The 5th Crystal Engineering and Emerging Materials Workshop of Ontario & Quebec

Montreal, 16-19 July 2018

CEMWOQ-5

The 5th Crystal Engineering and Emerging Materials Workshop of Ontario and Quebec

July 16-19, 2018
McGill University, Montreal, Canada

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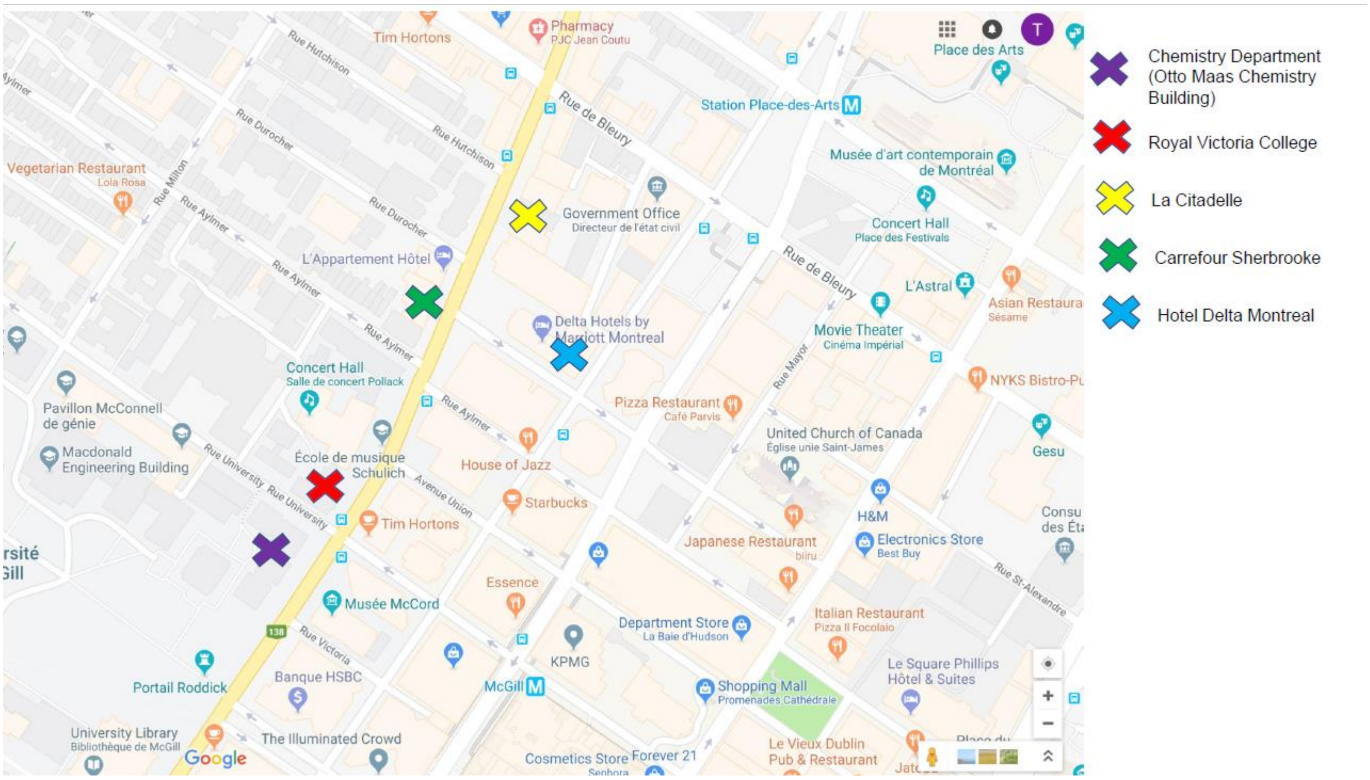
How to Get Here

The following map highlights the location of the conference venue (Chemistry Department), as well as the suggested accommodation options.



Lunches and Conference Dinner

Pizza or box lunches will be provided to participants during lunch breaks on Tuesday, Wednesday and Thursday (17-19 July).

The CEMWOQ-5 Conference Dinner will be held at the Thomson House, McGill University Graduate Students Club, on Wednesday (18 July 2018) at **7:30 pm**, which is 1 hour after the end of the poster session. The Thomson House is located a short (15-20 min) uphill walk from the Chemistry Department, so please leave yourself enough time between the poster session and the dinner to arrive timely.

If you have any particular food requirements (allergies, etc) that have not been listed in your registration forms, please e-mail us as soon as you can.

The cost of the dinner is included in the conference registration ☺

Workshop: Crystal structure solution and refinement using powder X-ray diffraction

16th July, Room 112 (Purves Lecture Hall), Otto Maass Building, Montreal

Organized by: **Luzia S. Germann** (Max Planck Institute for Solid-state Research, Stuttgart)
Mihails Arhangelskis (McGill University, Montreal)

This course gives a short introduction to crystal structure solution and refinement from powder X-ray data. We will begin with a general overview of available methods of structure solution and refinement, highlighting their advantages and limitations.

Following the theoretical introduction, we will continue with an interactive exercise on crystal structure determination from powder data using the program EXPO. For this exercise to be most useful, we would like to ask the attendees to bring their own laptops with preinstalled version of EXPO. The program is freely available for academic purposes and can be downloaded from http://www.ba.ic.cnr.it/softwareic/expo/expo2014-download/ following registration on that website (Windows, MacOS and Linux versions are available).

If you have any problems installing the software, please e-mail Dr Mihails Arhangelskis (mihails.arhangelskis@mcgill.ca)

The workshop will conclude with an interactive presentation highlighting potential difficulties encountered during structure solution and refinement. Common causes of errors and ways to avoid mistakes will be discussed.

Workshop timetable:

11:00-12:30 – Introduction into powder diffraction, Pawley and Rietveld refinement.

12:30-13:00 – Short break (coffee included)

13:00-14:30 – Demonstration of structure solution in EXPO.

14:30-15:00 – Final Exercise “What can go wrong with structure refinement”.

Meeting Program

Monday 16-Jul-18

10:00 am	–	4:00 pm	Registration
10:00 am	–	11:00 am	Registration for Workshop
11:00 am	–	3:00 pm	**Workshop –** "*Crystal structure solution and refinement using powder X-ray diffraction*"
3:30 pm	–	3:40 pm	Welcome Comments
3:40 pm	–	4:00 pm	Meeting Opening – **Dima Perepichka** (Department Chair, McGill University)
4:00 pm	–	5:00 pm	**Opening Plenary Lecture – Joel Bernstein** (New York University) "*Structural Chemistry, Fuzzy Logic and the Law*"
5:00 pm	–	5:20 pm	**Invited talk: Karthik Nagapudi** (GenenTech, Inc.) "High-throughput screening and scale-up of cocrystals, nanoparticles and amorphous solid dispersions using resonant acoustic mixing"
5:20 pm	–	5:40 pm	**Sandra Kaabel** (Tallinn University of Technology) "*Template-driven self-assembly of hemicucurbit[n]uril macrocycles in the solid state*"
5:40 pm	–	6:00 pm	**Aaron Smith** (University of Guelph) "*Old tools and new tricks in the analysis of peptide crystal frameworks*"
6:00 pm	–	6:30 pm	Reception

Tuesday 17-Jul-18

10:00 am	–	10:30 am	**Invited talk: Mario Wriedt** (Clarkson University) "*New Frontiers in Metal-Organic Frameworks: Spintronics and Tunable Gas Sorption*"
10:30 am	–	10:45 am	**Cameron Lennox** (McGill University) "*Mechanochemical synthesis of ultralight porous main-group imidazolate frameworks*"
10:45 am	–	11:05 am	**Maria Matlinska** (University of Alberta) "*Synthesis and Structural Characterization of Novel Alkaline Earth bioMOFs*"
11:05 am	–	11:20 am	Coffee Break
11:20 am	–	11:40 am	**Invited talk: Matthew Harrington** (McGill University) "*Liquid crystalline processing of high toughness bio-fibers fabricated by mussels*"
11:40 am	–	12:00	**Invited talk: Robert Schurko** (University of Windsor) "*NMR Crystallography and Solid-State NMR of the Periodic Table*"

12:00	–	12:20 pm	**Noemie-Manuelle Dorval Courchesne** (McGill University) “*Fabrication of functional protein-based materials*”
12:20 pm	–	1:30 pm	Lunch Break
1:30 pm	–	2:00 pm	**Invited talk: Ashlee Howarth** (Concordia University) “*Metal-Organic Frameworks for Adsorption and Detoxification of Hazardous Analytes*”
2:00 pm	–	2:15 pm	**Alex Stirk** (University of Windsor) “*Acid/Base Effected Dynamic Motion within a Stable fcu Zr Metal Organic Rotaxane Framework*”
2:15 pm	–	2:30 pm	**Nadia Stephaniuk** (University of Windsor) “*Inclusion Chemistry of Thiazyl and Selenazyl Radicals in MIL-53(Al)*”
2:30 pm	–	2:45 pm	**Nathan Doupnik** (University of Windsor) “*A novel bis-1,2,4-benzothaidazine pincer ligand: Synthesis, characterization and coordination chemistry*”
2:45 pm	–	3:00 pm	Coffee Break
3:00 pm	–	3:30 pm	**Invited talk: Krešimir Molčanov** (Rudjer Bošković Institute) “*Stacking of planar conjugated rings: a continuum of interactions ranging from dispersion to multicentric two-electron covalent bonding*”
3:30 pm	–	3:45 pm	**Danielle Dinsdale** (University of Guelph) “*Investigating the Reactivity of 1,2,3-Dithiadiazolyl-o-naphthoquinone Ligands Through Solvent-free Techniques*”
3:45 pm	–	4:00 pm	**Michelle Mills** (University of Guelph) “*Tuning Solid State Phase Transitions in Lanthanide-Radical Complexes*”
4:00 pm	–	4:15 pm	**Mitchell Nascimento** (University of Windsor) “*Crystal Engineering Approaches to Organic Ferrimagnets: Theory and Preliminary Results*”
4:15 pm	–	4:30 pm	Coffee Break
4:30 pm	–	5:00 pm	**Invited talk: Adam Duong** (Université du Québec à Trois-Rivières) “*Use Only What You Need and Contribute as You Can: Materials Design for Energy and Nanotechnology Applications*”
5:00 pm	–	5:20 pm	**Invited Talk: Eric McCalla** (McGill University) “*The Challenge of Understanding the Structure–Properties Relationship in Advanced Battery Materials*”
5:20 pm	–	5:40 pm	**Mike Hawkridge** (Malvern Panalytical) “*In operando data of Li-Ion batteries from XRPD laboratory diffractometers*”
5:40 pm	–	~7:00 pm	Poster Session

Wednesday 18-Jul-18

10:00 am – 10:30 am	**Invited talk: Yining Huang** (Western University) “*Probing the behaviour of gas molecules in MOFs by solid-state NMR*”
10:30 am – 10:45 am	**Mihails Arhangelskis** (McGill University) “*Towards prediction of structure, topology and stability of metal-organic frameworks*”
10:45 am – 11:00 am	**Cristina Mottillo** (Acsynam, Inc) “*Sustainable innovation meets MOF synthesis: rapid, scalable manufacture of highly porous metal-organic frameworks in* scCO$_2$”
11:00 am – 11:15 am	Coffee Break
11:15 am – 11:45 am	**Invited talk: Silvina Pagola** (Old Dominion University) “*Accessing charge transfer salt polymorphs by liquid-assisted grinding and vapor digestion: crystal structures from powders, reactant polymorphism, and solvent effects*”
11:45 am – 12:05	**Invited talk: Dmitriy Soldatov** (University of Guelph) “*Generation of cavity space in crystalline and amorphous organic solids with the help of strong hydrogen bonds”*
12:05 – 12:35 pm	**Invited talk: Karine Auclair** (McGill University) “*Solvent-Free Mechano-Enzymatic Reactions: “RAging” Biomass*”
12:35 pm – 1:30 pm	Lunch Break
1:30 pm – 2:00 pm	**Invited talk: Dominik Cinčić** (University of Zagreb) “*Metal-organic multicomponent halogen bonded solids: towards supramolecular control over structure and properties*”
2:00 pm – 2:20 pm	**Patrick Szell** (University of Ottawa) “*Cosublimation: A Rapid Route towards Halogen Bonded Cocrystals Yielding Otherwise Inaccessible Architectures*”
2:20 pm – 2:35 pm	**Daniel Therien** (McGill University) *“Using chitinase enzymes under solvent-free conditions to break down chitin”*
2:35 pm – 2:50 pm	Coffee Break
2:50 pm – 3:20 pm	**Invited talk: Christian Pellerin** (Université de Montréal) “*Photomobility of Azomaterials in the Solid State*”
3:20 pm – 3:40 pm	**invited talk: Louise Dawe** (Wilfrid Laurier University) “*A Scaffolded Approach to the Integration of Crystallography in Undergraduate Curriculum and Research*”
3:40 pm – 4:00 pm	**Fabian Hammerer** (McGill University) “*Enabling beta-glucosidase enzymatic activity under high-speed ball-milling*”
4:00 pm – 4:15 pm	Coffee Break
4:15 pm – 4:45 pm	**Invited talk: Barry Blight** (University of New Brunswick)

			“*A Swellable Polymer/MOF Composites for the Containment and Degradation of Organophosphorous Contaminants”*
4:45 pm	–	5:00 pm	**Blaine Fiss** (McGill University)
			“*Mechanochemical Functionalization of Polymers with Solid Phosphorylating Agents and Synthesis of Flame-Retardant Cellulose Nanocrystals*”
5:00 pm	–	5:20 pm	**Farukh Ali** (University of Guelph)
			“*Solid-State Green Synthesis of Diketopiperazines (DKPs)*”
5:20 pm	–	5:35 pm	**Johannes Kreutzer** (Nature Communications)
			“*Publishing in Nature and Nature Research Journals*”
5:35 pm	–	~6:30 pm	Poster Session
7:30 pm	–	10:00 pm	Dinner

Thursday 19-Jul-18

10:00 am	–	11:00 am	**Closing Plenary Lecture – James D. Wuest** (Université de Montréal)
11:00 am	–	11:20 am	Coffee Break
11:20 am	–	11:40 am	**Luzia S. Germann** (Max Planck Institute for Solid-state Research)
			“*Magic combination of X-ray diffraction with solid state NMR*”
11:40 am	–	12:00	**Invited talk: Ken Maly** (Wilfrid Laurier University)
			“*Self-Assembly of Polycyclic Aromatic Hydrocarbons in the Solid State and in Liquid Crystals for the Preparation of New Materials*”
12:00	–	12:20 pm	**Louis A. Cuccia** (Concordia University)
			“*Expanding the Scope of Viedma Ripening*”
12:20 pm			**Closing Words - Louis A. Cuccia** (Concordia University)

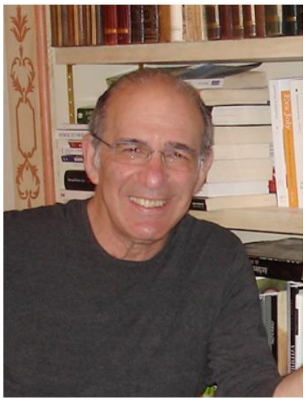
Poster List

#	Name	Affiliation	Title
1	Ryan Johannson	University of Ottawa	Non-Covalent Pnictogen-Bonded Cocrystals Formed with Mechanochemistry studied by $^{121/123}$Sb NQR Spectroscopy
2	Dominique Leckie	University of Windsor	Transition Metal Complexes of the 1,3,2-Dithiazolyl Radical
3	Kayrel Edwards	McGill University	Preparing hydrogen-bonded photo-reversible materials
4	Alicia McTaggart	Concordia University	Growth characteristics of silica-carbonate microstructures under the influence of Chicago Sky Blue Dye
5	Paola Marino and Zvart Ajoyan	Concordia University	Green Applications of Metal–Organic Frameworks
6	Matt McTaggart	Royal Military College of Canada	Confinement-induced reaction spontaneity in a water solvated nanosystem
7	Nguyen Thi Phuong Thao	Concordia University	Solid Phase Deracemization of a Chlathrate: from Mechanochemical Synthesis to Viedma Ripening of Tri-o-thymotide
8	Willem Verduyn	University of Guelph	A novel organic radical exhibiting magnetic bistability
9	Lara Watanabe	University of Windsor	Exploring the Reactivity of Tetrathiocins with d-block Metals
10	Jean-Louis Do	McGill University	“From Olefin Metathesis to the Friedländer Reaction: Mechanochemical Catalysis for the Synthesis of Nitrogen Heterocycles”
11	Igor Huskić	McGill University	“Engineering Rare Earth Oxalates for Selective Separation of Scandium from Lanthanides”
12	Patrick Julien	McGill University	Simple Binaphthol Linkers for Multifunctional Coordination Polymers and Metal Organic Frameworks
13	Filip Topić	McGill University	Steroids as coformers in cocrystallization with PAHs and heterocycles
14	Ghada Ayoub	McGill University	Mechanochemistry vs. solution growth: striking differences in bench stability of a cimetidine salt based on synthetic method
15	Shaghayegh Ostadjoo	McGill University	Salt-free Enzymatic Hydrolysis of Xylan

16	Jenny Oh	Concordia University	Spontaneous Resolution and Chiral Amplification in Co-Crystals
17	Tristan Borchers	McGill University	Developing “Soft-Bonding” Composite Materials from Hydrophylic Polymers and Azp Dys
18	Christopher J. Barrett	McGill University	Cocrystals of Azo Chromophores as Engineered Optical Materials
19	Ricky Tran	McGill University	Periodic DFT calculations for studying thermodynamic properties and Raman spectra of halogen-bonded cocrystals
20	Joseph M. Marrett	McGill University	Supercritical carbon dioxide enables rapid, clean, and scalable conversion of a metal oxide into zeolitic metal-organic frameworks
21	Shaodi Li	McGill University	Green solid-state synthesis of SIFSIX metal-organic frameworks
22	Hatem Titi	McGill University	“Mechanochemical Synthesis based on Resonant Acoustic Mixing”
23	Athena Fidelli	McGill University	Cu(II) Frameworks from a “Mixed-Ligand” Approach
24	Athanassios Katsenis	McGill University	Understanding the Thermodynamic Driving forces Underlying Mechanochemical Transformations of Metal Organic Frameworks (MOFs)
25	Daniel Therien	McGill University	Using chitinase enzymes under solvent-free conditions to break down chitin
26	Robin S. Stein	McGill University	McGill Chemistry Characterization (MC2) Facility
27	Christopher W. Nickels	McGill University	Innovations in Mechanochemistry Instrumentation
28	Guvanch Gurbandurdyyev	McGill University	Preference for *crs*-Topology in a Series of Isostructural Metal 5-Methyltetrazolates

Abstracts of Oral Presentations

Opening Plenary Lecture



Structural Chemistry, Fuzzy Logic and the Law

Prof. Joel Bernstein
Department of Chemistry (Emeritus),
Ben-Gurion University of the Negev,
Beer Sheva, Israel 84120
New York University Abu Dhabi/Shanghai

While chemistry is considered to be one of the exact sciences, much of the reasoning in the practice of chemistry is not based on absolutes – “always” and “never” – but rather on general rules and exceptions to those rules. This means that in the practice of their discipline, chemists necessarily resort to what is often called “fuzzy logic”. Some of those chemists are recruited to serve as consultants and expert witnesses in patent litigations that necessarily involve technological and scientific issues often including chemistry. As a result of the fuzzy nature of much of chemical logic, accomplished, well established chemists can find themselves on opposite sides of a courtroom, each representing what he or she honestly believes is correct science, even though in terms of the legal question to be addressed, they are diametrically opposed. In this talk I will provide examples of these aspects of the relationship between the fuzzy logic of chemistry and the role of expert witnesses in patent litigation.

Closing Plenary Lecture

Engineering New Crystalline Molecular Materials

Prof. James D. Wuest
Département de chimie
Université de Montréal, Montreal
Pavillon J.-Armand Bombardier, 5155, Chemin de la rampe
Montréal, Québec, Canada, H3S 5G4

A powerful strategy for making new molecular materials with predictably ordered structures is based on modular assembly, using components with selected geometries and an ability to take part in specific intermolecular interactions. The scope and usefulness of this strategy will be illustrated by describing the design and synthesis of modules that permit (1) the construction of hydrogen-bonded networks with permanent porosity, (2) the assembly of crystalline covalently-bonded carbon-based networks analogous to diamond and graphite, and (3) the preparation of ordered carbon-based materials with optoelectronic properties of potential use in devices such as batteries and solar cells.

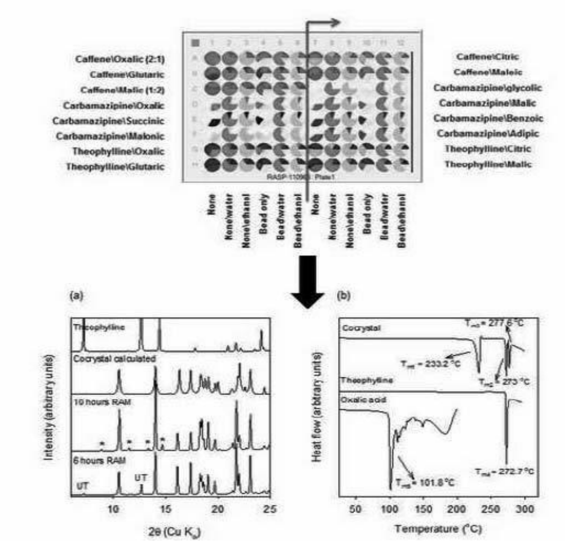
Invited Talk

High-throughput screening and scale-up of cocrystals, nanoparticles and amorphous solid dispersions using resonant acoustic mixing

Karthik Nagapudi*, Dennis Leung, Evelyn Yanez, and Colin Masui

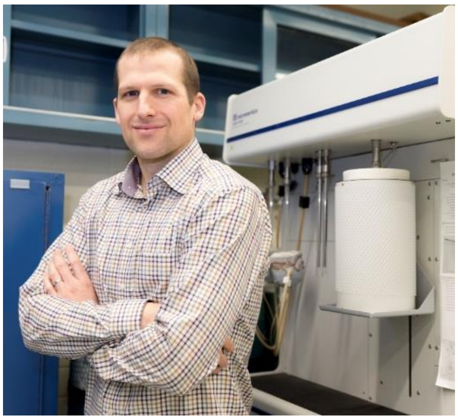
Genentech, Inc.

This talk will explore the effectiveness of resonant acoustic mixing (RAM) for screening and scale up of cocrystals and nanoparticles. 16 cocrystal systems were selected as test cases based on previous literature precedent. A 96 well plate set up in conjunction with zirconia beads was used for cocrystal screening using RAM. A success rate of 80% was obtained in the screen for plates containing solvent or solvent plus Zirconia beads. A proof of concept production of hydrated and anhydrous cocrystals of 1:1 Theophylline Citric acid system at a 400 mg scale was demonstrated using solvent and bead assisted RAM. The RAM parameters of acceleration and mixing time were optimized using a DOE approach to enable scale up of 2:1 Theophylline Oxalic acid cocrystals at an 80-gram scale with a net yield of 94%. In a similar vein, RAM can also be used for the production of nanoparticles. The utility of RAM in screening and scale up of nanoparticles will also be discussed using an internal compound as an example. RAM is an environmentally friendly mechanochemical technique for both high throughput screening and scaled up production of cocrystals and nanosuspensions.



Invited Talk

New Frontiers in Metal-Organic Frameworks: Spintronics and Tunable Gas Sorption



Prof. Mario Wriedt
Department of Chemistry and Biomolecular Science
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Web: wriedt-lab.com

Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal clusters or ions connected by polytopic organic linkers. Their framework structures, pore environment, and functionality make them uniquely tunable by the choice and connection of metal and organic building blocks, allowing the design of innovative materials with customized properties.

My research programs all address interrelated fundamental aspects of the design, synthesis, and characterization of functional MOF materials. This presentation is a comprehensive overview on the achievements of my "Functional Materials Design & X-ray Diffraction Laboratory" over the past five years. I am going to show how systematic investigations of important structure-property relationships will pave the way for new developments in advanced materials for spintronics[1-3] and gas sorption applications such as hydrogen storage or carbon capture[4-5].

[1] *CrystEngComm*, **2018**, *20*, 1011.
[2] *Inorg. Chem.*, **2017**, *56*, 6965.
[3] *J. Am. Chem.* Soc., **2015**, *137*, 9254.
[4] *Dalton Trans*., **2017**, *46*, 6853.
[5] Chem. Mater., **2016**, *28*, 7825.

Invited Talk

Liquid crystalline processing of high toughness bio-fibers fabricated by mussels

Prof. Matthew J. Harrington

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

Marine mussels (Mytilus spp.) produce protein-based biopolymeric fibers known as byssal threads that exhibit toughness exceeding most synthetic polymer materials, as well as the capacity to self-heal. Byssal threads have thus emerged as important archetypes for bioinspired design of sustainable, next-generation polymers. X-ray diffraction combined with *in situ* mechanical testing has revealed that the mechanical prowess of byssal threads emerges from the hierarchical, semi-crystalline organization of the collagenous protein building blocks[1]. Recent investigations of thread formation process employing confocal Raman spectroscopic imaging and traditional histology reveal that prior to self-assembly, the constituent proteins are apparently pre-organized in secretory vesicles in a smectic-like liquid crystal mesophase[2]. During formation, vesicles coalesce following a suspected pH transition, retaining and locking in the structural order of the smectic phase during the process. This suggests that the LC phase is crucial for achieving hierarchical organization under biological-friendly conditions. While our understanding of the assembly process is still developing, these findings offer potentially transformative insights into how humans might improve polymer processing technologies towards more sustainable practices, while still achieving remarkable material performance.

1. Reinecke, A., Bertinetti, L., Fratzl, P., Harrington, M.J. (2016) Cooperative behavior of a sacrificial bond network and elastic framework in providing self-healing capacity in mussel byssal threads. *Journal of Structural Biology*. **196**, 329–339
2. Priemel, T., Degtyar, E., Dean, M.N., Harrington, M.J. (2017) Rapid self-assembly of complex biomolecular architectures during mussel byssus bio-fabrication. *Nature Communications*. **8**, 14539.

Invited Talk

Metal-Organic Frameworks for Adsorption and Detoxification of Hazardous Analytes

Prof. Ashlee J Howarth

Department of Chemistry and Biochemistry,
Concordia University, 7141 Sherbrooke St W.
Montreal, QC, H4B 1R6

Metal-organic frameworks (MOFs) are structurally diverse, porous materials comprised of metal nodes bridged by organic linkers. Through careful choice of nodes and linkers, the chemical and physical properties of MOFs can be elegantly tuned and materials with very high surface area and porosity can be obtained. As a consequence, MOFs have been explored for many potential applications including, but not limited to, gas storage and release, chemical separations, catalysis, drug delivery, light harvesting and energy conversion and the remediation of contaminated water. MOFs offer an interesting platform for use as adsorbents, as well as catalysts for contaminant detoxification, particularly since the advent of MOFs that are highly stable in aqueous solutions and under varying pH conditions. In this presentation, Zr-based MOFs are explored as platform materials for the adsorption, removal and detoxification of various harmful analytes.

Invited Talk

Stacking of planar conjugated rings: a continuum of interactions ranging from dispersion to multicentric two-electron covalent bonding

Krešimir Molčanov, Biserka Kojić-Prodić

Rudjer Bošković Institute, Zagreb, Croatia
E-mail: kmolcano@irb.hr

Stacking of aromatic rings is a well-known type of intermolecular interaction. It is usually considered as rather weak (typically <1 kcal mol^{-1}), and is assumed that it is an exclusive property of aromatic rings; the fact that other types of planar conjugated rings also stack is usually overlooked. Misconceptions about the very nature of stacking are numerous, and are reflected in a variety of names used (often misleading): π···π interaction, π-stacking, πinteraction, aromatic interaction, stacking interaction, etc.

However, there is a growing amount of evidence that all rings stack, and that aromaticity is not a *conditio sine qua non* for formation of π-stacks. Stacking of planar organic radicals has been used in design of organic semiconductors and magnetic materials. Our detailed studies have shown that interactions between quinoid rings and semiquinone radicals are by an order of a magnitude stronger than interactions between aromatics.

As a result of numerous X-ray charge density studies on different types of stacked rings, we propose a generalised model of stacking, which accounts for both aromatic and non-aromatic rings. Our results show that: 1) non-aromatic planar polyenic rings can stack; 2) interactions are more pronounced between systems/rings with little or no π-electron delocalisation (e.g. quinones) than those involving delocalised systems (e.g. aromatics); 3) the main component of the interaction is electrostatic/multipolar between closed-shell rings; 4) interactions between radicals involve a significant covalent contribution. Thus, stacking covers a wide range of interactions and energies ranging from weak dispersion to non-localised two-electron multicentric covalent bonding ('pancake bonding').

Invited Talk

Use Only What You Need and Contribute as You Can: Materials Design for Energy and Nanotechnology Applications

Prof. Duong Adam,
Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada, G9A 5H7,
E-mail: adam.duonguqtr.ca,
website: www.duonglab.ca

Nowadays, improvements in the fields of chemistry, physics and engineering have allowed better understanding of the structure-property relationships. As a result, many efforts have been made to precisely control the composition, the structure and the properties of materials to develop numerous fields such as photovoltaics, batteries, energy conversion, energy storage and nanotechnology, and so forth. Functional materials have therefore significant impacts on our lives styles such as energy, transportation, life science and environment. Increasing efficiency and improved reliability of promising technologies can then be achieved by the design of new materials. Here, we have prepared a series of Metal-Organic Polymers (MOPs) and Mixed Metal-Organic Polymers (MMOPs) with well-defined and tunable properties. Remarkably, MOPs and MMOPs display reversible chromism and have bandgap energy promising for sensor technology and light harvesting.

Invited Talk

Probing the behaviour of gas molecules in MOFs by solid-state NMR

Prof. Yining Huang

Department of Chemistry,
The University *of* Western Ontario,
London, Ontario, Canada
E-mail: yhuang@uwo.ca

A major advance in materials chemistry in recent years is the emergence of hybrid organic-inorganic solids known as metal-organic frameworks (MOFs) with unique properties such as modularity, tunable pore sizes/functionality, high surface areas and permanent porosity. Among numerous applications, MOFs are well-suited for the capture of greenhouse gases (CO_2) and the storage of energy carrier gases (H_2, CH_4). With the rapid growth of MOF applications in gas adsorption, comes the need for new characterization strategies.

Solid-state NMR (SSNMR) spectroscopy is a powerful technique for MOF characterization. It provides key information on the behavior of gas molecules in MOF channels/cages and the effect of adsorption on framework structure. This talk will focus on our recent work investigating CO_2, H_2 and CH_4 adsorption in several representative MOFs. ^{13}C and ^{2}H SSNMR are employed to directly monitor the dynamic behavior of gaseous molecules inside MOF pores. NMR results allow one to determine the number of adsorption sites, identify the location of binding sites, gaining physical insight into the nature and strength of host-guest interactions between gaseous molecules and MOF framework. The information gained from SSNMR studies are complementary to that obtained from X-ray diffraction.

Invited Talk

Accessing charge transfer salt polymorphs by liquid-assisted grinding and vapor digestion: crystal structures from powders, reactant polymorphism, and solvent effects

Prof. Silvina Pagola

Old Dominion University, Dept. of Chemistry and Biochemistry
4402 Elkhorn Avenue
Norfolk, USA
E-mail: spagola@odu.edu

The electron donor tetrathiafulvalene (TTF) forms charge transfer salts (CTS) with *p*-benzoquinone derivatives (electron acceptors), such as chloranil (CA), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), 2,5-dichloro-*p*-benzoquinone and chloranilic acid (CAH_2). CTS can be neutral, mixed-valence or ionic. Mixed valence CTS, typically showing segregated TTF columns as a crystal packing motif, can give rise to organic metals. Although the latter are most often grown as single crystals by electrocrystallization, liquid-assisted grinding (LAG) has been used to selectively synthesize CTC polymorphs.[1] In general, for TTF-CA (**I**), TTF-DDQ (**II**)[2] and TTF-CAH_2 (**III**) is observed that grinding with high polarity solvents (*e.g.*, water and DMSO) leads to ionic CTC, while mixed valence or neutral polymorphs are obtained using medium to low polarity solvents. For **III**, protic, medium polarity solvents (MeOH, EtOH, isopropanol, and 1-butanol) also yield the ionic form.

LAG often yields powders which afford crystal structure determination from synchrotron X-ray powder diffraction, and the structures of the black TTF-CA, the green TTF-2,5-dichloro-*p*-benzoquinone, and a new, likely neutral TTF-CAH_2 polymorph will be shown. The latter is a small band-gap semiconductor, as determined from its FT-IR absorption border (300 K – 10 K), even though its crystal structure possess segregated CAH_2 and TTF columns.

Moreover, there are two TTF polymorphs (orange and brown forms), and the orange transforms to the brown form by neat grinding. The orange TTF as reactant seems to favor the formation of the ionic TTF-CA, requiring smaller quantities of polar solvents in LAG, and in combination with most solvents by vapor digestion.[1]

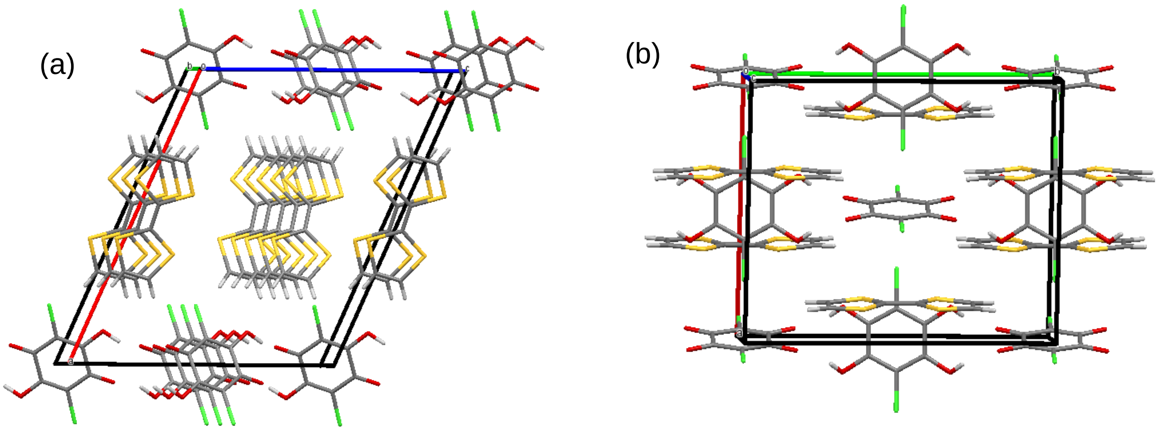

Figure 1: Crystal structures of (a) the “burgundy” TTF-CAH_2, and (b) the “ionic” TTF-CAH_2 polymorph.

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Invited Talk

Metal-organic multicomponent halogen bonded solids: towards supramolecular control over structure and properties

Prof. Dominik Cinčić[1], Vinko Nemec[1], Katarina Lisac[1], Filip Topić[2], Tomislav Friščić[2]
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Halogen bonding has emerged as a mode of assembly that is complementary to hydrogen bonding, and is currently the only class of σ-hole interactions commonly used in crystal engineering.[1] Over the past two decades research into halogen bonding has mostly focused on organic systems. However, the use of halogen bonding to direct the assembly of metal−organic building blocks remains largely unexplored. An overwhelming majority of reported studies and strategies for incorporating metals into halogen-bonded architectures have focused on single component solids.[2] Synthesis of multi-component metal–organic materials with organic halogen bond donors has received much less attention.[3] This presentation will provide an overview of some of the work related to metal-based halogen-bonded cocrystals that we have pursued recently.[4-7] Also, this presentation will outline our experiment- and theory-based efforts, including as of yet unpublished results, directed towards discovering and utilizing halogen bonding interactions for the construction of new functional solids.

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Invited Talk

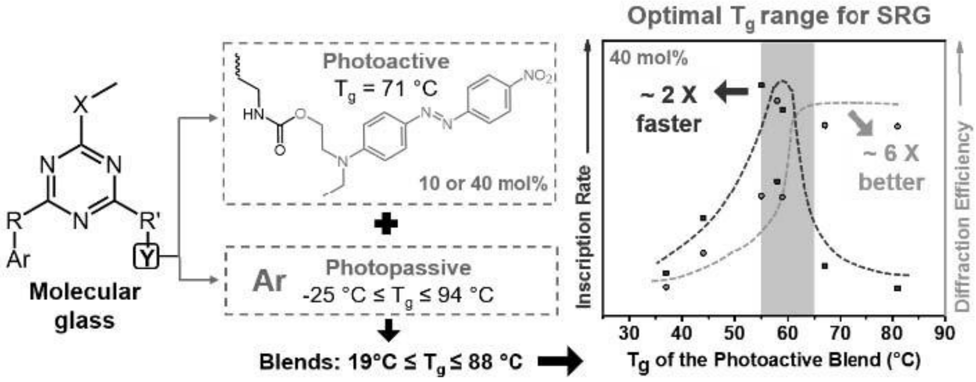
Photomobility of Azomaterials in the Solid State

Prof. Christian Pellerin,[1] Audrey Laventure,[1] Jaana Vapaavuori,[1] Ribal Georges Sabat,[2] Olivier Lebel[2]

[1]Université de Montréal; [2]Royal Military College of Canada

The molecular-scale photoisomerization of azobenzene (azo) derivatives can translate into macroscopic motions and other photomechanical effect. This phenomenon can be used, among others, to prepare surface relief gratings (SRGs). This mass transport is puzzling since it occurs in the solid state at temperatures well below the glass transition temperature where the segmental motion of the material is normally frozen.

We have used infrared spectroscopy (IR) to investigate, from a molecular point of view, the changes occurring in a Disperse Red 1-containing molecular glass under irradiation (gDR1). Results show a gradient of molecular environment where very large changes are observed around the azo moiety but none for the triazine core and ancillary groups of the molecular glass. To decouple the azo concentration and the thermal properties of the material, we have then studied mixtures of the photoactive gDR1 with a series of photopassive molecular glasses. Molecular design of these passive glasses allowed tuning the Tg of the blends while maintaining photoactivity constant. The IR, UV-visible and light diffraction results reveal optimal conditions for the inscription of SRGs in solid-state amorphous azomaterials.



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Invited Talk

A Swellable Polymer/MOF Composites for the Containment and Degradation of Organophosphorous Contaminants

Yaroslav B. Kalinovskyy,[a] Alex J. Wright [a] Simon J. Holder,[a] Prof. **Barry A. Blight** [a,b]

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Recently we have been exploring how small molecule interactions with MOF nodes can act as effective hydrolysis catalysts for organo-phosphorus substrates (both benign and biologically hazardous).[1-3]In particular we have demonstrated how we can enhance the hydration of node defects by reaction in water under microwave irradiation, and in turn enhancing the rate of hydrolysis.[6] This work is further underpinned in parallel by the development of a polymer support termed High Internal-Phase Emulsion (HIPE) polymer that has the capability to swell in the presence of these hazardous materials.[7]

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Invited Talk

The Challenge of Understanding the Structure–Properties Relationship in Advanced Battery Materials

Prof. Eric McCalla
Department of Chemistry, McGill University, Montreal

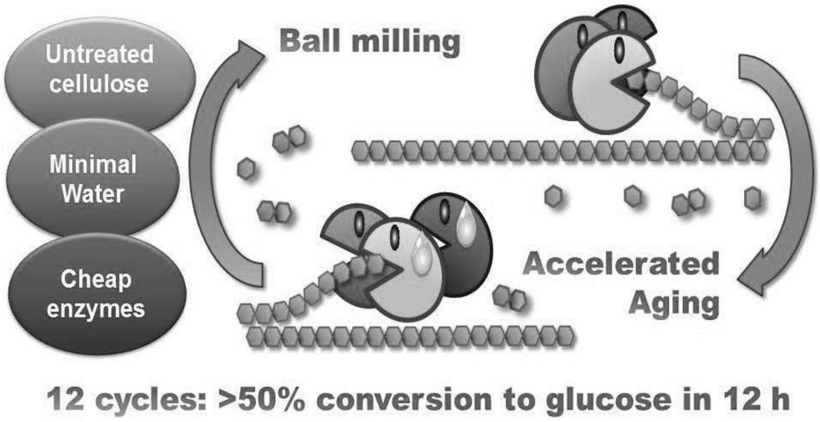
It is becoming evident that advanced batteries will play a critical role in a number of essential sustainability applications, including widespread implementation of electric vehicles and off-grid energy storage to support intermittent renewable energy sources. To achieve the very demanding targets set by these applications, novel materials are being designed for Li-ion batteries wherein oxygen redox is being harnessed in the electrochemistry. These show a considerable energy density improvement compared to traditional electrode materials where only transition metals compensate the charge transferred during battery operation. However, many challenges have been encountered; some related to the nature of the starting materials while others are related to the structural transformations taking place during electrochemical cycling. Here, two topics will be presented where crystallography has brought fundamental understanding that has both clarified confusion existing in the field and guided further design of next-generation materials. The first is a combinatorial study wherein thousands of samples were characterized by XRD and analysed to determine the phase stabilities at play during synthesis. The dramatic impact of cooling rates has had particular consequences to both academic and industrial research. The second topic will be a survey study of model systems that resulted in a broad understanding of the possible mechanisms at play when these materials are used in a battery. Of note, the harnessing of oxygen redox must be done in such a way to prevent oxygen gas production.

Invited Talk

Solvent-free Mechano-enzymatic Reactions: “RAging” Biomass

Prof. Karine Auclair,
Department of Chemistry, McGill University, Montreal

Enzymes are typically manipulated as dilute aqueous solutions. This is however remote from their natural environment. For example it is well-recognized that the cell is a highly crowded environment, with a total molecule concentration estimated to ~400 mg/mL. Most enzymes have evolved to perform under high macromolecular crowding. Other enzymes, such as cellulases, xylanases and chitinases, are excreted by microorganisms and work directly on the moist, solid surface of their substrate, in the absence of bulk solvent. From this perspective, we envisaged that some enzymes might have evolved to work optimally in the absence of bulk water. We have recently developed a new efficient way to perform biocatalysis in the absence of bulk solvent. Our process, coined reactive aging or RAging, is based on alternating periods of brief, gentle milling, followed by aging. RAging is especially promising for biomass degradation as it enables the reactivity of poorly soluble and chemically recalcitrant substrates, such as cellulose and chitin among others. This presentation will summarize our adventures with enzymes at work in a solid matrix.



Invited Talk

A Scaffolded Approach to the Integration of Crystallography in Undergraduate Curriculum and Research

Prof. Louise N. Dawe, B.Ed., Ph.D.
Department of Chemistry and Biochemistry, Wilfrid Laurier University, Waterloo
Twitter: @LouiseDawe

Project scaffolding, as a tool to achieve learning outcomes, supports the immediate construction of knowledge by the learner, provides the basis for the future independent learning, and enables learners to reach otherwise unattainable goals.[1] The 2014 International Year of Crystallography provided an opportunity for the redesign of a required third year course on Chemical Literature and Communication at Wilfrid Laurier University. While course outcomes were based on recommendations for information literacy[2], a scaffolded approach to student projects, thematically based on the exploration of crystallography, was employed.[3] In addition to providing an overview of project scaffolding practices, examples for the integration of small molecule crystallography into first year general chemistry through senior undergraduate capstone courses will be discussed. Finally, recent research progress in fundamental areas of crystallography (polymorphism and coordination chemistry[4,5]), carried out by undergraduates in my research program, will be included in the context of learning outcome mastery throughout the degree program.

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Invited Talk

Self-Assembly of Polycyclic Aromatic Hydrocarbons in the Solid State and in Liquid Crystals for the Preparation of New Materials

Prof. Kenneth E. Maly

Department of Chemistry and Biochemistry, Wilfrid Laurier University, Waterloo

Polycyclic aromatic hydrocarbons bearing flexible side chains are more soluble than their unsubstituted analogs and can often self-assemble via π stacking interactions in solution and the solid state, as well as form liquid crystalline phases. In the liquid crystalline state, noncovalent interactions play an important role in determining the stability of the liquid crystalline phase. In this presentation, I will highlight strategies used to improve π-stacking interactions polycyclic aromatic hydrocarbons in order to prepare compounds that exhibit stable columnar liquid crystal phases. In particular, I will describe the effects of substitution patterns and electronic effects of substituents on the liquid crystallinity of a series of alkoxy-substituted dibenzanthracenes. We will also describe the factors influencing liquid crystallinity of a series of dibenzopentacenequinones. Finally, the effect of heteroatom substitution on self-assembly of a series of acene analogs will be described.

Invited Talk

Generation of cavity space in crystalline and amorphous organic solids with the help of strong hydrogen bonds

Dmitriy V. Soldatov, Aaron J. Smith, Travis A. P. Fillion
University of Guelph, Guelph

Our research focuses on the design of organic-based materials with cavity space. We utilize so-called non-self-complementary molecules that cannot pack closely due to their geometry or the positioning of hydrogen bond sites. The latter case leads to H-bonded frameworks incompatible with close packing in the solid state.

Two strategies utilized in our recent studies will be illustrated. Short hydrophobic peptides were used to create co-crystals and crystalline inclusion compounds with bioactive molecules. Dendrimers with peripheral amide groups were used to make non-crystalline solids with pores accessible to gases. In both cases strong H-bonds were used as a key element in the creation of porous 3D framework, but in two different ways. In peptides, the H-bond was used to build a 2D supramolecular motif, or "supermolecule", that is non-self-complementary due bulky side groups in the peptide backbone. In dendrimers, the H-bond was used to prevent inclusion of peripheral groups of the molecule into interstitial spaces of adjacent molecules in the solid. The common feature of these two very different examples is the tendency of molecules to form all possible strong H-bonds in the solid which supersedes their tendency to a close van der Waals mode of packing.

Invited Talk

NMR Crystallography and Solid-State NMR of the Periodic Table

Sean T. Holmes, Austin A. Peach, David A. Hirsh, Christopher A. O'Keefe, Jacqueline E. Gemus, Stanislav L. Veinberg, and **Robert W. Schurko**
Department of Chemistry and Biochemistry, University of Windsor, Windsor

NMR crystallography is an emerging discipline that combines solid-state NMR (SSNMR) spectroscopy, X-ray diffraction (XRD) methods, and computational approaches for the purposes of refining and determining molecular-level structures in a wide array of solids, including crystalline, semi-ordered, and amorphous materials.[1-3] SSNMR can be utilized to provide information on interatomic distances, structural assignments, local atomic/molecular symmetries, and/or characterization of structural disorder; these data, when used in combination with XRD and/or computational methods, can elicit structures that rival those determined by neutron diffraction methods.

The majority of modern NMR crystallographic studies rely upon the measurement of chemical shifts (typically from ^{1}H, ^{13}C, or ^{15}N NMR spectra), and comparison to magnetic shielding values of refined structures obtained from plane-wave density functional theory (DFT) calculations. An increasing number of studies have utilized data from numerous NMR-active nuclides across the periodic table, including metal nuclides with large chemical shift anisotropies and quadrupolar nuclides (i.e., nuclear spin > 1/2).

In this lecture, first, I will present a discussion of NMR crystallographic studies conducted in my group, with a focus on structural refinements aided by ^{14}N, ^{17}O, ^{35}Cl, ^{111}Cd and ^{195}Pt solid-state NMR data. Then, I will discuss some of the methods designed by my group that allow for rapid acquisition of SSNMR spectra crucial for NMR crystallographic studies.[4] Finally, I will outline a powerful method for refining crystal structures that uses dispersion-corrected plane-wave DFT, which relies upon the accurate measurement and computation of electric field gradient (EFG) tensors.[5]

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Regular Talks

In operando data of Li-Ion batteries from XRPD laboratory diffractometers

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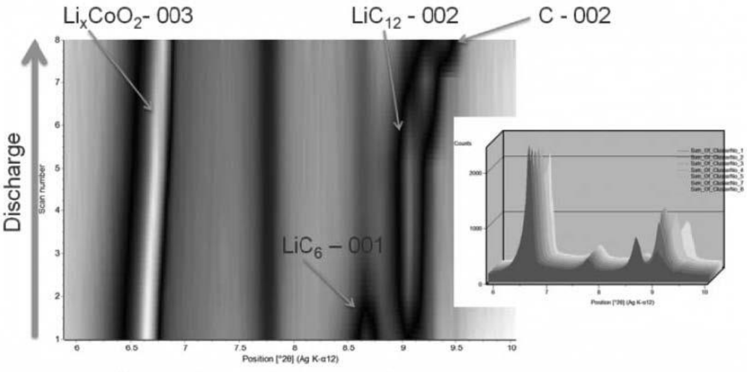

Virtual charge/discharge axis – Summed clusters

Typically *in operando / situ* X-ray diffraction experiments of commercial Lithium-Ion batteries are carried out on synchrotron beam lines due to the high brilliance sources and the possibility to use high-energy radiation. In this presentation however we will cover how to quickly collect high (Rietveld) quality XRPD data of commercial Lithium-Ion batteries during charge/discharge cycles on a laboratory XRPD diffractometer equipped with an X-ray tube with Silver anode and an area detector optimized for high energy Xrays. Further, we will discuss how to extract accurate phase quantities as well as crystallographic information automatically from multiple scans by using complex fitting model consisting of Pawley phases to model the fixed components (Aluminum and Copper electrodes), Rietveld phases to model variable components like $Li_{1-x}CoO_2$, LiC_6, LiC_{12} + Carbon and Profile fit peaks to model the polymer separator. Additionally we will address how Cluster analysis can be used to group and pre-sort the huge amount of raw data that is generated during the experiment. Cluster analysis can also be used for example to sort all scans of one or many experiments along a virtual charge/discharge axis.

Cosublimation: A Rapid Route towards Halogen Bonded Cocrystals Yielding Otherwise Inaccessible Architectures

Patrick M.J. Szell,[1] Shaina A. Gabriel,[1] Estelle Caron-Poulin,[1] Olivier Jeannin,[2] Marc Fourmigué,[2] David L. Bryce[1]
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Several synthetic techniques are available for the preparation of halogen-bonded adducts including traditional solvent-evaporation methods and mechanochemistry [1]. Although vapor deposition has been investigated, it has mainly focused on surfaces [2, 3]. With the intention of reducing solvent usage and experimental times, here we explore the potential of *co*sublimation as a synthetic technique for preparing halogen bonded cocrystals, focusing on the C-I⋯N motif involving nitrogen-containing heterocycles. We have selected 4 donors and 4 acceptors, and prepared all 16 combinations via the following methods: solvent evaporation, cosublimation in a sealed glass tube, and cosublimation in a sublimation apparatus. We show that the crystals obtained from overnight cosublimation performed in a glass tube are suitable for single-crystal X-ray diffraction. We report five new crystal structures, two of which are, to date, unobtainable through other methods (see Figure 1). Furthermore, we show that cosublimation can be used to rapidly prepare and purify bulk samples using a simple sublimation apparatus, enabling the scalable preparation of halogen-bonded cocrystals using common laboratory equipment.

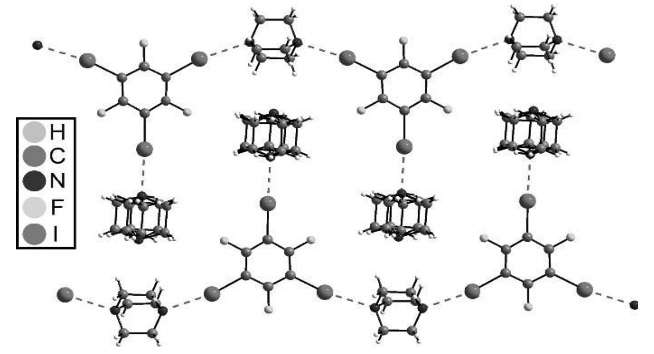

Figure 1: Depiction of the crystal structure of (1,4-diazabicyclo[2.2.2]octane)2(1,3,5trifluoro-2,4,6-triiodobenzene), featuring a tritopic donor fully saturated with C-I⋯N halogen bonds, observed only in the cosublimation product.

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Regular Talks

Template-driven self-assembly of hemicucurbit[*n*]uril macrocycles in the solid state

Sandra Kaabel,[1,2] Robin S. Stein,[2] Riina Aav[1] and Tomislav Friščić[2]
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Chiral cyclohexanohemicucurbiturils (cycHC[*n*]) are barrel-shaped macrocyclic receptors capable of binding anionic (Fig. 1, right) and electron-rich guests, and could therefore be applied in a range of target structures, such as sensors, in asymmetric catalysis or as components in pharmaceutical delivery systems.[1] The synthesis of 6- and 8-membered cycHC[*n*] proceeds in strong acids, where the target macrocyclic product is dictated by the choice of the anionic template.[2,3,4]

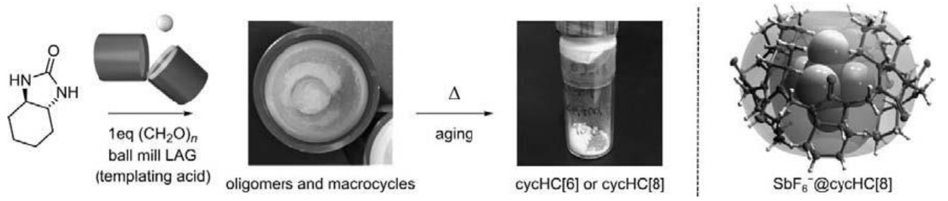

Fig. 1 General scheme for the solid state synthesis of cycHC[*n*] (left) and an anion inclusion complex of cycHC[8] with $SbF6^-$ (right)

Recently, we have investigated solid state approaches for the synthesis of cycHC[*n*]. Mechanochemistry is a rapidly advancing "CleanTech" synthetic technique, which uses mechanical agitation to achieve chemical transformations in the absence of bulk solvents.[5] Applications of solvent-free mechanosynthesis of covalently-bonded nanocapsules have revealed improved reaction yields, product selectivity and isolation.[6] We found, that the synthesis of cycHC[*n*] from cyclohex-1,2diylurea and paraformaldehyde proceeds selectively and quantitatively in a solvent-free template-directed process.(Fig. 1, left) Liquid-assisted grinding (LAG) of the reactants with a catalytic amount of acid produces a set of polymerization products from which a desired macrocyclic product can be amplified in the presence of a suitable supramolecular template. Besides providing a green route for the synthesis of these macrocycles, by removing the bulk of used acid and solvents, these solvent-free processes offer unique examples of supramolecular control over reversible covalent bond formation in the solid state.

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Acid/Base Effected Dynamic Motion within a Stable *fcu* Zr Metal Organic *Rotaxane* Framework

Alexander J. Stirk, Hazem Amarne, Jacqueline E. Gemus, Christopher A. O'Keefe, Robert W. Schurko and Stephen J. Loeb*
Department of Chemistry & Biochemistry, University of Windsor, Windsor

A new T-shaped [2]rotaxane ligand has been designed and synthesized. The 24crown-6-ether macrocycle is wrapped around a benzimidazole motif and mechanically bound in place with two methoxy stopper groups. The organic linker contains two carboxylic acid groups to allow for formation of a Metal-Organic *Rotaxane* Framework (MO*R*F) with zirconium(IV) ions. Structural analysis by VT-PXRD and Materials Studio show the MO*R*F to be isostructural to the reported Zr MOF PCN-57[1] with a rotaxane-tetramethyl ligand incorporation ratio of 1:1. The rotaxane linkers were rationalized using Materials Studio to inhabit both the tetrahedral and octahedral cavities allowing for the above experimental ratio. Solid-State ^{2}H (deuterium) NMR spectroscopy shows free rotation of the ^{2}H labelled 24-crown-6 ether interlocked macrocycle. Dynamic motion was observed at elevated temperatures and when the benzimidazole core is both neutral and protonated within the framework and found to exhibit different modes of dynamic motion.

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Investigating the Reactivity of 1,2,3-Dithiadiazolyl-o-naphthoquinone Ligands Through Solvent-free Techniques

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Department of Chemistry, University of Guelph, Guelph

A series of non-innocent 1,2,3-dithiadiazolyl-o-naphthoquinone ligands has been designed. These bidentate ligands have been isolated and structurally characterized in three oxidation states: closed-shell cation, neutral radical, and closed shell anion.[1] Our current interest lies in modifying these ligands to access a radical anion oxidation state. In creating coordination complexes of the radical anion species, we aim to develop molecule-based materials with properties such as activated conductivity and magnetic ordering.

Cyclic voltammetry (CV) studies on our modified ligands, which are closed-shell in the neutral oxidation state, indicate that reduction to a radical anion species is electrochemically irreversible. However, preliminary electron paramagnetic resonance (EPR) data suggests that we can isolate a radical anion species when using $SbPh_3$ to simultaneously reduce and coordinate the ligand. Thus, we speculate that electrochemical irreversibility is due to significant electronic rearrangement as opposed to decomposition. One ligand in particular, 4-methoxy-naphtho[1,2-d][1,2,3]dithiazole-5-one, o-DTANQOMe, has shown to be promising in solvent-free mechanochemical reactions that involve grinding the reagents together and heating under vacuum to grow X-ray quality crystals. Preliminary structural data, EPR, and CV is presented.

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Tuning Solid State Phase Transitions in Lanthanide-Radical Complexes

Michelle B. Mills, Willem R. Verduyn, Mohamed Ghazzali, Dmitriy V. Soldatov, Rodolphe Clérac, and Kathryn E. Preuss
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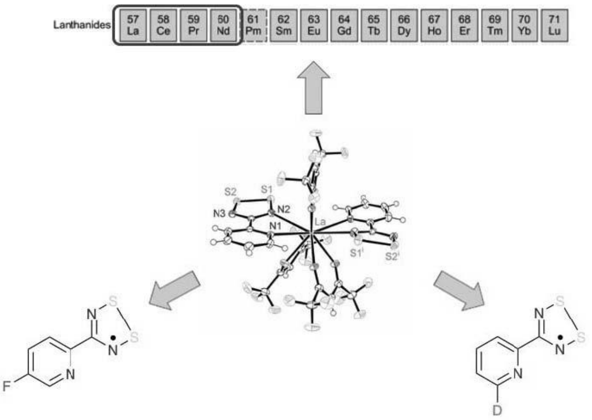

We have recently reported[1] a radical-La(III)-radical coordination complex,La(hfac)$_3$(pyDTDA)$_2$, where reversible pancake bonding between thiazyl radicals leads to switchable magnetic properties in the solid state; hfac = 1,1,1,5,5,5hexafluoroacetylacetonato-; pyDTDA = 4-(2´-pyridyl)-1,2,3,5-dithiadiazolyl. Pancake bonds 'rupture' in a two-step sequence with increasing temperature, accompanied by small changes in geometry and changes in magnetic properties. A re-entrant phase transition is observed. A theoretical model has been developed that predicts this phase transition behavior.

Using a crystal engineering approach to materials design, we have identified specific important contacts in La(hfac)$_3$(pyDTDA)$_2$ that can be exploited to tune the switchable magnetic behaviour. The temperature at which the phase transitions occur can be tuned by varying the lanthanide ion (La-Nd) in an isostructural series. We have also made efforts to tune the switchability by modifying the thiazyl radical ligand. Weakening the pancake bonding by incorporating an electronegative halogen results in major changes to the magnetic properties. Preliminary efforts to disrupt important intermolecular contacts have been made by synthesizing a pyDTDA derivative with a specific hydrogen atom replaced by deuterium. Magnetic and structural data will be presented that illustrate the results of each rational change to the design of the molecule.

Regular Talks

Enabling beta-glucosidase enzymatic activity under high-speed ball-milling

Fabien Hammerer, Shaghayegh Ostadjoo, Tomislav Friščić, Karine Auclair
Department of Chemistry, McGill University, Montreal

It has recently been discovered that enzymatic transformations can be conducted in solvent-free conditions using solid-state chemistry techniques like ball milling. We recently reported the digestion of cellulose into glucose combining cellulases (sets of enzymes specialized in cellulose hydrolysis), ball-milling, accelerated aging (i.e. static incubation at mild temperature) and the minimal amount of water.[1] This technique called RAging allows the fast and efficient conversion of microcrystalline cellulose and untreated biomass into highly concentrated glucose and/or xylose solutions.

During the process, we observed that ball-milling provoked the accumulation of cellobiose, glucose dimer, which was converted into glucose during the following aging period. This peculiar result led us to investigate the solvent-free behavior of β-glucosidase (BGL), the enzyme responsible for the hydrolysis of cellobiose. The study revealed that both the milling frequency and initial mixture composition play a crucial role in the preservation of enzymatic activity. BGL quickly deactivates when milled in the presence of its substrate alone but we found that the addition of a passive component (biopolymer, plastic, metal oxide) helped conserve the enzyme's structure and activity even at high milling speeds and over extended periods of time. These results provide important insights into how to improve our cellulose process and promote solvent-free mechano-enzymatic transformations for a large range of sensitive enzymes.

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Fabrication of functional protein-based materials

Prof. Noémie-Manuelle Dorval Courchesne
Department of Chemical Engineering, McGill University, Montreal

Nature has evolved microorganisms, macromolecular protein assemblies and biopolymers with exquisite properties. Of particular interest and are protein materials, which can display complex nanoscales features, modular structures, and tunable surface chemistry. Furthermore, proteins can often be easily genetically engineered to tune their properties and rationally design novel materials with custom functions. Such properties are very useful for creating scaffolds and for coordinating the assembly of nanoscale materials in a variety of devices for environmental, bioenergy or biomedical applications. Using protein structures as building blocks to assemble devices provides a sustainable and environmentally-friendly alternative to conventional inorganic or polymeric materials used for the fabrication of consumer goods.

Here, we present examples of protein-based materials that we assemble to produce macroscopic functional thin films, gels and coatings. We also describe potential applications for protein structures with novel physical properties, including the ability of transporting charges, absorbing light or exhibiting binding affinities for different targets.

Synthesis and Structural Characterization of Novel Alkaline Earth bioMOFs

Maria A. Matlinska, Michelle Ha, Guy M. Bernard, Bryden Hughton, Abishek Iyer, Arthur Mar and Vladimir K. Michaelis*
Department of Chemistry, University of Alberta, Edmonton

Alkaline earth phosphates are the minerals essential for assisting the formation of skeletal tissue.[1] Deficiencies in these components are strongly linked to bone tissue disorders such as osteoporosis.[1] Worldwide, 9+ million fractures a year are caused by osteoporosis, alone.[2] Therefore, the demand for effective materials to enhance skeletal durability is very high. Bisphosphonates are primary pharmaceuticals used to suppress bone dissolution. The optimal use of bisphosphonates requires adequate calcium intake, that is why there is an increasing interest in potential drug candidates comprising Ca^{2+} and bisphosphonate molecule as an alternative to separate supply of these two substances.[3,4] Our research attempts to develop novel alkaline earth MOFs based on earlier work by Shi *et al*,[4] with varying the ratios of Ca^{2+} and Sr^{2+} in 3D structures that contain bisphosphonate linkers. As strontium and calcium are significant candidates in maintaining normal bone density and fine-tuning the rate at which ions and bisphosphonate are released, it is important to investigate methods of incorporating these cations into new phosphonate-based materials. The synthetic approach involves hydrothermal method. Using solid-state nuclear magnetic resonance (NMR) spectroscopy and powder X-ray diffraction we contrast the structures of the prepared biomaterials. Their potential to promote formation of hydroxyapatite is assessed with simulated body fluid tests. We use ion exchange experiments and GIPAW, a DFT based method to investigate the release patterns of metal ions into solution to model their structure and potential for bioavailability. Finally, we use human osteosarcoma cells to assess calcification ability of the newly synthesized materials.

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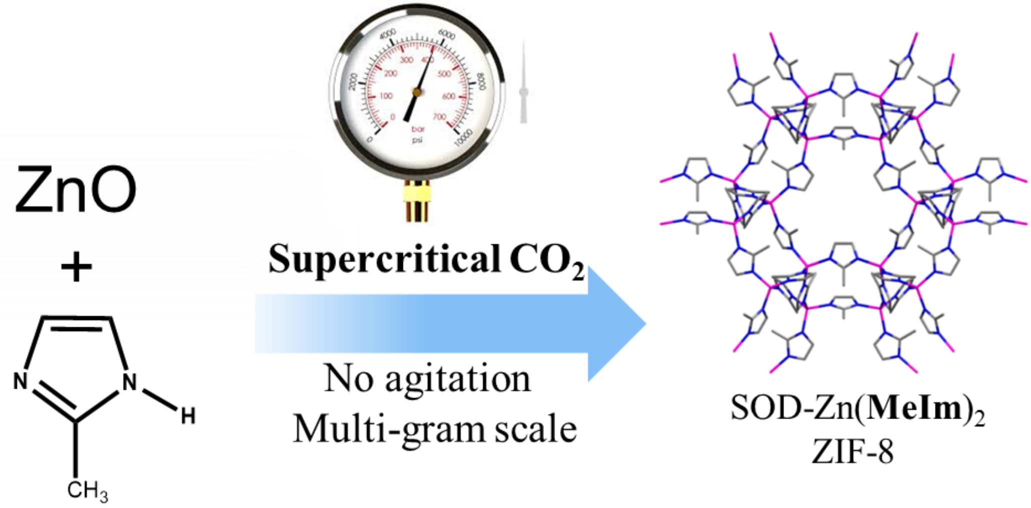
Sustainable innovation meets MOF synthesis: rapid, scalable manufacture of highly porous metal-organic frameworks in $scCO_2$

Cristina Mottillo. Acsynam, Inc. Montreal

Metal-organic frameworks are a recently commercialized class of porous adsorbent materials,[1] which are being thoroughly investigated for implementation in technologies such as gas storage, food preservation, and hydrocarbon separation. It is the design and discovery of new MOF structures with improved stability and heightened functionalities that has accelerated their route to commercialization within the past five years. However, it is also becoming increasingly clear that the development of efficient and economical methodologies for MOF manufacture is an imperative for their adoption on an industrial scale[2]. Mechanochemical[3] and accelerated aging[4] methods are examples of recently developed methodologies which reduce the solvent, high temperatures, and corrosive reagents sometimes associated with traditional solvothermal MOF synthesis. We now demonstrate that the synthesis of high surface area MOFs can be achieved rapidly and efficiently using supercritical carbon dioxide ($scCO_2$) from readily available metal oxides and solid organic linkers.[5] Reacting metal oxides (eg. ZnO) and organic ligands (eg. various imidazoles) in $scCO_2$ results in the rapid (ca. 5 min) and quantitative formation of MOFs such as the prototypical ZIF-8. This work presents a versatile, environmentally-friendly, and virtually solvent-free alternative for MOF synthesis that is scalable to at least 0.5 Kg, and contradicts previous conceptions about the ability for $scCO_2$ to activate highly insoluble metal precursors such as metal oxides.



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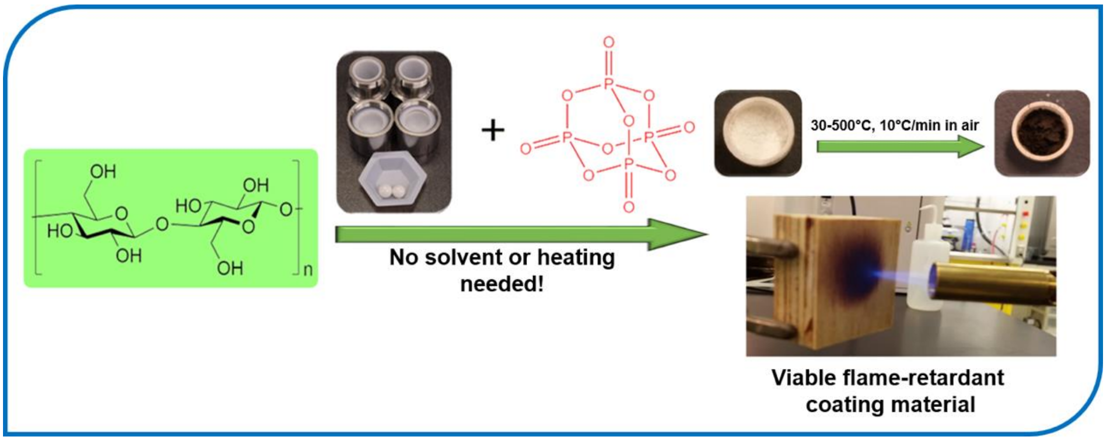
Mechanochemical Functionalization of Polymers with Solid Phosphorylating Agents and Synthesis of Flame-Retardant Cellulose Nanocrystals

Blaine G. Fiss, Lucius Hatherly, Robin S. Stein, Tomislav Friščić, Audrey Moores
Department of Chemistry, McGill University, Montreal

Flame-retardant materials are used extensively in areas ranging from general construction and textiles to the aerospace and automotive industries. Typically, these industries employ halogenated organic molecules or inorganic phosphates as flame-retardant materials. However, the toxicity of these materials, both to the environment and human health, has become a topic of greater concern. New flame-retardants are needed which are both effective at preventing the ignition and propagation of fire, while being environmentally benign, both in their design and usage. Herein we describe a new mechanochemical synthesis of both covalently phosphorylated polymers and cellulose nanocrystals using phosphorus pentoxide as greener alternatives to traditional flame-retardant materials. Magic angle spinning (MAS) NMR and thermogravimetric analysis (TGA) were used to determine the phosphate content and thermal stability of the resulting material, respectively. Initial measurements show phosphate loadings on average of 4700 mmol/kg compared to 1700 mmol/kg as proposed in literature. Preliminary tests also show their feasibility as protective coatings on wood substrates.



Old tools and new tricks in the analysis of peptide crystal frameworks

Aaron J Smith, Dmitriy V Soldatov
Department of Chemistry, University of Guelph, Guelph

Crystal frameworks created out of peptides offer eco-friendly and bio-compatible solutions to storage, delivery and separation challenges across a wide range of fields including pharmaceutical, agricultural and cosmetic industries. By selecting hydrophobic R groups on the peptide backbone, a cavity space maybe created in the framework between the hydrogen bonded peptide layers. This cavity space can incorporate secondary molecules with various shapes, sizes and functional groups, due to the remarkable flexibility of the peptide framework. After the creation of a series of new peptide crystals containing secondary molecules, we set out to quantify the framework flexibility and gain a deeper understanding of other features like hydrogen bonding motifs, layer distortions and porosity. Currently in the literature there are various tools, conventions and schemes for peptides, but none of them allow for a comprehensive description, comparison and quantification of all the parameters of interest. By combining these finding with a new set of measurements, we have been able to gain a new understanding of the peptide framework and establish a general method for future analysis.

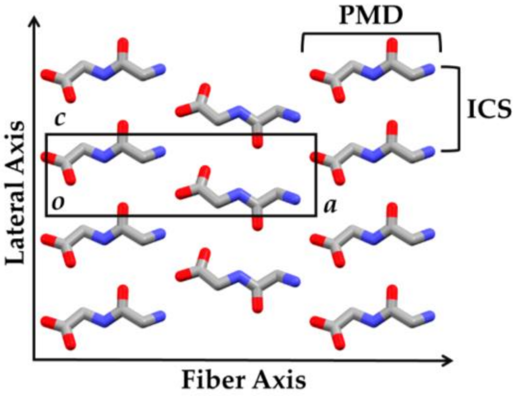


Figure 1: Schematic of peptide layer with labeling

Expanding the Scope of Viedma Ripening

Prof. Louis A. Cuccia,
Department of Chemistry & Biochemistry, Concordia University, Montreal

The focus of our research centers on conglomerate crystals constructed from achiral building blocks. Attrition-enhanced deracemization of conglomerate crystals was first demonstrated by Viedma in 2005 with sodium chlorate and is now widely known as ‘Viedma ripening’. This simple yet effective method for chiral amplification of conglomerate crystals has spawned great interest from both practical and fundamental perspectives. Numerous examples of Viedma ripening in conglomerate crystal systems, with either chiral or achiral building blocks, have since been explored. Herein, the scope of Viedma ripening is further widened. Examples include: (*i*) chiral inclusion compounds of tri-*o*-thymotide (TOT), (*ii*) conglomerate co-crystals of tryptamine with various achiral carboxylic acids, and (*iii*) conglomerate crystals that exhibit mesoscale twisting, such as decacyclene and hippuric acid.

Regular Talks

Inclusion Chemistry of Thiazyl and Selenazyl Radicals in MIL-53(Al)

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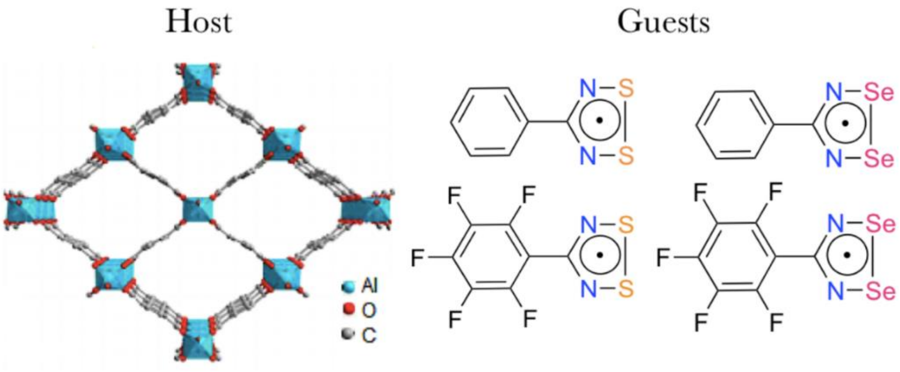
Department of Chemistry & Biochemistry, University of Windsor, Windsor

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, its selenium analogue (PhDSDA), and the fluorinated analogues of each (C_6F_5DTDA and C_6F_5DSDA), into the porous metal-organic framework host MIL-53(Al). These inclusion complexes have been characterized by powder X-Ray diffraction, DSC, TGA and EPR spectroscopy. Reactivity studies are discussed.



Solid-State Green Synthesis of Diketopiperazines (DKPs)

Farukh I. Ali, Dmitriy V. Soldatov
University of Guelph, Department of Chemistry, Guelph

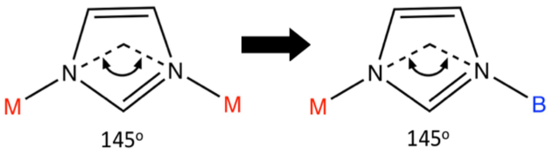
Short peptides and their corresponding cyclic peptides (DKPs) are biologically active molecules with important applications in medicine, pharmaceutics and food industry. In pharmaceutical and food industry, it is seen that processing and storage of peptides materials leads to a degradation process which mainly results into DKPs. Our study is an attempt to rationalize, optimize and generalize this degradation process to develop a solid-state synthetic route to form DKPs. These smallest cyclic peptides are interesting due to their rigid cyclic structure, H-bond capabilities, substituent group stereochemistry, chiral nature and resistance to proteolysis.

In this study, we investigated the solid-state physical and chemical transformations of peptides induced by heating. The experiments were carried out in a range of conditions using a thermogravimetric analyzer, differential scanning calorimeter and ventilation oven. The changes were monitored through the release of volatiles (TGA-FTIR, oven) and thermal effects of reactions (DSC). The final products were analyzed by FTIR, NMR, GC-MS and XRD methods. We found that some dipeptides undergo intramolecular conversion to DKPs 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 DKPs.

Mechanochemical synthesis of ultralight porous main-group imidazolate frameworks

Cameron Lennox[a*], Joshua Crew[a,b], Jean-Louis Do[a,c], Ashlee J. Howart[c,d], Omar K. Farha[d], and Tomislav Friščić[a]

a) Department of Chemistry, McGill University; b) School of Chemistry, Cardiff University, Cardiff, Wales, UK; c) Department of Chemistry & Biochemistry, Concordia University; d) Department of Chemistry, Northwestern University, Evanston, IL, USA



Metal-organic frameworks (MOFs) have been established as the go-to tunable, porous materials yet their synthesis still poses significant challenges both in terms of yield and efficiency, as well as with respect to environmental impact. [1] Boron imidazolate frameworks (BIFs)[2] are a rare example of a main group MOFs that are analogous to a class of materials known as zeolitic imidazolate frameworks. The general design of BIFs replaces the metal nodes of a zeolitic imidazolate framework with alternating monovalent cations (*e.g.* Li^+, Cu^+) and tetrakis(imidazolato)borate anions. Such a structure, based on alternating metal and boron nodes, makes these frameworks particularly attractive as lightweight microporous materials, in comparison to most other MOF materials. Until this point, the synthesis of these materials has relied on solvothermal conditions. Through efforts in the development of solvent-free mechanochemical routes[3] for the assembly of a wide range of BIF materials, we now show that liquid assisted grinding (LAG) and ion-and-liquid assisted grinding (ILAG) can influence the topological selectivity, crystallinity, and porosity of desired frameworks. While the mechanochemical route has provided simultaneously a cleaner, faster access to such frameworks, it has also expanded upon which metal cations can be used as well as the associated topologies of such materials.

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Regular Talks

Towards prediction of structure, topology and stability of metal-organic frameworks

Mihails Arhangelskis,[a] Zamirbek Akimbekov,[b] Athanassios D. Katsenis,[a] G.P. Nagabushana,[b] Ghada Ayoub,[a] Andrew J. Morris,[c] Tomislav Friščića[a] and Alexandra Navrotsky[b]

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[b] Peter A. Rock Thermochemistry Laboratory, University of California, Davis, USA;
[c] School of Metallurgy and Materials, University of Birmingham, UK

Metal-organic frameworks (MOFs) are microporous materials of emergent technological importance for gas storage and separation, catalysis, sensing devices and other advanced applications. The diversity of available ligands makes development of MOFS with specific properties a challenging task. New, cutting-edge computational methods are expected to bridge the gap between structures and properties of MOF materials and make their design more target-specific. This can be achieved by rationalizing thermodynamic aspects of MOF formation and topological transformations, explaining topological preferences of different systems and predicting the most likely structures for a given metal-ligand system.

This presentation will outline our recent advances in using periodic density functional theory (DFT) calculations[1] to characterizing and even predicting MOF systems. We will show how calculations can be used to rationalize the sequence of MOF topological interconversions occurring under mechanochemical conditions.[2] Furthermore, we will present the first direct comparison of DFT-calculated energies of MOF polymorphs compared with experimental calorimetric measurements. We will report a case of theory-driven synthesis of a new zeolitic imidazolate framework (ZIF) material, where the predicted topological preferences were verified with experiment.

Finally, we have endeavored to explore the topological preferences and stabilities of framework structures based on the recently isolated pentazolate (**pnz**$^-$) ligand.[3,4] The structure of pentazolate anion, exhibiting five nitrogen atoms potentially available for creation of coordination bonds, makes it an excellent ligand for exploring topological diversity. During the study we have obtained energy landscapes for pentazolate frameworks containing zinc and cadmium metals, explored their topological preferences and evaluated the energetic properties of these materials.

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Regular Talks

Using chitinase enzymes under solvent-free conditions to breakdown chitin

J.P. Daniel Therien, Fabien Hammerer, Tomislav Friščić, Karine Auclair
Department of Chemistry, McGill University, Montreal

It is estimated that 7 million tons of crustacean shell waste is generated annually worldwide, with most simply being discarded into landfills and the ocean. One of the major components of crustacean shells, chitin, is the most abundant nitrogen-containing biopolymer found on the planet. Given the renewable feedstock of chitin, breaking it down into its monomer N-acetylglucosamine is of potential commercial interest to multiple sectors, especially with the potential to derivatize N-acetylglucosamine into chemicals such as glucosamine and 3-acetamido-5-acetylfuran. However, current methods to break down chitin typically employ harsh conditions (such as strong acids and bases), and therefore lack sustainability in the long run. While enzymes open the door toward more sustainable reactions, the class of enzymes capable of breaking down chitin, called chitinases, are poor at hydrolyzing chitin in solution. Our group has developed a new method of treating chitin biomass using enzymes under solvent-free conditions using a combination of mechanochemistry techniques including ball milling and accelerated aging (static incubation) repeated over many cycles, which we call reactive aging (RAging). Our group has previously demonstrated this approach to be effective for cellulose and plant biomass without the need for harsh chemicals or substrate pre-treatment[1]. Our results thus far demonstrate that we can efficiently hydrolyze chitin using RAging and can extend this process to acetic acid treated biomass with a significant improvement in the yield when compared to reactions done in solution.

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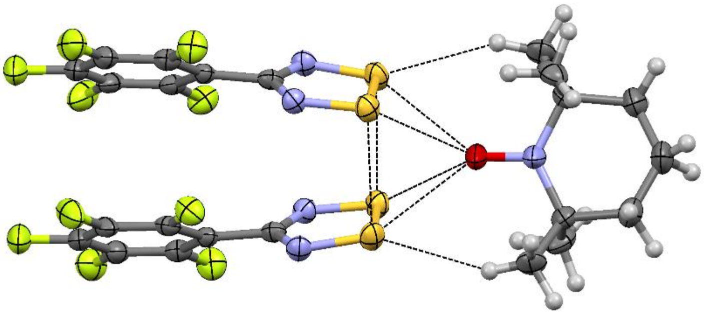
Crystal Engineering Approaches to Organic Ferrimagnets: Theory and Preliminary Results

Mitchell A. Nascimento, Elodie Heyer, Joshua Clarke, Jeremy M. Rawson*

Conventional ferrimagnets comprise two different metal ions A and B with different spins which are antiferromagnetically coupled to one another, resulting in a net spontaneous magnetization equal to $M = |g_AS_A - g_BS_B|$. Here we propose that co-crystallisation of different $S = ½$ organic radicals with even modestly dissimilar g factors can lead to an observable spontaneous magnetic moment. Recent results directed towards the synthesis of an expanded family of radical-radical cocrystals using structure-directing synthons are discussed.



Regular Talks

Magic combination of X-ray diffraction with solid state NMR

Luzia S. Germann,[a*] Robin S. Stein,[b] Igor Moudrakovski,[a] Tomislav Friščić,[b] Robert E. Dinnebier[a]
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It is impossible to understand physical properties of solid materials without the knowledge of their crystal structure.[1] Not all materials can be obtained as single crystals, especially during milling processes. Therefor single crystals of suitable quality for structure determination are sometimes not available. Hence, X-ray powder diffraction methods are a favorable way to obtain structural information on those materials. One main drawback of powder diffraction is the loss of information during the projection of 3D reciprocal space onto 1D scattering angle. As a result, space group symmetry cannot always be assigned unambiguously. On the other hand, solid state NMR is an excellent complementary method to assert space group symmetry.

In this presentation, I will highlight the strength of the combination of solid state NMR with X-ray powder diffraction to solve *ab initio* crystal structures of metal organic polymers and cocrystals.[2-4]

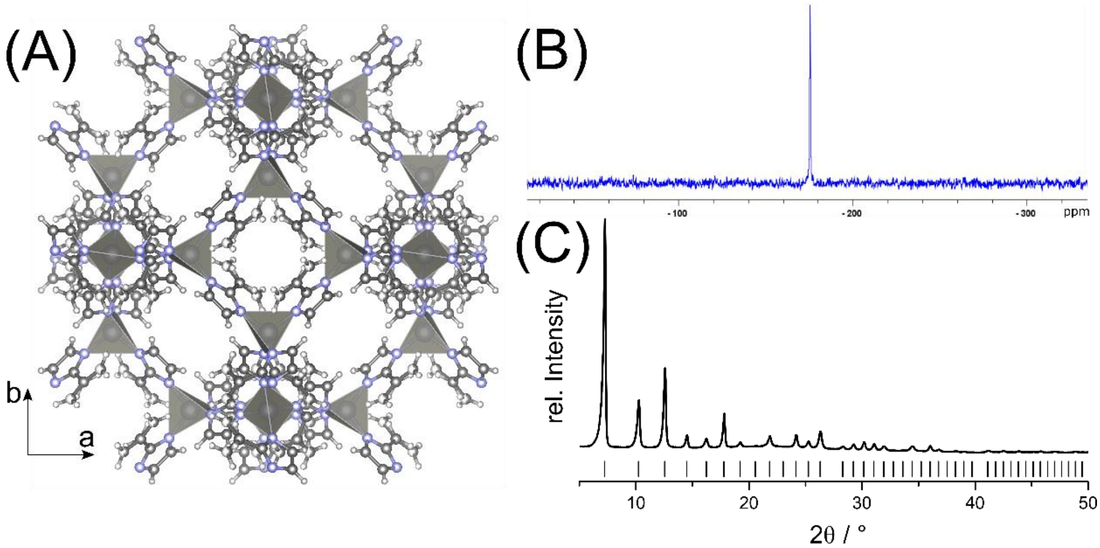

Figure 1: (A) Crystal structure, (B) ^{15}N ssNMR spectrum and (C) X-ray powder diffraction pattern of SOD-Zn(**VIm**)$_2$.

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A Novel bis-1,2,4-benzothiadiazine pincer ligand: synthesis, characterization and coordination chemistry

Nathan Doupnik, Konstantina Pringouri, Muhammad U. Anwar and Jeremy M. Rawson*
University of Windsor

The development of polydentate N-donor ligand sets with tuneable coordination chemistry is desirable for the construction of new functional materials. The pincer N-based bis-chelate 2,2';6',2'' terpyridine (terpy, Fig. 1, left) is known to form stable complexes with a variety of transition metals which have found uses in solar cells, light emitting electrochemical cells, luminescent systems, and non-linear optical devices. Related ligand-metal complexes such as Co^{II}(terpy)2 has been shown to demonstrate thermal spin-crossover.[1] The family of 1,2,4-benzothiadiazines (btdaH) with sulfur in various oxidation states (II/IV/VI) have attracted attention for both materials and pharmaceuticals applications. The applications for 1,2,4-benzothiadiazine molecules and their derivatives are commonly dictated by the oxidation state of the sulfur atoms. Benzothiadiazines in the S(VI) oxidation state are commonly found in pharmaceuticals such as thiazide medications to treat hypertension.[2] The S(IV) systems are uncommon but recently have been reportedly accessed through aerial oxidation of the S(II) state in the presence of Lewis acidic metals and basic species.[3] The S(II) derivatives have shown reversible 1e$^-$oxidation reactions to generate stable radicals and have been exploited in the synthesis of paramagnetic liquid crystals and as molecular conductors.[4-5] My research has focused on the development of a novel pincer ligand, 2,6pyridyl-bis-benzothiadiazine (bis-btdaH2, Fig. 1, right), designed to offer a tridentate mer-binding coordination geometry. This presentation will focus on ligand synthesis and reactivity towards first row transition metal ions.

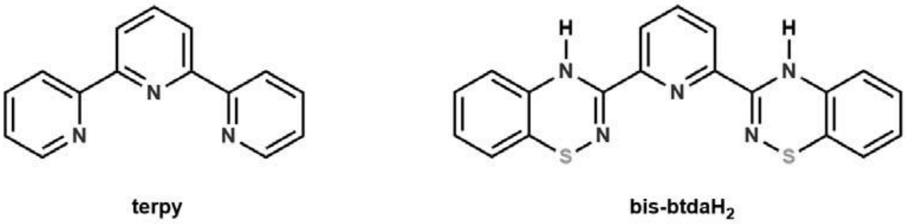

Fig. 1 Molecular structure of terpy (left) and 2,6-pyridyl-bis benzothiadiazine (bis-btdaH2, right).

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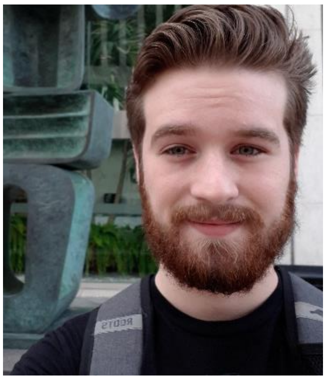
Publishing in Nature and Nature Research Journals

Dr. Johannes Kreutzer
Associate Editor, Nature Communications

This presentation will outline a range of different Nature research journals, as well as other journals published by the Nature Publishing Group (NPG), including their scope and different ways of dissemination and highlighting research at NPG.

Poster Abstracts



1. Non-Covalent Pnictogen-Bonded Cocrystals Formed with Mechanochemistry studied by $^{121/123}$Sb NQR Spectroscopy

R. Johannson, C. Leroy, D. L. Bryce
Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Canada.

A pnictogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a pnictogen atom (N, P, As, Sb, Bi) in a molecular entity and a nucleophilic region in another, or the same, molecular entity. Here, we report new pnictogenbonded adducts between SbF_3 and $SbCl_3$ with various Lewis bases (N, S, and O electron donors) prepared via mechanochemical ball milling. Pnictogen bonding is investigated by $^{121/123}$Sb (I = 5/2 and 7/2, respectively) NQR spectroscopy[1] and powder X-ray diffraction, along with SSNMR (^{13}C CP/MAS) spectroscopy when appropriate. DFT calculations of NMR parameters as well as natural localized molecular orbital analyses complement the experimental findings. Observed frequency shifts in the NQR spectrum upon cocrystallization are on the order of 0.1 to 10 MHz and clearly reveal the formation of pnictogen bonds to antimony. This work provides a novel probe of pnictogen bonds and pnictogen bond formation, a class of interactions for which unique applications in catalysis have recently been uncovered.[2]

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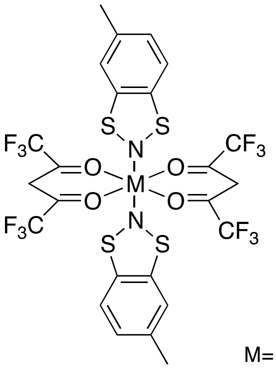
2. Transition Metal Complexes of the 1,3,2-Dithiazolyl Radical

Dominique M. Leckie (leckied@uwindsor.ca) and Jeremy M. Rawson* (jmrawson@uwindsor.ca)
University of Windsor

The field of single molecule magnets has provided access to systems in which individual bits of data can be stored at the molecular (nm and sub-nm) scale. Here the energy barrier to reversal of the magnetization is given by DS^2 where D reflects the magnetic anisotropy and S is the spin ground state of the complex. Most SMMs are based on 3*d* or 4*f* metal ions as a source of both D and S but the use of paramagnetic ligands (the so-called "metal/radical approach") has attracted attention to increase the spin ground state in polynuclear complexes. Extensive work by Preuss has investigated both 3*d* and 4*f* metal complexes of dithiadiazolyl radicals.[1] The related dithiazolyl radicals have been poorly studied in comparison.[2] Here, we present the synthesis and characterization of a series of mononuclear complexes of 4-methyl-benzo-1,3,2-dithiazolyl, MBDTA, with $M(hfac)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) using X-ray diffraction, EPR spectroscopy and SQUID magnetometry.



M= Mn, Fe, Co, Ni, Cu, Zn

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3. Preparing hydrogen-bonded photo-reversible materials

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Many photo switchable materials have azobenzene incorporated covalently into their backbones because the reversible trans-cis isomerization of azobenzene makes it an effective photo switch. However, systems using non-covalent interactions, such as hydrogen bonding, have garnered much attention due to the relatively strong, selective and directional nature of the hydrogen bond. It has already been shown that when azobenzene is hydrogen bonded to a polymer, the optical and mechanical properties of the polymer changes. The majority of the polymers utilized in making these supramolecular hydrogen bonded azobenzene systems are synthetic polymers.

Instead of using synthetic polymers to develop these supramolecular complexes, biodegradable and bio-sourced polymers can be used. Therefore, we aim to prepare hydrogen bonded self-assembled guest-host complexes by mixing a range of substituted azobenzenes with biodegradable and bio-sourced polymers. These materials will display improved optical and mechanical properties when compared to the host polymers and will also be capable of assembly and disassembly. The materials will be characterized using liquid NMR, powder XRD, FT-IR spectroscopy and ellipsometry. The photo-induced birefringence and kinetics of the *trans-cis* isomerization will also be studied.

4. Growth characteristics of silica-carbonate microstructures under the influence of Chicago Sky Blue Dye

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Spurred by lessons learnt from the ability of nature to “design” biominerals with a high degree of control over their shape, size, mineral phase and hierarchical assemble over multiple length scales, a multitude of bottom-up research strategies have been geared towards developing self-assembled inorganic materials having superior functionality and complexity. Of particular interest are 3D nano-crystalline composite materials, characterized by long-range orientational order and highly curved surfaces, which can be synthesized from the coupled reaction of the carbonates of barium, strontium and aragonite-type calcium carbonate with silica in alkaline (pH ~10-11.9) environments under the influence of atmospheric CO2. These silica-carbonate microstructures include cardioidal sheets, helicoids, “worms”, flower-like and globular structures. In this work, we aim to show how the size and predominant morphologies of silica-carbonate microstructures can be tuned as a function of sulphonated azo dye concentration in addition to its method of incorporation in the crystallization solution. Indeed, this research also provides indirect evidence for accelerated growth rates of the microstructures from solutions containing dye as implied by an increase in size relative to control experiments without dye during a growth period of 1.5-2 hours. Directed strategies to control both shape and size are of fundamental importance since it is well-known that the chemical composition and physical properties of a material are intimately connected to its function. Light and scanning electron microscopy (SEM) are the principle tools used for the characterization of the as-formed microstructures.

5. Green Applications of Metal–Organic Frameworks

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Department of Chemistry & Biochemistry, Concordia University
†authors contributed equally

Our environment is suffering greatly due to many global issues including, but not limited to, waste disposal, natural resource depletion, and air, water and soil pollution. The relatively new field of chemistry, green chemistry, embraces and implements the notion of inventing and designing chemical products and processes that seek to mitigate and/or eliminate the use/generation of hazardous substances. Metal–organic frameworks (MOFs) are an intriguing class of hybrid porous materials[1] that are comprised of metal nodes bridged by organic linkers. MOFs have been studied in traditional green chemistry applications such as catalysis, as well as many other green applications including energy conversion and storage, and pollution remediation, amongst others.[2]

MOFs have shown significant potential for the remediation of air pollution[3] as well as water pollution[4] owing, in part, to their high surface area and tunable pore shapes and sizes which makes them highly modular adsorbent materials. MOFs can be functionalized *de novo* and post-synthetically[3] and can be tuned to encapsulate a variety of guest molecules.[5] In addition, the judicious choice of organic linkers and metal nodes allows for the design of materials with open metal sites which have been shown to aid in air and water pollution remediation[6] as well as other green applications including carbon dioxide capture,[7] and hydrogen storage.[8] Towards reducing our reliance on fossil fuels, MOFs have been studied in solar energy applications, including light harvesting, energy transfer, and as catalysts[9] for the conversion of solar energy to fuels.[10,11]

This poster presentation will highlight the recent progress made towards the use of MOFs in wide-ranging green applications.

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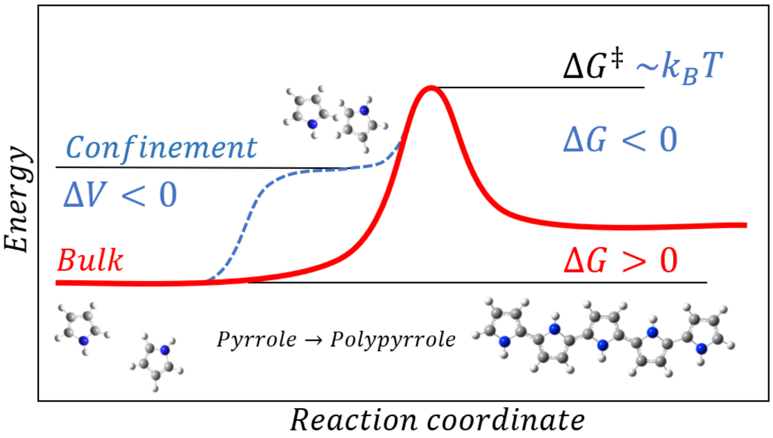
6. Confinement-induced reaction spontaneity in a water solvated nanosystem

Matt McTaggart, Cécile Malardier-Jugroot
Royal Military College of Canada

Enzymes are water soluble amphiphilic co-polymers that self-assemble into structures that catalyze the biochemical processes they serve. As efficient and precise as enzymes are, they did not evolve to serve human purpose but biological need. By identifying the necessary and sufficient physico-chemical properties we aim to develop synthetic analogues that take full advantage of evolution and artifice.

Poly(styrene-*alt*-maleic anhydride) is an amphiphilic co-polymer that self-assembles to create water soluble structures with wetted hydrophobic interiors whose minimum dimension is 2.5 nm. Solvation energy minimization drives low solubility molecules to become confined within the SMA structures with an unexpectedly high packing density. We used disk-chopper neutron spectrometry to find that the translational diffusion of pyrrole (C_4H_5N) immediately fell from the bulk liquid value to one equivalent to polypyrrole. Polymerization then occurred spontaneously and following zeroth-order kinetics, neither of which have been previously reported. We are using the GROMACS molecular dynamics software to match simulation results to our experimental data and determine the effective pressure felt by the pyrrole under confinement
Spontaneous compression and polymerization only occurs under nanoscale confinement, implicating both water and the SMA nanostructure in a systems-level emergent effect.



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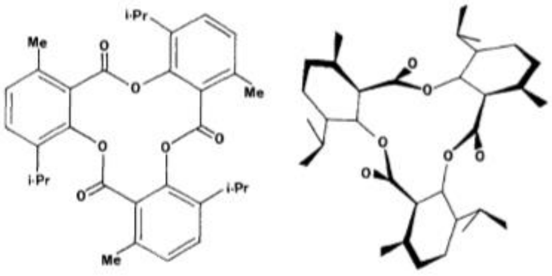
7. Solid Phase Deracemization of a Chlathrate: from Mechanochemical Synthesis to Viedma Ripening of Tri-*o*-thymotide

T. P. Thao Nguyen, Jean-Louis Do, Lei Ma and Louis A. Cuccia
Department of Chemistry & Biochemistry, Concordia University



Clathrates are a branch of inclusion compounds where a guest molecule is encapsulated inside a host crystal lattice. The chemistry of chlathrates is studied since the middle of the twentieth century and reports the discovery of new inclusion compounds and hosts, as well as their pragmatic applicability in chemical analyses and molecular separation processes.(1) Our compound of interest, tri-*o*-thymotide (ToT), exhibits a remarkable propensity to complex with more than 100 guest molecules on crystallization. (2) The 12-member-ring molecular conformation, constrained by a rotation around a single bond, adopts a chiral three-propeller shape configuration (either M or P) which is dynamically racemizing in solution, but preserved during conglomerate crystallization. (3) In light of the rich research history of ToT, we present a novel approach to its synthesis using simple one-pot mechanochemistry and revisit the study of chiral amplification and discrimination using attrition-enhanced deracemization, also known as *Viedma ripening* (4).

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8. A novel organic radical exhibiting magnetic bistability

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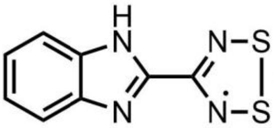
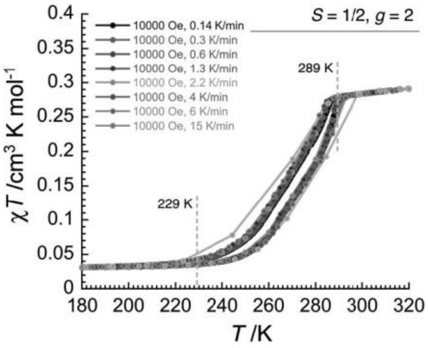
Magnetic bistability, resulting in rate-independent magnetic hysteresis, is a technologically relevant property because it imparts memory. Materials that exhibit this type of behaviour are important for possible device, sensor, and safety equipment design. We have successfully synthesized a new organic radical HbimDTDA (4-(2’benzimidazolyl)-1,2,3,5-dithiadiazolyl) that exhibits rate-independent hysteresis via a crystal-to-crystal phase transition. The material switches between diamagnetic and paramagnetic states in response to temperature by the reversible breaking and formation of pancake bonds. Magnetic and structural data for HbimDTDA that illustrate hysteretic behaviour are presented. Initial efforts in the development of Fe(II)-based spin-crossover materials using HbimDTDA as a ligand and the production of a radical anion, bimDTDA, will also be described.





9. Exploring the Reactivity of Tetrathiocins with *d*-block Metals

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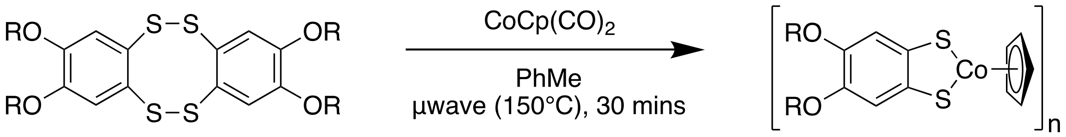
University of Windsor

Although metal dithiolene complexes were discovered in the 1960s, their commercial applications are still very limited. These complexes exhibit intense colors, multiple oxidation states, reversible redox reactions and the ability to take on different geometric conformations, which make them ideal in a variety of materials applications. Their diverse nature allows them to be used in areas such as building blocks for enzymatic modelling, conductivity, magnetism and in the field of nonlinear optics. To date, many dithiolate complexes contain strongly electron-withdrawing groups, such as $(NC)_2C_2S_2^{2-}$ and $(F_3C)_2C_2S_2^{2-}$, while the π-conjugated dithiolates predominately contain benzenedithiolate and toluene dithiolate. More recently, it has been shown that alkoxy-functionalized bis(benzo)-1,2,5,6-tetrathiocins are able to undergo oxidative addition to low valent group 10 metal complexes (Ni, Pd, Pt). This presentation will explore the reactivity of the group 9 metal, Co, with tetrathiocins.



1 R = Me, n = 2
2 R,R = $CH_2CH_2(OCH_2CH_2)_3$, n = 1
3 R,R = $CH_2CH_2(OCH_2CH_2)_4$, n = 1

The synthesis of the cobalt complexes CpCo(dt) (dt = dithiolate ligand) was achieved through microwave reactions of $CpCo(CO)_2$ with the respective bis(benzo)-1,2,5,6-tetrathiocin. The complexes were characterized by single crystal X-ray diffraction, NMR spectroscopy and other molecular spectroscopy techniques (FT-IR) to confirm their synthesis. The reaction equilibrium between $16e^-$ monomer and $18e^-$ dimer will be discussed.

10. From Olefin Metathesis to the Friedländer Reaction: Mechanochemical Catalysis for the Synthesis of Nitrogen Heterocycles

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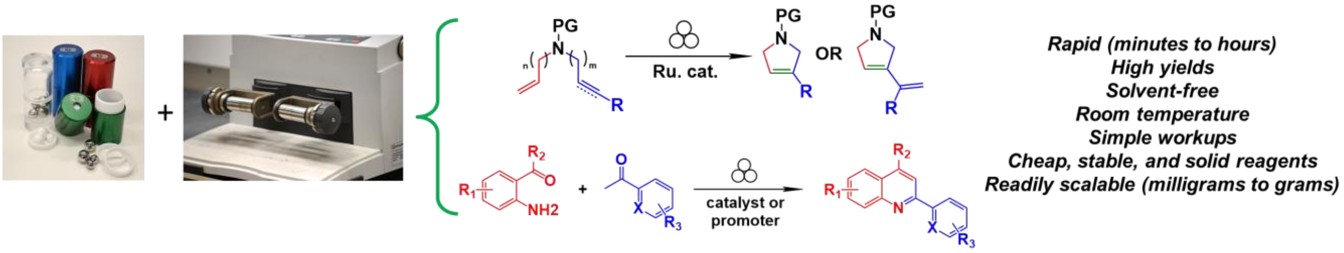
The fields of homogeneous and heterogeneous catalysis have seen tremendous growth over the years as a consequence of rapid advances in technology, as well as computational and coordination chemistry. Catalytic processes have become pivotal in numerous fields ranging in scales from industrial to academic and have enabled the preparation of a vast library of novel compounds, from small molecules to polymeric materials. Such processes, however, have not deviated much from solution-based routes with comparatively few explorations in the solid-state.



Rapid (minutes to hours)
High yields
Solvent-free
Room temperature
Simple workups
Cheap, stable, and solid reagents
Readily scalable (milligrams to grams)

Mechanochemical reactions encompass the use of mechanical force to affect a chemical transformation and have gained increased attention in recent years providing opportunities for unique, cleaner, and more efficient reactions.[1-2] In this context, herein we present the application of mechanochemistry as the enabling element for cleaner and more efficient metal and Lewis acid catalysis. Specifically, we have developed solvent-free strategies for ruthenium-catalyzed olefin metathesis[3] and the Lewis acid-catalyzed Friedländer reaction in the synthesis of nitrogen heterocycles of pharmaceutical and materials science relevance. This presentation will outline the potential of mechanochemistry in conducting rapid, solvent-free, and room temperature transformations of commercially available and specialty organic molecules.

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11. Engineering Rare Earth Oxalates for Selective Separation of Scandium from Lanthanides

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Department of Chemistry, McGill University

Scandium, along with yttrium and other lanthanide elements, is considered as a rare earth element (REE). This categorization has less to do with the relative abundance of these elements (scandium is as abundant as cobalt) and more to the scarcity of viable ores and the difficulty in separation and purification of these elements. Common processes for REE extraction and separation involve volatile organic liquids, synthetically demanding custom ligands, and concentrated mineral acids[1]. As a means to minimize the cost and environmental impact of such separation, we utilize the already common process of precipitation of REE cations from solution by oxalic acid[2] as a means for REE separation.

Lanthanides form 2- or 3-D tightly bound frameworks with oxalate anions which results in the low solubility of these materials in aqueous media. By incorporating other ions in the framework, the stability of the framework in aqueous environment can be decreased and the solubility of the materials can be greatly increased.

Herein we explore the solid-state reactivity of eight rare earth oxides (Sc, Y, La, Yb, Eu, Gd, Lu and Nd) with oxalic acid and its salts (Na, K and NH_4), revealing new metal-organic architectures based on scandium and suggesting a mild, environmentally-friendly route for their separation.

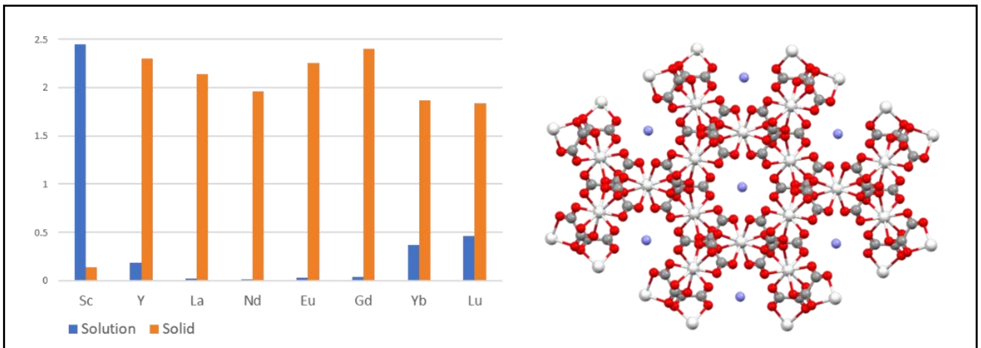

Figure 1. Left: Results of separation of Sc from other REE elements. Right: Crystal structure of $Sc(NH_4)(C_2O_4)_2$.

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12. Simple Binaphthol Linkers for Multifunctional Coordination Polymers and Metal Organic Frameworks

Patrick Julien, Hatem Titi, Robin D. Rogers, Tomislav Friščić
Department of Chemistry, McGill University

Metal-organic frameworks (MOFs) have emerged as promising multifunctional materials incorporating porosity, chirality, and optically active molecules. 1,1′-binaphthol (BINOL) based ligands are of interest due to their highly stable axial chirality, optical properties, and their potential for post-synthetic modification. This work explores the coordination chemistry of readily synthesized and affordable BINOL dicarboxylates as building blocks for a variety of coordination polymers and frameworks[1]. Through the careful selection of additives and linkers we are able to assemble interesting architectures under mild synthetic conditions with various metal ions in diverse oxidations states. We are currently utilizing this generalizable synthetic approach to rapidly explore and identify novel coordination polymers and structures which exhibit multiple properties such as porosity, chirality, and/or luminescence. Ultimately, we hope to create multifunctional materials amenable for applications in catalysis and sensing.

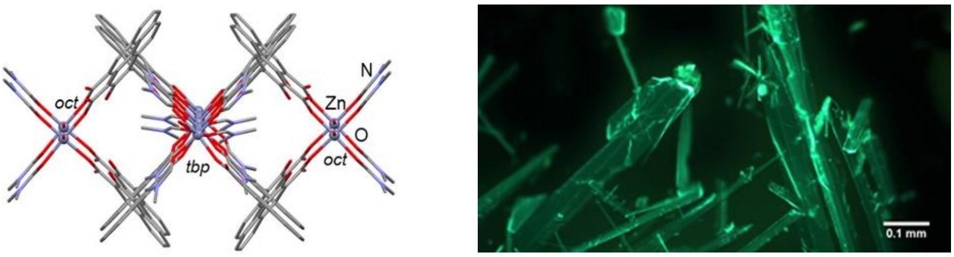

Figure 1. Structure (left) and fluorescence (right) of Zn- BINOL-3,3′-dicarboxylate coordination polymer[1].

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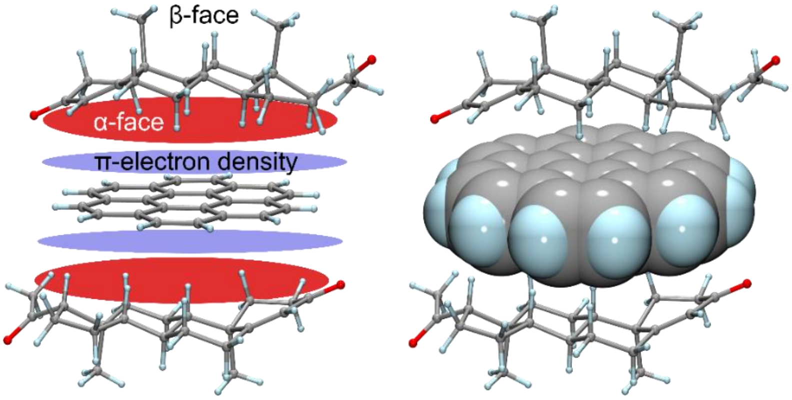
13. Steroids as coformers in cocrystallization with PAHs and heterocycles

Filip Topić, Davin Tan, Karen J. Ardila-Fierro, Tomislav Friščić
Department of Chemistry, McGill University

Currently, function and biological behaviour of steroids are believed to be mainly determined by terminal chemical groups attached to their backbone. Recently, however, some of us revealed there may be another way for steroids to recognize and bind other molecules, named the α···π interaction, so far observed in solid-state complexes of the steroid sex hormone progesterone with electron-rich, planar aromatic molecules (arenes). This interaction forms specifically between one face of the progesterone molecule, known as the α-face, and the arene π-electron cloud. Importantly, the small number of other steroids explored so far suggest that such supramolecular assembly is highly dependent on the fine detail of the steroid backbone, thus paralleling their behaviour in biological systems. In the context of supramolecular chemistry, α···π interaction can enable the design of new solid-state materials with potential use in drug delivery.



We set out to explore the limits of the cocrystallization strategy with progesterone, using larger PAHs such as perylene and coronene, and polyaromatic heterocycles such as phenanthridine, phenanthroline and others. The cocrystal screening was conducted mechanochemically, i.e. by liquid-assisted grinding, and the successful formation of a cocrystal established by powder X-ray diffraction and ATR-IR spectroscopy. A number of cocrystals were successfully obtained and their structures determined by single-crystal X-ray diffraction.

Our results demonstrate impressive reliability of the α···π interaction, witnessed by a relatively high rate of successful cocrystallization with the investigated coformers. On the other hand, the stoichiometry of the cocrystals is unpredictable, with all of 1:1, 2:1 and 3:1 steroid-to-coformer stoichiometries observed.

14. Mechanochemistry vs. solution growth: striking differences in bench stability of a cimetidine salt based on synthetic method

Ghada Ayoub, Vjekoslav Štrukil, László Fábián, Cristina Mottillo, Huizhi Bao, Audrey Moores, Davor Margetić, Mirjana Eckert-Maksić and Tomislav Friščić
Department of Chemistry, McGill University; Institute Ruđer Bošković, Zagreb, Croatia

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.

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15. Solvent-free Enzymatic Hydrolysis of Xylan

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Vascular plant biomass is an abundant renewable feedstock that could be exploited for biorefinery-based production of fuels, heat, commodity chemicals, and other commercially valuable products. Hemicelluloses, a vast group of complex, noncellulosic branched heteropolysaccharides consisting of various combinations of xylose, arabinose, mannose, glucose, galactose and *O*-acetyl-4-*O*-methylglucuronic acid residues, make up 10-30% of the dry weight of vascular plants. A major challenge in the bioconversion of lignocellulosic feedstocks is the high cost of converting the cellulosic and hemicellulosic components to fermentable sugars, including deconstruction of the recalcitrant complex matrix of lignocellulosic materials. Enzyme-mediated degradation of lignocellulosic biomass is a multi-step process that takes place in a heterogeneous reaction system, in which highly recalcitrant and water-insoluble polymer is hydrolyzed by enzymes at the solid-liquid interface.

Here, we present an efficient bioconversion of xylan to fermentable sugars under mechanochemical conditions without bulk solvent. Mechanochemical conditions help disrupt the cell wall structure thereby providing the enzymes access to their polysaccharide substrates. Using an inexpensive fungal xylanase without pretreatment of the substrate, bulk solvent, base/or acid our method gives high yields (80-100%) of reducing end sugar for conversion of the xylan in biomass.

16. Spontaneous Resolution and Chiral Amplification in Co-Crystals

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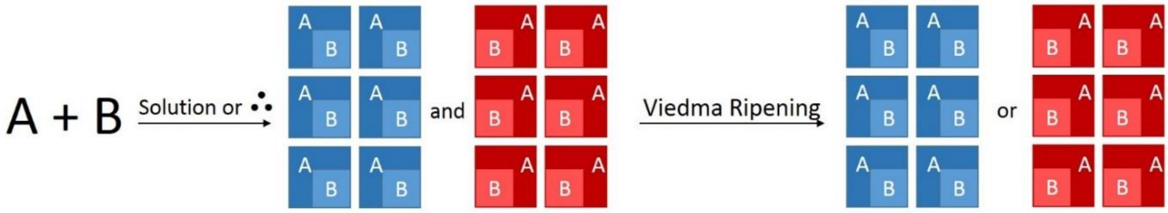
Department of Chemistry & Biochemistry, Concordia University

Achiral molecules can sometimes crystallize into one of the sixty-five non-centrosymmetric space groups to generate enantiomorphic conglomerate crystals.[1][2][3] Co-crystals are crystalline solids containing two or more molecular components usually in a stoichiometric ratio.[4] Herein, tryptamine (A) was able to co-crystallize with each of four different achiral carboxylic acids (B): *trans*-cinnamic acid (1), 4-chlorocinnamic acid (2), 4-chlorobenzoic acid (3), and 2-thiophenecarboxylic acid (4), to form optically active conglomerate co-crystals, linked by hydrogen bonds and quaternary ammonium salt bridges. The crystals' optical activity was investigated by solid-state circular dichroism (CD). The deracemization of these four co-crystal systems was further studied using Viedma Ripening, an attrition-enhanced deracemization process developed by Cristobal Viedma.[5] Tryptamine (A) itself also crystallizes as a chiral conglomerate, consequently, we will describe our efforts to influence the direction of mirror symmetry breaking in the cocrystals by using chiral tryptamine as a starting material in the Viedma ripening process.



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17. Developing "Soft-Bonding" Composite Materials from Hydrophylic Polymers and Azo Dyes

Tristan Borchers, Kayrel Edwards, Christopher J. Barrett
Department of Chemistry and School of Environment, McGill University.

Utilizing supramolecular interactions between hydrophilic polymers and photoactive dyes, we developed a series of photoactive polymers. Azobenzenes are used as photo-switches because of their fast, powerful and reversible trans-cis isomerization. Previous work in our group has utilized supramolecular forces with the presence of azobenzenes to form materials capable of exhibiting optical storage, being used as a humidity sensor, or molecular machine.[1,2,3,4] In the following poster we will present results regarding the use of electrostatic interactions to develop biocompatible photoactive crosslinked polymers, as well as photoactive surfaces developed through layer by layer (LBL) stacking of alternating dye/polymer. Separate layers are held together by electrostatic interactions between the oppositely charged polymer and dye. The material exhibited excellent optical clarity, as well as showing a linear relationship between absorbance and the amount of bilayers. Additionally the material has shown to display a unique effect when irradiated at low power, below the threshold of photo degradation. Following irradiation, a clear spot can be seen at the location of the laser beam. Further investigation is needed to understand this phenomenon.

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18. Cocrystals of Azo Chromophores as Engineered Optical Materials

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This poster describes the investigation of the design, synthesis, and optical properties of azo-dye based cocrystals. Azobenzenes have long been studied as a versatile chromophore for optical materials such as dyes, colourings, and photo-switches for photo-alignment or photo-actuation applications. The crystal engineering of fluorinated azobenzenes(co)crystals for dichroic and photo-mechanical properties has recently been explored by our collaboration, and represents novel materials towards various optical photo-phenomena, including photo-mechanical motion. Building upon the knowledge that simple, often two-component cocrystals can be designed to exhibit dichroism by parallel alignment of the chromophore within a crystal, we then describe the creation and dichroism of materials of greater complexity, achieved by the incorporation of a greater number of components. It demonstrates that the dichroic properties of these materials are tolerant of dynamic disorder provided that the azo molecules remain aligned, and also presents the expansion of our work from purely organic cocrystals to the realm of organic/inorganic salts.

19. Periodic DFT calculations for studying thermodynamic properties and Raman spectra of halogen-bonded cocrystals

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Department of Chemistry, McGill University

Intermolecular interactions, utilized in guiding self-assembly of cocrystals, are critical in the fields of crystal engineering and materials chemistry. Apart from the most highly studied class of intermolecular interactions, hydrogen bonding, a relatively new class of molecular recognition and self-assembly processes, halogen bonding, have surfaced in the past few decades as an effective and reliable way of controlling assembly of crystal structures.[1-2] In these interactions, a halogen bond, or more specifically its sigma hole, acts as an electrophilic site or halogen bond donor, interacting with sites that are high in electron density or halogen bond acceptors. In this study, we analyse the mechanochemical transformations between multiple stoichiometries of 1,4-triiodobenzene (1,4-tfib) and phenazine cocrystals, utilizing computational periodic density functional theory (DFT) calculations in CASTEP.[3] Firstly, thermodynamic properties of these structures were calculated, elucidating enthalpies of formation and enthalpies of interconversions between cocrystal stoichiometries. Next, free energy phonon calculations, a powerful tool in modelling atomic vibrations and calculating thermodynamic functions such as entropy and Helmholtz free energy, were performed. By computing these properties, we were able to evaluate the thermodynamic outcomes of cocrystal transformations as a function of temperature. In addition, our calculations were used to map vibrational frequencies to atomic motion, thereby assisting in the interpretation of experimental Raman spectra.

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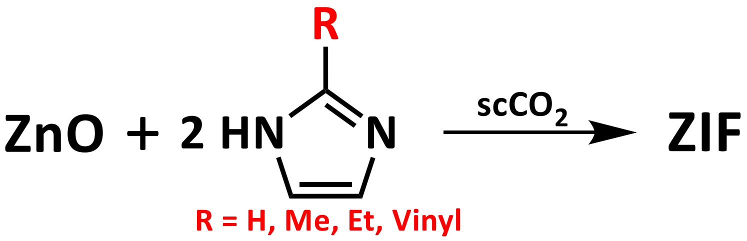
20. Supercritical carbon dioxide enables rapid, clean, and scalable conversion of a metal oxide into zeolitic metal-organic frameworks

Joseph M. Marrett, Cristina Mottillo, Christopher W. Nickels, Jean-Louis Do, Gandrath Dayaker, Luzia S. Germann, Robert E. Dinnebier, Ashlee J. Howarth, Omar K. Farha, Tomislav Friščić, Chao-Jun Li

Supercritical carbon dioxide ($scCO_2$) has found widespread use in polymer synthesis[1], chemical separations[2] and even activation of microporous metal-organic frameworks (MOFs)[3]. Recently, syntheses of MOFs in $scCO_2$ media have been reported but have required specialized metal precursors[4] or ionic liquid additives[5] to enable reactivity *via* solubilization of the metal source, limiting the ease for potential industrial scale-up of these techniques. Surprisingly, we find that $scCO_2$ enables the rapid and complete conversion of a *metal-oxide* to zeolitic imidazolate frameworks (ZIFs), a class of MOF whose structures mimic those of natural zeolites, in a clean and readily scalable fashion without the need for catalytic additives, organic solvents, or other auxiliaries. More specifically, we show that homogenous solid-state mixtures of zinc oxide and a substituted imidazole are cleanly and quantitatively converted to a ZIF, such as the well known ZIF-8, within minutes upon exposure to $scCO_2$.



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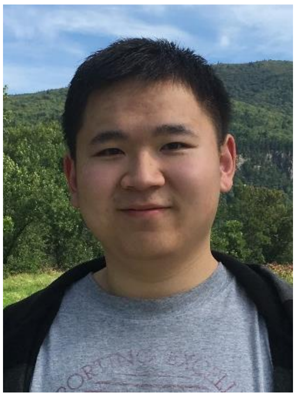

21. Green solid-state synthesis of SIFSIX metal-organic frameworks

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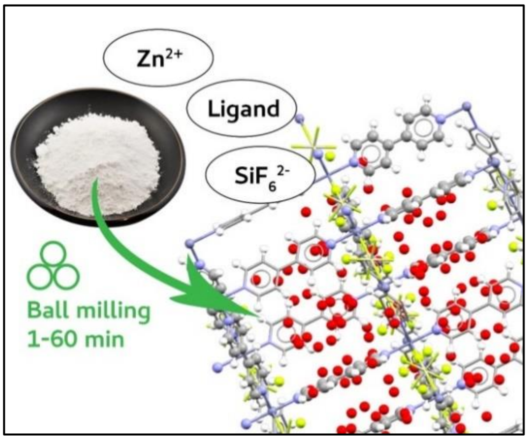
Microporous metal-organic frameworks (MOFs) are promising candidates for carbon capture and gas separation,[1,2] due to their high, tunable internal surface areas, which render them well suited for sequestration and separation of greenhouse gases (GHGs). Among these materials, the SIFSIX class of MOFs have been particularly promising for direct air capture of CO_2 and CH_4.[1,2]



SIFSIXes consist of two-dimensional square-grid sheets held apart by anionic SiF_6^{2-} pillars; each sheet is composed of transition metal ions (*e.g.* Ni^{2+}, Cu^{2+}, or Zn^{2+}) and ditopic ligands, such as 4,4'-bipyridine.[1] However, the known synthetic routes for SIFSIX materials are lengthy, require large solvent volumes, and depend on metal precursors that are often hazardous.[3,4] In addition, SIFSIXes are often unstable when exposed to water,[5] which severely hinders their longevity and commercial application. 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. We also discuss the effects of water exposure in the context of these reactions, and our efforts to mitigate them.

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22. Mechanochemical Synthesis based on Resonant Acoustic Mixing

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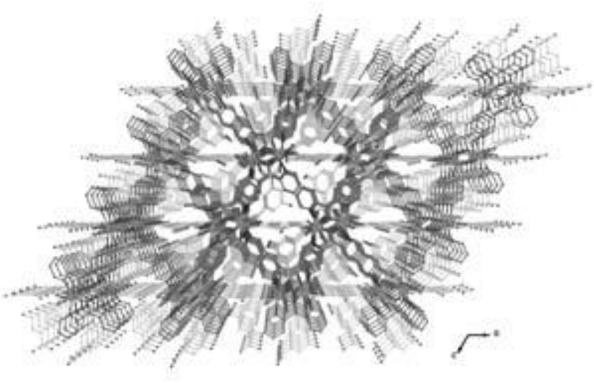
In recent years, organic synthesis has become increasingly oriented toward alternative and non-conventional methodologies, with the aim of achieving synthetic procedures that are cleaner, safer as well as more energy- and materials-efficient. Of particular interest in the development of Green Chemistry techniques for research and manufacturing is mechanochemistry, i.e. chemical reactivity induced or sustained through mechanical force. Mechanochemical reactions have attracted the attention of a wide range of chemistry researchers, not only providing cleaner, safer routes to conduct room-temperature and solvent-free synthesis, but also permitting the synthesis of previously inaccessible molecular targets. However, the applications of mechanochemistry are hindered by difficulties of reaction scale-up, as laboratory-scale ball milling processes are not readily adaptable to manufacturing-scale planetary or attrition mills. In order to resolve this long-standing problem of mechanochemical synthesis, we now present the use of resonant acoustic mixing (RAM) as a novel mechanochemical method that permits chemical transformations on milligram, as well as multi-gram scales, without introducing major changes in equipment design. By using a selection of organic transformations, including condensation, catalytic coupling, and ring expansion processes, this presentation will illustrate the general applicability, as well as scalability, of the mechanochemical RAM methodology.

23. Cu(II) Frameworks from a “Mixed Ligand” Approach

Athena M. Fidelli, V. G. Kessler, Giannis S. Papefstathiou
Department of Chemistry, University of Athens

Over the last years, we have been witnessing the born of a new field within the realms of molecular and supramolecular chemistry, which aspires to forge bonds between the fields of Metal-Organic Frameworks (MOFs) and Molecular Nanomagnets (MNMs) [1]. Both materials, MOFs [2] and MNMs [3] are interesting in their own right for their chemistry, aesthetics and properties. Making MOFs from MNMs or SMMs is not trivial, since it requires the controlled aggregation and organization of magnetic building blocks into designed 3D architectures. Inspired by the aforementioned synthetic challenge, we developed a “mixed-ligand” approach, which relies on the utilization of both “cluster-making” and “polymer-making” ligands. Our attention was drawn towards reaction blends containing di-2-pyridyl ketone (py_2CO) and simple bridging ligands. Given the ability of py_2CO to undergo metal-assisted transformation, generating polydentate ligands, that have provided access to a plethora of polynuclear metal complexes [4], we reasoned that a reaction blend of py_2CO/poly-carboxylate or py_2CO/poly-phosphonate will lead to polymeric complexes comprising polynuclear metal complexes. Through the “mixed ligand” strategy, in the chemistry of Cu^{II}, both coordination polymers (1D, 2D and 3D) and extended hydrogen-bonded frameworks have been isolated depending on the reaction conditions. In all cases, both “cluster-making” and bridging ligands have been incorporated into the structures, in which di-2-pyridyl ketone has undergone several metal-assisted transformations to yield CuII structural units. Topological analysis was additionally performed for all the compounds synthesized through this strategy, while magnetic studies were carried out for all the coordination polymers based on $[Cu_2\{(py)_2C(OH)O\}H_2O]^{3+}$ subunits.



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24. Understanding the Thermodynamic Driving forces Underlying Mechanochemical Transformations of Metal Organic Frameworks (MOFs)

Athanassios D. Katsenis[1], Mihails Arhangelskis[1], Gandrath Dayaker, Alexandra Navrotsky[2] and Tomislav Friščić[1]

Mechanochemistry has been successfully utilized as a synthetic technique in almost all areas of chemistry, including coordination polymers and microporous frameworks.[1,2] Specifically, mechanochemistry has been demonstrated especially efficient as a technique to explore the phase landscape of zeolitic imidazolate frameworks (ZIFs) and deliberately build families of either true MOF polymorphs (i.e. isocompositional frameworks) or families of isoreticular (i.e. based on the identical three--dimensonal network) MOFs based on judiciously designed organic ligands.[3,4] We have previously shown that mechanochemical syntheses of MOFs often proceed through multi-step reaction mechanisms where intermediate metastable phases appear before the formation of the final product.[3,5] Herein we provide a direct evaluation of the underlying thermodynamic driving forces to explain the course of the abovementioned interconversions by combining both calorimetric measurements and theoretical investigations based on periodic density functional theory (DFT).[4] In particular, we explore for the first time the relationship between the resulting frameworks and the different substituents of the organic ligands and how using computational approaches can provide a step towards crystal structure prediction of metal organic frameworks. In this presentation we will summarize our synthetic, computational and experimental studies, directed towards improving the fundamental understanding of both the thermodynamics of mechanochemical processes, and of factors controlling topology and stability of MOFs.

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25. Using chitinase enzymes under solvent-free conditions to break down chitin

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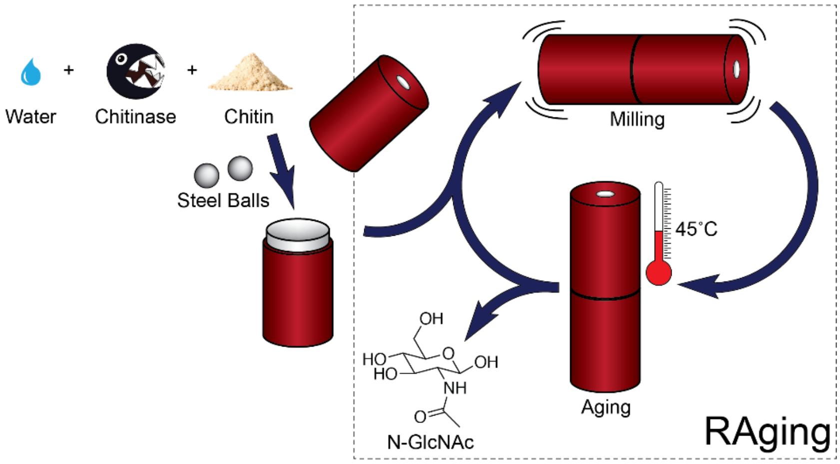
It is estimated that 7 million tons of crustacean shell waste is generated annually worldwide, with most simply being discarded into landfills and the ocean. One of the major components of crustacean shells, chitin, is the most abundant nitrogen-containing biopolymer found on the planet. Given the renewable feedstock of chitin, breaking it down into its monomer N-acetylglucosamine is of potential commercial interest to multiple sectors, especially with the potential to derivatize N-acetylglucosamine into chemicals such as glucosamine and 3-acetamido-5-acetylfuran. However, current methods to break down chitin typically employ harsh conditions (such as strong acids and bases), and therefore lack sustainability in the long run. While enzymes open the door toward more sustainable reactions, the class of enzymes capable of breaking down chitin, called chitinases, are poor at hydrolyzing chitin in solution. Our group has developed a new method of treating chitin biomass using enzymes under solvent-free conditions using a combination of mechanochemistry techniques including ball milling and accelerated aging (static incubation) repeated over many cycles, which we call reactive aging (RAging). Our group has previously demonstrated this approach to be effective for cellulose and plant biomass without the need for harsh chemicals or substrate pre-treatment[1]. Our results thus far demonstrate that we can efficiently hydrolyze chitin using RAging and can extend this process to acetic acid treated biomass with a significant improvement in the yield when compared to reactions done in solution.



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26. McGill Chemistry Characterization (MC^2) Facility

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The McGill Chemistry Characterization (MC^2) facility is a multi-user facility that provides instrumentation and expertise on a wide variety of analytical and microscopy techniques. Our instrumentation currently includes mass spectrometry, single-crystal and powder diffraction, NMR and EPR spectroscopy, AFM (including MFM and STM), and TGA, DSC, FTIR, and UV-Vis. We serve both the experienced and novice investigators and our services include training for independent use, analytical services and full support from our experienced staff.

Our facilities are located in McGill's Department of Chemistry in the Otto Maass building and the Pulp and Paper Research Centre. We serve over 200 researchers from academia, government labs, and industry each year.

27. Innovations in Mechanochemistry Instrumentation

Christopher W. Nickels (Form-Tech Scientific, Inc), Shalisa Oburn (University of Iowa), Leonard R. MacGillivray (University of Iowa), Tomislav Friščić (McGill University)

In the past 10 years mechanochemical reactions, *i.e.* solvent-free transformations induced or sustained by milling, grinding, shearing or stretching, have transformed from a laboratory curiosity to a generally applicable, versatile methodology to conduct clean, rapid chemical transformations.[1] So far, mechanochemistry has established itself as a unique methodology to conduct solvent-free chemical transformations with freedoms akin to those of solution-state synthesis, not only in organic chemistry, but also in pharmaceutical materials science, metal-organic and organometallic chemistry, as well as coordination chemistry, synthesis of microporous metal-organic frameworks (MOFs) and nanoparticle materials.[2] However, despite the successes and broad acceptance of mechanochemistry as a synthetic methodology, there has been almost no effort to develop mechanochemical instrumentation to suit mechanochemists' needs, as most existing instrumentation is based on designs developed for the needs of particle size reduction and metallurgical alloying. This presentation will outline our recent, not yet presented, innovations in developing mechanochemical instrumentation suitable for chemists.

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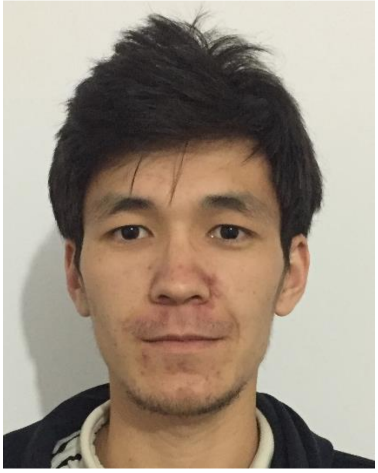

28. Preference for *crs*-topology in a series of isostructural metal 5-methyltetrazolates

Guvanch Gurbandurdyyev[1,2], Joseph Marrett[1], Igor Huskić[1], Hatem M. Titi[1], Mihails Arhangelskis[1] and Tomislav Friščić [1*]
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Metal azolate frameworks (MAFs) are a class of metal-organic framework (MOF) which are composed of cationic metal nodes and anionic azolate linkers, most commonly imidazolates, triazolates, and tetrazolates. Some types of MAFs have been studied extensively, specifically ones based on imidazolate linkers and divalent zinc nodes which adopt zeolitic topologies, while others based on more exotic metal-linker combinations remain less explored.[1]
In this work, we present a series of isostructural MAFs based on the 5-methyltetrazolate linker and a group of divalent transition metal nodes (Zn, Cu, Co, Ni). Unexpectedly, we find that the topology adopted by these MAFs under the vast majority of experimental conditions, one based on octahedral coordination (CN = 6), is not particularly dense and contains voids which may confer microporosity. This finding defies the conventional wisdom that the densest structure is always the most stable, but recent computational work in the group on related metal-pentazolate systems[2] supports our experimental findings, indicating that higher coordination numbers can make up for, and overcome, stability lost by a lowered packing coefficient. Recognizing these types of systems, where open structures are inherently stable, may represent a valuable tool for the design of functional MOFs with increased durability and permanence of porosity for industrial and scientific applications.

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