



uOttawa

# 1<sup>st</sup> Workshop on Luminescence & Magnetism in Molecules & Materials (*LM*<sup>3</sup>)



March 11<sup>th</sup>, 2019 – University of Ottawa

STEM building, room 201

## Schedule

9:40-10:00	Welcome coffee
10:00-10:05	Opening remarks
10:05-10:35	<i>Simon Trudel</i> "Magnetic Nanomaterials: from Unconventional Magnetism to Unexpected Photoluminescence" [ <b>invited</b> ]
10:35-10:55	<i>Emille M. Rodrigues</i> "Lanthanide-Based Luminescent Nanoparticles: from the Synthesis to Potential Technological and Biomedical Applications"
10:55-11:15	<i>Artiom Skripka</i> "Decoupling Theranostics with Rare Earth Doped Nanoparticles: Wavelength Specific Functional Response"
11:15-11:35	<i>Nicholas C. Obitte</i> "In Vitro Evaluation of the Theranostic Potential of UCNPs-Drug Blend Entrapped in Calcium Alginate Beads for Targeted Delivery"
11:35-11:55	<i>Isabel Gessner</i> "Tailoring Inorganic Nanocrystals for Biomedical Applications"
11:55-13:30	Lunch break
13:30-13:50	<i>Lucas V. Besteiro</i> "Designing Energy-Saving Glasses with Embedded Plasmonic Nanoparticles"
13:50-14:10	<i>Ilias Halimi</i> "Harnessing the Synergy between Upconverting Nanoparticles and Lanthanide Complexes in a Multi-Wavelength Responsive Hybrid System"
14:10-14:30	<i>Daniele Benetti</i> "Semiconducting Nanomaterials for Solar Energy Harvesting Devices"
14:30-14:50	<i>Paul Richardson</i> "Single-Molecule Magnetism – Fundamentals and Characterization"
14:50-15:20	<i>Selvan Demir</i> "Employing Radical Ligands in Lanthanide-Based Single-Molecule Magnet Design" [ <b>invited</b> ]
15:20-15:45	Coffee break
15:45-16:05	<i>Gabriel Brunet</i> "Crystalline Transformations of Nanoporous Materials"
16:05-16:25	<i>Diogo A. Galico</i> "Temperature and Oxygen Optical Probes Based on Lanthanide Ion Complexes Chemically Bonded to Polydimethylsiloxane"
16:25-16:45	<i>Katie L. M. Harriman</i> "Ligand Effects in 4f-Amido Single-Molecule Magnets"
16:45-17:00	Concluding remarks

Invited contributions

## Employing radical ligands in lanthanide-based single-molecule magnet design

Selvan Demir

Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA

Molecules that possess an energy barrier to spin inversion have intriguing potential applications in areas such as magnetic refrigeration, molecular spintronics and high-density information storage. For these applications, however, key performance characteristics such as large spin-relaxation barriers and high magnetic blocking temperatures are required. Lanthanides have been proven to be particularly well-suited for the design of single-molecule magnets owing to their large magnetic moments and magnetic anisotropy that stem from strong spin-orbit coupling of the 4f orbitals. By using lanthanide ions such as Tb<sup>3+</sup>, Dy<sup>3+</sup>, and Er<sup>3+</sup> which possess intrinsically large orbital angular momentum, significantly higher barriers and blocking temperatures can be achieved. A general methodology to enhance single-molecule magnet properties in mononuclear lanthanide complexes comprises matching the ligand field symmetry with the anisotropic electron density distribution of the maximal  $M_J$  state. Employing this methodology, we will present the synthesis of mononuclear rare-earth metallocene complexes that function as new f-metal-based single-molecule magnets. Another particularly successful approach to improve blocking temperatures is to generate strong magnetic exchange between lanthanide centers through the employment of radical bridging ligands. If the magnetic exchange coupling is large enough then quantum tunneling of the magnetization can be attenuated. Here, we will further present the synthesis of multiple bimetallic radical-bridged lanthanide-based single-molecule magnets and describe effective suppression of quantum tunneling pathways using various organic bridging radical ligands. In addition, we combine both methodologies and demonstrate with the first series of N<sub>2</sub><sup>3-</sup> radical-bridged metallocene complexes that the combination of axial magnetic anisotropy provided by the cyclopentadienyl ligands with the strong magnetic exchange coupling enabled by the inorganic N<sub>2</sub><sup>3-</sup> radical results in exceptionally large magnetic hysteresis loops which remain open up to high temperatures.



### Bio

Selvan Demir studied chemistry at the University of Cologne and received her Diploma in 2007. She conducted research on scandium solid state chemistry with Prof. Gerd Meyer and scandium organometallic chemistry with Prof. William J. Evans at the University of California, Irvine earning her Dr. rer. nat. in 2010. In 2011, Selvan accepted a DAAD Postdoctoral Fellowship and began her postdoctoral research on lanthanide-based single-molecule magnets and porous aromatic frameworks with Prof. Jeffrey R. Long at the University of California, Berkeley. She was also a postdoctoral research affiliate at the Lawrence Berkeley National Laboratory working on neptunium, plutonium, and americium chemistry with Dr. David K. Shuh, before starting her independent career as a junior professor of inorganic chemistry at the University of Göttingen in 2016. Since 2019, Selvan is an assistant professor of chemistry at the Michigan State University. Her research interests are in the areas of synthetic organometallic chemistry and molecular magnetism, with special emphasis on the chemical reactivity of f-elements.

## Magnetic nanomaterials: From unconventional magnetism to unexpected photoluminescence

Simon Trudel

*Department of Chemistry, Institute for Quantum Science and Technology, University of Calgary*

Magnetic materials find use in a variety of applications, and still offer new surprises in terms of unexpected physical behaviours. In this talk, I will present recent work on two areas of nanomagnetism. First: the study of unexpected, and yet-to-be fully understood magnetism in nanostructures of coinage metals – Cu, Ag, and Au. For Au, we show that the capping ligand can tune the magnetism of similarly sized thiolate-coated Au NPs.

Second: the design of new nanoparticulate metal-oxide nanomaterials for use as contrast agents in magnetic resonance imaging. Our focus has been in the design of contrast agents for high-field MRI. We investigate several parameters, such as low-molecular weight capping ligands, magnetochemical series across mixed metal ferrites, and the serendipitous discovery of photoluminescence in new Mn-based agents.



### **Bio**

Dr. Simon Trudel joined the Department of Chemistry and Nanoscience Program at the University of Calgary in November 2009 as an Assistant Professor, and rose to the rank of Associate Professor in 2015, and Director of the Nanoscience Program in 2018. Simon leads a nanomaterials-focused research group, interested in the structure-property relationships that govern functionality in nanoscale materials. In particular, the magnetic and catalytic properties of metallic and metal-oxide nanoarchitectures are of great interest to his work. In addition to academic endeavours, he has ventured into the entrepreneurial world by co-founding a spin-off company based on his academic work, and likes to explore the beautiful backcountry of the Canadian Rockies on skis, boots, and crampons.

Oral contributions (in order of presentation)

**Lanthanide-based luminescent nanoparticles: from the synthesis to potential technological and biomedical applications**

Emille Martinazzo Rodrigues,<sup>a,b</sup> Fernando Aparecido Sigoli,<sup>a</sup> Teresa Pellegrino<sup>b</sup>

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In this talk, it will be presented the synthesis, structural, luminescent and magnetic characterizations of lanthanide-based nanoparticles (NP), mainly with NaLnF<sub>4</sub> composition. The adjustment of the thermal decomposition method conditions to drive the nanoparticles formation in different crystalline phases and core@shell nanostructuration will also be explained. It will be presented the proof of concept of the potential technological application of such materials as non-contact temperature sensors with high relative thermal sensitivity. In the last part of the talk, it will be included a short presentation on strategies of post-synthesis modification of NaLnF<sub>4</sub> nanoparticles towards NP colloidal stability and biocompatibility. Such modifications can result in interesting colloidal NP for diverse biomedical applications, such as T1 MRI contrast agents, and as internal radiotherapy agents.

**Decoupling theranostics with rare earth doped nanoparticles: wavelength specific functional response**

Artiom Skripka,<sup>a</sup> Vitalijus Karabanovas,<sup>b</sup> Greta Jarockyte,<sup>c,d</sup> Riccardo Marin,<sup>a</sup> Vivienne Tam,<sup>a,e</sup> Marta Cerruti,<sup>e</sup> Ricardas Rotomskis,<sup>f</sup> Fiorenzo Vetrone<sup>a</sup>

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Theranostics constitutes integrated therapeutic and diagnostic functions in a single drug-probe system, promising example of which are rare-earth doped nanoparticles (RENPs). It is common to believe that theranostic multi-functionality of RENPs has to occur simultaneously; yet, on-demand control of therapy and diagnostics would make a move towards safer and more precise nanomedicines. We are exploring the possibility to optically decouple the diagnostic and therapeutic features of RENPs by using excitation wavelengths that can trigger these features individually. This paradigm shift will bring RENPs closer to routine biomedical research and clinic, as true multi-functionality can be attained.

**In Vitro Evaluation of the Theranostic Potential of UCNPs-Drug Blend Entrapped in Calcium Alginate Beads for Targeted Delivery**

Bridget Chizobam Obitte,<sup>a</sup> Nicholas Chinedu Obitte,<sup>b</sup> Fabian Ifeanyichukwu Ezema,<sup>a</sup> Eva Hemmer<sup>c</sup>

<sup>a</sup> *Department of Physics and Astronomy, Faculty of Physical Sciences, University of Nigeria, Nsukka.*

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<sup>c</sup> Department of Chemistry and Biomolecular Sciences, University of Ottawa

The biomedical applicability of upconverting nanoparticle (UCNPs) is a huge gold mine yet to be fully explored. Hence the fast growing research interest by material and biomedical scientists. There is scarce literature report focusing on the impact of pharmaceutical dosage forms and coloaded drug on the luminescence behavior of constitutive UCNPs. Therefore, our present study sought to evaluate the effect of co-loading diclofenac sodium with ytterbium and erbium co-doped Sodium Yttrium fluoride on the emission behaviour of the UCNPs, and the relationship between targeted drug release and luminescence. UCNPs were synthesized via the solvothermal method using either oleic acid, span 85 or triacetin and characterized. The UCNPs and diclofenac potassium (1:2 ratio) were subsequently entrapped in calcium alginate beads and dissolution testing experiments in aqueous acid and phosphate buffer solutions (pH 6.8 and 7.4) simulating the gastrointestinal tract pH were carried out. The beads liberally permitted luminescence credited to the entrapped nanoparticles. The beads displayed varying time-dependent luminescence after contact with the different dissolution media. In conclusion, calcium alginate bead is a promising carrier for co-loading UCNPs and diclofenac potassium intended for site specific theranostic targeting.

## Tailoring inorganic nanocrystals for biomedical applications

Isabel Gessner, Sanjay Mathur

*Institute of Inorganic Chemistry, University of Cologne, Germany*

The exceptional properties of materials at the nano-scale have aroused a huge increase in their demand for a broad variety of applications including biomedicine. Due to their high biocompatibility, stability and the abundance of iron in our environment, which results in low costs of iron-based materials, iron oxide nanoparticles (IONPs) have become prevalent in the field of nanomedicine. In our workgroup, Fe<sub>3</sub>O<sub>4</sub> IONPs have been synthesized using a range of well-established synthetic procedures. By changing the reaction conditions and applying suitable surface ligands, the morphology, surface charge and dispersibility of IONPs could be tuned according to the desired application allowing for a reproducible fabrication of optimized and highly efficient vectors. The high MRI contrast obtained for IONPs prepared in this work was exploited for the visualization of next generation electronic brain implants during *ex vivo* experiments. Moreover, the covalent attachment of specific RNA strands to the surface of magnetic beads could be used for the first time for the intracellular capturing and purification of microRNAs and marker proteins. As an outlook, the use of dye functionalized lanthanide-doped nanoparticles as a model to monitor drug release from a nanoparticle-based delivery vehicle will be presented.

## Designing Energy-Saving Glasses with Embedded Plasmonic Nanoparticles

Lucas V. Besteiro,<sup>a,b</sup> Xiang-Tian Kong,<sup>a,c</sup> Zhiming Wang,<sup>a</sup> Federico Rosei,<sup>b</sup> Alexander O. Govorov<sup>a,c</sup>

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Plasmons are resonant, collective charge carrier excitations. Nanocrystals made of different plasmonic materials can provide sharp resonances from UV to near IR by changing their geometry and, by creating tailored nanoparticle ensembles, we can design specific transmission profiles that filter out particular spectral bands. I will discuss this idea in the context of energy-saving windows. These are used to block UV and IR radiation from the solar spectrum while remaining transparent to visible light, aiming to reduce the energy expenditure of active cooling systems in warm climates. By considering this approach, we offer alternatives to current industrial standards, with comparable efficiencies and potentially lower costs.

## Harnessing the synergy between upconverting nanoparticles and lanthanide complexes in a multi-wavelength responsive hybrid system

Ilias Halimi,<sup>a</sup> Riccardo Marin,<sup>a</sup> Dylan Errulat,<sup>a</sup> Yacine Mazouzi,<sup>a</sup> Giacomo Lucchini,<sup>b</sup> Adolfo Speghini,<sup>b</sup> Muralee Murugesu,<sup>a</sup> Eva Hemmer<sup>a,c</sup>

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Amalgamation of different optically active materials is a lively field due to the number of applications for which such composites can be exploited. Indeed, the interaction between semiconductors, metallic nanoparticles, inorganic phosphors and/or organic fluorophores joined in composed systems has led to the preparation of devices with superior capabilities in terms of light harvesting, molecule or ion sensing, temperature probing, photoluminescence color and lifetime tuning.

Upconverting nanoparticles (UCNPs) are particularly valuable species in the frame of optical systems based on energy transfer mechanisms since they (i) allow for the control of the interaction and relative placement between the moieties of choice at the nanometer scale, (ii) feature high surface-to-volume ratio, favoring surface interactions while minimizing bulk effects, and (iii) showcase near-infrared operational capabilities, a paramount asset in contexts like light harvesting and biomedical applications.

Inspired by this, we here present a unique solid-state hybrid system composed of films of dinuclear fluorescent lanthanide ( $\text{Ln}^{3+}$ ) complex  $[\text{Ln}_2\text{bpm}(\text{tfaa})_6]$  ( $\text{Ln} = \text{Tb}$  or  $\text{Eu}$ ) and UCNPs using a straightforward drop-cast methodology. The system displays visible emission under near-infrared excitation, simultaneously stemming from sub-10-nm UCNPs and  $[\text{Ln}_2]$  complexes, the latter species being otherwise directly excitable only using UV-blue radiation. In light of the results of steady-state – including power-dependent – and time-resolved optical measurements, we identified the radiative, primarily ligand-mediated nature of the energy transfer from  $\text{Tm}^{3+}$  ions in the UCNPs-to- $\text{Ln}^{3+}$  ions in the complexes. Hyperspectral mapping and electron microscopy observations of the surface of the hybrid system confirmed the continuous and concomitant distribution of UCNPs and lanthanide complexes over the extensive composite films.

Key features of the hybrid system are the simultaneous UV-blue and near-infrared light harvesting capabilities and their ease of preparation. These traits render the presented hybrid system a formidable candidate for the development of photoactivated devices capable to operate under multiple excitation wavelength and to transduce the absorbed light into narrow, well-defined spectral regions.

## Semiconducting nanomaterials for solar energy harvesting devices

Daniele Benetti, Federico Rosei

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To reduce our dependence on fossil fuels and control the greenhouse emissions, it is necessary to transit to more sustainable sources of energy. This challenge may be addressed by the so-called 3<sup>rd</sup> generation solar cells. In the last decade, these devices have rapidly improved in terms of photoconversion efficiency and became one of the most cost-effective alternatives to the commercially available silicon cells, due to simple, low-cost materials and fabrication process. In our group, we explore how the semiconducting materials interact with each other and how, by applying suitable modulations of the interfaces of nanomaterials, we can control proprieties, such as charge injection and light management, in order to improve the final performances of the device

## Single-Molecule Magnetism – Fundamentals and Characterization

Paul Richardson, Muralee Murugesu

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Single-molecule magnets (SMMs) have been a field of great interest in inorganic and materials chemistry for nearly 30 years, with great advancements in relaxation times and blocking temperatures having been reported within the past 2 years (Science, 2018, 362, 1400). Therefore, the proper understanding and interpretation of data related to SMMs is of the utmost importance. This seminar will cover the fundamental properties of SMMs and will discuss the various characterization methods and their analysis.

## Crystalline Transformations of Nanoporous Materials

Gabriel Brunet,<sup>a</sup> Koen Robeyns,<sup>b</sup> Damir A. Safin,<sup>a</sup> Tom K. Woo,<sup>a</sup> Muralee Murugesu<sup>a</sup>

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Crystalline sponges have recently become extremely attractive materials due to the fact that we can perform “crystal-free” crystallography on molecules that were previously impossible to crystallize. Here, we present our investigations into the stability and dynamic uptake behaviour of nanoporous frameworks, and focus on the key host-guest interactions that drive molecular encapsulation. Notably, we introduce new methods to visualize guest adsorption behaviours and confinement effects, thereby improving the scope of the crystalline sponge method beyond a simple crystallographic tool.

## Temperature and oxygen optical probes based on lanthanide ion complexes chemically bonded to polydimethylsiloxane

Diogo Alves Galico, Fernando Aparecido Sigoli

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Europium(III) and terbium(III) benzoylacetate complexes were chemically bonded to the polydimethylsiloxane polymer functionalized with the ethyldiphenylphosphine oxide ligand resulting in self-supported membranes that allows a ratiometric temperature optical probing with high thermal sensitivity. The obtained results for these systems indicate a  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer, which collaborates with the system high sensitivity. Besides that, a membrane containing the europium(III) benzoylacetate complex and the ethylantracence group (eant) that have a strong oxygen-sensitive blue emission was synthesized, giving rise to a simultaneous temperature and oxygen ratiometric optical probe. The obtained results for this system indicate an anthracene  $\rightarrow Eu^{3+}$  energy transfer.

## Ligand Effects in 4f-Amido Single-Molecule Magnets

Katie L. M. Harriman, Muralee Murugesu

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Lanthanide single-molecule magnets (SMMs) have become ubiquitous in the development of molecular magnetic materials due to their intrinsic magnetic anisotropy. This feature of rare earth ions has produced high performance SMMs with very large

energy barriers to spin reversal and blocking temperatures which exceed that of liquid nitrogen (77 K). Both the strength of the electrostatic metal-ligand interactions as well as the local symmetry about the 4*f*-ion has a direct effect on the splitting of the crystal-field microstates, and as a result the performance of the material. To this end, amido-based ligands are ideal bases for 4*f*-ions as they allow for a direct study of the structure-property relationships (N-Ln-N bond lengths and angles), and in turn allow for manipulation of the properties *via* chemical modifications (R-group substitutions in NR<sub>2</sub>) in order to obtain idealized geometries at the metal center. This presentation will outline synthetic routes and the subsequent challenges faced in tuning the local symmetry and the solid-state structures of lanthanide-amido SMMs as well as an investigation into their slow relaxation dynamics *via* SQUID magnetometry.

**The organizers:**

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