH) is a dynamic discipline that applies scientific methods to answer questions relating to the art objects and cultural heritage. TAH relies on both modern, non-destructive analytical chemical methods and history of chemistry. It also depends on combined expertise of art historians, conservators, curators, chemists, and historians of science and technology. Thus, you will closely collaborate with art historians and museum personle for this project

The aim of the project is to explore art objects from the Malcove Collection at University of Toronto's Art Museum. The choice and number of actual art objects and questions will depend on the art historians and curators (first lesson in TAH: the initial research questions usually come from the art members of the team!). Once when the initial steps are completed, the number of chemistry students required for the project will be determined.

- Learning outcomes: understanding the role of physical sciences in art and, more general, in humanities, developing interdisciplinary communication skills, hands-on handling and analysis of museum objects, report writing skills, applying non-destructive analytical methods
- Required training certificates: understanding of analytical techniques important in technical art history available at UTSC: X-ray fluorescence and reflectance infrared techniques
- 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.

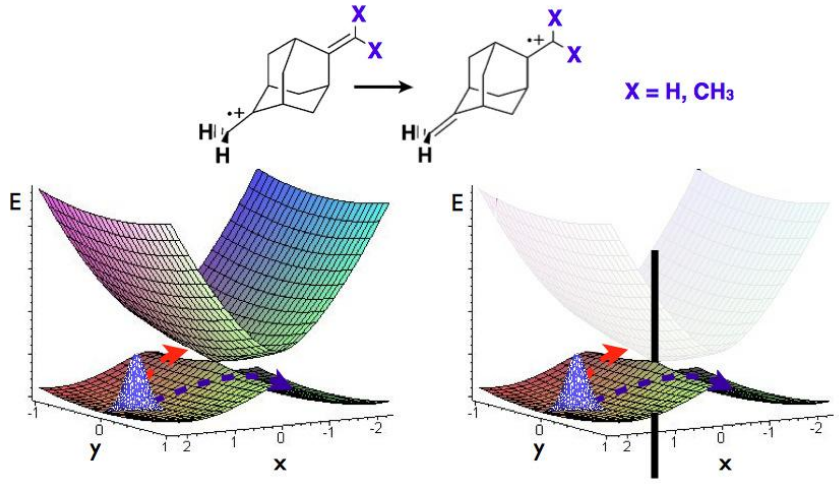
Project #7

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.utsc.utoronto.ca/~aizmaylov/**

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.utsc.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)

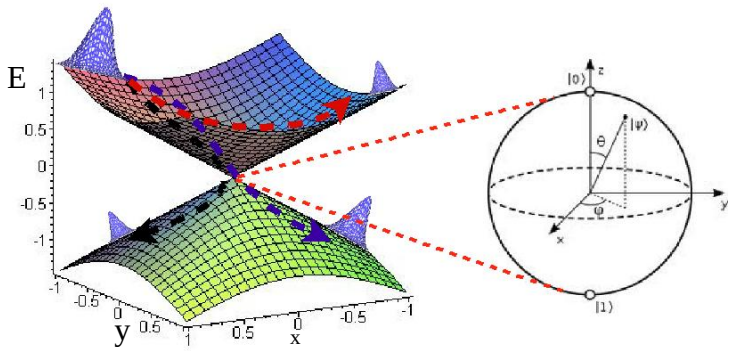
Project #9

Supervisor: **Artur Izmaylov** 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.utsc.utoronto.ca/~aizmaylov**

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 #11

Supervisor: **Kagan Kerman** Co-supervisor (if any): **M. Simpson**

Office: **SW533** Sub-discipline: **Bioanalytical Chemistry**

Laboratory: **SW221** Course code: **CHMD90/91**

e-mail: **kagan.kerman@utoronto.ca** # of students: **1**

Web: **http://www.utsc.utoronto.ca/~kkerman/**

ELECTROCHEMICAL OXIDATION OF DISSOLVED ORGANIC MATTER

Dissolved organic matter (DOM) functions as an intermediate in microbial metabolic processes and facilitate the cycling of multi-oxidation state metals in biogeochemical redox reactions [1]. Quinone functional groups associated with DOM are frequently cited as important organic moieties responsible for the redox activity of inorganic contaminants [2]. Electrochemical study of DOM would lead to a better understanding of the structural components responsible for redox behavior, such as quinones and nitrogen and sulfur (N/S) functional groups [3-5]. This project will utilize voltammetric techniques (differential-pulse, square-wave and stripping) coupled with NMR spectroscopy. DOM isolates from diverse sources will be tested using platinum as well as nanoparticle-modified carbon working electrodes. The electrochemical profiles of DOM will be correlated with the NMR data to understand their structural details and redox-active moieties.

- This project requires a team effort with graduate students, and is co-supervised with Professor Myrna Simpson (DPES, UTSC).
- A student working on this project will gain experience in electroanalytical techniques and NMR spectroscopy.
- Student is expected to present the research results in weekly group meetings (tentatively Friday afternoons).

References:

[1] Lovley D. R., Coates J. D., Blunt-Harris E. L., Phillips E. J. P., and Woodward J. C. (1996) Humic substances as electron acceptors for microbial respiration. *Nature* 382, 445–448.

[2] Struyk Z., and Sposito G. (2001) Redox properties of standard humic acids. *Geoderma* 102, 329–346.

[3] Nurmi J. T., and Tratnyek P. G. (2002) Electrochemical properties of natural organic matter (NOM), fractions of NOM, and model biogeochemical electron shuttles. *Environ. Sci. Technol.* 36, 617–624.

[4] Fimmen, R. L., Cory, R. M., Chin, Y.-P., Trouts, T. D., McKnight, D. M. (2007) Probing the oxidation-reduction properties of terrestrially and microbially derived dissolved organic matter. *Geochim. Cosmochim. Acta* 71, 3003-3015.

[5] Tian, M., Wen, J., MacDonald, D., Asmussen, R. M., Chen, A. (2010) A novel approach for lignin modification and degradation. *Electrochem. Commun.* 12, 527-530.

Project #12

Supervisor: **Kagan Kerman** Co-supervisor (if any):

Office: **SW533** Sub-discipline: **Bioanalytical Chemistry**

Laboratory: **SW221** Course code: **CHMD90/91**

e-mail: **kagan.kerman@utoronto.ca** # of students: **1**

Web: **http://www.utsc.utoronto.ca/~kkerman/**

IMMUNOCHIPS FOR AMYLOID-BETA USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Alzheimer's disease (AD) is a progressive and irreversible neurodegenerative dementia marked by substantial impairments to episodic memory and cognitive functions. Approximately 60% of all late-onset cases of dementia are attributed to AD, which is estimated to afflict more than 500,000 Canadians [1][2]. The amyloid cascade hypothesis attributes AD pathogenesis to an imbalance in amyloid-beta (Abeta), a small 4 kDa peptide capable of undergoing spontaneous self-association to form neurotoxic supramolecular assemblies. Notably, soluble oligomers have been identified as the more relevant toxic species of Abeta relative to later stage fibrillar aggregates and has since become a critical target for future drug therapy development.

We will be developing a rapid, disposable electrochemical immunosensor for determination fibril and oligomer distribution over the course of Abeta aggregation. To this effect, conformation-specific antibodies will be immobilized onto the surface of a gold CD electrode to monitor the inhibition of distinct aggregate states. Surface binding events will be determined by impedance spectroscopy, in which antigen-antibody interactions are quantified as a function of charge transfer resistance across the electrode interface. The efficacy of a small library of novel sym-triazine-derived aggregation modulators to reduce toxic oligomer formation will be evaluated. The results are expected to demonstrate the utility of impedimetric immunosensing for comprehensive identification of effective Abeta aggregation modulators.

- This project requires a team effort with graduate students, and is co-supervised with Professor Ian Brown (Biological Sciences, UTSC). Biosafety certificate is required.
- A student working on this project will gain experience in biosensor development using electroanalytical and biological techniques.
- Student is expected to present the research results in weekly group meetings (Friday afternoons).

References: [1] Blennow, K., et al. (2006) Lancet 368, 387-403.[2] Rising Tide: The impact of dementia on Canadian society <www.alzheimer.ca/>

Project #13

Supervisor: Bernie Kraatz Co-supervisors:

Office: ESCB 5th floor Sub-discipline: Inorganic/ Biological

Laboratory: ESCB 5th floor Course code: CHMD90

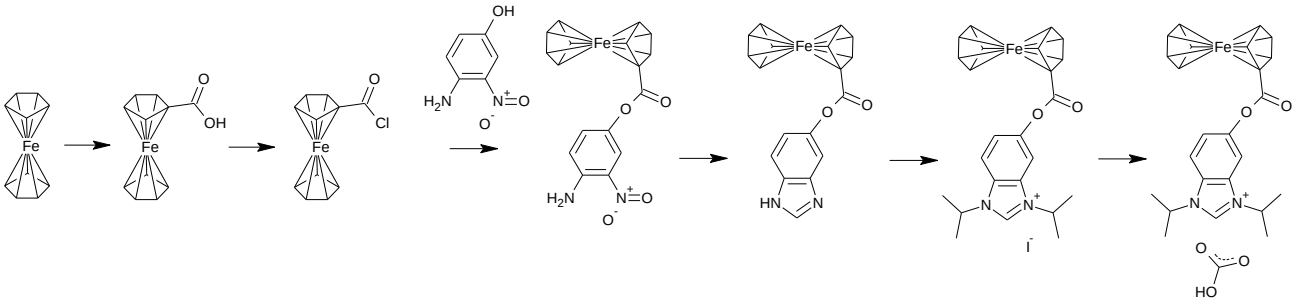
e-mail: bernie.kraatz@utoronto.ca # of students: 1

Web: http://www.utsc.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.utsc.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 diasteromers 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 interations. 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 of 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.

Project #18

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

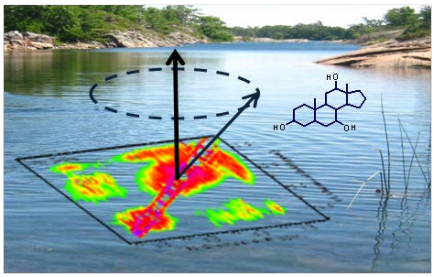
Office: **SY324** Sub-discipline: **Organic/Analytical/Environmental**

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 it 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 with 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 #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-dimetional real-time scans. Conventional MRI relies on the ^{1}H-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/

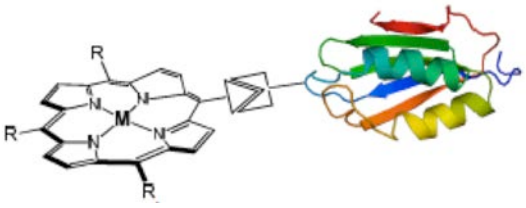
DESIGN AND SYNTHESIS OF MRI CONTRAST AGENT FOR COVALENT PROTEIN LABELING

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

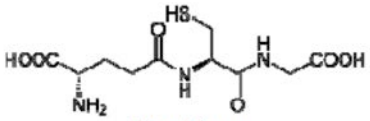
Supervisor: Ronald Soong **Co-supervisor (if any): Andre Simpson**
Office: SY324 **Sub-discipline: Analytical/Biological**
Laboratory: SY050 **Course code: CHMD90**
e-mail: ronald.soong@utoronto.ca **# of students: 1**
Web: **http://www.utsc.utoronto.ca/~asimpson/**

^{19}F 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 ^{1}H NMR resonances of glutahiones are often indistinguishable from other metabolites due to serve spectral overlap. However, the thiol (SH) group can be activated to form disulfide bonds, allowing us to add NMR observable ^{19}F tag for detection. ^{19}F 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 ^{19}F tag through disulfide bond linkage in standard Glutathiones and in biological tissue extracts.

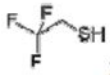
Learning outcomes :

- 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.

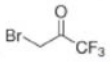


Glutathione

Possible ^{19}F Tag



2,2,2-Trifloroethanethiol



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

Supervisor: Bernie Kraatz

Co-supervisor: Shadi Dalili

Office: ESCB 5th floor

Sub-discipline: Inorganic/ Biological/ Organic

Laboratory: ESCB 5th floor

Course code: CHMD90

e-mail: bernie.kraatz@utoronto.ca

# of students: 1

Web: http://www.utsc.utoronto.ca/~bkraatz/

Synthesis and properties of thiourea and thioamide-containing pro-drug analogs

Techniques that have been widely used in drug discovery include mass spectrometry, coupled with gas and liquid chromatography. These methods possess high accuracy; however, they are time-consuming, expensive and not immediate. Thus, these standard techniques are not suitable for the screening of large libraries of compounds, resulting in the lack of new pro-drugs for the treatment of bacterial infections. Hence, there is a need for new high-tech platforms capable of reliably screening large libraries of newly developed synthetic pro-drugs in real-time. We plan to synthesize thiourea and thioamide-containing pro-drug analogs, and develop a novel high-throughput enzyme based screening platform for testing these analogs. These analogs could potentially be used to treat Tuberculosis (TB), although further bacterial testing must be done for confirmation.

The enzyme cyclohexanone monooxygenase (CHMO), which catalyzes environmentally friendly reactions with excellent selectivity, will be used in a proof of concept test with thiourea. It is expected that CHMO will cause the pro-drug thiourea to be converted into its active oxidized form, thus enabling the drug to treat bacterial infections. Analogs synthesized will be tested in a similar platform with CHMO for activity.

- Learning outcomes: 1- Gain experience in synthesis of various thiourea and thioamide-containing pro-drug analogs and advanced synthetic techniques; 2- Gain expertise in spectroscopic characterization methods (NMR, IR, MS); 3- Gain experience in the development of high-throughput enzyme based screening platform for pro-drug discovery; 4- Gain expertise in electrochemical techniques and methodology
- Required training certificates: WHMIS
- Expectations of students: 1- Work effectively and collaboratively with graduate students and postdoctoral fellows; 2- Participate fully in all group activities and meetings; 3- Submit monthly written updates on progress of project; 4- Communicate with supervisor weekly on progress of project; 5- Maintain safe and clean lab environment; 6- Document all results and data in proper scientific format and adhere to scientific journal templates for reporting of spectra data

Supervisor: **Ronald Soong** Co-advisor: **Artur Izmaylov**

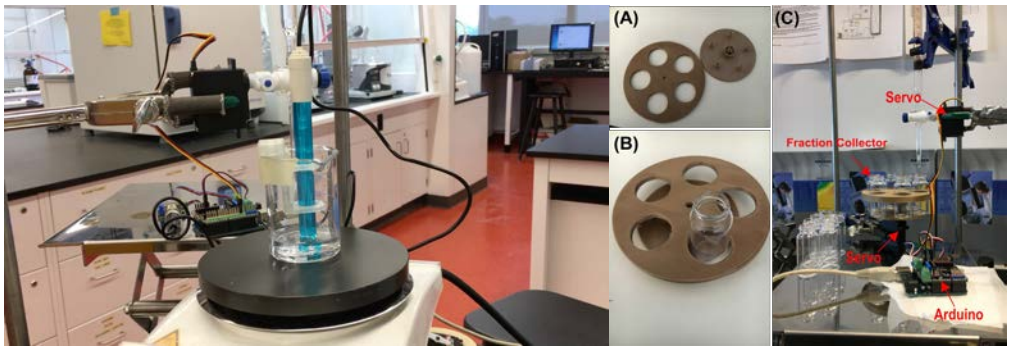
Office: **SW155B** Sub-discipline: **Instruments**

Laboratory: Course code: **CHMD90/91**

e-mail: ronald.soong@utoronto.ca # of students: **1**

Construction and Evaluation of Portable Analytical Instruments Based on the Arduino Microcontroller

A microcontroller is a micro-computer that is small and generally inexpensive. They are low-powered and can be powered through a variety of ways, including a USB connection, a wall socket, and a 9V battery[1]. Several types of microcontrollers are commercially available; the specific microcontroller studied here is called the Arduino. In this project, the student will be tasked with designing and making analytical instruments for undergraduate experiments. The goal is to create these low cost instruments such that they are affordable. The student is encourage to be creative while applying their knowledge in chemistry. The instruments that the student will be building will be 1) An auto-titrator 2) A cellphone spectrophotometer 3) auto-pipeter. Through designing and making these instruments, the student will gain hand-on experience with microelectronics and engineering in addition to basic analytical chemistry.



Supervisor: **Andre Simpson** co-supervisor: **Ronald Soong**

Office: **SY324** Sub-discipline: **Analytical/Biological**

Laboratory: **SY050** Course code: **CHMD90**

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Investigating ^{15}N as an important nucleus to better understand biochemical processes through *in-vivo* NMR

D. magna are the standard organism used globally for aquatic toxicity testing. The present method used by regulatory bodies to assess aquatic toxicity of a compound is the "21 day reproducibility test". If no perturbations are noted in reproducibility then the chemical is deemed to be safe at that concentration. However, the literature has repeatedly reported more subtle effects such as DNA damage, changes to metabolic pathways, bioaccumulation, permanent binding can be missed using this standard approach as such there is great need to develop more informative, sensitive and rapid methods to truly evaluate aquatic toxicity.

In-vivo NMR, has the potential to monitor not only the entire molecular fingerprint of an organism in real time but also relates changes in the molecular profile to uptake, transformation, binding, bio-concentration and secretion of a contaminant species. As such *in-vivo* NMR provides the technical framework required to understand "how" and "why" certainly chemicals are toxic, information desperately needed by regulators to set more meaningful standards. Despite its considerable potential *in-vivo* NMR has not yet been applied to evaluate toxicity in an environmental context.

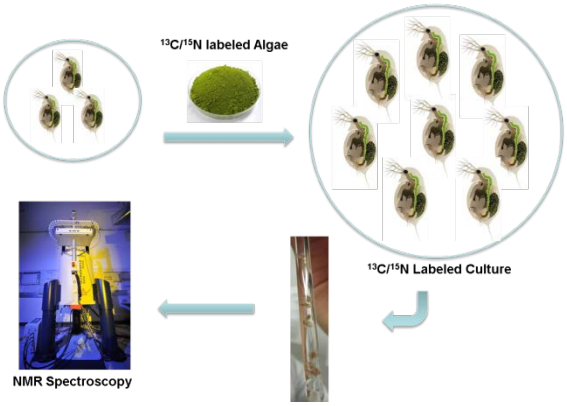
Optimizing the depth and variety of information that can be obtained via *in-vivo* NMR will be critical to comprehensively evaluate toxic pathways. With this in mind ^{15}N NMR (1D and multidimensional) will be explored as a potentially powerful tool to study metabolites, proteins and other biomolecules *in-vivo*. Organisms will be fed a diet of ^{15}N labelled algae and various NMR schemes will be developed to observe and differentiate metabolites and macromolecules *in-vivo*. It is anticipated ^{15}N labelling will provide a wealth of novel information complimentary to common NMR studies focusing on ^{1}H and ^{13}C.

Learning outcome

(1) The student will receive hands-on training on culturing and isotopic labelling *D. Magna*

(2) The student will receive training on using advanced NMR spectroscopy required for *in-vivo* studies.

(3) The student will learn about different statistical methods for data analysis and interpretation.



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 co-authored scientific publication, we expect the student to be involved in this process as required.

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Investigating ^{31}P as an important nucleus to better understand energetic processes through *in-vivo* NMR

D. magna are the standard organism used globally for aquatic toxicity testing. The present method used by regulatory bodies to assess aquatic toxicity of a compound is the "21 day reproducibility test". If no perturbations are noted in reproducibility then the chemical is deemed to be safe at that concentration. However, the literature has repeatedly reported more subtle effects such as DNA damage, changes to metabolic pathways, bioaccumulation, permanent binding can be missed using this standard approach as such there is great need to develop more informative, sensitive and rapid methods to truly evaluate aquatic toxicity.

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Optimizing the depth and variety of information that can be obtained via *in-vivo* NMR will be critical to comprehensively evaluate toxic pathways. With this in mind ^{31}P NMR (1D and multidimensional) will be explored as a potentially powerful tool to study metabolites (such as ADP, ATP, phospholipids etc.) and biomolecules RNA/DNA *in-vivo*. Organisms will studies *in-vivo* and *in-vitro* after chemical extraction. High resolution NMR from extracts will be useful for assignments of broader signal in ^{31}P *in-vivo* NMR. It is anticipated ^{31}P NMR provide a wealth of novel information complimentary to common NMR studies focusing on ^{1}H and ^{13}C.

Learning outcome

(1) The student will receive hands-on training on culturing *D. Magna*

(2) The student will learn various extraction approaches.

(3) The student will receive training on using advanced NMR spectroscopy required for *in-vivo* studies.

(4) The student will learn about different statistical methods for data analysis and interpretation.

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 co-authored scientific publication, we expect the student to be involved in this process as required.

Supervisor: **Andre Simpson** co-supervisor: **Ronald Soong**

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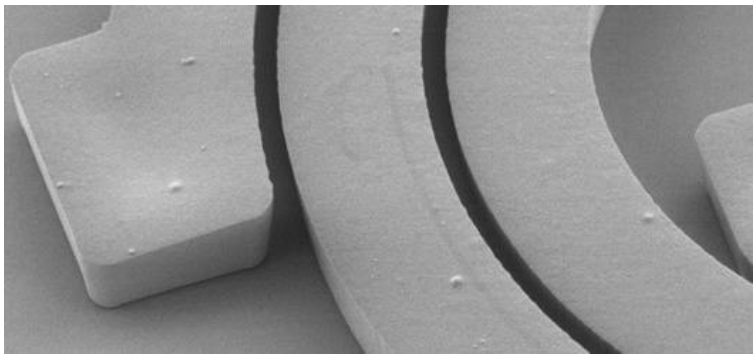
The Application and Development of Micro Surface Coil NMR.

NMR spectroscopy is arguably the most powerful tool in modern research with the ability to provide unprecedented levels of information regarding molecular structure and interactions. However, the relatively low sensitivity of NMR is it's main drawback. Recently, new nanolithography techniques allow the "printing" of NMR coils as small as individual cells. Such coils provide theoretical mass sensitivities ~50 times higher or time savings of ~2500 times in comparison to conventional NMR technology.

However, when moving to such small samples questions become: "how do we handle such samples?", "how do we retain the sample on the coil?", "how do we prevent evaporation?", "can organisms be kept alive on these coils?", "how small can we go?", and "what are applications of coils of varying diameter?"

The D90 student with work alongside graduate students and PI's to assist in answering these questions. The student will be immersed in all areas of the project and will learn a diverse array of techniques, application and theory. The student will test various applications that include plants, cells, organisms, tissue, small fruits/seeds. In both static and flow orientations.



Learning outcome

(1) The student will receive hands-on training on handling tiny samples using microscopes.

(2) The student will receive training on using advanced NMR spectroscopy, including advanced water suppression, advanced acquisition and spectral interpretation approaches.

(3) The student will learn about theory and application of cutting edge, globally unique, micro-coil NMR technology.

(4) The student will work with a diverse range of chemical, environmental and biological samples.

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 co-authored scientific publication, we expect the student to be involved in this process.

Supervisor: **Andre Simpson** co-supervisor: **Ronald Soong**

Office: **SY324** Sub-discipline: **Analytical/Biological**

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Understanding real-time bioaccumulation and transformation of perfluorinated contaminants in *Daphnia magna* using *in-vivo* NMR

D. magna are the standard organism used globally for aquatic toxicity testing. The present method used by regulatory bodies to assess aquatic toxicity of a compound is the "21 day reproducibility test". If no perturbations are noted in reproducibility then the chemical is deemed to be safe at that concentration. However, the literature has repeatedly reported more subtle effects such as DNA damage, changes to metabolic pathways, bioaccumulation, permanent binding can be missed using this standard approach as such there is great need to develop more informative, sensitive and rapid methods to truly evaluate aquatic toxicity.

In-vivo NMR, has the potential to monitor not only the entire molecular fingerprint of an organism in real time but also relates changes in the molecular profile to uptake, transformation, binding, bio-concentration and secretion of a contaminant species. As such *in-vivo* NMR provides the technical framework required to understand "how" and "why" certainly chemicals are toxic, information desperately needed by regulators to set more meaningful standards. Despite its considerable potential *in-vivo* NMR has not yet been applied to evaluate toxicity in an environmental context.

In this project *in-vivo* NMR will be used to monitor the real time uptake, biotransformation and binding of perfluorinated contaminants which are now found ubiquitously in our environment. Perfluorinated hydrocarbons are present in human blood in the ppb range (50 ppb average in the public) to ppm range (3M workers). The chemicals exhibit complex toxicity that is not well understood. NMR has a key role to play in understanding the toxicity of PFC's for example our group showed that PFOA and PFOS interact preferentially and irreversibly with Sudlow's site I and II on human serum albumin when introduced to human blood. However, at present there have been no studies of PFC's *in-vivo*. The chemicals themselves will be monitored by a range of NMR approaches to understand and explain their biological uptake, accumulation, transformation and secretion. *In-vivo* NMR holds great potential to understand the impact of chemicals prior to mass release into the environment.

Learning outcome

(1) The student will receive hands-on training on culturing *D. Magna*

(2) The student will receive training on using advanced NMR spectroscopy required for in-vivo studies.

(3) The student will learn about different statistical methods for data analysis and interpretation.

Required Training: WHMIS

Our expectation from students: Hard working, open minded student, with interests in more than one area of chemistry**.**

Supervisor: Ruby Sullan
Co-supervisor (if any): NA
Office: EV566
Sub-discipline: Biophysical Chemistry
Laboratory: EV 506-523
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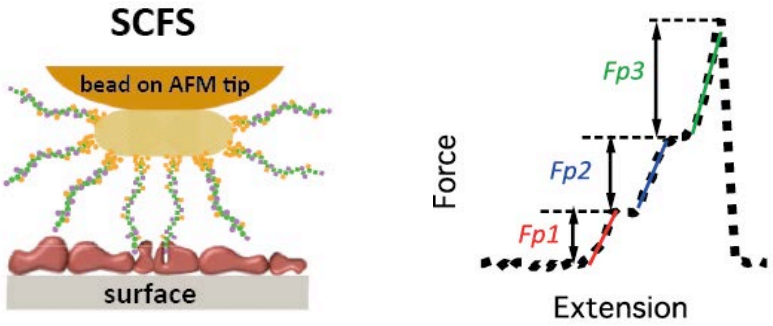
Interaction forces between *E. coli* and PDMS substrates of varying stiffness: Single cell force spectroscopy

Central to the initiation and maturation of biofilms are the bacterial cell surface adhesion molecules (adhesins) that mediate initial attachment between the cell and a wide range of surfaces. The chemical nature of these surfaces as well as the biochemical characteristics of the adhesins has been a focus of numerous studies. An important gap that remains to be filled is how bacterial adhesion depends on the stiffness of the underlying substrate. Nothing is currently known about the underlying molecular mechanisms and mechanical forces that govern this substrate-stiffness dependent bacterial adhesion. The goal of this CHMD90/91 research project is to quantify the interaction forces between *E. coli* (wild-type and knockout mutants) and polydimethylsiloxane (PDMS) substrates of varying stiffness using atomic force microscopy (AFM)-based single cell force spectroscopy (SCFS). This will quantify the degree of contribution of the key adhesins that mediate the initial attachment and growth of bacteria to substrates of varying stiffness, at the single-cell level.

- In this project, the student will learn to grow and manipulate bacteria, and measure forces of interactions with substrates using the AFM. The student will acquire and analyze force-extension curves to quantitatively characterize bacterial adhesion.
- The student is required to take WHMIS and Biosafety trainings prior to lab work.
- The student is expected to carry out experiments and analyze data as pre-discussed with the supervisor, meet weekly with the supervisor to track research progress, and write a final thesis report at the end of the project.



References:

[1] Friedrichs, J, et al. A practical guide to quantify cell adhesion using single-cell force spectroscopy. *Methods*, **2013**, 60, 169-178.
[2] Sullan RM, et al. Single-cell force spectroscopy of pili-mediated adhesion. *Nanoscale*, **2014**, 6, 1134-43.