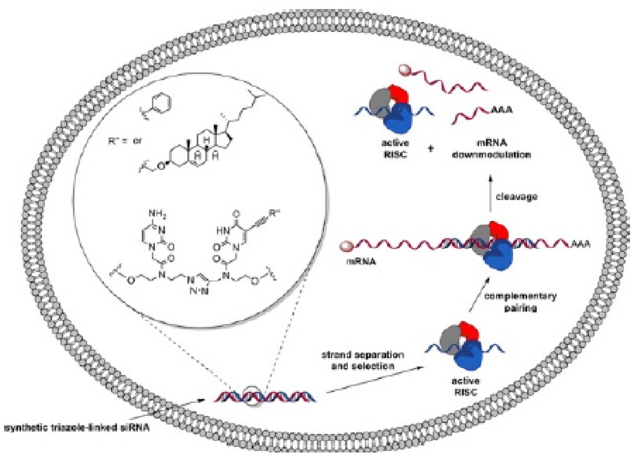
4th Year Thesis Projects in Chemistry

Professor Jean-Paul Desaulniers, Associate 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.

Project 1. Chemical Synthesis of Novel Short-Interfering RNAs



In this project, an undergraduate exchange student will work closely with other members of the lab, aimed at synthesizing new types of chemically-modified short-interfering RNAs. 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.

Selected Publications Involving Undergraduate Students

1) M. L. Hammill, **A. Patel**, **M. A. Alla**, and J.-P. Desaulniers. "Stability and Evaluation of siRNAs Labeled at the Sense Strand with a 3'-Azobenzene Unit" *Bioorg. Med. Chem. Lett.* **2018**, *28,* 3613-3616.

2) L. Salim, C. McKim, and J.-P. Desaulniers. "Effective Carrier-Free Gene-Silencing Activity of Cholesterol-Modified siRNAs" *RSC Advances* **2018**, 8, 22963-22966.

3) S. G. Forrester, J. Foster, **S. Robert**, **L. Salim**, and J.-P. Desaulniers. "Efficient Synthesis of the $GABA_A$ Receptor Agonist *trans*-4-Aminocrotonic Acid (TACA)" *Bioorg. Med. Chem. Lett.* **2017**, *27,* 4512-4513.

4) **B. J. Peel**, G. Hagen, **K. Krishnamurthy**, and J.-P. Desaulniers. "Conjugation and Evaluation of Small Hydrophobic Molecules to Triazole-Linked siRNAs" *ACS Med. Chem. Lett.* **2015**, *6*, 117-122.

5) T.C. Efthymiou, **V. Huynh**, **J. Oentoro**, **B. Peel**, and J.-P. Desaulniers. "Efficient Synthesis and Cell-Based Silencing Activity of siRNAs that Contain Triazole Backbone Linkages" *Bioorg. Med. Chem. Lett.* **2012,** *22*, 1722-1726.

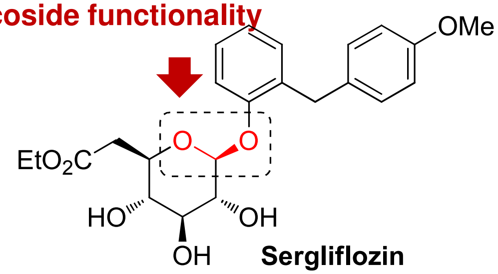
More information: Visit http://faculty.uoit.ca/desaulniers/home.htm.

Dr. Yuri Bolshan

Associate Professor

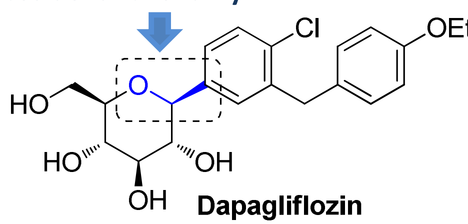
Pharmaceutical/Synthetic Organic Chemistry
Science Building, Room 4070

Natural but unstable
***O*-glycoside functionality**



Sergliflozin

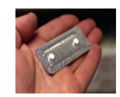
Unnatural and stable
***C*-glycoside functionality**



Dapagliflozin

Increased chemical and metabolic stability

vs



Intravenous vs Oral therapy

OUR RESEARCH

Development of methodologies for the synthesis of unnatural *C*-glycosides and β–and γ-amino acids

Incorporation into anticancer drugs to improve their pharmacological properties.
Emphasis: antileukemic drugs

γ-amino acids are known neurotransmitters
Emphasis: Huntington's disease
Parkinson's disease, pain

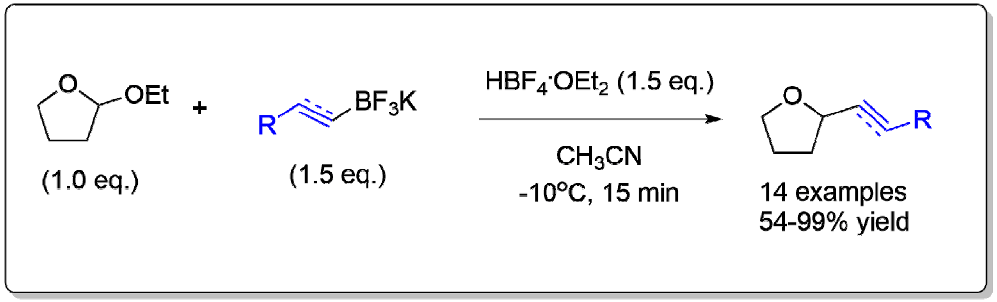
Synthesis of inhibitors for epigenetic proteins that modify DNA and control genes' expression

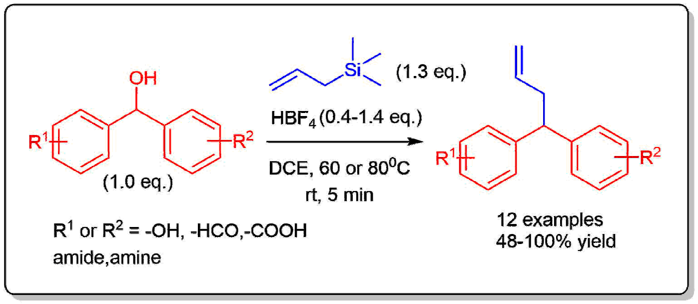
β–amino acids are metabolically more stable than α-amino acids
Emphasis: synthetic analogs of natural antibiotics

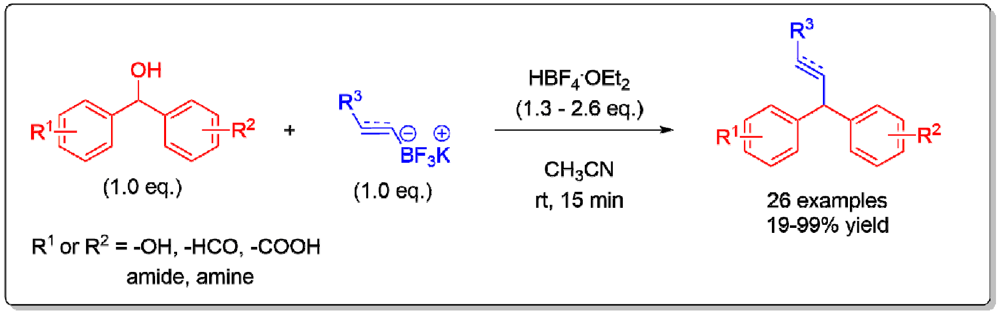
Dr. Yuri Bolshan

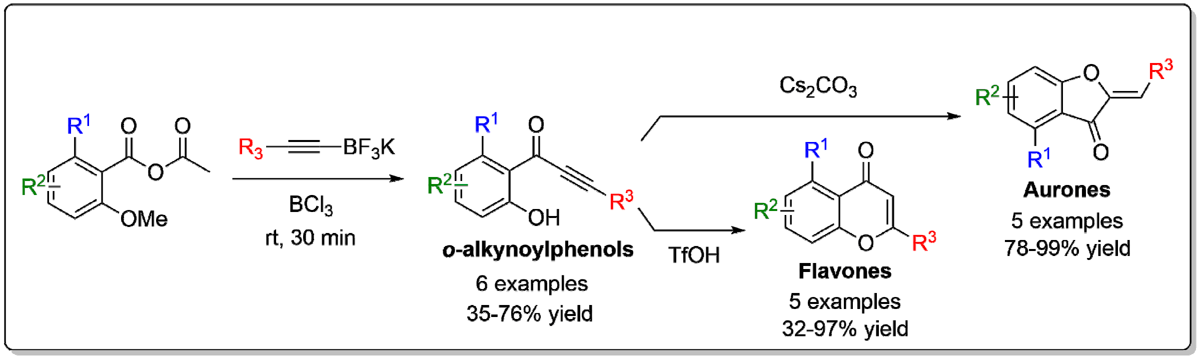
Associate Professor

Pharmaceutical/Synthetic Organic Chemistry
Science Building, Room 4070



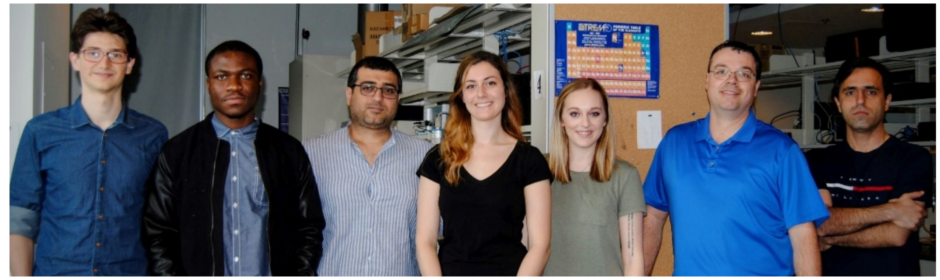




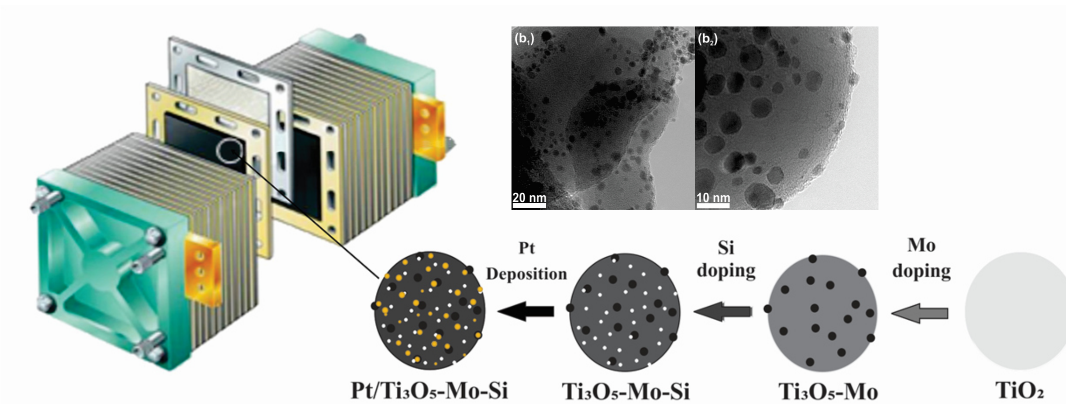


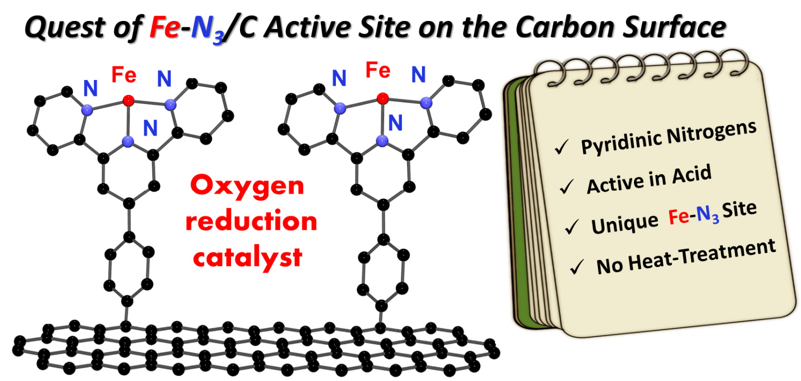
Dr. Brad Easton

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



Research Interests: electrochemistry, materials chemistry, fuel cells, sensors, carbon surface chemistry, H_2 production



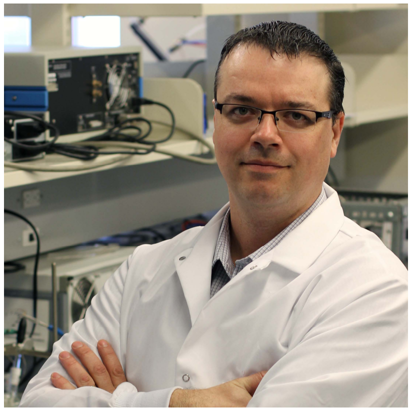


Selected publications based on undergraduate thesis:

- **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.

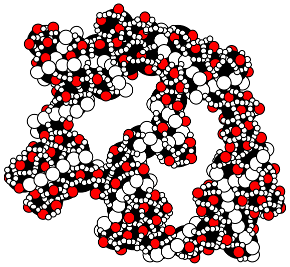
Dr. Brad Easton

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



Available thesis projects for 2019/20

1. *Electrochemical stability of novel metal oxide-based fuel cell supports*
2. *Support effects related to photo-enhanced electro-oxidation of organic fuels*
3. *The preparation of coordination based functional electrochromic materials and metal wires on conductive surfaces.*
   (co-supervised with Dr. Zenkina)



Dr. Fedor Naumkin

Associate Professor

Ph.D. (Russian Academy of Sciences)

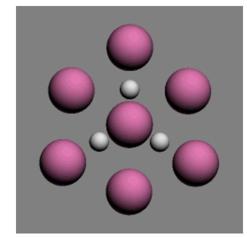
Research profile

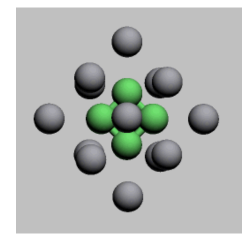
The <u>Computational Nanochemistry</u> research deals with design of new nanosystems (atomic and molecular complexes, clusters, and interfaces), analysis of their structures, properties, and their inter-relationships.

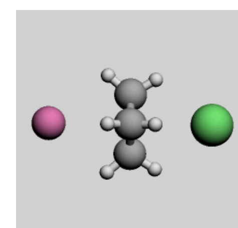
Of specific current interest are novel systems with molecules trapped (1) between counter-ions or (2) inside metal cluster cages

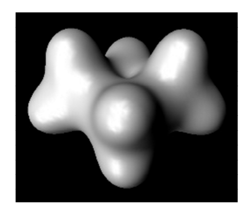
Various possible applications include:

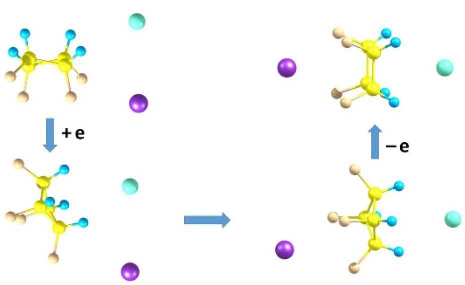
- new tuneable nanocatalysts and materials,
- building blocks with desired shapes and electronic properties,
- light detection and utilization, molecular electronics and machinery,
- efficient matter and energy storage at molecular level,
- molecular self-assembly and induced reactions, etc.

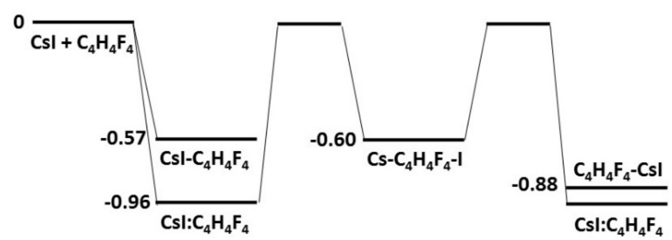


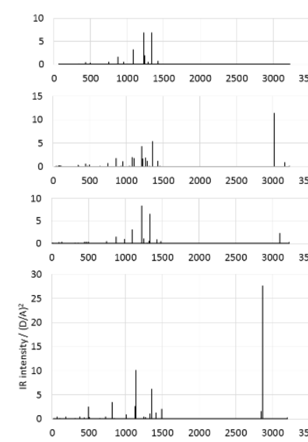












Dr. Fedor Naumkin

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

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

These systems are to be suitably designed based on the molecule geometries, their structures optimized in terms of energy, stability and other properties studied.

<u>Project 1</u> focusses on polarity and IR spectra, both being enhanced and sensitive to the system structure. Dimerization as 1st step in self-assembly will also be involved.

<u>Project 2</u> concentrates on the reaction barriers evolution inside the complex due to the contributions from mechanical pressure and electric field of the ions.

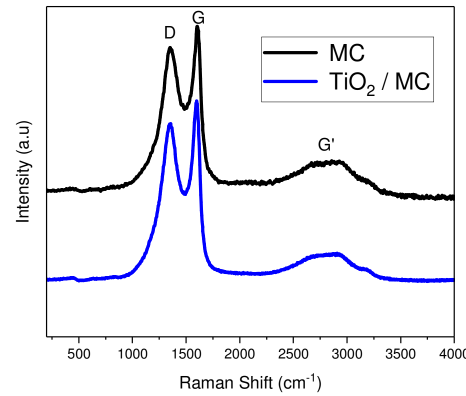
In either project the student will acquire practical experience of working with state-of-the-art quantum-chemistry software and modern visualization tools, on high-performance computing facilities accessible at and through the UOIT.

Selected publications (* marks students):

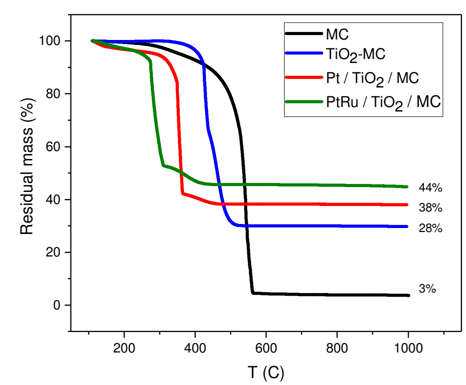
- M. Sullivan* and F. Y. Naumkin, Exploring the effects of ion-pair trapping on IR spectra and isomerization of polar molecules. To be published (2019).
- S. Kerr* and F. Y. Naumkin, Noncovalently bound complexes of polar molecules: Dipole-inside-of-dipole vs dipole-dipole systems. New J. Chem. 41 (2017) 13576.
- B. Cochrane* and F. Y. Naumkin, Reshaping and linking of molecules in ion-pair traps. Chem. Phys. Lett. 643 (2016) 137.

Prof. Liliana Trevani

Associate Professor (Chemistry-Materials Chemistry)
PhD in Chemistry – University of Buenos Aires, Argentina
PDF – Memorial University, Newfoundland, Canada
Research Associate – University of Guelph, Ontario, Canada

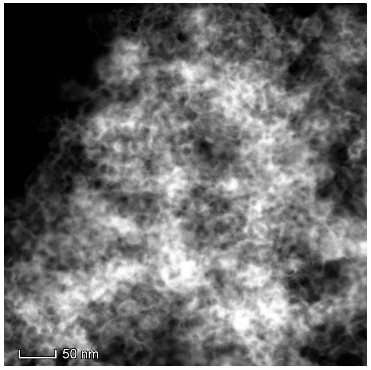


Available thesis projects (2019-2020):



Fabrication of nano-metal structures for plasmonic sensing of pharmaceutical drugs (co-supervised with Prof. Nisha Agarwal, Physics, UOIT)

Development of hybrid carbon nanostructured materials for energy storage and conversion.



Contact: liliana.Trevani@uoit.ca
Website: www.liliana-Trevani.com

Prof. Liliana Trevani

Fabrication of nano-metal structures for plasmonic sensing of pharmaceutical drugs

(Project co-supervised with Prof. Nisha Agarwal, Physics, UOIT)

The project is aimed to investigate the synthesis and characterization of supported metal nanomaterials in silica matrices for surface enhanced Raman scattering (SERS). The application of these nanostructures for the detection of low concentrations of target molecules (including pharmaceutical drugs) will be also investigated. The student will gain experience in several analytical and physical/chemical characterization techniques.

For additional information, see for instance: Jiang et al., Applied Surface Science 378, 181-190 (2016)

Development of hybrid carbon nanostructured materials for energy storage and conversion.

The thesis project will focus on the synthesis and characterization of novel composite carbon structures for applications in the field of energy storage and conversion. Carbon materials will be produced by carbonization of polymeric materials synthesized in the presence of hard- and soft-templates with the aims of controlling the surface area and pore size distribution of the final products. The deposition and catalytic activity of metal and metal oxide nanoparticles on these materials will be also investigated in collaboration with a graduate student. The student will explore several analytical and physical/chemical techniques used for the characterization of nanomaterials, including electrochemical methods.

For additional information, see for instance: Bruno et al., Colloids and Surfaces A: Physicochemical. Eng. Aspects 362, 28-32 (2010). Forouzandeh et al., J. Electrochemical Society, 165(6), F3230-F3240 (2018)

Prof. Olena Zenkina

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

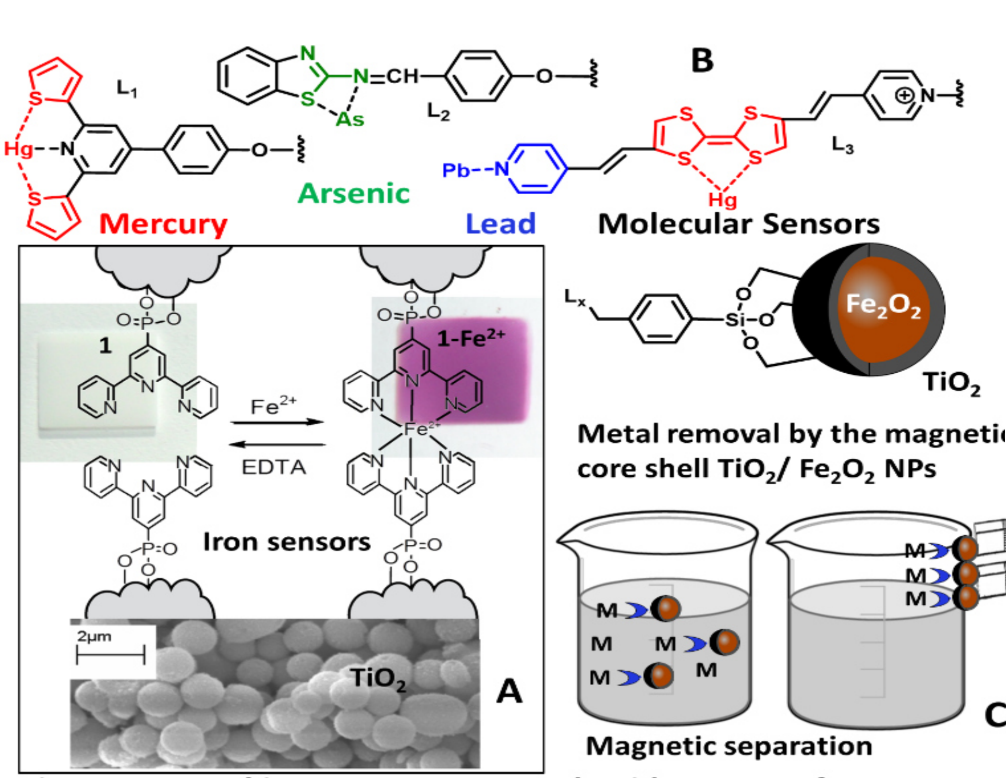
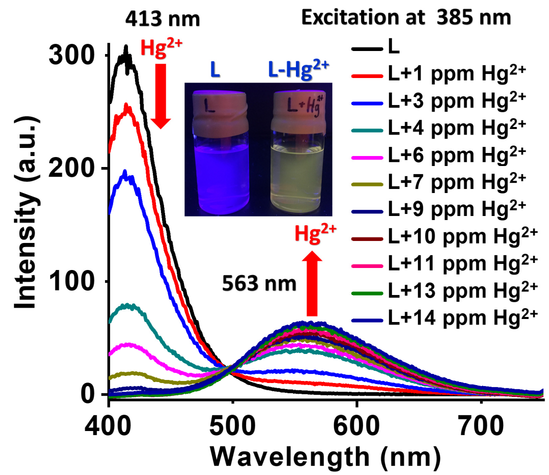
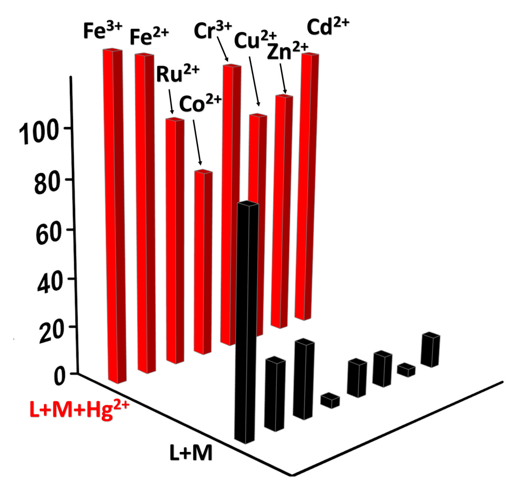


Figure 1: Metal ion sensors on metal-oxide nanosurfaces.
A: Fe^{2+}; B: $Hg^{+/2+}$, Pb^{2+}, $As^{3+/5+}$. C: Removal of metal ions.



Mercury Sensors



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. “*Eur. J. Inorg. Chem.* 2016, *22*, 3530-3535.

Undergraduate student authors marked in red

Prof. Olena Zenkina and Prof. Brad Easton

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

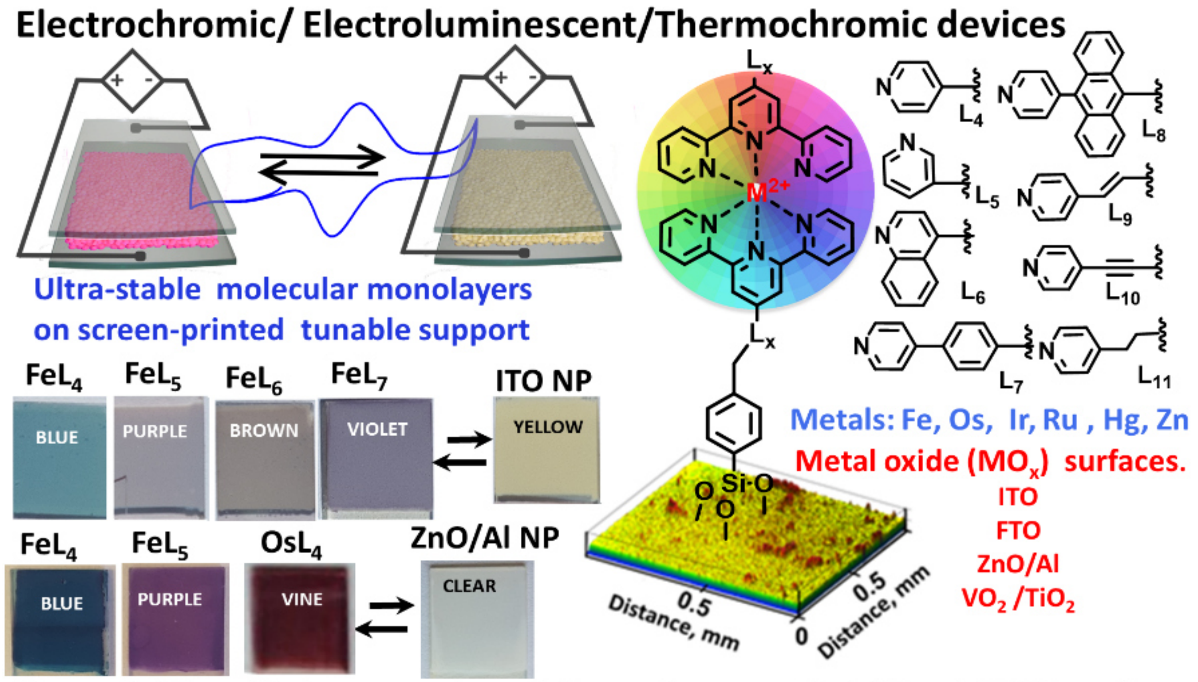


Figure 3. "Smart" chromogenic metal complexes on "intelligent" MO_x surfaces.

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.

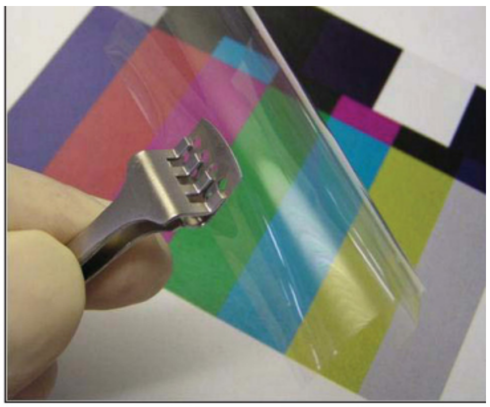
Allan, J. T. S.; Quaranta, S.; Ebralidze, I. I.; Egan, J. G.; Poisson, J.; Laschuk, N. O.; Gaspari, F.; Easton, E. B.; Zenkina, O. V., *ACS Applied Materials & Interfaces* **2017,** *9* (46), 40438-40445.

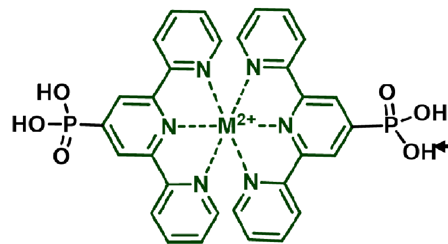
Undergraduate student authors marked in red

Prof. Olena Zenkina

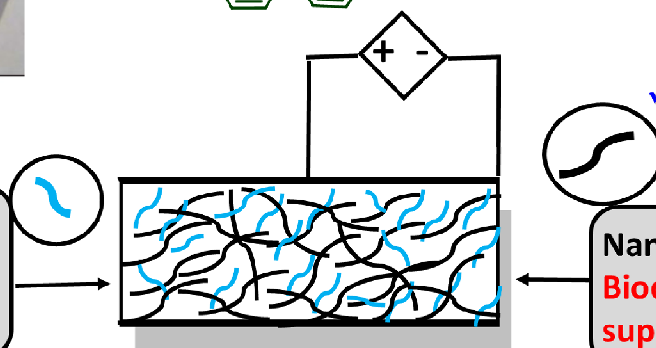
3. Nanocellulose based conductive surfaces for smart molecular materials.

Adv. Funct. Mater. **2014**, *24*, 1657–1663





Phosphonate linker
Covalent robust attachment,
Water-soluble ink materials



✓ Transparent, flexible, conductive, rough, foldable surfaces

Silver nanowires:
Enhanced conductivity

Nanocellulose, or nanofabrics
Biodegradable high surface area support, cell wall rupturing effect

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!

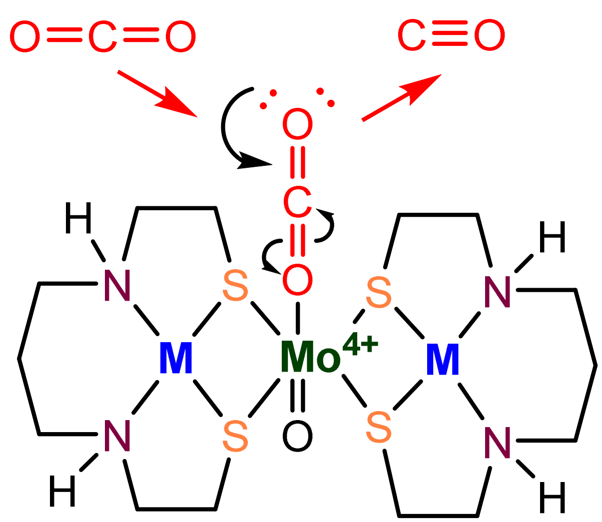
Dr. Kevin Coulter

Research Area: Inorganic and Organic Synthesis, Electrocatalysis

Objective: 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) → H_2 (g) + O_2 (g) E0 = +1.23 V
2. CO_2 reduction: $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ $E^0 = -0.38$ V

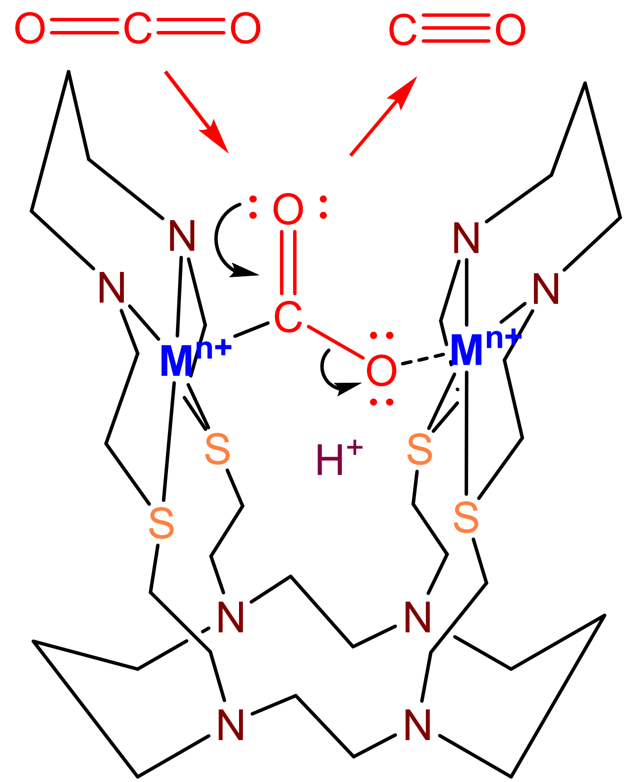
Project#1. Synthesis of linear [11]aneN_2S_2 and macrocyclic [14]aneN_2S_2 ligands and their metal complexes; testing for CO_2 reduction activity



M = Cu(II), Ni(II)

Dr. Kevin Coulter

Project#2. Synthesis of macrotricyclic ([14.9.9]aneN8, [14.9.9]aneN4S4, [14.15.15) face-to-face binuclear ligands and their metal complexes, testing for CO_2 reduction activity.



M^{n+} = $Ni^{2+/+}$, $Co^{3+/2+}$, $Cu^{2+/+}$, $Mo^{4+/3+}$

Project#3. Synthesis of μ-Oxo Transition Metal Clusters and Testing for Water Splitting Activity.