

# 46<sup>th</sup> POMS at UQAM

*Physical-Organic Mini-Symposium*

*Université du Québec à Montréal*

**Nov 2-4 2018**

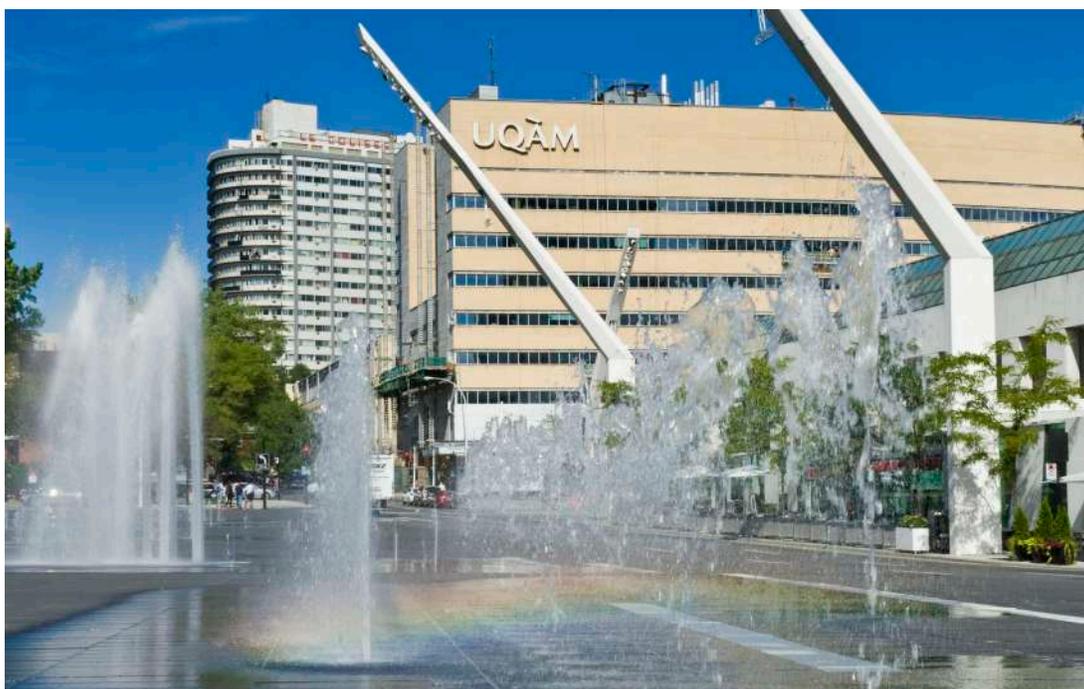


## 46<sup>th</sup> Physical Organic Mini Symposium (POMS)

Hosted by: Mathieu Frenette

**Université du Québec à Montréal (UQAM)**

**November 2-4 2018**



## Foreword

Thank you, students and professors, for coming to UQAM as we host our first POMS in its 46 years of existence—in fact, the POMS conferences and our Faculty of Science are almost exactly the same age. Indeed, UQAM is a young university. It may surprise you to hear that our chemistry department has only started offering PhD degrees in 2009! Since 2009, however, our department has been on a hiring spree. More than half of our department's professors were hired during this time—this has created a very dynamic and research-motivated environment that I am very grateful to be a part of.

POMS was my first conference experience as an undergraduate student, more than a few years ago, and I always enjoyed attending a POMS conference at every stage of my scientific career. Like many new parents who realize how much their own parents worked to raise them; I now appreciate the organizing efforts for the many conferences I gleefully attended in the past. I am grateful for the help/push to organize this conference by Ken Maly and, particularly, for the help afforded by my students Taylor Hope, Antoine Juneau, Ehsan Hosseininassab, Taraneh Javanbakth and Asma Boushah. A big 'thank you' is due to Pascale Beauchemin for administrative help and the department, faculty and NanoQAM for the generous financial support.

Have a wonderful conference and have fun in Montreal!

Your Conference Organizer,  
Mathieu Frenette



# Schedule for POMS 2018 @ UQAM

## Friday November 2<sup>nd</sup> 2018

19:00-22:00  
Welcome Mixer



### Benelux

245 rue Sherbrooke West, Montreal, QC

<https://goo.gl/maps/PSXqMHZ8kum>

Beer, Wine or Drink + snacks provided

Reasonably priced food is also available (Paninis and "Euro dogs")



**Saturday November 3<sup>rd</sup> 2018**

**All talks in SH-3420**

*Important Note:* All outside building doors are locked during the weekend. A security guard will open the main doors at 200 Sherbrooke street West (on Sherbrooke street).

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**8:30**      **Registration, Coffee and muffins**  
–            **+ Uploading morning presentations in SH-3420**

**9:00**

Pavillon Sherbrooke, 200 Rue Sherbrooke Street West, Montréal, QC H2X 3Y7  
<https://goo.gl/maps/dS8MRkSvJz82>

**Main Entrance (registration) and SH-3420 (coffee and muffins)**

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**9:00**      **Opening Remarks in SH-3420** by Mathieu Frenette, Conference Organizer

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First Session Chair: **Christopher Caputo**

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**9:10**      **Renaud Milette Lamarche** (r\_miclet@live.concordia.ca), Rolf Schmidt, Christine DeWolf  
*Concordia University*  
Deposition of Thiol  $\omega$ -Functionalized Phenolic Surfactant from the Air-Water Interface

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**9:30**      **Antonius Van Kessel** (antonius.vankessel@mail.mcgill.ca), Richard Lincoln and Gonzalo Cosa  
*McGill University and University of Warsaw*  
Using Fluorescence Microscopy to Study Lipid-Derived Electrophile Chemistry

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**9:50**      **Katarzyna Jodko-Piórecka** (katarzyna.jodko-piorecka@mail.mcgill.ca), Celine Prell, and Gonzalo Cosa  
*McGill University and University of Warsaw*  
Monitoring the Transfer of Oxidative Power Through the Lipid Membrane with a Tocopherol-Based Fluorescent Probe

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20-minute Break

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Second Session Chair: **Heidi Muchall**

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**10:30** **Adrian Schwan** (schwan@uoguelph.ca), Matthew Sing, Lilly U. Ho, Erwin J. Remigio, and Eric Nicol  
*University of Guelph*  
A Computational Assessment of the Formation and Breakdown of Triaryl-1,4-Oxathiins

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**10:50** **Taylor Hope** (hope.taylor@courrier.uqam.ca), Yohann Gagné, Christopher J. Legacy, Marion H. Emmert, and Mathieu Frenette  
*Université du Québec à Montréal*  
Mechanistic Insights into Fe Catalyzed  $\alpha$ -C-H Oxidations of Tertiary Amines: Non-Radical Pathways For Base-Metal Catalyst

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**11:10** **Philippe Archambault** (archambault.phil@gmail.com), Gilles Peslherbe, and Heidi Muchall  
*Concordia University*  
Electron Density Topology Investigation of P-Stacking in GAAA Tetraloop Containing Oligonucleotides

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**11:30** **Sharon Pinus** (sharon.pinus@mail.mcgill.ca) and Nicolas Moitessier  
*McGill University*  
Computational Design And Synthesis Of Asymmetric Catalysts

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Lunch Break in SH-4800 (1h20min)  
Please put up your posters in SH-4800

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Third Session Chair: **Ken Maly**

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**13:10** **Natalia Sannikova** (nsanniko@sfu.ca), Marco Farren-Dai, Andrew J. Bennet  
*Simon Fraser University*  
<sup>19</sup>F NMR Spectroscopy as a Tool to Probe Glycoside Hydrolases Mechanisms

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**13:30** **Sven Bourgois** (sbour085@uottawa.ca), Anabel E. Lanterna, and Juan C. (Tito) Scaiano  
*University of Ottawa*  
Heterogeneous Photocatalytic Heck Reactions Between Benzylic Halides and Vinyl Arenes

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- 16:00**     **Poster Presentations in SH-4800**
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- 17:50**
- P1**     **Hu Zhang**, pH- and photo switching studies of poly(acrylic acid-co-coumarin) as well as its brushes grafted to silica surfaces
- P2**     **Abdel Al Ahmad**, Component Exchange for Property Tailoring
- P3**     **Li Zhang**, Computational Study into the Origin of  $^{17}\text{O}$  Chemical Shift Changes in Solvated Acetone
- P4**     **Janet Gaba**, Computational study of weak interactions in cyclic trimers of model phenolic surfactants
- P5**     **Philippe Archambault**, Computational investigation of  $\text{CH}_3\text{SNO}_2$  and the effects of protonation on the electronic structure
- P6**     **Thibault Amiaud**, Towards Electrochemically Mediated Fluorescence For Reversible Fluorescence Turn-On/Turn-Off
- P7**     **Yohan Gautier**, Understanding The Electrochromic Effect Of Azomethines Via Structure-Property Studies
- P8**     **Marie-Hélène Tremblay**, Exploiting Intramolecular Hydrogen Bonding for Fluorescence Modulation
- P9**     **Monika Wałęsa-Chorab**, Photopolymerization of Electractive Layers for Electrochromic Applications
- P10**    **Alexandre Malinge**, Synthesis and Characterization of Liquid Crystalline Tetraoxapentacene Derivatives
- P11**    **Alexandre Malinge**, Solvato/fluorochromic properties of an electronic push-pull benzothiadiazole fluorophore
- P12**    **Chengzhang Yao**, Pushing the Visible Emission Envelop: Developing NIR Emitters
- P13**    **Lei Hu**, Towards NIR Fluorophores: A Photophysical and Electrochemical Study
- P14**    **Julia McCain**, Development of Dormant Photosensitizers for Antimicrobial Photodynamic Therapy
- P15**    **Meghan Heer**, Efficient Photoconversion of Thiones to Ketones: Exploring Ethers as a Source of Oxygen
- P16**    **Wenzhou Zhang**, Dormant Singlet Photosensitizer Based on ROS
- P17**    **Bowen Wang**, Selective Alkene Isomerization and Semi-hydrogenation using  $\text{MoS}_2\text{CoOx@TiO}_2$  Heterogeneous Photocatalyst
- P18**    **Aya Sakaya**, Mapping Redox Activity in Supported Lipid Bilayers
- P19**    **Ehsan Hosseininassab**, Mechanism and kinetics for the secondary autoxidation of fluorene
- P20**    **Tananeh Javanbakht**, Réaction des nanoparticules d'oxyde de fer avec peroxyde d'hydrogène
- P21**    **Michael Lerond**, Towards a Fully Organic Stretchable and Conductive Material for Hole Injection Layers
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**Sunday November 4<sup>th</sup> 2018**

**All talks in SH-3420**

*Important Note:* All outside building doors are locked during the weekend. A security guard will open the main doors at 200 Sherbrooke street West (on Sherbrooke street).

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**8:30 Coffee and muffins in SH-3430**

– + Uploading morning presentations in SH-3420

**9:00**

Pavillon Sherbrooke, 200 Rue Sherbrooke Street West, Montréal, QC H2X 3Y7

Main Entrance doors on Sherbrooke street only

<https://goo.gl/maps/dS8MRkSvJz82>

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**9:00 Opening Remarks in SH-3420** by Mathieu Frenette, Conference Organizer

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**9:10 Ken Maly** (kmaly@wlu.ca)

*Wilfrid Laurier University*

Self Assembly of Polycyclic Aromatic Hydrocarbons: Design of New Columnar Liquid Crystalline Materials

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**9:30 Christopher B. Caputo** (caputo@yorku.ca)

*York University*

Using Fluorescent Probes to Accurately Measure Lewis Acidity

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**9:50** Genesis Infante, Ryan Dean, Djihane Damoo, and **Sara Eisler** (seisler@unb.ca)

*University of New Brunswick*

Controlling 5-exo/6-endo-*dig* Cyclizations of Heterocyclic Alkynylamides: Accessing Unusual Pyrrolones and Pyridinones

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**10:10 Thomas Baumgartner** (tbaumgar@yorku.ca)

*York University*

An Unexpected 'Step-Conjugated' Biphosphole via Unique P-P Bond Formation

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30-minute Break

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**11:00** Monika Wałęsa-Chorab, Marie-Hélène Tremblay, Heather L. Filiatrault, Antoine Leliège, **Will Skene** (w.skene@umontreal.ca)  
*Université de Montréal*  
Strategies For Improving Electrochromic Device Performance

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**11:20** **Tao (Toby) Zeng** (TobyZeng@cunet.carleton.ca)  
*Carleton University*  
Theoretical studies in singlet fission: material search and mechanism exploration

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**11:40** **Jérôme Claverie** (jerome.claverie@usherbrooke.ca)  
*Université de Sherbrooke*  
Self-assembled colloids as hierarchical catalysts for artificial photosynthesis

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# Deposition of Thiol $\Omega$ -Functionalized Phenolic Surfactant from the Air-Water Interface

R. Milette Lamarche<sup>1</sup>, R. Schmidt<sup>1</sup>, C. DeWolf<sup>1</sup>

<sup>1</sup> Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke St W., Quebec Canada, H4B 1R6

E-Mail address (corresponding author): Christine.Dewolf@concordia.ca

Self-assembly from solution is a useful way to create monolayer film but offer limited degree of control over the final self-assembled monolayer (SAM) organisation. An alternative that we are exploring is the pre-assembly of the monolayer at the air-water interface. Using an  $\omega$ -functionalized thiol surfactant in a Langmuir monolayer enables by deposition, accompanied by chemisorption, onto a gold substrate. This approach should permit variation of the organization that is not attainable using SAMs. Furthermore, it may be possible to form the monolayer in the presence of analytes of interest in the subphase, allowing the monolayer to organize in the ideal organization to selectively absorb the analytes once transferred onto a solid substrate.

To demonstrate the viability of this approach we use  $\omega$ -thiolated phenolic surfactants. Phenols have been shown to interact strongly with metals and certain class of proteins, potentially allowing the monolayer formed to be used as biosensor. Phenolic surfactants also show strong headgroup interactions which allows them to form strongly cohesive films. For an  $\omega$ -thiolated surfactant (a bola amphiphile) this can prevent the  $\omega$ -thiol from penetrating into the subphase, forcing it upward for contact with the gold upon deposition. This is, however, dependent on the conditions in which the monolayer is created and on the length of the alkyl chain. First, we elucidates the impact of an  $\omega$ -thiol on the phase behaviour of the phenolic surfactant. Comparison of the thiol and methyl terminated surfactants using Langmuir isotherms, ellipsometry, Brewster angle microscopy, grazing incident x-ray diffraction and AFM enabled a determination of the thiol location and selection of an appropriate deposition strategy (Langmuir-Blodgett vertical deposition on either the upstroke or the downstroke). Other approaches to modify the film organization will be presented and include mixed monolayers (thiolated and non-thiolated) and subphase pH.

# Using Fluorescence Microscopy to Study Lipid-Derived Electrophile Chemistry

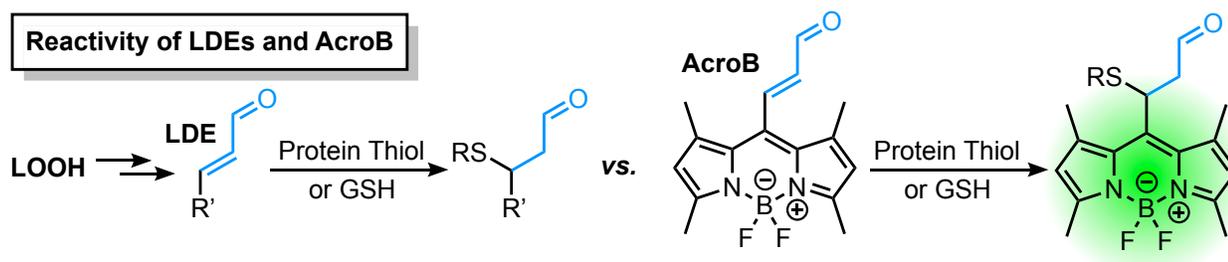
Antonius T.M. Van Kessel, Richard Lincoln and Gonzalo Cosa

Department of Chemistry and Quebec Centre for Applied Materials (QCAM), McGill University, Montreal, Quebec

[antonius.vankessel@mail.mcgill.ca](mailto:antonius.vankessel@mail.mcgill.ca); [gonzalo.cosa@mcgill.ca](mailto:gonzalo.cosa@mcgill.ca)

Lipid-derived electrophiles (LDEs) are reactive degradation products of the lipid hydroperoxides (LOOH) formed during lipid peroxidation.<sup>1</sup> While LDEs can act as important cellular signals through alkylation of nucleophilic residues (e.g. protein thiols) on specific sensor proteins, high levels of LDEs cause undesired protein alkylation and are implicated in the pathogenesis of neurodegenerative diseases.<sup>1</sup> Improved understanding of cellular LDE chemistry may be obtained through the application of photochemistry and fluorescence microscopy principles, as was pioneered by our group's development of AcroB (see figure below).<sup>2</sup> AcroB is an LDE analogue bearing the acrolein moiety, the electrophilic warhead of many LDEs, linked to a BODIPY chromophore. Upon reaction with a cellular nucleophile (protein thiol or glutathione, GSH), AcroB becomes fluorescent, allowing mapping of LDE reactivity and monitoring of adduct trafficking in live cells.<sup>2</sup> We are now undergoing work to alter the physical properties of AcroB in order to influence the cellular targets of the probe.

In order to further investigate the applicability of our probes to study the fundamental role of LDEs in cell physiology, we aim to alter the cellular concentration of LDE targets and observe the response with our fluorogenic probes. The ability of our probes to respond to changes in cellular metabolism will enable the future study of how LDE chemistry influences physiology and pathology using fluorescence strategies.



<sup>1</sup>Schopfer, F.J. *et al. Chem. Rev.* **2011**, *111*, 5997.

<sup>2</sup>Lincoln, R. *et al. J. Am. Chem. Soc.* **2017**, *139*, 16273.

# Monitoring the Transfer of Oxidative Power Through the Lipid Membrane with a Tocopherol-Based Fluorescent Probe.

Katarzyna Jodko-Piórecka,<sup>1,2</sup> Celine Prell,<sup>1</sup> and Gonzalo Cosa<sup>1</sup>

<sup>1</sup> Department of Chemistry, McGill University, Montréal, QC,

<sup>2</sup> Faculty of Chemistry, University of Warsaw, Warsaw, Poland

[katarzyna.jodko-piorecka@mail.mcgill.ca](mailto:katarzyna.jodko-piorecka@mail.mcgill.ca); [gonzalo.cosa@mcgill.ca](mailto:gonzalo.cosa@mcgill.ca)

The transfer of oxidative power across lipid membranes by antioxidants and their associated radicals may offer cells a mechanism to control redox reactions and associated cell signaling events, despite the hydrophobic barrier imposed by the lipid bilayer. It may further provide chemists with the ability to control the oxidative environment in compartmentalized systems.

Herein, using the fluorogenic probe **H<sub>4</sub>BPMHC** consisting of an  $\alpha$ -tocopherol ( $\alpha$ -toc) chromanol moiety coupled to a BODIPY fluorophore, we have developed a fluorescence assay to monitor the kinetics of tocopheroxyl radical (TO $\cdot$ ) transfer across the membrane barrier in model lipid systems. Effectively, the probe was embedded in the liposomal membrane separating a highly oxidative external environment (containing a water-soluble initiator of peroxidation) from a highly reductive intravesicular environment (containing ascorbic acid). The probe, oxidized to a tocopheroxyl radical on the outer leaflet of the liposomal membrane, undergoes translocation to the internal leaflet where it is regenerated by the ascorbic acid encapsulated in the liposome. As a result, the oxidative power is effectively transported from one side of the liposomal membrane to the other. To evaluate the dynamics of antioxidant radical transport through membrane, we compared the efficiency of regeneration for tocopheroxyl radicals derived from either  $\alpha$ -tocopherol, PMHC (an analogue of  $\alpha$ -tocopherol lacking the long phytol tail) or the probe **H<sub>4</sub>BPMHC**.

Our results indicate that **H<sub>4</sub>BPMHC** can be used to monitor the free radical transfer through the nanometer thick lipid membrane barrier along a redox gradient. The dynamics of the transfer depend on the lipids composing the membrane and on the type of chromanol-based antioxidant acting as the carrier of oxidative power. The mobility of chromanol-based antioxidants across the bilayer, and consequently their radical scavenging efficiency, is modulated by steric factors, namely aliphatic tail length of antioxidants. Kinetic studies performed on our system underscore that smaller molecules (PMHC) transmit this oxidative power more readily.

In general, the proposed methodology provides a tool to study the transmembrane movement of lipid soluble antioxidants and to determine the factors modulating the rate of radical transfer across the lipid bilayer. It can be used to assess the mobility of different radicals in lipid membranes, or to study the synergistic effects between antioxidants present in different compartments.

# A Computational Assessment of the Formation and Breakdown of Triaryl-1,4-Oxathiins

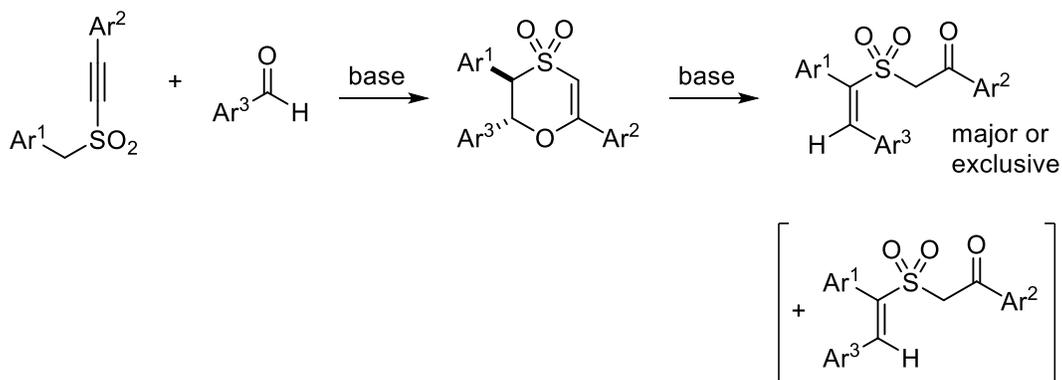
Adrian L. Schwan, Matthew Sing, Lilly U. Ho, Erwin J. Remigio and Eric Nicol

Department of Chemistry, University of Guelph, Guelph, ON, Canada, N1G 2W1

[schwan@uoguelph.ca](mailto:schwan@uoguelph.ca)

A synthesis of the 2,5,6-triaryl-5,6-dihydro-1,4-oxathiin ring system in its S,S-dioxide form has been achieved through treatment of various benzyl alkynyl sulfones with base and an aldehyde. The mechanism has been speculated previously<sup>[1]</sup> and presumably involves deprotonation of benzyl alkynyl sulfone and subsequent attack of the added aldehyde. The so-formed oxyanion cyclizes onto the triple bond, and product forms after proton transfer(s). The reaction conditions invariably suffer from the formation of a by-product arising from base-induced breakdown of the oxathiin.

Computational studies were performed with explicit counterion inclusion in order to fully understand both the steps required for the preparation of the oxathiins, and the mode of breakdown, which produces a conjugated enone with unexpected double bond geometry. The oxathiin formation mechanism is generally supported by these investigations. On the other hand, the computational work suggests involvement of an important Li-to-aryl interaction on the way to delivering the cis alkene. The presentation will present the various intermediates involved along with their relative energies.



<sup>1</sup> Ho, L.U.; Shkooor, M. Gh.; Hossain, M.S.; Deen, M.C.; Soldatov, D.V. and Schwan, A.L. *J. Sulfur Chem.*, **2013**, 34, 79.

# Electron Density Topology Investigation of $\pi$ -Stacking In GAAA Tetraloop Containing Oligonucleotides

Philippe Archambault, Gilles Peslherbe, and Heidi Muchall

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montreal, Quebec

[archambault.phil@gmail.com](mailto:archambault.phil@gmail.com); [heidi.muchall@concordia.ca](mailto:heidi.muchall@concordia.ca)

Non-covalent interactions are the driving force for the folding and stability in nucleic-acid structures, and hydrogen bonding and  $\pi$ -stacking between bases are the fundamental structural properties at the core of nucleic acids research. In many single stranded RNA macromolecules, the presence of non-Watson-Crick pairing between nucleobases results in ill-defined networks of non-covalent interactions. As a consequence, large RNA structures remain unrealistic to predict from their sequence alone.<sup>1</sup> While experimental techniques, such as NMR spectroscopy, have been successful at revealing  $\pi$ - $\pi$  interactions<sup>2</sup>, their effectiveness to accurately characterize individual interactions quickly diminishes as the size of the RNA increases. As a result geometric inferences for distances and angles or from overlap criteria (for hydrogen bonding and  $\pi$ -stacking, respectively) become common practice for structural prediction purposes.

As non-covalent interactions can be determined unambiguously from the electron density,<sup>3</sup> we aim to use computational methods based on density functional theory and the quantum theory of atoms in molecules (QTAIM) to characterize the  $\pi$ - $\pi$  stacking interactions from r(GGGCGAAAGCCU) NMR structures.<sup>4</sup>

<sup>1</sup> Lerman, Y. V.; Kennedy, S. D.; Shankar, N.; Parisien, M.; Major, F.; Turner, D. H. *RNA* **2011**, *17*, 1664–1677.

<sup>2</sup> Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019-1027.

<sup>3</sup> Bader, R. F. W. *Atoms in Molecules: A Quantum Theory* Clarendon Press: Oxford, 1990.

<sup>4</sup> Jucker, F. M.; Heus, H. A.; Yip, P. F.; Moors, E. H. M.; Pardi, A. *J. Mol. Biol.* **1996**, *264*, 968-980.

# Computational Design and Synthesis of Asymmetric Catalysts

Sharon Pinus<sup>1</sup>, and Nicolas Moitessier<sup>1</sup>

<sup>1</sup> Department of Chemistry, McGill University, Montreal, Quebec

[sharon.pinus@mail.mcgill.ca](mailto:sharon.pinus@mail.mcgill.ca); [nicolas.moitessier@mcgill.ca](mailto:nicolas.moitessier@mcgill.ca)

Asymmetric catalysts are catalysts that in addition to increasing the reaction's rate, also favor the formation of one enantiomer over the other. These catalysts are therefore important for the synthesis of chiral compounds (i.e. drugs, pesticides, materials, etc.).

Three main fields of asymmetric catalysis have been developed: transition-metal based catalysis, in which the active species is a metal complex; asymmetric organocatalysis - small organic molecules acting as catalysts - and biocatalysis, involving the use of enzymes. The former suffers from two major drawbacks: a) Transition metals are often toxic, making them unsafe to work with and incompatible with the synthesis of safe pharmaceuticals. b) Most used metals (e.g., palladium, platinum), are rare and thus very expensive. The latter option suffers from a narrow substrate scope due to high specificity and sometimes from poor stability. More recently, it was established that small organic molecules, such as proline (a natural amino acid), could catalyze reactions (e.g., Diels-Alder) and induce enantioselectivity. Thereafter, the field of organocatalysis started gaining momentum. **The benefits of organocatalysis are appealing: reduced toxicity, lower price and greater availability.** Many of these catalysts could be synthesized from enantiopure starting materials (i.e. natural products) which are available in the enantiopure form.

Although several efficient asymmetric organocatalysts for different chemical transformations have been synthesized and reported in the past 20 years, progress in the field is slow due to the difficulty in predicting selectivity in advance. Consequently, we drew inspiration from the field of drug discovery, where recent advances in computational chemistry tools have enabled the use of software which could predict the binding ability of a molecule to a known target, thus reducing the number of molecules that need to be synthesized experimentally. Our group has developed a computational tool, ACE (Asymmetric Catalyst Evaluation), designed to predict the stereochemical outcome of reactions (%ee and transition states) using a catalyst. ACE does not require expertise in computational chemistry and is meant to be used by organic chemists to evaluate the selectivity of newly designed catalysts **prior** to synthesis. As such, the structure can be optimized *in silico* and only a small number of catalysts would need to be synthesized and tested. ACE is part of the VIRTUAL CHEMIST platform, developed by our group, that can be used to create a library of potential catalysts and test them *in silico* for their selectivity, prior to synthesis. Current efforts in our lab involve the computational aided design, synthesis and testing of novel organocatalysts, with a focus on the Diels-Alder cycloaddition. We will present the development of the software and its application to the discovery of novel Diels-Alder cycloaddition catalysts. This has been done by virtual screening conducted on a database (virtual library) of previously reported asymmetric compounds. In addition, the future potential of the software will be presented.

# **<sup>19</sup>F NMR Spectroscopy as a Tool to Probe Glycoside Hydrolases Mechanisms**

Natalia Sannikova,<sup>1</sup> Marco Farren-Dai<sup>1</sup> and Andrew J. Bennet<sup>1</sup>

<sup>1</sup> Department of Chemistry, Simon Fraser University, Burnaby, BC

[nsanniko@sfu.ca](mailto:nsanniko@sfu.ca); [bennet@sfu.ca](mailto:bennet@sfu.ca)

Due to the importance of sugars in living systems, enzymes that remove carbohydrates (glycosidases or glycoside hydrolases, GHs) are essential in many biological events, such as cell recognition, anti-bacterial defense strategies and pathogenesis mechanisms. Deficiency in specific glycoside hydrolases can result in various lysosomal storage diseases leading to many developmental problems and a reduced life expectancy. This makes glycosidases attractive targets for drug discovery. Thus, an improved understanding of their mechanisms of action can aid in the design of tight-binding transition state analogue inhibitors as potential lead compounds for therapeutic development.

Kinetic isotope effects (KIEs) are a powerful tool for investigating enzyme mechanisms so as to elucidate transition state structures that occur during the catalytic cycle. The Bennet group has developed a new methodology for the measurement of competitive kinetic isotope effects on enzyme-catalyzed reactions by quantitative <sup>13</sup>C-NMR spectroscopy.<sup>1</sup> However, the use of <sup>13</sup>C-NMR spectroscopy has certain disadvantages: i) lower sensitivity in comparison to other NMR active nuclei (<sup>1</sup>H, <sup>19</sup>F, <sup>31</sup>P); ii) potentially complex syntheses from available starting materials; and iii) overlapping NMR peaks leading to the need for extensive spectral deconvolution. To overcome those difficulties <sup>19</sup>F can be used as a sensitive NMR active probe nucleus for KIE measurements.<sup>2</sup> As part of a continuing effort to characterize glycoside hydrolase mechanisms and expand the scope of our existing NMR methodology, KIEs for several GHs have been measured by <sup>19</sup>F NMR spectroscopy. KIEs on Family 55 (GH55) inverting exo-1,3-β-D-glucanase and GH15 inverting amyloglucosidase will be discussed.

<sup>1</sup>Chan, J. *et al. Nat. Chem. Biol.* **2010**, *6*, 405-407.

<sup>2</sup>Chan, J. *et al. J. Am. Chem. Soc.*, **2012**, *134*, 1212-1220.

# Heterogeneous Photocatalytic Heck Reactions Between Benzylic Halides and Vinyl Arenes

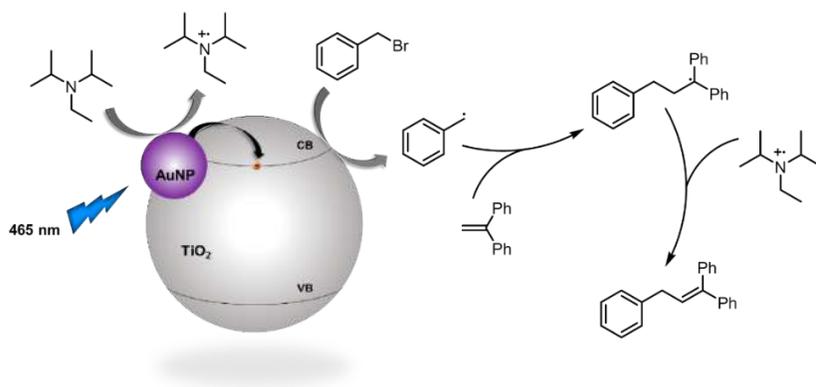
Sven C. Bourgeois, Anabel E. Lanterna, Juan C. Scaiano

Department of Chemistry and Biomolecular Sciences and Centre for Advanced Materials Research (CAMaR), University of Ottawa. 10 Marie Curie, Ottawa, ON K1N 6N5, Canada

[sbour085@uottawa.ca](mailto:sbour085@uottawa.ca)

The field of photoredox catalysis has emerged as a prominent approach to synthetic chemistry over the past decade, offering powerful strategies in the activation of small molecules with high selectivity under milder conditions compared to their thermally driven counterparts. Despite all these advantages there currently are only a limited number of photoredox catalysts available, the most common of which suffer from very high costs, poor reusability and decreased ease of separation. The use of inorganic semiconductors, such as  $\text{TiO}_2$ , has emerged as a convenient alternative to expensive and toxic transition metal complexes. Its use as a photocatalyst has been widely explored as an alternative heterogeneous photoredox catalyst. Heterogeneous photo-catalysis can provide both facile catalyst separations and potential reuse. The main disadvantage of the use of pure nanometric  $\text{TiO}_2$  as a photocatalyst is the large band gap ( $>3.1\text{eV}$ ) of this semiconductor that can only absorb UV light ( $<400\text{ nm}$ ). Decorating  $\text{TiO}_2$  with noble transition metals such as Pd, Au or Cu, among others, can overcome this problem as the resulting materials usually absorb light in the visible region.

We present here our efforts to apply gold supported titanium dioxide to the Heck-type coupling of vinyl arenes to benzylic halides using photoredox catalysis.



Scheme 1. Proposed mechanism for the  $\text{Au}@\text{TiO}_2$  catalyzed coupling of benzylic halides and vinyl arenes.

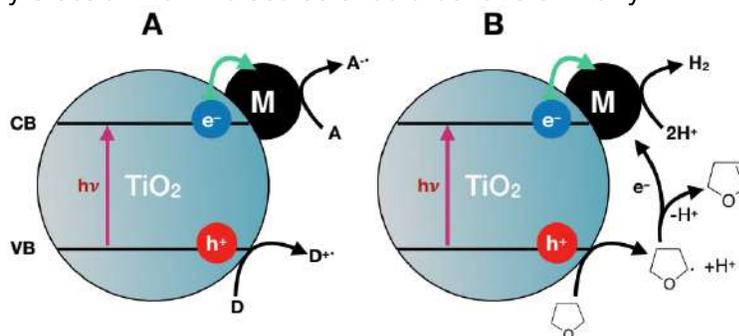
# Trapping of Photogenerated Semiconductor Holes by Ethers. An Over-Looked Highly Efficient Photochemical Free Radical Source

Andrew Hainer, Nancy Marina, Paolo Costa, Stefanie Rincon, Anabel Lanterna, Juan (Tito) Scaiano  
Department of Chemistry and Biomolecular Sciences and Centre for Advanced Materials Research (CAMaR), University of  
Ottawa. 10 Marie Curie, Ottawa, ON K1N 6N5, Canada  
ahain055@uottawa.ca ; titoscaiano@mac.com

Titanium Dioxide ( $\text{TiO}_2$ ) has been used as an alternative heterogeneous photocatalyst. Its activity has been explored from the synthesis of organic molecules<sup>1,2</sup> to the degradation of contaminants. Here we envision that  $\text{TiO}_2$  semiconductor properties can also be used as a very efficient source of free radicals. Thus, the photogenerated electrons and holes in the semiconductor can participate in both reduction and oxidation pathways, respectively. The advantages of this approach are that it can form single radicals as opposed to common free radical initiators which generate radical pairs, and the ease of separation of the catalyst post reaction. We therefore aimed to explore the effectiveness of a variety of ethers for radical generation based on our proposed mechanism (Scheme 1).

In this work, we evaluated the generation of free radicals by monitoring the trapping of the generated radicals with TEMPO, as well as by monitoring the formation of the  $\text{H}_2$  gas side-product, the other half of the redox cycle. The materials tested in our experiments were nanometric  $\text{TiO}_2$  decorated with various metal nanoparticles such as Pd, Pt, Au, Co, Cu, and Ni (denoted as  $\text{M@TiO}_2$ ). These metal decorations help by increasing the lifetime of the reactive photogenerated electron-hole pair of the semiconductor. With these catalysts we found that radicals were efficiently generated and trapped by TEMPO with most ethers tested, and that monitoring the formation of hydrogen gas is effective for screening. It was also found that the addition of TEMPO decreased the formation of hydrogen gas, helping support our proposed mechanism. Competition experiments also gave insight into the mechanism, concluding that the electrophilicity of the hole resembles that of alkoxy radicals, the most commonly used free radical initiators. The loss of some stereoelectronic control gave support for a proton coupled electron transfer (PCET) instead of the hydrogen atom transfer (HAT) commonly found with alkoxy radicals.

Overall, we found that the photogenerated semiconductor holes are very electrophilic and can easily generate free radicals, as demonstrated with common cyclic and acyclic ethers. We also expect that other moderately electron-rich molecules should behave similarly.



Scheme 1: general mechanism (a) and proposed mechanism (b) of  $\text{TiO}_2$  photoredox catalysts.

<sup>1</sup>Tyagi, A. *et al. Catal. Sci. Technol.* **2017**, *7*, 2616-2623

<sup>2</sup>Marina, N. *et al. ACS Catal.* **2018**, *8*, 7593-7597

# 21<sup>st</sup> Century Medicinal Waters, Does the Sun Do More Than You Think?

Morgan Vallieres, Anabel Lanterna, and J.C. Scaiano

University of Ottawa, Ottawa, Ontario

[mvall095@uottawa.ca](mailto:mvall095@uottawa.ca)

Contamination of water is a growing global concern that not only affects natural biological communities, but also is threatening human life. Industrial waste, pesticide runoff and sewage are among the main sources of the pollution. Most research will mention the presence of these compounds in our aquatic systems, they will mention “degradation” but fail to explore the degradation mechanism and more importantly, to identify the products.<sup>1</sup> What these molecules transform into after prolonged exposure to solar light is extremely valuable knowledge for our safety and the environment. These are factors to consider when we want to understand how to proceed to eliminate them. Previous research conducted by our group,<sup>2</sup> ventured into the idea of using various semiconductor-based catalysts, particularly metal-decorated TiO<sub>2</sub>, that can use sacrificial electron donors (SED), contained in river or contaminated waters, to generate hydrogen gas, and in the process modify or destroy the organic contaminants. As shown in the diagram below the formation of H<sub>2</sub> in pure water (panel a) requires its oxidation (O<sub>2</sub> formation), a reaction that is rather inefficient; whereas the presence of a SED (with methanol as an example, panel b), can greatly improve the H<sub>2</sub> formation as they are easy to oxidize.

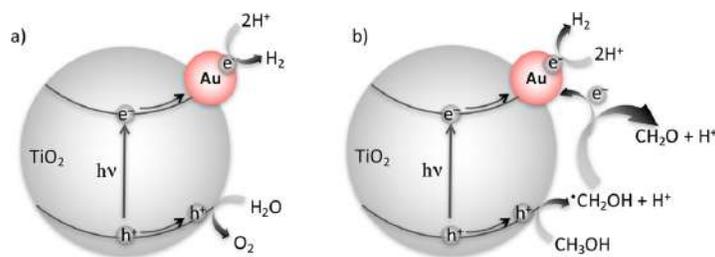


Figure 1. (a) Water splitting and (b) methanol splitting upon UV excitation, illustrated for Au@TiO<sub>2</sub>.<sup>2</sup>

In this work we present our interests in exploring the degradation of a particular set of contaminants, pharmaceuticals, and their use as SED for the production of H<sub>2</sub>. Molecules such as ibuprofen, naproxen and estrogen are regularly disposed into the water, causing major changes in the aquatic environment. In order to study the degradation of these materials, we employ Pd-decorated TiO<sub>2</sub> in the presence of various pharmaceutical compounds upon UV light irradiation and follow the formation of H<sub>2</sub>, as a test of degradation. We recreate conditions which mimic those found in aquatic environments in a pH range from 6.5-8, using K<sub>2</sub>CO<sub>3</sub>. We address concerns about catalyst leaching and expect to improve catalyst reusability. Finally, we plan the design of a flow system by incorporating the catalyst on a more rigid support, such as glass wool, and expect to degrade these contaminants in real aquatic systems.

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- 2) Hainer,Andrew; Vallieres, Morgan; Scaiano, Juan; Anabel,Lanterna, Photocatalytic Hydrogen Generation Using Metal-Decorated TiO<sub>2</sub>: Sacrificial Donors vs True Water Splitting. ACS Energy, 2018, 3, 542-545.

# Redox Active Conducting Polymer Design for Energy Storage

Danny Chhin<sup>1</sup>Steen Schougaard<sup>1</sup>

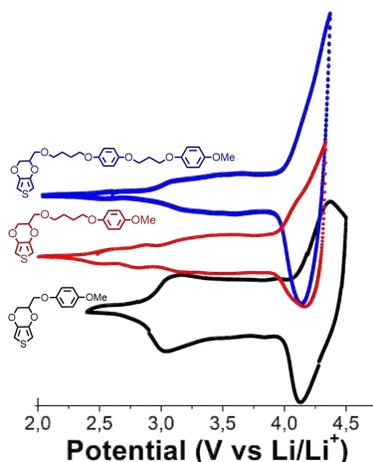
<sup>1</sup> Nanoquam, Département de Chimie, Université du Québec à Montréal, Montréal, Québec

[chhin.danny@gmail.com](mailto:chhin.danny@gmail.com); [schougaard.steen@uqam.ca](mailto:schougaard.steen@uqam.ca)

Reversible redox behavior in organic molecules have been observed in numerous biological processes to metabolize nutrients into energy such as photosynthesis for plants and electron transport in living cells. In fact, many redox-active organic molecules possess high energy density and are readily available from the biomass. Hence, the interest of redox-active organic molecules for electrochemical energy storage. However, they generally make poor electrode material. In part because redox-active organic molecules possess low electronic conductivity. Therefore, a large quantity of conductive additive is needed to process them into effective electrode at the cost of the electrode energy density. Moreover, the redox-active organic molecules are soluble in most electrolyte battery. As a result, they leech out from the electrode which leads to rapid energy fade.

To overcome these limitations, the redox-active organic molecules can be tethered to a conducting polymer backbone to form a redox active conducting polymer.<sup>1</sup> Thus, the conducting polymer acts as a molecular wire that conducts electron to the pendant redox-active site and at the same time prevents their dissolution in the electrolyte. In practice, this has proven to be less efficient than expected as steric and coulombic interaction between the conducting polymer backbone and the pendant redox moiety can interfere with the performances of the hybrid material e.g. polymerization of the monomer, electronic conductivity, redox reversibility.

There is still poor understanding of the electrochemical performances of redox active conducting polymer in relation to its chemical and structural design. Herein, we report the performances of various design of redox active conducting polymer based on a 3,4-ethylenedioxythiophene (PEDOT) backbone grafted with electron rich aromatic moieties.<sup>2,3,4</sup>



<sup>1</sup> Park K-S, Schougaard SB, Goodenough JB. **2007**, *Adv Mater.* 848–51.

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# Catalytic Farming: Reaction Rotation Extends Catalyst Performance

Ayda Elhage, Anabel E. Lanterna\*, Juan C. Scaiano\*

Department of Chemistry and Biomolecular Sciences and Centre for Advanced Materials Research (CAMaR),  
University of Ottawa. 10 Marie Curie, Ottawa, ON K1N 6N5, Canada

[alantern@uottawa.ca](mailto:alantern@uottawa.ca), [jscaiano@uottawa.ca](mailto:jscaiano@uottawa.ca)

Visible-light-mediated photo-redox catalysis has emerged as a valuable concept in organic synthesis avoiding the undesired photodegradation of organic molecules under UV exposure. On the other hand, the efforts to prepare photo-responsive materials is a growing field in heterogeneous catalysis, where the combination of easy separation, minimal product contamination, and catalyst reusability are major assets that can be combined with the use of light, usually connected with milder reaction conditions. The use of heterogeneous catalysis has key advantages compared to its homogeneous counterpart, such as easy catalyst separation and reusability. However, one of the main challenges is to ensure good performance after the first catalytic cycles. Active catalytic species can be inactivated during the catalytic process leading to reduced catalytic efficiency, and with that loss of the advantages of heterogeneous catalysis. Here we present an innovative approach in order to extend the catalyst lifetime based on the crop rotation system used in agriculture. The catalyst of choice to illustrate this strategy, Pd@TiO<sub>2</sub>, is used in alternating different catalytic reactions, which reactivate the catalyst surface, thus extending the reusability of the material, and preserving its selectivity and efficiency. As a proof of concept, different organic reactions (Scheme 1)<sup>1-3</sup> were selected and catalyzed by the same catalytic material during target molecule rotation.



Scheme 1. Reaction rotation for catalytic farming of Pd@TiO<sub>2</sub>.

1. Elhage, A.; Lanterna, A. E.; Scaiano, J. C., Tuneable photocatalytic activity of Palladium-decorated TiO<sub>2</sub>: non-hydrogen mediated hydrogenation or isomerization of benzyl-substituted alkenes *ACS Catal.* **2017**, *7*, 250.
2. Elhage, A.; Lanterna, A. E.; Scaiano, J. C., Light-Induced Sonogashira C-C Coupling under Mild Conditions Using Supported Palladium Nanoparticles *ACS Sustainable Chem. Eng.* **2018**, *6*, 1717.
3. Marina, N.; Lanterna, A. E.; Scaiano, J. C., Expanding the Color Space in the Two-Color Heterogeneous Photocatalysis of Ullmann C-C Coupling Reactions *ACS Catal.* **2018**, 7593.

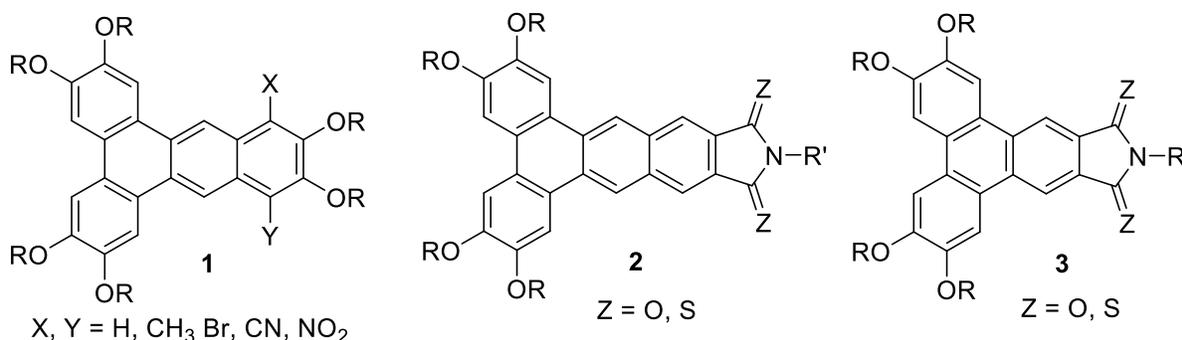
# Self-Assembly of Polycyclic Aromatic Hydrocarbons: Design of New Columnar Liquid Crystalline Materials

Kenneth E. Maly

Department of Chemistry and Biochemistry, Wilfrid Laurier University, Waterloo, ON

[kmaly@wlu.ca](mailto:kmaly@wlu.ca)

Polycyclic aromatic hydrocarbons bearing flexible side chains are more substituted than their unsubstituted analogs and can often self-assemble via pi stacking interactions in solution and the solid state, as well as form liquid crystalline phases.<sup>1</sup> In the latter state, noncovalent interactions play a key role in determining the stability of the liquid crystalline phase. Here we will explore the effect of structure of the aromatic core and substituents on liquid crystalline properties. In particular, we will compare the liquid crystalline a series of alkoxy-substituted triphenylenes and dibenzanthracenes (e.g. **1**) with different substituents attached to the aromatic core and show that a combination of electron-withdrawing substituents and flexible chains leads to broad liquid crystalline phases.<sup>2,3</sup> Based on these results, we have prepared a series of triphenylene and dibenzanthracene imides and their thionated analogs (**2** and **3**).<sup>4,5</sup> We will describe the effect of thionation on self-association in solution and in the liquid crystalline state.



<sup>1</sup> T. Wohrle *et al.* Chem. Rev. **2016**, *116*, 1139; S. Kumar, Chem. Soc. Rev. 2006, *35*, 83.

<sup>2</sup> J. A. Paquette, C. J. Yardley, K. M. Psutka, M. A. Cochran, O. Calderon, V. E. Williams and K. E. Maly, *Chem. Commun.* **2012**, *48*, 8210.

<sup>3</sup> J.A. Paquette, K.M. Psutka, C.J. Yardley, and K.E. Maly, *Can. J. Chem.* **2017**, *95*, 399.

<sup>4</sup> K. Psutka, K. Bozek and K. Maly, *Org. Lett.* **2014**, *16*, 5442.

<sup>5</sup> K. M. Psutka and K. E. Maly, *RSC Adv.* **2016**, *6*, 78784.

# Using Fluorescent Probes to Accurately Measure Lewis Acidity

Christopher B. Caputo<sup>1</sup>

<sup>1</sup> Department of Chemistry, York University, Toronto, ON

[caputo@yorku.ca](mailto:caputo@yorku.ca)

The recent renaissance in main-group chemistry has focused the development of new Lewis acids for applications in main-group catalysis as an integral component of the rapidly expanding research area of frustrated Lewis pair (FLP) chemistry. Lewis acid strength is an important parameter for establishing their utility in practical applications. Several techniques developed to measure the strength over the past few decades include the Gutmann-Beckett and fluoride ion affinity methods. Nevertheless, these have been subject to criticism, the former providing a misrepresentation of the true Lewis acidic nature of several compounds, while the latter utilizing computational calculation to give only an estimate of Lewis acid strength. Herein, we report a fluorescence-based method for accurately determining the strength of a range of main-group element-based Lewis acids. Utilizing a dithienophosphole oxide architecture, we were able to mimic the structural motif of the widely employed Gutmann-Beckett method. This allowed us to correlate the optical response to the strength of the Lewis acid in an efficient manner. Comparing the optical response to commonly used methods that employ <sup>31</sup>P NMR chemical shifts or quantum-chemical calculations strongly suggest that our method using fluorescent Lewis acid-base pairs is more reliable. Moreover, our method provides a direct measure of the Lewis acidity of a given solution with direct implications to the overall utility of a Lewis acid in practical applications.

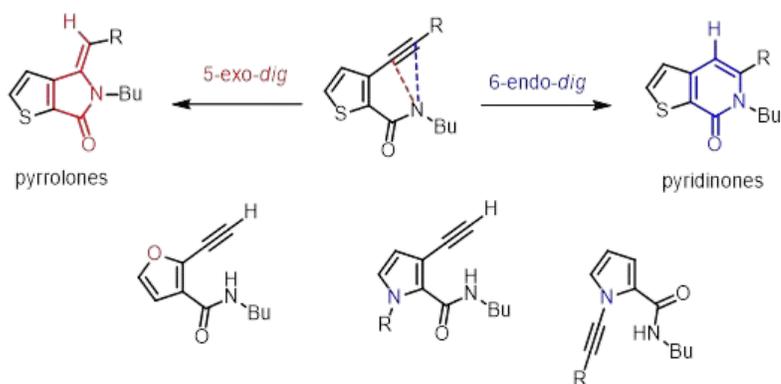
# Controlling 5-Exo/6-Endo-Dig Cyclizations of Heterocyclic Alkynylamides: Accessing Unusual Pyrrolones and Pyridinones

Genesis Infante, Ryan Dean, Djihane Damoo, and Sara Eisler<sup>1</sup>

<sup>1</sup> Department of Chemistry, University of New Brunswick, Fredericton, NB

seisler@unb.ca

5-Exo and 6-endo cyclizations in heterocyclic alkynylamides provide access to extended structures that are either very difficult to access, or are currently unavailable by other methods. However, these cyclization reactions can be unreliable, and mixtures of products are often formed. To determine how to control the competing 5-exo- and 6-endo-*dig* cyclization pathways, a series of computational studies was performed. It was found that shifting the favourability toward one or the other pathways could be achieved by controlling various structural features. Experimental results reflecting theoretical predictions will also be presented.



# An Unexpected 'Step-Conjugated' Biphosphole via Unique P-P Bond Formation

Zisu Wang,<sup>1</sup> Nayanthara Asok,<sup>2</sup> Joshua Gaffen,<sup>2</sup> Yael Gottlieb,<sup>3</sup> David Bi,<sup>2</sup> Chris Gendy,<sup>2</sup> Roman Dobrovetsky<sup>3</sup> and Thomas Baumgartner<sup>1,2</sup>

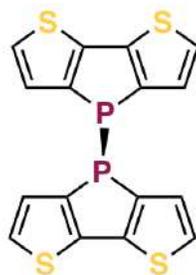
<sup>1</sup> Department of Chemistry, University of Calgary, Calgary, AB, Canada

<sup>2</sup> Department of Chemistry, York University, Toronto, ON, Canada

<sup>3</sup> School of Chemistry, Tel Aviv University, Tel Aviv, Israel

[tbaumgar@yorku.ca](mailto:tbaumgar@yorku.ca)

The synthesis of a  $\pi$ -conjugated organophosphorus species with bridging P-P unit is reported.<sup>1</sup> Due to the pyramidal geometry of the phosphorus centers, the new molecular scaffold provides intriguing electronic communication throughout the three-dimensional structure via  $\pi$ - $\sigma$ - $\pi$  conjugation in stepwise fashion. The new species was serendipitously found to be accessible via an unprecedented reaction of the corresponding *P*-amino-phosphole precursor through mediation with the hard Lewis acid BF<sub>3</sub>. We provide detailed mechanistic studies toward a suitable reaction mechanism that was also verified via computational means. Moreover, we elaborate the utility of the novel biphosphole via P-functionalization that lends further proof for the step-conjugation provided by the unique phosphorus-based molecular architecture.



<sup>1</sup> Wang, Z. *et al. Chem*, **2018**, 4, online (DOI : 10.1016/j.chempr.2018.08.022).

## Strategies for Improving Electrochromic Device Performance

Monika Wałęsa-Chorab<sup>1,2</sup> Marie-Hélène Tremblay,<sup>1</sup> Heather L. Filiatrault,<sup>1</sup> Antoine Leliège<sup>1</sup>  
and W.G. Skene<sup>1</sup>

<sup>1</sup>Département de chimie, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7,  
Canada.

<sup>2</sup>Current address: Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b,  
61614 Poznań, Poland  
w.skene@umontreal.ca

Electrochromic devices undergo reversible color change with applied potential. Such devices have found uses in a wide range of applications from wallet size smart card displays to large area architectural glass. This smart-glass has the advantage of reducing building operational costs. While an extended palette of colors is possible with organic polymers, their synthesis can be tedious. In contrast, azomethines can be prepared by catalytic condensation. They are additionally advantageous as the heteroatomic bond is intrinsically electron withdrawing. An alternating  $\pi$ -donor-acceptor arrangement is therefore possible when they are prepared from electron rich aromatics. A wide range of colors that span the visible spectrum are therefore possible with relatively low molecular weight azomethines. Despite this, azomethines lag behind their all-carbon counterparts in electrochromic device performance. Strategies for improving the electrochemical switching performance of azomethines will be presented. Ways of modulating the color and electrochemical resistance of the colorful azomethines will also be discussed.

# Theoretical studies in singlet fission: material search and mechanism exploration

Tao Zeng

Department of Chemistry, Carleton University, Ottawa, Ontario K1S 5B6, Canada

Singlet fission (SF) converts one short-lived singlet exciton to two long-lived triplet excitons. It can potentially enhance the power conversion efficiency in organic photovoltaic devices [i]. In the new concept of intramolecular singlet fission (iSF), chromophore units are covalently bonded and it is easier to adjust intermolecular morphology to facilitate SF. However, the detailed iSF mechanism is still unclear. In this presentation, our recent works in SF are discussed. Through performing quantum chemistry calculations and quantum dynamics simulations, we investigated the small size effects in iSF and presented a step-by-step picture for the through-liner iSF [ii, iii]. With the new understanding, we proposed a strategy to enhance the iSF efficiency by making appropriate substitution on the linker. We also explored the significance of azaborine substitution in designing SF chromophores [iv].

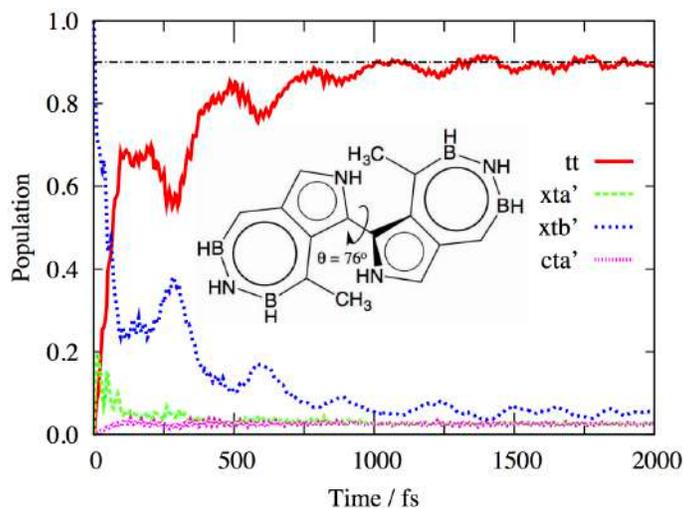


Figure. 1. Evolutions of populations of relevant states in intramolecular singlet fission.

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[ii] T. Zeng and P. Goel, *J. Phys. Chem. Lett.* **7**, 1351 (2016).

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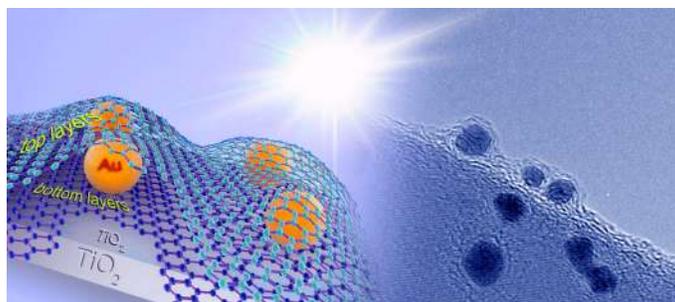
[iv] T. Zeng, S. K. Mellerup, D.-T. Yang, X. Wang, S. Wang, and K. G. Stamplecoskie, *J. Phys. Chem. Lett.* **9**, 2919 (2018).

# Self-assembled colloids as hierarchical catalysts for artificial photosynthesis

Jerome Claverie

Université de Sherbrooke, Sherbrooke, Qc, Canada

Semiconducting nanostructures are currently under intense scrutiny for their ability to harvest light, and to generate charge carriers which can promote the splitting of water or the reduction of CO<sub>2</sub>, leading to the sustainable formation of fuels such as hydrogen, methanol or methane. Two main routes are currently exploited. In the first one (so called Z scheme), the nanostructure is bound to the surface of an electrode, which either serves of photoanode or of photocathode. Such nanostructures, which are usually constructed by a top-down approach, can incorporate an exquisite level of refinement and complexity, but a limited active surface. Another approach consists in incorporating both the anode and the cathode within a single nanoparticle. This approach leads to materials with high surface and commensurate catalytic activity. However, usual bottom-up synthetic methods usually do not afford a high level of sophistication on the spatial arrangement of the various phases constituting these nanoparticles. To address this problem, we have developed methods whereby inorganic/organic hybrid colloids are first self-assembled before being converted into highly active photocatalysts which are able to split water under visible light. With this method in hand, we were able to conceive and prepare sophisticated free-standing photocatalytic nanoparticles with high activity in water splitting under visible light. Thus, colloid self-assembly is a powerful method to design photocatalysts for artificial photosynthesis. This communication will present several examples of nanoparticle architectures including various examples of heterojunctions, plasmonic and/or upconverting photocatalysts, and semiconductors exploiting whispering gallery mode resonances.



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# **P1: pH- and Photo Switching Studies Of Poly(Acrylic Acid-Co-Coumarin) as well as its Brushes Grafted To Silica Surfaces**

Hu Zhang, W. G. Skene\*<sup>a</sup> and Suzanne Giasson\*<sup>ab</sup>

<sup>a</sup>Department of Chemistry, Université de Montréal, C.P. 6128, succursale Centre-Ville, Montréal, QC, H3C 3J7, Canada.

<sup>b</sup>Faculty of Pharmacy, Université de Montréal, C.P. 6128, succursale Centre-Ville, Montréal, QC, H3C 3J7, Canada  
E-mail: w.skene@umontreal.ca; suzanne.giasson@umontreal.ca

We report the preparation of a responsive poly(acrylic acid-co-7-(2-methacryloyloxyethoxy) -4-methylcoumarin) (P(AA-co-CMA)) copolymer by reversible addition-fragmentation chain-transfer (RAFT) and its brushes grafted from silica substrates. For the P(AA-co-CMA) copolymer, it can be prepared by polymerizing directly from acrylic acid and coumarin monomers. The photo-responsive behaviors of the hydrophilic and hydrophobic were investigated by UV-Vis absorption spectroscopy in water. In solution, the copolymers could be reversibly cross-linked and de-cross-linked using two different wavelengths of light. The results demonstrate that the cross-linking density can be adjusted with irradiation time (or the intensity). Although the photocleavage of coumarin photodimers appeared incomplete, a reversible photocontrol of the crosslinking density could be achieved to a certain degree. With the polymer solution repeatedly exposed to alternating UV light at  $\lambda > 310$  nm and  $\lambda < 260$  nm for 10 cycles, the reversible change in the dimerization degree (cross-linking density) was observed. In order to graft polymer brush to the silicon wafer, the same RAFT agent was firstly immobilized onto its surface. Then the similar RAFT polymerization was conducted. The polymer brush layer was analyzed using AFM and ellipsometry in air and buffer solution. Preliminary study showed that the thickness of the polymer brush in solution can be reversibly tuned by cross-linking and de-cross-linking of the coumarin component using the UV-Vis light, much as the same way with the free copolymers.

# P3: Computational Study into the Origin of $^{17}\text{O}$ Chemical Shift Changes in Solvated Acetone

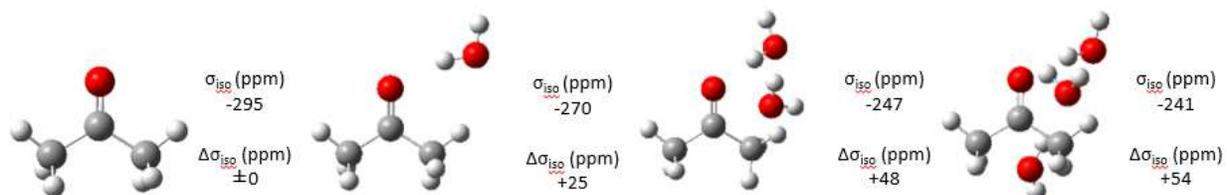
Li Zhang and Heidi Muchall

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montreal, QC

[li.zhang.20181@mail.concordia.ca](mailto:li.zhang.20181@mail.concordia.ca); [heidi.muchall@concordia.ca](mailto:heidi.muchall@concordia.ca)

The chemical shift of a nucleus is susceptible to changes in the nuclear environment. Besides structural changes, an important environmental factor is the influence of the solvent. Thus, H-bonding in neat alcohols can be disrupted by solvents in dilution studies, and the signal of the hydroxyl proton wanders upfield over a quite large range; not surprisingly, the chemical shift of oxygen in carbonyl compounds is also solvent-dependent. For acetone, the experimental  $\delta^{17}\text{O}$  is 572 ppm in the neat sample, 535 ppm in water, 568 ppm in acetonitrile, and 580 ppm in hexane, and the range of  $\Delta\delta$  observed is about 50 ppm on the  $\delta^{17}\text{O}$  scale of about 800 ppm.<sup>1</sup> It has been suggested that, in the absence of H-bonds, the observed shifts might be due to changes in the C=O bond length through the polarity of a solvent.<sup>1</sup> Nowadays, computational studies of implicit and explicit solute-solvent interactions can uncover the origin of solvent-induced chemical shift changes.

We will present the impact of both solvent fields and individual solvent molecules on the  $^{17}\text{O}$  isotropic shielding in acetone.



[1] 1:1 Dilution data, water reference: H.A. Christ, P. Diehl. *Helv. Phys. Acta* **36**, 170 (1963).

## P4: Computational study of weak interactions in cyclic trimers of model phenolic surfactants

Janet Gaba,<sup>1,2,3</sup> Christine DeWolf,<sup>2,3</sup> and Heidi Muchall<sup>1,3</sup>

Concordia University, Montreal, Quebec:

<sup>1</sup>Centre for Research in Molecular Modeling

<sup>2</sup>Centre for Nanoscience Research

<sup>3</sup>Department of Chemistry and Biochemistry

[janet.gaba@mail.concordia.ca](mailto:janet.gaba@mail.concordia.ca); [christine.dewolf@concordia.ca](mailto:christine.dewolf@concordia.ca); [heidi.muchall@concordia.ca](mailto:heidi.muchall@concordia.ca)

Lipid assemblies at interfaces have structures that depend on their intermolecular interactions. Experimental work<sup>1,2</sup> shows that both hydrogen-bonding and  $\pi$ -stacking interactions affect the behaviour and organization of phenolic surfactant monolayers. However, the locations and strengths of these interactions remain unclear. Grazing incidence x-ray diffraction (GIXD) data have yielded information on the lateral organization of these systems, allowing the determination of individual interactions using electronic structure methods.

Preliminary results have been obtained using  $\omega$ B97X-D (DFT) and GFN-xTB (semiempirical) methods for *p*-alkylphenol, *p*-alkoxyphenol, and alkyl *p*-hydroxybenzoate cyclic trimer model systems, and some larger assemblies, in both the gas phase and implicit water solvent. Lipid models upright themselves more with increasing tail length. Particular systems show a loss of the cyclic trimer motif in water, in favor of a "2+1" stacked arrangement. Additionally, in larger assemblies evidence of potential long-range  $\pi$ - $\pi$  stacking is observed.



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<sup>2</sup> Schmidt, R.; DeWolf, C. *Langmuir* **2004**, *20*, 3284-3288.

## P5: Computational investigation of CH<sub>3</sub>SNO<sub>2</sub> and the effects of protonation on the electronic structure

Philippe Archambault, Vinod Parmar, Ann English, and Gilles Peslherbe

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montreal, Quebec

[archambault.phil@gmail.com](mailto:archambault.phil@gmail.com); [gilles.peslherbe@concordia.ca](mailto:gilles.peslherbe@concordia.ca)

Protonation and deprotonation are fundamental steps in many chemical and biochemical reactions. Considering them becomes especially important when an acidic or a basic microenvironment is produced (i.e. by residues within a protein's active-site) as reactivity and stability of reaction intermediates can be heavily influenced by protonation or deprotonation. After thionitrates (RSNO<sub>2</sub>) were proposed as active intermediates in organic nitrate decomposition, there has been a growing interest in understanding their reactivity and stability<sup>1,2</sup> as organic nitrates can act as prodrugs for nitric oxide (NO) which is a powerful vasodilator.<sup>3</sup> RSNO<sub>2</sub> are shown to be stable in the presence of an acidic environment furthering the need to investigate not only RSNO<sub>2</sub> but the effects of protonation on the electronic structure and reactivity as well.

In this work we will present the use of high-level *ab initio* calculations to perform a systematic study of the electronic structures of CH<sub>3</sub>SNO<sub>2</sub> (model compound for thionitrates) and its protonated forms.

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## **P6: Towards Electrochemically Mediated Fluorescence for Reversible Fluorescence Turn-On/Turn-Off**

Thibault Amiaud<sup>1</sup> and W.G. Skene<sup>1</sup>

<sup>1</sup>Département de chimie, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.

w.skene@umontreal.ca

Desired properties of electroactive compounds are reversible electrochemistry. When these compounds are highly conjugated, they undergo color changes when subjected to applied potentials. Incorporating an electroactive moiety into a conventional fluorophore can lead to electrochemically mediated fluorescence modulation. The fluorescence of conventional fluorophores can also be electrochemically switched with pendant groups. Towards developing electroactive fluorescence switches, various electrofluorophores will be presented along with their electrochemistry and fluorescence.

## **P7: UNDERSTANDING THE ELECTROCHROMIC EFFECT OF AZOMETHINES VIA STRUCTURE-PROPERTY STUDIES**

Yohan Gautier<sup>1</sup> and W.G. Skene<sup>1</sup>

<sup>1</sup>Département de chimie, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.

w.skene@umontreal.ca

An electrochromic behavior is typically defined as the change in absorption with applied potential. When the absorption occurs in the visible, the electrochemically mediated color switching can be observed by the common user. This has potential uses in various applications, notably architectural smart glass for modulating the temperature of buildings. Conjugated azomethines consisting of low molecular weight trimers have demonstrated electrochromic properties. Despite this, little is known about the true effect of molecular structure on the electrochromic properties. Towards this end, a series of structurally similar azomethines were prepared. These were investigated for understanding the effect of modifying both the terminal substitution and the central aromatic on the electrochromic properties, with particular focus being placed on the redox potential, electrochemical reversibility, and electrochemically mediated color changes. The results of this extensive study will be presented.

## **P8: EXPLOITING INTRAMOLECULAR HYDROGEN BONDING FOR FLUORESCENCE MODULATION**

Marie-Hélène Tremblay<sup>1</sup> and W.G. Skene<sup>1</sup>

<sup>1</sup>Département de chimie, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.

w.skene@umontreal.ca

Despite the relative ease of azomethine preparation compared to their all-carbon counterparts, their properties can be limited. For example, bold colors that span the entire visible spectrum are possible with relatively low molecular weight conjugated azomethines. However, their fluorescence is nearly none existent. Even when highly fluorescence fluorophores are connected to azomethines, their intrinsic emission is quenched by the heteroatomic bond. External stimuli can be used to mitigate the efficient fluorescence deactivation modes of azomethines. It will be demonstrated that hydrogen bonding is a viable means intrinsic azomethine quenching. It will be shown that engaging the supramolecular contacts leads to emission enhancement.

## **P9: PHOTOPOLYMERIZATION OF ELECTRACTIVE LAYERS FOR ELECTROCHROMIC APPLICATIONS**

Monika Wałęsa-Chorab<sup>1,2</sup> and W.G. Skene<sup>1</sup>

<sup>1</sup>Département de chimie, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.

<sup>2</sup>Current address: Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61614 Poznań, Poland

w.skene@umontreal.ca

Azomethines have the advantage of being easily prepared by the catalytic condensation of aryl amines and amines. The resulting bond is chemically robust and it can resist hydrolysis. When electroactive precursors are used for the preparation of azomethines, the products are also electroactive. Indeed, they undergo reversible color switching with applied potential. The collective electroactivity and robustness of azomethines make them ideally suited for electrochromic applications. The robustness of the azomethine will be demonstrated by sustaining conventional photolithography. It will be shown that low molecular weight azomethines can be immobilized on electrodes and their electrochromic properties demonstrated.

## P10: Synthesis and Characterization of Liquid Crystalline Tetraoxapentacene Derivatives

Alexandre Malinge,<sup>2</sup> Lana K. Hiscock,<sup>1</sup> Brooke M. Raycraft,<sup>1</sup> Monika Wałęsa-Chorab,<sup>2</sup> Coralie Cambe,<sup>2</sup> Hi Taing,<sup>3</sup> S. Holger Eichhorn,<sup>3</sup> Louise N. Dawe,<sup>1</sup> Kenneth E. Maly<sup>1</sup> and W. G. Skene<sup>2</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, Wilfrid Laurier University, 75 University Ave. W., Waterloo, ON, N2L 3C5, Canada

<sup>2</sup>Département de Chimie, Université de Montréal, CP 6128, Centre-ville Montreal, QC, H3C 3J7, Canada

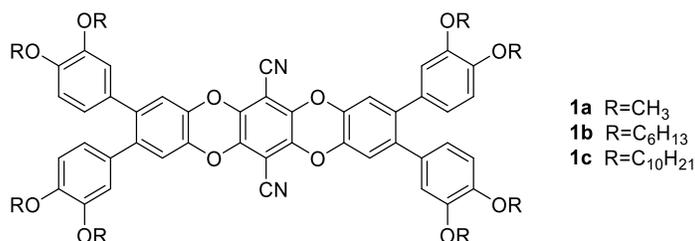
<sup>3</sup>Department of Chemistry and Biochemistry, University of Windsor, Essex Hall, 401 Sunset Ave., Windsor, ON, N9B 3P4, Canada

[alexandre.malinge@gmail.com](mailto:alexandre.malinge@gmail.com) ; [w.skene@umontreal.ca](mailto:w.skene@umontreal.ca)

Fluorescent columnar liquid crystals could have potential applications as semiconductors in organic photovoltaic cells, field effect transistors and light emitting diodes.<sup>1,2</sup> However, the emission of the core observed in solution is usually quenched in ordered phases.<sup>3,4</sup>

Here, the tetraoxapentacene has been studied as a core for columnar liquid crystals because of its emission and straightforward preparation.<sup>5,6</sup> Our approach is to append alkoxy-substituted aryl groups (1a-c) to promote aggregation-induced emission (AIE) in order to exhibit fluorescence.<sup>7,8</sup>

Indeed, the energy consumed, in solution, by the rotation of functional groups in the molecule leads to a non-radiative decay. However, in solid state, the free rotation of those groups is restrained and a radiative decay (AIE) is observed.



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## **P11: Solvato/fluorochromic properties of an electronic push-pull benzothiadiazole fluorophore**

Alexandre Malinge, Coralie Cambe, Mathieu Frémont, Lei Hu and W. G. Skene

*Département de Chimie, Université de Montréal*

[alexandre.malinge@gmail.com](mailto:alexandre.malinge@gmail.com) ; [w.skene@umontreal.ca](mailto:w.skene@umontreal.ca)

The fluorescence properties of a benzothiadiazole core flanked by a triphenylamine donor and aldehyde acceptor were studied.

A large shift in the emission spectrum was observed between 540 to 750nm by changing the polarity of the solvent. This effect is called “solvatochromism” and it is a useful property for sensors and molecular switching applications.

Furthermore, high quantum yields were measured in solution (up to 95% in toluene) and in solid state (55%). They are desired properties for its use in optoelectronics. The electrochemistry, spectroelectrochemistry, and spectroelectrofluorescence were also examined and they will be presented.

## **P12: PUSHING THE VISIBLE EMISSION ENVELOPE: DEVELOPING NIR EMITTERS**

Monika Wałęsa-Chorab,<sup>1,2</sup> Chengzhang Yao, Georges Turner and W.G. Skene<sup>1</sup>

<sup>1</sup>Département de chimie, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.

<sup>2</sup>Current address: Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61614 Poznań, Poland  
[w.skene@umontreal.ca](mailto:w.skene@umontreal.ca)

Fluorophores are ubiquitous in a large range of applications such as biological imaging and organic electronics. While fluorescence in the visible region has its advantages it is also a severe limitation. Emission in the NIR would be advantageous for both biological probes and organic emitting devices to address many of the shortcomings of visible fluorophores. Towards this means, we investigated conjugated fluorophores having an electronic *push-pull* configuration. We examined the effect of a heavy heteroatom in the core aromatic on the spectroscopic and electrochemical properties, along with the emission quantum yields. These are complemented by theoretical calculations to appreciate the fluorophore's photophysical properties.

# P13: Towards NIR Fluorophores: A Photophysical and Electrochemical Study

Chengzhang Yao,<sup>a</sup> Hu Lei,<sup>a</sup> Mathieu Frémont,<sup>a</sup> Laurie Walach,<sup>a</sup> Georges Turner,<sup>a</sup> W. G. Skene<sup>a</sup>

<sup>a</sup>Department of Chemistry, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.

Email: huleify@gmail.com; w.skene@umontreal.ca

**Abstract:** Fluorophores are compounds that emit light when irradiated. This property has been useful for a wide range of applications, including sensors and organic electronics.<sup>1</sup> Extending the range of emission fluorophores from the visible region into the NIR is advantageous for both biological imaging<sup>2</sup> and organic electronics applications.<sup>3</sup> This can in part be done by incorporating complementary strong electron donors and acceptors into the fluorophore. Such an electronically *push-pull* fluorophore gives rise to an intramolecular charge transfer. The effect of different electronic withdrawing groups (NO<sub>2</sub> vs CN) on the photophysical and electrochemical properties for understanding NIR emission behavior will be presented. To fully appreciate the properties, the spectroelectrochemistry, spectroelectrofluorescence, and quantum yields will be presented.

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## **P14: Development of Dormant Photosensitizers for Antimicrobial Photodynamic Therapy**

Julia McCain,<sup>1</sup> and Gonzalo Cosa<sup>1</sup>

<sup>1</sup> Department of Chemistry, McGill University, Montreal, QC

[julia.mccain@mail.mcgill.ca](mailto:julia.mccain@mail.mcgill.ca); [gonzalo.cosa@mcgill.ca](mailto:gonzalo.cosa@mcgill.ca)

Photodynamic therapy (PDT) is an established therapeutic technique for the treatment of diseases such as cancer and bacterial infections. PDT uses light-sensitive compounds called photosensitizers which, upon photoexcitation, undergo rapid intersystem crossing from the singlet to the triplet excited state, next sensitizing singlet oxygen ( $^1\text{O}_2$ ), a cytotoxic reactive oxygen species (ROS). Light activation allows for spatiotemporal control of photosensitizer activity. A risk of this approach is damage to surrounding healthy tissues when the light treatment is applied. A new level of control, activation of an otherwise dormant photosensitizer by reaction with a chemical cue, would mitigate undesired activity in healthy tissues.

In 2016, our group reported a dormant photosensitizer that activates upon scavenging of ROS. The new compound delivers  $^1\text{O}_2$  specifically in cells under oxidative stress associated with increased metabolic activity and ROS generation. The dormant photosensitizer combines a photosensitizing boron-dipyrromethene (BODIPY) dye with the antioxidant chromanol ring of  $\alpha$ -tocopherol as a trap. The trap quenched excited states of the photosensitizer via intramolecular photoinduced electron transfer (PeT), preventing the sensitization of  $^1\text{O}_2$  by the triplet excited state of the photosensitizer. ROS-mediated oxidation of the trap moiety prevented the quenching, activating the photosensitizer. We aim to increase the dynamic range of the photosensitizer-trap system by tuning the BODIPY redox properties, ensuring that the compound is completely inactive until, upon reaction with ROS, it becomes highly efficient in sensitizing  $^1\text{O}_2$ .

## P15: Efficient Photoconversion of Thiones to Ketones: Exploring Ethers as a Source of Oxygen

Meghan Heer,<sup>1</sup> Taylor Hope,<sup>1</sup> Ken Maly,<sup>2</sup> Mathieu Frenette<sup>1</sup>

<sup>1</sup>Département de Chimie, Université du Québec à Montréal, Montréal, Québec

[mheer055@uottawa.ca](mailto:mheer055@uottawa.ca); [frenette.mathieu@uqam.ca](mailto:frenette.mathieu@uqam.ca)

The purpose of this project is to identify the mechanism in the photoconversion of a dithioimide liquid crystal to its parent imide. The dithioimide liquid crystal species was synthesized by Prof. Ken Maly's group from Wilfred Laurier University in Waterloo, Ontario for the purpose of improving the self-assembly of the compound in columnar mesophase systems over a wide range of temperatures so they can be used in liquid crystal displays.<sup>1</sup>

In the presence of molecular oxygen, thione to ketone photoconversions are well understood.<sup>2</sup> For our dithioimide, however, the photoconversion still proceeds in the absence of molecular oxygen and in anhydrous ether solvents (tetrahydrofuran and diethyl ether). Strangely, the thione to ketone photoconversion fails in dichloromethane and chloroform, which points to ethers as an unprecedented source of oxygen for this reaction. The addition of oxygen, peroxides, or water to the ether solvent did not appreciably vary the reaction yield nor the rate of reaction. Laser-flash photolysis studies showed the triplet state of the dithioimide, but this excited state was unaffected by THF. Instead, it appears the singlet state is reacting with THF; increasing amounts of THF lowers the initial yield of triplet dithioimide, but not its lifetime. To confirm the ether solvent as the ultimate source of oxygen, isotopically-enriched water was purchased and the synthesis of 18-O THF is underway.

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## P16: Dormant Singlet Photosensitizer Based on ROS

Wenzhou (Kevin) Zhang,<sup>1</sup> Julia McCain,<sup>1</sup> Roger Bresolí- Obach,<sup>2</sup> Dr. Santi Nonell,<sup>2</sup> and Dr. Gonzalo Cosa<sup>2</sup>

<sup>1</sup> Department of Chemistry, McGill University, Montréal, Québec

<sup>2</sup> Institut Químic de Sarrià, Universitat Ramon Llull, Barcelona, Spain

[[wenzhou.zhang@mail.mcgill.ca](mailto:wenzhou.zhang@mail.mcgill.ca)]; [[gonzalo.cosa@mcgill.ca](mailto:gonzalo.cosa@mcgill.ca)]

Photodynamic therapy for the treatment of cancer and other diseases employs photosensitizers to promote the production of singlet oxygen to eliminate pathological tissue. Due to the cytotoxicity of singlet oxygen, it is imperative to have a high degree of control over its production. Previously, our group has reported a dormant photosensitizer based on a boron-dipyrromethene (BODIPY) chromophore where a chromanol trap moiety serves as a dormant/active control switch via photoinduced electron transfer. Reactive oxygen species (ROS) trigger activation of the sensitizer upon oxidation of the chromanol segment <sup>[1]</sup>. Building on our previous work we developed a new chromophore with enhanced switching capabilities. Herein we present the results.

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## P17: Selective Alkene Isomerization and Semi-hydrogenation using $\text{MoS}_2\text{CoO}_x\text{@TiO}_2$ Heterogeneous Photocatalyst

Bowen Wang, Kieran Duke, Anabel E. Lanterna\*, Juan C. Scaiano\*

<sup>1</sup> Department of Chemistry and Biomolecular Sciences and Centre for Advanced Materials Research (CAMaR), University of Ottawa. 10 Marie Curie, Ottawa, ON K1N 6N5, Canada

[[bwang060@uottawa.ca](mailto:bwang060@uottawa.ca), [titoscaiano@mac.com](mailto:titoscaiano@mac.com), [alantern@uottawa.ca](mailto:alantern@uottawa.ca)]

Alkenes are important in both industry and academia.<sup>1</sup> Especially some stereoselective alkenes are the key intermedia in synthesis of natural and industry products.<sup>2</sup> Platinum and palladium complexes are the most widely used catalysts for isomerization or hydrogenation reactions because of their high reaction rates.<sup>3-4</sup> Previous studies in the group have shown the tunability of Pd-decorated  $\text{TiO}_2$  materials, where the reaction can be directed towards either olefin isomerization or hydrogenation by subjecting the catalyst to different excitation wavelengths.<sup>5</sup> Despite the catalyst great activity, more inexpensive alternatives with similar efficiencies are always beneficial in terms of industrial applications. This research centers around the development of alternative materials to Pd-decorated composites, utilizing earth-abundant elements such as Mo and Co. We chose  $\text{MoS}_2$  due to its ability to catalyze the adsorption of hydrogen with near zero free energy,<sup>6</sup> which makes it a promising catalyst for H-transfer reactions. In particular, we found that multi-metal composites like  $\text{MoS}_2\text{CoO}_x\text{@TiO}_2$  materials can photocatalyze olefin isomerizations more efficiently than  $\text{Pd@TiO}_2$  under UV light irradiation. It is known that the Co can create edge sites along the  $\text{MoS}_2$  layer, generating more catalytic reactive areas on the material surface. Additionally, the catalyst proved to be suitable for alkyne semi-hydrogenation to furnish the corresponding alkene. The results demonstrate that the earth abundant materials can serve as efficient heterogeneous photocatalysts to replace expensive palladium catalysts in the synthesis of alkenes.



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## **P18: Mapping Redox Activity in Supported Lipid Bilayers**

Aya Sakaya, Andres Durantini, Tara Sverko, Vicent Wieczny and Gonzalo Cosa\*

Department of Chemistry and Quebec Center for Advanced Materials, McGill University, Montréal, Québec

[aya.sakaya@mail.mcgill.ca](mailto:aya.sakaya@mail.mcgill.ca); [gonzalo.cosa@mcgill.ca](mailto:gonzalo.cosa@mcgill.ca)

Supported lipid bilayers (SLB) have gained wide attention as assembly scaffolds, owing to their ability to self-assemble into well-defined fluid structures, allowing the compartmentalization and direct assembly of components of interest in a fluid platform. An excellent model of cellular membranes, supported lipid bilayers offer the opportunity to mimic and study processes occurring across these fluid mosaics such as respiration, transport and signaling.

In this study, we have explored redox reactions within supported lipid bilayers, proof of concept experiments intended to address the response of membrane embedded redox systems. Experimentally, a supported lipid bilayer was formed on top on an indium tin oxide (ITO)-coated glass, mimicking the lateral fluidity of a cell membrane. H4CIPrB-PMHC, a redox sensitive fluorogenic probe analogous to  $\alpha$ -tocopherol (Vitamin E) was incorporated within the SLB, and its electrochemical and optical properties were studied using spectro-electrochemical (SEC) total internal reflection fluorescence (TIRF) microscopy. We will discuss the general methodology, results, and implications of the work in the context of electron transport through relay redox systems.

## **P21: Towards a Fully Organic Stretchable and Conductive Material for Hole Injection Layers**

Michael Lerond,<sup>1</sup> Adam Manssouri,<sup>2</sup> Fabio Cicoira<sup>1</sup> and W.G. Skene<sup>2</sup>

<sup>1</sup>Département de génie chimique, Polytechnique de Montréal, Montréal, Québec

<sup>2</sup>Département de chimie, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.

[w.skene@umontreal.ca](mailto:w.skene@umontreal.ca)

A series of poly(dimethylsiloxane) (PDMS) functionalized with 3,4-propylenedioxythiophene (ProDOT) pre-monomers were synthesized. The resulting macromonomers were polymerized via chemical oxidation involving the substituted thiophenes. The resulting elastomer exhibited good stretchability. It also exhibited conductive properties when doped by adding ProDOT units prior to the polymerization. The preparation and subsequent polymerization of the stretchable conductive substrate will be presented.