



**The 4th Crystal Engineering and Emerging Materials Workshop of
Ontario and Quebec
(CEMWOQ-4)**

**May 26 – 28, 2017
Wilfrid Laurier University
Waterloo, Ontario**

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Saturday, May 27, 2017

8am – 9am Workshop registration (Main Entrance, Science Building)

All lectures will take place in the Science Building, Room N1044

9am – 9:50am Plenary Lecture 1 - Christer B. Aakeröy
"Crystal engineering from molecules to materials"

9:50am – 10:10am Jan Christophson
"Halogen-Bonded Azobenzenes: Design of Optically Responsive Crystals and the Discovery of a Soft Photolithographic Effect"

10:10am – 10:30am Michelle Mills
"Thiazyl vs. selenazyl: How rational manipulation of intermolecular interactions impacts magnetic properties"

10:30am – 11am Coffee break and informal discussions

11am – 11:50am Plenary Lecture 2 - Prof. Dr. Vladimir P. Fedin
"Porous coordination polymers: from synthesis and structure to functional properties"

11:50am – 12:25pm Poster preview flashtalks

12:25pm – 12:40pm CEMWOQ-4 Group Photo

12:40pm – 2pm Lunch

2pm – 2:30pm Professor Delia Haynes
"Host-guest systems based on the pamoate ion"

2:30 – 2:50pm Stephen Dale
"A density-functional examination of the magnetic states of electrides and the evolution of piezomagnetic behaviour under pressure"

2:50pm – 3:10pm Aaron Smith
"New Layered Inclusion Compounds of Short Chain Leucine Containing Peptides"

3:10pm – 3:30pm Courtney Dickie
"Coordination Chemistry and Magnetization Dynamics of Lanthanide(III) Complexes with Applications as Single-Ion Magnets"

3:30pm – 4pm Coffee break and informal discussions

4pm – 4:30pm Professor Stephen Loeb
“MIMs in MOFs: Organizing Mechanically Interlocked Molecules Inside Metal-organic Frameworks”

4:30pm – 4:50pm Nimer Murshid
“Metal Carbonyl Complexes (MCCs): From Water Insoluble Structures to Multifunctional Stable Aqueous Nanovesicles”

5pm – 6:30pm Poster session (Atrium, First Floor Science Building)

7pm – 10pm Conference dinner at The Hawk's Nest

11:50am – 12:25pm Poster preview flashtalks

11:50am – 11:55am Daniel Cutler
“Exploring the Coordination Chemistry of mpmH as a new ligand in 3d-Cluster Chemistry”

11:55am – 12pm Jacqueline Gemus
“In Pursuit of Mixed-Linker ZIFs: Multinuclear SSNMR to Characterize the Products of Mechanochemical Reactions”

12pm – 12:05pm Nadia Stephaniuk
“The inclusion chemistry of 4-phenyl-1,2,3,5-dithiadiazolyl radical, and its selenium analogue, into the porous metal-organic framework host MIL-53(Al)”

12:05pm – 12:10pm Farukh Ali
“Diketopiperazines (DKPs): Solid State Synthesis and Co-crystallization”

12:10pm – 12:15pm Ghada Ayoub
“Effect of the preparation methods on the physicochemical properties of the cimetidine salt”

12:15pm – 12:20pm Andy Tsang
“ α -Lipoic Acid for the Design of Pharmaceutical Co-crystals”

12:20pm – 12:25pm Michael Brand
“Clean, Solvent Free Synthesis of Metal-organic Frameworks from Simple Reagents in the Solid State”

Sunday, May 28, 2017

8am – 9am Workshop registration (Main Entrance, Science Building)

All lectures will take place in the Science Building, Room N1044

9am – 9:30am Professor John Wallis

“Interactions and Reactions Between Substituents in Peri-Naphthalene Systems
– Crystallography, Charge Densities and Solid State NMR Studies”

9:30am – 9:50am Nicole Cathcart

“Rational design of nanoscale building blocks for sensing applications”

9:50am – 10:10am Lucia Myongwon Lee

“Chalcogen Bonding in Supramolecular Chemistry: N-substituted benzo-2,1,3-selenadiazoles as building blocks”

10:10am – 10:30am John Hayward

“Pyridinium groups as σ -hole activators: Investigating chalcogen bonding in a series of zwitterionic thiopheno-thioureas”

10:30am – 11am Coffee break and informal discussions

11am – 11:50am Plenary Lecture 3 - Dr. Marc Fourmigué

"Halogen-bonded co-crystals: implications in crystal engineering and molecular conductors"

11:50am – 12:15pm Student awards and closing remarks

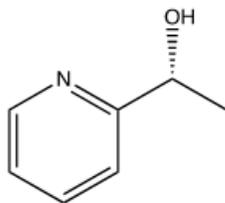
Poster Abstracts
Saturday, May 27, 5-6:30pm
Science Atrium

1. Ligand Design -Towards Chiral Single Molecule Magnets

Parisa Abbasi, Amy Pham, Daniel Cutler, Theocharis Stamatatos and Melanie Pilkington*

Department of Chemistry, Brock University, 1812 Sir Isaac Brock Way, St. Catharines, ON, L2S 3A1, *mpilkington@brocku.ca

Single-Molecule Magnets (SMMs) are coordination complexes of paramagnetic metal ions that display slow relaxation of magnetization below their blocking temperature that are currently intensively researched due to their potential applications as memory storage devices. The introduction of chirality into this family of molecules creates opportunities for new properties such as magnetochiral dichroism (MChD), as well as potential applications in the field of multiferroics. In recent years we have developed synthetic strategies to chiral organic ligands for the assembly of chiral spin crossover complexes.[1] We have now extended this approach to target the preparation of small chiral, organic ligands with functionality suitable for the self-assembly of polynuclear clusters. Following this strategy, the synthesis of the chiral mpmH ligand (**1**) and its preliminary coordination chemistry together with select first row transition metal ions will be presented, as a first step towards the discovery of a new family of chiral SMMs.



mpmH (1)

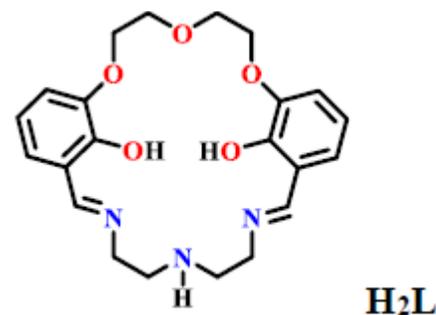
1. Q. Wang, S. Venneri, N. Zarrabi, H. Wang, C. Desplanches, J.-F. Letard, T. Seda, M. Pilkington, *Dalton Trans*, **2015**, 44, 6711.

2. Heterodinuclear complexes of a macrocyclic compartmental ligand for the design of Single Molecule Magnets

Zineb Ras Ali, Jeffery Regier and Melanie Pilkington*

Department of Chemistry, Brock University, 1812 Sir Isaac Brock Way, St. Catharines, ON, L2S 3A1, *mpilkington@brocku.ca

Single molecule magnets (SMMs) are molecules which are magnetized in the presence of an external magnetic field and retain their magnetization once the field is removed. This slow relaxation is due to an 'energy barrier' U to reversal of the magnetization which depends on D , the magnetic anisotropy and S (for transition metals) or J (for lanthanides). For Ln-based SMMs, the intrinsic anisotropy of their coordination complexes can be enhanced by targeting the preparation of complexes with an appropriate ligand field. In recent years we have employed N3O2 and N5 Schiff-base macrocycles to confer $D5h$ symmetry on Ln(III) ions which has afforded a new family of Ln-SMMs.[1,2] Extending this concept we are currently investigating the coordination chemistry of the compartmental ligand, **H2L** which contains two discrete N3O2 and O5 binding pockets that can support pentagonal bipyramidal coordination geometry. The synthesis and coordination chemistry of this ligand with first row transition metal and lanthanide ions will be presented together with magnetic and *ab initio* studies of selected complexes.



1. E.L. Gavey, Y. Beldjoudi, J.M. Rawson, T. Stamatatos, M. Pilkington, *Chem. Commun.* **2014**, 50, 3741.
2. E.L. Gavey, M. Pilkington, *Polyhedron*, **2016**, 108, 122.

3. Diketopiperazines (DKPs): Solid State Synthesis and Co-crystallization

Farukh I. Ali, Andy Tsang, Dmitriy V. Soldatov

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

DKPs are the smallest cyclic peptides which have rigid cyclic structure, hydrogen bonding capabilities, substituent group stereochemistry, chiral nature and resistance to proteolysis. Due to these characteristics DKPs have distinctive and exciting physical and chemical properties which make them very useful for medicinal chemistry, pharmaceutical and food industry. Recently, these ubiquitous molecules have attracted attention not only due to their numerous biological activities and various therapeutic possibilities but also as reliable supramolecular synthons for non-covalent assembly. Although various DKPs have been synthesized in the solution, their formation in the solid state has not been synthetically utilized.

In this study, we investigated the thermally induced solid state synthesis of DKPs from short peptides. The chemical transformations were monitored in a thermogravimetric analyzer, differential scanning calorimeter and ventilation oven through the analysis of released volatiles and thermal effects of the reactions. Post-heating products were analyzed by FTIR, NMR, GC-MS and XRD methods. We found that some dipeptides undergo intramolecular condensation upon heating to produce their cyclic products. Later, DKPs were evaluated as co-crystallization agents against pharmaceutically active ingredients. Various combinations of DKPs with pharmaceutically active ingredients were screened with PXRD while single crystals were studied using single crystal XRD. DKPs have shown promising results as co-crystallization agents for the design and synthesis of new molecular materials.

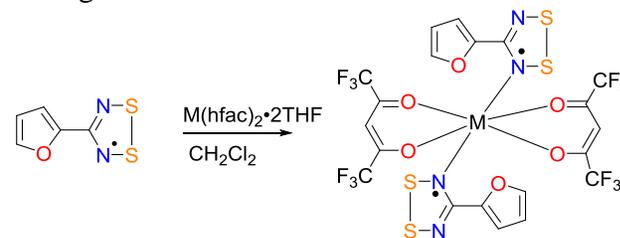
4. Synthesis of Paramagnetic Ligand using 1,2,3,5-dithiadiazolyl (DTDA)

Saleh Alofi and Kathryn Preuss

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Five-membered ring heterocyclic thiazyl radicals are a common class of organic compounds characterized by the inclusion of sulfur and nitrogen¹. In the past, ligands derived from 1,2,3,5-dithiadiazolyl (DTDA) have been synthesized and reported in our group². complexes involving thiazyl radicals continue to show interesting features (ferromagnetism, antiferromagnetic, coupling) in the solid state and demonstrate the great potential of 1,2,3,5-DTDA radicals as building blocks for the development of molecular magnets in materials chemistry. The aim of this project is to synthesis 4-(2'-furyl) - 1,2,3,5-dithiadiazolyl (fDTDA) radical. Complexes of the fDTDA ligand will be synthesized using paramagnetic metal ions such as Mn^{II}, Co^{II} and Ni^{II} to create monodentate coordination in the solid state. The ligand f(DTDA) contains an N-O chelation site for metal coordination with spin density present to allow for magnetic coupling. Previously, our group reported a paramagnetic Mn(hfac)₂ complex of 4-(2'-cyanofuryl-5')-1,2,3,5-dithiadiazolyl with antiferromagnetic coupling between the radical ligand and the metal center³. This previous has been considered as the first evidence of coordination to metal can be attached via nitrogen atom regardless of assistance of chelation.



1. Rawson, J. M.; Alberola, A.; Whalley, A. *J. Mater. Chem.* **2006**, 2560.
2. Preuss, K. E. *Coord. Chem. Rev.* **2015**, 289.
3. Hearn, N. G. R.; Hesp, K. D.; Jennings, M.; Korocok, J. L.; Preuss, K. E.; Smithson, C. S. *Polyhedron*, **2007**, 26, 2047.

5. Effect of the preparation methods on the physicochemical properties of the cimetidine salt

Ghada Ayoub, Vjekoslav Štrukil, Cristina Mottillo, Tomislav Friščić*

Salts and cocrystals of active pharmaceutical ingredients (APIs) are of great interest in drug formulations due to their improved pharmaceutical properties, most importantly their solubility, overall stability, and bioavailability.¹ Synthesis and discovery of pharmaceutical salts and cocrystals can be approached by different methods.^{2,3} This presentation will outline a systematic study of how the physicochemical properties of new solid forms of the highly conformationally flexible model API cimetidine are affected by the choice of mechanochemical or solution-based preparation techniques. The presented results, which identify new salts and salt solvates of cimetidine, represent one of the so far very few studies of the striking effect that mechanochemical preparation methods could have on the physicochemical properties of nominally identical materials. Specifically, we will describe a difference in thermal stability of single crystals of a cimetidine solvate salt obtained from solution, compared to the nominally identical material made by liquid-assisted ball milling. The observed stability differences, which serendipitously led to the discovery of a new polymorph of a cimetidine salt, are most likely explained by particle size differences. Overall, the presented work highlights the importance for deeper studies of the so far neglected effect of mechanochemical synthesis on the stability of the resulting material.

1. Friščić, T.; Jones, W., *Farad. Discuss.*, **2007**, *136*, 167-178.
2. Zhang, G. G. Z.; Henry, R. F.; Borchardt, T. B.; Lou, X.; *J. Pharm. Sci.*, **2007**, *96*, 990-995
3. Friščić, T.; *J. Mater. Chem.*, **2010**, *20*, 7599-7605

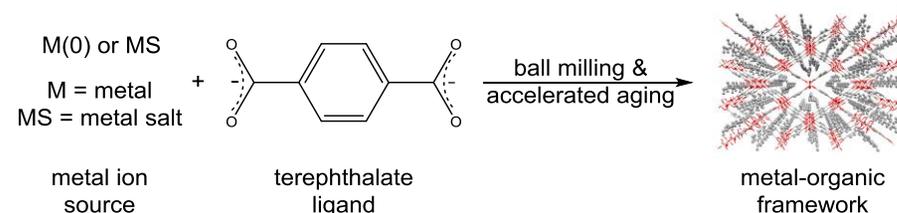
6. Clean, Solvent Free Synthesis of Metal-organic Frameworks from Simple Reagents in the Solid State

M Brand^{a,b}, C Mottillo^{a,c}, J.-L Do,^a T Friščić^{*a}

a) Department of Chemistry, McGill University, 801 Sherbrooke St. W., H3A 0B8 Montreal, Canada. b) School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT, Wales, UK.
c) ACSYNAM Inc., 4685 Rue Jeanne-Mance, Montréal, Québec H2V 4J5, Canada.

Interest in metal-organic frameworks (MOFs) has increased dramatically over the past two decades.¹ With numerous applications ranging from gas storage and separation to drug storage and delivery arising from their highly tuneable properties, MOFs are becoming highly relevant in academia and industry². Until recently, the production of MOFs has largely depended on solution-based methodologies, which often require high temperatures and the use of toxic or corrosive reagents. Recent synthetic strategies aimed at improving the efficiency and safety of MOF synthesis, which include such solid-state methodologies as mechanochemistry and accelerated aging, have demonstrated the ability to accomplish the spontaneous assembly of MOFs from basic, more economical feedstocks such as metal oxides.^{3,4} We now present new solid-state strategies that allow the simple, effective synthesis of terephthalate-based MOFs, such as the commercially-relevant MIL-53, directly from simple reagents, including raw metals. This new methodology provides an environmentally-friendly alternative to conventional MOF synthesis, while offering the opportunity to recycle metal waste into valuable microporous metal-organic products.

[1] Wang, C.; Ho, Y. *Scientometrics*. 2016, **109**, 481. [2] Czaja, A. U.; Trukhan, N.; Muller, U., *Chem. Soc. Rev.*, 2009, **38**, 1284. [3] Julien, P. *et al.*, *J. Am. Chem. Soc.* 2016, **138**, 2929. [4] Mottillo, C. *et al.*, *Green Chem.*, 2013, **15**, 2121.

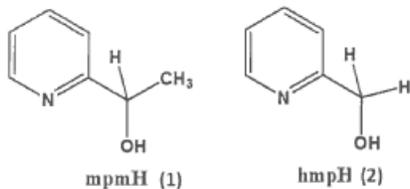


Poster 7:

Exploring the Coordination Chemistry of mpmH as a New Ligand in 3d-Cluster Chemistry

Daniel Cutler, Parisa Abbasi and Melanie Pilkington

Single-Molecule Magnets (SMMs) are coordination complexes of paramagnetic metal ions that display slow relaxation of magnetization below their blocking temperature that are currently intensively researched due to their potential applications as memory storage devices. The introduction of chirality into this family of molecules creates opportunities for new properties such as magnetochiral dichroism (MChD), as well as potential applications in the field of multiferroics. We have thus recently initiated a new program of research aimed at the development of small, potentially chiral chelating ligands for the discovery of metal clusters with unprecedented structural motifs and novel magnetic and/or electronic properties. Our first target ligand, α -methyl-2-pyridine-methanol or mpmH (**1**), previously unexplored in the field of 3d-cluster chemistry, possesses similar coordination features to the well studied 2-(hydroxymethyl)pyridine or hmpH system (**2**), but subtly differs in its steric and electronic nature. The synthesis, structural and preliminary magnetic properties of coordination complexes of (**1**) together with select first row transition metal ions (e.g. Cu(II)) will be presented.



8. Design of new molecular magnetic materials utilizing 4-(benzimidazol-2'-yl)-1,2,3,5-dithiadiazolyl paramagnetic ligands

Declan M. Dejordy, Michelle B. Mills, Tobie Wohlhauser, Dmitriy V. Soldatov, Kathryn E. Preuss

One approach to the design of molecule-based magnetic materials is the “metal-radical approach,” which utilizes paramagnetic ligands linked to paramagnetic metals. Our group has developed a number of 1,2,3,5-dithiadiazoyl (DTDA) radicals for use as ligands. These species have the potential for strong intermolecular interactions because of their close contacts in the solid state, the manipulation of which may lead to the development of new materials. Some interesting interactions that often occur in DTDA radical complexes include dimerization, electrostatic contacts, and π -stacking between the thiazyl radical and aryl substituent group.

We present the synthesis, characterization, and phase transition behaviour of a new DTDA radical. 4-(Benzimidazol-2'-yl)-1,2,3,5-dithiadiazolyl (bimDTDA) undergoes a solid-state phase transition from a diamagnetic dimer at low temperature to a paramagnetic phase at room temperature. BimDTDA can be used as a neutral ligand, and has been coordinated to Gd(hfac)₃ (hfac = Hexafluoroacetylacetonate). Magnetic data, single-crystal XRD, and PXRD data of bimDTDA and the coordination complex will be presented.

9. In Pursuit of Mixed-Linker ZIFs: Multinuclear SSNMR to Characterize the Products of Mechanochemical Reactions

J.E. Gemus,^a C.A. O'Keefe,^a T. Friščić,^b and R. W. Schurko^a

^a Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, Canada

^b Department of Chemistry and FRQNT Centre for Green Chemistry and Catalysis, McGill University, Montréal, QC, Canada

Zeolitic Imidazole Frameworks (ZIFs) are a class of porous molecular frameworks consisting of divalent metal nodes that are joined together by imidazolate linkers,¹ and can be made using either one type of imidazolate or more than one type (i.e., a *mixed-linker ZIF*). The latter case has been shown to improve flexibility and selectivity in the molecular sorting properties of the ZIFs.² Mechanochemical synthesis (MS), a technique that offers quantitative yields with little or no solvent, has been used to make ZIFs; however, MS has been applied only to single-linker ZIFs, with little or no application to mixed-linker ZIFs. Extensive studies of MS have been conducted using powder X-ray diffraction (pXRD); however, this technique is ill-suited to identification and characterization of dilute or disordered species, complicating its application in studying ZIFs with non-uniform distributions of different linkers. Solid-state NMR (SSNMR) is useful as a complementary technique, as it can yield structural information on both dilute and amorphous species. I will present the findings of a multinuclear SSNMR study (¹H, ¹³C, ¹¹¹Cd), in combination with pXRD data, which has been used to characterize the products of MS reactions involving multiple imidazolate linkers to aid in the rational synthesis of tailor-made frameworks.

[1] A. Phan *et al.* *Acc. Chem. Res.* **2010**, *43*, 58

[2] K. Eum *et al.* *J. Am. Chem. Soc.* **2015**, *137*, 12

10. Structural Effects of Ln³⁺-ions in Nanoparticles: a Solid-State NMR Study

D.A. Hirsh,¹ X. Zhang², F.C.J.M. van Veggel² and R. W. Schurko,¹

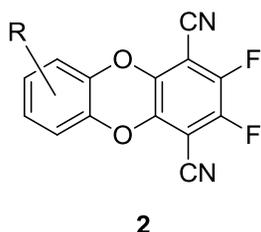
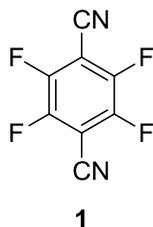
1. Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, N9B 3P4 Canada
2. Department of Chemistry, University of Victoria, PO BOX 3065, Victoria, BC, V8W 3V6 Canada

The unusual optical properties of rare-earth nanocrystals (RE-NCs) doped with lanthanide ions (Ln³⁺) make them attractive for applications in LEDs, photovoltaics, and biological imaging. SSNMR is an ideal technique for characterizing RE-NCs given its sensitivity to local molecular structure. The presence of Ln³⁺ ions complicate the acquisition of SSNMR spectra, however, as most are paramagnetic. The recent development of ultra-fast MAS probes ($\nu_{\text{rot}} > 40$ kHz) has enabled the acquisition of NMR spectra of these paramagnetic materials. Herein, we present a multinuclear (¹⁹F, ²³Na, ⁸⁹Y) SSNMR study of NaYF₄ NCs loaded with varying amounts of paramagnetic Er³⁺ and Tm³⁺ dopants. Such careful structural analysis is key to the logical design of novel materials with improved bulk properties.

11. Synthesis and Characterisation of Dicyanotetraoxapentacenes as Novel Liquid Crystalline Materials

L.K. Hiscock, Brooke Raycraft, Kenneth E. Maly

Discotic liquid crystals typically consist of a disc-shaped, rigid polycyclic aromatic hydrocarbon (PAH) core bearing peripheral flexible chains. In the columnar liquid crystalline phase molecules form extended pi-stacked arrays allowing for charge transport along the columnar axis and makes these materials attractive candidates as organic semiconductors. Variation of the molecular structure allows for tuning of the liquid crystalline properties and can also give rise to several types of liquid crystalline phases. We are currently exploring tetraoxapentacene derivatives as discotic liquid crystals because they exhibit LC phases and interesting fluorescence, and can readily be prepared by nucleophilic aromatic substitution of commercially available tetrafluoroterephthalonitrile. This approach allows for a diversity of structures starting from compound **1**. Another approach provides asymmetric pentacenes from **2** which can be substituted with a second, different nucleophile.



12. A comparison of dispersion agents to optimise liquid phase exfoliation of few layer graphene from graphite in aqueous solution.

Kelly, Wright, Dr Andrew Vreugdenhil

Presented here is a comparison of dispersion agents to facilitate the exfoliation of graphene from graphite in aqueous solution. Liquid phase exfoliation (LPE) was used to exfoliate graphene from graphite using ultrasonication. Polyvinylpyrrolidone (PVP), Carboxymethyl cellulose (CMC), Triton™X-100 (T-X), Pluronic ®123 (P-123) and Chitosan (CHI) were compared on their ability to produce few layer graphene (FLG) dispersions. PVP yields a FLG dispersion with the highest quality of FLG flakes and the highest concentration suspension, 0.305 ± 0.05 mg/mL. CMC, T-X and P-123 had limited success producing dispersions. CHI had no success in producing a FLG dispersion. Raman spectroscopy was used to determine FLG flake quality using peak fitting of the 2D band, and the intensity ratio of the D and G band was used to calculate the mean flake size. UV-vis spectroscopy was used to determine concentrations of the FLG dispersions using the Beer-Lambert Law.

13. Discotic Liquid Crystals with Internal Side Chains as Potential Organic Semi-Conductors

Junghoon Ko, Hi Taing, S. Holger Eichhorn

Most discotic liquid crystals follow the conventional design consisting of a polyaromatic core surrounded by 3 or more side chains. This design yields liquid crystals with small stacking distances of 3 - 4 Å between molecules within the same column but large distances of 20-40 Å between molecules of adjacent columns. Although this approach favours 1-dimensional charge transport along columnar stacks, the insulating layer of aliphatic side-chains hinders charge carriers from shifting to neighbouring columns once they reach defect sites. For most applications of electronic devices, a reasonably fast charge transport in all three dimensions is preferred to circumvent trapping of charge carriers at the numerous defect sites. Presented here is a unique approach to discotic columnar liquid crystals which incorporates a small number of short, inwardly-pointing side-chains to promote columnar mesomorphism, while avoiding interference with the lateral close-packing of aromatic cores. This design features a 1,3,5-triazine core substituted with bithiophene units which contain side-chains at the 3 position of the outer thiophene ring. For comparison, discotic 1,3,5-triazine derivatives with more traditional designs featuring external side-chains were also synthesized by attaching various alkylthiophene groups.

14. Exploring the Mechanochemical Synthesis of 1,1'-Bi-2-naphthol (BINOL)

Ryan Kung, Patrick A. Julien, Tomislav Friščić*

Department of Chemistry, McGill University, Montreal, QC, Canada

Mechanochemical reactions, conducted for example by ball milling, are being increasingly explored for achieving green and efficient chemical transformation, with a particular advantage of circumventing the need for bulk organic solvents. However, reports of catalytic milling reactions of crystalline materials remain limited and, in general, poorly understood. The central compound in this presentation, 1,1-bi-2-naphthol (BINOL) is a versatile ligand that has been used in a wide variety of metal-based and organocatalytic systems. The molecule itself is usually synthesized *via* a copper-catalyzed C-H activation and coupling reaction in solution.

This presentation will describe a catalytic mechanochemical approach for the synthesis of BINOL, and explore the effects of various copper catalysts and additives such as sub-stoichiometric amounts of solvents or desiccants. In particular, we will show that mechanochemical synthesis of BINOL can proceed faster and at lower temperature than the equivalent solution syntheses. As such, the mechanochemical synthesis of BINOL provides not only an interesting and green synthetic method, but provides fundamental insights into the behavior of catalytic milling reactions of crystalline solids.

1. James, S. L.; *et al. Chem. Soc. Rev.* **2012**, *41*, 413-447.
2. Nakajima, Makoto, *et al. Chem. Pharm. Bull.* **1998**, *46* (11), 1814-1815.

Poster 15:

Green mechanochemistry of open SIFSIX metal-organic frameworks

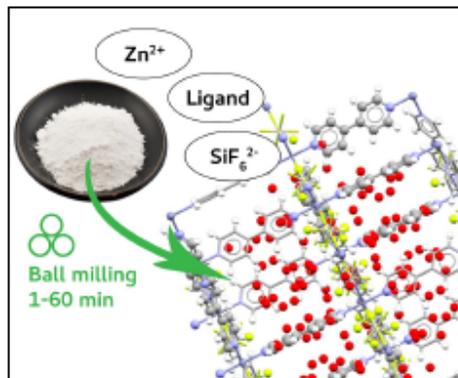
Shaodi Li^a, Cristina Mottillo^a, and Tomislav Friščić^a

^aDepartment of Chemistry, McGill University, Montreal, Quebec, Canada

^bACSYNAM Inc., Montreal, Quebec, Canada

Microporous metal-organic frameworks (MOFs) are becoming highly sought for uses in carbon capture and gas separation,^{1,2} due to their high and tunable internal surface areas, as well as thermal and chemical stability which render them well suited for sequestration and separation of greenhouse gases (GHGs). The SIFSIX class of MOFs have been noted as particularly promising for direct air capture of CO₂ and CH₄.^{1,2}

The SIFSIX materials consist of two-dimensional square-grid sheets held apart by anionic SiF₆²⁻ pillars; each sheet is composed of transition metal ions (e.g. Ni²⁺, Cu²⁺, or Zn²⁺) and ditopic ligands, such as pyrazine or 4,4'-bipyridine.¹ However, the currently available synthetic routes for SIFSIX materials are lengthy, require large solvent volumes, and depend on often toxic and hazardous metal precursors.^{3,4} Here, we describe our efforts to synthesize SIFSIX materials in a "greener" manner by adopting a solid-state approach, based on mechanochemical reaction of select zinc salts and compatible ligands. The presented milling reactions provide a new route for SIFSIX synthesis, which considerably reduces reaction time and eliminates the need for bulk solvents.



References

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16. Synthesis of porous zeolitic imidazolate frameworks from a metal oxide in supercritical carbon dioxide

Joseph Marrett, Dr. Tomislav Friščić

Porous metal-organic frameworks (MOFs) have emerged as materials widely applicable to a variety of areas including selective gas capture¹, catalysis,² and chemical separation.³ Conventionally, MOF synthesis requires large volumes of organic solvent, extensive heating, and corrosive metal salts,⁴ limiting the feasibility of "green" and efficient scale-up for industrial production.⁵ With this in mind, more environmentally-friendly alternatives to conventional MOF synthesis have recently been developed, including mechanochemical⁶ and accelerated aging⁷ methods. These techniques offer reduced energy inputs and require little to no organic solvent, but often still demand the addition of catalytic additives to achieve complete conversion from metal oxides. We show here that microporous MOFs from the zeolitic imidazolate frameworks (ZIFs) class of materials¹ can be produced directly and rapidly from a metal oxide using supercritical carbon dioxide (scCO₂) as the reaction medium, without the use of catalysts or traditional organic solvents. Specifically, we find that solid mixtures of zinc oxide and imidazole derivatives react within minutes to form open ZIFs such as the widely studied ZIF-8 in complete conversion, when exposed to supercritical carbon dioxide. The resulting methodology is a clean, fast, and highly scalable alternative for the synthesis of microporous MOF materials.

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17. Transition metal coordination complexes of *N*-(3-cyanophenyl)-*N'*-pyridin-2-ylurea

Tristen Moyaert, Louise Dawe

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N-(3-cyanophenyl)-*N'*-pyridin-2-ylurea (L1) was synthesized by reaction of 2-aminopyridine with 3-cyanophenylisocyanate. Upon reaction with transition metal salts (Ni(NO₃)₂, Co(NO₃)₂, and Cu(ClO₄)₂), mononuclear M(L1)₂²⁺ complexes were obtained, that formed one dimension chains *via* further metal coordination to solvent, or anions. Synthesis and crystal structures will be presented.

18. Expanding the Family of Palladium-DTDA Metal Complexes

Mitchell A. Nascimento and Jeremy M. Rawso

Dithiadiazolyl radicals have been shown to be a versatile class of stable neutral radicals, with potential applications ranging from magnetic materials[1], luminescent materials[2], conductive materials[3], and as paramagnetic ligands for metal complexes including recent reports of single molecule magnet activity[4]. However, complexes of DTDA as paramagnetic ligands are quite rare, including examples by Preuss, Rawson, Banister and Boere where the heterocycle undergoes oxidative addition with S-S bond cleavage or coordinates as a 7 pi radical. Discussed here are some recent attempts at the synthesis of new Pd-DTDA complexes, with the goal of expanding this family of complexes and providing further insight into the reactivity and physical properties of these versatile radical ligands.

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19. Applications of ^{35}Cl SSNMR for the study of HCl Pharmaceutical Cocrystals

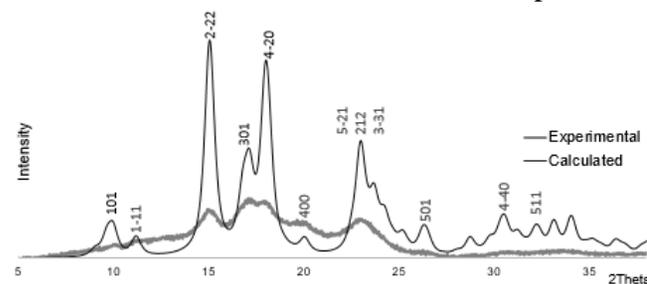
A.A. Peach, D.A. Hirsh, and R.W. Schurko* <rschurko@uwindsor.ca>, University of Windsor, Windsor, ON, Canada, N9B 3P4.

Active pharmaceutical ingredients (APIs) can be synthesized in a variety of solid forms (e.g., salts, hydrates, amorphous structures), each of which can have distinct physicochemical properties, such as stability, solubility, and/or bioavailability. In turn, these properties impact the manner in which the dosage form is manufactured (this often involves a number of complex organic components, including starches, sugars, and polymers). As such, there has been a growing interest in creating simpler formulations in the form of API cocrystals, where the API is cocrystallized with a pharmaceutically acceptable coformer to produce a single solid phase.¹ Fluoxetine HCl, the active ingredient in the antidepressant Prozac, is known to form cocrystals via slow evaporation from mixtures with three coformers: benzoic acid, fumaric acid, and succinic acid.² Structural characterization of these cocrystals is crucial for understanding the mechanisms of their formation, and to permit the rational design of new cocrystals with novel structural motifs and favourable pharmaceutical properties. First, we will demonstrate the use of ^{35}Cl solid-state NMR (SSNMR) as a structural probe of the chloride anions in fluoxetine HCl cocrystals. ^{35}Cl NMR spectra can easily distinguish between the API and the cocrystal, and can be used to monitor the formation of the product, as well as for detection of impurities. Second, we will explore an alternative method for cocrystal formation via mechanochemical synthesis, and demonstrate the superiority of our new synthetic methods over conventional recrystallization methods.

[1] *CrystEngComm* **2014**, *16*, 3451. [2] *J. Am. Chem. Soc.* **2004**, *126*, 13335.

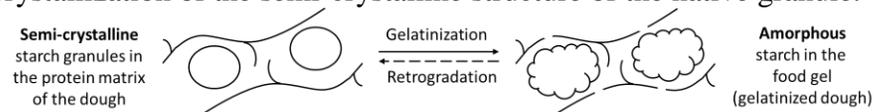
20. Monitoring the re-crystallization of starch during staling of the wheat flour bread

I. Poloz <ipoloz@uoguelph.ca>, D.V. Soldatov, Department of Chemistry, J.E. Bock Department of Food Science, University of Guelph



Starch is a naturally occurring polysaccharide. In the wheat flour the molecules of branched

(amylopectin) and linear (amylose) polymers pack in a semi-crystalline granule with onion-like structure of alternating crystalline and amorphous lamellas. In the flour dough, the starch granules are present unchanged in their semi-crystalline state, but incorporated in an H-bonded protein matrix. The flour and flour dough yield a similar powder X-ray diffraction pattern corresponding to the crystal structure of A-amylose reported previously.¹ Upon heating in the presence of water the starch granules gelatinize that involves loss of the granular structure and crystallinity. Retrogradation is a reverse process leading to a partial re-crystallization of the semi-crystalline structure of the native granule.



Powder X-ray diffraction was used as a technique to monitor the changes in the starch crystalline structure during the storage of baked breads. Crystallinity of the samples was calculated as a function of temperature and time. The results of this study will be presented and discussed.

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21. NEW DERIVATIVES OF 1,2,4-BENZOTHIADIAZINES AND THEIR COORDINATION CHEMISTRY

Konstantina Pringouri, Muhammad U. Anwar, and Jeremy M. Rawson*

The family of 1,2,4-benzothiadiazines with sulfur in various oxidation states (2/4/6) have attracted attention for both materials and pharmaceuticals applications.¹ The redox behaviour of the S(II) derivatives is central to our studies in developing polydentate N-donor ligand sets with tunable coordination chemistry for the construction of new functional materials.² My research has focused on the development of a range of derivatives of these heterocycles in which the group at the C(3) position is varied to include pyridyl (L^1H) and pyrimidine (L^2H) rings (Fig. 1), thereby offering strong N,N'-donor systems for metal coordination. Their reactivity towards first row transition metal ions has been explored and the effect of the counter-ions examined. In the presence of oxygen, an alternative reaction outcome is observed in which the thiadiazine ring is oxidized to its S-oxide forming a range of polynuclear complexes.

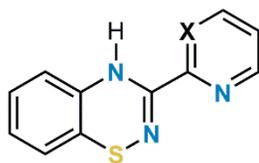


Fig. 1 Molecular structure of 1,2,4-benzothiadiazine, where X = CH (L^1H), N (L^2H).

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- ² E. R. Clark, J. J. Hayward, B. J. Leontowicz, D. J. Eisler and J. M. Rawson, *CrystEngComm*, 2014, **16**, 1755

22. Biasing Nematic Over Columnar Mesomorphism by Molecular Design

Hi Taing, Jacob Rothera, Stephan Holger Eichhorn*

University of Windsor, Department of Chemistry and Biochemistry

Nematic mesophases, although common in calamitic systems, are rarely observed for discotic liquid crystals as they prefer to assemble into columnar mesophases. As a result, the structure-property relationship for discotic nematic liquid crystals is still poorly understood and their properties have been little studied. Nematic discotic liquid crystals have potential applications as high pressure lubricants and as organic semiconductors that possess 3-D rather than 1-D charge transport typically observed in columnar mesophases. Presented here are nematic discotic liquid crystals based on trithienyl triazine derivatives bearing alkyl carboxylate or vinyl cyano acetate groups. The chosen design of using a small, conformationally flexible aromatic core with only three side-chains promotes nematic over columnar mesomorphism most likely because the interactions between cores and the packing volume of side-chains are insufficient for creating microphase segregation into columnar stacks. Also, the star-shape of the molecules would generate a large degree of free volume if the compounds arrange into freely rotating columnar stacks. The single crystal structure of an ester with ethyl side-chains reveals a co-planar layered arrangement of the trithienyl triazine cores that requires the side-chains of neighboring molecules to fill the space in between the thiophene groups. We hypothesize that this packing motive remains the same for esters with longer side-chains but the crystalline phase is destabilized with increasing length of the alkyl chains to favour a nematic mesophase. Particularly rare is the nematic and columnar polymesomorphism observed for the related trithienyl triazines containing vinyl cyano acetate groups. The formation of a low temperature columnar mesophase, in addition to the high temperature nematic mesophases, is reasoned with stronger core-core interactions due to the increase in size of the conjugated core and additional dipolar interactions.

23. Copper(II)-mediated synthesis of 2-aminobenzothiazoles

Zachary Schroeder, Richard Edwards, Lana Hiscock, Louise N. Dawe*

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Herein, a novel route to 2-aminobenzothiazole derivatives, via copper(II)-mediated rearrangement of alkyl- and aryl substituted thioureas, is presented. This has been accomplished using greener solvents where possible, and offers the further advantages that this reaction does not require heat, or any added oxidant. In a further attempt to minimize the environmental impact of this synthetic process, the transformation has been explored through solvent-free mechanochemistry, and preliminary results indicate this to be an equally viable route to product formation. Further mechanistic and theoretical considerations are being investigated.

24. The development of a conductive two-component, UV crosslinked sol-gel system containing Polyaniline and the silica sol-gel precursors: 3-Methylacryloxypropyltrimethoxysilane and Tetraethoxysilane

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This work describes our attempt to encapsulate Polyaniline (PANI) in a U.V. crosslinked, two component silica sol-gel coating. This coating comprised of 3-Methylacryloxypropyltrimethoxysilane (MaTMS) and Tetraethoxysilane (TEOS) can be used in corrosion inhibition. Two component crosslinked sol-gel systems tend to demonstrate better adhesion and chemical resistance than non-crosslinked, or single component gels. In our research lab we routinely use a two component sol-gel system, specifically a γ -Glycidoxypropyltrimethoxysilane (GPTMS): TEOS combination, which can be chemically crosslinked with an amine. The inclusion of PANI in this system and the introduction of the amine crosslinker led to the precipitation of PANI, resulting in poor coating quality. This work shows that PANI's stability in aqueous solution is pH dependant and at a basic pH PANI precipitates out of solutions. Herein, we demonstrate that the use of stoichiometric amounts of 1M HNO₃ and Isopropanol as a co-solvent creates a sol that undergoes hydrolysis within five minutes of stirring under ambient conditions. Upon heating at 60⁰C for 25 minutes the sol undergoes condensation. We will subsequently demonstrate that PANI forms a stable solution with the sol-gel precursors and photo-initiator in Isopropanol with stoichiometric amounts of 1M HNO₃. This solution remains stable upon dip-coating and exposure to UV light. The resulting coatings have a better visual quality than the GPTMS: TEOS coatings.

Poste 25
Nadia Stephaniuk, Jeremy Rawson
University of Windsor

Host-guest interactions have recently become a growing area of study within the scientific community, where the intrinsic chemistry affiliated with the binding and activity of these interactions can be directly correlated to the applications these complexes possess, such as gas storage materials, sensors, activators, and in heterogeneous catalysis. In particular, inclusion complexes possessing radical guests offer the potential for strong communication between both the host and guest and/or the guest molecules themselves, where the nature of the host-guest interactions lead to the effects in which the host can modify the guest properties, or conversely, the guest affects the host structure. This presentation will describe the inclusion chemistry of 4-phenyl-1,2,3,5-dithiadiazolyl (PhDTDA) radical, and its selenium analogue (PhDSDA), into the porous metal-organic framework host MIL-53(Al). The inclusion of the PhDTDA and PhDSDA radicals into MIL-53(Al) was achieved through gas phase diffusion, and led to a colour change in the host from white to red and purple, respectively. The characterization of these inclusion complexes was confirmed through powder X-Ray diffraction, EPR spectroscopy, and Differential Scanning Calorimetry. Reactivity studies of these radicals within the host framework will be discussed.

26. Removal of Se (IV) and Se (VI) with Activated Carbon Produced using Recycled H₃PO₄

Oliver Strong, Andrew Vreugdenhil

Toxic anions such as selenium and arsenic, are difficult to remove from contaminated ground water. Activated carbon (AC) has a large surface area that makes it an ideal sorbent for water filtration, but it is ineffective at removing selenium anions without surface functionalization. In this work, AC was prepared using recycled phosphoric acid. The AC produced using recycled phosphoric acid maintained high surface areas ($1643 \pm 140 \text{ m}^2\text{g}^{-1}$). The AC was treated in two steps using incipient impregnation. A base wash was used to adjust the pH of the AC, followed by iron loading with iron (II) chloride. The resulting Fe-AC was then used for the removal of Se (IV) and Se (VI) in solution. Results showed adsorption of Se (IV) to the Fe-AC surface, and no observable uptake of the Se (VI).

27. Development of Panchromatic Dyes Using the Subchromophore Behaviour Found in Non-symmetrically Substituted 1,3,5-Triazine Cores

Hi Taing, Jacob Rothera, Menandro Cruz, S. H. Eichhorn*

The attachment of 3 different heterocycles to a 1,3,5-triazine core has shown to exhibit additive subchromophore behaviour, where each substituent has its own absorption. This phenomenon was utilized to generate panchromatic dyes with specific absorption peaks that span the UV and visible spectrum. Unpredictably, a triazine derivative containing both a strong donor and strong acceptor group on the same molecule gave rise to an additional absorption peak at longer wavelengths, which was attributed to an electronic communication between the meta-substituents. UV-Vis and TD-DFT studies indicate this communication occurs intra- and intermolecularly. In addition, single crystal XRD has shown that these asymmetrically substituted triazines form disordered crystalline phases or higher ordered mesophases.

28. α -Lipoic Acid for the Design of Pharmaceutical Co-crystals

Andy Tsang, Samuel Netzke, Dmitriy V. Soldatov

α -Lipoic acid (ALA) has the potential to be used for new formulations of pharmaceuticals where it acts as a co-crystallization agent. ALA is a naturally occurring compound found in plants and animals as a cofactor for mitochondrial energy production. It is also used in the treatment of diabetes and heavy metal poisoning, and as an antioxidant. These different functions have gathered interest among the public and research community as both a drug and a nutritional supplement. ALA has been shown to form co-crystals but only one crystal structure has been reported. ALA has a relatively low melting point of $\sim 60^{\circ}\text{C}$, and the co-crystallization with nicotinamide increased its thermal stability by 20°C ¹.

Various combinations of ALA with bioactive molecules containing hydrogen bonding functional groups were screened with powder X-ray diffraction for the formation of co-crystals. Crystals suitable for single crystal X-ray diffraction analysis were grown and characterized. Thermodynamic stability and other properties of the co-crystal were also studied by determining the phase diagram of the corresponding binary system using differential scanning calorimetry. The results of these studies will be presented.



*Active Pharmaceutical Ingredient

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29. Molecular-Level Structure and Dynamics in Hydrated Active Pharmaceutical Ingredients: A Solid-State NMR Study

N. Veinberg, S.T. Holmes, D.A. Hirsh, and R.W. Schurko,*
University of Windsor, Windsor, ON

The pharmaceutical properties of active pharmaceutical ingredients (APIs) are highly dependent on their molecular-level structures. Many APIs are crystallized as HCl salts to improve their stability and solubility; these can crystallize into polymorphic and pseudopolymorphic forms (e.g., hydrates or solvates), each of which can have distinct physicochemical properties. In particular, the anhydrous and hydrated forms of HCl salts of APIs can have drastically different stabilities, shelf lives, and/or bioavailabilities. Our group has demonstrated, via the use of ^{35}Cl solid-state NMR (SSNMR), a correlation between the ^{35}Cl electric field gradient (EFG) tensor parameters and the numbers and types of short H...Cl bonds involving the Cl^- anions in anhydrous samples.¹ However, these relationships are not clear for hydrated HCl APIs, due to the mobility of the water molecules and ambiguities in hydrogen atom positions.² I will present a systematic ^{35}Cl SSNMR study of several HCl API hydrates, in order to develop structural correlations between ^{35}Cl EFG tensors and local Cl^- anion environments. A combination of ^{35}Cl SSNMR, pXRD, quantum chemical calculations, and variable-temperature ^2H SSNMR will provide information on how the water molecules affect the molecular structures of hydrated HCl APIs. These findings may prove useful for high throughput analysis of APIs, hydrate/anhydrate identification, and detection of impurities and disproportionation products.

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30. Organometallic host materials based on antimony(III) and (V) compounds

L. Visontai, K. E. Preuss*, D. V. Soldatov*

So-called non-self-complementary host molecules possess irregular geometries which prevent efficient crystal packing. This packing efficiency can be increased by incorporating guest molecules into void spaces which hosts cannot occupy, resulting in an overall decrease in lattice energy. Such irregular-shaped compounds are ideal candidates for host materials due to their propensity to form inclusion compounds, or ‘clathrates’. Selectivity of these materials can be enhanced through the rational design of host species, culminating in the development of what are termed ‘clathrate sorbent materials’. A major potential application of clathrate sorbents would be in the separation of chemical species, including homologues, isomers and possibly enantiomers.

Several types of non-self-complementary hosts exist in literature including ‘trefoil’ shaped molecules such as triphenylmethane and ‘humming top’ hosts such as modified metal dibenzoylmethanates. The remarkable clathratogenic properties of these compounds have been attributed to their distinct molecular geometries.

Our focus is on developing a new class of organometallic host materials based on Sb(III) and Sb(V) compounds. Using an Sb centre allows for greater design flexibility than in typical carbon-based materials because Sb adopts different geometries in the III and V oxidation states. It is therefore possible to significantly alter the clathratogenic properties of these compounds through small chemical modifications. The synthesis and characterization of these materials will be presented, with an emphasis on single crystal and powder XRD, TGA, and ^1H NMR data.

Poster 31:

Multinuclear Solid-State NMR Spectroscopy Ionic Cocrystals
C.S. Vojvodin, D.A. Hirsh, I. Huskic, T. Frišćić and R.W. Schurko.*

The rational design of multi-component single-phase materials known as cocrystals is a flourishing area in crystal engineering. Cocrystals have distinct properties in comparison to their pure constituent components (e.g., solubility, stability, etc.)^[1] providing a means of tailoring the physicochemical properties of a crystalline solid form. As such, there has been much recent interest in the synthesis of cocrystalline forms of active pharmaceutical ingredients (APIs), for use as dosage formulations. While there have been numerous reports of the synthesis of API cocrystals, there are relatively few papers describing methods for rational synthesis or mechanisms of cocrystal formation. Solid-state NMR (SSNMR) is well suited for studying the formation of cocrystals, since it is sensitive to the local structural changes that result from the intermolecular interactions in cocrystals (e.g., hydrogen bonding).^[2,3] In this poster, we present a multinuclear (³⁵Cl, ²³Na, ¹³C, ²H, and ¹H) SSNMR study of NaCl:Urea:Hydrate cocrystals made via mechanochemical syntheses. SSNMR, in tandem with pXRD and thermogravimetric methods, allow for the identification of distinct cocrystalline phases, the detection of impurities, and the potential monitoring of mechanisms of cocrystal formation. Characterization of these simple model systems, accompanied by *NMR crystallographic characterization* via quantum chemical computations,^[4] will develop a methodological framework for future studies of increasingly complex cocrystals of APIs and pharmaceutically acceptable cofomers.

[1] *Pharm. Res.*, **2006**, *23*, 1888-1897; [2] *J. Phys. Chem. Lett.* **2014**, *5*, 3340. [3] *Mol. Pharm.* **2013**, *10*, 999-1007; [4] *CrystEngComm*, **2013**, *15*, 8599.

32. Nanoscale Building Blocks: Plasmonic Metal and Photoelectrochemically Active Metal Oxide Nanoparticles for Renewable Energy Applications

Nicole Cathcart, Patrick Campbell, Nimer Murshid and Vladimir Kitaev

Size- and shape-uniform nanoparticles and nanostructures function as well-defined nanoscale building blocks (NBBs) in a variety of applications. Convenient tailoring of NBB composition, surface chemistry, size-dependent functional properties and self-assembly enables versatile design of novel materials based on NBBs. With respect to renewable energy applications, plasmonic metal nanoparticles can enhance sunlight absorption with a wavelength conveniently tunable by the NBB dimensions. Photoelectrochemically active metal oxide NBBs, such as hematite and manganese (III,IV) oxides, are effective in oxygen evolution, as well in remediative photodegradation. We will present our work on well-defined NBBs at Laurier.

Also Presenting:

Poster 33: Richard Edwards

Poster 34: Elodie Heyer and Ines Taarit

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