Conference Report: 2nd China-India-Singapore Symposium on "Crystal Engineering, 20-23 November 2012, Guanzhou, China.

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The China-India-Singapore symposium series on "Crystal Engineering" was conceived with the idea to bring together researchers working in the field of crystal engineering from the countries China, India, and Singapore. This symposium series was aimed to discuss and acknowledge recent advances in the field of crystal engineering happening in the south Asian region. The first China-India-Singapore Symposium on Crystal Engineering (CISSCE) was held at National University of Singapore (NUS) from 30th July - 2nd August, 2010. The 2nd China-India-Singapore Symposium on Crystal Engineering was recently held at Guangzhou, China during 20th - 23rd November 2012. A total of 37 researchers from China, India and Singapore presented their work ranging from the research areas of pharmaceutical solids, materials science and computational chemistry. The 2nd CISSCE highlighted some of the recent developments in the field of organic, bioorganic, metal organic hybrid (metal complexes and coordination polymers), pharmaceutical and organic-semiconductor materials achieved through the applications of crystal engineering. This report is an attempt to provide reader a glimpse of some of the recent research work undergoing in various laboratories in China, India and Singapore in the field of crystal engineering that was discussed in the symposium.

Study of Strong and Weak Intermolecular Interactions

The role of intermolecular interaction is very fundamental in understanding the molecular association in all states of matter. It is very important to understand their nature, origin and their relative strengths to ascertain the interaction hierarchy operating within a supramolecular assembly that dictates molecular associations. Prof. Naresh Patwari (Indian Institute of Technology Bombay, Mumbai, India) highlighted the role of π-π stacking interactions in a combined experimental and theoretical study. In his presentation, Prof. Patwari presented the study of nature, strength and orientational preferences of π-π stacking interactions in the hetero-dimers of phenylacetylene with polysubstituted N-heterocyclic aromatic rings performed with the help of IR-UV double resonance spectroscopy.[1] Dr. Tejender S. Thakur (CSIR-Central Drug Research Institute, Lucknow, India) discussed an important issue related to the molecular level understanding of crystallization processes with an example of formaldehyde crystal structure. Dr. Thakur showed that, the detailed structural insight into the molecular recognition process can be obtained from theoretical calculations by studying the systematic build up of a supramolecular assembly through small molecular clusters using the aufbau principle.[2] Such studies have implications in understanding the crystal nucleation and growth processes.

Crystal Engineering of Organic Solids

Understanding the crystallization process is very important to crystal engineering. The control over various solid forms of a given compound cannot be achieved without the complete understanding of the crystal structure landscape. Prof. Gautam R. Desiraju (Indian Institute of Science, Bangalore, India) in his presentation put forth this idea with some examples from his research work. He discussed about the identification of high energy crystalline phases of benzoic acid by sampling the crystalline phases of mono and polyfluorinated benzoic acids.[3] In another example he discussed about the sampling of various co-crystals of orcinol with mono and bi-N-acceptor co-former systems with the help of high throughput crystallography. Thereby, permitting the sampling of the structural landscape for a co-crystallization reaction for other members of the 1,3-dihydroxybenzene family with mono and bi-N-acceptor co-formers.

Pharmaceutical co-crystals

Pharmaceutical co-crystals is one of the very active and important topics of research for both academia and industry where researchers are working towards the goal of designing novel co-crystal based solid formulations of active pharmaceutical ingredients (APIs) for improving their physicochemical properties. Several new techniques and methodologies are being developed and employed in order to obtain a suitable solid form of the API with desired physicochemical properties. The first 1st China-India-Singapore Symposium on Crystal Engineering had also seen active discussions and presentations on this topic. In this symposium, Dr. Venu R. Vangala, Dr. Srinavasalu Aitipamula from the Institute of Chemical and Engineering Sciences, Singapore and Dr. Ram K. R. Jetti (Mylan Laboratory, Hyderabad, India) highlighted the application of crystal engineering in the study of pharmaceutical solids. Dr. Vangala presented a talk on the usefulness of twin screw extrusion (TSE) method for performing the large scale manufacturing of co-crystals of APIs.[4] Dr. Vangala emphasized the usage of TSE as a clean, green and an efficient method for the bulk production of co-crystals of APIs with an example of co-crystallization of a poorly soluble API, Nitofurantoin (NF) with 4-hydroxybenzoic acid (HBA). Dr. Aitipamula discussed the topic API co-crystal hydrates and their aqueous solubilities by taking the examples of caffeine–4-hydroxybenzoic acid (1:1) hydrate, piracetam–4-hydroxybenzoic acid (1:1) hydrate and griseofulvin–acesulfame (2:1) hydrate.[5] Dr. Ram K. R. Jetti's talk was focused on tautomeric polymorphism, a less known type of polymorphism with an example of API, triclabendazole, a veterinary anthelmintic drug. Dr. Jetti presented two polymorphic forms and various co-crystal and salts of triclabendazole in which the API existing as either two tautomeric forms.[6] Through this study, Dr. Jetti showed that co-crystallization can be very helpful to ascertain the tautomeric and conformational preference of triclabendazole in the solid state.

Donor-acceptor complexes and organic semiconductor materials

In recent years, the design and fabrication of new semiconductor materials has moved beyond traditional inorganic based semiconductors. Tremendous amount of progress has been noted in the field of organic semiconductors and polymers, as they offer much wider scope for future developments of novel functional materials with tuneable optical, electrochemical, and electrical properties. Crystal engineering principles in particular has provided a great deal of help in designing this class of materials by providing a toolkit for modulating various interactions involved in directing their self-assembly and adjusting properties for better performance. Dr. Pritam Mukhopadhyay's research group at Jawaharlal Nehru University, New Delhi, India is working towards the design and synthesis of novel functional organic material for charge transfer applications by modulating the inter- and intra-molecular donor-acceptor interactions. Dr. Mukhopadhyay discussed the design aspects of several functional materials synthesized by their research group for sensing, radical ion general and ferroelectric applications.[7] Dr. Suhrit Ghosh (Indian Association for the Cultivation of Science, Kolkata, India), discussed about the various design strategies adopted in their laboratory to facilitate the self-sorting of aromatic bis-(trialkoxybenzamide)-functionalized dialkoxynaphthalene (DAN) donor and napthalene-diimide (NDI) acceptor based chromophores and to avoid alternate donor-acceptor stacking.[8] Dr. Ghosh showed that, the self-sorting of donor-acceptor assembly can be achieved by a careful choice of amide side chain lengths of the donor and acceptor chromophores. Dr. Satish Patil's (Indian Institute of Science, Bangalore, India) discussed the application of crystal engineering principles in the design of organic semiconductor polymer materials. Dr. Patil showed that, the electronic transport properties of these molecular semiconductors can be fine tuned by modifying intermolecular interactions present in the solid by chemical substitution and/or by extending conjugation. Prof. Christian Kloc of Nanyang Technological University, Singapore, presented their recent research work on the design and synthesis of binary organic semiconductors compounds. Prof. Kloc discussed some the interesting examples of organic semiconductors and their properties studied by his research group.

Some applications of organic crystal engineering

The response of a material to the change in temperature determines its thermal properties such as thermal conductivity, thermal diffusivity, thermal expansion etc. Most of the solids usually show small thermal expansion with increase in temperature generally termed as positive thermal expansion (PTE). However, in some very unusual cases a decrease in volume with increase in temperature termed as the negative thermal expansion (NTE). Such a phenomenon is very rare in the case of organic solids. Dr. Binoy Krishna Saha (Pondicherry University, Pondicherry, India) presented a case study of 1,3,5-benzenetricarboxylic acid (BTA) and 2,6-dimethylaniline (DMA) co-crystal hydrate that shows negative thermal expansion along *b*-axis in a variable temperature experiments.[9] Dr. Huaqiang Zeng's research group at National University of Singapore, Singapore is working towards the design and synthesis of bio-inspired folding helices and macrocycles for their potential use in ion and water transport applications. Dr. Zeng explained that these foldamers are designed by incorporating suitable functional group in the molecular backbone that facilitates the formations of inward pointing intramolecular interactions and hence direct the folding of structural into helical or circular shapes.[10] Dr. Parthasarathi Dastidar, (Indian Association for the Cultivation of Science, Kolkata, India) presented the application of supramolecular synthons in synthesizing a series of organic-salt-based low molecular weight gelators derived from tert-butoxycarbonyl (Boc)-protected L-amino acids and dicyclohexyl/dibenzyl secondary amines. [11] Dr. Dastidar, discussed about the nitrobenzene gel of dicyclohexyammonium Boc-glycinate (GLY.1) synthesized in their laboratory that displayed remarkable load-bearing and self-healing properties at par with the clay- and polymer-based gels

Crystal Engineering of Co-ordination Compounds

Crystal engineering of co-ordination compounds involves the self-assembly of metal ions and organic ligands that leads to two different classes of co-ordination compounds. (1) The co-ordination complexes having metal ions linked to organic ligands that results in discrete molecular units with the supramolecular structure held by intermolecular interactions and (2) co-ordination polymers (or popularly known as metal organic frameworks) in which metal ions are linked through bridging organic ligands forming an extended polymeric network structure. The study of co-ordination compounds have attracted much attention in recent years due to their intriguing structures and potential applications in adsorption and separation, ion-exchange, gas storage, catalysis, and so on. Prof. Tong-Bu Lu (Sun Yat-Sen University, Guangzhou, China) presented work form some of their recent studies on the polyazamacrocyclic ligands (polyaza cryptands) based complexes and their utility in photocatalytic reactions. Prof. Lu showed that the polyaza cryptands, having a tripodal skeleton, contains two binding sites suitable for forming di-nuclear metal coordination complexes and can be utilized for the activation of nitriles and bicarbonates ligands.[12] Prof. Sandeep Verma's (Indian Institute of Technology Kanpur, Kanpur, India) research group has been working on the synthesis and characterization of novel supramolecular architecture based on metal-nucleobase complexes and study of their catalytic properties. Prof. Verma, showed that nucleobases can also be attached to the carbon nanotube (CNT) surface to obtain functionalized single-wall/multi-wall (sw/mw) CNTs and can be utilized for synthesizing metal-CNT hybrids.[13]

Crystal engineering of metal organic frameworks (MOFs) (co-ordination polymers)

Prof. T. S. Andy Hor's research group at Institute of Materials Science and Engineering, Singapore is working towards the synthesis and the applications of novel co-ordination polymers and other organometallic solids constructed using the flexible nitrogen-rich ligands such as N-heterocyclic carbenes designed in their laboratory. Prof. Hor discussed the catalytic applications of Iron(II) complexes synthesized from functionalized amine-pyrazolyl tripodal ligands for the cross-coupling of aryl-Grignard with alkyl halides under ambient conditions.[14] Prof. Rong Cao (Fujian Institute of Research on the Structure of Matter, Fuzhou, China) addressed the difficulties in construction of coordination polymers using flexible ligands. Prof. Cao pointed out several factors (number of rotable bonds, pH, temperature, solvent and counter ions) that affect the design and assembling of coordination polymers having flexible ligands. Prof. Cao also pointed out that, the high ligand flexibility makes the crystal structure determination of these CPs more difficult as they mostly leads to amorphous solids or shows high disorder in their crystal structures.[15] Prof. Xian-He Bu's (Nankai University, Tianjin, China) gave an overview of the progress made in their laboratory towards the design and synthesis of novel multi-functional coordination architectures designed from several organic ligands and various metal ions. Prof. Bu also discussed several functional aspects such as porosity, magnetic behavior and luminescent properties shown up by these metal-organic framework compounds.[16]

Metal organic frameworks obtained from functionalized imidazolate ligands and their analogues

Zeolitic imidazolate frameworks (ZIFs) are an important class of metal-organic frameworks composed of tetrahedral metal ions e.g. Zn(II) or Co(II), linked by substituted organic imidazole ligands that that gives an isomorphic 4-connected topology as zeolites. The tetrahedral metal ion provides the requisite zeolitic topology while, the functionalized imidazolate linkers provide required chemical/structural diversity to ZIFs for their potential industrial applications. Prof. Jian Zhang (Fujian Institute of Research on the Structure of Matter, Fuzhou, China) discussed some of the examples on zeolitic imidazolate frameworks (ZIF) obtained from various substituted imidazolate ligands. Prof. Zhang discussed about doping strategies employed to obtain anionic ZIFs (AZIFs) in which the tetrahedral Cu(I) centre is doped into ZIFs to replace Zn(II) or Co(II) sites in the neutral ZIFs.[17] Prof. Zhang also discussed about the partial substitution of imidazolate ligands in ZIFs by these modified imidazolate ligands to generate another subclass of ZIF known as TIF-As, and hybrid zeolitic imidazolate frameworks (HZIFs). Prof. Wei-Yin Sun from Nanjing University, Nanjing, China presented their work on the crystal engineering of metal-organic frameworks obtained using the 4-imidazole-containing ligands.[18] Prof. Sun showed that the 4-imidazolate, based frameworks, exhibits high chemical stability in organic solvents (boiling benzene, methanol), water and alkaline solution (up to 1 M NaOH) and also showed very good gas adsorption capabilities for CO_2, CH_4, N_2 and H_2. Prof. Dan Li's research group at Shantou University, Shantou, China has been working on the fabrication of various azolate based metal-organic clusters/cages/frameworks their characterization and studying various applications in storage, recognition and catalysis. Prof. Li discussed about the gyroidal Zn(II) MOFs (STU-1) with **gie** topology, obtained from imidazolate ligand (L=1,2-bis((5H-imidazol-4-yl)methylene) hydrazine).[19]

Crystal engineering of ammonium metal-formate frameworks (AMFs)

Prof. Zhe-Ming Wang, from Peking University, Beijing, China discussed about the ammonium metal-formate frameworks (AMFs), another subclass of metal organic frameworks (MOFs) and the study of their phase transitions behaviours and resultant dielectric anomalies. Prof. Wang discussed about the structural aspects of some of the ammonium-magnesium-formates based frameworks namely, $[NH_4][Mg(HCOO)_3]$, $[CH_3CH_2NH_4][Mg(HCOO)_3]$ and $[NH_3(CH_2)_4NH_3][Mg_2(HCOO)_6]$ synthesized in their laboratory.[20]

Crystal engineering of metal cluster based coordination polymers and complexes

Prof. Jie-Peng Zhang of Sun Yat-Sen University, Guangzhou, China presented the crystal engineering of a new series of 13 highly porous iso-reticular metal carboxylate frameworks, with nine-connected **ncb** topology constructed from the trinuclear $M_3(\mu_3\text{-}O)(RCO_2)_6(T)_3$/ $M_3(\mu_3\text{-}OH)(RCO_2)_6(T)_3$ clusters, (M = Cr, Fe, Co, Ni, etc.) using the pyridylbenzoates and naphthalenedicarboxylates linkers.[21] Prof. Zhang discussed about the simple geometrical approach employed for predicting the pore size/shape modulation of these frameworks obtained by systematically altering the length of the two types of linkers. Prof. A. Ramanan, (Indian Institute of Technology Delhi, New Delhi, India), highlighted the utility of metal-carboxylate synthons as a reliable synthon for the crystal engineering of novel coordination polymers. Prof. Ramanan, discussed about the supramolecular design and synthesis of polyoxomolybdate coordination polymers and other polyoxomolybdate metal-organic solids obtained under varying experimental conditions that are constructed using these metal-aminocarboxylate synthons.[22] Prof. Guo-Yu Yang's group at Fujian Institute of Research on the Structure of Matter, Fuzhou, China is working on synthesis of oxometalate clusters of transition metals, main group elements and lanthanides, and porous frameworks and non-linear optical materials constructed from these oxygen-based cluster units. Prof. Yang highlighted the difference and challenges associated with the synthesis of these cluster organic frameworks in comparison to MOFs.[23] Prof. Quan-Ming Wang (Xiamen University, Xiamen, China), discussed the synthesis of polynuclear coinage metal (Ag, Au etc) cluster complexes designed in their laboratory. Prof. Wang showed that, metal cluster complexes based phosphorescent luminophores are much advantageous as the emissive metal cluster core can be protected from quenching by suitable choice of peripheral ligands. Prof. Wang showed that, the various ligand protected coinage Au/Ag metal cluster complexes synthesized in their laboratory show very good phosphorescent properties both in solution and in the solid state at room temperature.[24] Prof. Xian-Ming Zhang of Shanxi Normal University, Linfen, China presented the topic of crystal engineering of novel copper clusters based coordination frameworks. Prof. Zhang discussed that, reducing ligands such as halide, pseudo-halides, N- and S-containing ligands under hydrothermal condition normally results in Cu(I) cluster compounds. However, a mixed-valence or Cu(II) cluster compounds can be obtained by suitable choice of hydrothermal reaction conditions. Prof. Zhang discussed structure and properties of various Cu_4S_3, Cu_5S_4, Cu_6S_4, $Cu_{19}S_{12}I_4$, Cu_4O, Cu_4Br_6 and Cu_8Br_6, based compounds synthesized by their research group.[25] Prof. S. Natarajan (Indian Institute of Science, Bangalore, India), discussed about the synthesis of novel open-framework compounds templated by the thiosulfate and borate anions designed in their laboratory. Prof. Natarajan pointed out that, mainly the silicates, arsenates, phosphites, sulphates, sulfites, selenates are being used in the preparation of open framework structures whereas, and there is no precedence of the use of thiosulfates and borates anions. Dr. Soumyajit Roy (Indian Institute of Science Education and Research, Kolkata, India), reviewed the subject of soft-oxometalates (SOMs). Dr. Roy also showed some of the examples and properties of soft-oxometalates studied by their research group.[26]

Homo and heterometallic 3d-4f Lanthanides based coordination compounds and metal–organic frameworks

Design and synthesis of Lanthanides based metal organic frameworks has attracted attention of many researchers due to their unusual structure and properties. The high spin ground states and high spin-orbit coupling of lanthanide metal ions make these compounds an attractive choice for making potential single-molecule magnets and single chain magnets. Prof. Peng Cheng from Nankai University, Tianjin, China discussed examples of some of the novel homo- and heterometallic (3*d*-4*f*) Lanthanides based metal–organic frameworks (Ln-MOFs) constructed from furan-2,5-dicarboxylic Acid (H_2FDA) designed in their laboratory and their luminescent and magnetic properties arising from 3*d* and/or 4*f* electrons.[27] Prof. La-Sheng

Long (Xiamen University, Xiamen, China), presented the construction of high-nuclearity 3*d*-4*f* metal clusters templated by anions generated in situ. Prof. Long emphasized that, these high nuclearity lanthanide-transition metal clusters not only act as the ideal model systems for understanding the magnetic interactions between *d*- and *f*-electrons, but also exhibit unique properties in comparisons to their homo-metallic analogues or their lower nuclearity cognates.[28]

Applications of metal organic frameworks in asymmetric catalysis

The uniform porosity, adjustable pore size and easily accessible catalytic sites make MOFs a suitable choice as catalysts for performing various molecular transformations. New functionalized materials can be constructed by integration of well-known and efficient homogeneous catalysts (such as, metallosalens, metalloporpyrins and Ti-BINOLate complexes) into MOFs for making them more effective for catalysis. There are very few research groups working on incorporating such molecular catalysts into the MOFs for exploring them for catalytic applications, especially in asymmetric catalysis. Prof. Yong Cui (Shanghai Jiaotong University, Shanghai, China), presented the design and synthesis of dicarboxyl/pyridyl-functionalized chiral metallosalen frameworks for asymmetric catalysis and separation studied in their research group. Prof. Cui, discussed, the synthesis $[Zn_8L_4Cl_8]$ framework obtained by the self-assembly of homo-chiral enantiopure pyridyl functionalized ligand H_2L (prepared by the Schiff base condensation of 5-tert-butyl-3-(4-vinylpyridyl)salicylaldehyde and enantiopure 1,2-diaminocyclohexane followed by reduction with NaBH4) with $ZnCl_2$.[29]

Applications of metal organic frameworks in solid state reactions

Prof. J. J. Vittal (National University of Singapore, Singapore), highlighted the application of coordination polymers in performing [2+2] photochemical cycloaddition reactions. Prof. Vittal showed that chemical reactivity of coordination polymers can be exploited for their potential applications in the regio- and stereo-selective synthesis of organic compounds that cannot be easily obtained by traditional synthetic routes. Prof. Vittal discussed the single-crystal-to-single-crystal [2+2] photodimerization reactions of coordination polymers composed of interdigitated pillared 2D network of 4-styrylpyridine (4-spy) units resulting in 100% conversion of 4-spy ligand into 1,3-bis(4’-pyridyl)-2,4-bis(phenyl)cyclobutane.[30] Prof. Miao Du (Tianjin Normal University, Tianjin, China), discussed the topics of single-crystal to single-crystal transformation induced by external stimuli in the self assembly of coordination polymers. Prof. Du presented the issue of supramolecular isomerism and structural conversion observed between the coordination compounds obtained 3,5-bis-(2-pyridyl)-4-amino-1,2,4-triazole (2-bpt) with silver(I)nitrate.[31]

Porous Organic Frameworks and Covalent Organic Frameworks

Prof. Guang-Shan Zhu's group at Jilin University, Jilin, China has been working on the synthesis of novel class of porous organic materials, namely the porous aromatic frameworks (PAFs) and the study of their membranes for applications in gas storage and gas separation technology. Prof. Zhu discussed some of the porous aromatic frameworks namely, PAF-1, PAF-2 and PAF-36 designed and synthesized in their laboratory. Prof. Zhu presented that the PAF-1 synthesized from tetrakis(4-bromophenyl)methane using the nickel(0)-catalyzed Yamomoto-type Ullmann cross-coupling reaction showing very good gas storage properties with high Langmuir surface area of 71 m^2 g^{-1}.[32] Covalent organic frameworks (COFs) belong to another class of porous materials having extended organic structures. Dr. Rahul Banerjee (CSIR-National Chemical Laboratory, Pune, India) and co-workers showed that a very stable and crystalline covalent organic frameworks (COFs) can be obtained with the help of new synthetic strategy involving the use of a combination of reversible and irreversible organic reactions.[33]

3D Electron Diffraction from Transmission Electron Microscope (TEM)

Prof. Shilun Qiu, discussed about the application of novel structure determination method employing the 3D electron diffraction (ED) data obtained from specially designed transmission electron microscope (TEM) in obtaining the structural details of micro-size porous crystalline materials such as Zeolites and MOFs. Prof. Qui showed that, the 3D electron diffraction technique could be very useful for obtaining valuable structure information even for the porous organic framework materials having extremely short life time under electron beams. Followed by this; Diliang Zhang from Prof. Qiu's research group presented a short tutorial on structure solution of porous crystalline materials by 3D electron diffraction using TEM.

The 2nd CISSCE symposium was another very successful meeting for the crystal engineering community in the south Asian region. Leading experts from the participant countries with diverse research interests had the opportunity to discuss, exchange ideas and experiences, establishing new partnerships.

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