4^{th}-Year Chemistry Thesis Projects 2022-2023 Academic Year

Table of Contents

Application for Thesis Information and Instructions

OntarioTech UNIVERSITY

4th-Year Chemistry Thesis Projects 2022-2023

Introduction

The thesis option consists of two courses: CHEM 4410U and CHEM 4420U. Each course constitutes 3 credit hours of the 120 credit hours required for an honours degree. Students are expected to enroll and pass CHEM 4420U immediately following CHEM 4410U. Under most circumstances, these courses will be taken in the fall and winter semesters of the student's final academic year.

The completion of the honours thesis is expected to require at least 230 hours of work on the part of the student (i.e., an average of 9 hours per week in each of the two semesters). The majority of this time will be spent in the laboratory conducting original research under the supervision of a faculty member. The evaluation of the chemistry honours thesis will be based on three components: i) in-lab performance; ii) oral defence of the thesis; iii) written dissertation. Both the student and the faculty supervisor should familiarize themselves with policies and procedures governing the honours thesis. These guidelines should not be interpreted as superseding any regulations described in the university calendar or general policies of the Faculty of Science.

Qualification for the Honours Thesis

To qualify for the honours thesis in chemistry a student must:

1. Have completed 90 credit hours toward their degree by the beginning of the fall semester of the year in which they intend to take CHEM 4410U / 4420U.
2. Have a GPA of 2.0 and be in clear academic standing.
3. Have passed at least four of: CHEM 3040U, CHEM 3120U, CHEM 3220U, CHEM 3520U and CHEM 3540U.

Students who have not completed 90 credit hours at the end of their third-year may be admitted provisionally to CHEM 4410U if they can show that they will have completed 90 credit hours by the start of the fall semester.

Selection of a Project

Each year faculty members in the Faculty of Science willing to supervise undergraduate theses in chemistry will provide a list of thesis projects from which a student may choose. Normally, a student completing a program in chemistry will do a project under the supervision of one of the chemistry faculty members. However, projects from other disciplines (or even other Faculties) may also be acceptable as long as the research involves significant chemistry content. Such projects require the approval of the Chemistry Undergraduate Studies Committee.

Students may apply to work on a project by completing the "Honours Thesis Application" form available on the Faculty of Science website. The completed form is submitted by email to the current Undergraduate Program Director (UPD) for Chemistry **(olena.zenkina@ontariotechu.ca in 2022.)** Acceptance by an individual supervisor is not guaranteed and is at the sole discretion of the supervisor. Students must apply to work on a project by **April 30** of the year prior to starting the research project. The UPD will inform students asap (by May 31^{st} at the latest) if they have been selected by a supervisor and are approved to register in CHEM 4410U/4420U.

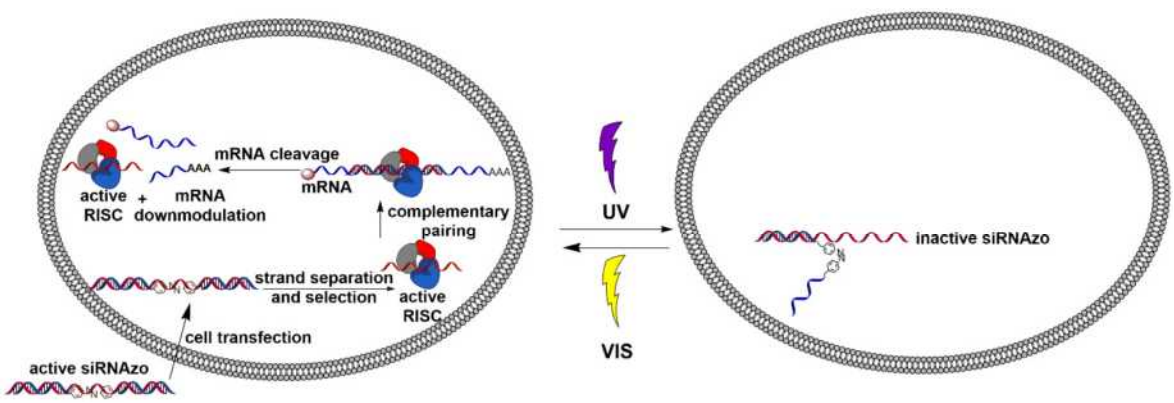
Professor Jean-Paul Desaulniers, Professor – Research Profile

The Desaulniers research group in Chemical Biology uses tools of organic chemistry, biochemistry, biophysical chemistry, and molecular biology to target, probe, and understand various components of gene expression. Organic chemistry is a powerful research tool for biology, because it allows us to answer key questions of biological importance. Diverse projects in our group range from the use of synthetic organic chemistry to generate new molecules with potential beneficial properties, to cell-based biological characterization of macromolecular-ligand interactions.

Research Projects for Chemistry Students for the 2022-2023 Academic Year

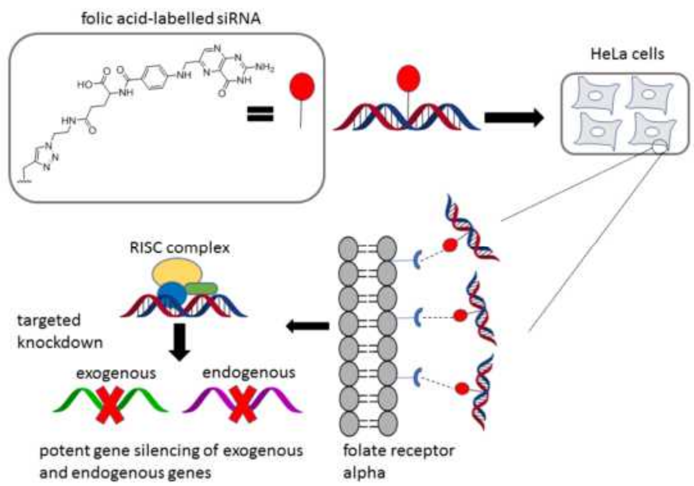
Project 1. Chemical Synthesis of Photoswitchable siRNAs

In this project, an undergraduate exchange student will work closely with a senior PhD student aimed at synthesizing new types of chemically-modified short-interfering RNAs that have photoresponsive properties. Through the use of organic chemistry, the student will synthesize phosphoramidite building blocks, and synthesize RNAs on solid-phase resin. This multi-disciplinary project will expose the exchange student to wide range of experimental techniques in a state-of-the art laboratory.



Project 2. Synthesis of Folic-Acid Derivative Phosphoramidites for Nucleic Acids

Recently, we have identified that folic-acid tagged siRNAs are excellent vectors for delivery of siRNAs into cells. To improve the synthetic utility of the chemistry, we are investigating the synthesis of folic acid phosphoramidites, that could allow for facile site-specific incorporation into a library of oligonucleotides. The student working on this project will be exposed to organic chemistry, and solid-phase synthesis.



Selected Publications (students bolded)

1) **L. Salim**, E. Goss, and J.-P. Desaulniers. "Synthesis and Evaluation of Modified siRNA Molecules Containing a Novel Glucose Derivative" *RSC Advances* **2021**, *11*, 9285-9289.

2) **L. Salim** and J.-P. Desaulniers. "To Conjugate or to Package? A Look at Targeted siRNA Delivery via Folate Receptors" *Nucleic Acid Ther.* **2021**, *31*, 21-38.

3) **M. L. Hammill**, G. Islam, and J.-P. Desaulniers. "Reversible Control of RNA Interference by siRNAzos" *Org. Biomol. Chem.* **2020**, *18*, 41-46.

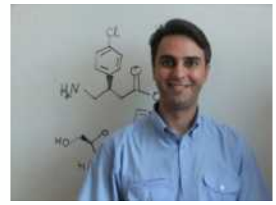
4) **L. Salim**, G. Islam, and J.-P. Desaulniers. "Targeted Delivery and Enhanced Gene-Silencing Activity of Centrally-Modified Folic Acid-siRNA Conjugates" *Nucleic Acids Res.* **2020**, *48*, 75-85.

5) **K. Tsubaki**, **M. L. Hammill**, **A. J. Varley**, M. Kitamura, T. Okauchi, and J.-P. Desaulniers. "Synthesis and Evaluation of Neutral Phosphate Triester Backbone-Modified siRNAs" *ACS Med. Chem. Lett.* **2020**, *11*, 1457-1462.

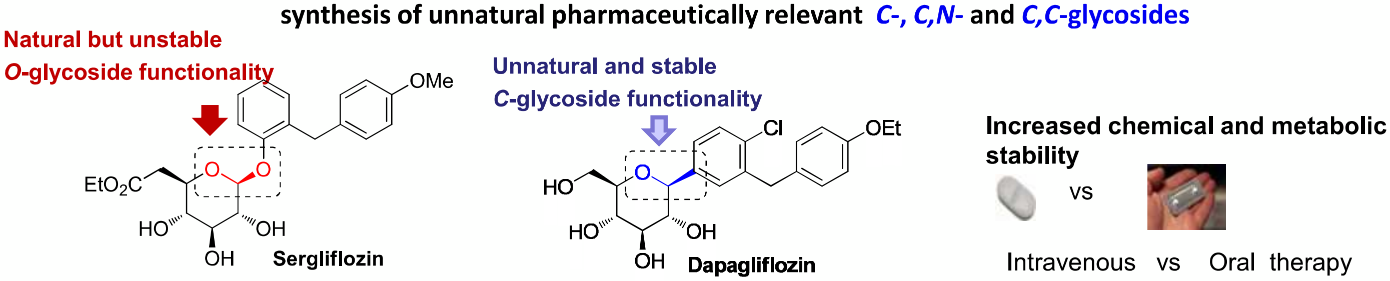
More information: Visit http://jpdesaulniers.com and check us out on Twitter (@JP_Desaulniers and @DesaulniersLab).

Dr. Yuri Bolshan
Associate Professor

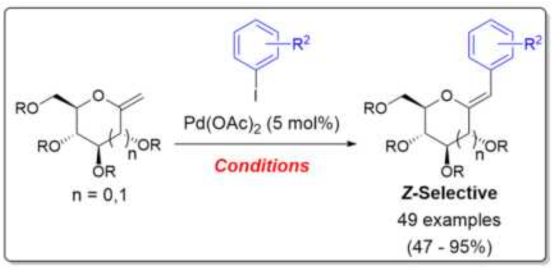
Pharmaceutical/Synthetic Organic Chemistry
Science Building, Room 4070



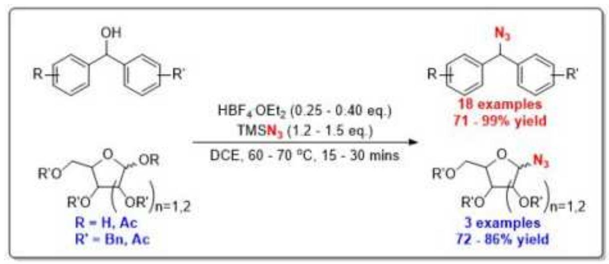
Development of Brønsted acid and metal-catalyzed methodologies for the synthesis of unnatural pharmaceutically relevant *C-*, *C,N-* and *C,C-glycosides*



Selected publications



J. Regier, S. Ghanty, Y. Bolshan*
J. Org. Chem. **2022**, 87, 1, 524–530



J. Regier, R. Maillet,* Y. Bolshan
Eur. J. Org. Chem. **2019**, 2390−2396

*R. Maillet – undergraduate thesis student

Dr. Fedor Naumkin

Associate Professor of Chemistry
Ph.D. (General Phys. Inst., Russ. Acad. Sci.)

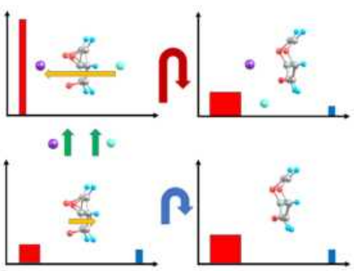
Research profile

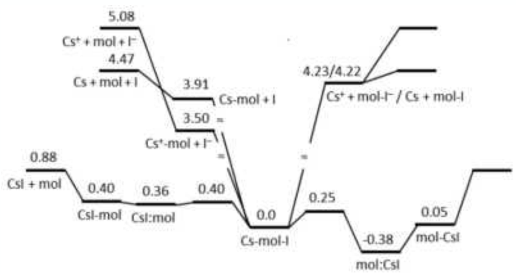
The Computational Nanochemistry research deals with the design of new nanosystems (clusters, intermolecular complexes, molecular junctions & interfaces),
prediction and analysis of their structures, properties, and their inter-relationships.
Of specific current interest are novel systems with molecules:

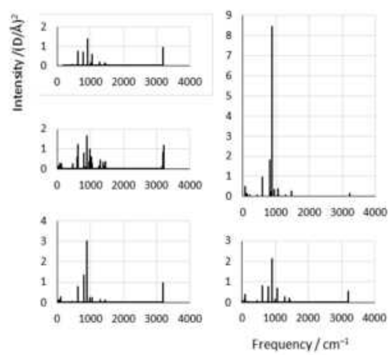
(1) trapped between counter-ions and stimulated to isomerise/react;
(2) linked by metals in assemblies with controllable shape alterations.

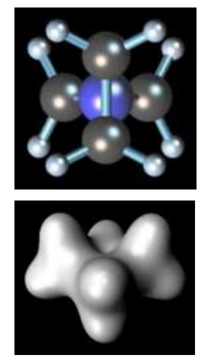
Various possible applications include:

- building blocks for materials with desired properties,
- light detection and utilization, molecular electronics and machinery,
- efficient energy storage at molecular level,
- molecular self-assembly and induced reactions, etc.









Dr. Fedor Naumkin **Contact: Fedor.Naumkin@uoit.ca**

- ***Project 1. Modelling of highly polar supramolecular species with enhanced IR activity and self-assembly capability.***
- ***Project 2. Evaluation of field-induced reactions of molecules trapped between counter-ions.***

The student will computationally investigate a series of insertion complexes of molecules trapped in counter-ion pairs.

These systems are to be suitably designed, their structures optimized in terms of energy, stability, polarity, IR spectra and other properties studied.

Project 1 focusses on the polarity and IR spectra, enhanced and system-structure sensitive. Dimerization as 1st step in self-assembly may also be involved.

Project 2 concentrates on the reaction barriers evolution inside the complex due to the mechanical pressure and electric field of the ions. A hyper-valence case may be included.

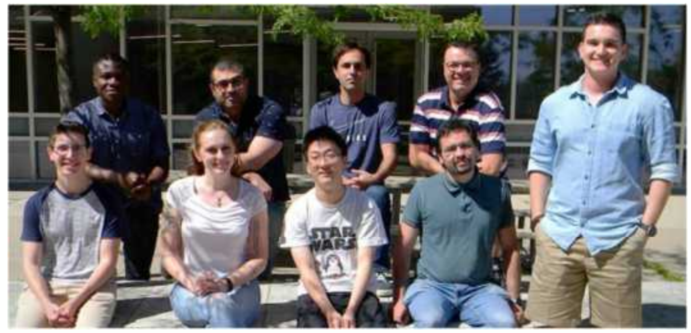
In either project the student will acquire practical experience of working with a state-of-the-art quantum-chemistry software and modern visualization tools, on high-performance computing facilities accessible at and through the UOIT.

Selected publications (* marks students):

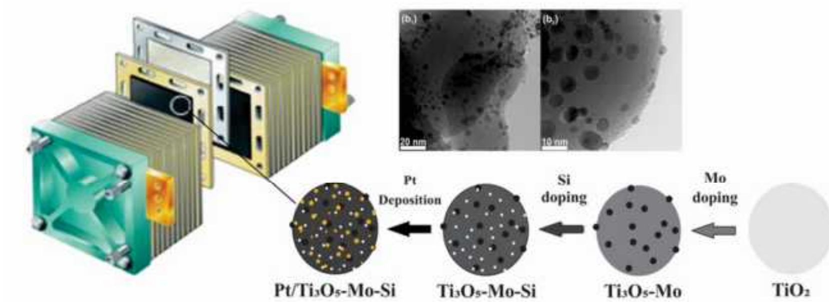
- S. Kerr* and F. Y. Naumkin, Field-assisted isomerization of a molecule intra-complexed with a counterion-pair, tracked via IR spectra. *To be submitted* (2021).
- M. Sullivan* and F. Y. Naumkin, Supramolecular complexes with insertion-enhanced polarity and tuned IR spectra. *Int. J. Quantum Chem.*, 121, e26534 (2021).
- M. Sullivan* and F. Y. Naumkin, Highly polar insertion complexes with focused IR spectra and internal field-inhibited isomerization. *ChemPlusChem*, 85, 2438-45 (2020).

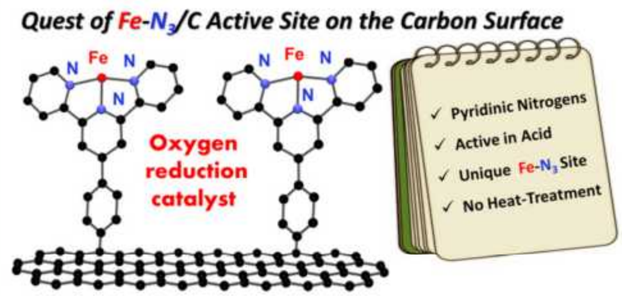
Dr. Brad Easton

Professor (Chemistry)
Ontario Tech Research Excellence Chair in Electrochemical Energy Materials
http://www.bradeaston.ca/



Research Interests: electrochemistry, materials chemistry, fuel cells, sensors, carbon surface chemistry, electrochromics





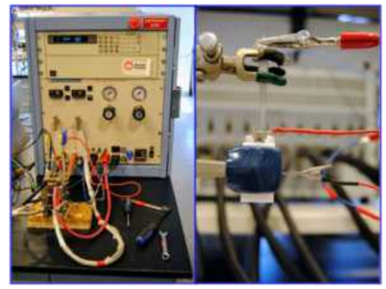
Selected publications based on undergraduate thesis:

- **J. Poisson, H.L. Geoffrey,** I.I. Ebralidze, N.O. Laschuk, J.T.S. Allan, A. Deckert, E.B. Easton, O.V. Zenkina, J. Phys. Chem C., 122 (2018) 3419 – 3427.
- **K. M. Yarrow**, N. E. De Almeida, E. B. Easton, "The impact of pre-swelling on the stability of Nafion/SS composite membranes", *J. Therm. Anal. Calorim.*, 119 (2015) 807 - 814.
- **O. Reid**, F. S. Saleh, E. B. Easton, "Determining electrochemically active surface area in PEM fuel cell electrodes with electrochemical impedance spectroscopy and its application to catalyst durability", Electrochimica Acta, 114 (2013) 278 – 284.

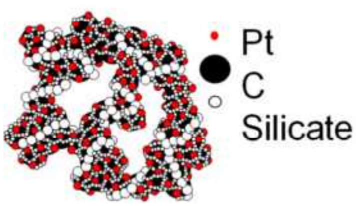
Dr. Brad Easton

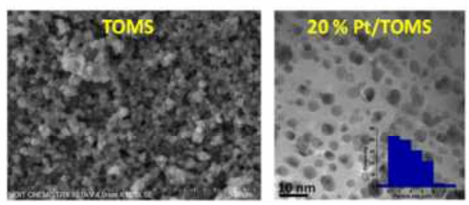
Professor (Chemistry)
Ph.D. (Memorial University of Newfoundland)
http://www.bradeaston.ca/

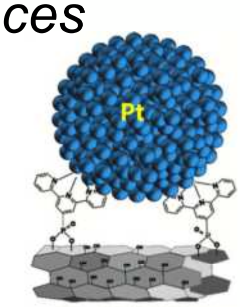
Available thesis projects for 2022/23



1. *Electrochemical stability of novel metal oxide-based fuel cell supports*
2. *Novel catalysts for electrochemical breathalyzer devices*
3. *The preparation of coordination based functional electrochromic materials on conductive surfaces (co-supervised with Dr. Zenkina)*



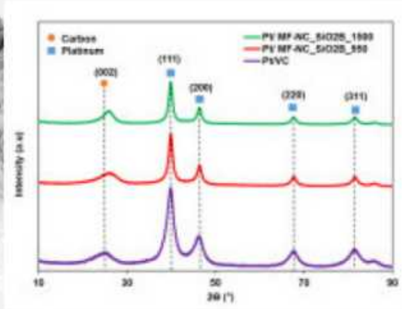


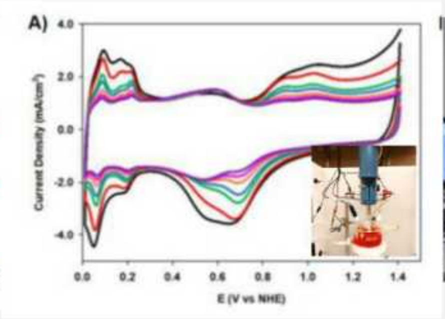


Professor Liliana Trevani, Associate Professor

Research Areas: physical chemistry (electrochemistry and thermodynamics) and materials science

Applications: energy storage and conversion, remediation, sensors, and hydrothermal chemistry





Honours Thesis Projects in Trevani's Group (2022-2023)

Water quality monitoring and safe water production

Even though access to water is recognized as a human right by the United Nations, there are still numerous regions where access to potable water is not guaranteed, challenging their economic development and growth. Work in this area in our group is intended to contribute to identifying and quantifying contaminants and developing low-cost potable water production systems. Below are two Honours Thesis projects offered in this area.

- **Project #1** aims to develop materials and methods for detecting contaminants in water. The student's work will focus on the synthesis and characterization of materials and their assembly in sensing devices to detect target organic and inorganic species in aqueous media.
- **Project #2** focuses on developing materials for safe water production and environmental remediation. The student will synthesize materials, including nano and mesoporous carbons, with tailored surface properties to eliminate target inorganic and organic species from water.

Both projects will require access to sophisticated experimental characterization techniques, and they will also provide opportunities for hands-on training in analytical chemistry. Both projects will involve the participation of graduate students.

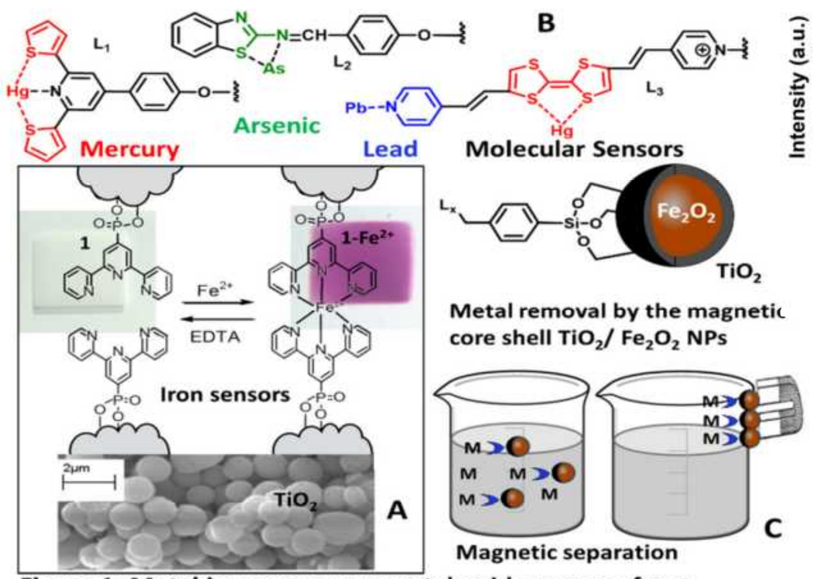
Development of electrodes for high temperature and pressure applications

Accurate water chemistry control under high temperature and pressure conditions is critical to many industrial processes, including the nuclear power industry. Because of the requirements, there is a need for specially designed sensors that can withstand extreme conditions without degradation. The student will develop and characterize electrodes for high temperature and pressure aqueous media conditions as part of this project. Chemical and electrochemical studies will be carried out to evaluate the electrodes' performance and improve their design.

For more information about these projects, please get in touch with Prof. Liliana Trevani (liliana.trevani@uoit.ca)

Prof. Olena Zenkina

1. Preparation of surface confined materials for selective metal ion sensing and removal of heavy metals/



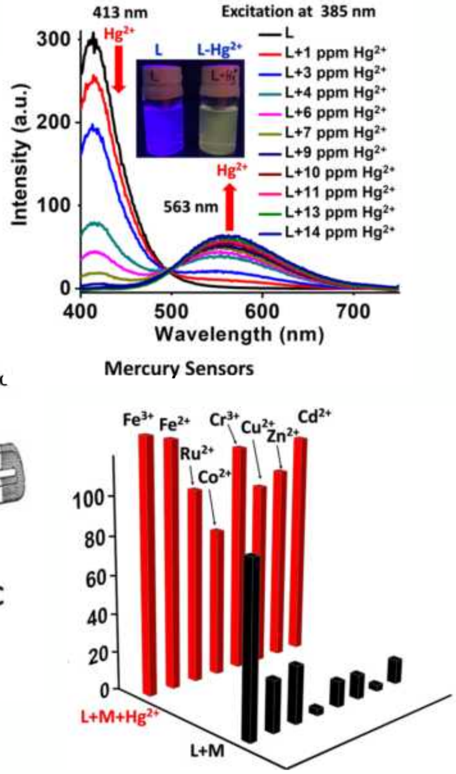


Figure 1: Metal ion sensors on metal-oxide nanosurfaces. A: Fe^{2+}; B: $Hg^{+/2+}$, Pb^{2+}, $As^{3+/5+}$. C: Removal of metal ions.

References: Undergraduate student authors marked in red

Egan J., Hynes A. J., Fruehwald H. F., Ebralidze I. I, King S. D., Alipour M.E.R., Naumkin F.Y., Easton B. E., Zenkina *O.V Journal of Materials Chemistry C.,* 2019, 7,10187. *Inside Cover Article.*

Laschuk N. O., Ebralidze I. I., Quaranta S., Kerr S., Egan J. G., Gillis S., Gaspari F., Latini A., Zenkina O.V., *Materials & Design*, **2016**, *107*, 18–25.

Laschuk N. O., Ebralidze I. I., Spasyuk D., Zenkina O. V. “*European Journal of Inorganic Chemistry* **2016**, *22*, 3530-3535.

Prof. Olena Zenkina and Prof. Brad Easton

2a The preparation of coordination based functional electrochromic materials and metal wires on the conductive surfaces.

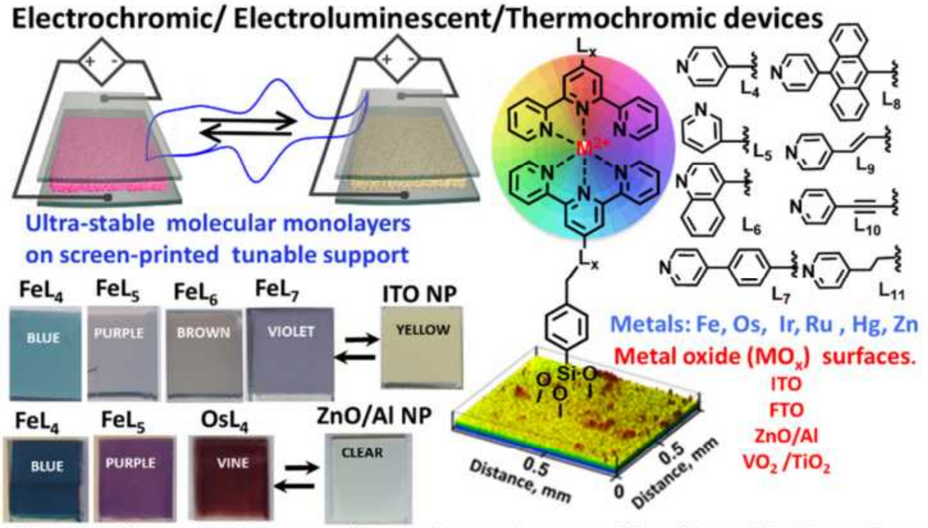


Figure 3. "Smart" chromogenic metal complexes on "intelligent" MO_x surfaces.

References: Undergraduate student authors marked in red

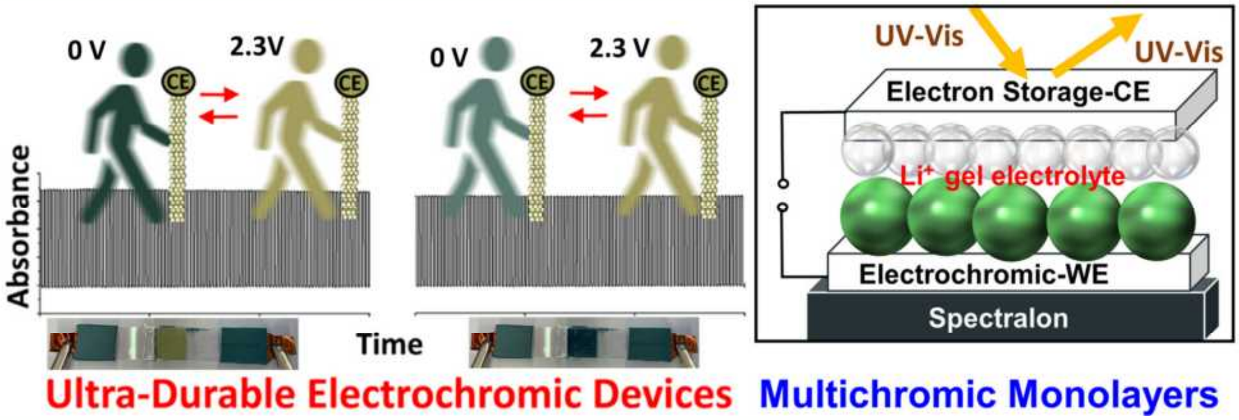
Ahmad, R.; Di-Palo, V..; Bell M..; Zenkina, O. V., Easton, E. B., *In Press. ACS Energy Mater.* **2022.**

Laschuk N.O., Ebralidze I.I., Poisson J., Egan J.G., Quaranta S., Cusden H., Allan J.T.S., Naumkin F., Gaspari F., Easton B., Zenkina O.V. *ACS Applied Materials & Interfaces.* **2018**, *10* (41), 35334–35343

Poisson, J.; Geoffrey, H. L.; Ebralidze, I. I.; Laschuk, N. O.; Allan, J. T. S.; Deckert, A.; Easton, E. B.; Zenkina, O. V., *J. Phys. Chem. C* **2018,** (122), 3419−3427.

Prof. Olena Zenkina and Prof. Brad Easton

2b. Optimization of the architectures and long term performance of electrochromic and energy storage devises.



References: Undergraduate student authors marked in red

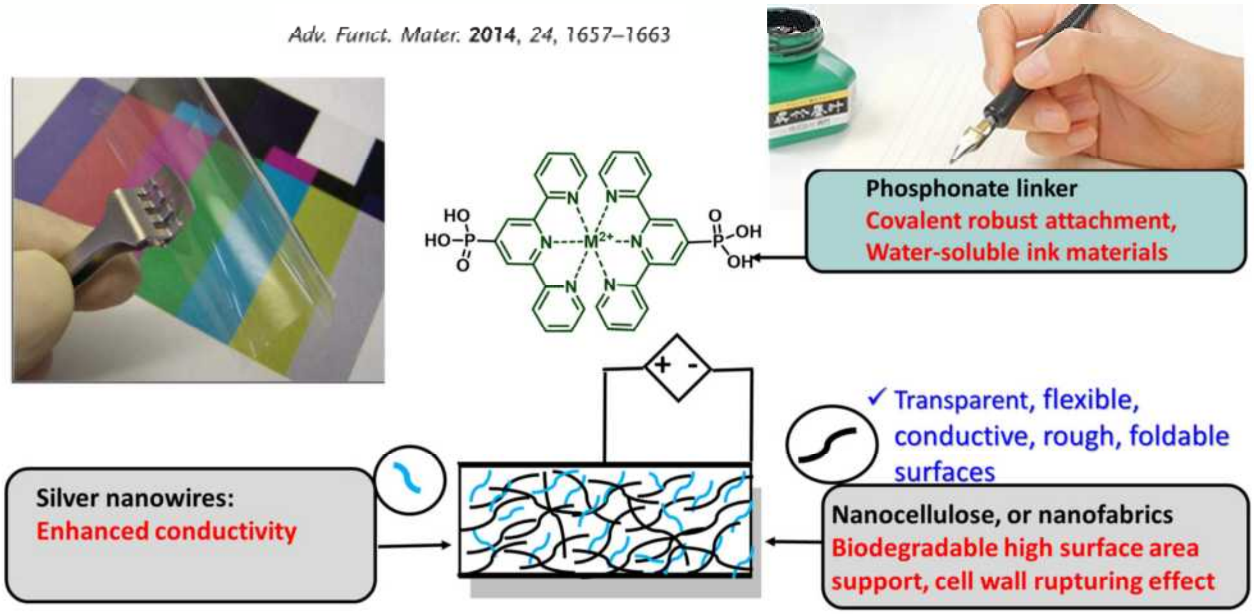
Ahmad, R.; Di-Palo, V..; Bell M..; Zenkina, O. V., Easton, E. B., *In Press. ACS Energy Materials.* **2022.**

Laschuk N.O., Ebralidze I.I., Poisson J., Egan J.G., Quaranta S., Cusden H., Allan J.T.S., Naumkin F., Gaspari F., Easton B., Zenkina O.V. *ACS Applied Materials & Interfaces.* **2018**, *10* (41), 35334–35343

Poisson, J.; Geoffrey, H. L.; Ebralidze, I. I.; Laschuk, N. O.; Allan, J. T. S.; Deckert, A.; Easton, E. B.; Zenkina, O. V., *J. Phys. Chem. C* **2018,** (122), 3419−3427.

Prof. Olena Zenkina

3. Nanocellulose based conductive surfaces for smart molecular materials.



We interested to make a water-soluble ink of different colours from well-defined transition metal complexes and to be able to "write" (covalently introduce electrochromic molecules) on the transparent biodegradable nanopaper. Novel materials may allow an easy electrochemically switching between colours and/or erasing of colours.

We target erasable, bendable transparent, multicolour electrochromic paper.

This is totally new research direction in our group.

We will closely collaborate with group of Prof. Easton on Electrochemistry side of this project!

Honours Projects
Dr. Kevin Coulter (Associate Teaching Professor)

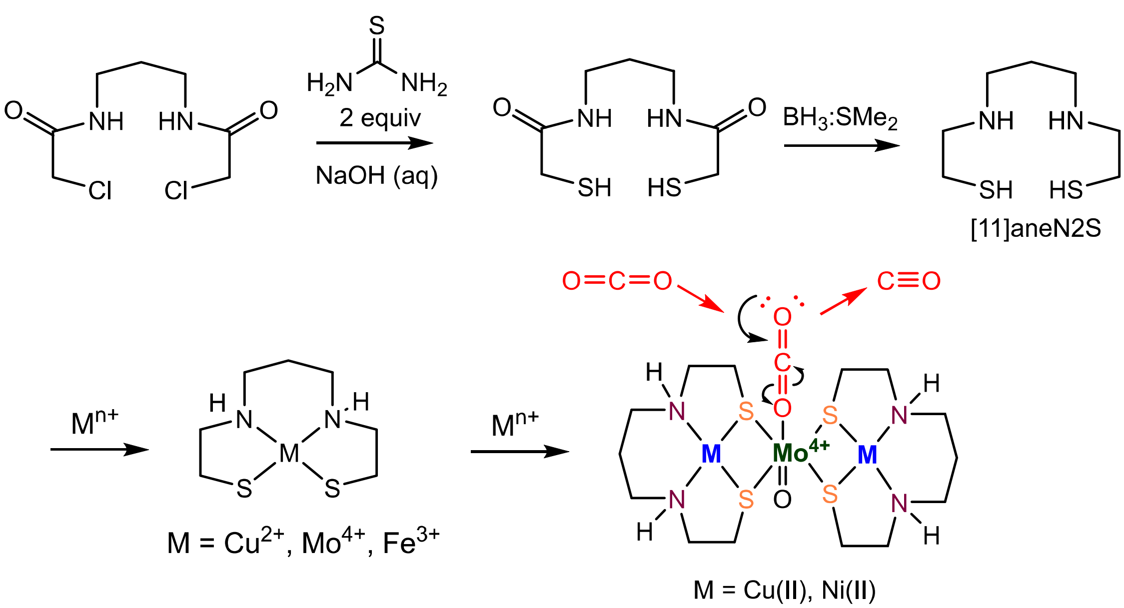
The focus of these Honours projects is to test both novel and existing Inorganic metal complexes for their activity as catalysts for the key “solar fuels” reactions:

1. Water splitting: H_2O (l) $\longrightarrow$ H_2 (g) + O_2 (g) $E^0 = -1.23$ V
2. CO_2 reduction: $CO_2 + 12\ H^+ + 12\ e^- \longrightarrow CH_3CH_2OH + 3\ H_2O$ $E^0 = 0.084$ V

NOTE: K. Coulter Honours Projects will be run over the Summer and Fall terms (not winter) when the undergraduate lab is more available

Project 1(a). Synthesis of N_2S_2 ligand complexes and Determination of CO_2 reduction activity

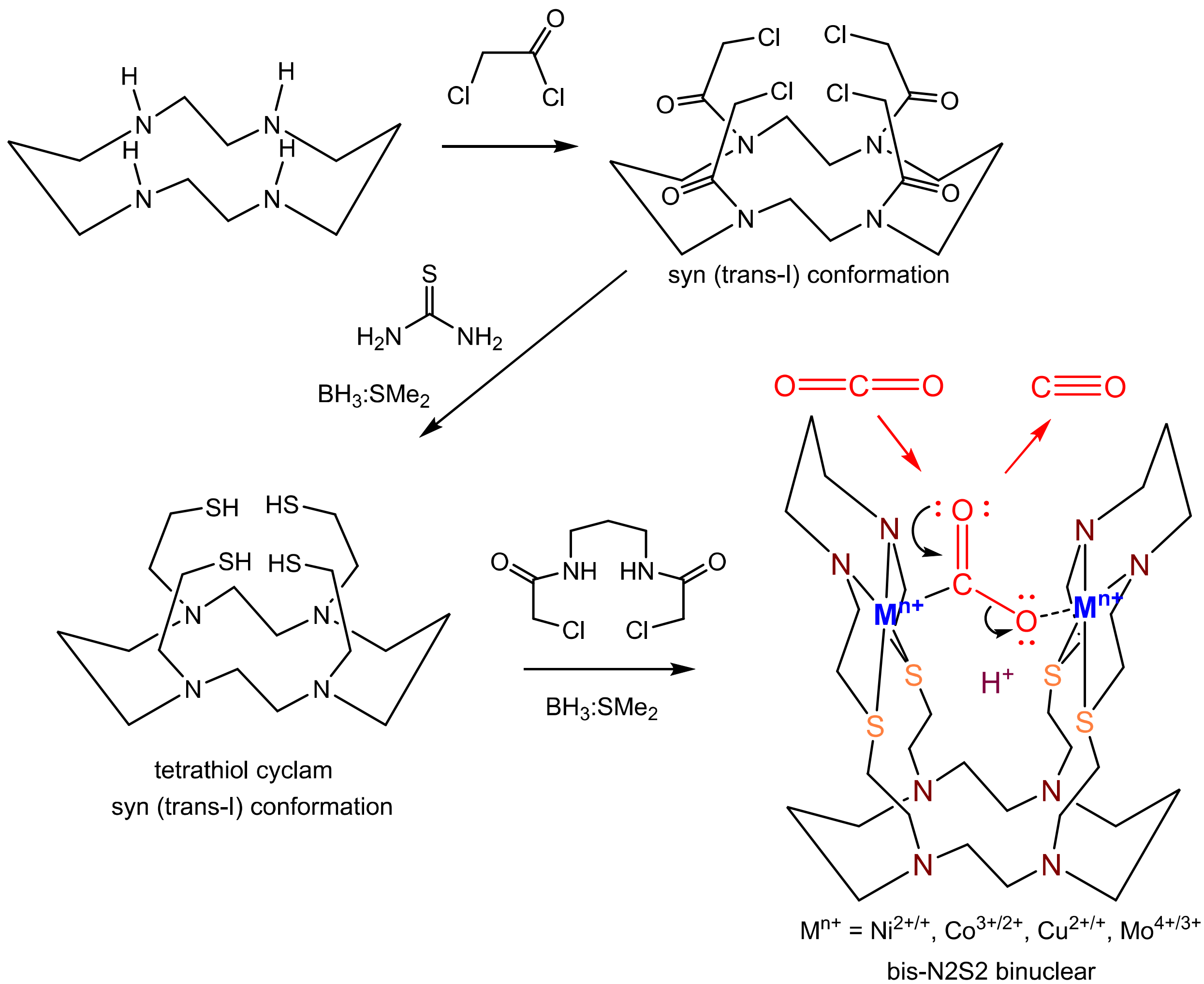
Although a few metal complexes of the [11]aneN2S ligand below have been reported[1], their activity for catalytic electroreduction of CO_2 was not determined. It was also reported[1] that additional metal coordination can form the trinuclear complex shown, which could have enhanced CO_2 reduction activity through metal ion cooperation where the second metal could assist in abstracting the O^{2-} oxide from the CO_2. The novel synthetic route below would avoid the volatile toxic reagents (H_2S or ethylene sulfide) used in previous methods, and the diamide intermediate will be non-volatile thereby avoiding a strong thiol stench. Also, the intermediate [11]aneN2S diamide can be used as a synthon to prepare the bis-N2S2 binuclear ligand in project 2(c) below.



1. Lawrance, *J. Chem. Soc. Dalton Trans.* **1976**, 939; *ibid* **1976**, 942

Project 1(b). Synthesis of bis-N_2S_2 binuclear ligand complexes and Determination of CO_2 reduction activity

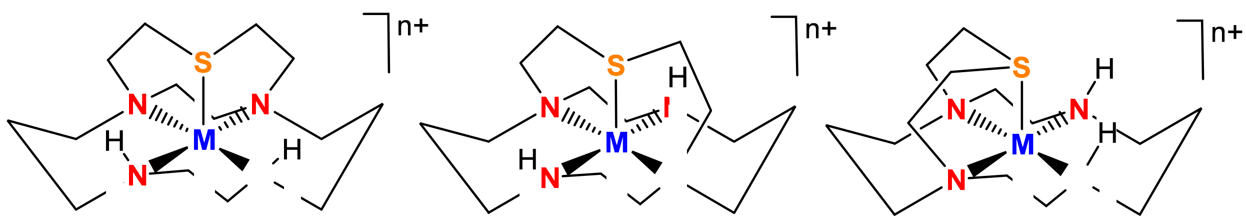
To use the methodology from project 1(a) to make the novel tetrathiol cyclam and bis-N2S2 binuclear ligands and their metal complexes, and determine their CO_2 reduction activity. The tetra(α-chloroamido)cyclam has been reported[1] and is known to adopt mostly the syn trans-I configuration with all four arms on the same side of the ring. Binuclear complexes are of great interest for small molecule catalysis and may exhibit enhanced CO_2 reduction activity through metal ion cooperation where the second metal could assist with additional electron transfer and/or in abstraction of the O^{2-} oxide from the CO_2.



1. Alex McAuley, S. Subramanian and T. Barclay *Dalton Trans.*, 2010, **39**, 9956–9961

Project 2. Synthesis of N_4S Macrobicycles

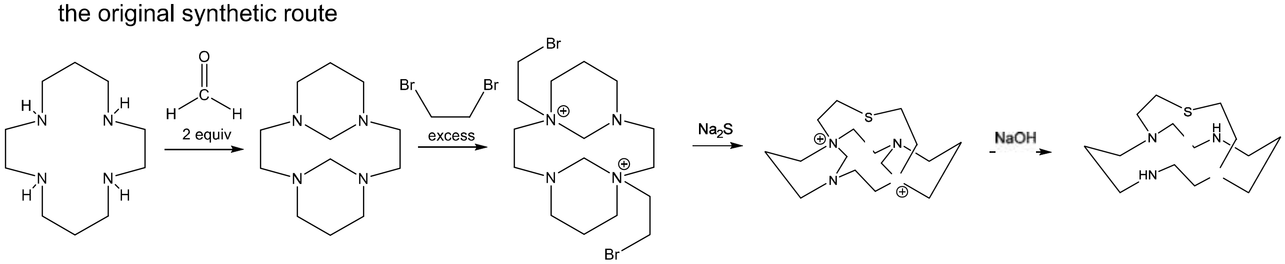
The three isomeric N4S macrobicyclic ligands (below) were synthesized in my thesis work, but their metal complexes have never been tested for CO_2 reduction activity. These ligands are based on the well studied [14]aneN_4 ligand "cyclam" where $Ni(cyclam)^{2+}$ and $Co(cyclam)^{3+}$ complexes have been shown to be electrocatalysts for reduction of CO_2 to CO with both high rate constants and Faradaic efficiencies, and surprising selectivity for CO_2 reduction over H^+.[1,2] It is of interest to re-make these N4S bicycle complexes and determine their activity for electroreduction of CO_2 because the apical soft thioether donor helps stabilize the reduced Ni^+ and Co^+ oxidation states. Some time ago, Dr. Etsuko Fujita at Brookhaven National Laboratory had expressed interest in obtaining samples of these complexes to study their CO_2 reduction activity via the pulse radiolysis technique using the 2 MeV Van de Graaff electron accelerator at BNL. The synthesis of the hemi-N4S bicycle isomer was very low yield, and a new method for regioselective di-alkylation of the 1,11 (diagonal) N's of cyclam has since been reported[3] that can be used to solve the problem of the original synthetic route[4].



[9]aneN4S   hemi-N4S   [10]aneN4S

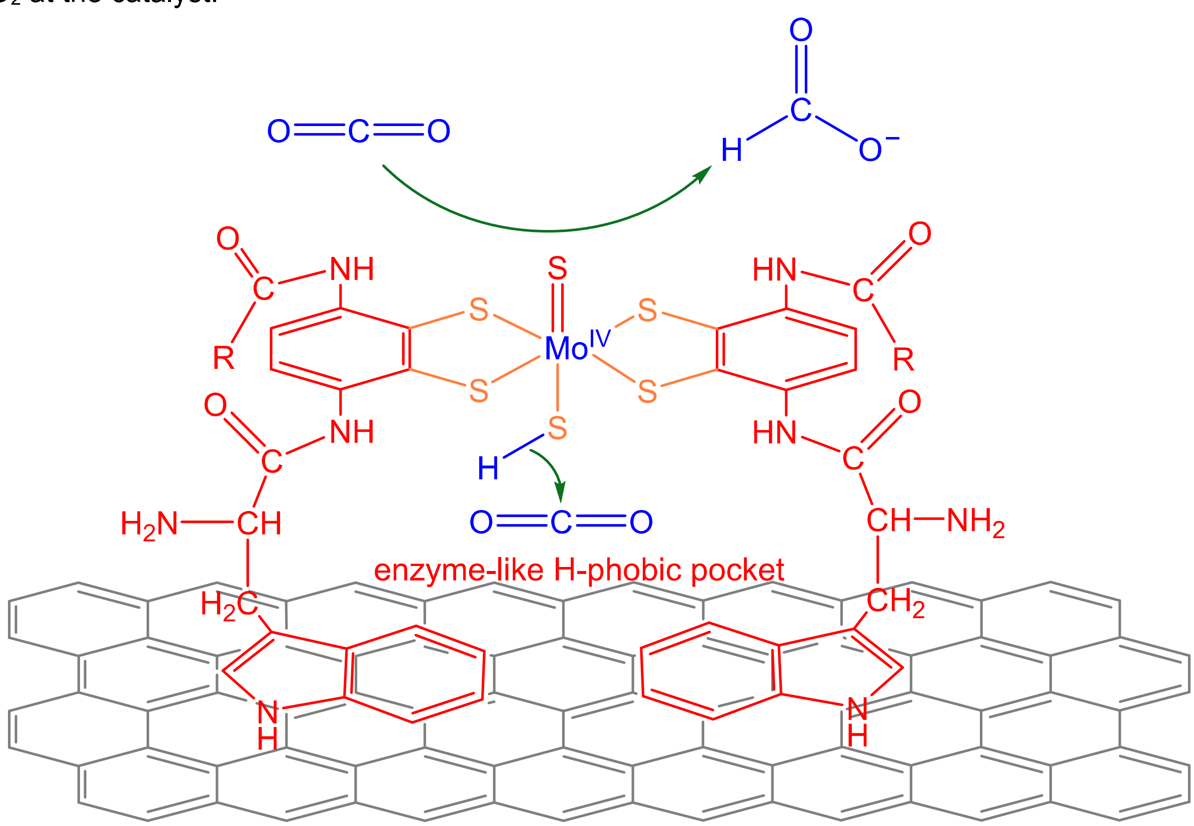
1. Kubiak *et al Inorg. Chem.* **2012**, *51*, 3932−3934; Sauvage et al J. Am. Chem. Soc. 1986, *108(24)*, 7461; Eisenberg et al *J. Am. Chem. Soc.* **1980**, *102*, 7361
2. Fujita *et al Energy Environ. Sci.*, **2012**, *5*, 9502; Fujita *et al J. Am. Chem. Soc.* **1991**, *113*, 1, 343-353
3. Guilard *et al Eur. J. Org. Chem.* **1998**, 1971-1975

4. Proposed synthetic route to make hemi-N4S bicycle avoiding the excessively rigid diamide intermediate used in the original synthetic route



Project 3. Synthesis of metal complexes with hydrophobic "footings" for adsorption on to carbon electrodes to facilitate increased activity for CO_2 reduction catalysis (co-supervised with Dr. Liliana Trevani)

The goal of this project is to increase the activity of CO_2 reduction catalysis of metal complexes by mitigating the problem of the low solubility of CO_2 in water and the low rate of diffusion of non-polar CO_2 to the polar metal catalyst. An ideal solution would be to emulate the enzyme carbonic anhydrase and CO_2 reduction enzymes (FDH, CODH and FMD) that have a hydrophobic pocket at the active site to attract the non-polar CO_2. It is very difficult to synthesize ligands that have a similar hydrophobic pocket but a more feasible solution would be to add "hydrophobic footings" to the ligands and adsorbing the complex to the non-polar surface of a carbon electrode to form a pocket. A quick search of the literature to see if anything has been reported on creating a hydrophobic pocket found an article[1] reporting that a superhydrophobic surface was generated on a Cu dendrite electrode by adsorbing 1-octadecanethiol, inspired by the structure of gas-trapping cuticles on subaquatic spiders, which resulted in a large increase in the Faradaic efficiency of CO_2 reduction to ethanol, from 4% without to 17% with the hydrophobic surface, and from 9% to 56% for CO_2 reduction to ethylene, showing the importance of having a hydrophobic pocket to attract and accumulate CO_2 at the catalyst.



1. "Bio-inspired hydrophobicity promotes CO_2 reduction on a Cu surface" Wakerley D, Lamaison S, Ozanam F, Menguy N, Mercier D, Marcus P, Fontecave M, Mougel V. *Nature materials.* **2019** Nov;18(11):1222-7

Chemistry Honors Thesis Application Form for 2022-2023

Student Information			
Student Name			
Student ID No.			
Chem Program			
E-Mail Address			
Student Qualifications			
Current GPA*			
Grades in Chemistry**			
Lists other courses (and grades) that may be of interest to a potential supervisor			

*Final approval pending marks as of end of April.

** Input "IP" for courses that are currently in progress.

Preferred Thesis Projects	
1st Choice Supervisor: (TTTF)***	
1St Choice Project Title:	
2nd Choice Supervisor: (TTTF)***	
2nd Choice Project Title:	
3rd Choice Supervisor: (TTTF or TF)***	
3rd Choice Project Title:	

*** TTTF = Tenured or Tenure-Track Faculty; TF = Teaching Faculty.

Supervisor Acceptance (Office use only, not to be filled out by student)	
Project Title: Name	

Supervisor Name	
Supervisor Signature	
Date	
UPD Approval Date	
UPD Signature	

Email completed form the thesis project coordinator by April 30th 2022.

Acceptance by a supervisor is not guaranteed and is at the sole discretion of the supervisor. Students are encouraged to contact potential supervisors to discuss potential projects before applying. Please provide at least two potential thesis supervisors.