Chemical Crystallography and Crystal Engineering in India

Crystal engineering, as defined by G. R. Desiraju in 1989, is the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties. The subject therefore consists of three different enterprises: (1) understanding interactions; (2) formulating design strategies for new solids; (3) property enhancement towards functional materials. These three stages are both distinct and interconnected and all stages are needed to obtain new solids with desired properties. Because of the very general nature of the sequence, Interactions $\rightarrow$ Structure $\rightarrow$ Properties, crystal engineering has become an umbrella discipline, which draws into its fold several current themes of scientific interest. Here we have chosen to describe the research in crystal engineering that is ongoing in India. The distinct yet interconnected nature of the subject is matched by the distinct yet interconnected nature of all the research groups in India working on many attributes of crystal engineering.

G. R. Desiraju is an organic chemist by training and perhaps one of the first crystallographers in India with a completely chemistry background. He has played a major role in the discovery, development and growth of the subject of crystal engineering. He is noted among chemists and crystallographers for his work on C–H•••O hydrogen bonding. Over the years he wrote many monographs and reviews related to crystal engineering. In crystals, recurring and thus robust recognition patterns between molecules mediated by non-covalent interactions are termed supramolecular synthons, defined by Desiraju in 1995. In the beginning of his career, Desiraju's research was devoted to establishing the new concepts of weak interactions and supramolecular synthons. In recent years, his research focuses on the consolidation and validation of the concepts and postulates in crystal engineering. Currently, he focuses on exploring the concept of structural landscape in crystal engineering, design strategies to achieve multi component single crystals (cocrystals), halogen bonding, nanoindentation studies of molecular crystals, cocrystal screening, polymorphism and pharmaceutical cocrystals.

Following G. R. Desiraju's work, a vertical take-off of the subject of crystal engineering happened in India during the last two decades. Over 50 research groups in India are actively pursuing research in crystal engineering and its allied fields such as host-guest complexes, network solids, pharmaceutical salts, hydrates, cocrystals, polymorphs, non-linear optical and magnetic materials, photo-luminescence, gas storage MOFs and solar cell devices. A. Nangia of University of Hyderabad and CSIR-NCL, Pune has been working on different topics of crystal engineering namely polymorphism, pharmaceutical cocrystals and design and synthesis of solid-state assemblies. T. N. Guru Row has been working on charge density analysis in molecular crystals in IISc, Bangalore. He is actively working on characterization and identification of the region of overlap between hydrogen bonds and van der Waals interactions, quantitative identification of the proton transfer region in organic crystals, evaluation of intermolecular interactions involving "organic fluorine", halogen bonding, interhalogen⋯interchalcogen interactions as structure directing components in crystal engineering. J. N. Moorthy from IIT-Kanpur has been working in the area of supramolecular chemistry and crystal engineering. His work focuses on guest-induced structural mimicry giving rise to multicomponent crystals and self-assembly based on charge-assisted hydrogen bonds. The central focus of P. Dastidar's (IACS, Kolkata) research is developing functional materials that range from organic to metal-organic to inorganic materials. He is involved in developing soft materials such as

supramolecular gels, functional coordination polymers and has also invented a process to improve the free-flow property of common salt through habit modification. C. M. Reddy is working in Indian Institute of Science Education and Research (IISER) Kolkata. His research interests focuses on mechanical properties of organic crystals which includes bending crystals. His group's research also includes other branch of crystal engineering such as solid-state pharmaceutical chemistry, pharmaceutical crystallography, mechanical properties and crystal growth and polymorphism in Active Pharmaceutical Ingredients (APIs). B. K. Saha in Pondicherry University has been focusing on the thermal expansion of organic crystals, host-guest chemistry in crystalline materials and solid-state photodimerization. Deepak Chopra works on *in situ* cryocrystallography and electron density analysis in molecular crystals at IISER, Bhopal. R. G. Gonnade, a scientist at CSIR-NCL, Pune, is actively working on organic crystal chemistry which covers the wide area in solid state chemistry ranging from polymorphism, structural phase transition and organic solid state reactions using single crystal X-ray crystallography. T. S. Thakur in CDRI, Lucknow, is interested in designing multicomponent crystals of drugs and pharmaceutically relevant compounds using supramolecular synthon approach, crystal structure prediction (CSP) and experimental charge density (ECD). Among the other groups working in the field of crystal engineering, B. Sarma from Tezpur University and R. Thakuria from Gauhati University are actively working on drug nucleation at the functionalized interface, organic nanocrystals and pharmaceutical crystallization

Metal Organic Frameworks (MOFs)/ Coordination Polymers (CPs)

In the last decade, research on the topic of metal organic frameworks (MOFs) has opened up extensively amongst the researchers in India. MOFs, also well-known as coordination polymers (CPs), are a class of hybrid materials formed by the self-assembly of metal ions or clusters and polydentate bridging ligands, typically under mild conditions. Due to virtually limitless combinations of metals and ligands, and the void space within the networks, these types of materials have been widely employed for gas storage, catalysis, optical applications, separations, sensing and light-harvesting. Thanks to the concept of crystal engineering, by the judicious selection of the metal node and the linker units, one can easily tune the functionality and the porosity of the MOFs/CPs. A lot of research groups across India are currently working on MOFs/CPs based research. P. K. Bharadwaj at IIT, Kanpur is actively working on the chemistry involving the synthesis of MOFs/CPs. His research group has used MOFs for the storage of gases of strategic importance and used some of these materials as heterogeneous catalysts and for proton conduction. V. Chandrasekhar at IIT, Kanpur is working on the synthesis of magnetic MOFs and single molecule magnets. S. Natarajan at IISc, Bangalore has carried out mechanistic studies to correlate the principles of coordination chemistry using the MOFs/CPs structures. Ligand exchange reactions, luminescence and magnetic studies are further being done on such solid materials. R. Murugavel's group at IIT, Bombay focuses on the development of suitable thermally unstable molecular precursors for ceramic phosphates, and the generation of functional secondary building units of zeolites, thereby unraveling the structure. S. Verma's (IIT, Kanpur) research interest is based on the designing of supramolecules, clusters, and MOFs/CPs using linkers of biological significance, thereby introducing the idea of bio-MOFs/CPs. P. S. Mukherjee at IISc, Bangalore has been working on the crystal engineering aspects of organometallic materials, organic nano structures, molecular sensors and catalysis in nanocages. A. Ramanan's (IIT, Delhi) research activity highlights the design and synthesis of MOFs for separation based applications. K. Biradha's research at IIT-Kharagpur highlights topochemical solid state reactions and metal organic gels. R. Banerjee (CSIR-NCL, Pune) is actively working on the synthesis

and design of functional porous MOFs, porous organic cages and covalent organic frameworks (COFs) for gas storage, CO_2 capture, separation, catalysis, proton conductivity, fuel cell applications and drug delivery. Similarly, T. K. Maji's (JNCASR, Bangalore) work also highlights the synthesis and the structural characterization of MOFs/CPs for gas storage, separation, catalysis, optical and magnetic properties. S. Ghosh's (IISER, Pune) research interest is based on synthesis of MOFs/CPs for separation, gas storage, conductivity, sensing, chemical industry, energy and environmental applications. S. Konar (IISER, Bhopal) is interested in designing nanoscopic molecular clusters, cages and MOFs for materials application. The overarching objective of S. Roy's (IISER, Kolkata) group is to understand how simple interactions can lead to complex materials such as MOFs, soft-oxometalates (SOMs), and polyoxometalates (POMs) in photo-catalysis. R. Mondal (IACS, Kolkata) and D. Ghosal (Jadavpur University) work on the synthesis of functional porous MOFs/CPs and supramolecular materials as storage materials. Similarly, M. C. Das (IIT, Kharagpur), and S. P. Biswas (IIT, Guwahati) focus on the application of MOFs for gas/vapor/liquid adsorption, CO_2 capture, proton conducting membranes for fuel cells, heterogeneous catalysis and sensing. Considering the unique properties and the versatile application of MOFs/CPs, this particular research area in crystal engineering is expected to develop considerably in the near future.

Further reading

1. G. R. Desiraju, Crystal Engineering. The Design of Organic Solids; Elsevier: Amsterdam, **1989**
2. G. R. Desiraju, *J. Am. Chem. Soc.* **2013**, *135*, 9952-9967
3. K. Banerjee, *Nature*, **1930**, 125, 456.
4. G. R. Desiraju, *J. Indian Inst. Sci.* **2014,** *90*. 1-6
5. G. R. Desiraju, *Angew. Chem., Int. Ed.,* **1995**, *34*, 2311–232 (b) G. R. Desiraju, *Angew. Chem. Int. Ed.,* **2007**, *46*, 8342–8356
6. S. Tothadi, G. R. Desiraju, *Chem. Commun.* **2013,** *49*, 7791-7793 (b) R. Dubey, N. A. Mir, G. R. Desiraju, *IUCrJ*, **2016**, *3*, 102-107 (c) M. K. Mishra, U. Ramamurty, G. R. Desiraju, A. D. Bond, *Angew. Chem., Int. Ed.* **2014**, *53*, 13102−13105. (d) S. P. Gopi, S. Ganguly, G. R. Desiraju, *Mol. Pharmaceutics*, **2016**, *13*, 3590–3594.
7. A. Nangia *Acc. Chem. Res.*, **2008**, *41*, 595. (b) G. Bolla, A. Nangia, *Chem. Commun.* **2015,** *51*, 15578-15581
8. S. P. Thomas, M. S. Pavan, T. N. G. Row, *Chem. Commun.***2014**, *50*, 49-51 (b) D. Chopra, T. N. G. Row, *CrystEngComm* **2011**, *13*, 2175−2186.
9. J. N. Moorthy, P. Natarajan, P. Venugopalan, *Chem. Commun.* **2010**, *46*, 3574-3576
10. P. Dastidar, *Chem*. *Soc*. *Rev*. **2008**, *37*, 2699-2715.
11. S. Ghosh, C. M. Reddy, *Angew. Chem., Int. Ed.,***2012** *51*, 10319-10323 (b) G. R Krishna, R. Devarapalli, G. Lal, C. M. Reddy *J. Am. Chem. Soc.* **2016,** *138*, 13561-13567
12. S. Bhattacharya, B. K. Saha, *Cryst. Growth Des.* **2013,** *13*, 3299-3302
13. D. Chopra, *Cryst. Growth Des.***2012***, 12*, 541-546
14. R. Tamura, S. Iwama, R. G. Gonnade, *CrystEngComm.,* **2011**, *13*, 5269 -5280
15. T.S Thakur, S.S. Singh, **2015**, *15*, 7, 3280-3292
16. B. Saikia, P. Bora, R. Kharioda, B. Sarma, *Cryst. Growth Des.* **2015**, 15, 5593-5603
17. K. K Sarmah, A. Sarma, K. Roy, D. R. Rao, R. Thakuria, *Cryst. Growth Des* **2016**,*16*, 1047-1055
18. 1. V. Chandrasekhar, B. Murugesapandian, *Acc. Chem. Res.*, **2009**, *42*, 1047-1062.
19. S. Sen, N. N. Nair, T. Yamada, H. Kitagawa, P. K. Bharadwaj, *J. Am. Chem. Soc.*, **2012**, *134*, 19432-19437.
20. P. Mahata, D. Sarma, C. Madhu, A. Sundaresen, S. Natarajan, *Dalton Trans.*, **2011**, *40*, 1952-1960.

21. A. C. Kalita, N. Gogoi, R. Jangir, S. Kuppuswamy, M. G. Walawalkar, R. Murugavel, *Inorg. Chem.*, **2014**, *53*, 8959-8969.
22. S. Verma, A. K. Mishra, J. Kumar, *Acc. Chem. Res.*, **2010**, *43*, 79-91.
23. Howlader, P. Das, E. Zangrando, P. S. Mukherjee, *J. Am. Chem. Soc.,* **2016**, *138*, 1668-1676.
24. K. Biradha, A. Ramanan, J. Vittal, *Cryst. Growth Des.*, **2009**, *9*, 2969-2970.
25. (a) K Biradha, R Santra *Chem*. *Soc*. *Rev*. 2013, 42, 950-967 (b) S. Samai, K. Biradha *Chem. Mater.*, 24, 1165-1173
26. S. C. Sahoo, T. Kundu, R. Banerjee, *J. Am. Chem. Soc.,* **2011**, *133*, 17950-17958.
27. R. Halder, R. Matsuda, S. Kitagawa, S. J. George, T. K. Maji, *Angew. Chem. Int. Ed.,* **2014**, *126*, 11966-11971.
28. S. S. Nagarkar, S. M. Unni, A. Sharma, S. Kurungoot, S. K. Ghosh, *Angew. Chem. Int. Ed.*, **2014**, *53*, 2638-2642.
29. P. Rangaraj, S. Parshamoni, S. Konar, *Chem. Commun.*, **2015**, *51*, 15526-15529.
30. K. Das, S. Roy, *Chem. Asian J.*, **2015**, *10*, 1884-1891.
31. S. Bala, S. Bhattacharya, A. Goswami, A. Adhikary, S. Konar, R. Mondal, *Cryst. Growth Des.*, **2014**, *14*, 6391-6398.
32. B. Bhattacharya, A. Halder, L. Paul, S. Chakrabarti, D. Ghosal, *Chem. Eur. J.*, **2016**, *22*, 14998-15005.
33. A. Pal, S. Chand, S. Senthilkumar, S. Neogi, M. C. Das, *CrystEngComm.*, **2016**, *18*, 4323-4335.
34. R. Dalapati, B. Sakthivel, A. Dhakshinamoorthy, A. Buragohain, A. Bhunia, C. Janiak, S. Biswas, *CrystEngComm***, 2016**, *18*, 7855-7864.