Welcome to

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CEMWOQ 6.5

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CODE OF CONDUCT

Policies are adapted from the American Crystallographic Association Statements and Policies (https://www.amercrystalassn.org/statements-policies)

Diversity: The organizing committee for the Crystal Engineering and Emerging Materials Workshop of Ontario and Quebec (CEMWOQ) is committed to including participation by people of different age, gender identity and expression, race, nationality, ethnicity, physical ability, marital status, sexual orientation, socioeconomic status, military or veteran status, or any other facet of social diversity.

Code of Conduct: Recording, taking photography, or screenshots of another individual's presentation without the explicit permission from that individual is not permitted.

All participants should treat each other with respect and consideration. Personal attacks directed toward other participants, harassment, intimidation, or discrimination in any form will not be tolerated. Disruption of talks at oral or poster sessions will also not be tolerated.

Examples of unacceptable conduct include, but are not limited to, verbal comments related to gender, sexual orientation, disability, physical appearance, body size, race, religion, national origin, inappropriate use of nudity and/or sexual images in Zoom meetings or in presentations, or threatening or stalking any participant.

Consequences for Violating the Code of Conduct: Anyone requested to cease unacceptable behavior will be expected to comply immediately. CEMWOQ-6.5 organizers may take any action deemed necessary and appropriate, including immediate removal from the meeting. CEMWOQ-6.5 organizers may prohibit attendance by anyone violating this code of conduct at any future meeting.

Reporting Violations of the Code of Conduct: If you are the subject of unacceptable behaviour or have witnessed any such behaviour, please immediately notify a CEMWOQ-6.5 organizing committee member. This can be done through the Chat function on Zoom, or by writing to cemwoq6p5@gmail.com.

Conference Venue

The workshop is being host through the conferencing application Zoom (https://zoom.us/). Information on how to join the meeting will be distributed to your institutional E-mail address (used for conference registration) shortly before the start of the meeting. You should not share the meeting invitation with anyone else. All registered participants will receive a link.

Timing

You should plan to join the meeting at least **10 or 15 minutes early**. You will arrive into a virtual waiting room where your name will be verified against the official list of registered participants. Please ensure that your name, as associated with your Zoom login, is the same as the name that you used to register for the conference.

If you arrive late, or you have to leave the meeting and return, you will again go through the process of being verified in the waiting room before being admitted to the conference.

Once you are admitted to the meeting, your microphone will be muted. You will only be able to “unmute” yourself if the meeting host enables this, for example, when asking questions or during the poster session. When speaking, you must be respectable and adhere to the CEMWOQ-6.5 Code of Conduct.

Only presenters will have the ability to share their screen. You will have the ability to turn on and off your own video, but you must adhere to the CEMWOQ-6.5 Code of Conduct. If you are unmuted and find that your own audio is breaking up, you should turn off your video.

During sessions, if you would like to ask a question, it is recommended that you “raise your hand”. This can be done by first clicking on the icon labeled "Participants" at the bottom center of your computer screen. Then at the bottom of the window on the right side of the screen, click the button labeled "Raise Hand." If you are called upon by the host to ask your question, you will be unmuted. When you are done asking your question, or if there is insufficient time to get to your question, you should lower it by clicking the same button, now labeled "Lower Hand."

Posters for the poster session will be hosted at four different meeting links. Poster numbers for each link will be distributed by email to your official email address shortly before the poster session. You can join and leave each of these meetings in order to see all the posters that you would like. Once you arrive at the meeting, tell the host which poster number you would like to see, and the host will send you to the “Zoom breakout room” where that poster is being presented. Once you have seen the presentation you can leave the breakout room and return to the main room. The host will then send you to the next poster number that you would like to see. If you would prefer not to unmute yourself, once admitted to a poster meeting, you can change your Zoom display name to the poster number you would like to see. If you change your Zoom display name, you must continue to adhere to the CEMWOQ-6.5 Code of Conduct.

Organizing Committee

Louise Dawe is an associate professor in the Department of Chemistry and Biochemistry at Wilfrid Laurier University. She is vice-chair of the Canadian National Committee for Crystallography and organizes the annual Canadian Chemical Crystallography Workshop. She is also a member of the International Union for Crystallography (IUCr) Calendar Sub-Committee and is a co-editor of the IUCr's journal *Acta Cryst. C*. Louise co-organized CEMWOQ-4 with her colleague Prof. Ken Maly at Wilfrid Laurier University in 2017.

Tomislav Friščić is a Professor at McGill University. He obtained his B.Sc. degree with Prof. Branko Kaitner at the University of Zagreb (2001, Croatia), followed by a Ph.D. with Prof. Leonard R. MacGillivray at the University of Iowa (USA, 2006). After a post-doctoral stay with Prof. William Jones at the University of Cambridge and Pfizer Institute for Pharmaceutical Materials Science (2008), he was a Herchel Smith Research Fellow at the University of Cambridge until joining McGill University (2011). His group is investigating the solid state as a medium for cleaner, new chemistry, and has been involved in CEMWOQ since 2013.

Luzia S. Germann was born in Interlaken, Switzerland. She obtained her B.Sc. and M.Sc. from the University of Bern under the supervision of Samuel Leutwyler (2013) and Piero Macchi (2015), respectively. She did her Ph.D. at the Max Planck Institute for Solid State Research in the group of Robert E. Dinnebier, where she monitored solid-state reactions of functional molecular materials using *in situ* X-ray powder diffraction. She is currently a postdoc in the Friščić-group, funded by the Swiss National Science Foundation, working on green synthesis and *in situ* monitoring of mechanochemical reactions. Luzia was a co-organizer of CEMWOQ-5, hosted at McGill, where she jointly organized a workshop on powder X-ray diffraction with Mihails Arhangelskis.

Ashlee J. Howarth was born and raised in London, Ontario. She obtained her undergraduate degree from the University of Western Ontario in 2009, and then went on to do her PhD in inorganic materials chemistry at the University of British Columbia under the supervision of Michael O. Wolf. Before joining the faculty at Concordia, she completed an NSERC Postdoctoral Fellowship at Northwestern University with Joseph T. Hupp and Omar K. Farha. At Concordia, the Howarth research group is focused on the design and synthesis of rare-earth metal–organic frameworks targeting applications in wastewater remediation, catalysis, and chemical sensing. Ashlee was a co-organizer of CEMWOQ-6 hosted at Concordia in 2019.

Dylan Shields grew up in the Cincinnati, Ohio area before getting his PhD from Dr. Anna Gudmundsdottir at the University of Cincinnati. His PhD research focused primarily on determining solid-state photoreaction mechanisms using pump-probe spectroscopy, X-ray crystallography, and quantum mechanical calculations. However, Dylan's favorite research topic during his PhD was his work on photomechanical crystals. By understanding the factors that controlled these crystalline reactions, the photoinduced mechanical effect in the crystals could be modulated by simple substitutions to perform different macroscopic applications. Upon graduation from the University of Cincinnati, Dylan accepted a post-doctoral research position at McGill University in the Friščić group, where he will be working on hypergolic materials, crystallography and solid-state reactions.

Nick Vukotic was born in Dubrovnik, Croatia. He completed his Ph.D. in Chemistry (2014) at the University of Windsor under the supervision of Stephen J. Loeb, working on incorporating dynamic interlocked molecules into metal-organic frameworks. He then pursued a career in industry developing X-ray diffraction instrumentation as Principal Scientist at PROTO. In 2019, he joined the faculty at the University of Windsor as an NSERC/PROTO Industrial Research Chair in X-ray Diffraction and Crystalline Materials. His research program is focused on the creation of stimuli-responsive crystalline materials for drug release applications and the development of new research tools to study solid-state dynamics via XRD. Nick has been involved since CEMWOQ-3 was hosted in Windsor in 2015.

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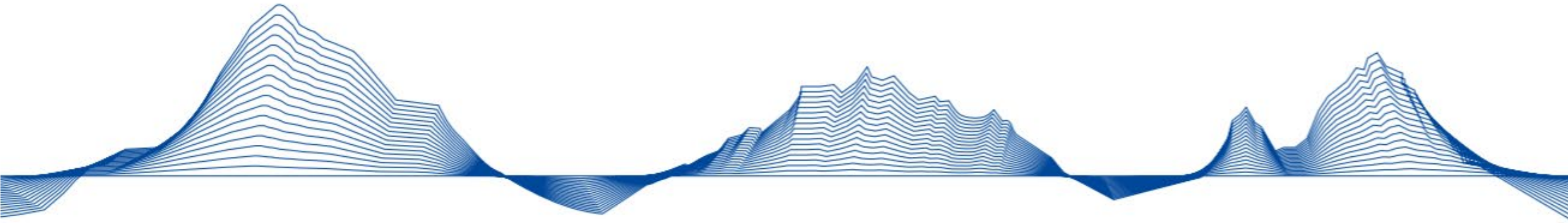

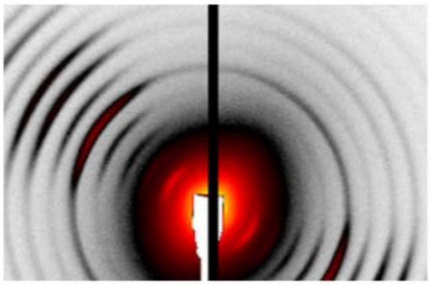

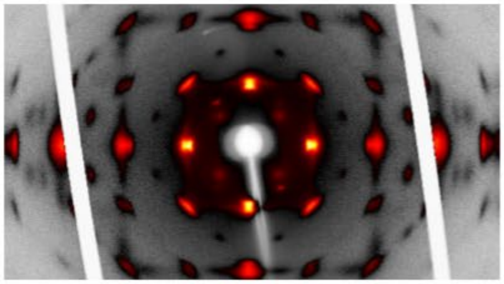

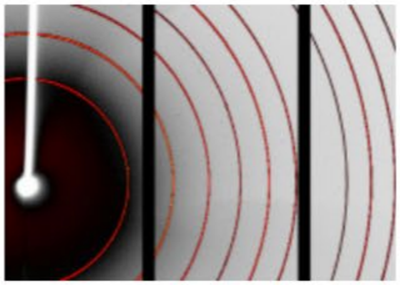

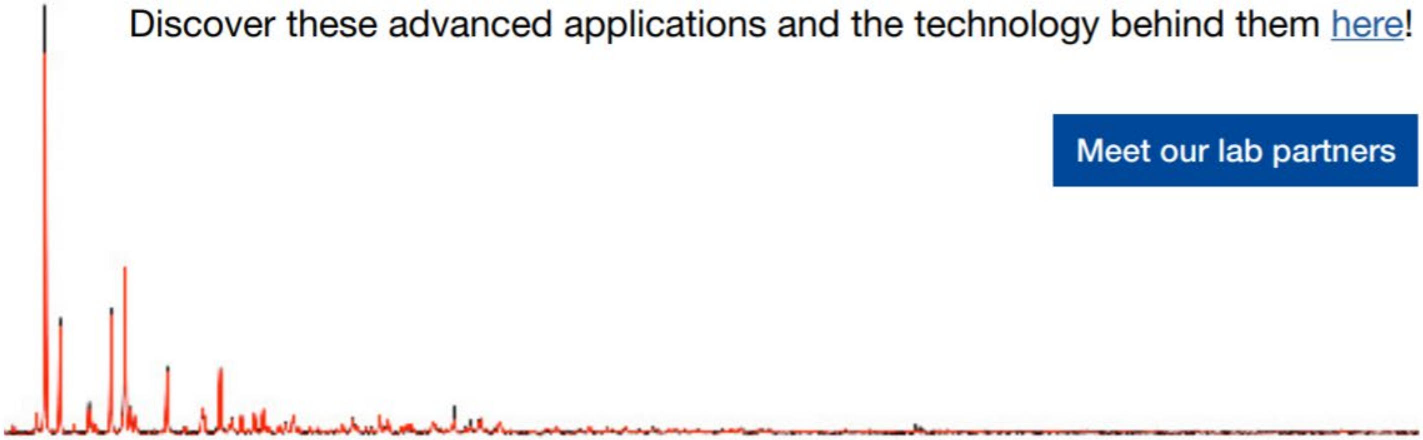

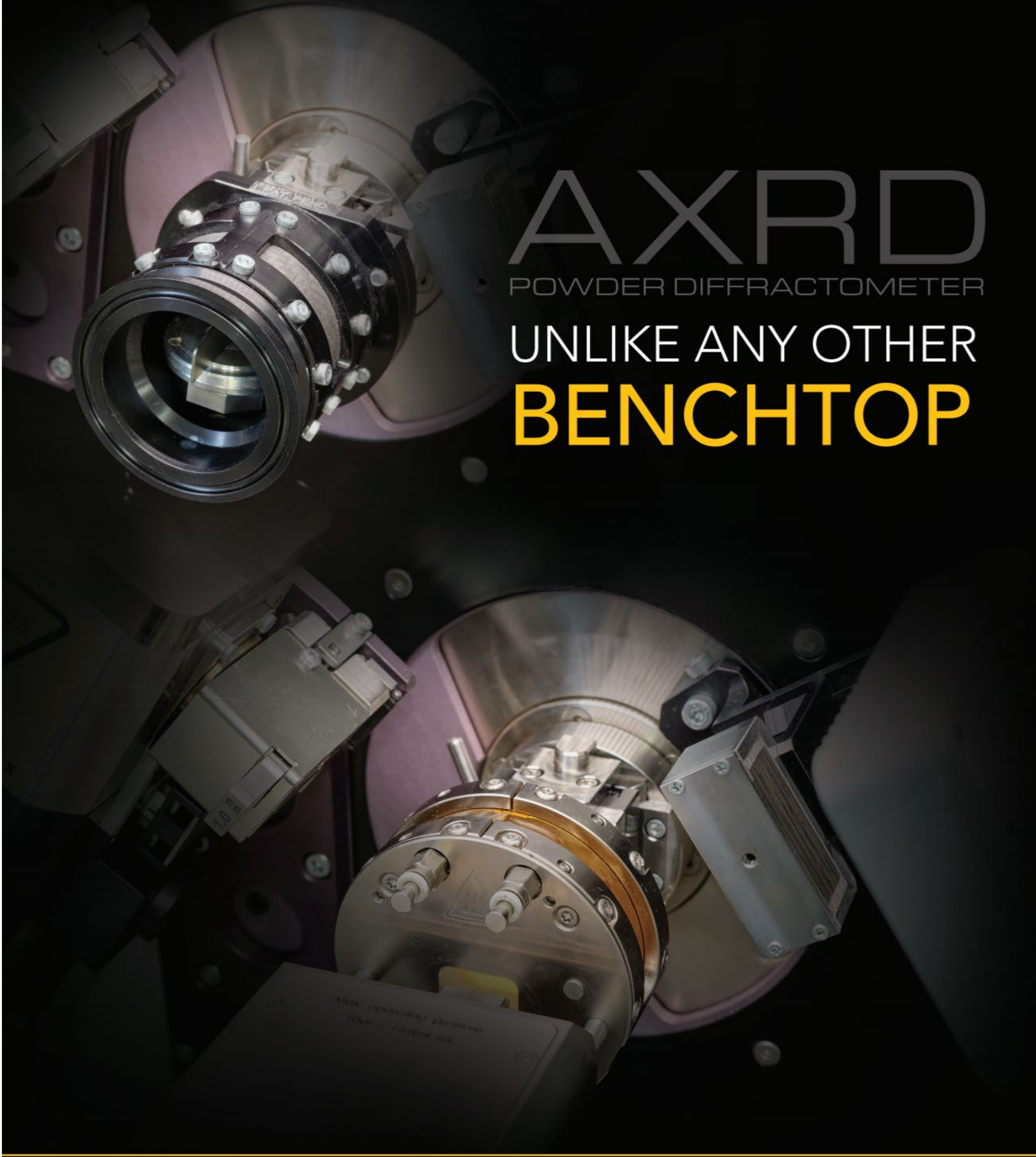
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Meeting Schedule

Saturday May 30, 2020:*Times listed in EST, GMT-4*

9:30-10:00am Morning Social

10:00-10:30am Omar K. Farha (Invited), Northwestern University

Programmable Smart Sponges for Protection

10:30-11:00am Gautam R. Desiraju (Invited), Indian Institute of Science

Some reminiscences of the early days of C-H...O hydrogen bonding: as seen through a representative paper

11:00-11:15am Coffee break (15 min)

11:15-11:30am Durga Prasad Karothu, New York University Abu Dhabi

Thermally Actuating Multifunctional Molecular Crystals

11:30-11:45am Mingoo Jin, Hokkaido University

A novel platform of luminescent crystalline molecular rotors via N-heterocyclic carbene metal complexes: Designing molecular rotations and luminescence in solid-state mediated by functionalized rotation-axis.

11:45am-12:00pm Krunoslav Užarević, Ruđer Bošković Institute

Rapid, clean and scalable synthesis of microporous functional MOFs and their non-conventional forms via mechanochemistry

12:00-12:15pm Benjamin Wilson, University of Windsor

Precise Spatial Arrangement and Interaction Between Two Different Mobile Components in a Metal-organic Framework

12:15-1:15pm Lunch Break

1:15-1:45pm Jillian Buriak (Invited), University of Alberta

The Twists and Turns of Incommensurate 2D Crystals

1:45-2:00pm Daniel Rainer, University of St Andrews

Mechanochemically assisted hydrolysis in the ADOR process

2:00-2:15pm Luzia S. Germann, McGill University

What is Crystallography?

2:15-2:30pm Coffee Break (15 min)

2:30-3:00pm Kristin M. Hutchins (Invited), Texas Tech University

Self-Assembly, Molecular Motion, and Thermal Expansion Behavior of Organic Crystals

3:00-3:15pm Feng Xibo, Dalhousie University

Piezochromism in Molecular Crystals: A Computational Study

3:15-3:30pm Rana Faryad Ali, Simon Fraser University

Solution-Phase Engineering of Second Harmonic Active Lithium Niobate Nanocrytals with Tunable Dimensions and Crystallinity

3:30-3:45pm Coffee Break (15 min)

3:45-4:15pm Michael T. Ruggiero (Invited), University of Vermont

Characterizing and controlling material function with terahertz vibrational spectroscopy

4:15-4:30pm Graeme Day, University of Southampton

Cocrystals: a computational survey and machine learning model of stabilisation energies

4:30-4:45pm Michael Ferguson, McGill University

Simulated indentations of aspirin and meloxicam crystals: a molecular- level study of mechanochemistry.

4:45-5:00pm Coffee break (15 min)

5:00-5:30pm Alex J. Stirk (Invited), Apotex Pharmachem Inc.

So You've Decided to Make a Generic Pharmaceutical

5:30-7:00pm Dinner Break

7:00-8:30pm Poster Session

Sunday May 31, 2020:*Times listed in EST, GMT-4*

8:30-9:00am Morning Social

9:00-9:30am Hajime Ito (Invited), Hokkaido University

Mechanical Response of Gold(I) Complexes

9:30-9:45am Simon M. Vornholt, University of St Andrews

Evaluating and Understanding the Performance of MOF-Polymer Composites for Medical Device Applications

9:45-10:00am Vinicius Martins, University of Western Ontario

Evaluating the impact of H_2O *on* CO_2 *capture in an ultramicroporous MOF via solid-state NMR spectroscopy*

10:00-10:15am Coffee break (15 min)

10:15-10:45am Leonard J. Barbour (Invited), Stellenbosch University

Developing complementary in situ methods for characterising porous crystalline materials

10:45-11:00am Soumya Mukherjee, Technical University of Munich

Ultramicropore Control of Molecular Sieving

11:00-11:15am Christopher Taylor, University of Southampton

Minimising polymorphic risk through cooperative computational and experimental exploration

11:15-11:30am Coffee Break (15 min)

11:30-12:00pm Jonathan W. Steed (Invited), Durham University

Supramolecular Gels: Control & Pharmaceutical Application

12:00-12:15pm Ahmad Sousaraei, Madrid Institute for Advanced Studies in Nanoscience

Reversible Protonation of Porphyrin MOFs as the Working Principle for Colorimetric Sensor Tags for Biogenic Amines

12:15-12:30pm Gustavo Santiso-Quinones (Sponsor), ELDICO Scientific AG

Electron Diffractometer: A Novel Device for Monitoring Nano-Crystalline Particles

12:30-1:30pm Lunch Break

1:30-2:00pm Graciela Díaz de Delgado (Invited), University of the Andes

Polymorphs, salts, and solvates of an Active Pharmaceutical Ingredient

2:00-2:15pm Gonzalo Campillo-Alvarado, University of Iowa

Escape from an Organic Crystal: Guest Transport Properties of a Boron-Based Molecular Machine

2:15-2:30pm Penghao Li, Northwestern University

Mechanical Interlocking in Triptycene-Based Hydrogen-Bonded Organic Frameworks

2:30-2:45pm Coffee Break (15 min)

2:45-3:15pm James Mack (Invited), University of Cincinnati

Stereoselective mechanochemical reactions through solid state ion pairing

3:15-3:30pm Dylan Shields, University of Cincinnati

Gas Powered Crystals: Photomechanical Diazide Crystals Produced by Photoinduced Gas Release

3:30-3:45pm Nan Liu, University of Ottawa

Water dispersible ligand-free rare earth fluoride nanoparticles: water transfer versus NaREF$_4$*-to-*REF$_3$ *phase transformation*

3:45-4:00pm Coffee break (15 min)

4:00-4:15pm Sandamini Ulpanhewa Vidanalage, University of Western Ontario

Understanding the Formation of Microporous Materials using In-Situ Solid-State MAS NMR Spectroscopy

4:15-4:30pm Lauren Macreadie, Massey University

Hydrocarbon adsorption within MOFs containing a 3D-linkers

4:30-5:00pm Darren Brouwer (Invited), Redeemer University

NMR Crystallography of Zeolites and Related Materials

5:00pm Closing Remarks and Social

Poster Presentations

Poster Number	Name	Affiliation	Breakout Room
Meeting Room 1 (Zoom Meeting Invite to be Sent by Email on May 30)			
1	Aamod Desai	University of St Andrews	1-1
2	Abeer Shunnar	Khalifa University of Science and Technology	1-2
3	Aditya Narayan Jhariya	University of Bradford	1-3
4	Andrew Kelly	Georgetown University	1-4
5	Anoop Kumar Saini	University of Delhi	1-5
6	Arthi Ravi	IISER Thiruvananthapuram	1-6
7	Asia Almuhana	University of Nottingham	1-7
8	Austin Peach	Florida State University	1-8
9	Avantika Hasija	Indian Institute of Science Education and Research	1-9
10	Bahar Karadeniz	Rudjer Boskovic Institute	1-10
11	Bartosz Mazur	Wroclaw University of Science and Technology	1-11
12	Blaine Fiss	McGill University	1-12
13	Carlos L. Santana	Webster University	1-13
14	Celymar Ortiz-de León	University of Iowa	1-14
15	Changan Li	University of Iowa	1-15
16	Chi Feng	Hokkaido University	1-16
17	Chi Yang Cheng	University of Southampton	1-17
18	Christopher Hartwick	University of Iowa	1-18
19	Daliah Farajat	Concordia University	1-19
Meeting Room 2 (Zoom Meeting Invite to be Sent by Email on May 30)			
20	Daniel Cutler	The University of Edinburgh	2-1
21	Deepak Kumar	Lovely Professional University	2-2
22	Dina Deyneko	Lomonosov Moscow State University	2-3
23	Dominique Leckie	University of Windsor	2-4
24	Dorothy Jones	Georgetown University	2-5
25	Federica Zanca	University of sheffield	2-6
26	Gabriele Delle Monache	Brock University	2-7
27	Georges Denes	Concordia University	2-8
28	Hatem M. Titi	McGill University	2-9
29	Israt Ali	Chinese Academy of Sciences	2-10
30	Jay Quentin	University of Iowa	2-11

31	Jean-Louis Do	Concordia University, McGill University	2-12
32	Jesus Daniel Loya	Texas Tech University	2-13
33	Joseph Marrett	McGill University	2-14
34	Josh LeDrew	Wilfrid Laurier University	2-15
35	Lana Hiscock	Wilfrid Laurier University	2-16
36	Lara Watanabe	University of Windsor	2-17
37	Laurelle Joseph	University of Cape Town	2-18
38	Matteo Lusi	University of Limerick	2-19
Meeting Room 3 (Zoom Meeting Invite to be Sent by Email on May 30)			
39	Mihails Arhangelskis	University of Warsaw	3-1
40	Mitch Nascimento	University of Victoria	3-2
41	Navkiran Kaur Juneja	Texas Tech University	3-3
42	Nayera Abdelaziz	University of Cincinnati	3-4
43	Parag Roy	Birla institute of Technology	3-5
44	Patrick Julien	University of Notre Dame	3-6
45	Poulami Chakraborty	Indian Association For the Cultivation of Science (IACS)	3-7
46	Pranay Ninawe	Indian Institute of Science Education and Research (IISER)	3-8
47	Prashant Kumar Pandey	Georgetown University	3-9
48	Prashant Kumar	University of Liverpool	3-10
49	Pratibha Kumari	Indian Institute of Technology Indore	3-11
50	Protap Biswas	Indian Association for the Cultivation of Science (IACS)	3-12
51	Qixuan Zheng	Texas Tech University	3-13
52	Rama Oktavian	University of Sheffield	3-14
53	Ranjit Thakuria	Gauhati University	3-15
54	Raymond Schireman	University of Vermont	3-16
55	Rishika Rai	IISER Thiruvananthapuram	3-17
56	Ritesh Haldar	Karlsruhe Institute of Technology	3-18
57	Roohollah Hafizi	University of Southampton	3-19
Meeting Room 4 (Zoom Meeting Invite to be Sent by Email on May 30)			
~~58~~	~~Samantha J. Kruse~~	~~Webster University~~	~~4-1~~
59	Sandipan Roy	Maharishi Markandeshwar Deemed to be University	4-2
60	Sandeep Kumar	Indian Institute of Technology Ropar	4-3
61	Sandra Kaabel	McGill University	4-4

62	Sergey Aksenov	Kola Science Centre RAS	4-5
63	Shivani Sharma	Indian Institute of Science Education and Research	4-6
64	Sourabh Bera	Indian Association For the Cultivation of Science (IACS)	4-7
65	Souvik misra	Indian Institute of Engineering Science and Technology	4-8
66	Sudhir Mittapalli	University of Hyderabad	4-9
67	Tamae Seo	Hokkaido University	4-10
68	Tomislav Stolar	Ruđer Bošković Institute	4-11
69	Upasana Banerjee	University of Cincinnati	4-12
70	Vahid Safarifard	Iran University of Science and Technology	4-13
71	Victor Quezada Novoa	Concordia University	4-14
72	Vignesh Athiyarath	IISER Thiruvananthapuram	4-15
73	Vinko Nemec	University of Zagreb	4-16
74	Xiaodan Ding	Texas Tech University	4-17
75	Zeinab Mohamed Saeed	Khalifa University	4-18
76	Zihui Song	University of Vermont	4-19
77	Amit Mondal	Indian Institute of Science Education and Research (IISER) Kolkata	4-20

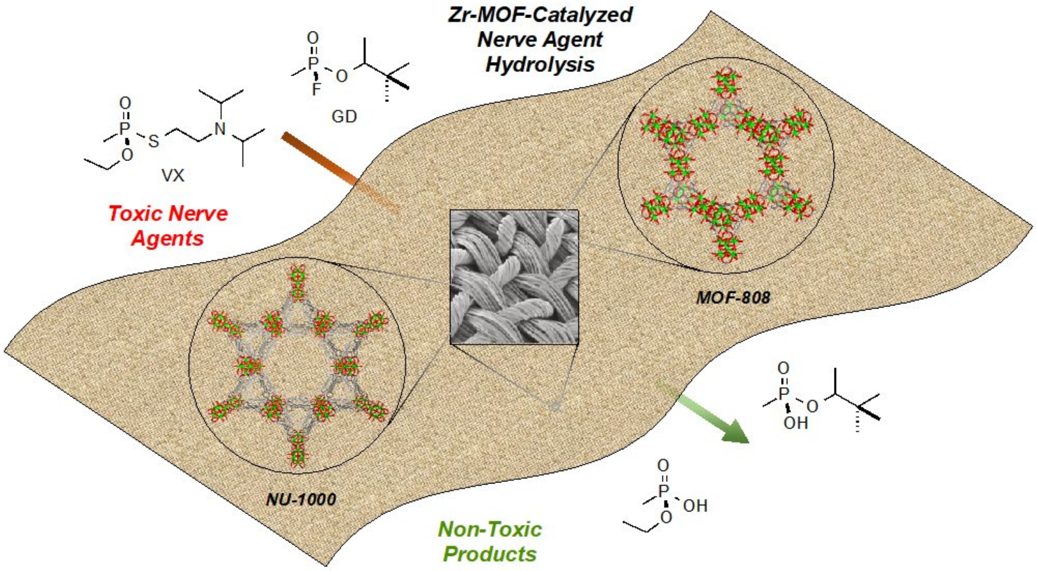
**Note, poster abstracts are at the end of the program, following the abstracts of invited and contributed speakers.

ABSTRACTS OF INVITED TALKS

Programmable Smart Sponges for Protection

Omar K. Farha, Northwestern University

This talk will focus on metal–organic frameworks (MOFs) from basic research to implementation and commercialization. MOFs are a class of porous, crystalline materials composed of metal-based nodes and organic ligands that self-assemble into multi-dimensional lattices. In contrast to conventional porous materials such as zeolites and activated carbon, an abundantly diverse set of molecular building blocks allows for the realization of MOFs with a broad range of properties. We have developed an extensive understanding of how the physical architecture and chemical properties of MOFs affect material performance in applications such as catalytic activity for chemical warfare agent detoxification.



Some reminiscences of the early days of C-H...O hydrogen bonding: as seen through a representative paper

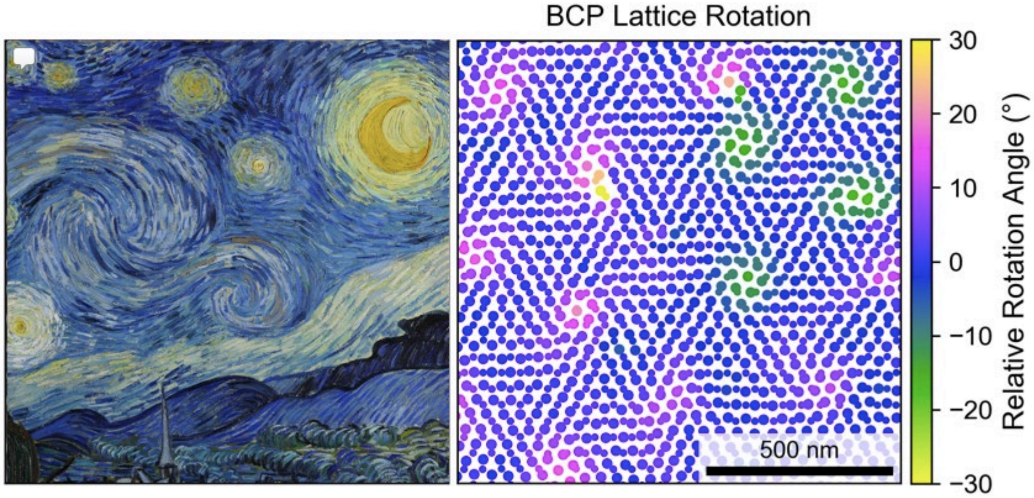
Gautam R. Desiraju, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore

Today, C-H...O hydrogen bonds in crystal structures of oxygenated compounds are practically taken for granted. This was not the case, say 30 years ago. There was a great vagueness and confusion regarding these interactions. Do they exist, was the biggest question. If they do exist, are they like 'regular' hydrogen bonds? How does one characterize them? Are they really important in determining crystal structures? And so on. Our group started looking at these questions from the mid-1980s. The early 1990s were a particularly productive period. In this talk, I will select just one paper from those times and try to indicate how we used to proceed on our way in answering these questions. It's important in science to understand the motivations behind certain publications. These are not always obvious in the formal prose that is contained in the paper. However, an appreciation of such factors and circumstances, even 30 years later, is always useful because it is this hidden aspect that is often the key in research that attempts to push forward hitherto unknown concepts and ideas.

The Twists and Turns of Incommensurate 2D Crystals

Cong Jin, Brian A. Olsen, Erik J. Luber, Jillian M. Buriak, University of Alberta

Incommensurate and Moiré superlattices have been of great interest to the physics community for decades – from 2D organized atomic assemblies of noble gases on graphite, to the very recent (2018-present) discovery that bilayers of 2D materials exhibit remarkable properties such as superconductivity and ferromagnetism. Tiny distortions on the subatomic scale appear to be responsible for these correlated physical properties. Here we will describe a tunable system that is two orders of magnitude larger (figure below) and hence much easier to study and probe, which provides fundamental insights into the registration and forces between incommensurate 2D lattices. Over 140 combinations of hard periodic patterns on silicon prepared by e-beam lithography, and soft self-assembling block copolymer (BCPs) patterns were examined. The energetics and relaxation of this broad range of commensurate and incommensurate lattices could be studied and reproduced with computational simulations. Static distortion waves, first predicted in 1977 and only observed experimentally in 2016, were observed in almost all 140 combinations investigated, and thus their formation appears to be a central route to energy minimization of these incommensurate lattice-based crystals.



Left: van Gogh’s Starry Night. **Right:** 2D incommensurate lattice of self-assembled BCPs on a hard silicon surface revealing static distortion waves (chiral spirals, pink and green).

Self-Assembly, Molecular Motion, and Thermal Expansion Behavior of Organic Crystals

Kristin M. Hutchins, Texas Tech University

Thermal expansion (TE) is the response of a material to a change in temperature. Materials that undergo well-controlled TE are useful in high precision instruments, sensors, and aerospace applications. Controlling and predicting TE behaviors of organic molecular solids connected through noncovalent interactions remains challenging because directing self-assembly of component molecules in three dimensions is not trivial. Here, we describe our efforts to design organic crystals that undergo molecular motion in response to temperature as a platform for achieving large TE. We direct solid-state self-assembly via noncovalent interactions including hydrogen or halogen bonds to yield one-dimensional chains and two-dimensional sheets and discuss the impact of these interactions on TE behavior. We also describe the use of cooling rate to access dynamic motion, reversibility, or trapped phases (Figure 1).

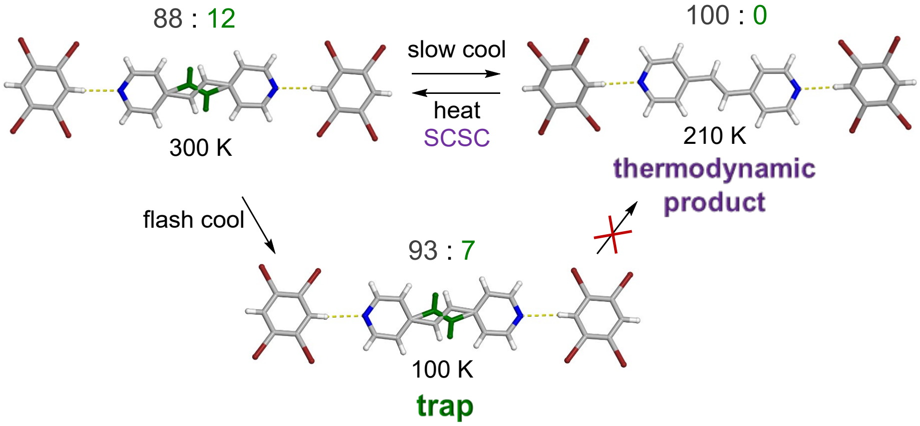


Figure 1. X-ray crystal structures showing molecular motion and cooling-rate-dependent access to thermodynamic (ordered) and trapped states in a co-crystal.

Characterizing and controlling material function with terahertz vibrational spectroscopy

Michael T. Ruggiero, University of Vermont

Over the past two decades, terahertz time-domain spectroscopy has become a valuable technique for the characterization of solid samples, primarily due to its sensitivity to bulk molecular packing arrangements. However, in recent years the role that specific terahertz vibrations play in a number of important physical phenomena has become increasingly apparent, with numerous studies highlighting how terahertz motions are directly responsible for the proper functioning of materials, ranging from enzymatic catalysis to solid-state phase transformations. In this work, terahertz spectroscopy is used to study a number of solid-state material phenomena, including the role of electron-(THz)phonon coupling for charge carrier dynamics in organic semiconductors, gas loading in porous materials (metal-organic frameworks and hydroquinone clathrates), and polymorphic/order-disorder transitions in molecular crystals. In all cases, specific terahertz motions exist that are responsible for these specific phenomena, enabling a direct 1-to-1 mapping of critical processes to a signal low-frequency vibrational resonance. Finally, recent work in using terahertz radiation to coherently control solid-state phase transitions will be discussed, and future directions into this exciting area of vibrational spectroscopy with be explored.

So You've Decided to Make a Generic Pharmaceutical

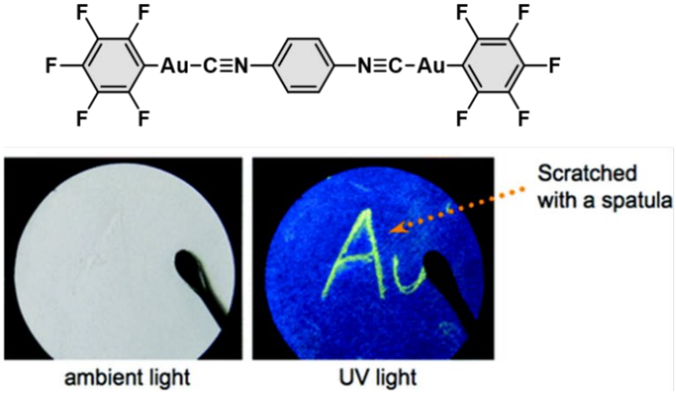
Alex J. Stirk, Apotex Pharmachem, Inc.

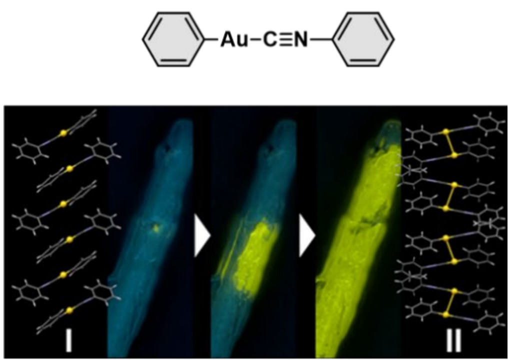
The solid-state form of a pharmaceutical is an extremely important consideration to an innovative (brand) pharmaceutical company, and doubly so for a generic one. When developing a new pharmaceutical there are many pitfalls that one must avoid in order to bring it to market so it may help patients in need. Some of these pitfalls are chemical in nature, while others legal. This talk outlines the do's and do not do's of crystal engineering a hypothetical successful generic pharmaceutical. The differences between industrial and academic concerns will also be discussed with an attitude towards helping both fields understand each other.

Mechanical Response of Gold(I) Complexes

Hajime Ito, Hokkaido University

Mechanical behaviors of organic and organometallic compounds recently attract considerable attention from many researchers. We have been focusing on gold(I) isocyanide complexes from 2008. We found that these many gold(I) isocyanide complexes are crystallized into several polymorphs and show various mechano-responding functions like luminescent mechanochromism, mechanical-triggered single-crystal-single-crystal (SCSC) structure change, contacting-induced SCSC, mechano-triggered reversible SCSC, non-centrosymmetric to centrosymmetric SCSC upon grinding, NIR mechanochromism, and photo- and thermo- salient phenomena. The details of these phenomena were investigated by single-crystal and powder XRD, optical and thermal measurements, as well as theoretical calculations. These mechano-responsive crystals significantly show "trans-scale correlations" between the molecular-level structural alternations and the changes in macroscopic properties.





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Developing complementary in situ methods for characterising porous crystalline materials

Leonard J. Barbour, Stellenbosch University

In order to understand solid-gas inclusion processes at the molecular level it is important to correlate physico-chemical data (e.g. sorption isotherms and calorimetric analysis) with structural data. It is therefore desirable to carry out structural elucidation and calorimetric analysis under conditions that closely mimic those of the sorption/desorption experiments. However, the crystallographic analysis of samples under controlled gas environments poses significant technical challenges, particularly given the limited space associated with the sample compartment of standard commercial diffractometer. In this regard, an environmental gas cell has been developed in parallel with a pressure-programmed differential scanning calorimeter. Use of these complementary techniques has provided new insight into features such as pressure-induced phase transformations that give rise to inflections and hysteresis in sorption isotherms. The influence of guest molecules on aspects such as gate-opening[1,2] and changes in network interpenetration[3-5] will be discussed.

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Supramolecular Gels: Control & Pharmaceutical Application

Jonathan W. Steed, Durham University

Gels are formed by hierarchical self-assembly either because of hydrophobic effects in water or by more directional interactions such as hydrogen bonding in less polar solvents (Fig. 1). Low molecular weight gelators based on small-molecules (LMWG) are emerging as pharmaceutical crystallization media. Particular attractions of LMWGs to the scientific community are the reversible nature of the interactions between the gelator molecules, the wide (essentially unlimited) range of solvents that can be gelled and the possibility of tuning the gels' behaviour by introducing responsive or switching functionality. This presentation focuses on the control crystallization by manipulating the materials properties of small molecule (supramolecular) gels and the nature of the gel fibre surface. We show how concepts firmly rooted in supramolecular host-guest chemistry and supramolecular self-assembly can be married with the materials science of soft matter in order to control and manipulate bulk materials properties.[1] The application of these kinds of switchable gels as novel media for pharmaceutical crystal growth is emerging [2] and the lecture will demonstrate by a number of case studies how gel phase crystallization fits into the wider toolbox of solid form screening.

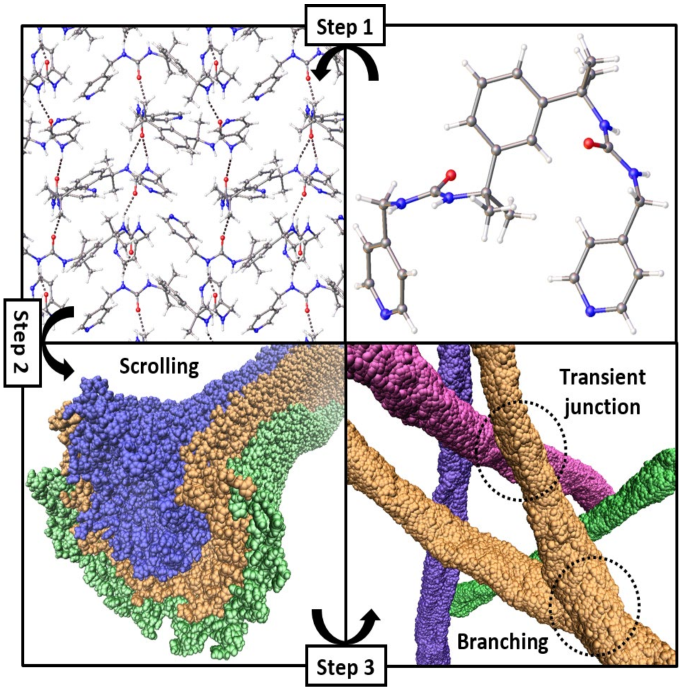

Figure 1. Assembly of a supramolecular gel by (1) layering, (2) scrolling and (3) entanglement.

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Polymorphs, salts, and solvates of an Active Pharmaceutical Ingredient

Graciela Díaz de Delgado, University of the Andes, Venezuela

Active Pharmaceutical Ingredients (APIs) are versatile materials which continue to attract a great deal of interest from solid-state scientists in the permanent search for better and safer pharmaceutical formulations. The diverse nature of these materials provide a myriad of possibilities for reactions, substitutions, polymorphism, salts and solvate formation, which may influence significantly their physical and pharmaceutical properties. A lot of effort is invested in the study of mechanisms to enhance the solubility and bioavailability of the API or to improve the stability during the manufacturing process, storage, and transport.

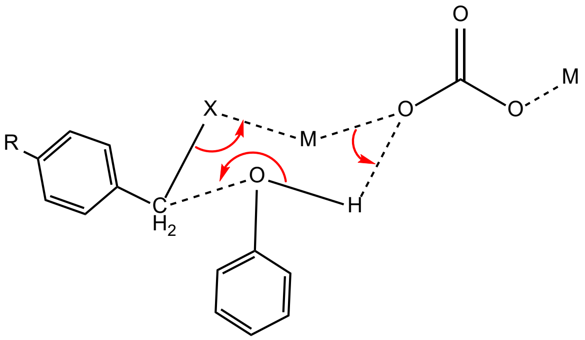
The structures of polymorphs, salts, solvates, and metal derivatives of several APIs, synthetized in our laboratory, have been determined using laboratory and synchrotron powder and single crystal X-ray diffraction data. The solid-state behavior of the different materials is monitored by FT-IR and TGA/DSC analyses. Particular attention is paid to phase transformations in the solid state. Hirshfeld surface analysis and energy framework calculations provide a deeper insight into intermolecular interactions. This presentation will be centered on flunixin, a common non-steroidal anti-inflammatory drug.

This talk contains work carried out by many undergraduate and graduate students from our laboratory. In particular, the contribution of M.C. Dávila, A.J. Dugarte, M.Sc. J.E. Contreras and Prof. J.M. Delgado (ULA-Venezuela), Prof. J.A. Henao and Dr. R.A. Toro (UIS-Colombia) and Prof. H. Camargo (UST-Colombia) are gratefully acknowledged. Access to the CSD has been possible through the FAIRE Programme of the CCDC.

Stereoselective mechanochemical reactions through solid state ion pairing

James Mack, University of Cincinnati

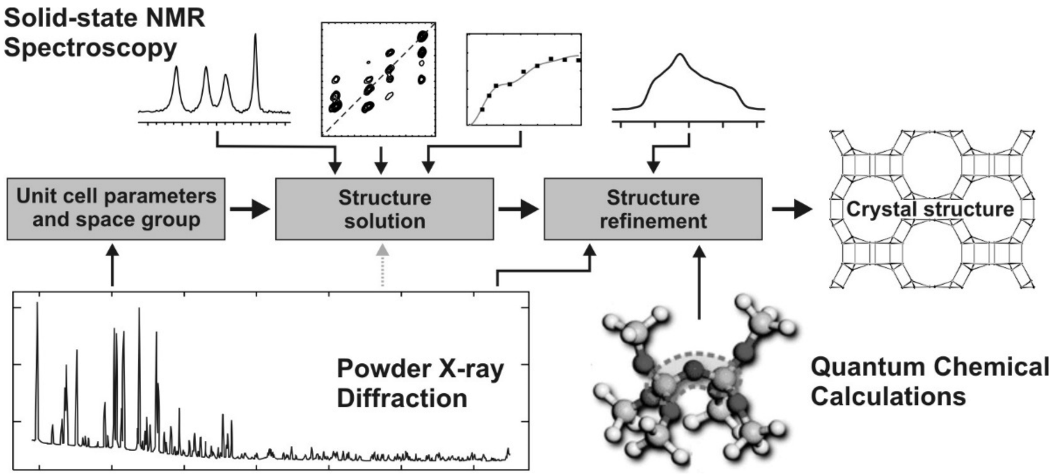
The allure of mechanochemistry is nearing a tipping point. With the rapid growth of articles about it, it is becoming clear that this once obscure discipline is becoming increasingly mainstream. There are many reasons for this, some are interested in improved laboratory safety as well as simpler, cheaper reaction procedures that allow for more efficient use of research time resulting in increased productivity. Many of the fundamental principles that govern this technique are still absent from the literature. We recently developed a better understand of how solid state ion pairing can create mre selective and safer reaction conditions than can be observed in solution. This approach takes advantage of the lack of a solvent shell to incorporate weaker and safer bases to drive reactions to completion through specific ion pairing pathways. The most efficient reactions contained larger and more polarizable cation and anion pairs.



NMR Crystallography of Zeolites and Related Materials

Darren H. Brouwer, Redeemer University

Solid-state nuclear magnetic resonance (SSNMR) spectroscopy is an important technique for structural characterization of solid materials. Due to the fact that it provides *local* structural information about the environments of NMR-active nuclei, SSNMR is highly complementary to diffraction techniques whose strength lies in providing information about the *long-range* periodic structure of a material. By combining solid-state NMR and diffraction techniques with various computational methods (modelling, density functional theory, etc), powerful approaches to structure determination of materials are being developed. These integrated structure determination strategies in which SSNMR spectroscopy plays a crucial role is broadly referred to as *NMR crystallography.* This talk will provide an overview of our NMR crystallography strategies for solving and refining zeolite crystal structures. Additionally, the application of this NMR crystallography approach to the structure determination of layered silicates that lack full 3D crystallinity, a considerably more challenging problem, will also be described.



ABSTRACTS OF CONTRIBUTED TALKS

Thermally Actuating Multifunctional Molecular Crystals

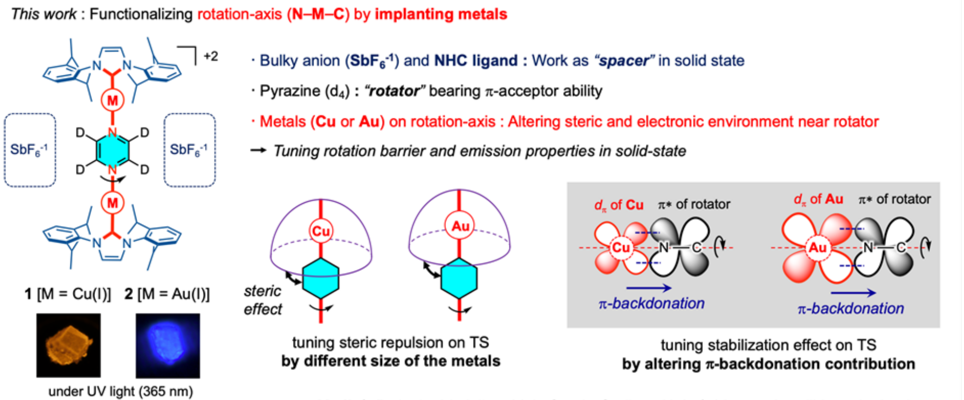
Durga Prasad Karothu, Rodrigo Ferreira, Luca Catalano, Ghada Dushaq,
Mahmoud Rasras, Panče Naumov, New York University Abu Dhabi

There has been growing interest in mechanically responsive molecular crystals that shows reversible and unusually large positive and negative thermal expansion triggered by external stimuli owing to their pivotal role in the design of actuators for soft robotics, artificial muscles, microfluidic and electrical devices. However, controlling molecular motion to execute huge thermal expansion in crystals remains a formidable challenge and their strong deformations usually lead to their destruction. Here we report a single crystal of simple organic compound exhibiting giant thermal expansion actuated by collective reorientation of molecules in the crystal lattice which is reversible after more than fifty heating and cooling cycles. Such atypical molecular motion, revealed by single crystal X-ray diffraction and microscopy analyses, drives an exceptionally large expansion along the length of the crystal. The applicability as an actuator with electrical properties is demonstrated by displaying reversible dielectric, capacitance, conductance and current measurements. The large shape change of the crystal with remarkable durability and electrical properties, suggests that this material is a strong candidate as a microscale multifunctional thermal actuating material.

A novel platform of luminescent crystalline molecular rotors via N-heterocyclic carbene metal complexes: Designing molecular rotations and luminescence in solid-state mediated by functionalized rotation-axis

<u>Mingoo Jin</u>[1], Ando Renpei[2], Marcus Jellen[3], Miguel A. Garcia-Garibay[3], Hajime Ito,[1] [1]:Department of Engineering, Hokkaido University, [2]: Graduate School of Chemical Engineering and Science, Hokkaido University; [3]: University of California, Los Angeles

Designing molecular motions in solid-state is a crucial subject because of the fundamental rule in a molecular machine and solid-state functional materials. Molecular rotations in solid state have been generally governed by a steric and electronic environment near the rotator, however there are still few methods to control the molecular dynamics in rational way due to the difficulties on manipulating and demonstrating these factors in highly dense media. Herein, we will describe a newly designed platform for the crystalline molecular rotors with a rotation-axis functionalization via implanting transition metals (Cu or Au) on the axel aimed at the rational design of molecular rotation and luminescence in solid-state.
The designed rotors **1** and **2** were prepared by using bulky N-Heterocyclic Carbene (NHC) ligand and anions (SbF$_6^{-1}$) as spacer, deuterated pyrazine as rotator having □-accepting ability, and Cu(I) or Au(I) metals between the NHC ligand and the rotator as rotation-axis. The rotor **1** and **2** yielded the luminescent crystals emitting in red and blue, respectively, and construct the analogue crystal structure; the spacers (bulky NHC ligands and SbF$_6^{-1}$) built a packing environment allowing for the rotator to occur rotation in crystal. Variable temperature (VT) ^{2}H solid-state (SS) NMR of crystal **1** and **2** revealed that both crystals show 2-fold rotation and a clear difference in rotation frequency ($k_{\text{rot.}}$). The $k_{\text{rot.}}$ of Cu(I) rotor **1** is ranging from 200 kHz to 2.80 MHz under 300 K to 340 K, and the rotation barrier (E_a) is assigned as 12.3 kcal/mol. On the other hand, the Au(I) rotor **2** shows faster rotation than Cu(I) complex **1**; the $k_{\text{rot.}}$ was ranging from 1.25 MHz to 13.5 MHz on 275 K to 325 K, and the E_a was 8.4 kcal/mol. DFT calculation of rotor **1** and **2** revealed the geometry of ground state and TS of rotation with the reasonably matched trend of rotation barrier given by the SS-NMR. Further analysis using NBO and SAPT analysis indicated that the stabilization energy via π-backdonation from metal to rotator have contributed to show the difference in the TS and the steric repulsive interactions were modulated by the different length of rotation-axis via the distinct size of Cu and Au. These results indicate that the functionalized rotation-axis via implanting transition metals can be a novel tool for manipulating molecular dynamics in solid-state. Further details with tuning the luminescent properties in solid-state will be described.



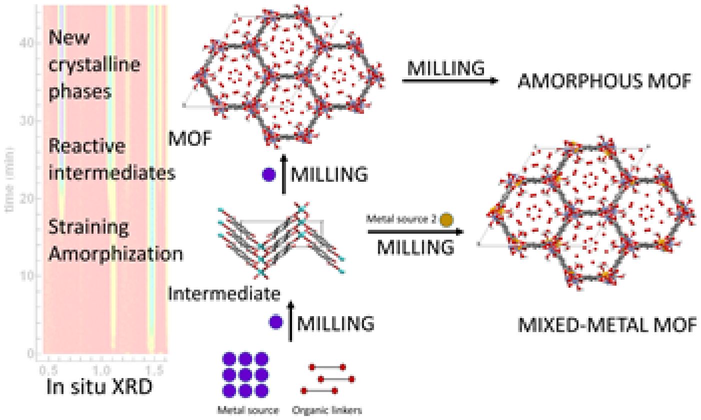
M. Jin*; R. Ando; M. Jellen; M.A. Garcia-Garibay; H. Ito*. Manuscript will be submitted soon.

Rapid, clean and scalable synthesis of microporous functional MOFs and their non-conventional forms via mechanochemistry

<u>Krunoslav Užarević</u>, Bahar Karadeniz, Tomislav Stolar, Valentina Martinez, Ruđer Bošković Institute

Porous metal-organic frameworks (MOFs)[1] are one of the most researched areas of modern materials science. These modular materials, whose structure and properties can be readily altered by careful choice of metal nodes and suitable organic linkers, are widely studied for gas storage and separation, catalysis, sensing, light-harvesting, and other applications.[2] The growing number of studies in the field resulted in the recent commercialization of several microporous MOFs on a laboratory scale. However, the standard synthetic procedures, involving an excess of organic solvents and harsh reaction conditions, still prevent their wider industrial application.

Here we present the application of mechanochemical reactions,[3] *i.e.,* reactions between solid reactants induced by mechanical force, for a rapid, green and room-temperature transformation of environmentally safe metal precursors, oxides or hydroxides into most relevant microporous MOFs, such as HKUST-1,[4] MOF-74[5] or zirconium-based MOFs of UiO,[6] and NU-[7] families. Mechanochemistry allows even for rapid and efficient synthesis and polymorphic control in complex porphyrinic zirconium MOFs.[8] We show here how the milling produces high-quality zirconium MOFs quantitatively in multigram quantities by using only a catalytic amount of "green" liquids, such as methanol or water.[9]



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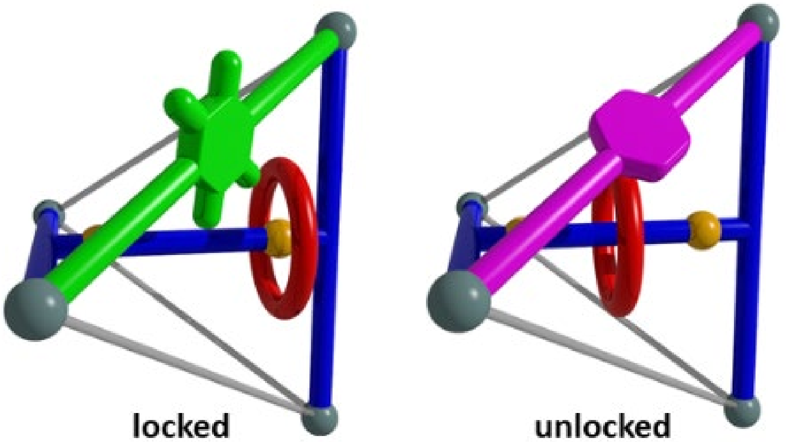
Precise Spatial Arrangement and Interaction Between Two Different Mobile Components in a Metal-organic Framework

Benjamin H. Wilson[1], Cameron S. Vojvodin[2], Ghazale Gholami[1], Louae M. Abdulla[1], Robert W. Schurko[2] and Stephen J. Loeb[1], [1]: *University of Windsor;* [2]: *Florida State University*

Much of the interest surrounding mechanically interlocked molecules (MIMs) is due to their applications as molecular machines.[1] The incorporation of molecular machines into the solid state, such as in metal organic frameworks (MOFs), is one approach to increase the complexity of these system and introduce interactions between multiple dynamic components.[2] Rotaxanes that feature translational motion of the macrocycle between recognition sites are known as molecular shuttles.[3,4] We have now utilized an H-shaped [2]rotaxane molecular shuttle linker, in combination with a suitable co-ligand, to cross-link the tetrahedral cavities of isostructural *fcu* MOFs **PCN-57** and **UiO-68** to give **UWDM-8** and **UWDM-9**.[5] This approach has also been extended to **UiO-68-d$_4$** and newly synthesized **UWCM-10**, containing a tetrazine rotor, to give **UWDM-9-d$_4$** and **UWDM-10** respectively. This approach allows for precise spatial arrangement of two different mobile components – a rigid rotor co-ligand and a rotaxane macrocycle. The interactions between these two components can be then probed utilizing variable temperature ^{2}H and ^{13}C solid-state NMR spectroscopy.



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Mechanochemically assisted hydrolysis in the ADOR process

Daniel N. Rainer,[a] **Cameron M. Rice,**[a] **Sharon E. Ashbrook,**[a] **Russell E. Morris**[a, b]
[a]University of St Andrews; [b]Charles University

The ADOR (Assembly-Disassembly-Organization-Reassembly) process provides a new methodology producing zeolites inaccessible through conventional procedures.[1,2] It revolves around the lability of Ge–O bonds towards hydrolysis, relative to Si–O, enabling controlled breakdown of the framework of a parent zeolite phase into its layered precursor analogue. Subsequent rearrangement of the layers, potentially aided by additives, and condensation leads to daughter materials exhibiting new frameworks.

Mechanochemical methods such as ball milling have great potential to improve chemical synthesis procedures in terms of efficiency and reduction of waste material. Applications in zeolite chemistry have already led to improvements in areas such as reaction time and required amounts of solvent.[3,4]

In an effort to increase the value of the ADOR process, especially in regard to possible industrial applications, the usage of low energy ball milling during the disassembly step of zeolite **UTL** was investigated. Both water and hydrochloric acid in different concentrations were used as hydrolysis agents, using increased zeolite/liquid ratios compared to previously published studies. Generally, partly disassembled and organized materials IPC-2P/IPC-6P were obtained, which act as direct precursors to their reassembled counterparts IPC-2 (**OKO**)[5] and IPC-6 (***PCS**).[6] PXRD patterns of as made products are indifferent to the acid concentration, however, reassembled materials vary significantly. Noticeable products of acid treated samples are obtained using 9 M HCl (**OKO**-type) and 12 M HCl (**PCR**-type). Experiments employing water as reagent also lead to materials with **OKO** framework.

The required volume of water for hydrolysis was also shown to be reducible to 100 µl for 500 mg of parent zeolite. This allows for a cost-efficient reaction with ^{17}O enriched water (40%). The product was successfully enriched with this NMR-active oxygen isotope demonstrating the possibility for a fast and feasible enrichment procedure with the presented methodology.

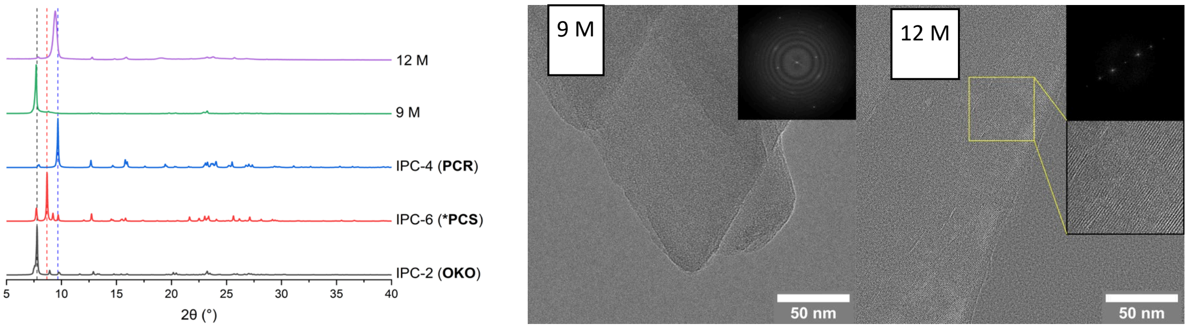

Figure 1. PXRD patterns (left) and TEM images with FFT inserts (right) of reassembled zeolite products from hydrolysis reactions with 9 M and 12 M hydrochloric acid.

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What is Crystallography?

Luzia S. Germann, McGill University

Crystals have fascinated humanity for centuries due to their inherent beauty and symmetry. The investigations date back far longer than the discovery of X-rays, neutrons, or electrons and consequently also diffraction techniques that appeared early in the 20th century. Some of the most important scientific discoveries are based on crystallographic investigations, with one of the most prominent example being the discovery of the double helix in DNA, leading to a Nobel prize in 1962 for Watson, Crick, and Wilkins. Despite the importance of crystallography in natural science, especially chemistry, and tremendous recent advancements in experimental setups and analytical tools, it appears that the basics of crystallography and the used techniques are decreasingly taught in higher education. Unsurprisingly, this can lead to mistakes and errors, in the best case it is only the misusage a terminology or definition, but it may also affect analysis and consequently lead to flawed interpretations.

This contribution highlights recent developments in experimental techniques in crystallography, discussing their challenges and advantages, also in respect to future education.

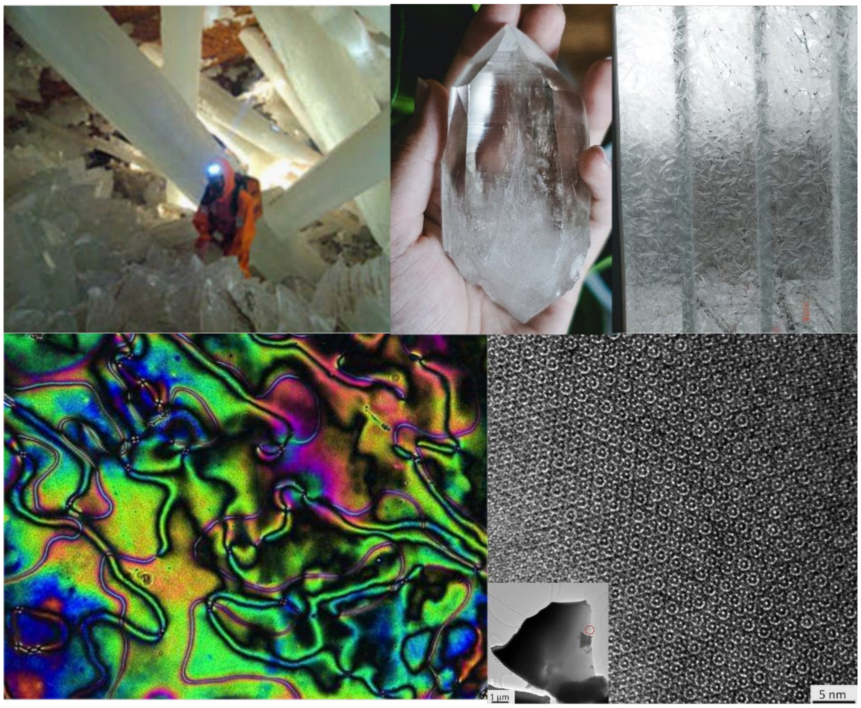

Figure 1: Different forms of crystals; From top left to bottom: selenite crystals in the “Crystal Cave of Gigants” in Naica, Mexico,[1] quartz crystal, ice on a window, a liquid crystal,[3] and $Al_{71}Ni_{24}Fe_5$ quasicrystal[4].

[1] picture courtesy of George Kourounis, [2] photo by Dani Costelo on Unplash, [3] *Silicone liquid crystal stiffens with repeated compression*, *Phys.Org.*, 29th April 2013, [4] Bindi *et al., Sci. Rep.*, **2015**, 9111.

Piezochromism in Molecular Crystals: A Computational Study

<u>Feng Xibo</u>, Axel D. Becke, and Erin R. Johnson, Dalhousie University

Piezochromism[1] refers to changes in the photoluminescence (PL) of certain molecular crystals in response to external pressure. This phenomenon has attracted much experimental research attention, due to potential applications in fields such as sensoring and memory devices. Computational modeling of piezochromism is of high theoretical interest, yet currently lacking. Herein, we present a computational effort to model and rationalize piezochromism in molecular crystals. The current methodology employs a combination of dispersion-corrected[2] solid-state and gas-phase density-functional theory (DFT), and the recent Virial Exciton Model by Becke[3]. Our study finds that piezochromism is primarily driven by the modification of the intermolecular interactions within the crystal lattice. We also point out that the origin of piezochromic PL shifts can be understood from both a chemical (polarizability) and a physical (band structure) perspective.

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Solution-Phase Engineering of Second Harmonic Active Lithium Niobate Nanocrytals with Tunable Dimensions and Crystallinity

Rana Faryad Ali, Byron D. Gates*, Simon Fraser University

Lithium niobate ($LiNbO_3$) is a unique photonic material, often referred to as the “silicon of photonics” due to its excellent optical properties. Lithium niobate based materials are used in photonic devices and sought for a diverse range of applications including optical modulators, acoustic-wave transducers, optical filters in mobile telephones, and wavelength converters in fiber optic based telecommunication systems. We advanced the development of solution-phase approaches for the preparation of lithium niobate ($LiNbO_3$) nanocrystals with an average, tunable size from 7 to 100 nm. This solution-phase process results in the formation of crystalline, uniform nanoparticles of $LiNbO_3$ at a reaction temperature of 220 °C with an optimal reaction time of as short as 30 h. Advantages of these methods include the preparation of single-crystalline $LiNbO_3$ nanoparticles without the need for further heat treatment or without the need for using an inert reaction atmosphere. The growth of these nanoparticles began with a controlled agglomeration of nuclei formed during a solvolysis step. The reactions subsequently underwent the processes of condensation, aggregation, and Ostwald ripening, which remained the dominant process during further growth of the nanoparticles. These processes did produce single-crystalline nanoparticles of $LiNbO_3$, suggesting an oriented attachment process. Average dimensions of the nanoparticles were tuned from 7 to ~100 nm by either increasing the reaction time or changing the concentration of the lithium salts used in the solvothermal process. The nanoparticles were also confirmed to be optically active for second harmonic generation (SHG). These particles could enable further development of SHG based microscopy techniques.

Cocrystals: a computational survey and machine learning model of stabilisation energies

David McDonagh, Christopher R. Taylor, Will Fyffe, Graeme M. Day, University of Southampton

We have previously published a large-scale computational study of the energetic driving force for cocrystal formation in molecular organic crystals, in which we calculated the energetic stability of 350 organic cocrystals relative to their pure phases of their constituent molecules [1]. The study demonstrated that observed cocrystals are almost always more stable than the pure components, but that simple descriptors, such as hydrogen bond counts and relative densities are only weakly predictive of a cocrystal's relative energetic stability. Here, we built on this work in an attempt to develop a predictive model for cocrystallisation using machine learning from molecular descriptors (i.e. no structural information on the cocrystal packing is used). We do so by training a Gaussian Process to calculated cocrystal stabilisation energies using only molecular descriptors. The motivation in attempting to learn stabilisation energies, as opposed to simply predicting if a given pair will cocrystallise, is to make the problem more tractable, by removing some of the many other variables that may impact successful cocrystallisation. The results demonstrate promise for this approach in targeting the most promising coformers in cocrystal design but point to the need for larger datasets.

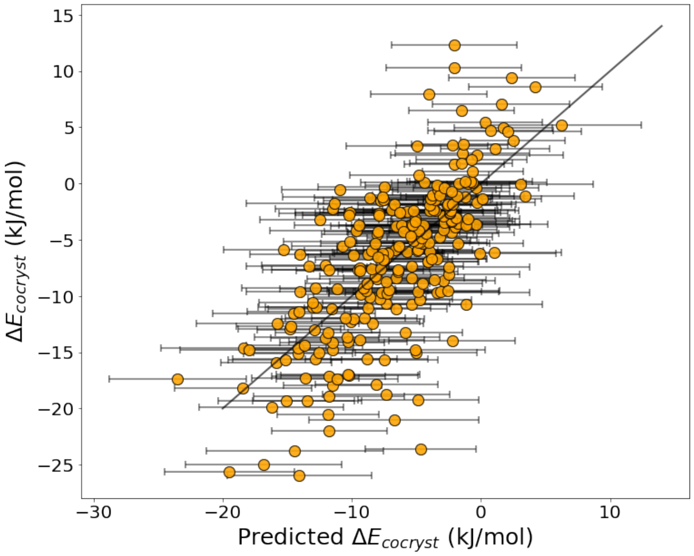

Figure 2. *Cocrystal stabilisation energies predicted by a Gaussian Process from molecular descriptors. Error bars show 1 standard deviation based the leave-one-out testing.*

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Simulated indentations of aspirin and meloxicam crystals: a molecular-level study of mechanochemistry.

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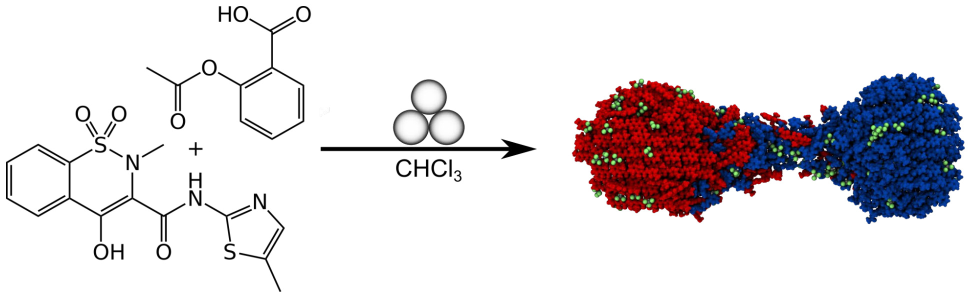
While mechanochemical methods continue to show their importance as an alternative synthesis, our view of the molecular-level events that occur during these processes remains restricted. In this work, indentations between grains of aspirin and meloxicam are modelled through molecular dynamics to simulate the initial stages of their known mechanochemical co-crystallisation. The effects of small amounts of solvent, in this case chloroform, are also included in the investigation. Simulations show i) the relatively facile mixing of materials during low-energy indentations in the absence, ii) the formation of a locally amorphous region focused at the contact point between the two grains, iii) plastic-like behaviour of the materials as a connective neck, Scheme 1, is formed between the grains upon their retraction, and that small amounts of solvent molecules have little to no effect at such an early stage of a reaction, indicating that their role comes into play during the later stages of the mechanochemical process.



Scheme 1: Mechanochemical indentation of aspirin (blue) and meloxicam (red) nanoparticles in the presence of chloroform.

Evaluating and Understanding the Performance of MOF-Polymer Composites for Medical Device Applications

Simon Vornholt, Morven Duncan, Stewart Warrender, Russell Morris*, University of St Andrews

Storage and delivery of biologically active gases for medical applications are amongst the most exciting potential uses for MOFs. Ni-CPO-27 (a 2,5-dihydroxytherephthalate framework with nickel as its nodes) shows exceptional storage and release properties for nitric oxide (NO)[1], a gas that exhibits anti-bacterial, anti-thrombotic and wound healing properties when delivered in low concentrations.[2] Employing MOFs as storage/release agents permits these advantageous properties to be harnessed by controllably delivering low concentrations of the gas, thus avoiding the toxicity associated with high concentrations. NO-releasing MOFs are therefore potentially very suitable for incorporation into medical devices such as catheters, which are a major cause of Healthcare Associated Infections.

Recent research has endeavoured to embed (meso-)porous materials into polymeric matrices as composites for the purpose of performing gas adsorption and separation.[3] MOF-polymer composite films provide an ideal model for MOF-containing components of potential medical devices, permitting analysis and development of critical properties prior to full device prototyping.

In this study, a series of MOF-polymer composites (containing 5-40 wt% MOF) have been synthesised, successfully loaded with NO and their stability to storage and NO release performance analysed. Intuitively, increasing the MOF loading level in the composites should result in higher concentrations of NO being released, however our results indicate that there is an optimum loading level for peak performance. Using focused ion beam assisted cross sectioning, 3D-reconstruction and SEM imaging we have studied the MOF's distribution throughout the polymer resin to understand this behaviour. We have shown that the concentration of NO released from the surfaces of these MOF-polymer composites can impart antibacterial efficacy. Moreover, this bactericidal activity is sustainable for longer than current commercially available antibacterial catheter coatings.

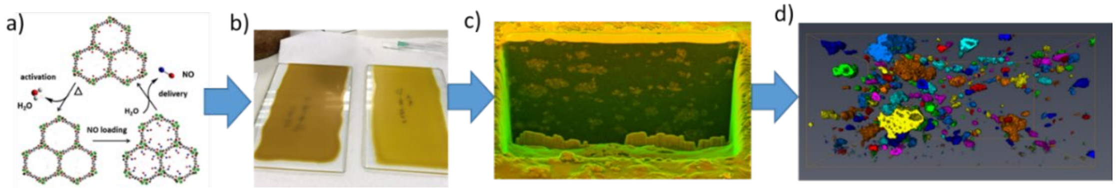


Figure 3: Nitric oxide (NO) sorption and SEM analysis of MOF-polymer composite. a) NO-loading and -release cycle of a typical CPO-27 material; NO is bonded to the open metal sites of the MOF, where its release is triggered by moisture b) MOF-polymer composite film synthesised with two different wt% MOF loadings c) Exposed MOF particles in a cross section of a 10 wt% MOF-polymer composite milled with a focused ion beam (FIB) assisted SEM and d) the 3D rendered volume that the MOF occupies inside the polymeric matrix of a 10 wt% film, each individual MOF-aggregate is represented with a new colour; data was acquired from a 3D reconstruction FIB-SEM experiment.

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Evaluating the impact of H_2O on CO_2 capture in an ultramicroporous MOF via solid-state NMR spectroscopy

Vinícius Martins, Brian E. G. Lucier, and Yining Huang, Western University

In the fight against climate change, a new class of porous materials namely metal-organic frameworks (MOFs) have emerged as promising candidates for CO_2 capture. However, recent studies have shown that the presence of water can drastically reduce their CO_2 adsorption capacity and even cause the collapse of the framework. Therefore, understanding the effect of water on the CO_2 adsorption in MOFs is critical to the development of water-stable MOFs for practical applications.[1]

Solid-state NMR spectroscopy has been widely employed as a complementary technique to X-ray diffraction in the study of host-guest interactions in MOFs. Herein, we have used a series of SSNMR techniques to study the effect of water on the adsorption behaviour of CO_2 in a ultra-microporous MOF ZnAtzOx.[2]

Variable-temperature ^{2}H and ^{13}C NMR studies of ZnAtzOx loaded with different concentrations of $^{13}CO_2$ and $^{2}H_2O$ have shown that these guest molecules occupy specific sites in the pores. Besides that, spectral simulations have shown that water undergoes a π flip-flop and liberational motions, while CO_2 molecules undergo a wobbling and hopping motions within the framework. Surprisingly, these motions remained very similar at different concentrations, suggesting that water does not drastically affect the adsorption of CO_2 within the framework.

Our results illustrate the power of SSNMR spectroscopy as a complementary technique to study the effect of water on the CO_2 adsorption in MOFs. Understanding the local structure and dynamics of CO_2 and D_2O in MOFs will further our knowledge for the development of water-stable MOFs for CO_2 capture.

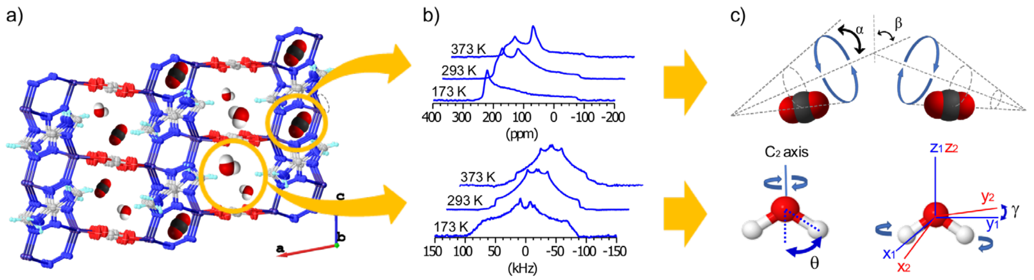

Figure 1. a) Illustration of the $^{13}CO_2$-D_2O co-loaded ZnAtzOx MOF; b) ^{13}C (top) and ^{2}H (bottom) variable temperature SSNMR spectra; and c) representation of the H_2O (top) and CO_2 (bottom) dynamics at 0.1 equivalent of CO_2 and 8% H_2O.

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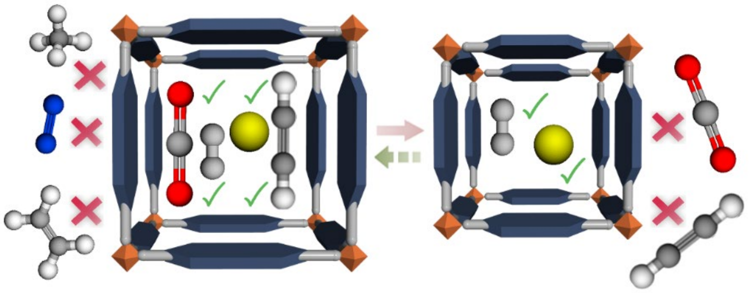
Ultramicropore Control of Molecular Sieving

Soumya Mukherjee, Michael J. Zaworotko*, Bernal Institute, Department of Chemical Sciences, University of Limerick

The high energy footprint of commodity gas purification and ever-increasing demand for gases require new approaches to gas separation.[1] Kinetic separation of gas mixtures through molecular sieving can enable *"ideal"* separation through molecular size or shape exclusion.[2] This is because molecular sieves exhibit pore windows of just the right size to block all larger gas molecules with little or no energy cost.[3] Physisorbents must exhibit just the right pore diameter to enable such ideal separation, but the 0.3-0.4 nm range relevant to small gas molecules is hard to control with precision.[4] For example, 0.30 nm is a dimension suitable for H_2 yet we are unaware of any previous reports of a molecular sieve for H_2 *vs.* slightly larger gas molecules such as CO_2 or N_2. We address this matter through study of the sorption properties of a new crystal engineered narrow pore variant of a reported metal-organic framework, calcium trimesate (**Ca-trimesate**) by reversible dehydration (Scheme 1).



Scheme 1 Pore contraction offers the first two-in-one molecular sieve **Ca-trimesate** where the phase behaviour is accompanied by distinct molecular sieving performances: the hydrated phase acts as a sieve for CO_2 and C_2H_2 (under ambient conditions) whereas the dehydrated phase is the first H_2 selective non-membrane solid sieve (under cryogenic conditions).

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Minimising polymorphic risk through cooperative computational and experimental exploration

Christopher R. Taylor, Matthew T. Mulvee, Domonkos S. Perenyi,
Michael R. Probert , Graeme M. Day, and Jonathan W. Steed, University of Southampton

We combine state-of-the-art computational crystal structure prediction (CSP) techniques with innovative experimental crystallization methods to understand and explore crystal structure in pharmaceuticals and minimise the risk of unanticipated late-appearing polymorphs.

Initially, we demonstrate the power of CSP to rationalise the known difficulty in obtaining polymorphs of the well-known pharmaceutical isoniazid. We go on to perform a blind CSP study on the related molecule iproniazid, predicting a significant risk of polymorphism. Employing a wide variety of experimental techniques, including gel-phase crystallisation,[1] our experimental colleagues initially obtained two of the predicted polymorphs, representing the first known non-solvated crystal structures of iproniazid. However, the most energetically stable structure from quantum-mechanical lattice energy calculations – i.e. the highest-ranked structure in a blind prediction – remained elusive.

However, by taking account of dynamical effects (including zero-point energy) through free energy calculations,[2] we predict that this third structure is in fact metastable, but becomes thermodynamically favoured at high pressure – a prediction confirmed by our experimental colleagues after painstaking high-pressure experiments obtained this third new form. We thusly demonstrate the power of CSP methods and the ability of our synergistic computational-experimental approach to “de-risk” solid form landscapes.

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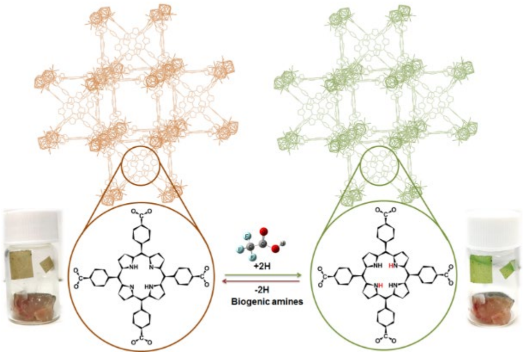
Reversible Protonation of Porphyrin MOFs as the Working Principle for Colorimetric Sensor Tags for Biogenic Amines

Ahmad Sousaraei[1,*], Carla Queirós[2], Francisco G. Moscoso[3], Ana M. G. Silva[2], Tânia Lopes-Costa[3], José M. Pedrosa[3], Luís Cunha-Silva[2], Juan Cabanillas Gonzalez[1,*], [1]Madrid Institute for Advanced Studies in Nanoscience; [2]University of Porto; [3]Universidad Pablo de Olavide

Smart methods and strategies for real-time detection of biogenic amines such as trimethylamine, histamine, putrescine and cadaverine released as bacterial metabolic products are increasingly more demanded.[1] Bacterial metabolic activity is crucial in different sectors such as healthcare monitoring, food industry, or industrial chain supply are only some examples.[2] Among the different transduction signals that can be employed for detection, those based on simple optical colorimetry are the most simple and cost-effective methods. Inorganic coordination polymers, also named metal-organic frameworks (MOFs), are hybrid materials that can be grown in the one, two and three-dimensional networks. These materials have been exploited in a wide range of applications.[3] Here, we report on the fast and full reversible protonation of a labile MOF with porphyrin as organic linker (*PCN224*) immobilized in PDMS polymer matrix, making mixed-matrix membrane (MMM).[4] Transition from the porphyrin planar conformation to an out-of-plane protonated conformation in solid state is achieved thanks to the pliability of the MOF, concomitant with a distortion of the crystalline structure with appearance of new diffraction peaks in the PXRD pattern. Full reversible de-protonation is achieved in only 10 seconds upon exposure the MOF to basic vapour. These findings are exploited to develop colorimetric tag sensors with capability to reveal the presence of biogenic amines.



Schematic presentation of hysteresis-free porphyrin protonation and subsequent de-protonation of the PCN224-MMM in presence of specific acid and raw fish

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Electron Diffractometer: A Novel Device For Monitoring Nano-Crystalline Particles

Gustavo Santiso-Quinones*, **Gunther Steinfeld**, **Eric Hovestreydt,**
Eldico Scientific AG

After the Science nomination for “Breakthrough of the year 2018”,[1,2] 3D-Electron Diffraction (3D-ED) using the continuous rotation method and X-ray crystallographic software, is gaining a lot of attention in the field of crystallography. In the past year many achievements using electron diffraction techniques have been made in the fields of organic molecules, polymorphism, material sciences, geological sciences, natural products, energetic materials, bio-molecules and many others.[2,3] Such experiments are done in a (modified)-Electron Microscope. Though the realization of such experiments still requires plenty of expertise and efforts and it can´t be applied on daily bases. Pioneers in the field of Electron Diffraction,[4] all agree that a dedicated device for the realization of such experiments, would be of great advantage to the crystallographic community. Though such a device doesn´t exists (up to now) at all. Therefore, it is a necessity that such a device could be made available for the realization of this exciting field of nano-crystallography. Eldico Scientific AG will present a new device which is dedicated exclusively for such purposes. The device, an Electron Difftactometer, is built and optimized for diffraction experiments. Furthermore, it uses exclusively the crystallographic approach (continuous rotation method) and crystallographic software. Experimental examples of the importance of such technique will be showcased too.

Acknowledgments: The authors wish to acknowledge and are grateful for the scientific work and scientific collaboration with Dr. Tim Grüne, Dr. Mauro Gemmi, and Dr. Ute Kolb. The experimental examples presented here are done in collaboration with all of them.

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Escape from an Organic Crystal: Guest Transport Properties of a Boron-Based Molecular Machine

Gonzalo Campillo-Alvarado,[a] Dale C. Swenson[a], Eva C. Vargas-Olvera,[b] Hugo Morales-Rojas,[b] Herbert Höpfl[b] and Leonard R. MacGillivray[a], [a]University of Iowa, [b]Universidad Autónoma del Estado de Morelos

The advent of synthetic molecular machines has been accompanied by an increased understanding of molecular dynamics. While motion has been attained in a variety of porous and robust frameworks constructed by metal-organic materials, molecular movement in close-packed organic crystals remains a fundamental challenge due to loss of structural integrity (i.e. crystallinity). Specifically, mechanisms of guest transport in organic solids, although of high interest for the materials community, remain poorly understood with only a few examples documented.

In this contribution, we describe a nonporous organic crystal that exhibits a single-crystal–to–single-crystal transformation (SCSC) upon guest release. Specifically, the close-packed system is based on a discrete host that contains a boronic ester unit (stator) coordinated to a motion-generating unit through B←N bonds. The motion that facilitates guest release has been identified by X-ray diffraction techniques (i.e. single-crystal-to-single-crystal transformation) and parallels the movement of a "rotisserie" in the macroscopic scale, which includes i) rotation and ii) stretching of the linker, and iii) titling of the boron stator.

Mechanical Interlocking in Triptycene-Based Hydrogen-Bonded Organic Frameworks

Penghao Li,[a] **and J. Fraser Stoddart**[a,b,c], [a]Northwestern University;
[b]Tianjin University; [c]University of New South Wales

Hydrogen bonded organic frameworks (HOFs), assembled from organic molecules by means of hydrogen bonding, are emerging as promising porous materials in conjunction with metal-organic and covalent-organic frameworks (MOFs and COFs) because of the ease of their synthesis under mild conditions and their solution processabilities that are generally not present in robust polymeric networks. Nevertheless, HOFs, compared to MOFs, still lack topological diversity. We have been exploring the use of triptycenes with peripheral aryl carboxyl groups as the building blocks for 3D HOFs. These peripherally extended triptycenes (PETs), which exhibit a rigid trigonal prismatic geometry, can form porous HOFs with a variety of complex mechanically interlocked network topologies. Herein, we will present (1) a rare example of interpenetration isomerism in HOF system, (2) the assembly of a porous supramolecular polyknot, and (3) the emergence of chirality from the chiral entanglement (Solomon link) of achiral networks, which are all based on the above-mentioned PET building blocks. We believe that these examples highlight the ability of supramolecular systems to create topologically complex architectures using geometrically simple building blocks.

Gas Powered Crystals: Photomechanical Diazide Crystals Produced by Photoinduced Gas Release

Dylan J. Shields[a], **Sujan Sarkar**[a], **Durga Karothu**[b], **Stefan Schramm**[b], **Pance Naumov**[b], **Anna Gudmundsdottir**[a], [a] University of Cincinnati, [b] New York University Abu Dhabi

Converting external stimuli, namely light, into macroscopic mechanical motions is fundamentally important to researchers intent on creating materials for sensing, molecular machinery, or biomimicking medical devices[1-4]. Much of the current research of these stimuli-responsive materials focuses on creating crystalline devices that work by strain induced by polymorph switching or reaction progression[5,6]. However, this talk will focus on a third and considerably less investigated pathway to for inducing crystalline motions: gas generation inside the crystal lattice[7]. This talk will cover a set of photomechanically active diazide crystals characterized by video microscopy, X-ray spectroscopy, and lattice energy calculations. Additionally, potential applications of these diazide crystals as potential devices will be discussed.

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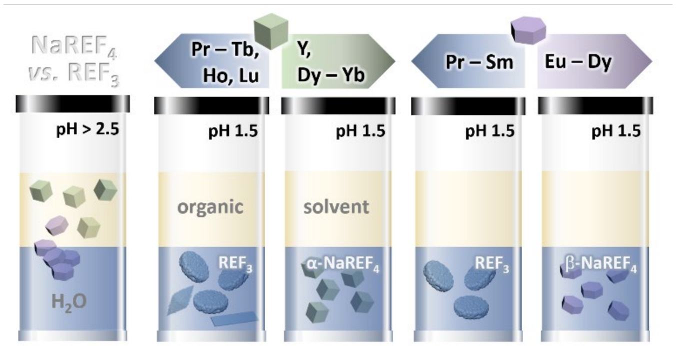
Water dispersible ligand-free rare earth fluoride nanoparticles: water transfer versus $NaREF_4$-to-REF_3 phase transformation

Nan Liu, **Nicholas Gobeil, Parrish Evers, Isabel Gessner, Emille M. Rodrigues and Eva Hemmer***, University of Ottawa

Water dispersible rare-earth (RE) based $NaREF_4$ nanoparticles (NPs) are promising host materials for doping with optically active lanthanide (Ln^{3+}) ions for diverse biomedical applications. In this work, we discuss the chemical stability of oleate-capped sub-10 nm α- and β-phase $NaREF_4$ NPs under the acidic conditions (pH<3) used for ligand removal to obtain such water-dispersible NPs.[1] In stark contrast to the generally considered good chemical stability of $NaREF_4$, these conditions were observed to pose a risk to phase transformation of the $NaREF_4$ NPs into much larger, hexagonal- or orthorhombic-phase REF_3, depending on the NP composition. A correlation between the thermodynamic stability of the α/β-$NaREF_4$ and the hexagonal/orthorhombic REF_3 phases – dictated by the RE ion choice – and the chemical stability of the NPs was found. $NaREF_4$ NPs based on lighter RE ions were more prone towards phase transformation, while those based on heavier RE ions exhibited stability. Also, given the large interest in luminescent NPs, optically active Ln^{3+} ions (Ln = Nd, Eu, Tb, Er/Yb) were doped into α/β-$NaGdF_4$ host NPs, and the dopant influence on the chemical stability was evaluated. Steady state and time-resolved spectroscopy unveiled spectral features characteristic for Ln^{3+} f-f transitions, before and after ligand removal. Overall, the results herein described emphasise the importance of minding the chemical procedure used for ligand removal of $NaREF_4$ NPs of different crystalline phases and RE compositions.



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Understanding the Formation of Microporous Materials using In-Situ Solid-State MAS NMR Spectroscopy

<u>Sandamini H. Alahakoon</u> and Yining Huang, Western University

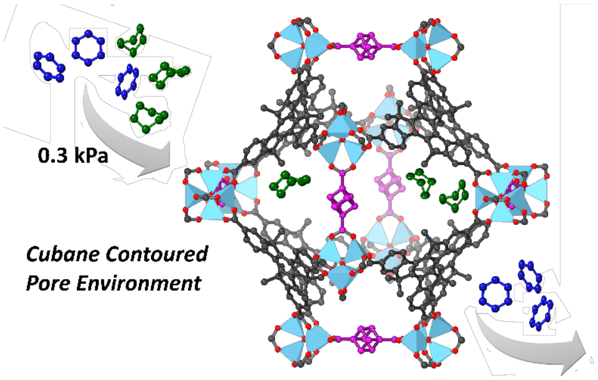
Zeolites and aluminophosphate-based ($AlPO_4$) molecular sieves are important microporous materials that have been widely used in industry for applications such as ion-exchange, gas separation/purification and catalysis. Zeolites and $AlPO_4$s are 3D-structured open frameworks built up of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra and the latter with $[PO_4]^{3-}$ and $[AlO_4]^{5-}$ tetrahedra sharing oxygens.

Even though much knowledge has been accumulated over last decades, the formation of $AlPO_4$-based molecular sieves is still not completely understood at a molecular level. This is because molecular sieves are prepared under hydrothermal synthesis conditions, which make it very difficult to monitor the crystallization process in real time. In this study, we employed an in-situ approach to study the crystallization of $AlPO_4$-11. Specifically, the formation of $AlPO_4$-11 was examined by in-situ high-resolution NMR under magic-angle spinning (MAS) condition, using a new commercially available NMR rotor that can withhold high-pressure and high-temperature. $AlPO_4$-11 was synthesized under dry gel conditions at 190 °C using di-*n*-propylamine as the structure-directing agent (SDA).

Evolution of the gel phases as a function of crystallization time was followed by in-situ ^{31}P and ^{27}Al MAS NMR to monitor the development of local environments of Al and P. ^{1}H MAS NMR is used to obtain information on the local structure of SDA. The $^{1}H \rightarrow {}^{31}P$ cross polarization enabled the differentiation of the $AlPO_4$-11 phosphorus sites among other coexisting phases. This in-situ MAS NMR allows one to obtain detailed structural information on the evolution of the intermediate phases leading to a better understanding of the formation of $AlPO_4$-11.

Hydrocarbon adsorption within MOFs containing a 3D-linkers

Lauren K. Macreadie[1]*, **Matthew R. Hill.**[2] **and Shane G. Telfer**[1], [1]Massey University,
New Zealand; [2]CSIRO, Australia



Aromatic ligands, with polycarboxylate or multitopic functionalities, govern the synthetic chemists' toolbox when forming metal-organic frameworks (MOFs) due to their rigid nature, commercial availability and their variable coordination modes. Conversely, despite their extensive success in creating a rich foundation for MOF development, restriction to solely phenyl interactions within adsorbates represents a possible limitation and reduced variation in the pore chemical environment of the materials.[1] Separation of hydrocarbons using low energy processes is a key area from an industrial standpoint where the strategic design of the MOF pore chemical environment can avoid energy expensive separations based on changes of phase.[2]

Cubane-1,4-dicarboxylic acid (H_2cdc) is a rigid, aliphatic dicarboxylate linker that contains eight carbon atoms arranged in a near-perfect cubic arrangement. Of notable interest is the structural similarity between H_2cdc and benzene-1,4-dicarboxylic acid (H_2bdc) – providing significant scope for the employment of the cubane molecule in MOF synthesis.[3] Through the incorporation of H_2cdc into prominent MOF architectures, we demonstrate the striking effects a contoured, aliphatic pore environment has on gas and hydrocarbon adsorption, compared with its aromatic counterpart, and explore the potential separation capacities these frameworks may pose.[1] Here we present a single-component ($[Zn_4O(1,4\text{-cdc})_3]_n$, CUB-5) and a multi-component ($(Zn_4O(\text{hmtt})_{4/3}(\text{bpdc})_{1/2}(\text{cdc})_{1/2}]_n$, CUB-30) MOF material which contain H_2cdc as an aliphatic linker. The stark difference in vapour adsorption between the topologically analogous frameworks highlights the importance of pore shape during the adsorption process.[1] Interestingly, both MOFs show promise for tuneable, selective hydrocarbon adsorption at low pressures, where CUB-5 shows a propensity for benzene adsorption at low partial pressures, providing a promising landscape for future investigations into benzene separations from an industrial standpoint.

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ABSTRACTS OF POSTER PRESENTATIONS

POSTER 1

Green Synthesis and Efficient Conversion of a Metal-Organic Framework (MOF) as Negative Electrode in Rechargeable Battery

Aamod V. Desai,[a,b] **Russell E. Morris,***[a,b] **and A. Robert Armstrong***[a,b], [a] School of Chemistry, University of St. Andrews, United Kingdom, [b] The Faraday Institution, Didcot, United Kingdom

The growing rise of global energy demands has propelled the development of sustainable energy systems. In this regard, devices offering versatile and efficient energy storage are highly sought after.[1] In particular, the realization of Li-ion battery (LIB) technology into commercial outlets has actuated the research further.[2] The growing span and applicability of this technology requires development of high-performing and sustainable electrode materials. Organic compounds or solids with organic backbones have shown immense promise as sustainable electrode materials, as they are composed of naturally abundant elements, can be functionalized and their electrochemistry is versatile.[3] Organic molecules are deployed as building blocks in the rapidly rising field of metal-organic frameworks (MOFs). These materials incorporate the features of individual components, especially the organic linkers, which can be modulated to tailor the chemical constitution. In the context of energy storage devices, MOFs have only recently garnered attention.[4] In addition to pristine materials, MOF-derivatives are attractive candidates as electrochemically nanostructure materials. Usually these derivatives are obtained by energy intensive processes. In the current work,[5] we demonstrate rapid, green synthesis of a s-block metal based MOF and its energy efficient transformation into active solid (Figure 1). The carbonaceous material functions as a promising anode material in rechargeable LIBs. The solid was found to present moderate low-rate capacities and cycling stability.

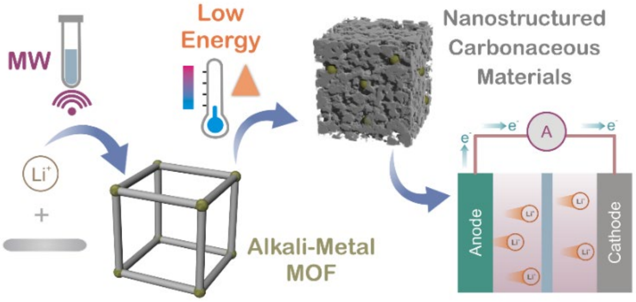

Figure 1. Schematic illustration of microwave-assisted synthesis of MOF and conversion into carbonaceous solid as anode in rechargeable batteries.

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POSTER 2

Mechanochemical screening of Ternary Molecular Ionic Cocrystals

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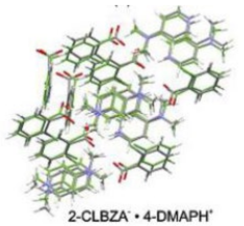
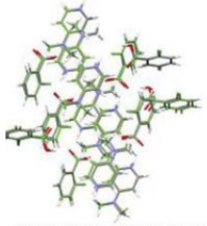
Ionic cocrystals (ICC) are a class of multi-component solid forms with the empirical formula $A^{-}BH^{+}N$ (A^{-} = anion, B^{+}= cation, N= neutral molecule or salt complex). The value of formulating active pharmaceutical ingredients (APIs) as molecular ICCs is that they allow the delivery of several therapeutic agents whilst facilitating the optimization of the physicochemical properties of the parent API [1]. Solution crystallization techniques are not suitable for the synthesis of higher-order cocrystals containing three or more chemical entities due to the inherent differences in the solubilities of the chemical species, which limits the construction of higher-order cocrystals. By contrast, we demonstrate here that mechanosynthesis [2,3] is a versatile technique for the synthesis of ternary molecular ICCs in essentially quantitative yield in less than 30 minutes of grinding with or without solvent. We also show ternary molecular ICCs can be synthesized step-wise or via one-pot liquid-assisted grinding techniques. Ternary molecular ICCs were synthesized via the cocrystallization of 4- dimethyl aminopyridine (4-DMAP) with a range of carboxylic acid coformers. The mechanosynthesis screen led to the facile crystallization of all known ICCs previously reported under solution crystallization screens as well as novel ICCs not previously reported. Furthermore, all the ICCs displayed sharp melting point endotherms ranging from 91.85℃ to 162.49℃ that are different from those of their salt counterparts. In conclusion, the mechanosynthesis of ternary molecular ICCs of the general type $A^{-}BH^{+}N$ is feasible and we show that mechanochemistry can provide a facile route for the synthesis of higher-order cocrystals with functional properties.



$2\text{-CLBZA}^{-} \bullet 4\text{-DMAPH}^{+}$



$2\text{-CLBZA}^{-} \bullet 4\text{-DMAPH}^{+} \bullet 2\text{-CLBZAH}$

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POSTER 3

Crystal engineering of multicomponent solids: Novel cocrystals of an anti-tuberculosis drug, isoniazid, with 1,3,5-triazine-based coformers

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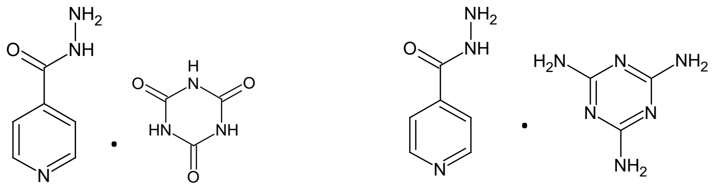
Crystal engineering strategies offers a paradigm for the facile design and synthesis of multicomponent crystals using self-assembly of complementary molecular solids. Recently, co-crystals, multicomponent crystals of active pharmaceutical ingredient (API) and co-former(s), are actively being explored due to their ability to fine tune biopharmaceutical properties of APIs.[1] In this poster contribution, we present discovery of two novel co-crystals of an anti-tuberculosis drug, isoniazid (**INA**),[2] with 1,3,5-triazine-based (cyanuric acid, **CYA** and melamine, **MEL**) coformers in the context of crystal engineering and their potential in modulating the physicochemical properties of API (Figure 1).



INA-CYA **INA-MEL**

Figure 1. Chemical structures of cocrystal components.

Results and discussion Screening for cocrystal formation have been performed using mechanical activation i.e. neat and liquid assisted grinding and the resulted materials were characterised by thermal (DSC, TGA) and powder X-ray diffraction (PXRD). The suitable qualities of crystals **INA** and **INA-CYA** have been generated using ethanol via solution crystallisation method and crystal structures were determined using single crystal X-ray diffraction. The crystal structure analyses confirm that **INA-CYA** has crystallised in orthorhombic $P2_12_12_1$ space group and is a 1:1 stoichiomtric cocrystal. The solid state packing suggests formation heterosynthons.

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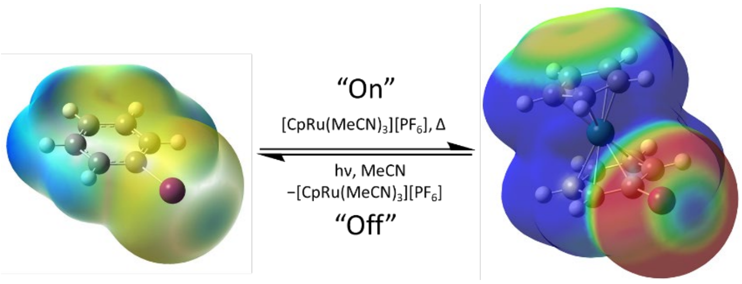
POSTER 4

η^6-Metalation/Demetalation of Simple Aryl Halides as a Means of Amplifying/Suppressing Halogen Bond Donor Capabilities

Andrew W. Kelly and K. Travis Holman, Georgetown University

Modular ON/OFF type control of Halogen Bonding(XBing) has been achieved with the reversible η^6 coordination of cyclopentadienyl ruthenium(II) moieties to simple aryl halides. This novel method for the activation of XB donors displays similar XB to the widely utilized fluorinated, nitrated, or otherwise electron-deficient ring XB donors, as demonstrated by single-crystal structures, ^{1}H-NMR experiments, and computational work. Unlike the aforementioned traditional donors, η^6 coordination of the ruthenium moiety occurs in a single “Click“-like step and is easily undone by simple exposure to light. These characteristics in combination are what has allowed for the ON/OFF control of XBing, providing not only a simple new method for the activation of XBs but a potential avenue to control solution state XB based aggregation.



POSTER 5

A New Multitalented Azine Ligand: Elastic Bending, Single-Crystal-to-Single-Crystal Transformation and a Fluorescence Turn-on Al(III) sensor

Anoop Saini, Delhi University

The design and synthesis of multi-tasking materials has attracted tremendous interest owing to their fascinating applications and economic viability. In the solid-state, crystalline materials are of paramount importance due to their potential applications in mechanical actuators, phototransistors, solar cells, light-emitting diodes and flexible electronics. The recent upsurge in the field of SCSC transformation reveals that transformed newer materials *via* external stimuli like light, heat and vapour have significant applications in sensor technology and gas storage. In organic ligands, the SCSC transformations are rare.

Here, we report a rare combination of two unique properties of an azine based ligand (**H_3L**): in a solid-state crystalline material it shows highly flexible and elastic behavior which on triggering with light results in slight deviation with phase transformation at the Single-Crystal-to- Single-Crystal (SCSC) level. Furthermore, in the solution state it acts as a highly selective, sensitive and reversible Al^{3+} sensor with a detection limit of 42 nM.

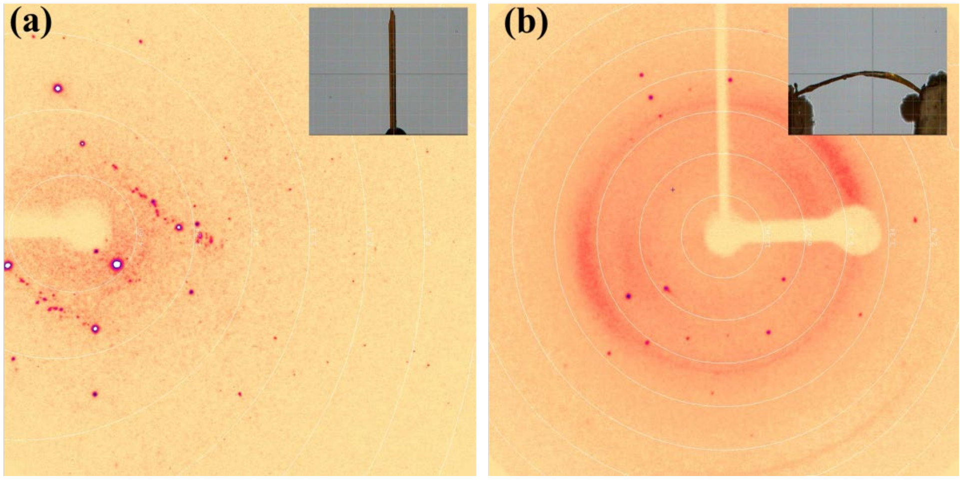


Figure 1. Diffraction images (Exposure time = 20 s) obtained from the mounted crystal and the inset shows the (**a**) original form and (**b**) bent form.

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POSTER 6

Tunable Mechanical Response from a Crystal Undergoing Topochemical Dimerization

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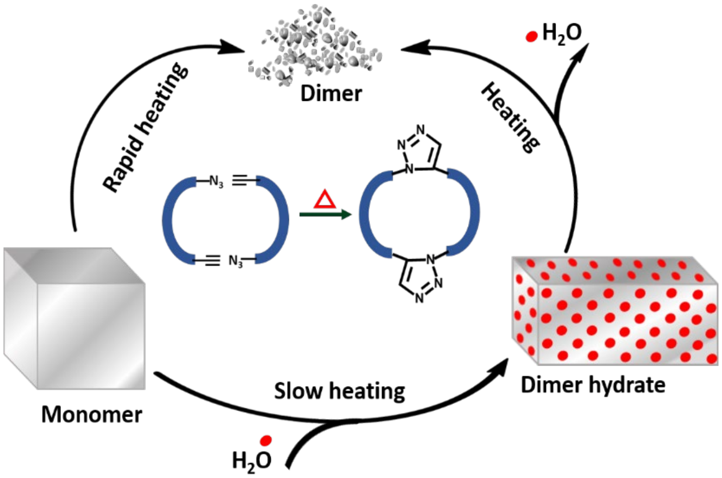
Research Thiruvananthapuram

Strain developed in crystals due to external stimuli causes mechanical response.[1] Crystals can bend, twist, explode, *etc.* in response to external stimuli, as a result of chemical reaction, polymorphic transition, conformational change or isomerization. Methods to tune such mechanical response are important for practical applications. Crystals of a monomer having azide and alkyne units pre-organized in a ready-to-dimerize orientation, show rate-dependent mechanical response by undergoing topochemical azide-alkyne cycloaddition (TAAC) reaction. When the rate of the reaction is fast, the crystals explode violently due to the sudden release of the strain. When the rate is slow, the crystal absorbs water from the surroundings, contemporaneously with the reaction, forming a dimer-hydrate, in a single-crystal-to-single-crystal (SCSC) manner. Upon dehydration, these hydrated crystals also explode. Thus, the strain gets stored by hydration and is released at will, by dehydration. Apart from the demonstration of storage of stimuli-induced strain and its harvest, we show the application of rate-dependent explosion in designing “turn-on” switches for automatic activation of remedial electrical circuits in case of a sudden rise in temperature.[2]



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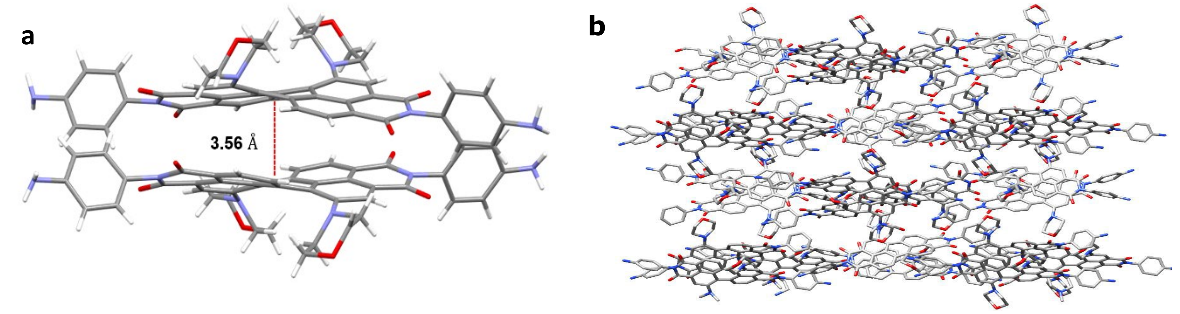
POSTER 7

FLOURESCENT POROUS HYDROGEN BONDING ORGANIC FRAMEWORKS (HOFs) USING PERYLENE DIIMIDE

Asia Almuhana, Neil R. Champness, University of Nottingham

Hydrogen-bonded organic frameworks (HOFs) are crystalline systems that are formed by self-assembly through hydrogen bonding. H-bonding connections feature a weak, flexible, directional, and reversible interaction indicating that HOFs show high crystallinity, solution processability, easy healing and purification. These unique advantages enable HOFs to be important for a variety of future applications. This study details the construction of HOFs using perylene diimides (PDIs) as building blocks, which usually are excellent fluorescent dyes. The building blocks are a series of PDI molecules functionalised with different H-bonding units at the imide-position, as well as the functionalisation of the bay area with a tertiary amine which leads to interesting optical and electronic properties. It has been observed that introducing electron donating substituents at the bay region has large effects in terms of the compounds UV/Vis maxima and consequently their colour. However, they have little impact upon the $E_{1/2}$ values of the two reduction processes but large effects in terms of the oxidation behaviour.



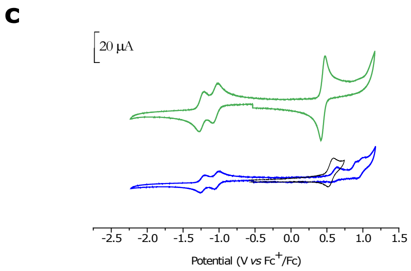


Figure. (a) Crystal structure of **G-PDI-1,** (b) The view of the 3D supramolecular organic framework of G-NH2PDI (HOFs), (c) Cyclic voltammograms recorded for **G-PDI-1** (top/green) and **B-PDI-1** (bottom/blue).

G-PDI-1: N,N'-di(tert-Butyl(4-aminophenyl) carbamate)-1,7-dimorpholino-3,4:9,10 perylenetetracarboxylic diimide.

POSTER 8

Mechanochemical Synthesis of Cocrystals of HCl Salts of Pharmaceuticals and their Structural Determination Using ^{35}Cl SSNMR and Dispersion-Corrected DFT Calculations

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[1] Florida State University, [2] University of Windsor, [3] National High Magnetic Field Laboratory, Tallahassee.

The solid forms of active pharmaceutical ingredients (APIs), including polymorphs, pseudopolymorphs, and amorphous solid dispersions, have unique properties such as stability and solubility that can affect their bioavaibility and shelf life. These properties are dependent on the molecular-level structure of the solid form of the API; as such, it is sometimes possible to modify these properties with targeted synthetic or preparative procedures. HCl salts of APIs are the most common solid forms with improved solubility and stability; however, it may be possible to further enhance these properties via the production of cocrystals (CCs). For this reason, cocrystalline forms involving an HCl API and a pharmaceutically acceptable coformer, have garnered recent attention.
In 2019, Borodi *et al.* demonstrated that mechanochemical (MC) methods could be used to produce CCs of promethazine HCl with four carboxylic acid coformers: fumaric acid, succinic acid, adipic acid, and oxalic acid.[1] Structural characterization of these CCs is crucial for understanding their mechanisms of formation, their solid-state properties, and the rational design of analogous CCs, as well as novel cocrystalline forms.

Herein, we describe the MC synthesis and characterization of HCl API CCs that were produced from a series of structurally homologous HCl API salts, including promethazine HCl (Ptz), chlorpromazine HCl (Cpz), and promazine HCl (Pmz). First, we present improved protocols for MC synthesis of previously reported Ptz CCs with reduced reaction times and high yields. Second, it is demonstrated that these protocols can be applied to produce novel CCs of Ptz, Cpz and Pmz. Then, ^{35}Cl SSNMR spectra are shown to be useful as spectral fingerprints for each HCl API and their corresponding CCs. This is because each solid form has a Cl^- ion environment(s) with a unique hydrogen bonding network, which results in distinct ^{35}Cl electric field gradient (EFG) tensor parameters, and concomitant second-order quadrupolar powder patterns that are clearly distinguishable.[2] Lastly, we discuss the use of dispersion-corrected plane-wave DFT calculations to refine model structures of several of these systems; comparison of experimentally measured and theoretically derived ^{35}Cl EFG tensor parameters are used as a metric for assessing the quality of the structures. We anticipate that these methods have potential for the design, preparation, and characterization of a cornucopia of HCl API CCs.

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POSTER 9

In situ cryocrystallization as a probe to investigate the crystal chemistry of –F and –CF_3 substituted benzaldehydes

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The molecular and crystal structure of low-melting of organic solids and liquids can be determined via *in situ cryo-crystallization* technique[1,2]. The understanding of the role of weak intermolecular interactions, in particular those involving organic fluorine, is of importance. Initial studies have been done on fluorobenzenes.[3] This method has find applications in in exploring and investigating a plethora of relatively weaker non-covalent interactions that supports the crystalline assembly such as N-H…F, C-H…F and F…F contact in fluorinated amines[4,5], C-H…O, C-H…F and F…O contact in fluorinated benzoyl chloride[6], C-H…π interactions in polymorphs of diphenyl ether[7] and C-H…O, N-H…N, C-H…N in furfural and its derivatives[8]. As a part of our ongoing investigation on fluorine centred interactions, a series of fluoro and/or trifluoromethyl substituted benzaldehydes, which are liquids at STP, are crystallized under non-ambient conditions using *insitu* cryocrystallization technique *via* OHCD (as shown in Fig 1.). The compound primarily consists of relatively weaker hydrogen bond donors and acceptors wherein the role of both electrostatics and dispersion is of relevance in the formation of the H-Bond. The anticipation of C-H…O, C-H…F, F…F, displaced π-stacking and interactions involving carbonyl's π -hole will be corroborated via several computational tools. The purpose of performing this challenging crystallization technique followed by computational evaluation is to appraise the role of weaker interactions which play a central role in the supramolecular chemistry of solids.

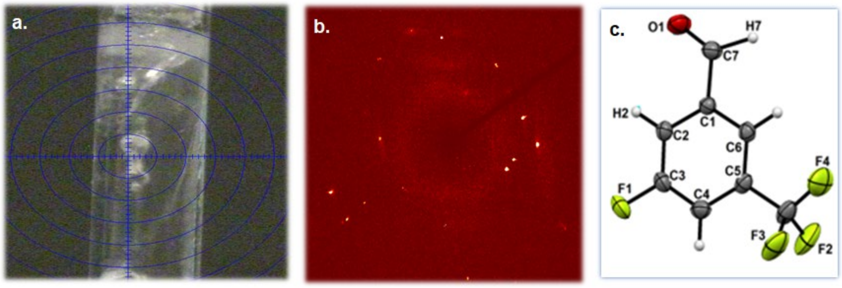

Fig 1. a. Crystallization of 3-fluoro-5-(trifluoromethyl) benzaldehyde (3F5CFBZ) in Lindemann capillary of 0.3mm diameter; b. X-ray diffraction image (Still Photo); c. ORTEP of 3F5CFBZ with 50% ellipsoidal probability

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POSTER 10

Mechanochemical synthesis and topology transformation in polymorphic Zr-MOF qubit candidates

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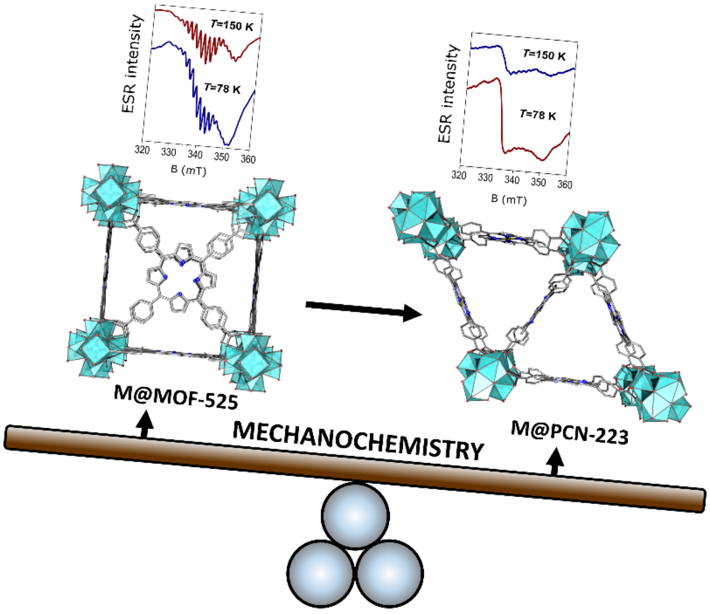
Among the large family of metal organic frameworks (MOFs), highly stable Zr-based MOFs are one of the most interesting members with various application areas owing to their stability, high porosity, high density of metal centres included in the cluster nodes, and varied types of topologies. However, the conventional synthetic method of pure phase polymorphs is still a challenge. Herein we present rapid, clean, high-yield mechanochemical synthesis of pure phase cubic MOF-525 and hexagonal PCN-223 polymorphs built on tetratopic porphyrin linker by liquid-assisted grinding technique.[1] In-situ powder X-ray diffraction monitoring performed at the DESY synchrotron source reveals that particular ball-milling conditions can induce the transformation from cubic to hexagonal phase, denoting MOF-525 to be a kinetic phase in this polymorphic system. Electron spin resonance (ESR) data of these polymorphic MOFs showed significant differences due to the different spatial arrangement and efficient separation of the metal centres (Cu(II), Mn(II) and Fe(III)) in the porphyrin rings, denoting them also as candidates for advanced spintronics applications.



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POSTER 11

Phonon induced deformations in microporous crystalline solids

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Phonons represent collective vibrations of the crystal structure which define instantaneous macroscopic deformations of the lattice. Low frequency phonons are often the precursors of structural deformations [1], in particular in the case of second order, continuous phase transitions. These deformations can define the symmetry and the structure of a new phase. They determine the thermodynamic properties of solids and their stability in the case of structural transformations.

The aim of this project is to investigate if phonons can be used to predict adsorption induced transformations in MOFs and how study of phonons can lead to understanding of the mechanism of deformation.

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POSTER 12

Solvent-free mechanosynthesis of ultrasmall nickel phosphide nanoparticles for catalyzing the hydrogen evolution reaction (HER)

Blaine G. Fiss[1], Nhu Nang Vu[2], Georgia Douglas[1], Trong-On Do[2]*, Tomislav Friščić[1]*, Audrey Moores[1]*, [1] McGill University, [2] Laval University, Québec City,

Despite the promise of hydrogen gas as a new energy resource, the environmentally-friendly design of catalysts for photocatalytic (PC) hydrogen evolution reaction (HER) from water remains a challenge. Metal phosphides are a low-cost, potentially accessible catalyst for this reaction, compared to the traditionally used precious metal systems.[1] However, the synthesis of metal phosphide nanomaterials currently involves highly reactive phosphorus sources, high temperatures and organic solvents. This presentation will outline the application of sodium phosphide as an excellent solid-state phosphorus source for the synthesis of nanoparticles below 3 nm in diameter, a size range previously not observed in mechanosynthesis of metal phosphides. The nanoparticles successfully promote the HER using graphitic carbon nitride as a photocatalytic support, generating 233.9 μmol g^{-1} h^{-1} of hydrogen, using broad spectrum light, at room temperature after only 3 hours.[2] The described mechanochemical method exhibits mass intensity (MI) >2.5 times lower than traditionally used solution-based methods, even after workup and washing of the product. Upon scaling up the reaction to a 2.5 gram scale, we were able to further improve the MI to 3 times less than traditional solvent-based methods, while reducing the energy demand more than 18-fold.

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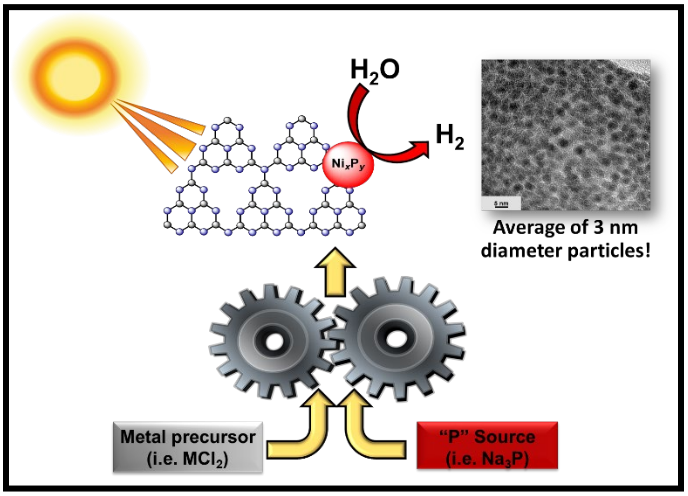


POSTER 13

Organic Networks based upon Halogen Bonding Interactions containing Nodes generated in the Solid State

Carlos L. Santana and Ryan H. Groeneman[*], Webster University

The ability to form purely organic networks continues to be an active area of research for crystal engineers. The number of reported organic solids still drastically lags behind the number of related metal-organic examples. Curiously, cyclobutane-based photoproducts, generated from a solid state [2 + 2] cycloaddition reaction, have been employed in the formation of these organic and inorganic frameworks. In particular, the most reported photoproduct has been *rctt*-tetrakis(4-pyridyl)cyclobutane that contains four identical pendant arms that can accept metal coordination bonds as well as different non-covalent interactions to form these extended solids. In this contribution, we will report the formation of the first purely organic diamondoid net based upon *rctt*-tetrakis(4-pyridyl)cyclobutane along with 1,4-diiodoperchlorobenzene as the divergent halogen bond donor. In addition, we will also report a ladder-like halogen-bonded network based upon *rctt*-tetrakis(5'-pyrimidyl)cyclobutane along with 1,4-diiodoperchlorobenzene. The formation and the resulting crystal structure of each network will be discussed.

POSTER 14

I Find Your Lack of Permeability Disturbing: Exploring Physicochemical Properties of 5-FU Multicomponent Crystals

Celymar Ortiz-de León and Leonard R. MacGillivray*, University of Iowa

With the number of diagnosed cancer cases growing from 12.7 million in 2008 to more than 14 million in 2012, cancer is one of the major causes of mortality. 5-fluorouracil (**5-FU)**, one of the highest-effective chemotherapeutic agents in the treatment of several cancers including liver, breast, gastrointestinal tract, ovary, and neck. Due to ease of isolation, grade of purity and physiochemical stability, crystalline solid forms of active pharmaceutical ingredients (APIs) are widely preferred over alternative forms of delivery. Studies on organic crystals have demonstrated that their solid-state properties are the consequence of the supramolecular arrangement of said entity. Hence, recent developments in the area of crystal engineering has given great focus to the design of optimal pharmaceutics by the formation of new solid forms assembled through noncovalent interactions comprising an API and a cocrystal former. Thus, the modulation of the physical and chemical properties (e.g. solubility, permeability, bioavailability) of the API in the solid state becomes possible.

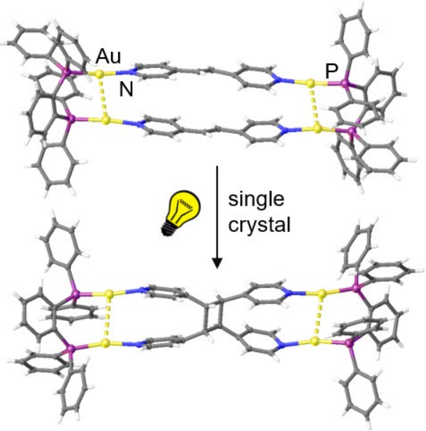
Our work explores the modulation of the physicochemical properties of **5-FU** through non-covalent interactions with resveratrol (**resv**) and 4,4’-bis(pyridyl)ethylene (**4,4’-bpe**). The three different compounds form a three-component assembly in the solid state. In the crystal, a molecule of resveratrol acts as a template through OH···N hydrogen bonds, organizing two molecules of **4,4’-bpe** into π-stackings. A third hydroxyl group on the resveratrol further interacts with a molecule of **5-FU**, which, in turn, forms a dimer that connects to another discrete assembly of resveratrol and 2(**4,4’-bpe**).

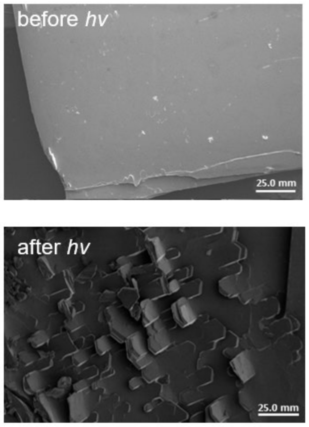
POSTER 15

Gold(I)···Gold(I) Interactions as Supramolecular Design Elements for Photo-responsive Macrocycles

Changan Li, Gonzalo Campillo-Alvarado, Dale C. Swenson and Leonard R. MacGillivray*, University of Iowa

Tetranuclear organogold(I) macrocycles were constructed using Au(I) coordination and aurophilic interactions. Diphosphine ligand (*i.e.*, 1,2-bis(diphenylphosphino)benzene, dppbz) was used to sustain aurophilic interactions and the formation of rectangular macrocycles involving olefins (*i.e.*, 1,2-bis(4-pyridyl)ethylene, bpe). The rigid $Au_2(dppbz)(CF_3COO)_2$ precursor self-assembles with bpe to afford a discrete $[Au_4(dppbz)_2(bpe)_2]^{4+}$ macrocycle in the solid state. The alkene undergoes a [2+2] photocycloaddition reaction. The photoreaction proceeds via a rare single-crystal-to-single-crystal (SCSC) transformation in quantitative yield that generates $[Au_4(dppbz)_2(4,4'\text{-tpcb})]^{4+}$(4,4'-tpcb = *rctt*-tetrakis(4-pyridyl)cyclobutane) stereoselectively and quantitively. We have also shown that expansion of the unit cell by the photocycloaddition generates ramps on the surfaces of the single crystals.



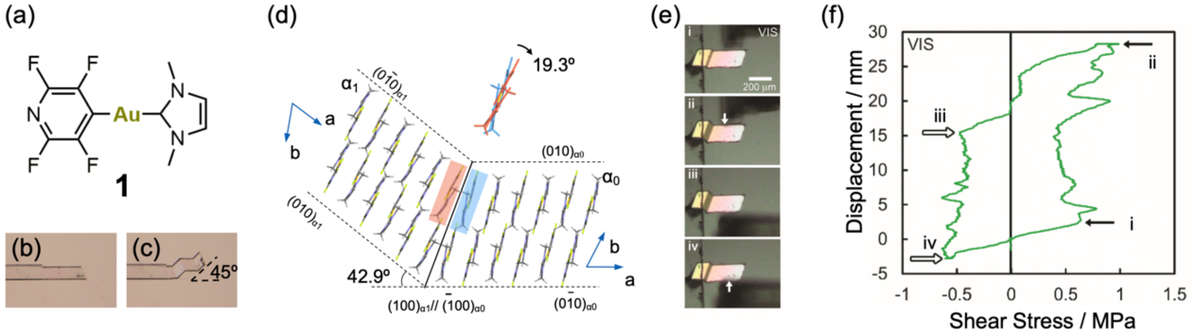


POSTER 16

Photoluminescent Ferroelastic Crystals of Gold Complexes

Chi Feng,[1] Tomohiro Seki,[1] Toshiyuki Sasaki,[2] Satoshi Takamizawa,[2] Hajime Ito[1,3],
[1] Hokkaido University, [2] Yokohama City University, [3] WPI-ICReDD, Hokkaido University

Ferroelasticity in molecular crystals represents macroscopic level plastic deformation with spontaneous strain upon mechanical stress. At the microscopic level, molecular orientational change takes place at the deformed moiety. The ferroelasticity has been well studied in inorganic alloy materials. But the ferroelasticity in organic molecular crystals is still not well researched.1) Moreover, there is no example of photoluminescent ferroelastic molecular crystals. In this work, we found that the *N*-heterocyclic carbene (NHC) gold(I) complex **1** shows a ferroelastic behavior with photoluminescence for the first time.2,3)



Crystals of compound **1** were prepared from dichloromethane/hexane solution (Fig. b). Under exposure to UV light, the crystal **1** exhibits blue photoluminescence. Upon applying mechanical force, the crystal **1** shows plastic bending with a bending angle of 45º (Fig. c). The effect of such deformation on the photoluminescence properties was then investigated. The bent moiety of crystal **1** shows an emission spectrum that is almost the same as the emission spectrum of the unbent moiety. Single-crystal X-ray diffraction analyses of the bent crystal **1** was performed. We found that a crystal twinning with molecular-level rearrangement at the bending moiety (Fig. d). The stress-strain measurement upon loading mechanical stress of the crystal of **1** indicates a hysteresis trace, confirming its ferroelastic property (Figs. e–f).

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POSTER 17

Evolutionary Chemical Space Exploration for Functional Materials

Chi Y. Cheng, Josh E. Campbell and Graeme M. Day, University of Southampton

We have recently developed a fragment-based materials discovery program which explores a user defined chemical space with a population of molecules that travels across the chemical space through an evolutionary type algorithm. By applying selection pressures onto each generation of molecules the evolutionary algorithm therefore directs the population towards a region of chemical space containing molecules with favourable target properties. As a first proof of concept we have applied this method to search for high performance small molecule organic semiconductors for a chemical space of aza-substituted polyaromatic hydrocarbons.[1] Since the performances of small molecule semiconductors can be highly dependent on its crystal structure, we carry out a two staged approach with the evolutionary algorithm acting as a first stage which suggests molecules from only molecular properties which are then fed into a crystal structure prediction[2] procedure with property evaluations on their predicted crystal structures. This led to the suggestion of a set of molecules with predicted crystal structure landscapes which predominantly contained crystals with high calculated carrier mobilities. These promising results therefore outlines and demonstrates a viable material discovery program for small molecules crystalline materials which offers many opportunities for further development.

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POSTER 18

Bisboronic diester complexes featuring ditopic receptor motif based 1,8 dipyridyl naphthalenes.

Christopher Hartwick, Gonzalo Campillo-Alvarado, Leonard R. MacGillivray,
University of Iowa

Derivatives utilizing the 1,8-substitution pattern of naphthalene frameworks have been used in various self-assembly processes in the solid state with. Aryl 1,8 napthalenes display a deviation from coplanarity approaching perpendicular orientation due to interactions between aryl groups. Applications using boronic acids have been found to bind nitrogenous compounds including pyridines and their derivatives using N→B bonding. Thus, diboronic ester adducts of 1,3-diboronic acid di-catecholates and 1,8 dipyridyl napthalenes continue to display such interactions while lone pair donation ensures close interactions between nitrogen and boron. Such substituted naphthalene reagents are based off of the 1,8 dipyridyl naphthalene (DPN), 1,8 di-4-ethylenylpyridyl naphthalene (DEPN), and 1,8 di-4-ethynylpyridyl naphthalene all form adducts with 1,3 benzenediboronic acid catechol diester.

POSTER 19

Exploring the Scope of the Mechanochemical Friedländer Synthesis

Daliah Farajat*, Jean-Louis Do*§, Tomislav Friščić§, Pat Forgione* and Louis A. Cuccia*, *Concordia University, § McGill University

The Friedländer reaction is used to synthesize quinolines, heterocyclic aromatic organic compounds that can be found in many natural and synthetic products. Quinoline derivatives often have important pharmacological properties, thus encouraging the discovery of new routes for their synthesis. While this reaction is readily carried out in solution under acid- or base-catalysed conditions, there are only a few investigations of the Friedländer condensation reaction carried out under solvent-free mechanochemical conditions. Mechanochemistry offers the potential advantages of shorter reaction times, milder reaction conditions, and compatibility with a greater number of functional groups – thereby avoiding many of the limitations often present in solvent-based Friedländer reactions. Insofar, the aim of this research is to expand the scope of mechanochemical Friedländer synthesis through systematically derivatizing the 2-aminocarbonyl and its ketone condensation partner (Figure 1). To-date, the reaction has been optimized and several products synthesized, including, 2-(4-bromophenyl)-4-phenylquinoline, 6-chloro-2-(4-bromophenyl)-4-phenylquinoline, 2-(4-methoxyphenyl)-4-phenylquinoline, and 6-chloro-2-(4-methoxyphenyl)-4-phenylquinoline at isolated yields of 94%, 84%, 98% and 89% respectively. A long term goal is to utilize this newly acquired knowledge to build scaffolds that can be pharmaceutically relevant.

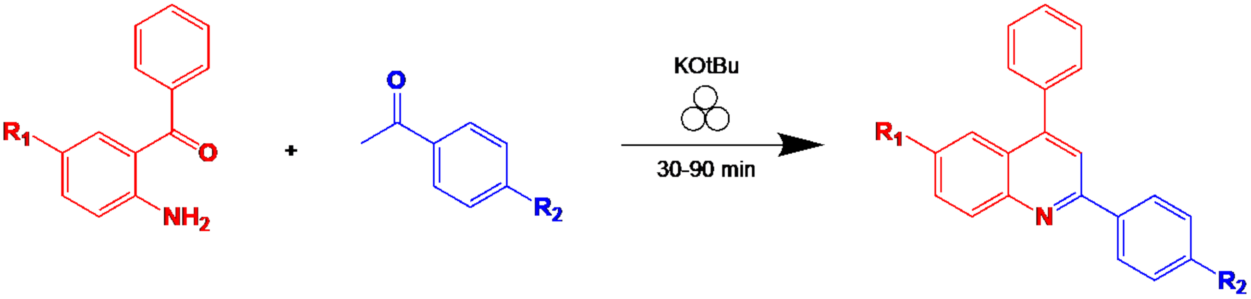

Figure 1. Proposed mechanochemical synthesis

POSTER 20

Towards polyoxometalates with Fe(III)? A family of molecular metal oxides

Daniel J. Cutler, [a] Alice Dearle,[a] Sergio Sanz,[a] Hector W. L. Fraser,[a] Edward Lee,[a,b] Sourav Dey,[c] Gary S. Nichol,[a] Marco Evangelisti,[d] Gopalan Rajaraman,[c] Jürgen Schnack,[e] Leroy Cronin [b] and Euan Brechin[a], [a] University of Edinburgh, [b] University of Glasgow, [c] Indian Institute of Technology Bombay, [d] CSIC-Universidad de Zaragoza, [e] Universität Bielefeld

There is an enormous size difference between the large polyoxometalates (POMs), usually synthesised from high oxidation state, diamagnetic metal ions (i.e. Mo, W and V)[1] and clusters built from paramagnetic, high spin (d^5) Fe(III) ions[2,3] despite both containing examples of compounds containing similar metal oxide cores.[4] The most closely related Fe(III) clusters to POMs being the Fe_{13} [5] and Fe_{17} [6] clusters, both are structurally related with alternating layers of tetrahedral and octahedral Fe(III)ions. The former has a α-Keggin structure and the latter the ε-Keggin structure with four capping Fe(III) ions. This has prompted us to speculate that large and very large Fe(III) molecular metal oxides, approaching the size and structural diversity of POMs, can be constructed, but with the terminal oxides replaced by simple monodentate ligands. The synthesis of such compounds would help to bridge the "gap" between the fields of molecular magnetism and POM chemistry. Thus, producing species with an myriad of potentially interesting physical properties, with applications in chemistry, physics, materials science, biology and medicine. Herein we present a series of such molecular Fe(III) oxides with a nuclearity up to 34 Fe(III) ions.

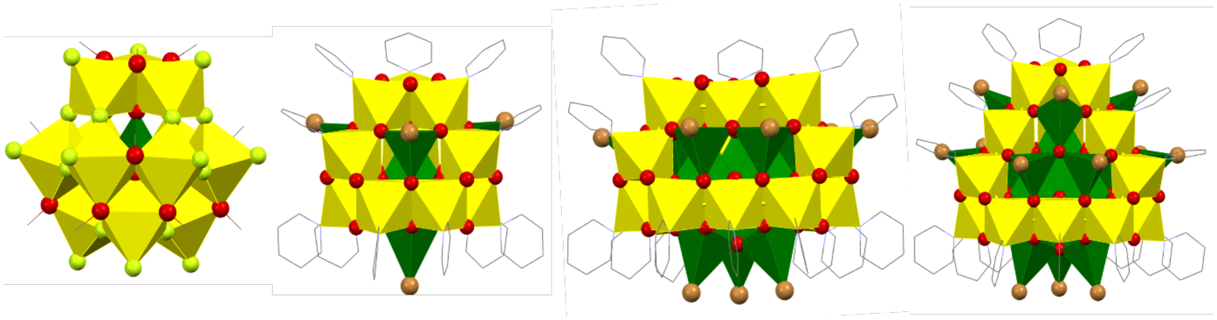

Figure 1. Polyhedral representations of four molecular oxide clusters from left to right Fe_{13}, Fe_{17}, Fe_{30} and Fe_{34}.

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POSTER 21

Nanostructured zinc oxide as a potential solar catalyst: crystal structures, properties and their applications

Deepak Sharma, Ajit Sharma*, Lovely Professional University

Metal oxide nanoparticles have shown solar catalytic properties. When the more surface area with intense crystal structure is available adsorption of target molecules will also be more as well as their photocatalytic reactions efficiency. Nanostructured zinc oxide (ZnO) for treatment of water with role of crystal structure is studied. Due to the more surface area and many other changes in chemical, biological and physical properties of nanoparticles that develop due to their size effects, these are gaining high interest in environmental cure. A nanorods shape crystal structure of ZnO are proved as effective photocatalyst. It has ability to degrade both biological and chemical impurities. The major drawback in the use of nanoparticles is that it is not easy to remove these after the treatment. The main issue related to elimination of pollutant from decontaminated water was found by growing various crystal structure of ZnO on some another co-dopant for visible light photocatalysis.

Keywords: Nanostructure; crystal structure; zinc oxide; photo-catalysis; degradation;

POSTER 22

NEW APPROACHES TO CRYSTAL CHEMICAL DESIGN OF PHOSPHORS BASED ON B-$CA_3(PO_4)_2$-TYPE HOSTS

Dina Deyneko[1], Sergey Aksenov[2], [1] Lomonosov Moscow State University, [2] Russian Academy of Sciences.

β-$Ca_3(PO_4)_2$ (β-TCP)-type compounds at the moment are considered as a host for rare-earth elements for producing phosphors for LED application[1]. type compounds are characterized by the variation of the space group based on the degree of distortion of the initial structure induced by heating/cooling and/or isomorphic substitutions. The polar structure with the non-centrosymmetric space group *R*3*c* and the unit cell parameters (*a* ~ 10.5 Å, *c* ~ 38 Å) has a phase transition to a non-polar structure with the space group $R\bar{3}c$ (with the same unit cell) under the heating. The further increasing of the temperature leads to formation another non-polar structure with the centrosymmetric space group $R\bar{3}m$, characterized by the reduced unit cell (*a* ~ 10.5 Å, *c* ~ 19 Å) in comparison with the initial ones. An hypothetical aristotype (parent phase) should be characterized by the space group $P\bar{3}1m$ and the following unit cell parameters: *a* ~ 6.1 Å, *c* ~ 6.3 Å.

A family of compounds $Sr_9R^{3+}(PO_4)_7$ (*R* = Sc, Cr, Fe, Ga, In) has a monoclinic (space group *C*2/*m*) crystal structure with the unit cell parameters of *a* ~ 18.4, *b* ~ 10.6, *c* ~ 9.0, β ~ 133°, which could be obtained from the space group $R\bar{3}m$. The further ordering processes is realized in the doubling of the *c* parameter and the unit cell parameters are *a* ~ 18.4, *b* ~ 10.6, *c* ~ 18.0, β ~ 133°, while the space group is *C*2/*c*. Trees of group–subgroup relations between different modifications of β-TCP-type compounds can be presented by Bärnighausen tree.

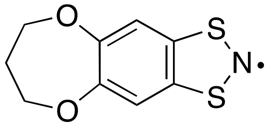
POSTER 23

Polymorphism and Magnetic Behaviour of a Novel Canted Antiferromagnet

Dominique M. Leckie[a], Justin Wrixon[a], Javier Campo[b], Mohammed Harb[a], and Dr. Jeremy M. Rawson[a,*], [a] University of Windsor, [b] University of Zaragoza

Thiazyl radicals have gained significant interest for their use as magnetic molecular materials. Among these radicals, the family of 1,3,2-dithiazolyl (DTA) derivatives have shown computationally that the majority of the unpaired electron resides on the S-N-S ring segment. While some DTA radicals dimerize via multi-centre bonding interaction or a pancake bond, their dimerization energy of approximately 0 kJ/mol allows many of these radicals to retain their paramagnetism in the solid state. DTA radicals which adopt pi-stacked structures often exhibit spin transition behavior in the solid state.[1-4] At low temperatures, a weak dimerization enthalpy favours formation of diamagnetic dimers, whereas at elevated temperatures, the effects of entropy dominate and a solid state phase transition to a paramagnetic monomer phase can be observed upon heating. Such materials where a phase transition is driven by heat, light, or pressure are suitable candidates for applications such as data storage.

Here, we present the synthesis and structures of the polymorphic dioxepinyl-benzo-1,3,2-dithiazolyl radical as well as careful methods to isolate the alpha and beta phase. The magnetic properties of the alpha phase are studied in-depth and exhibits a spontaneous magnetic moment at 3.8 K. Further characterization by variable temperature powder XRD, EPR, and DSC will be examined.



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POSTER 24

FAryl Amphiphile for the Morphology-Controlled Synthesis of Organic Semiconductor Microcrystals

Dorothy K. Jones, Nagarjuna Gavvalapalli, Georgetown University

Pi-conjugated organic molecular (PiCOM) semiconducting microcrystals (MCs) have great potential for use in photonic integrated circuits, optical waveguiding and lasing applications. This type of organic photonic integrated circuit would help overcome the some of the limitations faced by silicon-based integrated circuits, such as heat generation and bandwidth limitations. However, in order to fully realize the potential of PiCOM MCs for photonic and electronic applications, we need the ability to predictably generate MCs of different shapes and sizes. Currently the morphology-controlled synthesis of PiCOM MCs is mostly reliant on aliphatic surfactants, such as sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB), which lack structural diversity and thus do not provide tunable amphiphile-crystal facet interaction energies and generate a limited range of MC shapes. This poster will discuss how aryl amphiphiles can be used as shape-directors for the morphology-controlled synthesis of PiCOM MCs. By using an amphiphile with an aryl hydrophobe, the interaction energies between the shape-director and the crystal facets are increased due to the formation of pi-pi interactions. Additionally, differently shaped aryl hydrophobes can be synthesized, which further modulates the interaction energy between the shape-director and the crystal facets, which allows for a wider range of PiCOM MC shapes. This poster will show how two different aryl amphiphiles can be used to obtain differently shaped 9,10-diphenylanthracene MCs of with greater than 90% shape yield. Additionally, a proposed mechanism of how the aryl amphiphiles interact with the growing MC to dictate the final observed morphology will be discussed.

POSTER 25

High-throughput computational design and discovery of conductive materials in the CSD MOF subset

Federica Zanca[1], Sanggyu Chong[2], Bartomeu Monserrat[3], David Fairen-Jimenez[3], Peyman Z. Moghadam[1*], [1]University of Sheffield, Sheffield, [2] Korea Advanced Institute of Science and Technology (KAIST), [3] University of Cambridge

MOFs are innovative porous materials and have been widely studied for the past two decades for applications in different areas including gas storage, gas separation and catalysis. Here, we aim to study electrical conductivity in MOFs, a less explored but interesting property that can bring promising opportunities in energy storage and sensing application. Due to their high porosity and surface area, MOFs are poor electrical conductors. Here, to identify promising conductive structures, we performed high-throughput screening of the existing ca. 90,000 structures in the CSD MOF subset 1 — characterising the band gap and examining the presence or absence of metallic behaviour. The first set of selection criteria as developed based on the nature of MOFs' surface chemistry with a focus on the type of the secondary building unit and the ligand. We focused on MOFs containing open shell metals, metal clusters and highly conjugated linkers that can facilitate through-linker charge transfer between metals. The second set of criteria involved the presence of linkers containing metal-S, or -N coordination, redox-active linkers, π-π stacking, and mixed valence metals. For the ca. 1000 structures shortlisted, we then performed DFT calculations to derive useful insights into structure-conductivity relationships in MOFs, identify top-performing conductive MOFs, and to delineate key chemical and physical features in MOFs that influence their conductive properties for the first time. The results guide MOF researchers to assess and design conductive structures for electronics, energy storage and sensing applications.

POSTER 26

Pyridyl Alkoxide-Based Ligands in *3d/4f*-Metal Cluster Chemistry: Two Structurally Related Families with "Open Cubane"-like $\{Cu_2Ln_2\}$ and $\{Cu_4Ln_2\}$ Complexes with Single-Molecule Magnetic Behavior

Gabriele Delle Monache, Theocharis Stamatatos*, and Melanie Pilkington*, Brock University

Two families of $\{Cu_2Ln_2\}$ and $\{Cu_4Ln_2\}$ clusters (Ln= Gd(III), Tb(III), Dy(III)) have been prepared from benzoate ions and the chelating/bridging ligand 2,6-*bis*(1-hydroxyethyl)pyridine ($bhpH_2$, **1**), which are the only *3d/4f* clusters coordinated with $bhpH_2$ in the field to-date. Elucidation of their molecular structures by X-ray diffraction shows that the structural core of both sets of complexes are very similar, however magnetic susceptibility studies reveal that the Cu_2Ln_2 systems exhibit no slow relaxation of magnetization, whereas the Cu_4Ln_2 complexes are single molecule magnets (SMMs) at low temperature. The synthesis and magneto-structural studies of these two families of heterometallic clusters will be presented, highlighting how by carefully fine tuning their molecular structures, it is possible to suppress quantum tunnelling mechanisms (QTM) and switch on their SMM properties.

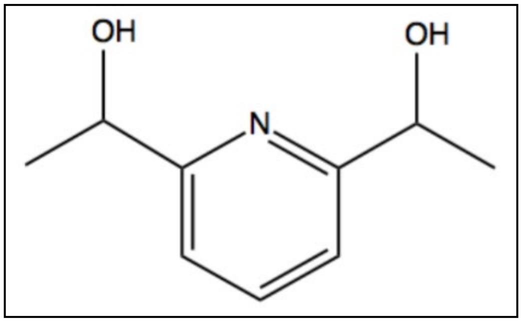

Figure 1: The molecular structure of $bhpH_2$ (**1**).

POSTER 27

From two-dimensional crystals to nanocrystallinity in $MSnF_4$ (M= Pb and Ba)

Georges Dénès[1,*], Abdualhafed Muntasar[1], M. Cecilia Madamba[1] , Juanita M. Parris[1], and Hocine Merazig[2], [1] Concordia University, [2] Université des Frères Mentouri de Constantine.

The structure of $MSnF_4$ (M= Pb and Ba) is derived from the MF_2 fluorite-type by a (√2, √2, 2) lattice transformation leading to a cubic → tetragonal relationship between the two structures, with doubling of the *c* axis resulting in a superstructure. The presentation will show how lattice strength consideration, combined with the presence of a stereoactive lone pair on tin(II) results in a two-dimensional structure due to the clustering of the lone pairs in parallel planes. This creates an unmanageable amount of preferred orientation that prohibits handling of crystals and their use for crystal structure determination. It is well known that milling breaks down crystals to smaller crystallites and therefore it reduces preferred orientation in polycrystalline samples. In this case, it was found that milling first enhances preferred orientation in $BaSnF_4$ (figure) instead of reducing it. So does hand grinding of α−$PbSnF_4$ in a mortar with a pestle. Further milling results in a tetragonal → cubic phase transition with formation of a nanophase. The presentation will emphasize how the combined use of X-ray and neutron powder diffraction with ^{119}Sn Mössbauer spectroscopy made it possible to understand the crystal structure of tetragonal $MSnF_4$ and to build a model of the nanophasic cubic structure as well as to establish that the latter contains two kinds of disorders, a positional disorder and an orientational disorder.

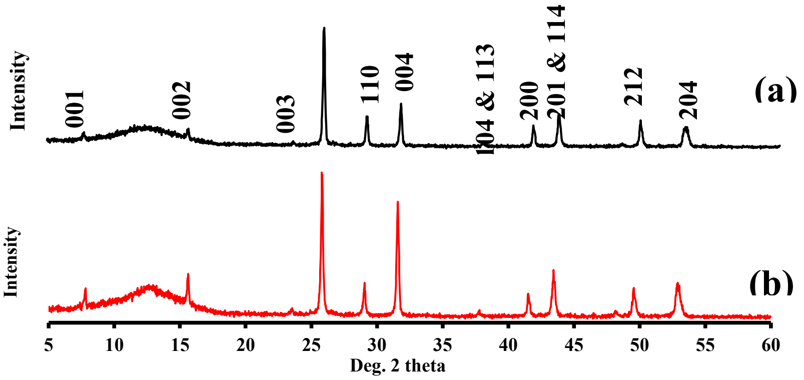

Figure: Effect of mild ball-milling on layered $BaSnF_4$: (a) before milling, (b) after milling for 2 minutes. The strong enhancement of the (00l) peaks after 2 minutes of milling shows a strong enhancement of the preferred orientation.

POSTER 28

New designs for solid hypergols

Hatem M. Titi,[1] Joe M. Marrett,[1] Mihails Arhangelskis,[1,2] Tomislav Friščić,[1] and Robin D. Rogers[3,] [1]McGill University,[2] University of Warsaw, [3] 525 Solutions, Inc.,

Hypergolic fuels, which spontaneously and rapidly ignite upon contact with an oxidizer, are a critical component of modern aerospace technologies. In that context, our team has been developing cleaner, safer and more environmentally-friendly hypergolic materials as potential replacement for currently used toxic and carcinogenic hydrazine. This presentation will provide an overview of our advances in development of hypergolic materials with ultrashort ignition delays (IDs) and tunable energy content based on concepts of crystal engineering, including new molecular solids, microporous metal-organic frameworks (MOFs) and cocrystals.[1,2]

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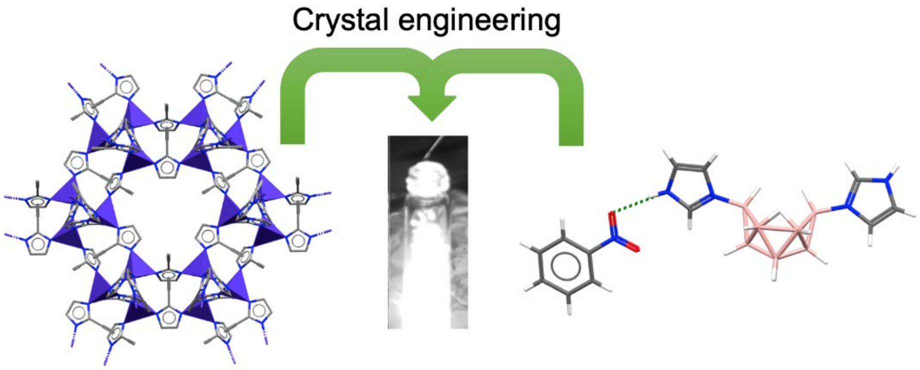
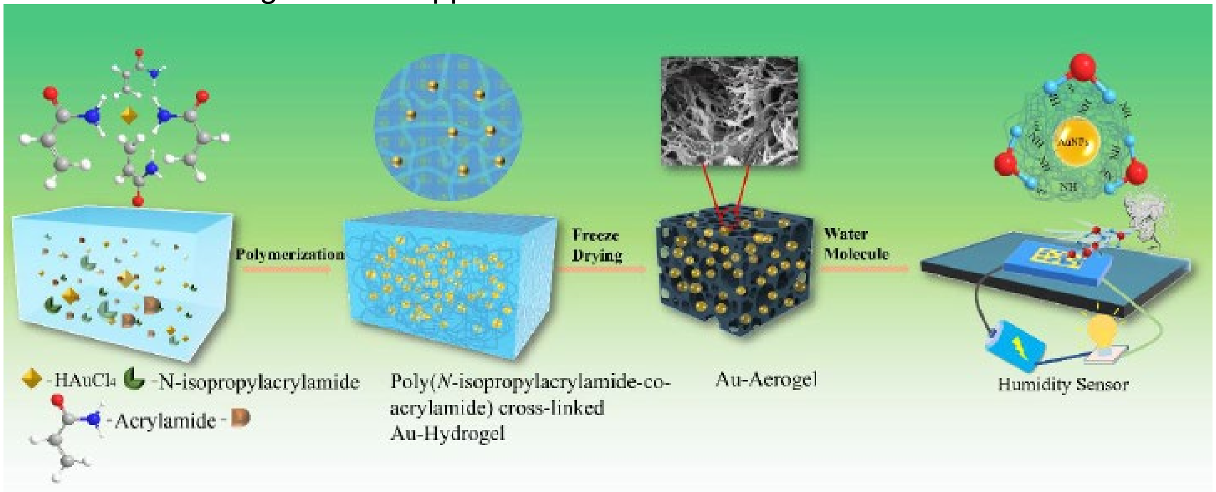


POSTER 29

Humidity responsive Polymer/Gold nanoparticles based hybrid Aerogel for real time Monitoring of Human breath

Israt Ali,[1,2] **Youju Huang,**[1,2] **Tao Chen,**[1,2] [1]University of Chinese Academy of Sciences, [2]Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences

Humidity sensor has received considerable attention in recent years because of its significance for air monitoring in agriculture, industries, goods stores and medical detections. Herein, we developed a simple, low cost and scalable fabrication strategy to construct a highly sensitive humidity sensor based on gold nanoparticles (AuNPs) and polymer system, by taking the advantage of conductivity and high surface area of gold aerogel. Such aerogel was fabricated by simple freeze drying method and showed conductivity, highly porous and low density structure. The combined gold nanoparticles (AuNPs) and Poly-N-isopropylacrylamide aerogel shown high sensitivity to water molecules due to the presence of amide group in PNIPAm. Interestingly, this report presents that the facile design of gold aerogel humidity sensor can be used to detect human breath under different health states such as sickness, high breath diseases, lungs problem and respiratory system problems, which is promising in practical flexible wearable devices for human health monitoring. In addition, the promising advantage of gold aerogel allow us in whistle tune recognition application. Schematic illustration of fabrication of aerogel and its application.



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POSTER 30

Hydrogen- and Halogen-Bonding in the Crystal Engineering of Photoreactive Solids

Jay Quentin, Dale C. Swenson, and Leonard R. MacGillivray, University of Iowa

Noncovalent forces such as hydrogen- and halogen-bonding (H- and X-bonding, respectively) are well established supramolecular synthons, capable of directing the self-assembly of multicomponent systems into supramolecular architectures. H-bonding, and - to a far lesser extent - X-bonding synthons have been successfully invoked in the crystal engineering of photoreactive solids. Specifically, ditopic H- or X-bond donor molecules can serve as Lewis-acidic templates capable of recognizing complementary Lewis-basic functionalities (e.g., N-atoms) on substrate molecules to form H- or X-bonding interactions with the substrate(s). As such, these relatively weak, reversible, and often directional interactions can often serve to preorganize two olefinic substrates into geometries amenable to topochemical solid-state [2+2] photodimerization to furnish 1,2,3,4-tetrasubstituted cyclobutanes. As a consequence of the highly ordered environment of the solid state as the reaction medium, these transformations are often quantitative and stereospecific, making such solid-state transformations powerful synthetic tools for accessing cyclobutanes.

We demonstrate here select examples of O-H···N and N···I interactions in directing the self-assembly of multicomponent systems into photoreactive cocrystals. Each cocrystal involves *trans*-1,2-bis(*n*-pyridyl)ethylene (*n* = 2 or 3) as the olefinic substrate, and either catechol or 1,*n*-diiodotetrafluorobenzene (*n* = 3 or 4) as the H- or X-bond donor coformer, respectively. In each case, UV irradiation of microcrystalline samples of the cocrystals furnishes the corresponding cyclobutane photoproduct quantitatively and stereospecifically.

POSTER 31

Exploring the Solution and Solid-state Self-assembly of Anionic Salicylic Acid-Based M_nL_{2n} and M_nL_n Metallohelicates

Jean-Louis Do,[1,2] Tomislav Friščić,[2] and Louis A. Cuccia[1], [1]McGill University, [2] Concordia University

Helicates are molecular materials consisting of metal- and/or organic-based components bridged through non-covalent interactions to form helical complexes. The versatility and relevance of these materials in the field of supramolecular chemistry have resulted in significant contributions towards our understanding of self-assembly, molecular recognition, interactions with biologically relevant molecules, and catalysis.[1-3] Studies on such compounds, however, have largely focused on their ability to encapsulate other molecules within their helical cavity and their templated self-assembly, typically in solution. Supramolecular helicates have been relatively underinvestigated as templates, components, and structure directing agents in the assembly of new, functional, and crystalline solid materials for pharmaceutical, materials, and catalytic applications.

Herein, we propose the design, study, and solid-state synthesis of helicates based on ligands derived from salicylic acid (Figure 1), directed towards new functional solids. The goal is to exploit the ease of synthesis and flexibility of salicylic acid and its derivatives as building blocks to prepare new supramolecular helicates whose structural designs may readily be adapted to the assembly of materials with potential applications in catalysis, drug delivery, light harvesting, and porosity. We also demonstrate the preliminary investigations using small, chiral organic additives in influencing the chirality of our metallostructures.

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POSTER 32

Co-crystals and salts of the anti-cholesterol drug bezafibrate

Jesus Daniel Loya, Selena J. Li, Daniel K. Unruh & Kristin M. Hutchins, Texas Tech University

Bezafibrate, an anti-cholesterol drug, is one of the many contaminants found in wastewater that is not readily removed. Water contaminants could potentially have adverse effects on humans and animals. Typically, co-crystallization is a common laboratory technique used to increase solubility or bioavailability of drugs. In our research, we use co-crystallization as a tool to better understand the intermolecular bonding and supramolecular behavior of bezafibrate with various acceptor molecules. By understanding these interactions, a material (e.g. polymer, membrane) can be properly designed to efficiently remove bezafibrate from wastewater. Attempts to co-crystallize bezafibrate had previously failed, we altered the approach by using acceptor molecules containing only hydrogen-bond acceptor sites. We were able to successfully synthesize the first co-crystals of bezafibrate. The intermolecular bonding behavior, and solution-state binding studies of the co-crystals were investigated. In an effort to design an efficient contaminant-removal material, we sought to make the interaction stronger between the drug molecule and the acceptor molecule. We modified the pK_a values of the acceptors so that we could synthesize the first salts of bezafibrate. Here, we will describe the synthesis of the first co-crystals and salts of bezafibrate, as well as the various supramolecular architectures we obtained.

POSTER 33

Metal-Organic Frameworks as Highly Tuneable Fuels

Joseph M. Marrett[1], Hatem M. Titi[1], Mihails Arhangelskis[12], Cristina Mottillo[1], Gandrath Dayaker[1], Robin D. Rogers[3], and Tomislav Friščić[1]*, [1]McGill University,[2] University of Warsaw, [3] 525 Solutions, Inc.,

Recent work in our group has demonstrated the possibility of installing specific chemical moieties on metal-organic frameworks (MOFs) to induce hypergolicity, the property of ignition upon contact with an oxidizer, in otherwise non-hypergolic materials.[1] More specifically, we found that the introduction of vinyl and ethynyl groups to the imidazolate linkers of zeolitic imidazolate frameworks (ZIFs) yields tuneable, high performance hypergolic materials with promising potential for application in the field of aerospace propulsion.[1,2] We have also evaluated the combustion enthalpies of 13 popular MOFs and ZIFs, discovering that their energetic content is generally similar to those of existing energetic materials and fuels on both a volumetric and gravimetric basis.[3] These two conclusions reveal a powerful and versatile platform for the development of energetic MOF materials with tuneable hypergolicity and high, tuneable energetic content for applications in aerospace propulsion. This presentation will detail our efforts in discovering and developing this platform and will demonstrate the large effect on energetic properties that subtle changes in the structure of a MOF can have.

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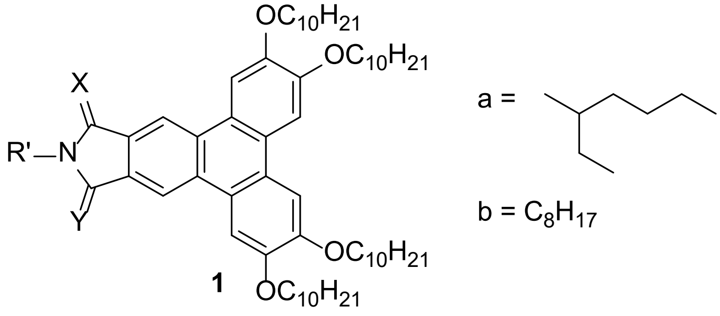
POSTER 34

Synthesis and Self-Assembly of Liquid Crystalline Triphenylenedicarboxythioimides

<u>J. LeDrew</u>[1], K. Psutka[1], H. Taing[2], S. H. Eichchorn[2], K. E. Maly[1], [1] Wilfrid Laurier University, [2] University of Windsor, Windsor, Ontario

With an increased interest in organic electronics, electron deficient discotic liquid crystals have garnered significant attention in recent years due to their potential applications in organic semiconductors, organic light-emitting diodes, and photovoltaics [1]. Imide-bearing materials (eg. perylene bisimides), have been used as electron accepting materials due to their high photochemical stability and charge transport properties [2]. Moreover, our lab has demonstrated that the thionation of imide-containing dibenzanthracenedicarboxyimides, lowered their lowest unoccupied molecular orbital (LUMO) energies and narrowed the highest occupied molecular orbital (HOMO)-LUMO band gaps, all while maintaining broad columnar phases and increased self-assembly [3]. Here, we will report the synthesis and properties of a series of novel triphenylenedicarboxyimides and thioimides (**1**). These materials displayed broad columnar phases in which the clearing point was affected by the degree of thionation [4]. In addition, thionation lead to a lowering of the LUMO energies and a narrowing of the HOMO-LUMO band gaps as well as an improvement in self-assembly in solution when compared to the parent imide derivatives [4]. Furthermore, the results obtained are consistent with those seen with the thionation of the dibenzanthracenedicarboxyimides and demonstrates that thionation can be used to tune the electronic properties of imide-containing discotic liquid crystals without any major consequential effects on their mesogenic properties. These results, combined with our novel approach, suggest that thionation may be a promising method for the future design of electron-deficient liquid crystalline materials.



1

X = Y = O
X = S, Y = O
X = Y = S

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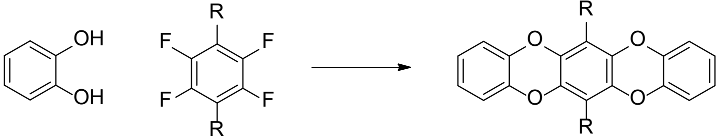
POSTER 35

Controlling π-Stacking Interactions in a Series of Novel Heteroacene Derivatives

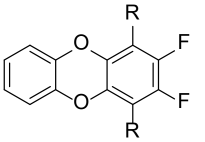
L. Hiscock, L. Dawe, K. Maly, Wilfrid Laurier University

The understanding and control of intermolecular forces allows for the creation of supramolecular architectures held together by relatively weak, flexible interactions. The exploitation of π-π stacking interactions can produce materials with dynamic properties such as crystal to crystal transitions.[1] Co-facial π-interactions are also important in the preparation of semiconducting organic materials,[2] however, face-to-face π-stacking is generally repulsive and often disfavoured.[3]

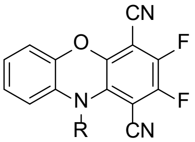
In our development of an S_NAr-based methodology for the synthesis of heteropentacene analogues **1a-c** we synthesised a series of electronically biased 1,2,3,4-tetrasubstituted dibenzodioxin (**2a-c**) and phenoxazine (**3a-c**) derivatives.[4] An examination of the crystal structures of **2a-c** and **3a-c** indicates that a combination of electronic bias and C−H substitution affords compounds which tend to π-stack in a co-facial, antiparallel manner. A search of the Cambridge Structural database for representative structures was also conducted. The results indicate such motifs could be valuable building blocks for supramolecular design of materials held together by co-facial π-π stacking interactions.



1a, R = CN
1b, R = F
1c, R = Br



2a, R = CN
2b, R = F
2c, R = Br



3a, R = H
3b, R = Et
3c, R = Bn

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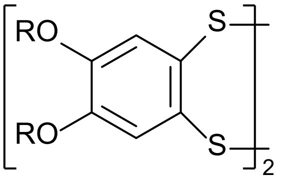
POSTER 36

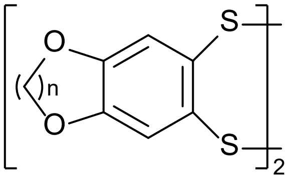
A Two-Step Synthesis of Group 10 Dithiolate Coordination Complexes Bearing A Crown-Ether Functionality And Na$^+$ Binding Studies

L. K. Watanabe,[a] Justin D. Wrixon,[a] Zeinab S. Ahmed,[a] John J Hayward,[a] Parisa Abbasi,[b] Melanie Pilkington,[b] Charles L. B. Macdonald[a,c] and Jeremy M. Rawson*[a,]
[a] University of Windsor, [b] Brock University, [c] Carleton University

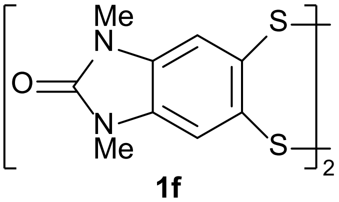
Metal dithiolene complexes exhibit intense colors, multiple oxidation states, reversible redox reactions and the ability to take on different geometric conformations, making them ideal in a variety of materials applications.[1] To date, many dithiolate complexes contain strongly electron-withdrawing groups, such as $(NC)_2C_2S_2^{2-}$ and $(F_3C)_2C_2S_2^{2-}$, while the π-conjugated benzo-dithiolates predominantly derive from commercial benzenedithiol or toluene dithiol ligands.[2] Recently we have explored the oxidative addition reactions of alkoxy-functionalized bis(benzo)-1,2,5,6-tetrathiocins to low valent group 10 metal complexes (Ni, Pd, Pt) as an alternative strategy to develop functionalized benzene dithiolate complexes.[3] In this presentation a library of tetrathiocins (**1a** – **1g**) are described with a particular focus on benzo-15-crown-5 complexes in which the benzo-15-crown-5 functionality is explored as a sensor for Na$^+$ cations. Structural studies reveal the coordination geometry of the Na$^+$ cation comprises the expected benzo-crown-5 O_5 donor set along with a variety of covalent and non-covalent interactions including coordinated solvent, bridging dithiolate S atoms and a Na…p interaction to the BPh_4 anion.

1a R = Me
1b R = Et

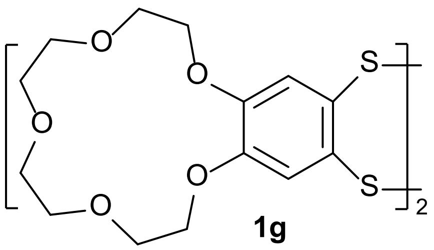




1c n = 1
1d n = 2
1e n = 3



1f



1g

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POSTER 37

Supramolecular modification of a novel imidazopyridazine antimalarial drug lead via co-crystal formation

Laurelle Joseph, Mino R. Caira and Kelly Chibale, University of Cape Town

The compound 6-(3-(cyclopropylsulfonyl)phenyl)-3-(4-(methylsufinyl)-phenyl)imidazo[1,2-*b*]pyridazine (henceforth IMP) was identified as one of the frontrunner lead compounds from a series of imidazopyridazine antimalarials synthesized by the H3D Drug Discovery and Development Centre. IMP was able to completely cure mice infected with the *Plasmodium berghei* strain of the malaria parasite following the oral administration of 4×50 mg/kg doses [1-2]. Although IMP displayed potent antimalarial activity, its poor aqueous solubility ($< 5\ \mu M$ at pH 6.5) is one of the liabilities towards its further development. One way in which the solubility of IMP could be enhanced is through supramolecular modification. This approach has been proven to produce alternative solid-state forms of APIs with improved physicochemical properties such as aqueous solubility [3-8].

The study to be presented describes the use of supramolecular methodology to prepare new solid-state forms of IMP, specifically co-crystals, salts, solvates and cyclodextrin inclusion complexes. Objectives include the full characterization of such new solid forms using X-ray, thermal and spectroscopic techniques and ultimately assessment of their utility in drug delivery.

Co-crystal screening techniques including virtual and experimental (neat/liquid-assisted grinding) approaches were used to identify possible hits. New co-crystals between IMP and the coformers succinic acid, adipic acid (Figure 1) and fumaric acid, as well as a salt with oxalic acid were prepared by co-precipitation and their crystal structures were solved using single crystal X-ray diffraction. The co-crystals were further characterized using HSM, TGA, DSC, ^{1}H NMR and FT-IR spectroscopy. TGA and ^{1}H NMR spectroscopy indicated 2:1 (IMP:coformer) stoichiometry for each co-crystal. The primary non-covalent interactions between IMP and the coformers are -COOH···O=S and -COOH···N(imidazole). Co-crystal formation was confirmed by examining the diagnostic bands in the FT-IR spectra. *In vitro* solubility studies indicate that the maximum solubility of IMP in simulated intestinal fluid obtained from the IMP·adipic acid co-crystal is significantly higher than that of the untreated IMP.

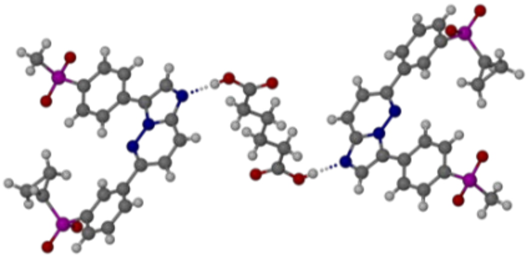

Figure 1: Hydrogen bonding interaction between IMP and adipic acid.

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POSTER 38

A solid solution of Cortisone and Hydrocortisone afford a tuneable Drug-Prodrug crystal form.

Matteo Lusi, University of Limerick

Recent medical progresses have enabled the treatment of many diseases, which may continue for extensive period of time in chronic cases. In this view, the realization of multi-drug formulations may simplify complex pharmaceutical regimens whilst reducing overall doses and potential side effects. For example the combination of a drug with its prodrug might help prolonging the optimal plasma concentration, hence reducing the daily drug administration.

In particular, solid homogeneous phases such as cocrystals are often more stable than mixtures and guarantee easier processing. Unfortunately the fixed stoichiometric of cocrystals prevents the fine tuning of the dose for each component.
Here we present a stable solid solution that combines an archetypal anti-inflammatory molecule such and hydrocortisone with its biological precursor cortisone (figure 1). Despite the lack of isostructurality, and the difference H-Bond capability, the solubility of the parent components is virtually complete enabling fine-tuning of the multidrug stoichiometry. Interestingly, the homogeneous product could not be obtained by standard crystallization techniques but only through Supercritical fluid (SCF) technologies using CO_2 as an antisolvent.

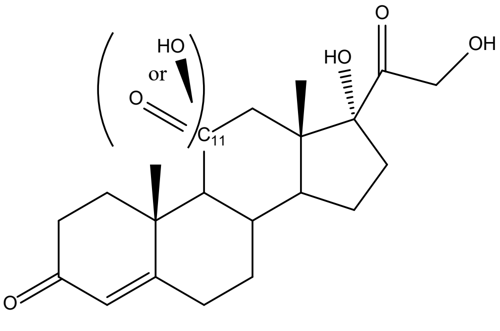

Figure 1: Structure of Cortisone and Hydrocortisone

POSTER 39

Theoretical studies of halogen-bonded cocrystallization using periodic DFT calculations

Mihails Arhangelskis,[1,2] Ricky Tran,[2] Katarina Lisac,[3] Filip Topić,[2] Sara Cepić,[3] Patrick A. Julien,[2] Christopher W. Nickels,[2] Andrew J. Morris,[4] Tomislav Friščić[2] and Dominik Cinčić[3], [1]University of Warsaw, [2]McGill University, [3]University of Zagreb, [4] University of Birmingham

Halogen bonding is a supramolecular interaction based on an attraction between electrophilic region (σ-hole) of a halogen atom and a nucleophilic donor atom.[1] The emergence of XB as an alternative to more commonly used hydrogen bonding opens a new path to the design of wide range of supramolecular architectures and multicomponent molecular crystals.[2]

In order to design new halogen-bonded materials more efficiently, it is crucial to understand the energy and directionality of the halogen bonds as a function of donor and acceptor atom types, while also considering the effects of supramolecular interactions besides XB (hydrogen bonding, π-π stacking etc.) This can be achieved by utilizing periodic density functional theory (DFT) calculations, which bring the accuracy of quantum chemical calculations to the realm of crystal structures.

This presentation will focus on the use of periodic density functional theory (DFT) calculations to understand the thermodynamic stability of halogen-bonded cocrystals. We have used periodic DFT to explain the formation of cocrystals with unprecedented halogen bonding interactions with the heavy, increasingly metallic elements of the pnictogen group (I···P, I···As, I···Sb).[3] In addition, our inability to synthesize the analogous cocrystal with I···Bi interaction was rationalized that way.

The presentation will continue with the application of periodic DFT calculations to study stoichiometric diversity of halogen-bonded cocrystals. The ability of periodic DFT calculations to predict stoichiometric interconversions will be demonstrated.[4]

Throughout the presentation the challenges in modelling crystal structures containing halogen bonds will be addressed.[5] Performance of various DFT methods (functionals and dispersion corrections) will be discussed.

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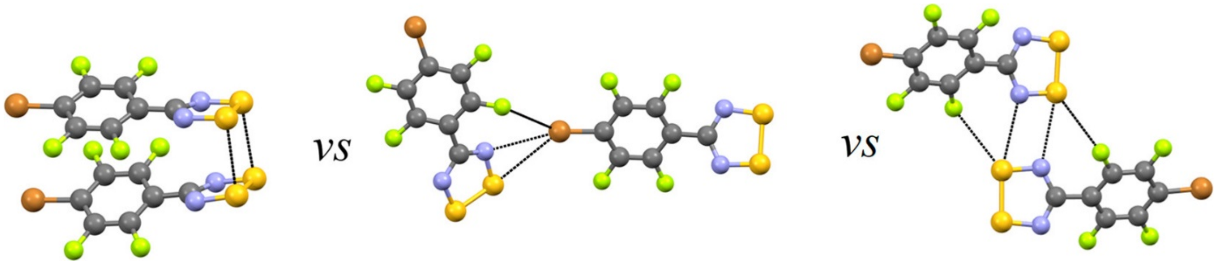
POSTER 40

An Investigation of Halogen Bonding as a Structure-Directing Interaction in Dithiadiazolyl Radicals

Mitchell A. Nascimento[a], Elodie Heyer[a], Robert J. Less[ab], Christopher M. Pask[ab], Ana Arauzo[c], Javier Campo[c], and Jeremy M. Rawson[ab], [a]University of Windsor, b) Cambridge University, c) University of Zaragoza

The preparation and characterization of halo-functionalized dithiadiazolyl radicals p-XC6F4CNSSN (X = Br (**1**) or I (**2**) is described. Compound **1** is trimorphic. The previously reported **1α** (Z′ = 1) comprises monomeric radicals, whereas **1β** comprises a mixture of one cis-oid π*−π* dimer and one monomer (Z′ = 3). **1γ** exhibits a single cis-oid dimer (Z′ = 2) in the asymmetric unit. We have only been able to isolate a single polymorph of **2**, isomorphous with **1α**. Both the bromo and iodo groups in **1** and **2** promote sigma-hole type interactions of the type C−X⋯N (X = Br, I), reflecting the strength of this interaction in heavier halo-derivatives. An analysis of intermolecular forces is made using dispersion corrected density functional theory (DFT) (UM06-2X-D3/LACV3P*) and compared to a unified pair potential model (UNI) embodied in the crystallographic software Mercury. While there is a correlation between DFT and UNI models, there are some discrepancies, although both reveal that a number of intermolecular contacts beyond the sum of the van der Waals radii are significant (>5 kJ mol−1). A natural bond order analysis of the intermolecular interactions reveals lone pair donation from the heterocyclic N atom to C−X or S−S σ* orbitals contributes to these intermolecular interactions with relative energies in the order C−I > SN-II > C−Br > SN-III. The magnetism of 2 reveals a broad maximum in χ around 20 K indicative of short-range antiferromagnetic interactions. DFT calculations reveal a set of three significant exchange interactions which propagate in two dimensions.

Reference: Nascimento, M. A.; Heyer, E.; Less, R. J.; Pask, C. M.; Arauzo, A.; Campo, J.; Rawson, J. M. An Investigation of Halogen Bonding as a Structure-Directing Interaction in Dithiadiazolyl Radicals. *Cryst. Growth Des.* **Article ASAP** DOI: 10.1021/acs.cgd.9b01698



POSTER 41

Effect of pedal motion or motion inability on thermal expansion of organic crystals

Navkiran Juneja, Daniel K. Unruh, and Kristin M. Hutchins, Texas Tech University,

Thermal expansion of materials is mostly dependent on chemical composition and usually correlates with the crystal structure, electronic structure, and defects of the materials. Materials with desirable physical properties and controllable thermal expansion properties are useful in designing devices such as thermomechanical actuators, sensors, and composites. Atoms in molecules are not stationary and hence they undergo certain molecular motions depending upon the type of symmetry of the molecules. Here, we focus on molecules with a skeleton similar to that of azobenzenes and stilbenes, which are capable of undergoing pedal motion. Incorporating such molecules into a multi-component solid via co-crystallization can be a captivating way to design materials with movements or unique thermal expansion properties. The dynamic processes or motions in crystals can be investigated using variable temperature X-ray diffraction analysis of the crystal. In this presentation, we describe co-crystals sustained by halogen and hydrogen bonds and the role that molecular motion and bond type play on thermal expansion properties.

POSTER 42

Study of Photodynamic Responsive Crystals of Organic Azides In Correlation to X-Ray Crystal Structure

Nayera Abdelaziz, Jeanette A. Krause and Anna D. Gudmundsdottir, University of Cincinnati

Our group previously reported the first detection of triplet vinylnitrenes in solution by preforming transient spectroscopy of azirine and isoxazole derivatives. We also studied solution photochemistry of 3-azido-1-indenone, which resulted in dimerization of vinylnitrene. Here, we are studying the solid-state photochemistry of 3-azido-1-indenones, which undergoes different photoreacivity from solution due to the rigid structure of the compound in solid state. We are correlating the photoreactivity of both unsubstituted, and substituted 3-azido-1-indenones, to their X-ray crystal structures. Also, we are studying mechanical response of the crystals to light.

POSTER 43

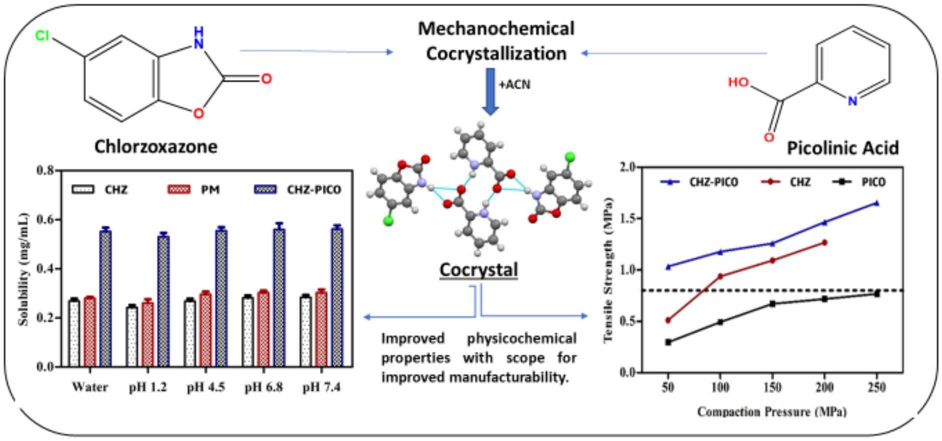
Application of mechanochemical cocrystallization to alter the physicochemical properties and to improve the manufacturability of chlorzoxazone.

Parag Roy and Animesh Ghosh, Birla Institute of Technology, Mesra,

Chlorzoxazone (CHZ) is a centrally acting muscle relaxant used for the treatment of muscle spasm. It is a BCS class II drug having poor solubility and high permeability and also have high cohesiveness, inferior flow property and compressibility, hence wet granulation is the only option for the manufacturing of conventional tablets. In this study, mechanochemical cocrystallization has been explored to prepare chlorzoxazone-picolinic acid (CHZ-PA) cocrystals to improve its poor physicochemical properties. The prepared cocrystal was characterized by different characterization techniques such as SCXRD, PXRD, DSC, TGA, FTIR. CHZ-PA cocrystals showed improved solubility in different pH media along with an enhanced dissolution rate. Tabletability studies were performed for the prepared cocrystal to investigate the powder compaction behavior. The manufactured CHZ-PA cocrystals showed better flowability and tabletability properties compared to the CHZ. Thus, it provides an opportunity to explore the direct compression technique for manufacturing an oral solid dosage form, which is much economically viable. Further, accelerated stability studies performed to demonstrate that the prepared cocrystals were stable under accelerated storage conditions for up to thirteen weeks.

The study demonstrates the significance of mechanochemical cocrystallization as a green synthesis approach to improve the physicochemical properties of an active pharmaceutical ingredient and also to improve the manufacturability of the drug to form a suitable dosage form.

Figure:



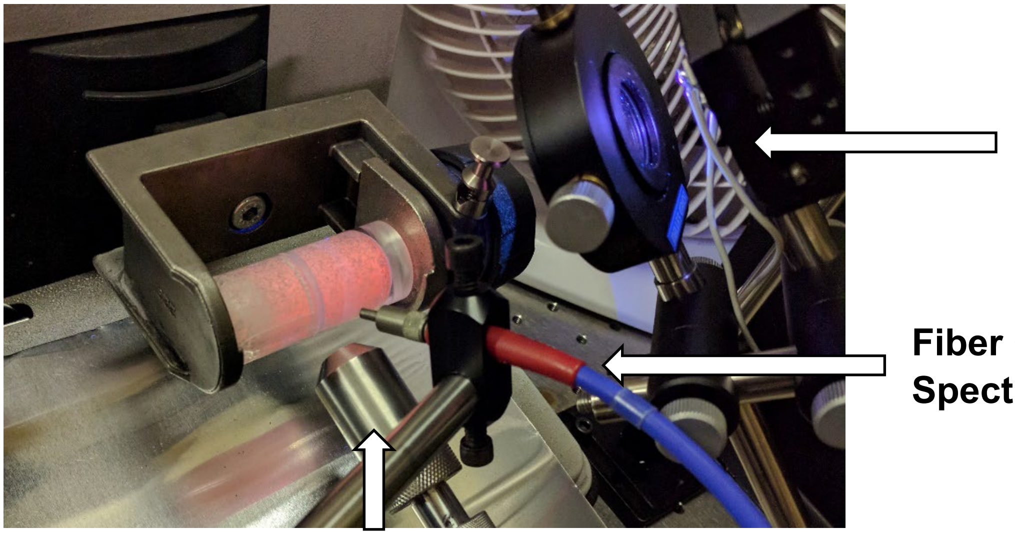
Improved physicochemical properties with scope for improved manufacturability.

POSTER 44

Tandem fluorescence and Raman spectroscopies for real-time monitoring of supramolecular structure by milling

Patrick A. Julien[1]*, Mihails Arhangelskis[1], Luzia S. Germann[3], Robin S. Stein[1], Martin Etter[2], Robert Dinnebier[3], and Tomislav Friščić,[1]* [1]McGill University,
[2]Deutsches Elektronen-Synchrotron, [3]Max Planck Institute for Solid-State Research

Mechanochemical methods are increasingly popular methods for conducting a wide variety of reactions including the screening and synthesis of cocrystals of active pharmaceutical ingredients (APIs). As tools to monitor milling reactions remain limited, the first use of real-time fluorescence spectroscopy to monitor a milling reaction is herein described. Combining simultaneous fluorescence and Raman spectroscopies reveals the amorphization and phase transition behavior of indometacin under continuous milling and reveals the kinetic profile of the formation of the indometacin-saccharin cocrystal via liquid assisted grinding. This easily accessible dual spectroscopic approach coupled with is a fundamental advance in studying the kinetics and mechanisms of milling reactions involving fluorescent materials.

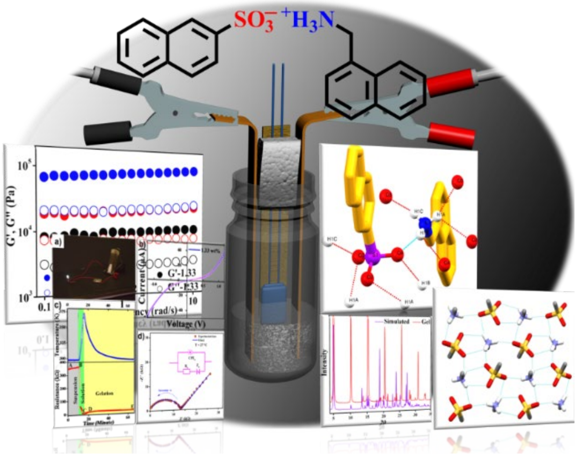


POSTER 45

A supramolecular hydrogel derived from a simple organic salt capable of proton conduction

Poulami Chakraborty, IACS, Kolkata

Developing proton conducting materials has become an attractive research goal because of their application in electrochemical power plants like fuel cells. Since liquid conducting materials e.g. liquid electrolytes have operational limitations like leakage problems, despite their high ionic conductivities and good contacts with electrodes, the need for developing mechanically rigid or quasi-solid alternatives has become obvious. Among the various alternatives, including organic conducting polymers, crystalline porous materials (metal- and covalent-organic frameworks (MOFs and COFs)) and polymer gel electrolytes (PGEs), supramolecular gel can be better offering the advantages of solid electrolyte devoid of various drawbacks faced by the above mentioned materials. In the present work,[1] the primary ammonium sulfonates (PAS) were targeted as potential supramolecular gelators expecting the resulting hydrogel to display proton conduction due to the possibility of generating activated water molecules mediated by hydrogen bonding involving the PAS moiety. With this background, we set out our quest for synthesizing new supramolecular gelators from organic sulfonates based on a detailed supramolecular synthon analysis through Cambridge Structural Database[2] search in sulfonate salts. We prepared a combinatorial library of PAS salts. Interestingly, one such salt namely N2SNm produced hydrogel displaying proton conductivity (1.2×10^{-4} S cm^{-1}) whereas both the xerogel and the as-synthesized bulk solid failed to show any measurable conductivity. Based on the single crystal structure of the gelator and powder X-ray diffraction of the hydrogel, we hypothesized the reason for the proton conductivity by hydrogel to be the participation of water molecules in the crystal lattice of the hydrogel network.



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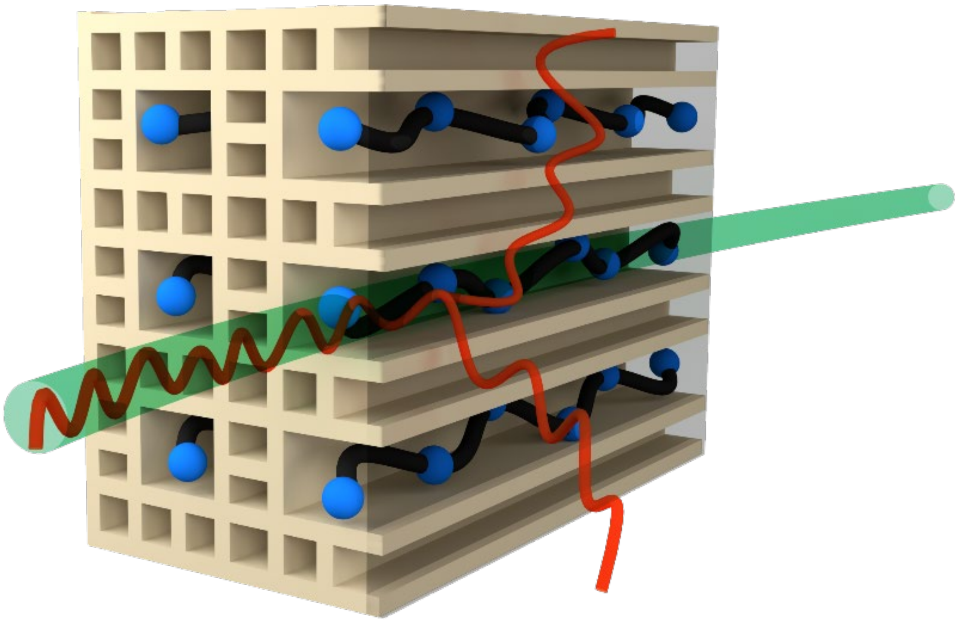
POSTER 46

Imparting Multifunctionality by Utilizing Biporosity in a Zr-Based MOF

Pranay Ninawe, **Nirmalya Ballav,** Indian Institute of Science Education and Research, Pune

An exquisite design strategy of selectively incorporating conducting polymers in a Metal-Organic Framework (MOF) was introduced, which resulted in decoupling of electrical and thermal conductivity along with significant retention in porosity. Owing to intrinsic bi-porous nature of UiO-66 framework, herein, we have introduced specialty monomers pyrrole (Py) and 3,4-ethylenedioxythiophene (EDOT) selectively inside one of the two distinct voids, which were then polymerized my extraneous oxidizing agents. An electrical conductivity enhancement of ~10^6 times was observed in both the nanocomposites compared to pristine MOF bringing them into semiconducting regime, along with significant decreased thermal conductivity. The process resulted in loading of ~12 wt% of polymers inside the voids, creating a balance between the electrical and thermal conductivities along with simultaneous porosity retention up to ~70%.



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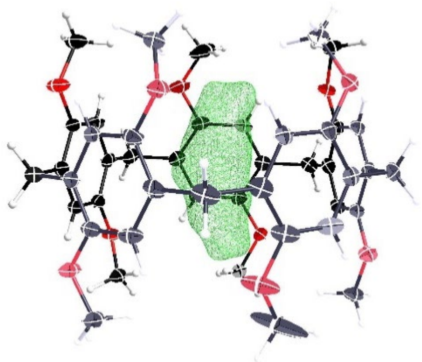
POSTER 47

DIMETHOXYPILLAR[5]ARENE AS A 0D POROUS MOLECULAR SOLID: SOLID FORMS IN THE CONTETX OF ROOM TEMPERATURE CO_2 SORPTION

Prashant Kumar Pandey, Georgetown University



CO_2 electron density map (green) inside a DMP5 cavity

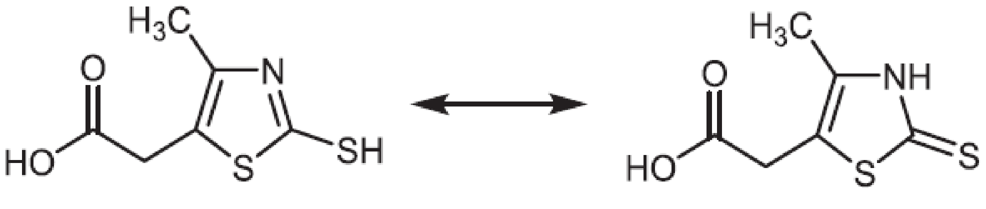
The term “porosity without pores” defines a curious case where the pores of a particular material are not accessible by channels leading up to it, such closed pores are referred to as 0D pores. Since the cavities in a 0D porous material are three dimensionally enclosed, they offer great selectivity and size sensitivity for guest molecules which differentiates 0D porous materials from other porous materials and network solids. Dimethoxypillar[5]arene (DMP5), first invented by Ogoshi and co-workers in 2008 are potential 0D porous materials, but its porosity has never been formally discovered. The demonstration of 0D porosity in DMP5 has far reached implications in studying selectivity and gas storage properties as it can be prepared easily from commercially available and cheap starting materials along with an easy recrystallization procedure. In the current research, set in motion by the quest for a guest-free porous (*β*) phase, DMP5 was shown to exist in three new polymorphic forms including a non-characterized meta-stable, close packed phase (*γ*), an empty crystalline non-porous phase (*α*) and an amorphous phase (a-DMP5). Both a-DMP5 and α-DMP5 phases were shown to transform to the tetragonal *β*-CO_2-DMP5 phase when pressurized with CO_2 (30-35 bar) with a high kinetic barrier for CO_2 release, retaining the guest CO_2 for upto 90 days, characteristic of a 0D porous molecule. Single crystals of gas clatharate *β*-CO_2@DMP5 and *γ*-DMP5 were obatined.

POSTER 48

Conductivity studies in two dimensional coordination polymers built with a thiazole based ligand

Prashant Kumar, University of Liverpool

Organic ligands bearing several donor atoms (i.e. N, O or S) have been a subject of considerable interest in the field of Chemistry and Material Science during the last few decades. In coordination chemistry, multidentate ligands coordinate to various metals yielding compounds that possess intriguing structural motifs and remarkable properties. In the field of advanced materials, the synthetic community shows a preference in the use of five and six-membered heteroaromatic systems. Several compounds based on thiophene and the azole rings have been reported, however the presence of N- and S-atoms in the thiazole five-membered ring gives to the resulting compounds desirable properties. 2-Mercapto-4-methyl-5-thiazoleacetic acid (H_2L) is a hybrid ligand and has five donor atoms (2S, 2O and 1N) exhibiting high versatility and coordination flexibility with a variety of metal ions. The different donor sites of heterocyclic thiones can bind with two or more metal ions in order to form metal complexes. Also, the size of the metal anion plays a significant role in the way the metal coordinates to the ligand and as a result in the final polymer's dimensions. Bearing all these in mind, in this work we have chosen to incorporate the commercial available ligand H_2L along with Zn and Cd salts to form coordination polymers. To the best of our knowledge, this is the first attempt to synthesize CPs with the use of H_2L as the main ligand. We report herein the conductivity properties of two compounds formulated as [ZnII(HL)2] (1) and [CdII(HL)2] (2). The FP-TRMC profiles for as-synthesized CPs 1 and 2 and a similar film made from organic linker H_2L, show maximum values of fΣm of 3.9 x 10^{-5} cm^2/V.s **1**, and 2.6 x 10^{-5} cm2/V.s **2** respectively, and a long carrier life time where / represent the photocarrier generation yield and fΣm is the sum of the generated charge carrier mobilities for both electrons and holes. The photo-conductivity kinetic traces decayed principally triple exponential manner. All of the kinetic traces exhibit pseudo-first order ones with long enough lifetimes as represented by k_3 of 4.2–5.0 x 10^4 s^1, suggesting that the signals were observed as the transient conductivity of free charge carriers after geminate charge recombination processes.



Form A

Form B

POSTER 49

Design and construction of a Dual Role fragile ligand: Mechanically Elastic Crystal and selective mitochondria imaging in live cell

Kumari Pratibha,[†] Verma Sanjay K.,[‡] Natarajan Kaushik,[§] Ansari Shagufi Naz,[‡] and Mobin Shaikh M. [*,†,‡,§], [†]Discipline of Biosciences and Bio-Medical Engineering
[‡]Discipline of Chemistry,[§]Discipline of Metallurgical Engineering and Materials Science,
Indian Institute of Technology Indore

The use of multitalented materials has been of great interest to researchers considering the vast array of potential applications and good economic viability.[1,2] Herein, we report the unique properties of a new Schiff base ligand (H_2L), synthesized and characterized by ^1H and ^{13}C NMR, and LCMS. Further, it has been authenticated by a single-crystal X-ray diffraction (XRD) study. In a solid state, H_2L can bend upon an externally applied stress and rapidly reverts to its original shape upon relaxation, revealing highly flexible and elastic bending properties. Powder XRD and Raman studies indicate high retention of crystallinity and chemical bonds even under stress (bend) conditions, which implies that the bending in H_2L is due to the intermolecular hydrogen bonding and C-H⋯π interactions. Moreover, in the solution state, H_2L is fluorescent, non-cytotoxic, and selectively labels mitochondria of live cells and tumor spheroids

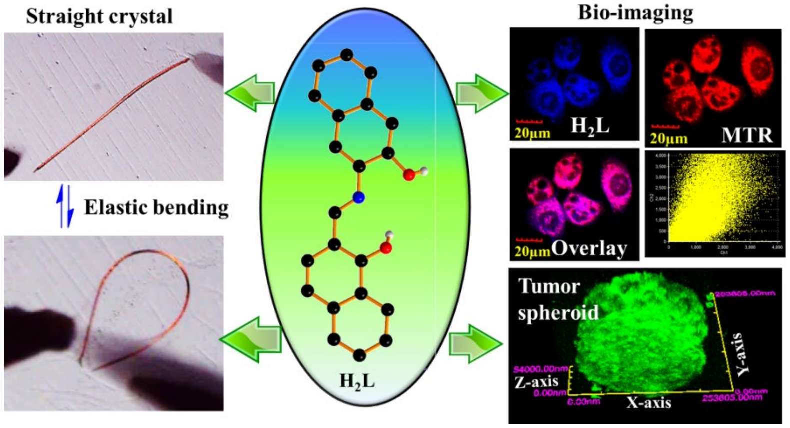


Fig. In solid state H_2L crystal is highly elastic (mechanical bending). In solution state label selectively label mitochondria of live cells and tumor spheroids.

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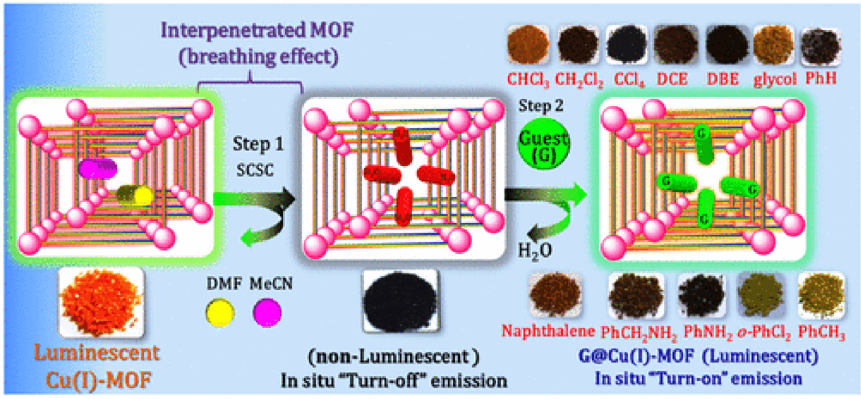
POSTER 50

Cu(I) Flexible Luminescent MOF, Trapping various guests with Guest-Responsive Turn-Off and Turn-On Luminescence and Mechanistic Study

Protap Biswas, Indian Association for the Cultivation of Science (IACS)

Flexible Cu(I) metal−organic framework [Cu(I)-MOF (1)] with well-defined nanoporous channel built with flexible terpyridine ligand offers a scaffold for the inclusion of different classes of guest molecules through a single-crystal-to single- crystal (SCSC) transformation in the vapour phase at ambient conditions with visual colour change. Thus, Cu(I)-MOF (1) offers potential platform for molecular recognition and undergoes guest responsive structural dynamism that can be triggered by interfacial interactions. Despite having the stable conformation of the rotational isomers liquid state, the less stable conformation of these molecules (eclipsed and gauche) is oriented into the MOF. The intermediate of all of the guest-exchanged processes appeared as a black material (H_2O@Cu(I)-MOF) prior to the encapsulation of each guest that happens through the SCSC manner followed by encapsulation of the guests in situ at ambient conditions through SCSC transformation. This confirms that the process is a two-step process leading through a common intermediate. The MOF loses its luminescence behaviour, removing lattice solvents in situ and appears as a black material, and it regains its luminescence property with the guests. Thus, the MOF displays both luminescence "turn-off" and "turn-on" before and after incorporation of the guests, respectively, leading to a common turn-off mechanism.



KEYWORDS: guest inclusion, SCSC transformation, breathing MOF, "turn-off" and "turn-on" luminescence, mechanistic study

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POSTER 51

Synthesis of Pharmaceutical Co-crystals and Pyridine-Functionalized Polymers

Qixuan Zheng, Samantha L. Rood, Daniel K. Unruh, and Kristin M. Hutchins,
Texas Tech University,

Increasing consumption of pharmaceuticals causes pollution of natural aquatic environments.[1] Traditional methods such as activated carbon absorption[2] and ozonation[3] can be less effective in removing pharmaceuticals. We investigated the chemical bonding behaviour of pharmaceuticals with potential receptors to design removal materials.

Here, we report co-crystallization of three pharmaceuticals (mefenamic acid (**MA**), naproxen, and diclofenac (**DFC**)) with five bipyridines (1,2-bis(4-pyridyl)ethylene, 4,4'-azopyridine (**AP**), 1,2-bis(4-pyridyl)ethane (**BPEth**), 1,3-bis(4-pyridyl)propane (**BPP**), and 4,4-dipyridyl). While all co-crystals exhibit at least one expected COOH···N hydrogen-bond synthon between the drug and bipyridine, we demonstrate three unique co-crystals **MA·BPP**, **DFC·BPEth**, and **DFC·AP** with unique supramolecular architectures (Figure 1). For example, the components of **DFC·AP** self-assemble into four-component rings that further assemble into columns. The included solvent can be removed by heating or exchanged with other solvents while maintaining crystallinity (Figure 1c).

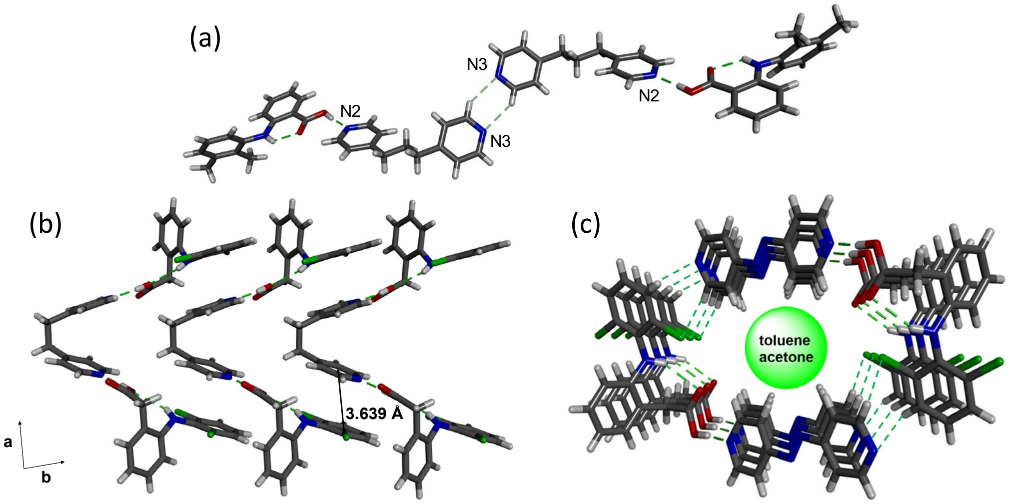

Figure 1. X-ray crystal structures of: (a) **MA·BPP**, (b) **DFC·BPEth**, and (c) **DFC·AP**.

Based on hydrogen bonds with contaminants, we synthesized both linear and crosslinked pyridine-functionalized polymers. Binding experiments confirmed the ability of the polymers to bind pharmaceutical molecules.

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POSTER 52

Computational Characterisation of Zr-oxide MOFs for Gas Adsorption and Separation Studies

Rama Oktavian[1], **Raymond Schireman**[2], **Guanming Huang**[1], **Michael T. Ruggiero**[2]*, **Peyman Z. Moghadam**[1]*, [1] University of Sheffield, [2] University of Vermont

Zirconium metal (Zr) has the ability to construct metal-organic framework (MOF) materials as metal nodes due to its superior hydrolytic, thermal, and chemical stability as well as forming strong interactions with oxygen atom. Because of this stability, Zr-oxide MOFs have been gaining much attention for gas adsorption and separation applications. Here, we report structure search methods within the Cambridge Structural Database (CSD)[1] through a number of "look-for-Zr-oxide-MOFs" criteria to identify and create a curated database of ca. 100 materials to date, bringing a unique record for all researchers working in this area. For all identified structures, we manually corrected the position of bridging hydroxyl groups and calculated the partial atomic charges for each MOF using systematic density functional theory (DFT) methods. We then identified top-performing MOFs for CO_2 adsorption via high-throughput grand Canonical Monte Carlo (GCMC) simulations. Through experimental verification of CO_2 adsorption in Zr-oxide MOFs[2,3], we reveal the importance of choosing the appropriate DFT functionals and basis sets to calculate Coulombic interactions at the Henry's regime for CO_2 adsorption (Figure 1).

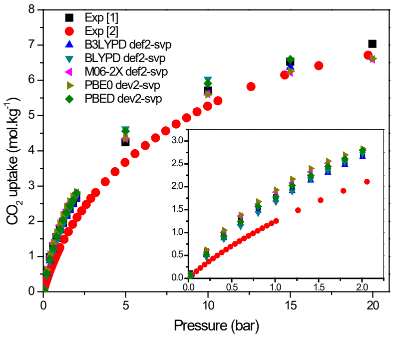

Figure 1. CO_2 adsorption isotherms in UiO-66 for different sets of partial charges obtained from DFT calculations.

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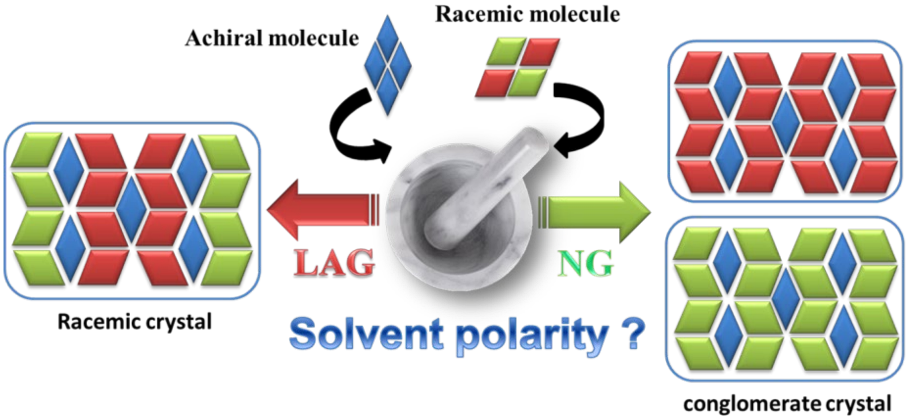
POSTER 53

Effect of Solvent Polarity in Mechanochemistry: Preparation of Conglomerate vs. Racemate

Ranjit Thakuria, Gauhati University, India

Chirality is always a fascinating topic to chemist due to its importance in the pharmaceutical industry. Majority of drug molecules available in the market are chiral and only one of the enantiomer provide the desired physiological activity; therefore, separation of enantiomer during synthesis is one of the essential steps in the drug development process. Compared to chiral chromatography crystallization is a cheaper alternative; however, this method is restricted to the possibility of crystallization as conglomerate from a racemic solution.[1] The racemization is a spontaneous process and 90–95% of chiral compounds undergo racemization; whereas formation of conglomerate is limited to 5–10%. On the other hand preparation of conglomerate during cocrystallization is even less probable. Moreover, it needs screening of suitable achiral coformer/ additive which is unpredictable and requires high through-put screening.

In this report, for the first time, synthesis of conglomerate as well as racemic salts of same system, achiral isoniazid (ISN) with racemic DL-tartaric acid (DL-ta) has been prepared using mechanochemistry (Scheme 1).[2] The plausible reason for obtaining conglomerate during NG as well as LAG with non-polar liquids may be the absence of hydrogen bonding donor/ acceptor sites in respective liquids that restricts formation of homochiral nucleation of enantiomeric clusters under mechanical grinding. The role of solvent polarity and dipole moment used during grinding is discussed.



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POSTER 54

Investigation of Polymorphism in the Organic Semiconductor TIPS-pentacene

Raymond Schireman and Michael T. Ruggiero, University of Vermont

TIPS-pentacene is a popular candidate for use in organic semiconductors due to its high charge carrier mobility and stability in common organic solvents.[1] The performance of TIPS-pentacene devices is directly related to its crystal structure. Previous research by Yang *et al.* has shown that the structure of thin-film crystallized TIPS-pentacene changes as a function of deposition temperature, and that it is possible to stabilize a high-temperature lattice structure that is suggested to represent a second polymorphic phase (Form II).[2] Importantly, Form II has improved charge carrier mobility compared to Form I, although the mechanism of increased performance remains elusive.[3] Thus, a detailed characterization of the atomic and bulk crystal structure as a function of temperature is critical. The goal of this research was to investigate the high-temperature crystal structure of TIPS-pentacene using periodic density functional theory (DFT) simulations. The DFT simulations revealed the presence of two potential energy minima, suggesting that the high-temperature structure observed by Yang *et al*. is indeed Form II, and not solely a thermal expansion of Form I. These results ultimately permit the underlying origins of the improved charge transport properties to be studied with atomic-level precision.

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POSTER 55

Synthesis of Various Pseudopolypeptides via Thermal Topochemical Azide-Alkyne Cycloaddition (TAAC) Reactions

Rishika Rai, Baiju P. Krishnan and Kana M. Sureshan*, Indian Institute of Science Education and Research Thiruvananthapuram, Kerala.

Attractive properties of peptide-based smart biomaterials have encouraged researchers to develop peptide mimics by surrogating the enzyme sensitive amide linkage. Functional as well as structural mimics of natural peptides (i.e. Peptidomimetics) have provided a wide scope of applications[1] in different fields. To overcome the difficulties associated with solution state synthesis (low yield, solubility issues, tedious manipulations, difficult purification etc.), we have employed topochemical reactions (reactions in crystal lattice) to develop various pseudo-polypeptides. Such lattice controlled reactions between pre-organized reacting motifs present in required proximity, provide distinct products.[2] We have synthesized simple dipeptides modified with azide and alkyne. Upon thermal activation, crystals of these dipeptides (based on L-Alanine and L-Valine) undergo not only topochemical Azide-Alkyne Cycloaddition (TAAC) reaction to form biopolymer mimics[3] but also show interesting response towards heating i.e. twisting (right-handed) along length of the crystals. Role of molecular chirality is further established in this rare phenomenon by studying the enantiomeric dipeptide crystals.[4] Extending in the same line, we have also explored heterochiralty in similar system constituting D and L amino acids. As anticipated, these crystals undergo TAAC polymerization but followed by cracking due to significant amount of strain developed.[5] Pursuing our interest in peptide-based biopolymers, we have achieved a variety of pseudo-polypeptide in gel state as well by employing similar principles on several other amino acids.

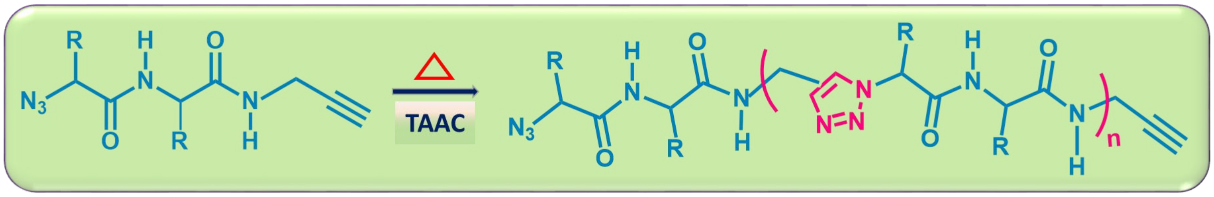

Figure 1. Dipeptide modified with azide and alkyne at the termini undergoes thermal topochemical

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POSTER 56

Controlling photoexcited states in metal-organic thin film by crystal engineering approach

Ritesh Haldar,[1] Marius Jakoby,[1] Antoine Mazel,[2] Marjan Kristić,[1] Wolfgang Wenzel,[1] Stéphane Diring,[2] Fabrice Odobel,[2] Ian A Howard,[1] Christof Wöll[1], [1] Karlsruhe Institute of Technology (KIT); [2] Université de Nantes.

Photoexcited electronic state of an organic chromophore is very sensitive to its surrounding environment. Geometry and inter-chromophore interactions are the prime factors, which decide the photon absorption, excited state dynamics, and radiative or nonradiative pathways. These are pivotal to the advancement of organic optoelectronics. Nevertheless, controlling chromophore assembly is a challenging task and unpredictability of the assembly process often leads to undesired photophysical processes. We will illustrate here that using crystalline metal-organic approach, it is possible to achieve desired photophysical processes in organic chromophores (acting as linker) and a predictive crystal engineering strategy can be employed.

We shall present two examples of 2D metal-organic thin films, fabricated using a liquid-phase epitaxy (LPE)[1] on functionalized surface as an oriented crystalline thin film. In the first example, an anisotropic energy transfer is revealed by enforced stacking of 2D metal-organic frameworks.[2] Second example illustrate a predictive crystal engineering strategy to tune excitonic coupling between naphthalenediimide chromophores (Figure 1).[3] These results reveal the prospect of crystal engineering towards optimization of excited state photophysics in metal-organic or organic materials.[4]

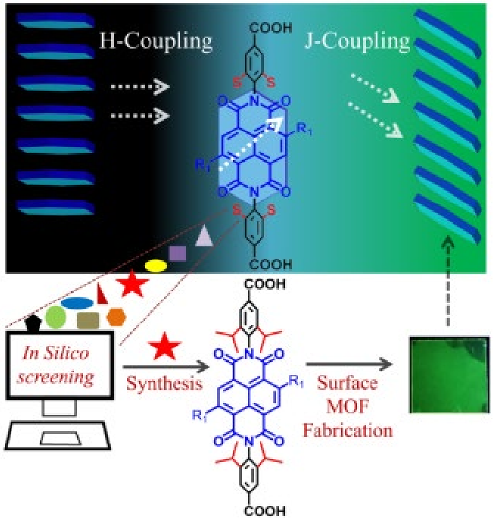

Figure 1: Illustration of a predictive crystal engineering strategy to tune excitonic coupling.

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POSTER 57

Δ-Machine learning high-fidelity energies for molecular crystal structure prediction

R. Hafizi, O. Egorova, D. Woods, and G. M. Day, University of Southampton,

Polymorphism is prevalent in organic molecular crystals because of their weak nature of packing forces. In a typical crystal structure prediction (CSP), tens of structures are typically found in the usual energetic range of polymorphism from the global minimum, some of which are separated by sub kJ/mol lattice energy differences. Consequently, a higher level of theory (e.g., hybrid DFT) is needed to evaluate the energetics of the sampled structures, tens of thousands of which are taken from the potential energy surface during the CSP. Being prohibitively demanding in terms of computational power, accurate evaluation of lattice energy is the bottleneck for a reliable prediction.
In this work, we report a multi-fidelity Δ-machine learning (Δ-ML) approach for describing the lattice energy difference between various levels of theory. To this aim, Gaussian Process Regression is used, which tends to outperform other ML methods for small data problems. As the case studies, the energy landscape of three small, but challenging, molecules are predicted by FIT+DMA force field. In the next step, we compare the efficiency of two computational methods in performing Generalized Gradient Approximation and hybrid DFT calculations. An optimized combination of these two is employed for re-ranking the structures in a 25 kJ/mol window from the global minimum, which in turn is used as the data set for ML training. We show that the trained ML model performs properly on predicting the hybrid DFT landscape and cost reduction, which is a promising achievement, especially for the investigation of the whole energy landscape of larger molecules.

POSTER 58

ORGANIZING THE ORGANIC SOLID STATE TO ACHIEVE [2+2] CYCLOADDITION REACTIONS VIA HALOGEN BONDING INTERACTIONS

Samantha J. Kruse,[1] **Eric Bosch,**[2] **Ryan H. Groeneman,**[1] Webster University,
Missouri State University

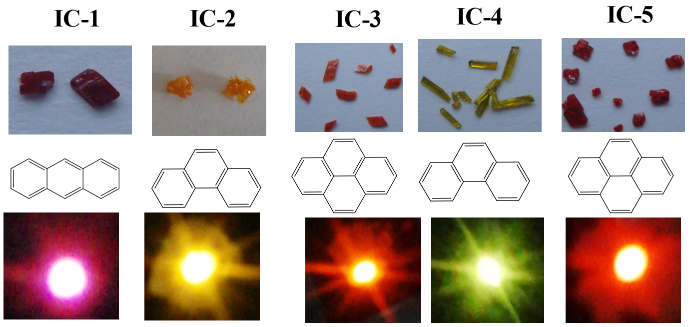
Over the last decade, the ability to align reactive olefins that will undergo a [2+2] cycloaddition reaction in the solid state has continued to be an active area of research. In order to align the reactant molecules in the required orientation and distance criteria for a photoreaction a template-based approach has proven to be very successful. In nearly all cases, hydrogen bonding interactions have been the driving force that positions the carbon-carbon double bonds in the correct orientation to undergo this solid-state photoreaction. Halogen bonding, however, has only been reported in a very limited number of examples where it templates photoreactions. In this contribution, we will report on halogen bonding templates that utilize **I•••N** contacts to organize the organic solid state to yield photoreactive co-crystals. X-ray crystal structures before photoreactions will be discussed, as well as the ability to form various isostructural co-crystals based upon nontraditional halogen bond donors.

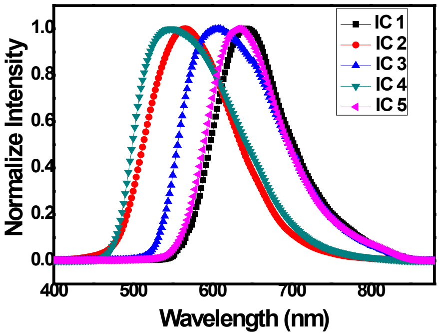
POSTER 59

Guest Responsive Tunable Solid-State Emissions of Supramolecular Two-Component Organic Hosts

Sandipan Roy*, Aastha, Vinit Mishra and Moumita Kotal, Maharishi Markandeshwar

Interest in tunable solid-state luminescent materials has evoked tremendously in recent years owing to their emerging applications in light emitting diodes, photovoltaic devices, sensors and lasers.[1] In this context, the development of solid state supramolecular two-component organic host systems based on non-covalent interactions (e.g.; hydrogen bonds) have great potential to exhibit tunable solid-state emissions induced by the inclusion of π-aromatic guest molecules. [2-6] Here, we have successfully developed two new supramolecular two-component organic hosts, denoted as $[H_3\mathbf{1}]_2[H_2\text{bpe}]$ and $[H_3\mathbf{1}]_2[H_2\text{bpy}]$, composed of 2,2',6,6'-tetracarboxybiphenyl ($H_4\mathbf{1}$) with 4,4'-bipyridylethylene (bpe) and 4,4'-bipyridine (bpy) molecules linked by charge-assisted hydrogen bonds. Both of these hosts were found to exhibit excellent aromatic guest inclusion abilities via remarkable exhibition of different colors in their corresponding inclusion complexes (**IC-1**–**IC-5**). The crystal structures of all inclusion complexes were analyzed in terms of hydrogen bonding between the two host components and host–guest interactions. Notably, the inclusion complexes exhibited multicolor emissions in the crystalline state implying the different extent of cation–π interactions between the pyridinium ions and π-aromatic guest molecules. These findings indicated that our supramolecular design strategy led to tune the structural and luminescence properties of inclusion complexes.





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POSTER 60

First Principles Study of Hydrogen Storage in Li-Decorated Metal−Carbyne Framework

Sandeep Kumar, Surinder Pal Kaur, and T. J. Dhilip Kumar, Indian Institute of Technology Ropar

The need for sustainable energy fuel is much higher than earlier. The use of hydrogen as a fuel is obstructed due to its low storage capacity in the storage medium. Here, a newly designed metal−carbyne framework (MCF) is decorated with Li atoms with an average Li binding energy of 1.94 eV. Two Li atoms are used to decorate each carbyne linker of the MCF. Here, using density functional theory calculations, we systematically investigated the adsorption of H_2 in Li-decorated MCF, namely $MCFLi_8$. It is found that four H_2 molecules are adsorbed in the molecular form on each Li in $MCFLi_8$ by Niu's charge polarization mechanism. Our findings revealed that the Li-decorated MCF exhibits a high hydrogen storage capacity at ambient conditions with adsorption−desorption energy ranging between 0.2 and 0.6 eV. Hirshfeld charge analysis and electrostatic potential maps show the charge transfer mechanism during the hydrogen adsorption. Born−Oppenheimer molecular dynamics simulations reveal the reversibility of adsorbed hydrogen at ideal pressure and temperature conditions. Thermodynamic usable capacity of adsorbed hydrogen at adsorption and desorption conditions is determined by calculating hydrogen occupation number. The gravimetric hydrogen density of 11.1 wt % is found for complete H_2 adsorbed in $MCFLi_8$. This study suggests that Li-decorated MCF can be a promising hydrogen storage material.

POSTER 61

Mechanoenzymatic degradation of polymers

Sandra Kaabel, J. P. Daniel Therien, Catherine Deschênes, Tomislav Friščić,
Karine Auclair, McGill University

The resilience of polymers to chemical, physical and biological degradation makes them valuable materials in human-made constructions and packaging, due to low production costs, favourable processing, and product properties.[1] Synthetic polymers that boast highest scale of production, such as polyethylene, polypropylene and polyethylene terephthalate are a major contributor to the accumulation of waste in landfills and oceans. Chemical recycling, through depolymerization, holds the potential to avoid disposal of plastics and recover their monomeric components for circular material manufacture, or for up-cycling to value-added chemicals.[2]

Recently our group demonstrated that cellulose[3], chitin[4] and xylan[5] can be efficiently depolymerized by their corresponding hydrolase enzymes in a moist-solid environment using mechanochemistry and aging. In contrast to the harsh solvents and reaction conditions generally used for the chemical hydrolysis of these natural polymers, enzymatic degradation methods present a promising environmentally benign alternative. A number of hydrolases have been identified for the depolymerization of petroleum-based polymers[6], and this presentation will outline our recent success in adapting the mechanoenzymatic methods[7] to the clean and efficient depolymerisation of plastics.

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POSTER 62

Topological Features and Modularity of Hybrid Inorganic Frameworks

Sergey Aksenov, Russian Academy of Sciences

Zeolites compose an important class of inorganic crystalline materials that have been widely used in technology. A family of microporous materials demonstrates that frameworks can be built by TO_4 tetrahedra and MO_6 octahedra (M – predominantly transitional metals: Ti, Nb, Zr, Sn, Fe, Mn, etc.). Such heteropolyhedral zeolite-like materials are also characterized by many useful physical and chemical properties and attract interest (especially titanium silicates) as ion-exchangers because of their efficient absorption of heavy elements from aqueous solutions.

The modern topological analysis of zeolite structures using the ToposPro software is based on the types of linkage of natural tiles, the smallest tetrahedral clusters, to form a framework structure. In this case, it can be also useful to characterize a topology of the heteropolyhedral frameworks as they represent the same 3D cationic nets.

Another way for describing complex structures of inorganic compounds is the modular approach, when the structure is described as a combination of a number of fragments – modules.

Both approaches have been recently applied for the analysis of hybrid lanthanide-based silicates, uranyl germanates and vanadates, borophosphates of transitional metals, and series of minerals and related compounds with heteropolyhedral frameworks. The relationships between such heteropolyhedral frameworks and tetrahedral framework types were found and described in details and hypothetical zeolite-type materials were predicted.

POSTER 63

Efficient capture of toxic oxoanions of Se(VI) and As(V) accompanied with direct crystallographic evidence in a water-stable cationic MOF

Shivani Sharma, Aamod Vikas Desai, Biplab Joarder, Sujit Ghosh,* Indian Institute of Science Education and Research (IISER Pune),

Remediation of oxo-anions of heavy metals such as selenium and arsenic hold tremendous significance as they have been listed by EPA among highly toxic compounds and priority environmental pollutants. Cationic MOFs, which are suitable receptors for such ions have not been explored for the concomitant capture of such oxo-anions which demands investigation. Herein, we demonstrate successful capture of oxo-anions of Se(VI) and As(V) via a Ni(II) based water stable cationic MOF accompanied with one of highest uptake value observed (~ 100mg/g for SeO_4^{2-} and ~ 85mg/g of $HAsO_4^{2-}$) in the domain of cationic MOFs. This ion-exchange/capture phenomenon was affirmed with direct crystallographic visualization of these extremely toxic anions within the voids of a water stable cationic MOF. The MOF exhibited selective capture owing to shape memory effect of SO_4^{2-} anions. The extended array of highly aligned SO_4^{2-} anions lying along crystallographic *c*-axis led to facile exchange with incoming toxic anions viz. SeO_4^{2-} and $HAsO_4^{2-}$. Moreover, the exchanged crystals were studied using single crystal X-ray diffraction which revealed interesting insights about the environment of the isolated anions within the framework. The selenate (SeO_4^{2-}) anion was located at the same positions as the (SO_4^{2-}) anion from which we inferred similar interaction site whereas $HAsO_4^{2-}$ was present at a variable location due to the larger size Such crystallographic visualization of the toxic anion within the framework serves as a guide for determining the interaction sites that will contribute directly to the development of materials targeted towards the capture of such toxic anions.

Figure 1: Schematic showing capture of toxic ions of selenium and arsenic by a water stable cationic MOF.

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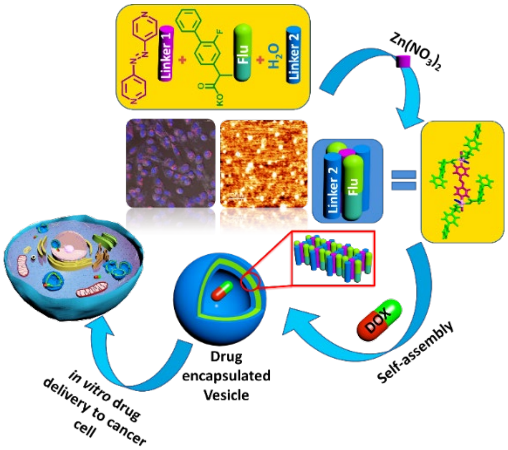
POSTER 64

Design and synthesis of Zn(II)-coordination polymers anchored with NSAIDs: Metallovesicle formation and multi-drug delivery

Sourabh Bera, Abhinanda Chowdhury, Koushik Sarkar and Parthasarathi Dastidar*, Indian Association for the Cultivation of Science (IACS)

A series of coordination polymers (**CP1-CP5**) synthesized from a bispyridyl linker namely 4,4´-azopyridine (**L**), selected non-steroidalanti-inflammatory drugs (NSAIDs) namely diclofenac (**Dic**), ibuprofen (**Ibu**), flurbiprofen (**Flu**), mefenamic acid (**Mefe**) and naproxen (**Nap**) and Zn(NO_3)$_2$ were characterized by single crystal X-ray diffraction. In the crystal structure of **CP3** it was observed that the metal coordinated water molecules were located opposite sides of the coordination polymer chain whereas in the crystal structure of **CP5** metal coordinated water molecules were located on the same side of the coordination polymer chain. The coordination polymer namely **CP3** derived from **Flu** was able to form metallovesicle in DMSO, DMSO/H_2O and DMSO/DMEM (biological media) as revealed by TEM, AFM and DLS but in case of **CP5** it was unable to form such vesicular aggregate. Metallovesicle formation by **CP3** was further supported by loading a fluorescent dye namely calcein as well as an anti-cancer drug doxorubicin hydrochloride (**DOX**) as revealed by UV-vis and emission spectra, and fluorescence microscopy. **DOX** loaded metallovesicle of **CP3** (**DOX@CP3-vesicle**) could be delivered *in vitro* to a highly aggressive human breast cancer cell line namely MDA-MB-231 as revealed by MTT and cell migration assays, and also cell imaging performed under laser scanning confocal microscope (LSCM). Thus, a proof of the concept for developing multi-drug delivery system derived from metallovesicle for delivering an anti-cancer drug to cancer cells is demonstrated for the first time.

Figure:



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POSTER 65

1,8-napthalimide based Transient hydrogel: kinetically trapped metastable gel with AIEE properties

Souvik Misra, Pijush Singh, Jayanta Nanda*, IIEST,Shibpur

Since last several years, scientists are studying several small molecules based on supramolecular systems to mimic living systems. However, most of them are in their equilibrium state. In recent days, scientists are paying much attention to create supramolecular models which are based on ‘out of equilibrium’ or ‘far from equilibrium’, ‘metastable’, ‘kinetically trapped’ and ‘fuel driven’. One of the most interesting properties of these kind of systems is time variable properties keeping the basic unit constant. We have synthesized 1,8-napthalimide based dipeptide compound which forms hydrogel in DMSO/water mixtures. This hydrogel is transient in nature and transformed into crystal with time. The conversion from one morphology to others was observed within few hours without using any external stimuli. The gel formation depends upon mainly three parameters : a) concentration of gelator, b) % of water in the mixture and c) time. FE-SEM study suggested morphology of dipeptide is transformed to sphere to fiber to helical fiber and helical fibers to crystal. It is believed that crystal state is the thermodynamically stable state, because whatever the starting concentration of gelator, % of water in mixture or time, system moves towards crystallization. It is observed that in lesser % of water, system is directly converted into crystal state without attending the metastable gel state. NMI-dipeptide (N2) showed J-type aggregation upon water addition and exhibits blue emission in the mixed solvent system. This molecules exhibit AIEE phenomenon in mixed solvent system. Interestingly, upon heating the crystalline material in the same solvent system, it forms again hydrogel.

POSTER 66

Cocrystals, Salts and Supramolecular Gels of Non-Steroidal Anti-Inflammatory Drug Niflumic Acid

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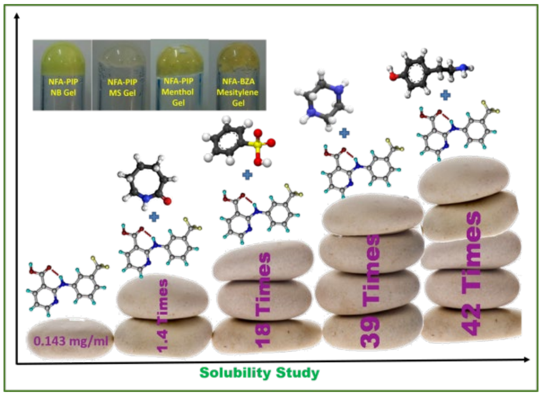
University of Hyderabad,

Niflumic acid (NFA) is a non-steroidal anti-inflammatory drug (NSAID) classified under the BCS (Biopharmaceutical Classification System) Class II category of poor aqueous solubility and high permeability. In an attempt to improve the physicochemical properties of NFA, particularly solubility and dissolution rate by cocrystallization and salt formation, cocrystals of NFA were prepared by using caprolactam (CPR, 1:1), 2-hydroxy pyridine (2HP, 1:1) and salts with piperazine (PIP, 1:0.5), benzenesulfonic acid (BSA, 1:1), benzyl amine (BZA, 1:1 and 2:2), and tyramine (TYA, 1:1). The new solid forms were characterized by powder X-ray diffraction, infrared spectroscopy, differential scanning calorimetry, and confirmed by single crystal X-ray diffraction. NFA–PIP and NFA–BZA II salts from nitrobenzene, methyl salicylate, menthol and mesitylene solvents showed an unexpected gelation behavior as confirmed by rheology experiments (frequency and amplitude sweep methods). Solubility and dissolution measurements for GRAS cocrystals and salts in 20% EtOH-water medium showed TYA and PIP salts to have improved solubility of 40 times (for both) and dissolution rates faster by 54 and 7 times respectively, while for BSA salt the improvement in solubility is 18 times and dissolution is 10 fold. Diffusion studies of NFA supramolecular gels in a Franz diffusion cell showed enhanced flux for NFA–PIP menthol gel, and moreover both piperazine and menthol are both pharmaceutically acceptable and this gel may, therefore, be suitable for topical treatment and high drug concentration at the target site. These studies show that apart from oral delivery of salts, topical drug delivery of Niflumic acid to avoid GI complications of is an approach to improve physicochemical properties and oral bioavailability of NSAIDs.



Reference:

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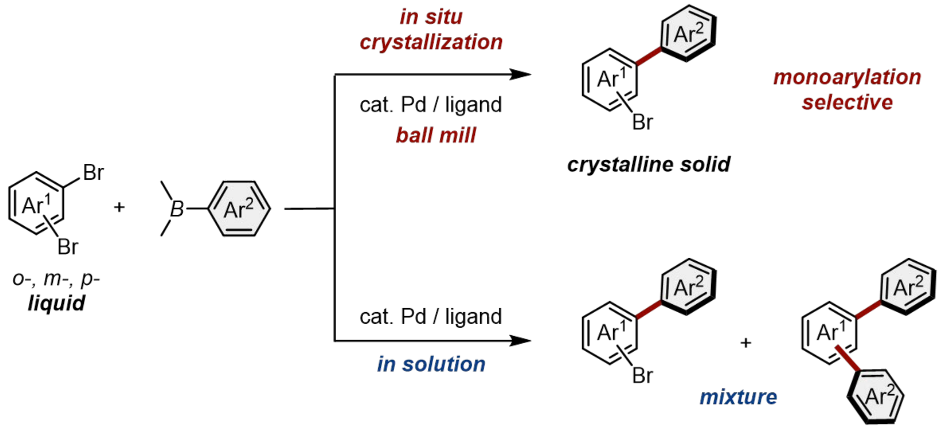
Poster 67

In Situ Crystallization Enables Selective Monoarylation of Dibromoarenes

Tamae Seo[1], Koji Kubota[1], Hajime Ito[1], Hokkaido University,

Since organic reactions using ball milling are conducted without organic solvents, the reactivity can be greatly influenced by the phase of the substrate (solid, liquid and gas).[1] Inspired by the unique reactivity profile under mechanochemical conditions, we envisioned that selective organic transformations by utilizing the *in situ* phase transition could be developed. In this study, we have developed *in situ* crystallization driven selective Suzuki-Miyaura cross-couplings of dibromoarenes using ball mill.[2] The reaction between liquid dibromoarenes and arylboronic acids in the presence of a palladium catalyst proceeded to provide crystalline solids of monoarylated products with high selectivity. In contrast, under solution-based conditions using the same catalytic system, the mixture of mono- and diarylated products was obtained with lower selectivity. The lower reactivity of the crystalline monoarylated products relative to the liquid starting materials should be attributed predominantly to the low diffusion efficiency of the former in the reaction mixture under mechanochemical conditions. The present study sheds light on a novel approach using *in situ* crystallization to design selective organic transformations that are difficult to achieve via conventional solution-based synthesis.



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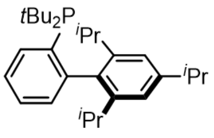
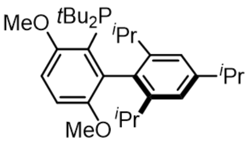


tBuXPhos

or



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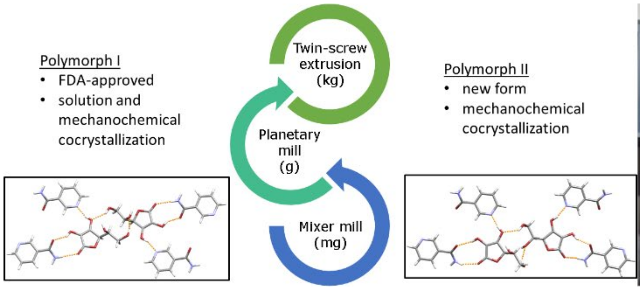
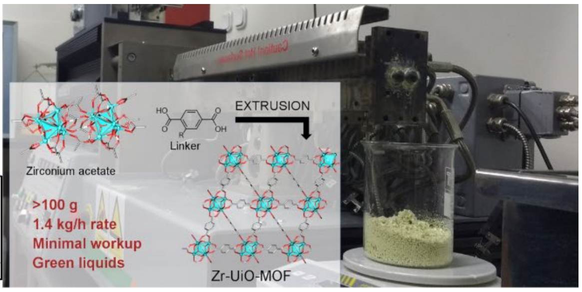
POSTER 68

Sustainable chemistry and engineering on a large scale: continuous manufacturing of pharmaceutical cocrystals and metal-organic frameworks by twin-screw extrusion

Tomislav Stolar [a], **Krunoslav Užarević** [a], [a]Ruđer Bošković Institute,

With the fast-increasing negative anthropogenic effect on the environment, it is of an urgent need to develop sustainable ways for the production of relevant materials. Mechanochemistry, i.e., chemical reactivity induced by mechanical action, has become a viable synthetic technique that relies on solvent-free or minimum-solvent procedures [1,2]. Twin-screw extrusion (TSE) is a large scale mechanochemical device that uses two co-rotating screws to transport, shear, and knead material along the barrel. Here we demonstrate efficient and scalable access to: (a) FDA-approved pharmaceutical cocrystals based on vitamin C and vitamin B3 with selective control of their polymorphic forms [3] and (b) zirconium metal-organic frameworks (MOFs) such as UiO-66-NH_2 which shows high activity for the catalytic breakdown of nerve gas simulants [4]. The properties of all materials produced on the large-scale were validated and show the potential of TSE procedures for the industrial-scale output.





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POSTER 69

Photoresponsive ‘self-stirring’ organic crystals caused by gas release

Upasana Banerjee, Jeanette A. Krause and Anna D. Gudmundsdottir, University of Cincinnati

Azido photochemistry has earned a lot of interest recently due to their wide application in synthesizing pharmaceutically significant heterocycles. We report a sustainable approach of synthesizing pyrrole from dieneazide derivatives using visible light LEDs and sunlight in crystals. Optical microscopy reveals self-stirring photomechanical response of the dieneazide crystals and was correlated with the intermolecular forces inside the crystal lattice to investigate the basis of high photoconversion in the solid-state.

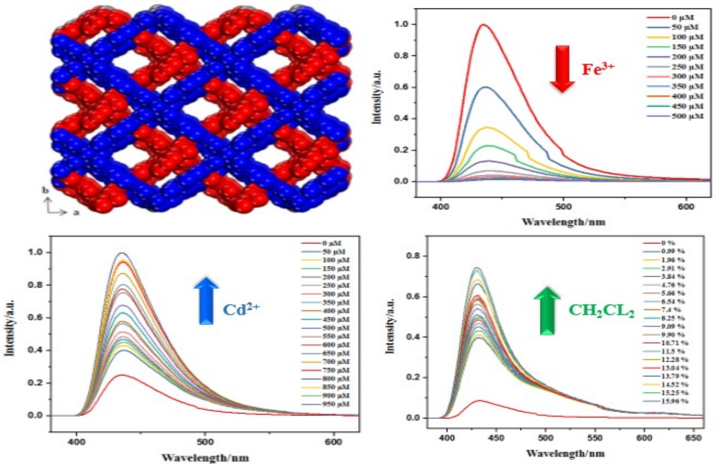
POSTER 70

Highly selective and sensitive sensing of metal ions and small molecules via a functional luminescent Zn(II)-based metal-organic framework

Yeganeh Davoudabadi Farahani, Mohammad Rad, Vahid Safarifard*, Iran University of Science and Technology

Recently, very much attention has been taken to the reconnaissance of heavy metal ions due to their prompt diffusion as environmental contaminants to the surroundings. The design and synthesis of sensitive and selective luminescent materials as chemical sensing agents is a fundamental goal in fluorescence assays [1]. Considering high porosity, large surface area, excellent photoluminescence property of metal-organic frameworks (MOFs), luminescent properties of a microporous azine-functionalized MOF, TMU-16, dispersed in different metal ions and solvents have been investigated systematically [2]. TMU-16 displays superb luminescence emission, and it can detect Fe(III) and Cd(II) ions with high selectivity, excellent sensitivity, and short response time (<1 min). The emission intensities of TMU-16 were quenched upon the addition of Fe^{3+} and increased upon the addition of Cd^{2+}. The detection limits of TMU-16 for Fe^{3+}/Cd^{2+} in DMF are estimated to be 0.2 and 0.5 μM, respectively. The effect of other metal ions on the fluorescence intensity of the MOF was studied and other metal ions showed low interference response in recognition of Fe^{3+} and Cd^{2+}. Furthermore, TMU-16 exhibits distinct solvent-dependent luminescent spectra with emission intensity significantly enhanced toward dichloromethane.

Graphical Abstract



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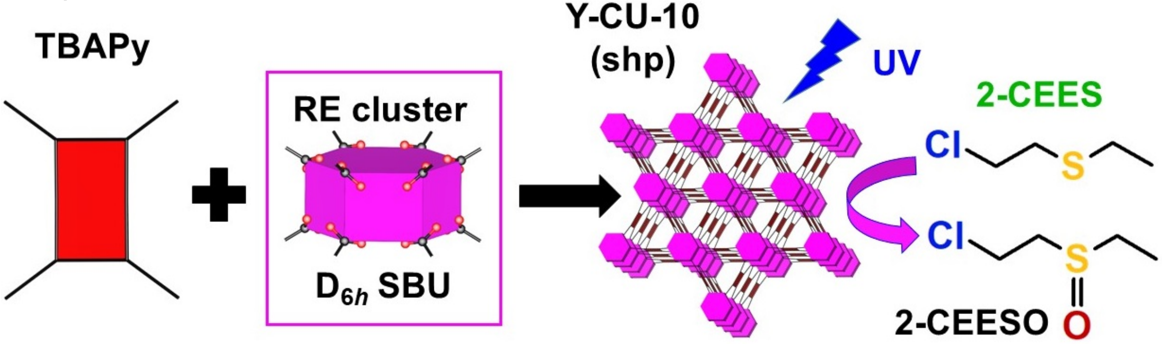
POSTER 71

A novel Rare-Earth Metal-Organic Framework and its potential Application in a Catalytic Photo-oxidation Reaction

Victor Quezada-Novoa,[a] Hatem Titi,[b] Amy Sarjeant and Ashlee J. Howarth[a]*,
[a]Concordia University, [b]McGill University

Metal–organic frameworks (MOFs) are a kind of hybrid crystalline material that has been intensively studied during the last few decades, in part for their potential applications in gas adsorption, sensing, and catalysis, among others.[1,2] MOFs have been synthetized from many of the metals on the periodic table, however, rare earth (RE) metals, including yttrium, scandium and the fifteen lanthanides, are gaining increasing attention for the intricate topologies and specific properties that RE-based MOFs can feature.[3,4] In this work, we present a novel RE-based MOF,RE-CU-10 (RE = Y(III) or Tb(III); CU = Concordia University). CU-10 features an **shp** topology, which is comprised from 12-connected RE-cluster nodes bridged by 4-connected organic linker, where the points of extension from the cluster create a secondary building unit (SBU) with D_{6h} symmetry. The obtained framework features high porosity through the presence of 1D triangular channels. The degradation of sulfur mustard simulant, 2-CEES, by production of singlet oxygen was evaluated and will also be presented, showing a degradation half-life comparable to the well-known NU-1000[5].



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POSTER 72

Single-Crystal-to-Single-Crystal syntheses of two Cross-laminated 1D-polymers *via* Topochemical Azide-Alkyne Cycloaddition Reaction

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The demand for polypeptide-mimics having triazole as the amide-surrogate has been increasing recently. Considering the interest in polyglycine-mimics, we synthesised a triazolyl-pseudo-polyglycine *via* Topochemical Azide-Alkyne Cycloaddition reaction.[1] We synthesized two glycine derived monomers N_3-Gly-Gly-NH-CH_2-C≡CH and N_3-Gly-Gly-Gly-CH_2-C≡CH and their SCXRD analysis revealed that they adopts a H-bonded criss-crossed layered packing such that the molecules in each layer are aligned in a head-to-tail manner and the complementary azide and alkyne motifs of adjacent peptides are at proximity in an orientation apt for their cycloaddition. Interestingly, each monomer is H-bonded with the ones which are aligned almost orthogonally in adjacent layers. Such an arrangement makes the 1D-array-like arrangement of monomers in one layer to be nearly orthogonal to similar arrays in alternate layers. At room temperature, the crystals of both monomers underwent spontaneous single-crystal-to-single-crystal (SCSC) polymerization *via* Topochemical Azide-Alkyne Cycloaddition (TAAC) reaction to form triazolyl-polyglycines. Due to the criss-crossed arrangement of the monomers, polymer-crystals evolved with a novel topology where 1D polymer chains formed cross-laminated alignement in alternate layers. In this novel topology, each polymer chain having *n* amide bonds formed H-bonding with *2n* polymer chains in adjacent layers. Such well packed arrangement in the crystal lattice resulted in enhanced mechanical properties and thermal stabilities of both the polymers. The topology adopted by these two fully organic polymers in single crystal is novel compared to existing lamellar or weave kind of topologies for 1D polymers.

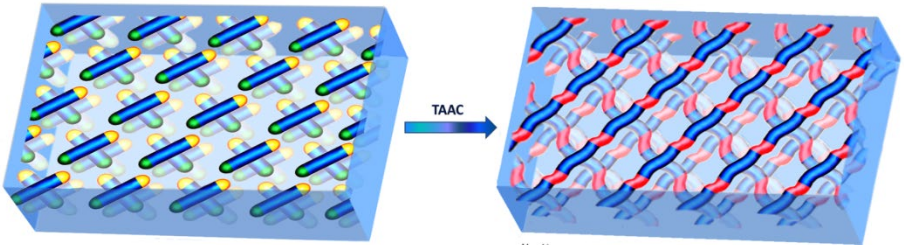

Figure 1. Single-crystal-to-single-crystal polymerization of peptide derivatives functionalized with azide and alkyne to cross laminated 1D polymers via Topochemical Azide Alkyne Cycloaddition (TAAC) reaction.

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POSTER 73

Recent strategies for metal-organic cocrystal engineering — imine ligands with peripherally located carbonyl or morpholinyl fragment oxygen atoms as halogen bond acceptors

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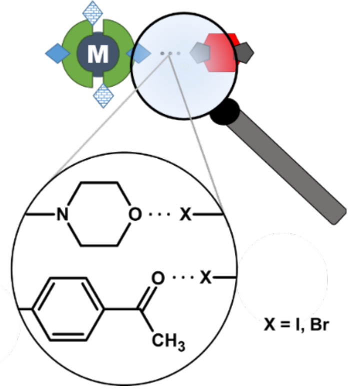
Halogen bonding[1] is a versatile intermolecular interaction that has been utilized for the synthesis of a wide range of molecular and ionic materials. However, the use of halogen bonding for crystal engineering of new materials based on metal-organic subunits remains poorly explored and a challenge.[2]

Recently, our team has introduced a strategy that exploits carbonyl and morpholinyl oxygen atoms as halogen bond acceptors that can be readily introduced into the periphery of imine (Schiff base) ligands of coordinately unsaturated metal complexes.[3–5] For example, using the carbonyl oxygen atom as the halogen bond acceptor enabled the synthesis of two isostructural metal-organic cocrystal families, based on copper(II) and nickel(II) centers.[4] Of note is that the accompanying thermal analysis results validated the hypothesis that macroscopic properties of such materials can be readily tuned without changes to the overall crystal structures: four isostructural compounds were obtained as a combination of equivalent copper(II) and nickel(II) complexes with one stronger and one weaker halogen bond donor, with thermal stability of the metal-organic cocrystal being clearly determined by choice of halogen bond donor and the metal center. This presentation will provide an overview of these and other recent results in developing increasingly reliable strategies to design and synthesize metal-based halogen-bonded materials with controllable properties.[5]



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POSTER 74

Thermal Expansion in Single-Component Crystals and Mixed Co-crystals

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Thermal expansion (TE) is the response of a material to temperature changes.[1] It is classified as positive, negative or zero TE. When the dimensions of materials are increased upon heating, it is called positive TE (PTE), which is the most common behavior in materials. Negative TE (NTE) or zero TE (ZTE) are rarer behaviors, which are determined by a decrease in size or nearly no change in size upon heating, respectively.

Organic molecules are capable of motion in the crystalline state. Dynamic pedal motion[2] can be characterized using variable temperature crystallographic studies, and our group has observed that large PTE occurs along the direction where motion happens.

In this presentation, we describe the synthesis and characterization of a series of halogen-bond donors containing motion-capable group olefin (C=C), azo (N=N), or imine (C=N) groups to investigate TE behaviors in single-component crystals (Figure 1). We also describe the design and synthesis of a series of three-component mixed co-crystals, which could provide a strategy for tuning TE in organic solids.

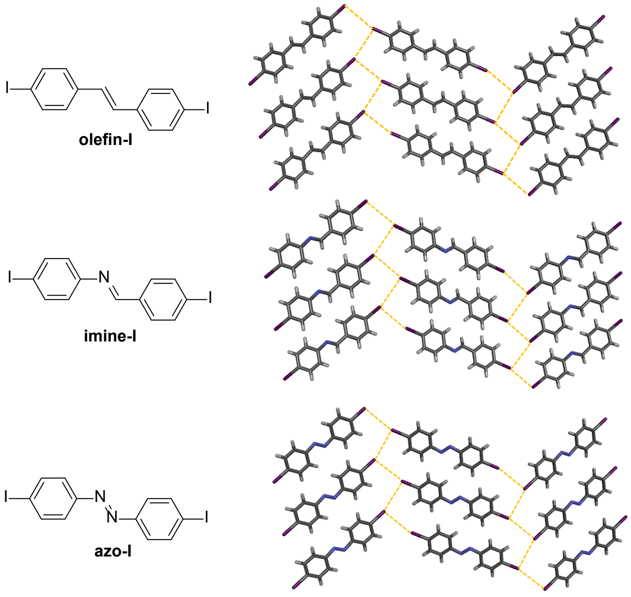

Figure 1. Chemical and X-ray structures of halogen-bond donor molecules.

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POSTER 75

Beyond binary cocrystals: mechanosynthesis of eutectic solid forms of polycyclic aromatic hydrocarbons with enhanced solid-state properties

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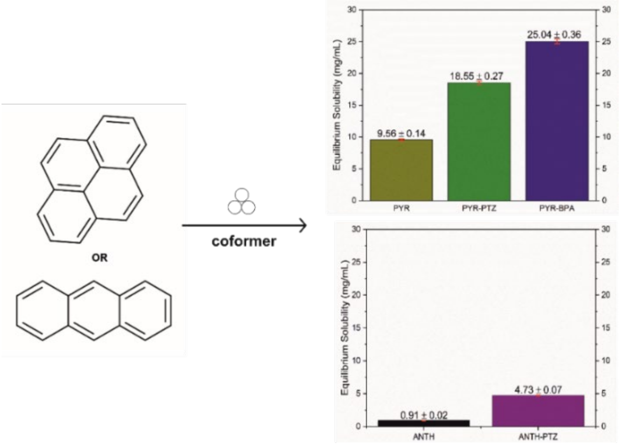
Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants that are ubiquitous in the environment and harmful to human health[1]. They also have low solubilities in polar solvents which limits their bioremediation potential. To modify PAH physicochemical properties (particularly, their solubility), mechanosynthesis was employed to efficiently prepare eutectic solid forms of PAHs in essentially quantitative yield. This was done using an "anti-crystal engineering" design principle[2] where synthon non-complementarity but molecular size similarity was found to be an important driver in eutectic formation. Computational structure prediction calculations show that none of the PAH-coformer combinations led to stable cocrystals relative to the stabilities of the component structures. This provided the rationale for why cocrystals were not observed during the mechanosynthesis experiments. Nevertheless, eutectic formation remains a challenging phenomenon to predict *a priori*. Phase diagrams and Tamman plots were constructed to better understand the thermal stability of each eutectic as a function of the composition. We find that eutectic solid formulations are desirable vehicles for physicochemical property optimization for molecules containing no heteroatoms. This is indicated by the observation of significant melting point depressions for the PAH upon eutectic formation that are in the range 30–50 °C. Moreover, equilibrium solubility measurements reveal that the eutectics lead to a ~2–5 fold enhancement in the PAH solubility.



- Equilibrium solubility enhancement (~2-5 folds).

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POSTER 76

Locating Solvent Molecules in Porous Solids Using Terahertz Spectroscopy

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Metal organic frameworks (MOFs) are a popular class of advanced porous materials, which have highly symmetric 3D structures and rich set of structural diversity. An important component to working with porous materials are the location to solvent molecules in the pores, which can alter bulk properties considerably. While X-ray methods are commonly used in this regard, it is not uncommon for it to present ambiguous results, making a definitive structural determination difficult. MIL-53(Al) is one such example, where its low-temperature phase (MIL-53(Al)-*np*) is believed to contain a co-crystallized water molecule in the pore of the framework. Specifically, two different space groups have been assigned, *P2/1c* and *Cc*, which produce nearly identical powder X-ray diffraction (PXRD) patterns. The differences between the two structures are subtle, with the *P2/1c* presenting a larger symmetry-unique building block. A complementary technique, terahertz time-domain spectroscopy (THz-TDS) has been used to aid in crystal structure predictions and to differentiate between similar crystals. In this study, PXRD, THz-TDS, and *ab initio* periodic density functional theory (DFT) calculations were combined to fully-uncover the correct three-dimensional structure of MIL-53(Al)-*np.* This methodology highlights the advantages of THz-TDS and how it can offer higher sensitivity for crystal structure evaluation compared to X-ray methods.

POSTER 77

Metal-like Ductility in Organic Plastic Crystals

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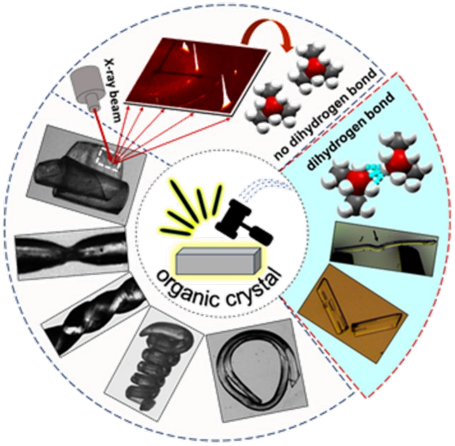
Abstract: Ductility, which is a common phenomenon in many metals, is difficult to achieve in molecular crystals. Organic crystals have been recently shown to bend plastically on one or two face specific directions, but they fracture when stressed in any other arbitrary directions. Here, we present an exceptional metal-like ductility and malleability in the isomorphous crystals of two globular molecules, BH_3NMe_3 and BF_3NMe_3, with characteristic tensile stretching, compression, twisting and thinning (increase of width over 500%). Surprisingly, the mechanically deformed samples, which transition to lower symmetry phases, not only retain good long range order, but also allow structure determination by single crystal X-ray diffraction. Molecules in these high symmetry crystals interact predominantly via electrostatic forces (B^-–N^+) and form columnar structures, thus forming multiple slip planes with weak dispersive forces among columns. While the former interactions hold molecules together, the latter facilitate exceptional ductility. On the other hand, the limited number of facile slip planes and strong dihydrogen bonding in BH_3NHMe_2 negates ductility. The structure-property correlation established in these aminoboranes with exceptional ductility and ability to retain crystalline order may enable designing highly modular, easy-to-cast crystalline functional organics, for applications in solid-state electrolytes, adaptable electronics (soft ferro/piezo/pyro-electrics), barocalorimetry (solid coolants), soft-robotics etc.



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