

PROGRAM and ABSTRACT BOOK



** Welcome to RISE 2019 and the University of Ottawa! **

Program at a Glance

Sunday, August 25th 2019

4:30 pm - 5:30 pm	Business Meeting (PIs only)	ARC 538
5:30 pm	Meet & Greet – Welcome Reception	ARC Lobby

Monday, August 26th 2019

All presentations will take place at **ARC 233**. Breaks will take place at the **ARC Lobby**.

9:20 am – 9:30 am	Welcome
9:30 am – 9:55 am	Paytan Robinson – <i>Investigating the Nature of Radical-Involved Halogen Bonding Systems through Spectroscopy</i>
9:55 am – 10:20 am	Sami George Sabbah – <i>Looking for Cationic Phenol: A Mechanistic Study of De-Aromatization Reactions Induced by Hypervalent Iodine via Theoretical and Spectroscopic Insights</i>
10:20 am – 10:45 am	Coffee Break
10:45 am – 11:10 am	Ahmed Ibrahim – <i>Development of Post-Synthetic Alterations of Bulk Carbon Nitride to Improve Photocatalytic Performance</i>
11:10 am – 11:35 am	Charles Xiacong Zhang – <i>Earth-Abundant Materials for Heterogeneous Photocatalysis</i>
11:35 am – 12:00 pm	Elvin Girineza – <i>Synthesis and Applications of Cu₂O/TiO₂ Nanoparticles for Photocatalyzed Glaser Coupling</i>
12:00 pm – 1:15 pm	Lunch Break
1:15 pm – 2:00 pm	Invited Lecture: Dr. Michelle Chretien
2:00 pm – 2:25 am	Coffee Break
2:25 pm – 2:50 pm	Manjot Grewal – <i>Tailoring the Structure of Lanthanide-doped Upconverting Nanoparticles</i>
2:50 pm – 3:15 pm	Ryan Karimi – <i>Unraveling Cellular Fluorescent Morphologies of Fluorogenic Lipid-Derived Electrophile Analogues</i>
3:15 pm – 3:40 pm	Luke Yang – <i>An Investigation towards Organic Magnets: Stable Radical Insertion on Fluorene Derivatives</i>
3:40 pm – 4:00 pm	Closing Remarks
6:00 pm	RISE Meeting Banquet (Alex Trebek Alumni Hall)

Tuesday, August 27th 2019

10:00 am – 12:00 pm	CAMaR Tour – Meeting point is the ARC Lobby
12:00 pm	End of RISE 2019

Special Guest and Keynote Lecturer:



Prof Michelle Chretien
Director, Centre for Advanced Manufacturing
and Design Technologies (CAMDT) at Sheridan
College

Michelle received her BSc in Chemistry from Dalhousie University and her PhD from the University of Ottawa for work in photochemistry and photophysics. Her PhD thesis was nominated for the Governor General's Medal and was awarded the IUPAC Prize for Young Chemists.

Michelle was an NSERC Post-Doctoral Fellow at the Centre for Biological Applications of Mass

Spectrometry in Montréal and has taught courses on photochemistry and mass spectrometry and the graduate and undergraduate level.

Michelle joined the Xerox Research Centre of Canada (XRCC) in 2007 and held a variety of roles including Senior Research Scientist, Product Manager, Program Manager for Strategic Research, Global Program Manager for Electronic Materials and Senior R&D Manager in Materials Science. Michelle has led scientists and engineers working on materials science and, with her team, has tackled challenges such as developing new materials and processes for 3D printing and printed, hybrid and flexible electronics. Michelle is currently an Adjunct Professor at McMaster University.

Michelle is passionate about the commercialization of innovation and public engagement in science. She is an active participant in the technology and innovation commercialization ecosystem, and sits on a number of committees and boards including:

- the Steering Committee for ReMAP, a Celesitca-led Network Centre of Excellence for accelerating novel electronics manufacturing technologies
- the Technical Advisory Board for IntelliFlex, an industry alliance focused on the flexible electronics industry
- the Selection Committee for the Ontario Scale-up Voucher Program

Michelle devotes time to various science outreach initiatives and has served as an elected member of the Inter-American Photochemical Society Advisory Board and RISE Canada. Michelle has published 21 scientific papers in peer-reviewed journals and holds 75 US patents on novel materials and marking technologies. In 2010, Michelle was recognized by PrintAction as one of the Canadian printing industry's Top 35 Under 35 for her technological contributions.

1 - Investigating the Nature of Radical-Involved Halogen Bonding Systems through Spectroscopy

Paytan Robinson^{1,2}, Xing Tong¹, Pierre Kennepohl¹

¹Department of Chemistry, University of British Columbia, Vancouver, BC, ²Department of Chemistry, St. Francis Xavier University, Antigonish, Nova Scotia

Halogen bonding (XB) has been identified as a potentially useful tool in molecular electronics. Dependent on the movement of electrons, molecular electronics will result in the formation of radicals as electrons are transferred in a system. This fact indicates radical-involved XB systems to be of particular interest. Previously in the Kennepohl lab, the stable radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) has been observed to form weak XBs with cationic halogenated molecules. Expanding on this, the nature of the XB interactions between TEMPO and a series of halogenated pyridinium salts (where X = Cl, Br, and I) is explored using spectroscopic methods to compare the XB strength for different XB donors (Figure 1), as well as to investigate thermodynamic properties of XB systems in solution.

¹H NMR titrations are performed to observe the relationship between increasing concentrations of TEMPO and the changing spectra of each pyridinium salt (constant concentration) in acetonitrile-d₃ solvent at room temperature (25 °C) and low temperatures (-35°C). The data indicate binding constants too small to determine, which suggest fairly weak XB interactions. This weak interaction was further confirmed when preparing crystals: proved too weak to result in crystals containing both XB donor and acceptor.

When compared, the chlorinated salts show a greater shift in NMR spectra than their counterparts. These salts (M2ClP, M4ClP) are further analyzed using Cl K-edge X-ray absorbance spectroscopy (XAS). Interestingly, for the largest ratio of M2ClP:TEMPO the data show an increase in absorption edge energy. Understanding this phenomenon would require more experimentation.

Overall, the interactions between TEMPO and our chosen XB donors proved to be relatively weak, which impeded our investigation into the nature of radical-involved XB systems. This suggests the need for better XB pairs in future trials. However, investing further time into investigating to interpret the XAS data may be worthwhile.

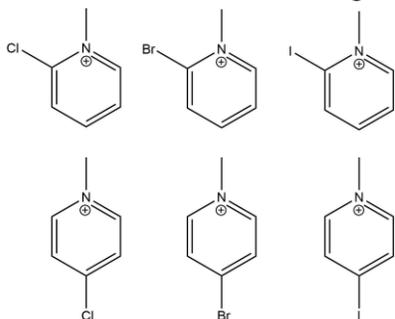


Figure 1. Halogenated pyridinium salts: (from left to right) M2ClP, M2BrP, M2IP, M4ClP, M4BrP, M4IP

2 - Looking for Cationic Phenol: A Mechanistic Study of De-Aromatization Reactions Induced by Hypervalent Iodine via Theoretical and Spectroscopic Insights

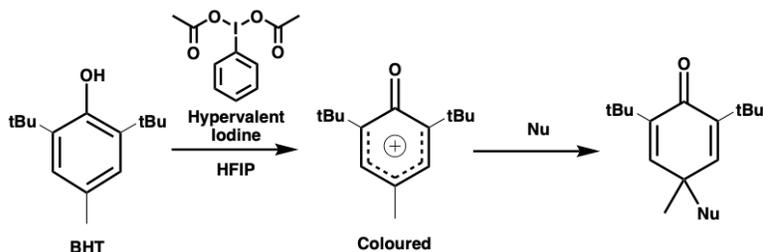
Sami George Sabbah^{1,2}, Antoine Juneau¹, Mathieu Frenette¹

¹Département de Chimie, Université du Québec à Montréal, Montréal, Québec,

²Department of Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario

Phenol de-aromatization constitutes a powerful synthetic approach to create highly functionalized 6-membered rings.¹ The reaction requires hypervalent iodine reagents in polar protic solvent—hexafluoroisopropanol is typically used—and is theorized to proceed through an unexpected cationic-phenol (phenoxenium) intermediate.² The mechanism of this reaction remains enigmatic due to the lack of experimental data in the literature.

The central focus of this study was to investigate the mechanisms proposed in the literature using density functional theory calculations as well as UV/Vis and Raman spectroscopy. Computational studies suggested the formation of an energetically favourable colourless iodine-phenol intermediate that dissociates into a coloured phenoxenium intermediate. We obtained good agreement between theoretical and experimental UV/Vis spectra on the formation of coloured intermediates consistent with phenoxenium intermediates for a range of phenolic compounds. Theoretical studies on various substituted phenols showed that butylated hydroxytoluene (BHT), a phenol with bulky R groups in the ortho position, produces a stable phenoxenium intermediate that can be freeze-quenched. A resonance Raman spectrum of this freeze-quenched red intermediate showed peak shifts that are indicative of a chemical transformation. We tentatively assign this Raman spectrum to a phenoxenium species and we are currently looking for phenoxenium reactive intermediates derived from other phenol derivatives. Our findings present promising strategies for elucidating the reaction mechanism, which will allow for advancements and practical implementation of this reaction in organic synthesis.



Reaction scheme for the de-aromatization of butylated hydroxytoluene (BHT) using hypervalent iodine in hexafluoroisopropanol (HFIP).

¹ Roche, S. P. & Porco, J.A. *J. Angew. Chem* **2011** 50(18), 4069.

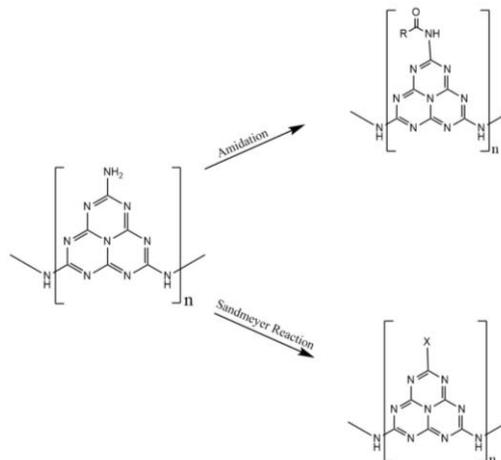
² Maertens G, Canesi S. *J. Top Curr Chem* **2016** 373, 223-41.

3 - Development of Post-Synthetic Alterations of Bulk Carbon Nitride to Improve Photocatalytic Performance

Ahmed Ibrahim^{1,2}, Robert Godin²

¹McMaster University, ²University of British Columbia

Graphitic carbon nitride (CN_x) is a promising photocatalyst that boasts facile synthesis and non-toxicity. Its development presents a potential alternative to fossil fuels and current solar energy conversion approaches. Promising photocatalytic hydrogen efficiencies have been reported using sacrificial electron donors but these routes are inherently unsustainable. Overall water splitting to generate O₂ and high energy H₂ is sustainable but current efficiencies are not high enough for commercial viability. Chemical and morphological alterations for CN_x are being investigated to improve its photocatalytic activity. The primary aryl amines of the CN_x heptazine rings provide a potential site for post-synthetic substitutions. Additionally, successful substitution in CN_x's bulk form would capitalize on its scalable and facile synthesis. Post-synthetic substitutions were targeted to enhance its semiconductor qualities by amplifying favourable electronic characteristics such as increased π-π stacking and charge transfer complex formation.^{1,2} In this project, we adapted traditional amide synthesis procedures using aromatic acyl chlorides to CN_x. Direct substitution of the heptazine aryl amines to halogens via a diazonium intermediate was also attempted using the Sandmeyer reaction. Products were purified via phase extraction and column separation, characterized using FT-IR, and their photocatalytic activities were assessed using the degradation of the azo dye methyl orange.³ Theoretical yields were not determined due to the lack of direct substitution and the inability to determine the ratio of acyl chloride to CN_x within the products. Amidation reactions yielded small amounts of organic-soluble product containing a mixture of acyl chloride and CN_x and large amounts of insoluble bulk containing the acyl chloride. Although amide formation in the products was inconclusive, FT-IR spectra revealed that the acyl chlorides and their corresponding carboxylic acids are present in the CN_x after extensive purification. These products have altered physical and spectral characteristics indicating intercalation of the acyl chlorides and potentially, substitution. Recovered bulk CN_x from the purified halogenation reactions showed no spectral change compared to the reactant bulk CN_x. In this presentation, the efficacy of the chosen synthetic methods will be discussed and the trends in photodegradation rates will be related to spectral and physical properties of the products.



¹ Kobayashi, Y. *et al. Nat. Mater.* **2016** 16(1), 109-114.

² Parini, V. P. *Russ. Chem. Rev.* **1962** 31(7), 408-417.

³ Yan, S. *et al. Langmuir.* **2010** 26(6), 3894–3901.

4 - Earth-Abundant Materials for Heterogeneous Photocatalysis

Charles Xiaocong Zhang^{1,2}, Anabel E. Lanterna¹, Juan C. Scaiano¹

¹Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario, ²Department of Chemistry, McGill University, Montreal, Quebec

It has been demonstrated Mo-Co based materials have great potential in light-harvesting processes – especially for photogeneration of H₂, where MoS₂ is used as an alternative to Pt- or Pd-based catalysts.¹ Nevertheless, Mo-based materials are practically unexplored in the field of photocatalytic organic transformations, with only a few examples reported for applications in fine chemistry.² The Scaiano group have worked with Co and Mo elements as co-catalysts (Mo-Co decorated TiO₂) for light-induced transfer hydrogenations; however, in those cases the catalyst only works under UV light.¹ Here we show the Mo-Co materials can show intrinsic photocatalytic activity in the absence of titania. To improve their heterogeneous properties, the materials are supported on glass wool (Mo-Co@GW), a strategy recently developed by the Scaiano group. The use of heterogeneous materials in catalysis usually facilitates the way the catalysts can be separated and reused.³ Glass wool is an ideal catalyst support because it is inexpensive, readily available, fairly robust, and its surface can be modified easily to achieve affinity towards catalytic materials.⁴

In this work we explore the use of MoCo@GW for different electron transfer reactions and we compare the efficiencies with the widely used Pd@TiO₂. Particularly, MoCo@GW is capable of catalyzing radical formations of cyclic ethers using UVA or visible light irradiation.⁵ A radical-trapping species, TEMPO, is used to monitor the radicals' formation. The TEMPO adduct is observed for cyclic ethers such as THF, dioxane, and benzodioxole. This material can also catalyse photoredox reactions, including the oxidation of 1-phenylethanol to acetophenone, indoline to indole, and tetrahydroisoquinoline to dihydroisoquinoline and isoquinoline under UVA or blue light irradiation.

Overall, the material is capable of catalyzing reactions involving one, two and up to four electrons, demonstrating the materials' ability for charge transfer. Additionally, the MoCo@GW can act under visible light irradiation, showing better efficiencies than Pd@TiO₂ photocatalysts.

¹B. Wang, et al. *J. Catal.*, **2019**, submitted.

²Z. Li, et al. *J. Photochem. Photobiol., C: Photochem. Rev.*, **2018**, 35, 39-55.

³J. C. Scaiano, A. E. Lanterna, *Pure Appl. Chem.*, **2019**, submitted.

⁴A. Elhage, et al. *Chem. Sci.*, **2018**, 9, 6844-6852.

⁵A. Hainer, et al. *J. Am. Chem. Soc.* **2019**, 141, 4531–4535.

5 - Synthesis and Applications of Cu₂O/TiO₂ Nanoparticles for Photocatalyzed Glaser Coupling

Elvin Girineza^{1,2}, Dreenan Shea¹, Geniece Hallett-Tapley¹

¹Department of Chemistry, St. Francis Xavier University, Antigonish, Nova Scotia,

²Department of Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario

Glaser coupling involves the oxidative homocoupling of terminal alkynes to form symmetrical 1,3-diynes and is the most widely used procedure to form such molecules.¹ These compounds have a wide variety of applications in the field of biology and material science including the synthesis of polymers and biologically active molecules.² In the past, expensive palladium catalysts were the classical way to catalyze such reactions. Currently, the use of copper salts in the presence of a base and an oxidant serve as an alternative method to mitigate expenses, although not without its own drawbacks such as the use of higher temperatures and long reaction times.³ However, the use of heterogenous copper nanoparticle functionalized semiconductors as a photocatalyst in Glaser coupling remains largely unexplored.

For cuprous oxide nanoparticle synthesis, a simple and safe in-situ synthesis method was adopted from previously published results⁴ using the addition of economic and environmentally-friendly TiO₂ as the supporting semiconductor. Furthermore, the photocatalytic capability of these Cu₂O nanoparticles in the Glaser coupling of phenylacetylene was found to be highly efficient at 10mM concentrations in the presence of a strong base of equal concentration and methanol solvent. The reaction times ranged from 15 minutes to 2 hours at ambient temperatures – much lower than literature values. By investigating the homocoupling efficiency at a variety of reaction conditions, it was determined that the reaction proceeds through a photooxidative mechanism reliant on the strength of the base used. In addition, the nanoparticles are fully recyclable at moderate light intensities and the reaction performance with TiO₂ as a supporting semiconductor is on-par or better than other supports which were tested including KNbO₃, KNb₃O₈, and optical-grade Nb₂O₅.

The promising nature of these results paves the way for a new environmentally friendly, economic, and highly-efficient standard by which Glaser coupling is carried out in the future.

¹ Sindhu, K. *et al. RSC Adv.* **2014**, 4 (53), 27867–27887.

² Zhang, S. *et al. Adv. Synth. Catal.* **2011**, 353, 1463-1466.

³ van Gelderen, L. *et al. Appl. Organometal. Chem.* **2013**, 27, 23-27.

⁴ Januário, E. R. *et al. J. Braz. Chem. Soc.* **2018**, 29 (7), 1527-1537.

6 - Tailoring the Structure of Lanthanide-doped Upconverting Nanoparticles

Manjot Grewal^{1,2}, Nikita Panov¹, Ilias Halimi¹, Emille Martinazzo Rodrigues¹, Tina Sun¹, Eva Hemmer¹

¹Department of Chemistry and Biomolecular Science, University of Ottawa, Ottawa, Ontario, ²Department of Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario

Lanthanide (Ln)-doped upconverting nanoparticles (UCNPs) have fascinating optical characteristics which makes them attractive for potential biomedical applications such as drug delivery and biological imaging.¹ In contrast to conventionally applied bioprobes that rely on the use of UV/visible light, the upconversion process that can take place in these materials enhances tissue penetration capability since NIR-light spectrally overlaps with the three biological windows.² Based on preliminary results in the HemmerLab, NaGdF₄-based UCNPs were synthesized using either Ln-chlorides or Ln-trifluoro acetates (Ln-TFAs) as precursors in a rapid microwave-assisted approach. Importantly, by choosing precursor chemistry in combination with reaction parameters (solvent, volume, time, temperature), two very different nanostructures became accessible.

Through the use of Ln-chlorides with water, acetic acid and ethanol as the solvent system, relatively large Ln³⁺-doped NaGdF₄ UCNPs with sizes in the 50-200 nm realm were synthesized. Doping with Tm³⁺(0.5%) and Yb³⁺(25%) or Er³⁺(2%) and Yb³⁺(20%) endows the NPs with visible luminescence under 980 nm irradiation. This optical behavior makes the NPs possible candidates for NIR-triggered drug release. Interestingly, the NPs obtained through this strategy appear porous in TEM and SEM. Such surface structure may be ideal for loading with photosensitizers or drugs and may overcome the need to grow a porous SiO₂ shell,³ thus, opening the door to more efficient drug delivery and photodynamic therapies.

In contrast, the microwave-assisted decomposition of TFA-precursors in organic high-boiling point solvents resulted in UCNPs of less than 10 nm in size. To overcome surface defect induced luminescence quenching – critical at such a small size scale –, undoped NaGdF₄ shells were grown onto the doped NaGdF₄: Yb³⁺(20%), Er³⁺(2%) core NPs. Spectroscopic studies revealed significantly brighter emission from core/shell (CS) structures with a 4 nm thick shell when compared to core-only UCNP.

Overall, through the microwave-assisted approach, optical probes for biomedical applications can be synthesized efficiently, while size and nanostructure can be controlled by using specific precursors, solvents, and reaction conditions.

¹ J. Xu *et al.* *J. Mater. Chem. B* **2014**, 2, 1791–1801.

² E. Hemmer *et al.* *J. Mater. Chem. B* **2017**, 5, 4365-4392.

³ S. He *et al.* *Chem. Commun.* **2015**, 51, 431-434.

⁴ Y. Wang *et al.* *CrystEngComm.* **2011**, 13, 1772-1774.

7 - Unraveling Cellular Fluorescent Morphologies of Fluorogenic Lipid-Derived Electrophile Analogues

Ryan Karimi^{1,2}, Antonius Van Kessel¹, Gonzalo Cosa¹

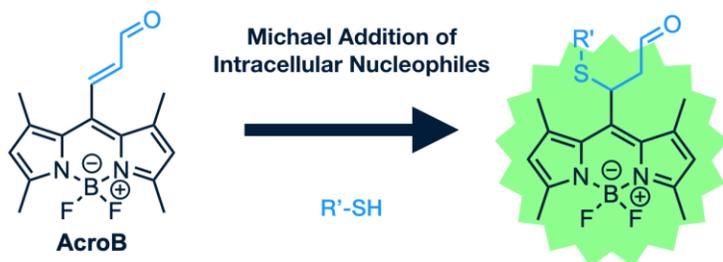
¹McGill University, ²University of British Columbia

Lipid-derived electrophiles (LDEs) are by-products of the chain-mediated reaction between polyunsaturated fatty acids and molecular oxygen, termed autoxidation. Autoxidation proceeds through a radical mechanism to form lipid hydroperoxides, which can further decompose to LDEs. These resultant LDEs include α - β -unsaturated ketones and aldehydes.

To counteract this mode of membrane autodegradation, eukaryotic cells have evolved intricate antioxidant systems to 'mop up' LDEs before they can initiate further oxidation events. This detoxification process usually proceeds through enzyme-mediated reactions with antioxidants (ex. glutathione) and subsequent cellular excretion of LDE-antioxidant adducts¹.

Previous work in our group has yielded a novel LDE-mimicking fluorogenic probe (AcroB), bearing an acrolein warhead that is sensitive to Michael addition. AcroB allows for real-time super-resolution mapping of cellular probe reactivity, as well monitoring of both cellular redox environments and the metabolic and excretion pathways for endogenously produced LDEs². However, there is still much to be understood about the intracellular targets of AcroB, the mechanisms of its trafficking, and the pathways of its export.

In this talk, I will present ongoing efforts to unravel the mechanisms that lead to distinct LDE-analogue fluorescent intracellular morphologies by way of imaging, high-throughput assay, and cellular fractionation studies. Analogues of AcroB with greater lipophilicity were also synthesized and characterized. This investigation of the intracellular behavior of AcroB has yielded insights into endogenous LDE reactivity, thus cementing AcroB's use as a tool to study intracellular LDEs.



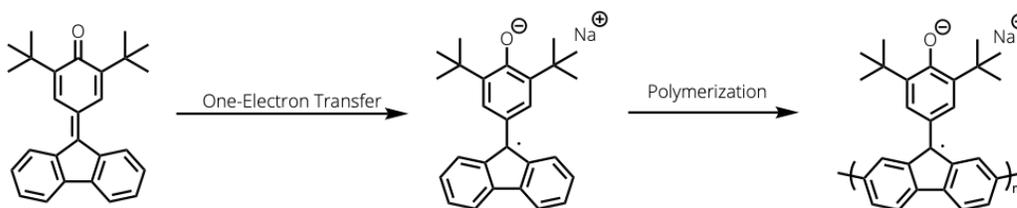
1. Schopfer, Francisco J., et al. *Chemical Reviews*, vol. 111, no. 10, 2011.
2. Lincoln, Richard, et al. *Journal of the American Chemical Society*, vol. 139, no. 45, 2017.

8 - An Investigation towards Organic Magnets: Stable Radical Insertion on Fluorene Derivatives

Luke Yang^{1,2}, Susan Cheng¹, Dwight Seferos¹

¹University of Toronto, ²University of British Columbia

Like spin-containing magnetic metals that have unpaired electrons in their d- or f-orbitals, magnetism can also be achieved by the introduction of radicals for organic molecules¹. However, radicals in organic molecules are typically featured with low stability under ambient temperature and pressure², which creates difficulties for the investigation of organic magnets. To solve the problem, fluorene derivatives were investigated because of its large aromatic system which helps to stabilize any introduced radical. A one-electron transfer was performed on the molecule 2,6-di-tert-butyl-4-(9H-fluoren-9-yl)cyclohexa-2,5-dien-1-one using sodium solid and the radical on the reaction product is detected by electron paramagnetic resonance. The electron paramagnetic resonance experiment revealed that due to the large π -conjugated system of the fluorene and the side chain, the compound is able to hold the radical under ambient temperature and pressure. The prepared fluorene derivative represents not only a stable organic radical species as itself but also a valuable precursor for a wide range of polymerizations. Propagation along 2,7 position of the fluorene polymerized with itself or other precursors may give substance that holds both magnetism and polymer properties.

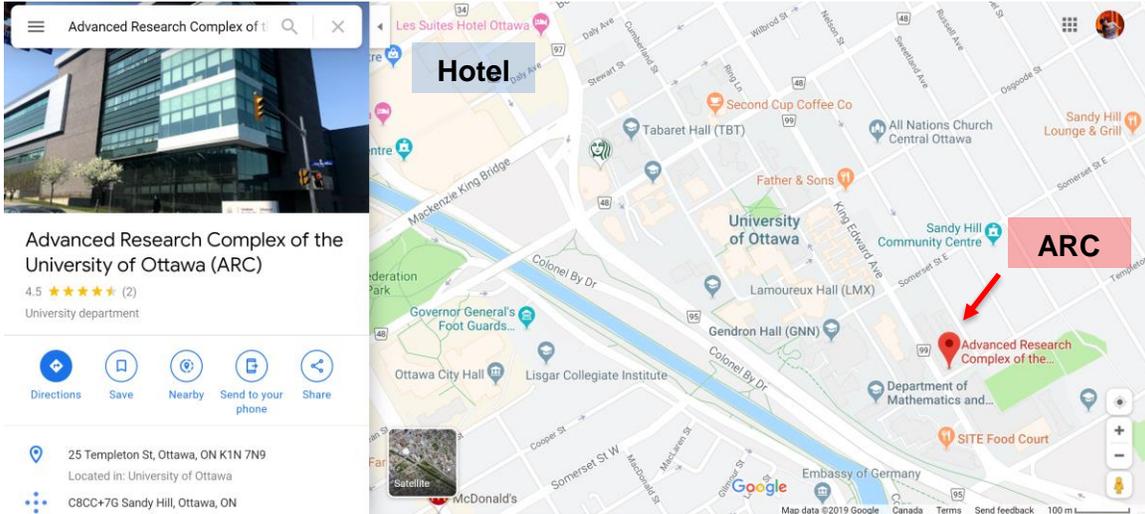


¹ Kamachi, M. *J. Macromol. Sci., Polym. Rev.* **2002**, *42*(4), 541–561.

² Zhang, K.; Monteiro, M. J.; Jia, Z. *Polym. Chem.* **2016** *7*(36), 5589–5614.

Locations

Sunday Evening and Monday Day Location:



Monday Dinner Location:

