

CEMWOQ 3

3rd Crystal Engineering and Emerging Materials Workshop of Ontario and Quebec

The 3rd Crystal Engineering and Emerging Materials Workshop of Ontario and Quebec

May 13-15, 2016

Windsor, Ontario, Canada

Hosted by:

The Department of Chemistry and Biochemistry

University of Windsor



University of Windsor

DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY

**The 3rd Crystal Engineering and Emerging Materials Workshop
of Ontario and Quebec - CEMWOQ-3
University of Windsor, Windsor, Ontario, Canada May 13-15, 2016**

Sponsors

- **PROTO Manufacturing** ○
- University of Windsor ○ Bruker AXS ○
- Royal Chemical Society ○ Pine Research Instrumentation ○
- Canada Research Chairs Program ○ American Chemical Society ○
- Cambridge Crystallographic Data Centre ○ Form-Tech Scientific ○

Conference Schedule at a Glance

| Time | Event | Location |
|--|--|---|
| Friday, May 13, 2016 2:00 pm - 5:00 pm | <i>Bruker Crystallography Workshop</i> | Centre for Executive and Professional Education at 167 Ferry St. - Room 103 |
| Friday, May 13, 2016 7:30 pm - 11:00 pm | <i>Friday-Night Mixer</i> | Craftheads Brewing Company 89 University Ave. W |
| Saturday, May 14, 2016 8:00 am - 8:50 pm | <i>Registration</i> | Centre for Executive and Professional Education at 167 Ferry St. - Main Atrium |
| Saturday, May 14, 2016 8:50 am - 6:50 pm | <i>CEMWOQ Day 1 Technical Program & Posters</i> | Centre for Executive and Professional Education at 167 Ferry St. - Room 116 |
| Saturday, May 14, 2016 7:00 pm - 9:00 pm | <i>Conference Dinner</i> | Mazaar Restaurant 372 Ouellette Avenue |
| Saturday, May 14, 2016 9:00 pm - Midnight | <i>PROTO Party</i> | The Bistro At The River 78 Riverside Drive W. |
| Sunday, May 15, 2016 9:00 am - 12:50 pm | <i>CEMWOQ Day 2 - Technical Program</i> | Centre for Executive and Professional Education at 167 Ferry St. - Room 116 |
| Sunday, May 15, 2016 1:00 pm - 2:30 pm | <i>Meeting of Conference Organizers: Past, Present and Future</i> | To Be Determined - a local restaurant most likely! |

Technical Program & Events

Bruker Crystallography Workshop

Friday, May 13, 2016 - 2:00 pm - 5:00 pm

Centre for Executive and Professional Education at 167 Ferry St. - Room 103

| Instructor: Charles Campana (Bruker AXS) | |
|---|---|
| Time | Lecture |
| 2:00 - 2:15 pm | <i>Registration</i> |
| 2:15 - 2:30 pm | Welcome - Jeremy Rawson (University of Windsor) |
| 2:30 - 3:30 pm | Diagnostics and Treatment of Problem Crystal Structures (Charles Campana, Bruker) |
| 3:30 - 4:00 pm | <i>Coffee Break</i> |
| 4:00 - 5:00 pm | Discussion |

CEMWOQ Friday-Night Mixer

Friday, May 13, 2016 - 7:30 pm - 11:00 pm

[Craftheads Brewing Company](#)

89 University Ave. W

CEMWOQ Day 1 - Technical Program

Saturday, May 14, 2016 - 8:00 am - 6:50 pm

Centre for Executive and Professional Education at 167 Ferry St. - Room 116

| Time | Event/Lecture |
|--|--|
| 8:00 - 8:50 | <i>Registration</i> |
| 8:50 - 9:00 | Opening remarks - Jeremy Rawson |
| <i>Chair: Louise Dawe (Wilfred Laurier University)</i> | |
| 9:00 - 9:30 | Tomislav Friščić (McGill University) |
| 9:30 - 9:50 | Pablo Martinez-Bulit (University of Windsor) |

| Time | Event/Lecture |
|---|---|
| 9:50 - 10:10 | Alex Mayo (University of Guelph) |
| 10:10 - 10:30 | David Hirsh (University of Windsor) |
| 10:30 - 11:00 | Coffee Break |
| <i>Chair: Rob Schurko (University of Windsor)</i> | |
| 11:00 - 11:50 | RSC CrystEngComm Plenary Lecturer: Omar Farha (Northwestern) <i>Design, Synthesis and Characterization of Catalytic Metal-Organic Framework Materials</i> |
| 11:50 - 12:20 | Team Talk: Dmitriy V. Soldatov and Andy Tsang (University of Guelph) <i>Supramolecular Materials Based on Short Peptides: Structure, Stability and Solid State Reactivity</i> |
| 12:20 - 12:30 | CEMWOQ Group Photograph |
| 12:30 - 14:00 | Lunch |
| <i>Chair: Tomislav Friščić (McGill University)</i> | |
| 14:00 - 14:20 | Sponsor Lecture: Nick Vukotic (PROTO Manufacturing) |
| 14:20 - 14:40 | Cristina Mottillo (McGill University) |
| 14:40 - 15:00 | Christopher O'Keefe (University of Windsor) |
| 15:00 - 15:30 | Kelong Zhu (University of Windsor) |
| 15:30 - 16:00 | Melanie Pilkington (Brock University) |
| 16:00 - 16:30 | Coffee Break |
| <i>Chair: Melanie Pilkington (Brock University)</i> | |
| 16:30 - 17:20 | Plenary Speaker: J.J. Vittal (National University of Singapore) <i>Solid State Photo-Reactivity of Metal Complexes, Coordination Polymers and Metal-Organic Frameworks Under UV Light</i> |
| 17:30 - 18:50 | Poster Session - Main Atrium |

CEMWOQ Conference Dinner
Saturday, May 14, 2016 - 7:00 pm - 9:00 pm
[Mazaar Restaurant](#) (372 Ouellette Avenue)

PROTO Party
Saturday, May 14, 2016 - 9:00 pm - Midnight
[The Bistro At The River](#) (78 Riverside Drive W.)

CEMWOQ Day 2 - Technical Program
Sunday, May 15, 2016 - 8:30 am - 12:50 pm
 Centre for Executive and Professional Education at 167 Ferry St. - Room 116

| Time | Event/Lecture |
|--|--|
| 8:30 - 9:00 | Registration |
| <i>Chair: Jeremy Rawson (University of Windsor)</i> | |
| 9:00 - 9:50 | Plenary Speaker: Amy Sarjeant (CCDC) How 827,948 Structures Can Improve our Understanding of Materials |
| 9:50 - 10:10 | Jean-Louis Do (McGill University) |
| 10:10 - 10:30 | Aaron Smith (Guelph) |
| 10:30 - 11:00 | Coffee Break |
| <i>Chair: Muhammad Anwar (University of Windsor)</i> | |
| 11:00 - 11:20 | Hi Taing (University of Windsor) |
| 11:20 - 11:40 | Yassine Beldjoudi (University of Windsor) |
| 11:40 - 12:00 | Farukh Ali (University of Guelph) |
| 12:00 - 12:30 | Ivani Malvestiti (McGill University) |
| 12:30 - 12:50 | Student awards and closing remarks |

CEMWOQ Day 2 - Meeting of Conference Organizers: Past, Present and Future
Sunday, May 15, 2016 - 1:00 pm - 2:30 pm
 Location To Be Determined - a local restaurant most likely!

Posters

| Poster Number | Title & Presenter |
|---------------|--|
| 1 | Truly Amphiphilic Octa-Alkylthio Substituted Tetraazaporphyrin Derivatives with Four Terminal Carboxylic Acid Groups - Elmahdy Abdulhamied (Windsor) |
| 2 | 1,2,5,6-Tetrathiocins As Ligands: A New Approach to Metal Dithiolene Complexes - Zeinab S. Ahmed (Windsor) |
| 3 | Synthesis and Surface Characterization of Novel Gold Nanoparticles Coated by a Cationic WS-TEMPO - Aisha Alsaleh (Windsor) |
| 4 | Switchable Materials using 4,5-Dioxonaphtho [1,2-d][1,2,3]dithiazolyl - Danielle R. Dinsdale (Guelph) |
| 5 | Solvent-free transformations of organic and pharmaceutical materials - Ahmed Fekri (McGill) |
| 6 | A simple set-up for in situ monitoring of vapour-induced reactions of pharmaceutical organic solids using a benchtop powder X-ray diffractometer - Igor Huskić (McGill) |
| 7 | Polymorphism, interconversion and porosity of a benzylpyridine-functionalized zwitterion - Leigh Loots (McGill) |
| 8 | Solid State Phase Transitions of Lanthanide-Radical Complexes: Breaking the Pancake Bonds - Michelle B. Mills (Guelph) |
| 9 | Exploring New Derivatives of 1,2,4-benzothiadiazines and their Coordination Chemistry - Konstantina Pringouri (Windsor) |
| 10 | Exploring the Re-entrant Phase Transition Behaviors of Lanthanide-Thiazyl Radical Complexes - Matt Ryu (Guelph) |
| 11 | Unusually Stable Gold Nanoparticles Protected by Large Dithiol Ligands - Sarah Salloum (Windsor) |
| 12 | Enantiomer-specific oriented attachment of guanidine carbonate crystals - Reajean Sivakumar (Concordia) |
| 13 | Developing Iron(II) Spin Crossover Compounds Using Pyrazolyl Borate and Thiazyl Radical Ligands - Ellen Song (Guelph) |

| Poster Number | Title & Presenter |
|---------------|---|
| 14 | T-shaped [2]rotaxane ligands for MOFs: a new design - Alexander Stirk (Windsor) |
| 15 | ^1H , ^{13}C , and ^{15}N Solid-State NMR Study of Halogen Bonded Frameworks Featuring Nitrogen-Containing Heterocycles - P.M.J. Szell (Ottawa) |
| 16 | Mechanochemistry as a Tool for Reaction Discovery: From Novel Copper-Catalyzed Mechanochemical C-N Coupling Reactions to Unique Crystal Structures - Davin Tan (McGill) |
| 17 | Dynamic Interlocked Metal-Organic Framework of Unsymmetrical Rotaxane - Christine To (Windsor) |
| 18 | Dynamic Motion of Multiple Molecular Spur Gears in Solution and Solid States - Yoshitaka Tsuchido (Windsor) |
| 19 | Organometallic host materials based on antimony(III) and (V) compounds - Laszlo Visontai (Guelph) |
| 20 | Mechanochemical Production of Halogen-Bonded $\text{P}=\text{O}\cdots\text{I}-\text{C}$ Solids and Characterization by Solid-State NMR Spectroscopy - Yijue Xu (Ottawa) |
| 21 | Templation effects and novel ZIF structures by solid state synthesis - Ivana Brekalo (Georgetown University) |

Abstracts

Lectures

Oral Presentation

Solid-State Green Synthesis of Piperazine-2,5-Diones

Farukh I. Ali and Dmitriy V. Soldatov*

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

Piperazine-2,5-diones are the smallest cyclic peptides. They have distinctive and exciting physical and chemical properties due to their rigid cyclic structure, hydrogen bonding capabilities, substituent group stereochemistry, chiral nature and resistance to proteolysis. These properties 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 synthones for non-covalent synthesis. Although various synthetic methods for piperazine-2,5-diones were developed in solution, their formation in the solid state has not been synthetically utilized.

In this study, we investigated the solid state intramolecular cyclization of peptides. The cyclization reaction was carried out in a range of conditions using a thermogravimetric analyzer, differential scanning calorimeter and ventilation oven. The progress of the reaction was monitored through the loss of water (TGA-FTIR, oven), thermal effects (DSC), and by comparing PXRD patterns. The final product was analyzed by FTIR, NMR, GC-MS and single crystal XRD methods. We found that a range of dipeptides undergo intramolecular cyclization upon heating. This process however was complicated by the formation of polymorphs and diastereomers of the cyclic product. Overall, this study gives insight into the comparative stability of dipeptides, solid state degradation of pharmaceutically active dipeptides, and most importantly the solid state green synthesis of piperazine-2,5-diones which is: benign and easy to conduct, highly atom efficient and solvent free, stereospecific and no-need-for-derivatives approach.

Oral Presentation

Recent developments of photo-responsive radicals: from fluorescence to photo-switching

Yassine Beldjoudi, Mitchell Nascimento, Igor Osorio Roman and Jeremy Rawson*

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

A careful tailoring of the crystal structure of the sulphur-nitrogen and selenium-nitrogen radicals form particularly stable radicals which exhibit long range order at temperatures higher than any other type of radical reported to date.¹ Since the Poly-Aromatic Hydrocarbons (PAHs) are well known to exhibit remarkable photonic and electrochemical properties, this paper describes our recent studies to prepare and investigate new structures comprising the electronic properties of the PAH moiety with those of the dithiadiazolyl moiety. Herein we report the synthesis and the crystal structure of a series of PAH-DTDAs radicals 1 – 3. In addition we report the UV/visible, the fluorescence and the magnetic properties of these different derivatives. Finally, the relative stability of each derivative has been studied using combinations of DSC, VT-PXRD, single crystal XRD.

1. (a) A.J. Banister, N. Bricklebank, I. Lavender, J.M. Rawson, C.I. Gregory, B.K. Tanner, W. Clegg, M.R.J. Elsegood, and F. Palacio, *Angew. Chem. Int. Ed. Engl.* 1996, 35, 2533. (b) R.I. Thomson, C.M. Pask, G.O. Lloyd, M. Mito, J. M. Rawson, *Chem. Eur. J.*, 2012, 18, 8629.

Oral Presentation

Exploring the Solid-state Reactivity of Noble Metals: Oxidative Mechanochemical Processing of Elemental Palladium and Gold

Jean-Louis Do and Tomislav Friščić*

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, PQ, Canada H3A 0B8

Noble metals, both elemental and their soluble derivatives, are highly valued. The ability to process and oxidize noble metals is of great interest to a number of relevant fields, ranging in scales from industrial to academic^{1,2}. Such processes, however, have traditionally required harsh conditions including, but not limited to, the use of high temperatures, strongly acidic or alkaline conditions, or toxic reagents^{3,4}. Using palladium and gold as models, we now demonstrate the so far unexplored ability to activate noble metals using clean, solvent-free chemistry based on mechanical

ball milling. In particular, the use of mechanochemistry enables unprecedented transformation of inert metals into diverse compounds at room temperature under mild conditions. We are able to rapidly and efficiently oxidize elemental palladium and gold into water soluble derivatives or, in one-pot orthogonal processes, prepare coordination complexes of varying architectures. We further demonstrate that these coordination complexes can easily be isolated and purified for further characterization and studies or may be immediately pulled into solution and used in catalytic processes.

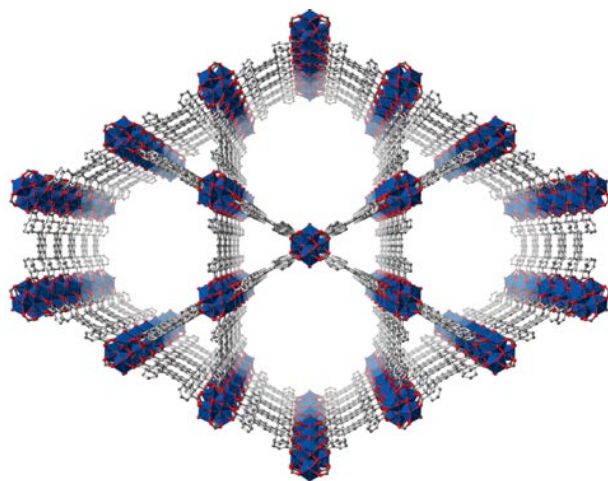
1. Lin, W. et al., *Angew. Chem. Int. Ed.*, 2010, 49, 7929-7932
2. Liu, Z. et al., *Nat. Commun.*, 2013, 4, 1855 doi: 10.1038/ncomms2891
3. Renner, H. et al., *Gold, Gold Alloys, and Gold Compounds*, Ullmann's Encyclopedia of Industrial Chemistry (Wiley-VCH Verlag GmbH, 2000)
4. Renner, H. et al., *Platinum Group Metals and Compounds*, Ullmann's Encyclopedia of Industrial Chemistry (Wiley-VCH Verlag GmbH, 2000)

Oral Presentation

Design, Synthesis and Characterization of Catalytic Metal-Organic Framework Materials

Omar K. Farha*

Department of Chemistry, Northwestern University, Evanston, IL 60208, USA



Metal-organic frameworks (MOFs) are an emerging class of solid-state materials built up from metal-based nodes and organic linkers. They exhibit permanent porosity and unprecedented surface areas which can be readily tuned through coordination chemistry at the inorganic node and/or

organic chemistry at the linkers. The high porosities, tunability, and stability are highly attractive in the context of catalysis. As exemplified by many catalytic enzyme assemblies in nature, site-isolation is a powerful strategy for performing catalytic reactions. MOFs provide an exciting platform for deploying catalysts in a site-isolated fashion and the cavities surrounding them can be engineered to conceptually mimic enzymes. This talk will address new advances in the synthesis and catalytic activity of MOF materials developed at Northwestern University.

Oral Presentation

Rapid Development of Mechanochemical Routes to Materials and Molecules

Tomislav Friščić*

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, H3A0B8, Canada

The past decade has seen an increasingly rapid growth of interest and uses of solid-state chemistry. For example, mechanochemical reactions,¹ conducted by grinding, milling or extrusion, are rapidly making progress as a more efficient, cleaner and room temperature alternative for pharmaceutical synthesis and materials screening (*e.g.* polymorphs, cocrystals), as well as organometallic and coordination chemistry, including the synthesis of microporous metal-organic frameworks (MOFs). This presentation will highlight our group's most recent efforts in developing mechanochemistry for the synthesis of active pharmaceutical ingredients (APIs)² and MOFs,³ and building up the mechanistic knowledge required to understand and rationally design mechanochemical reactivity.⁴

- 1) Friščić, *Chem. Soc. Rev.* **2012**, 41, 3493.
- 2) Tan *et al.* *Chem. Commun.* **2016**, 52, DOI: 10.1039/C6CC02015A5248
- 3) Katsenis *et al.* *Nature Commun.* **2015**, 6:6662.
- 4) Julien *et al.* *J. Am. Chem. Soc.* **2016**, 138, 2929.

Oral Presentation

Detection of Active Pharmaceutical Ingredients in Dosage Forms using DNP-Enhanced ³⁵Cl Solid-State NMR Spectroscopy

David A. Hirsh,¹ Aaron J. Rossini,^{2*} Lyndon Emsley,³ and Robert W. Schurko^{1,*}

1. University of Windsor, Department of Chemistry & Biochemistry, Windsor, ON, Canada N9B3P4
2. Iowa State University, Department of Chemistry, Ames, IA 50011-3111
3. Ecole Polytechnique Fédérale de Lausanne

(EPFL), Institut des Sciences et Ingénierie Chimiques, Lausanne, Switzerland CH-1015

Characterization of active pharmaceutical ingredients (**APIs**) is critical in the development and manufacture of dosage forms. APIs can crystallize in a variety of different solid forms (*e.g.*, polymorphs, hydrates, cocrystals, and salts) that have different physicochemical properties, which affect qualities of the final formulation like the shelf-life and bioavailability. Common methods for characterizing APIs in the bulk phase (*e.g.*, X-ray diffraction and ^{13}C SSNMR) cannot be applied to the study of many dosage forms, due to the presence of interfering signals from excipients that obscure those from the API. ^{35}Cl SSNMR is a powerful technique for characterizing APIs that are crystallized as HCl salts – more than half of all solid APIs are produced in this manner. ^{35}Cl NMR spectra provide unique spectral fingerprints of each form of an API without interference from the excipient (which does not contain Cl). Given the importance of identifying trace amounts of APIs in dosage forms (*e.g.*, low wt% APIs, polymorphs and/or impurities), there has been a focus on improving the lower detection limit of ^{35}Cl SSNMR spectra. Recently, dynamic nuclear polarization (**DNP**) has become a popular method for achieving high gains in S/N, but its application to wide-line spectra has been limited. Herein, I present the use of DNP to enhance static wide-line (> 100 kHz) ^{35}Cl patterns of APIs, with a focus on spectral quality, and a novel approach to increasing the DNP enhancement using periodic sample spinning (*i.e.*, the spinning-on spinning-off, **SOSO**, technique). I demonstrate the application of ^{35}Cl DNP SSNMR for the characterization of APIs in their bulk forms, as well as in dosage forms with low Cl contents. The potential uses of these techniques for polymorph differentiation, impurity identification, and the discovery of new solid phases are also discussed.

Oral Presentation

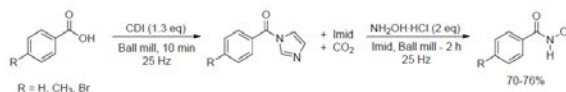
Mechanosynthesis of Hydroxamic acids

Ivani Malvestiti,^{1,2*} José G. Hernández,^{2,3} Tomislav Friščić,³ and Gareth O. Lloyd⁴

1. Universidade Federal de Pernambuco, Departamento de Química Fundamental, Recife, PE, Brazil, 50740-560,
2. McGill University, Department of Chemistry, Montréal, QC, Canada, H3A 0B8
3. RWTH Aachen University, Institute of Organic Chemistry, Landoltweg 1, Aachen, Germany,

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4. Heriot-Watt University, School of Engineering & Physical Sciences, Chemical Sciences, Edinburgh, United Kingdom, EH14 4AS



Scheme 1. Mechanochemical synthesis of hydroxamic acids.

The development of clean, solvent-free approaches to molecules and materials is an increasingly important area of modern chemistry, in particular in the context of pharmaceuticals. Mechanochemistry, *i.e.* chemical reactions induced or sustained by mechanical force and agitation, have emerged as a general and rapid approach for clean, high-yielding synthesis of pharmaceutically-relevant molecules and materials, at room temperature, and without the need for bulk solvents.[1] Hydroxamic acids are known to exhibit biological activities, *e.g.*, antibacterial, antifungal, anti-inflammatory, anti-asthmatic and metalloproteinase inhibitors, with the latter being due to their ability to coordinate to transition metal ions.[2] Syntheses of hydroxamic acids in solution and solution-solid phase have been described in the literature.[3-5] Direct condensation of a carboxylic acid and a nucleophile requires activation of the carboxylic acid and most methods, including large-scale processes, employ sacrificial coupling agents such as carbodiimides, acyl chlorides or *N,N'*-carbonyldiimidazole (CDI). The latter reagent has the advantage of being inexpensive, benchtop stable and generates imidazole as the byproduct.[6] This presentation will outline the development of the first solvent-free, mechanochemical route to hydroxamic acids, achieved by coupling of carboxylic acids and hydroxylamine hydrochloride, mediated by CDI (Scheme 1).

- [1] James et al. Chem. Soc. Rev. 2012, 41, 413; [2] Codd, Coord. Chem. Rev., 2008, 252, 1387; [3] Giacomelli, Porcheddu, Salaris, Org. Lett., 2003, 5, 2715; [4] Ho et al., J. Org. Chem. 2005, 70, 4873; [5] Usachova, Leitis, Jirgensons, Kalvinsh, Synth. Commun., 2010, 40, 927; [6] Métro et al. Chem. Eur. J., 2015, 21, 12787.

Oral Presentation

You Spin Me Right Round: MOFs Consisting of a Porphyrin and Mobile [2]Rotaxane Components

Pablo Martinez-Bulit, Christopher A. O'Keefe, Kelong Zhu, Robert W. Schurko,* and Stephen J. Loeb*

Department of Chemistry and Biochemistry, University of Windsor, Windsor ON N9B 3P4

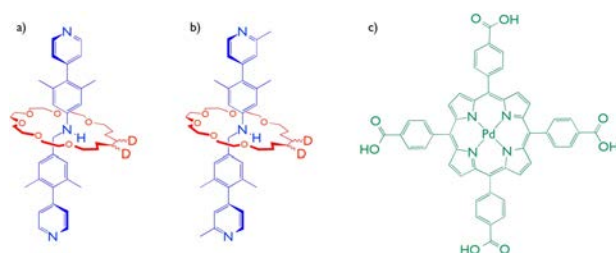


Figure 1. a) Rotaxane pillar L1, b) Rotaxane pillar L2, c) PdTCPP Porphyrin

Metal-organic Frameworks (MOFs) provide an ideal platform for ordering dynamic molecules, such as [2]rotaxanes. By tailoring the constituents of the MOF, it is possible to 'create' void space around the [2]rotaxane, which can be later utilized for the rotation or translation of the macrocyclic wheel.¹ In this work, we used a tetracarboxylate porphyrin (meso-tetrakis-4-carboxyphenyl-porphyrine (TCPP)) as a robust building block; it forms a 2D grid when combined with zinc(II) ions, that can be pillared using a suitable [2]rotaxane. The geometry of the grid forces the rotaxane molecules to be apart from each other, providing enough space for the mobile components to rotate. We synthesized two isostructural MOFs with PdTCPP and two different rotaxane linkers (Fig. 1), and studied the mobility of the wheel using ²H Solid-state NMR spectroscopy. We found that the structure of the rotaxane pillar can influence the rigidity of the framework; if the structure has less room for distortion, the macrocycle can move more freely. We also studied the influence of the solvent molecules inside the cavities of the MOF on the dynamics of the material, which revealed that solvent molecules can act as facilitators of the rotation, as seen in previous studies.²

1. Zhu et. al., *Nature Chem*, **2015**, 137, 514-519; Zhu et. al., *J. Am. Chem. Soc.*, **2014**, 136, 7403-7409.

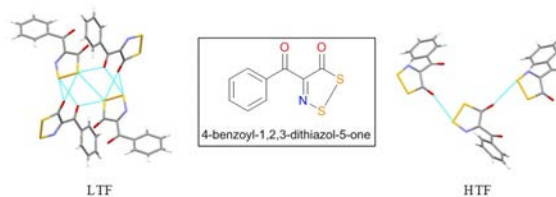
2. Dominguez et. al., *J. Am. Chem. Soc.*, **2002**, 124, 7719-7727

Oral Presentation

Phase Transition Behaviour of a Dimorphic System: The Role of Intermolecular Contacts Involving Sulfur

R. Alex Mayo and Kathryn E. Preuss*

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



Determining the significance of intermolecular contacts in the solid state is important in the fields of molecule-based materials and crystal engineering. Polymorphism provides an opportunity to study how intermolecular interactions, among the other thermodynamic factors, affect crystal packing. Typically, studies are performed on systems containing well-established supramolecular synthons, such as those that make use of hydrogen bonds. With growing evidence that sigma-hole "bonding" is a fundamental type of favourable interaction seen in close contacts in molecular crystals,¹ interactions other than hydrogen bonding may be considered as playing a major role in crystal packing.

We present the dimorphic system of the crystal forms of 4-benzoyl-1,2,3-dithiazol-5-one, where sulfur plays a major role in the crystal structure and unusual phase behaviour is observed. This enantiotropic system exhibits a transition at $T \sim 70$ °C, from a centrosymmetric low-density phase (the low temperature form, LTF), to a chiral high-density phase (the high temperature form, HTF). The potential energy surface relating the observed molecular conformations of 4-benzoyl-1,2,3-dithiazol-5-one in each form is determined by computational methods. The markedly different intermolecular contacts and interactions are characterized using single crystal X-ray diffraction data. Thermal behaviour is probed through DSC (Differential Scanning Calorimetry) experiments and VT-PXRD (Variable Temperature Powder X-Ray Diffraction).

1. Politzer, P.; Murray, J.S. and Clark, T., *Phys. Chem. Chem. Phys.*, **2013**, 15, 11178.

Oral Presentation:

Supramolecular imidazolium frameworks: design and self-assembly of hydrogen-bonded molecular solids with node-and-linker polarity inversion

Cristina Mottillo, Joanne Yu, Sameera Toenjes and Tomislav Friščić

McGill University, Department of Chemistry, Montreal, QC, Canada H3A 0B8



The design and synthesis of framework solids has become central to materials chemistry, owing to the importance of materials such as metal-organic frameworks in a wide range of industrial applications.¹ Hydrogen-bonded molecular frameworks are a relatively nascent class of materials which offer potential advantages over their metal-organic counterparts, in particular solubility in different solvents and low molecular weights. Nonetheless, rational design of such structures based on relatively weak supramolecular interactions is hindered by susceptibility of hydrogen bonds to solvent effects as well as their general sensitivity to linker functionalization. Thus, the design of hydrogen-bonded analogues of metal-organic frameworks (MOFs),² through the application of strategies normally used in the synthesis of MOFs, such as the node-and-linker approach, has remained less successful. We now present the development of a new class of hydrogen-bonded framework analogues of MOFs, called supramolecular imidazolium frameworks (SIFs), framework solids, which are assembled from imidazolium cationic linkers and anionic nodes to form open 2-dimensional nets of square grid topology.³ Whereas the initial development of SIFs employed tetrahedral SO_4^{2-} or SeO_4^{2-} nodes using an inverted node-and-linker design strategy, we now demonstrate the highly reliable formation of

hydrogen bonded **sql**-nets using planar squarate nodes and imidazolium linkers. The SIF structures are resistant to the presence of strong hydrogen-bonding interactions, *e.g.* with interstitial water and solvent molecules as well as linker functionalization, providing a foundation for the robust design of MOF-like molecular solids.

- [1] Zhou *et al.*, *Chem. Soc. Rev.* **2012**, 112, 673.
- [2] Eddaoudi *et al.*, *Chem. Soc. Rev.* **2015**, 44, 228.
- [3] Mottillo *et al.*, *Chem. Commun.* **2015**, 51, 8924.

Oral Presentation

Mechanistic Study of the Solid-State Synthesis of a Zeolitic Imidazolate Framework Using ^1H - ^{111}Cd CP/MAS SSNMR

Christopher A. O'Keefe,¹ Cristina Mottillo,² Tomislav Friščić² and Robert W. Schurko*¹

- 1. University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, N9B 3P4
- 2. McGill University, Department of Chemistry and FRQNT Centre for Green Chemistry, Montreal, QC, H3A 0B8

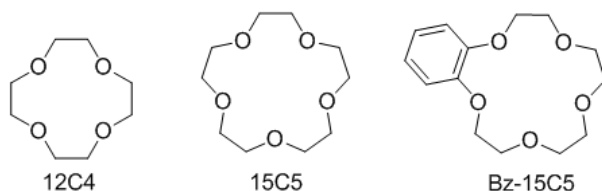
Mechanochemistry (MC, the use of mechanical forces to provide the activation energy for a reaction) and accelerated aging (AA, generating hybrid metal-organic materials under conditions of high humidity and slight heating) are two synthetic approaches that are consistent with the philosophy of green chemistry, as they use little solvent and non-toxic starting materials, and afford quantitative yields. Recently, these approaches have been applied to the synthesis of zeolitic imidazolate frameworks (ZIFs), which are a class of hybrid metal-organic compounds that have garnered great interest due to their uses in catalysis and gas storage. The mechanisms and factors affecting ZIF synthesis are largely unknown and likely very different from their solvothermal analogues. Recent mechanistic studies utilized both *in-* and *ex-situ* X-ray diffraction (XRD) experiments to identify products and intermediate phases with known structures; however, the identification of short-lived intermediate phases in low concentrations was not possible as their signals are obscured by those of the starting materials. Herein, we present a mechanistic study of the formation of a ZIF using both MC and AA synthetic techniques. First, we describe the use of multinuclear SSNMR (^{111}Cd , ^1H , ^{13}C and ^{14}N) to characterize a series of cadmium-containing ZIFs with known structures. This information is then used to elucidate the structure

of a ZIF that can be isolated from both MC and AA reactions. MC and AA reactions forming a cadmium-containing ZIF are monitored *ex situ* using ^{111}Cd CP/MAS SSNMR. Using this technique, it is possible to observe signals corresponding to both the intermediates and products of the reactions, which could potentially provide information on mechanisms of ZIF formation. The elucidation of the reaction mechanisms, and the determination of the factors that control the rates of formation and the final topologies of the ZIFs, all allow for the fine-tuning of these reactions to rapidly and cleanly produce the desired products.

Oral Presentation

Macrocyclic Ligands for Dual Property Ln(III) Single Molecule Magnets

Majeda Al Hareri and Melanie Pilkington*
Department of Chemistry, Brock University, 1812
Sir Isaac Brock Way, St. Catharines, ON, L2S3A1



Lanthanide ions display great potential in the field of molecular magnetism due to their large ground state spin values and high intrinsic magnetic anisotropies, which can be enhanced via the application of an appropriate ligand field. Many of the ligand systems employed to date however require multi-step syntheses and/or result in the isolation of coordination complexes which are unstable to air or moisture.¹ Our approach has been to exploit the inherently oxophilic nature of lanthanide ions together with stable, tuneable, oxygen-rich ligands such as crown ether macrocycles for the assembly of Ln^{III} complexes with interesting magnetic and electronic properties.^{2,3} Given that the atomic radii of Ln^{III} ions (where Ln^{III} = Tb, Dy, Ho, Er) are approximately 1 Å, the smaller, commercially-available crown ethers namely, 12-crown-4, 15-crown-5, and benzo-15-crown-5 with cavity sizes of 1.1-2.1 Å were chosen for this study. Employing a range of stoichiometric ratios and experimental conditions, a new family of complexes with 0- and 1-D structural topologies have been prepared. The structural, magnetic, and electronic properties of these systems will be presented.

1. D. N. Woodruff, R.E.P. Winpenny, R.A. Layfield, *Chemical Reviews*, **2013**, *113*, **7**, 5110.
2. E. L. Gavey, M. Al Hareri, J. Regier, L. D. Carlos, R. A. S. Ferreira, F. S. Razavi, J. M. Rawson, M. Pilkington, *J. Mat. Chem. C*, **2015**, *3*, 7738.
3. M. Al Hareri, E. L. Gavey, J. Regier, Z. Ras Ali, L. D. Carlos, R. A. S. Ferreira, M. Pilkington, *Chem. Commun.*, **2016**, submitted.

Oral Presentation

How 827,948 Structures Can Improve our Understanding of Materials

Amy A. Sarjeant¹, Shyam Vyas¹, Paul Sanschagrin¹, Neil Feeder², Colin Groom² and Suzanna Ward²

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Union Rd. Cambridge UK CB2 1EZ

The Cambridge Structural Database (CSD) now contains over 800,000 entries describing a vast array of crystal structures, from small drug-like compounds to massive metal-organic frameworks. This collection of structural information can be used to answer questions about stability, solubility, catalysis and more. This talk will feature several short stories of research success underpinning crystal engineering and our understanding of emerging materials from f-element complexes to rational drug design.

Oral Presentation

Flexible Peptide Microporous Framework

Aaron J. Smith, Melissa G. Ignacio, Sarah Hollywood and Dmitriy V. Soldatov*
University of Guelph, Department of Chemistry,
Guelph, ON, Canada N1G 2W1

When studying guest removal from a microporous framework, having the structure adapt to change instead of collapse of the framework or no change except for empty cavities, is less common. Recently our group discovered that trileucine – alcohol inclusion compounds however do demonstrate this uncommon behaviour, prompting a thorough analysis of the structures and flexibility of this unique series. Four new inclusion compounds of trileucine with ethanol, propanol, isopropanol and butanol were analysed. Extensive work was done to model these disordered systems using single crystal XRD analysis data. All structures display a layered motif with the guest

alcohol species in the interlayer space. However instead of head to tail hydrogen bonded sheets, peptides are bound 90 degrees to one another, still maintaining a 2D hydrogen bonded layer. Between these layers the leucine R groups form cavities in which the guest alcohol molecules are included. Looking at the entire series there are only slight changes in the overall structure when different alcohol molecules are incorporated, as only the interlayer distance expands significantly to accommodate the increase in guest size. Besides guest size, guest occupancy in the structure was also studied. This was done through thermogravimetric analysis (TGA) in combination with powder XRD analysis in order to analyze changes in the overall structure of the trileucine ethanol inclusion compound. Shifts in the resulting powder XRD lines show an adjustment in the interlayer distance when guest molecules left the structure, demonstrating that instead of collapse or rigidity, this structure changes as guest is lost. Further this change was in the interlayer dimension illustrating that it is the most flexible part of the entire structure.

Oral Presentation

Tailoring materials properties of polyaromatic 1,3,5-triazine derivatives with symmetric and non-symmetric substitution patterns

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

Department of Chemistry and Biochemistry,
University of Windsor

The electron deficient 1,3,5-triazine core has been typically used to generate donor- π -acceptor compounds where each peripheral arm acts as a subchromophore. Here, low-symmetry triazines have been developed with an atypical donor- π -acceptor structure where the triazine core is used as a π -bridge between meta-substituted donor and acceptor groups. These highly soluble non-symmetric triazine dyes form soft crystalline or disordered crystalline phases depending on their specific substitution patterns. One compound with meta-positioned strong donor and acceptor groups exhibits an unusual intramolecular charge transfer interaction, which was investigated in more detail by UV-vis spectroscopy studies and TD-DFT calculations. Also presented are several symmetric triazine derivatives that exhibit self-assembly into uncommon nematic discotic liquid crystalline phases. This occurrence is explained with a frustration between the optimization of

intermolecular interactions and the minimization of free volume.

Oral Presentation

Supramolecular Materials Based on Short Peptides: Structure, Stability and Solid State Reactivity

Dmitriy V. Soldatov*, Andy Tsang, Aaron J. Smith, Farukh I. Ali and Melissa G. Ignacio

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

The ability of peptides to form various supramolecular entities defines their role as the main building element of life. At the same time, these versatile molecules are rarely used in the design of supramolecular solid materials. Research conducted in our group focuses on the creation and study of crystalline inclusion compounds and co-crystals where short peptides are utilized as the main structural unit.

Our recent findings reveal an outstanding ability of short peptides to form H-bonded architectures incorporating molecules of a second kind. In some cases the architecture acts as a host framework, with the second molecule accommodated in cavities as a guest. Some of these frameworks demonstrate a remarkable flexibility not seen in most other host materials. This flexibility appears to be an essential factor allowing the peptide framework to survive drastic changes in the crystal structure as the guest molecules are replaced or removed from the cavities. In other cases the molecule of a second kind becomes an integral part of the H-bonded architecture in the so-formed co-crystals of peptide and a second molecule. Our research focuses on the structural aspects of all these materials, their thermodynamic and kinetic stability, and their potential uses in solid state organic synthesis or other applications.

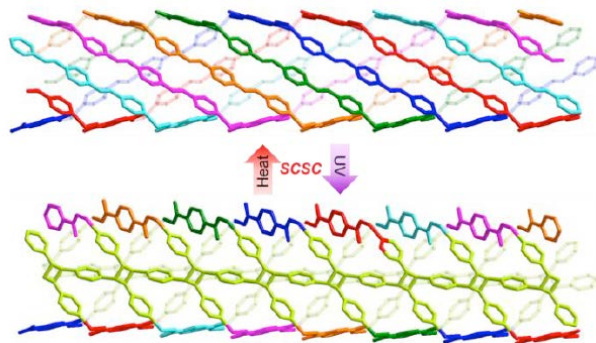
One recent example of our research is the solid state cyclization of diglycine and the use of the produced cyclic diglycine as a co-crystallization agent in the formation of pharmaceutically relevant co-crystalline materials. Our screening experiments conducted for the peptide showed selective formation of co-crystals with only few among a wide range of organic molecules tested. The peptide – sesamol pair was one of such successful combinations subjected to a detailed study to reveal the features of the crystal structure, thermodynamic stability and possible driving forces leading to the formation of this co-crystal.

Oral Presentation

Solid State Photo-Reactivity of Metal Complexes, Coordination Polymers and Metal-Organic Frameworks Under UV Light

J.J. Vittal

Department of Chemistry, National University of Singapore



For the past several decades [2+2] cycloaddition reaction has been studied extensively among the solid-state photochemical reactions. The classical work of Schmidt and co-workers in 1960's indeed paved both solid-state organic photochemistry and crystal engineering. The concept of aligning a pair of olefin bonds for photodimerization reaction goes beyond the organic molecules to successfully design photoreactive metal complexes, coordination polymers (CPs) and metal-organic frameworks (MOFs). The formation of cyclobutane rings and its reversible cleavage back to a pair of olefin bonds in the solid state could be used for making advanced materials for optical data storage, sensing, controlled guest release, pore size and surface functionalization in CPs and MOFs. Our laboratory has been interested in designing photoreactive crystals that can undergo solid state structural transformation by [2+2] cycloaddition reactions under UV light. These include structural transformation between different coordination polymers, post-synthetic modifications, polymerization of metal complexes, polymerization of organic ligands inside MOFs via [2+2] cycloaddition reactions forming hybrid structures comprising both organic and coordination polymers photosensitive behavior of metal complexes during photodimerization process under UV light, reversible formation and cleavage of cyclobutane rings in MOFs, and unusual [2+2] cycloaddition reactions between phenyl and olefin bonds. In this talk some of the recent developments in this area from our laboratory will be presented.

[1] R. Medishetty, J.J. Vittal, "Metal-organic frameworks for photochemical reactions", Editors: B Chen, G. Qian, Struct. & Bond. 2015, 157, 105-144.

[2] A. Chanthapally, J.J. Vittal, "Photoreactive Frameworks", "Metal-Organic Framework Materials", Editors: L.R. MacGillivray, C.M. Lukhart, John Wiley, 2014, 135-157.

[3] R. Medishetty, I.H. Park, S.S. Lee SS, J.J. Vittal, "Solid-state polymerization via [2+2] cycloaddition reaction involving coordination polymers", Chem. Commun.2016, 51, 3989-4001.

Oral Presentation

Reversible Mechanical Protection: A method to create novel Metal-Organic Frameworks / PROTO – *improve your science*

V. Nicholas Vukotic^{1,2}, Steven J. Loeb¹, Michael Brauss²

1. University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, Canada

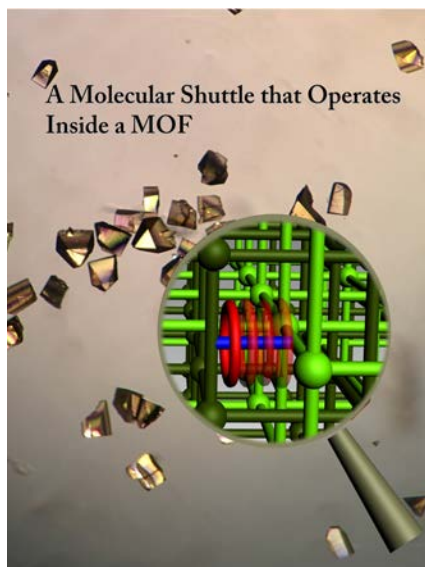
2. PROTO Mfg. Ltd., 2175 Solar Crescent, Oldcastle, ON, Canada, info@protoxrd.com

The development of functional materials such as metal-organic frameworks (MOFs) is an expanding area of research. The use of mechanically interlocked molecules (MIMs) as linkers in MOFs has shown that these components allow for the study of dynamics such as rotation and translation in the solid state, which was not previously possible. As a consequence of these studies another potential application of interlocked molecules became apparent. The ability to use the large macrocyclic component as a protecting group in the construction of novel MOFs and removing the macrocyclic component after by post-synthetic modification of the material. This presentation will describe the current work towards this application. This will be followed by a brief presentation by the primary event sponsor PROTO.

Oral Presentation

Installing Wheels and Crossbars between Interpenetrating Crystal Lattices

Kelong Zhu, Christopher A. O'Keefe, V. Nicholas Vukotic, Robert W. Schurko* and Stephen J. Loeb*
University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, Canada N9B 3P4



Metal-Organic Frameworks (**MOFs**) built from elongated organic linkers tend to interpenetrate. This phenomenon of interpenetration greatly reduces the pore size and thus the available space within the MOF structure. However, the interpenetration can be found useful in creating Metal-Organic Rotaxane Frameworks (**MORFs**) which contains a robust framework with dynamic components that can spin or translocate inside the material. Variable temperature ^{13}C CP-MAS SSNMR and ^{13}C 2D EXSY experiments demonstrated that in one of these materials the macrocyclic wheel can undergo a rapid to-and-fro (shuttling) motion along a 'crossing bar' built between struts of the interpenetrated frameworks. Thus, for the first time, we demonstrated that the translational motion of a molecular shuttle, can be organized, initiated and made to operate inside a crystalline, solid state material.

1. H. X. Deng, M. A. Olson, J. F. Stoddart, O. M. Yaghi, *Nat. Chem.*, **2010**, 2, 439–443
2. V. N. Vukotic, S. J. Loeb, *Chem. Soc. Rev.*, **2012**, 41, 5896–5906
3. K. Zhu, C. A. O'Keefe, V. N. Vukotic, R. W. Schurko, S. J. Loeb, *Nature Chem.*, **2015**, 7, 514–519

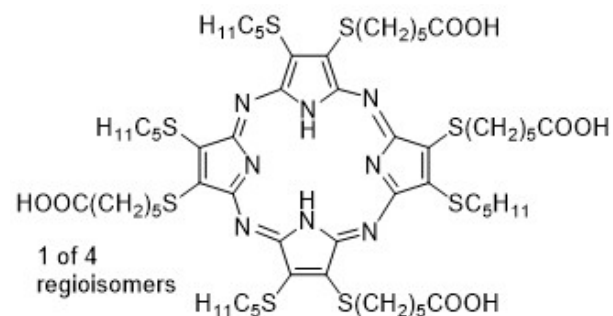
Posters

Poster Presentation #1:

Truly Amphiphilic Octa-Alkylthio Substituted Tetraazaporphyrin Derivatives with Four Terminal Carboxylic Acid Groups

Elmahdy Abdulhamied, Sarah Tran, and S.Holger Eichhorn*

University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, Canada N9B 3P4



Most known octa-alkylthio substituted tetraazaporphyrins (TAPs) have eight identical groups because their synthesis is much more straightforward. The generation of more amphiphilic TAPs, however, requires the attachment of at least two different types of substituents, one of hydrophilic and one of hydrophobic character. Amphiphilic TAPs are important building blocks for the formation of thin films by the LB and other techniques and the incorporation of TAPs into biological structures such as cell membranes. Presented here is the synthesis and properties of the first TAP containing four hydrophobic alkyl chains and four alkyl chains terminated with polar carboxylic acid groups. The synthetic approach required the development of a step-wise alkylation of sodium maleonitriledithiolate, which was best achieved by flow chemistry rather than batch reactions. The free-base TAP shown below was then prepared by the established cyclization in Mg propanolate. Its properties, such as solubility, thermal stability, and arrangement at interfaces, will be reported and compared to previously studied symmetric TAP derivatives with eight terminal carboxylic acid groups.¹

1. Ahmida, et al., *Soft Matter* 2013 (9,3) 811

Poster Presentation #2:

1,2,5,6-Tetrathiocins As Ligands: A New Approach to Metal Dithiolene Complexes

Zeinab S. Ahmed, Justin D. Wrixon and Jeremy M. Rawson*

University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, Canada N9B 3P4

Transition metal dithiolene complexes act as useful building blocks for diverse materials applications such as organic light emitting diodes, solar cell technologies, next-generation quantum computing applications, and as models for the active sites of

biologically important enzymes. Previously we have reported the oxidative addition of readily accessible tetra-methoxy-dibenzo-1,2,5,6-tetrathiocin (1) to zero-valent transition metals as a new approach to these complexes.¹⁻² Here we extend this process to include a wider range of tetrathiocins and explore their reactivity and substituent effects on the redox properties of the complexes.

1. J.D. Wrixon, J.J. Hayward, O. Raza and J.M. Rawson, *Dalton Trans.*, **2014**, 43, 2134.
2. J.D. Wrixon, J.J. Hayward and J.M. Rawson, *Inorg. Chem.*, **2015**, 54, 9384.

**Poster Presentation #3:
Synthesis and Surface Characterization of Novel Gold Nanoparticles Coated by a Cationic WS-TEMPO**

Aisha Alsaleh and Jeremy Rawson*

Department of Chemistry and Biochemistry,
University of Windsor, Windsor, ON, Canada
N8Y3E5

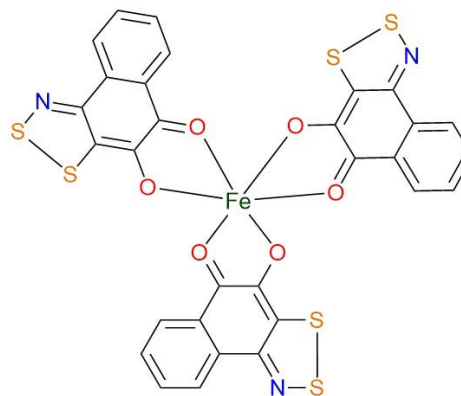
This paper reports the synthesis gold nanoparticles coated by a cationic WS-TEMPO (2, 2, 6, 6-Tetramethyl-4-[1-oxo- 6-(triethylammonio) hexylamino]-1-piperidinyloxy) as well as their surface characterization using EPR, Raman, IR and UV-Visible spectroscopies. The EPR spectra reveal that the radical is adsorbed onto the surface of the gold nanoparticles and the UV/vis spectra show that the plasmon surface band was blue shifted, indicating that the nanoparticles are stable when capped with radical. Kinetic studies reveal the blue-shift process appears second order, suggesting that the blue shift is associated with nanoparticle aggregation.

**Poster Presentation #4:
Switchable Materials using 4,5-Dioxonaphtho [1,2-d][1,2,3]dithiazolyl**

Danielle R. Dinsdale, Chad S. Smithson, and Kathryn E. Preuss*
University of Guelph, Department of Chemistry,
Guelph, ON

Spin crossover (SCO) and valence tautomeric complexes are quintessential examples of switchable molecular materials. SCO can occur for octahedral complexes of d^4 - d^7 1st row transition metals, where there can exist two different electronic states, low spin and high spin. Valence tautomerism involves an intramolecular electron transfer from the metal centre to a redox active

ligand. In both cases, the different spin states can be accessed through external perturbation (temperature, irradiation) and depending on the history, can confer a memory effect on the system, which is of high importance for practical application in memory, sensing, or switchable devices.



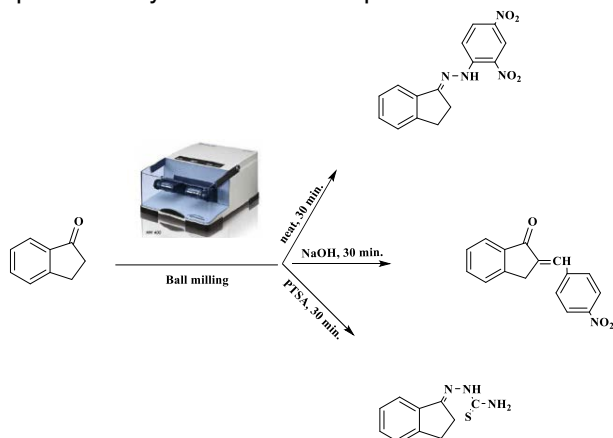
One of the current aims of SCO research is enhancing thermal hysteresis by increasing intermolecular interactions. This challenge may be met using thiazyl radicals, in particular using the thiazyl-based ligands developed by the Preuss group. 4,5-Dioxonaphtho[1,2-d][1,2,3]dithiazolyl, (o-DTANQ), is one such ligand that has been synthesized and characterized in the 1⁺, 0, and 1⁻ oxidation states by a previous group member. Crystal structures of the coordination complexes of the closed shell anion with Fe³⁺, Ga³⁺, and Sb⁵⁺ exhibit many intermolecular interactions through electrostatic contacts, while the neutral radical itself is able to co-crystallize with the protonated closed shell anion ligand, suggesting that multiple oxidation states can co-exist in the solid state. Current progress on the synthesis and characterization of materials created using o-DTANQ will be presented.

**Poster Presentation #5:
Solvent-free transformations of organic and pharmaceutical materials**

Ahmed Fekri and Tomislav Friščić
Department of Chemistry, Faculty of Science,
Mansoura University, Mansoura, Egypt and
Department of Chemistry, McGill University,
Montreal, Canada

The use of ball milling mechanochemistry to induce reactions between solids (mechanochemical synthesis) is rapidly emerging into a general and powerful route for the clean synthesis of molecules

and materials.[1] Whereas the elimination of bulk solvents in mechanochemistry offers an opportunity to vastly reduce the liquid waste streams associated with academic research and industrial manufacture, it also enables new, previously not reported transformations[2] to take place quickly, quantitatively and at room temperature.



One of the most attractive applications of mechanochemistry (and Green Chemistry in general) is in the context of active pharmaceutical ingredients (APIs, drugs) and derivatives (e.g. prodrugs), substances of primary importance for the pharmaceutical industry.

As a part of our research effort[3] towards the development of a clean approach to the synthesis of drugs, termed medicinal mechanochemistry,[4] we now report the mechanochemical syntheses of indanones, molecular structures found in anti-inflammatory, analgesic, anti-microbial and antiviral agents.

[1] James et al. Chem. Soc. Rev. 2012, 41, 413-447.

[2] Tan et al. Angew. Chem. Int. Ed. 2014, 53, 9321-9324.

[3] Tan et al. Chem. Commun. 2014, 50, 5248-5250.

[4] Tan, Loots and Frišćić, Chem. Commun. 2016, 52, DOI:10.1039/C6CC02015A

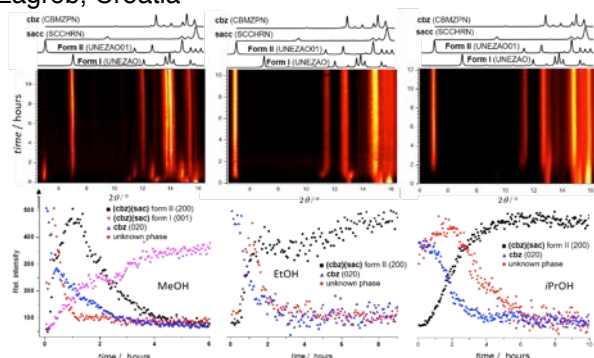
Poster Presentation #6:

A simple set-up for in situ monitoring of vapour-induced reactions of pharmaceutical organic solids using a benchtop powder X-ray diffractometer

Igor Huskić,¹ Jan-Constantin Christopherson,¹ Krunoslav Užarević,² Tomislav Frišćić*,¹

1. Department of Chemistry, McGill University, 801 Sherbrooke St. W. H3A 0B8 Montreal, Canada.

2. Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia



Cocrystals of active pharmaceutical ingredients (APIs) and their polymorphs are being intensely investigated for their role as advanced forms for drug delivery, in particular for their potential to improve the solubility, solid-state stability and bioavailability of drugs, and bring in new intellectual property. It is, therefore, not surprising that the discovery and development of new methods to screen for and synthesize cocrystal and polymorphs is a highly active area of pharmaceutical R&D. In that context, solvent-free or solvent-reduced techniques, such as liquid-assisted grinding mechanochemistry and solvent-mediated phase transformations of solids have garnered interest.^{1,2} However, perhaps the simplest and cleanest way to achieve transformations of molecular solids is through vapour-assisted transformations, known as vapour digestion or accelerated aging.^{3,4}

We now describe a simple setup for in situ continuous monitoring of vapour-induced transformations of organic solids using a benchtop X-ray powder diffractometer. As opposed to other commercially available, often quite expensive set-ups that usually only allow for water vapour atmosphere, this set-up provides a simple and inexpensive method to directly monitor the structural changes during accelerated aging reactions. Proof-of-principle application of this set-up to model pharmaceutical cocrystals reveals complex reactivity, transformations of reaction intermediates within minutes and novel, previously unreported phases.

1. S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Frišćić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell Chem. Soc. Rev. 2012, 41, 413B

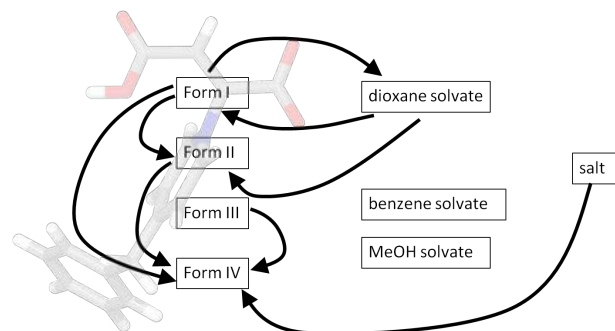
2. I. Sarceviča, L. Orola, K. P. Nartowski, Y. Z. Khimyak, A. N. Round and L. Fábíán, *Mol. Pharm.* 2015, 12, 2981.
3. J. Tian, S. J. Dalgarno, J. L. Atwood, *J. Am. Chem. Soc.* 2011, 133, 1399.
4. D. Braga, S. L. Giaffreda, F. Grepioni, and M. R. Chierotti, *CrystEngComm* 2007, 9, 879.

Poster Presentation #7:

Polymorphism, interconversion and porosity of a benzylpyridine-functionalized zwitterion

Leigh Loots,¹ J.P. O'Connor,² Tanya le Roex² and Delia A. Haynes²

1. Department of Chemistry, McGill University, 801 Sherbrooke St. W., H3A 0B8 Montréal, Canada
2. Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Stellenbosch 7600, South Africa



Zwitterions are most familiar in the form of amino acids in biological systems, but they are also well-established, and often highly reactive, intermediates in organic synthesis. In a recent investigation into cocrystallization of organic dicarboxylic acids and dibases we serendipitously discovered a series of pyridinium-derived zwitterionic compounds as crystalline solids.¹ Due to the awkward shape and strong hydrogen bonding potential of these zwitterions, we anticipated that they might prove to be good building blocks for organic hosts or porous materials. To this end, the solid-state behavior of one of these zwitterions – (2Z)-2-(4-benzylpyridinium-1-yl)-3-carboxy-1-hydroxyprop-2-en-1-olate – has been investigated in detail.² This molecule has been isolated in four polymorphic forms as well as three solvated crystal structures. Single-crystal as well as powder diffraction were used in conjunction with thermal analysis to investigate the properties and relationships between the different forms obtained. Solvent exchange and conversion experiments were performed as well as simple porosity studies.

1. L. Loots, D.A. Haynes, T. le Roex, *New J. Chem.*, 2014, 38, 2778.
2. L. Loots, J.P. O'Connor, T. le Roex, D.A. Haynes, *Cryst. Growth Des.*, 2015, 15, 5849.

Poster Presentation #8:

Solid State Phase Transitions of Lanthanide-Radical Complexes: Breaking the Pancake Bonds

Michelle B. Mills, Mohamed Ghazzali, Dmitriy V. Soldatov,* and Kathryn E. Preuss*

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

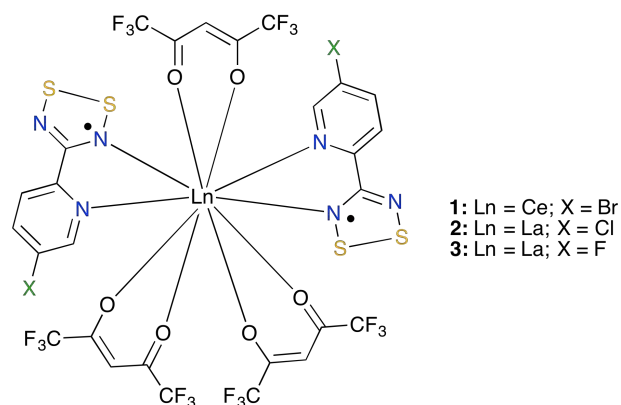


Figure 1: Line drawing of Ln(hfac)₃(X-pyDTDA)₂ complexes

We have recently reported¹ a radical-La(III)-radical coordination complex, La(hfac)₃(pyDTDA)₂, where reversible pancake bonding between thiazyl radicals leads to switchable magnetic properties in the solid state; hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-; pyDTDA = 4-(2'-pyridyl)-1,2,3,5-dithiadiazolyl. Pancake bonds 'rupture' in a two-step sequence with increasing temperature, accompanied by small changes in geometry and changes in magnetic properties, and a re-entrant phase transition is observed. A theoretical model has been developed that predicts this phase transition behavior. The temperature at which the phase transitions occur can be tuned by varying the lanthanide ion (La-Nd) in an isostructural series. Here we report preliminary results of recent attempts to generate new systems that undergo phase transitions similar to La(hfac)₃(pyDTDA)₂, by making variations to the structure of the thiazyl radical species. A series of Ln(hfac)₃(X-pyDTDA)₂, where X refers to the 5'-Br,² 5'-Cl, and 5'-F derivatives of pyDTDA (see figure 1) have been synthesized and characterized. Single crystal and powder X-ray data for three species at a variety of temperatures is presented.

1. Fatila, E. M.; Mayo, R. A.; Rouzières, M.; Jennings, M. C.; Dechambenoit, P.; Soldatov, D. V.; Mathonière, C.; Clérac, R.; Coulon, C.; Preuss, K. E. *Chem. Mater.*, **2015**, *27*, 4023.
2. Mills, M. B.; Hollingshead, A. G.; Maahs, A. C.; Soldatov, D. V.; Preuss, K. E. *CrystEngComm*, **2015**, *17*, 7816.

**Poster Presentation #9:
Exploring New Derivatives of 1,2,4-benzothiadiazines and their Coordination Chemistry**

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

Department of Chemistry and Biochemistry,
University of Windsor, Windsor, ON, Canada N9B 3P4

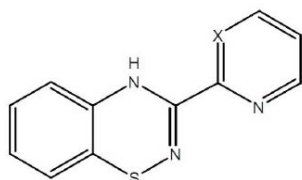


Fig. 1 Molecular structure of 1,2,4-benzothiadiazine, where X = CH, N.

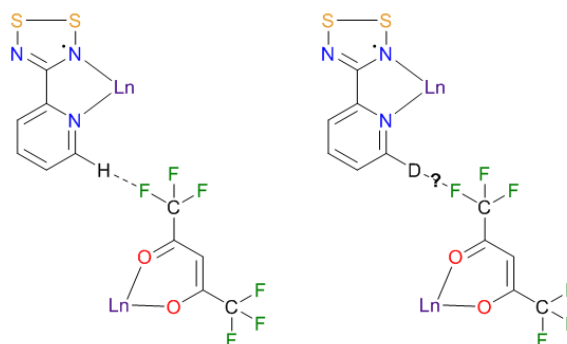
The family of 1,2,4-benzothiadiazines in various oxidation states have attracted attention for both materials and pharmaceuticals applications.¹ The development of polydentate N-donor ligand sets with tunable coordination chemistry is highly desirable for the construction of new functional materials.² We have developed a range of derivatives of the ligand in which the group at the C(3) position is varied to include pyridyl and pyrimidine rings (Fig. 1). Their reactivity towards first row transition metal ions is discussed.

¹ E. R. Clark, M. U. Anwar, B. J. Leontowicz, Y. Beldjoudi, J. J. Hayward, W. T. K. Chan, E. L. Gavey, M. Pilkington, E. Zysman-Colman and J.M. Rawson, *Dalton Trans.*, 2014, 43, 12996.

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

**Poster Presentation #10:
Exploring the Re-entrant Phase Transition Behaviors of Lanthanide-Thiazyl Radical Complexes**

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The Preuss research group has been exploring the chemistry of complexes of trivalent lanthanide metals with the bidentate spin-bearing ligand: 4-(2'-pyridyl)-1,2,3,5-dithiadiazolyl (pyDTDA). The 2:1 ligand to metal complexes with the general formula $\text{Ln}(\text{hfac})_3(\text{pyDTDA})_2$ exhibit re-entrant phase transition behavior in the solid state¹. It is hypothesized that this behavior can be influenced by contributions of various intermolecular interactions. One such interaction is a C-H...F-C contact between neighboring molecules in the solid state. We are probing the importance of this weak hydrogen bond by replacing the hydrogen atom involved with deuterium. It is hypothesized that, if this hydrogen bond is actually the primary component of the weak elastic interactions in the solid state structure, the temperature at which the phase transition occurs will be altered because the deuterium atom will significantly weaken the hydrogen bond enthalpy. Thus we aim to chemically tune the phase transition temperature, as well as provide evidence for the existence of weak C-H...F-C hydrogen bonding interactions in the solid state, a concept that has been gaining popularity in recent literature².

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**Poster Presentation #11:
Unusually Stable Gold Nanoparticles Protected by Large Dithiol Ligands**

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Gold nanoparticles (AuNPs) protected by a monolayer of organic ligands have been extensively studied over the past decades due to their potential applications in electronics, catalysis, drug delivery, optics, and biotechnology. One shortcoming of this approach is the limited chemical and thermal stability of AuNPs when protected with conventional aryl- or alkyl thiolate ligands. Presented here are AuNPs of high chemical and thermal stability that are protected by a specially designed dithiol ligand of overall hydrophobic character. Thermal stability of was monitored in solution and the solid phase by variable temperature UV-Vis spectroscopy, DSC, and TGA whereas chemical stability was probed by cyanide etching in solution and compared to reference AuNPs protected with octadecane thiolate. This new dithiolate ligand was also designed for the preparation of amphiphilic (Janus-type) AuNPs when co-deposited with a hydrophilic dithiolate ligand.

Poster Presentation #12:

Enantiomer-specific oriented attachment of guanidine carbonate crystals

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Oriented attachment, a non-classical crystallization phenomenon, describes the spontaneous self-assembly of adjoining crystals with common crystallographic orientations.¹ Introducing chiral recognition between crystals during oriented attachment enables enantiomer-specificity and the formation of homochiral structures. Herein, we report efficient enantiomer-specific oriented attachment for suspended crystals of guanidine carbonate to form mesoscale homochiral or enantioenriched aggregates under boiling or shaking conditions.² These aggregates display polyhedral macrostructures and their chirality was monitored using circular dichroism and polarized light microscopy.

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Poster Presentation #13:

Developing Iron(II) Spin Crossover Compounds Using Pyrazolyl Borate and Thiazyl Radical Ligands

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Spin-crossover (SCO) is a reversible change from high-spin to low-spin as a function of external parameters (temperature, irradiation, etc.) that occurs in some d^4 - d^7 metal complexes. Compounds exhibiting SCO and related phenomena have potential applications as molecular switches or data storage materials. Fe(II) SCO complexes are by far the most well-understood. Recently, poly-pyrazole borate ligands were shown to be effective in inducing SCO properties in Fe(II) species, e.g., $\text{Fe}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{bpy})$ and $\text{Fe}(\text{Tp})_2$.^[1,2] Our research group has developed a series of paramagnetic thiazyl-based ligands. These ligands can be viewed as radical analogues of 2,2'-bipyridine, 1,10-phenanthroline, and similar well-known diamagnetic ligands. Paramagnetic ligands can be used to enhance exchange coupling between paramagnetic metal ions, making them ideal for developing magnetic materials. Furthermore, because of their capacity to form dimers, our thiazyl-base ligands can be used as supramolecular synthons. The features of our ligands make them ideal candidates to induce or enhance hysteresis in Fe(II) SCO species, thereby creating materials with non-volatile data storage capabilities. Here, we present the synthesis and initial characterization of complexes $\text{M}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{L})$, where $\text{M} = \text{Fe}, \text{Mn}, \text{Ni}, \text{Zn}$ and $\text{L} = \text{bpy}, \text{pyDTDA}, \text{betaDTDA}, \text{phenDTA}$. IR spectroscopy and PXRD show promising results. We are currently learning how to grow single crystals of these species for structural and magnetic characterization.

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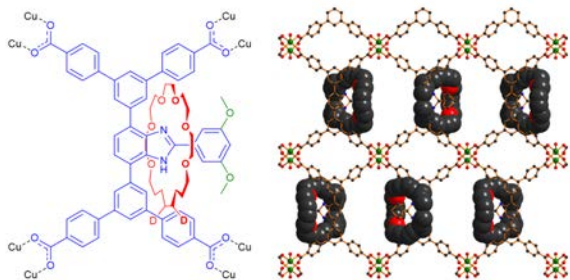
Poster Presentation #14:

T-shaped [2]rotaxane ligands for MOFs: a new design

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An evolution of the isophthalic T-shaped [2]rotaxane ligand has been synthesised. These new extended ligands, first produced by the Mukherjee group^[1], exhibit a high thermal stability with large accessible void space and pore volumes.



The basic organic skeleton was modified to contain a large [2]rotaxane stoppered with two methoxy groups. This new ligand was successfully incorporated into a copper containing metal organic rotaxane framework (MORF) with the same reported topology as shown by single crystal X-ray diffraction.

Poster Presentation #15:
¹H, ¹³C, and ¹⁵N Solid-State NMR Study of Halogen Bonded Frameworks Featuring Nitrogen-Containing Heterocycles

P.M.J. Szell, L. Brunet, R. Gill, S. Wan and D.L. Bryce*

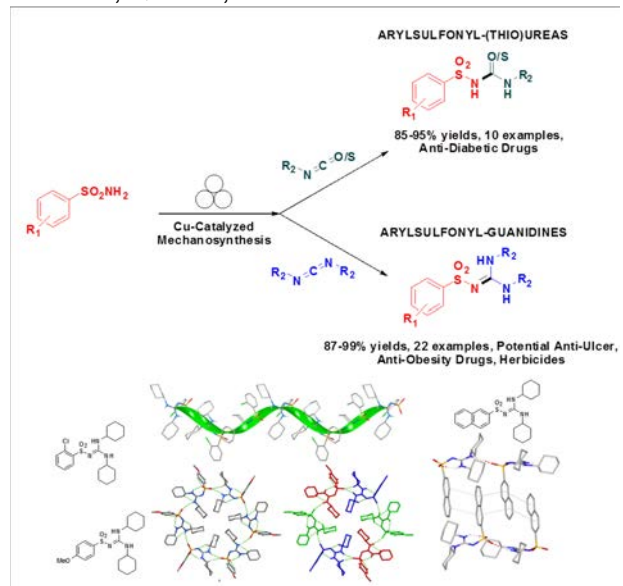
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Halogen bonding is a non-covalent interaction between the electrophilic region of a halogen (sigma-hole) and a Lewis base, which has gained popularity in the field of supramolecular chemistry. Despite recent advancements, halogen bonding remains relatively uncharacterized by NMR. Here, we report on a study of the chemical environment of the halogen bond by applying ¹H, ¹³C, and ¹⁵N solid-state NMR spectroscopy. Single crystal X-ray diffraction was used to characterize the frameworks formed between a series of fluorinated halogen bond donors (1,4-diiodotetrafluorobenzene, and 1,3,5-trifluoro-2,4,6-triiodobenzene) and several nitrogen-containing heterocycles (urotropin, 2,3,5,6-tetramethylpyrazine, acridine, phenazine). A series of novel crystal structures has been obtained which reveal the presence of a strong halogen bond between iodine and nitrogen.

Poster Presentation #16:
Mechanochemistry as a Tool for Reaction Discovery: From Novel Copper-Catalyzed Mechanochemical C-N Coupling Reactions to Unique Crystal Structures

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We recently demonstrated a simple, solvent-free mechanochemical approach for the synthesis of diverse sulfonyl-urea compounds, a successful class of drugs for combating Type II diabetes, by copper-catalyzed coupling of poorly nucleophilic sulfonamides and isocyanates.[1] Further exploration of this mechanochemical methodology revealed the first direct coupling of arylsulfonamides with carbodiimides, affording the one-step, solvent-free synthesis of arylsulfonyl-guanidines.[2] Attempts to reproduce this novel coupling in solution have so far failed. Whereas these results demonstrate mechanochemistry as a means to address the demands of pharmaceutical industries for cleaner and more efficient synthetic procedures,[3] they also demonstrate mechanochemistry as a versatile tool for reaction discovery, revealing synthetic approaches that are difficult or perhaps even impossible to achieve under conventional solution-based conditions.[4] The ability to access arylsulfonylguanidines rapidly, and on gram scale, also provides an opportunity to conduct a systematic investigation of the relative importance of hydrogen-bonding structural motifs in their solid-state structures.

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Poster Presentation #17:

Dynamic Interlocked Metal-Organic Framework of Unsymmetrical Rotaxane

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Mechanically interlocked molecules (MIMs), such as rotaxanes and catenanes have many potential applications as molecular machines and nanoscale devices.¹ We are interested in the incorporation of these interlocked systems into solid state materials via the formation of metal-organic rotaxane frameworks (MORFs). MORFs are of particular interest because of their dense organization of the molecular switches in the solid state. Recently, we developed a prototype material (UWDM-1) and showed using ²H and ¹³C CPMAS SSNMR that the wheel component of a rotaxane was capable of dynamic motion inside a MOF.² We have now synthesized an extended and unsymmetrical version of this type of rotaxane linker that allows for an increase in the void space inside the MOF, when compared to UWDM-1. This should allow for a more ordered lattice and an increase in free volume within the MOF.³ The structure of this material and the study of its dynamics by ²H SSNMR will be presented.

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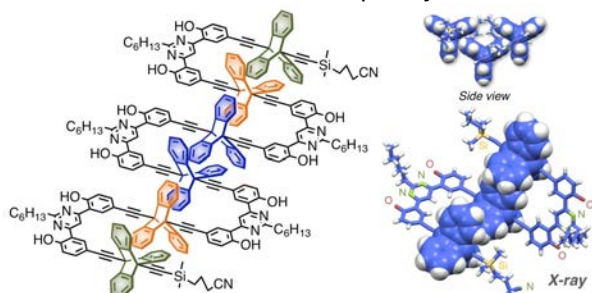
Poster Presentation #18:

Dynamic Motion of Multiple Molecular Spur Gears in Solution and Solid States

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Molecular Gears, composed of intermeshed trypticene units, are expected to be a key component of molecular machine systems in the future. However, research on the molecular spur gears, which is intermeshed in parallel, has been limited due to its structural complexity.



In addition, previous examples did not observe the gearing motion by VT NMR study in solution, because the rotational frequency of the trypticene units is faster than the NMR time scale. In this study, we have successfully synthesized molecular spur gears with multiple Tp units connected by a 4,6-bis(2-hydroxyphenyl)pyrimidine group. This backbone can maintain its U-shaped conformation by intramolecular OH...N hydrogen bonds. These compounds were fully characterized by NMR, IR, MS and Single Crystal X-ray Crystallography. Also, we have observed the dynamic motion of the molecular gears in solid state and in solution by solid-state NMR, DFT calculations and VT-NMR studies.

Poster Presentation #19:

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

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One of the most successful strategies in the design of new host materials is the creation of non-self-complementary molecules. Some irregular geometries facilitate packing which is more efficient in the presence of a guest than in the guest-free material.¹ For example, molecules with trigonal symmetry, e.g. the 'trefoil' shaped triphenylmethane, are known to possess clathratogenic properties.² Our focus is on developing a new class of organometallic clathrate sorbent materials based on antimony(III) and (V) compounds. Using an antimony centre allows for greater design flexibility than in typical carbon-

based materials because Sb adopts different geometries in the III and V oxidation states. Several antimony-based inclusion compounds are already known, covering a wide range of possible guest molecules.^{3,4} This project represents one of the earliest looks into the design, synthesis and characterization of main group clathrates for potential use in industrial applications.

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- (3) Sharutin, V. V.; Senchurin, V. S.; Sharutina, O. K.; Akulova, E. V. *Russ. J. Gen. Chem.* **2008**, 78 (12), 2344.
- (4) Kunkel, F.; Harms, K.; Kang, H.; Massa, W.; Dehnicke, K. Z. *Naturforsch. B Chem. Sci.* **1997**, 52 (2), 193.

Poster Presentation #20:

Mechanochemical Production of Halogen-Bonded P=O...I-C Solids and Characterization by Solid-State NMR Spectroscopy

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Mechanochemical liquid-assisted grinding (LAG), which requires only a few drops of solvent and overcomes the limitation of solubility, can provide a more environmentally friendly and effective method to prepare co-crystals. Here, we synthesized a series of novel halogen-bonded co-crystals of two phosphine oxides (Ph₃PO and CH₃Ph₂PO) and three different iodofluorobenzene compounds (*p*-C₆F₄I₂, *o*-C₆F₄I₂, and *sym*-C₆F₃I₃) by LAG [1] and slow evaporation. The halogen bonding (XB) geometry was first characterized by single-crystal X-ray diffraction. Solid-state NMR spectroscopy is a powerful tool to characterize the electronic and molecular structure associated with non-covalent interactions by measuring various fundamental NMR parameters including electric field gradient (EFG) and chemical shift (CS) tensors.[2] We describe a combined solid-state multinuclear magnetic resonance, single-crystal X-ray diffraction, and quantum chemical calculation study of the halogen-bonded co-crystals containing P=O...I-C motifs.[3]

CS tensors extracted from ³¹P CP/MAS NMR spectra provide indirect but strong indicators of the presence of XB. Further attempts at ³¹P single-crystal NMR experiments on these halogen-bonded single crystals are presented to provide unique structural insights into the effect of halogen bonding interactions on the ³¹P CS tensor orientations. ¹⁷O-labelled halogen-bonded compounds were also prepared using enriched Ph₃P¹⁷O as a starting material. ³¹P and ¹⁷O SSNMR spectra acquired at three different applied magnetic field strengths (9.4, 11.7, and 21.1 T) provide novel correlations between the XB geometry and measured NMR parameters: CS and EFG tensors, and *J*(³¹P, ¹⁷O) coupling. Density functional theory (DFT) calculations with periodic boundary conditions on crystal structures also reveal several notable trends relating various NMR observables ($\delta_{\text{iso}}(^{17}\text{O})$, *J*(³¹P, ¹⁷O) coupling) to the normalized XB distance parameter (*R*_{XB}). An additional natural localized molecular orbital (NLMO) analysis enables an interpretation of how various orbitals contribute to the observed correlations between the NMR parameters and the value of *R*_{XB}.

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Poster Presentation #21:

Templation effects and novel ZIF structures by solid state synthesis

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In the last decade Zeolitic Imidazolate Frameworks (ZIFs), a subclass of metal-organic frameworks, have been rising in popularity, due to their diverse topologies, good thermal and chemical stability, and large pore volumes, which could enable their use for gas storage, separation of gases, and catalysis.¹ However, traditional methods are energy demanding, use large quantities of organic solvents and expensive organic nitrates, and, above all, are often irreproducible and hard to control, giving mixtures of different ZIF frameworks in often low yields.

To improve the synthetic yield and make the syntheses more environmentally friendly, we have explored several different methods for solid-state ZIF synthesis, including neat² and liquid-assisted grinding³, slurring, and modified accelerated aging⁴ procedures. We have combined these methods with the use of different organic molecular templates, showing that we can reproducibly direct the polymorphic outcome of our syntheses to the desired product by templating a specific topological motif.

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