

Dario Braga,^{*a} Gautam R. Desiraju,^b Joel S. Miller,^c A. Guy Orpen^d and Sarah (Sally) L. Price^e

^aDipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy. E-mail: dbraga@ciam.unibo.it

^bSchool of Chemistry, University of Hyderabad, Hyderabad 500 046, India. E-mail: desiraju@uohyd.ernet.in

^cDepartment of Chemistry, University of Utah, Salt Lake City UT 84112-0850, USA. E-mail: jsmiller@chem.utah.edu

^dSchool of Chemistry, University of Bristol, Bristol, UK BS8 1TS. E-mail: guy.orpen@bristol.ac.uk

^eCentre for Theoretical and Computational Chemistry, Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ. E-mail: s.l.price@ucl.ac.uk

Received 30th July 2002, Accepted 16th August 2002

Published on the Web 30th August 2002

The first *CrystEngComm* discussion meeting on crystal engineering has demonstrated that the field has reached maturity in some areas (for example: design strategies, characterization of solid compounds, topological analysis of weak and strong non-covalent interactions), while the quest for novel properties engineered at molecular and supramolecular levels has only recently begun and the need for further research efforts is strongly felt. This Highlight article aims to provide a forward look and a constructive discussion of the prospects for future developments of crystal engineering as a bridge between supramolecular and molecular materials chemistry.

Dario Braga is Professor of Chemistry at the University of Bologna and Director of Bologna University College. He was awarded the Nasini Medal from the SCI and the FEDERCHIMICA prize. Dario Braga is currently Scientific Editor of *CrystEngComm*. His main scientific interests are in gas–solid and solid–solid reactions and in the crystal engineering exploitation of hydrogen bonding interaction between ions.



Dario Braga

Gautam R. Desiraju is Professor of Chemistry at the University of Hyderabad, India and member of the editorial board of *CrystEngComm*. He has received the



Gautam R. Desiraju

Third World Academy of Sciences Award in Chemistry and a Michael Visiting Professorship of the Weitzmann Institute of Sciences. Recently he was the recipient of a Ranbaxy Award in pharmaceutical sciences. His research interests are in the area of structural and supramolecular chemistry and include crystal engineering and drug design.

Joel S. Miller is a Distinguished Professor in the Department of Chemistry at the University of Utah. He is on the advisory boards of *Inorganic Chemistry*, *Advanced Materials*, *Chemistry-European Journal* and *Journal of Materials Chemistry* and is a member of the *Inorganic Synthesis Corporation*. He is a member of the editorial board of *CrystEngComm*. He was the recipient of the 2000 American Chemical Society's Chemistry of Materials Award for his discoveries in the area of molecule-based magnets.



Joel S. Miller

Guy Orpen is Head of the School of Chemistry and Professor of Structural Chemistry at Bristol University. He has been awarded the Meldola and Corday–Morgan Medals and Tilden Lectureship of the Royal Society of Chemistry. In 2000–2001 he held a Royal Society Leverhulme Senior Research Fellowship. He is author and co-author of over 400 research papers in the field of structural chemistry and is a member of the editorial board of *CrystEngComm*.



A. Guy Orpen

Sally Price is Professor of Physical Chemistry at University College London, and is a leading member of their Centre for Theoretical and Computational Chemistry. She is a member of the editorial board of *CrystEngComm*. Her initial scientific interest in the theory of intermolecular forces, and the development of realistic model intermolecular potentials, forms the basis for her current work on computational crystal structure and property prediction.



Sarah L. Price

Introduction

Crystal engineering is a flourishing field of research in modern chemistry, practised by scientists with interests in the modelling, design, synthesis and applications of crystalline solids with predefined and desired aggregation of molecules and ions.¹ The bottom-up construction of functional materials from molecules or ions is at the core of modern crystal engineering.² The idea is that of attaining collective crystal properties *via* an adequate choice of the building blocks and the growth of desired crystal structures in appropriate forms.³ Although the subject of crystal engineering is more than 30 years old,⁴ it has evolved considerably in recent times towards the interface between the supramolecular and solid state sciences.⁵ In this sense, it lies at the intersection of the 'top-down' and 'bottom-up' approaches towards materials design and fabrication. The area of crystal engineering is, therefore, highly interdisciplinary and attracts contributions from many traditional areas: organic chemistry, inorganic and organometallic chemistry, theoretical chemistry, crystallography and crystal growth. An ever-increasing number of scientists are directing their attention towards crystal engineering both as a means of developing sophisticated devices, and to learn how to control self-assembly and molecular recognition. Implicit in all this is an attempt to understand fundamental issues of nucleation and crystal growth.

A timely opportunity to discuss the state of the art in the field has been provided by the first *CrystEngComm* discussion meeting. The meeting focused on the topics of major undertaking at the beginning of 2002: polymorphism; intermolecular interactions; modelling crystals and theoretical crystal structure generation; synthesis of new structures and building strategies; crystal nucleation and growth; solid state reactivity, design and exploitation of the properties of molecular solids. The broad range of topics discussed at the meeting reflected the strong interdisciplinary character of this field and demonstrated that a need for a *discussion* was felt strongly by the crystal engineering community in this rapidly developing research area. The objective of this Highlight is twofold: on the one hand it should wrap together and summarise the subject matter of the five reviews and thirty regular papers presented and the meeting, whilst, on the other hand, attempting to envisage how the field will develop in the near future.

Properties and synthesis of molecular crystals

The application of crystal engineering will rest both on the ability to design and build crystal structures and the ability to interpret and exploit the properties of those crystal structures. The properties of crystalline matter are manifold and diverse. In this selection of papers those properties assessed include reactivity, optical, and electrical properties, and the synthetic efforts involve coordination networks from solution and inclusion chemistry in both molecular and extended lattice solids.

The exploitation of the reactivity of molecular crystals lies close to the origins of crystal engineering and is at the heart of the work of Fumio Toda as expounded in his Highlight article.⁶ In a series of illustrative examples he describes the application of host-guest chemistry in a variety of crystalline organic inclusion compounds. Remarkable inclusion compounds in which chiral crystal structures emerge from either racemic or achiral molecules are discussed and their ability to exchange guests is illustrated. The application of such compounds to the synthesis of species in which the crystal structure chirality is imprinted upon the (achiral) molecular components is an entrancing one. The realisation of a related strategy is achieved in a modified form in the case where an achiral guest undergoes photochemical reactions which are highly stereospecific when

carried out in a chiral crystalline phase and the handedness of the local environment is recorded in the product. The thermal reactions of chiral allenes in their (chiral) crystals lead to stereospecific cyclisations in a series of cases summarised in this article, and the relationship between the crystal structure and the selectivity is considered.

The opportunity to isolate unusual forms of familiar molecular entities or to perturb equilibria through the environment present in inclusion compounds represents another potential application of these species.⁶ Toda shows how carboxylic acids may be isolated in diol hosts and their behaviour studied in the absence of the usual hydrogen bonded dimerisation or polymerisation. Similarly tautomerisation-based equilibria can be frozen through co-crystallization of the appropriate tautomeric molecules as guests in suitable chiral hosts. As with the carboxylic acid studies, the opportunities here are more fundamental than applied – to aid the study of physical organic chemistry rather than to enable organic synthesis.

Toda has explained how the properties of inclusion compounds may be exploited to provide efficient and selective routes to a range of organic species with controlled stereochemistry. The microenvironment provided by the crystalline state and in particular the space in host-guest species allows considerable control of the reaction chemistry of organic species. Among the possibilities demonstrated are enantioselectivity, a range of different reaction types (including cyclisation, isomerisation and tautomerisation) of guest species, and reactions of the hosts in the form of chiral switching. The applications to synthesis described here are significant and far-reaching but so too are those to physical organic chemistry. Examples of crystal-to-crystal conversions are shown in Fig. 1.

MacGillivray and co-workers take up the theme of the reactivity of molecular solids by reporting the chemistry of tetrapyridylcyclobutane derivatives that may be selectively synthesized through co-crystallization of 1,2-dipyridylethenes with suitable hydrogen bond donors and subsequent templated stereoselective photodimerisation of the ethenes to yield the desired polytopic ligand species. In this paper two Cu(II) species are prepared based on *rac*-tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb).⁷ The first species is a discrete di-copper complex and the second includes a bis-sulfate bridged one-dimensional coordination network.

Hardie and Ahmad report a review of the inclusion chemistry of CTV (cyclotrivertatrylene) exploring the various roles of the shape and coordination and hydrogen bonding properties that CTV have in this chemistry.⁸ They go on to describe studies of the inclusion chemistry of CTV with transition metal species. In particular, they report preparation of an $[\text{Fe}(\text{OH}_2)_6]^{2+}/\text{H}_2\text{O}/\text{CH}_3\text{CN}/[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ salt in which the iron complex and the free water are involved in a hydrogen bond network linking the CTV molecules into a layer network. The CTV molecules further interact through arene-arene interactions forming arene-rich clusters in the structure. The similarities of this structure and that of the $[\text{Sr}(\text{OH}_2)_8]^{2+}$ analogue are striking. Similarly, they show that an $[\text{Ag}(\text{OH}_2)_2]^+/\text{H}_2\text{O}/\text{CH}_3\text{CN}/[\text{CB}_{11}\text{H}_{12}]^-$ system yields a structure isomorphous with that of a Na/DMF species. This observation of structural repetition with diverse chemical compositions is interesting and potentially important with the prospect of solid solutions of varied composition being in sight and the consequent novel properties arising.

Cole and Kreiling⁹ present work focused on the NLO properties of TCNQ derivatives and seek both structure/property relationships and the exploitation of these molecular properties in inducing non-linear (second harmonic generation, SHG) properties in the solid state. The structure/property relationship work is based on a survey of the Cambridge Structural Database (CSD) for suitable TCNQ derivatives. Various degrees of bond length alternation (BLA) in the quinoid (or zwitterionic) nucleus of the TCNQ derivative in the

of the range of structure types known for $\text{Ag}_2(\text{O}_2\text{CR})_2$ moieties in the CSD. The structural variability in these disilver moieties is striking as its similarity with the range of geometries known for carboxylic acids. The analogy and the structural mimicry it leads to clearly may have some useful applications in design strategies.

Formigué and co-workers report a study of the prospects of incorporating metal electron acceptor species into crystals containing an isostructural organic electron donor derived from tetrathiafulvalene.¹¹ They successfully prepared such a species by electrocrystallization and go some way to identifying the oxidation states of the component species. The success of this strategy may be helped by the consequences of fluorine segregation on the crystal structure formed. In effect, the shape and properties of the exterior of the molecular entities allow the central ethylene (or metal complex) moiety to be buried. The unusual salt does not have dramatic electrical conductivity properties but the proof-of-concept crystal structure may offer further opportunities to derive similar species with important electrical properties.

Kahr and co-workers report a series of studies on the optical properties of Ph_4X crystals ($\text{X} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ or Pb).¹² The properties reported include refractive index and optical rotation as well as induced optical properties such as electrogyration and electro-optic effects. This work clearly illustrates both the potential of molecular (organic) solids in offering properties not accessible in the conventional (inorganic) solid state, and also an understanding of how relatively small effects in an isostructural series can lead to substantial changes in the properties of the solids. Thus the sign of optical rotation changes within the series and its magnitude varies dramatically – in a way that can be plausibly related to the crystal structures. The importance of both classical (experimental) and computational studies of optical properties is emphasised in the work, not least because of the discovery of the substantial errors in the literature of the archetypal species.

Nucleation and growth, polymorphism, pseudo-polymorphism

The controlled preparation and characterization of different crystal forms of the same substance is one of the major issues of modern crystal engineering and solid state chemistry.¹³ Even though the discovery of polymorphs of molecular crystals or of their diverse solvate forms (*pseudo-polymorphs*) is often serendipitous, crystal polymorphism can, to some extent, be controlled.¹⁴ Indeed, it has been argued that the existence of more than one packing arrangement for the same molecular or ionic component(s) could be a major drawback for the purposed bottom-up construction of functional solids. Is polymorphism the *nemesis* of crystal engineering? This question has been addressed in the highlight by Davey *et al.*¹⁵ as well as in several contributions where a rational approach to polymorphism has been attempted.

The Highlight by Davey's group investigates aspects of the crystal nucleation process and tackles the relationship between intermolecular interactions in solution and in the solid-state, thus attempting a structural link between crystal structure and those solvent-mediated kinetic processes of molecular assembly on which nucleation is based. The following questions were asked by Davey in his Highlight. (i) Do critically sized clusters have to be crystalline or could they be amorphous? (ii) Do clusters exist with packings corresponding to all the potential polymorphs in a system? (iii) Are the cluster structures biased in any way by the nature of the solvent–solute interactions?

The process of crystallization involves a wide spectrum of procedures, such as supersaturation (a non-equilibrium stage that precedes the crystallization stage), salting out (addition of a common ion), evaporation of common organic solvents and

drowning out (the addition of a miscible non-solvent). The manner in which crystallization proceeds determines the outcome of the crystallization process, hence size and morphology of the crystals, or whether polymorphic modifications are obtained and the occurrence of solvates. The nature of the solvent–solute interactions, however, can play a significant role in determining whether an aggregate will evolve to a crystal or not. Through a number of examples Davey attempts to correlate the structure of clusters in solutions also in the case of polymorphic modifications. Although no actual direct data relate crystallinity to the formation of molecular clusters, the experiments on the templated nucleation of glycine and on the nucleation in other polymorphic systems such as dihydroxybenzoic acid (see Fig. 2) and sulfathiazole (see Fig. 3) suggest that molecular assembly in the liquid phase can indeed mirror the packings of the potential polymorphs that can be obtained from a crystallization process. The nature of the interactions between solvent and solute can play a significant role, as demonstrated in the case of saccharin. The relationship between *crystal growth units* and the intermolecular interactions that can be established between solute molecules and/or between these and the solvent is complex. In the cases discussed in the paper it is clear that molecular dimers are often common building blocks between solution and crystal and may act as a kind of 'structural messenger' between solution and crystal.

The paper by Steed and collaborators¹⁶ also addresses the issue of polymorphism. Their paper reports structural, thermal and NMR studies on the long known polymorphic modifications of GeHPh_3 and demonstrates the conversion of single crystals of the unstable β phase into the α form *via* a liquid phase thought to contain $(\text{GeHPh}_3)_2$ dimers, linked by a sixfold phenyl embrace. The nature of the intermolecular interactions bringing about this behaviour is discussed. Analogous behaviour is also found in the case of SiHPh_3 but not for CHPh_3 .

The paper by Grepioni and co-workers¹⁷ examines an intriguing case of concomitant polymorphism of organometallic solids and the existence of two isomorphous forms with different chemical compositions, which transform into the same substance upon thermal treatment. Crystallization of the organometallic cationic acid $[(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2\text{Co}^{\text{III}}]^+$ from acidic solutions produces two polymorphic crystals with the same chemical composition, namely $[(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2\text{Co}^{\text{III}}]^+[\text{Cl}^-]\cdot\text{H}_2\text{O}$, but different crystal structures and shape (called *cube* and *sword*). The sword-like crystals are isomorphous with the three-hydrated crystal $[(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})\text{Co}^{\text{III}}]\cdot 3\text{H}_2\text{O}$. All these three crystals transform into the anhydrous form $[(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})\text{Co}^{\text{III}}]$ upon thermal treatment.

The paper by Childs and Hagen¹⁸ describes a supramolecular aggregate formed by two molecules of the tri-carboxylic acid *cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid (Kemp's tri-acid, KTA) and four molecules of acetic acid. The aggregate is arranged in a centrosymmetric zero-dimensional (0D) motif while the 1D hydrogen bonded rod motif is

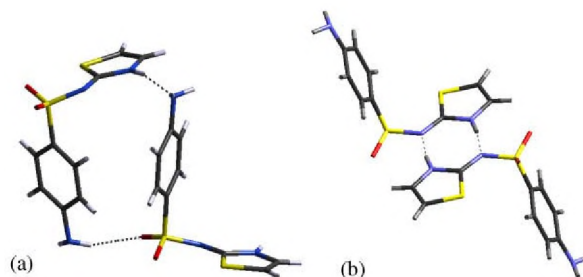


Fig. 2 Dimers of sulfathiazole described by Davey *et al.*¹⁵ (a) the dimer $R_2^2(18)$ of forms II, III and IV, and (b) the dimer $R_2^2(8)$ taken from form I.

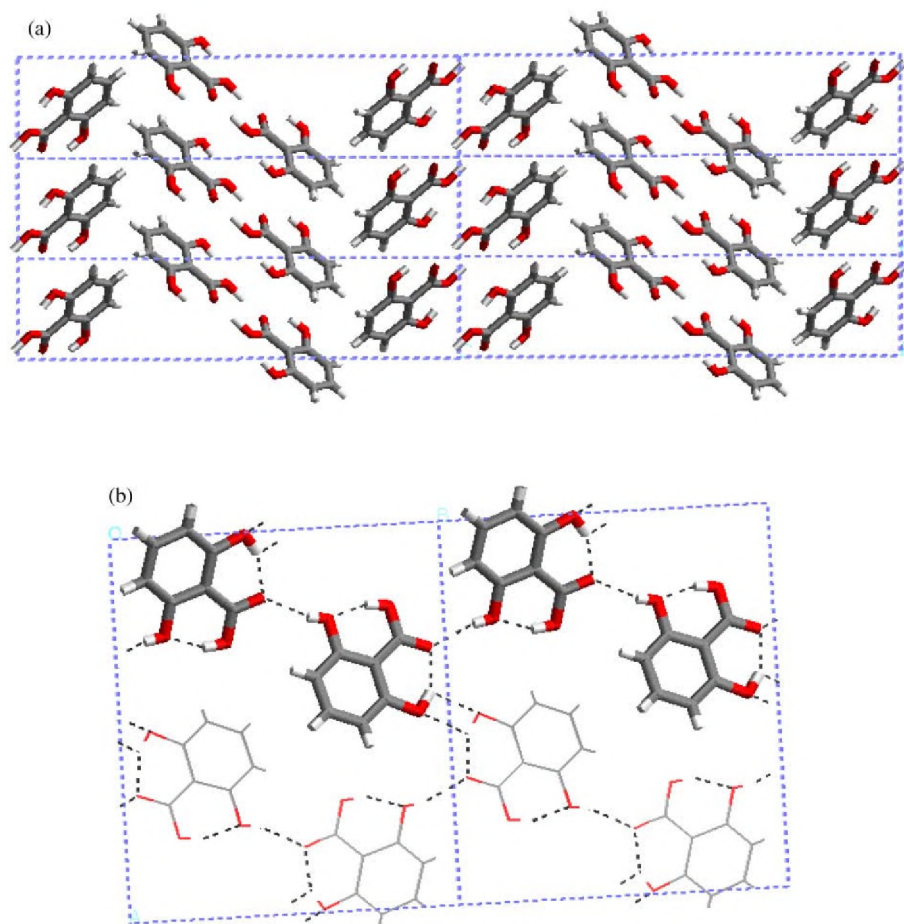


Fig. 3 Two polymorphic forms of 2,6-dihydroxybenzoic acid described by Davey *et al.*:¹⁵ (a) the metastable form is arranged in dimers, and (b) the stable form is arranged in a catemeric structure.

thermodynamically preferred by KTA under most conditions. The six-molecule 0D aggregate reported appears to behave like a large molecule with excellent self-recognition properties. Efficient centrosymmetric packing leads to maximized van der Waals contact and multiple C–H···O interactions between the aggregates.

The paper by Volkmer *et al.*¹⁹ describes the crystallization of (012) oriented calcite single crystals underneath monolayers of tetracarboxyresorc[4]arenes. These macromolecules possess several desirable properties, for example they form stable monolayers with finite-sized arrays of acidic residues, while the films exhibit novel supramolecular packing motifs. Crystal growth experiments with calcium carbonate have been performed underneath monolayers of *rccc*-5,11,17,23-tetracarboxy-4,6,10,12,16,18,22,24-octa-*O*-methyl-2,8,14,20-tetra(*n*-undecyl)resorc[4]arene spread at the air–water interface. It has been shown that the organic matrix influences the growth and morphology of the biomineral. In order to mimic structural aspects of the interaction between acidic proteins and biogenic calcite in calcified tissues, amphiphilic polyacids based on macrocyclic resorc[4]arene moieties have been employed in this study.

The paper by Beatty, Zaher and co-workers²⁰ investigates the crystal engineering of functional clay mimics. Clay-type materials with flexible pillars suitable for intercalation of small molecules or ions can be extremely useful. The authors investigate the utilization of a number of small organic acids that have mutually-orthogonal hydrogen bonding functionalities. The acids are allowed to react with secondary- and di-amines, leading to lamellar assemblies. These features are required for sheet formation that may serve as clay mimics (both in structure and in function) which we are investigating since these new clay mimics may be useful for organising

photopolymerisable substituents or for intercalation or host–guest applications.

The paper by Goldberg and collaborators²¹ extends previous studies of supramolecular porphyrin-based materials by investigating the assembly modes of [5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrinato]zinc with bipyridyl ligands. Supramolecular chemistry has been used as a stratagem to achieve the desired geometric order of porphyrin macrocycles in solution as well as in the solid state, and to synthesize a large variety of nanostructures as well as extended multiporphyrin architectures by non-covalent forces. The reactions lead to the formation of extended three-dimensional supramolecular architectures sustained by a concerted mechanism of metal–ligand (pyridyl–N···Zn) coordination and intermolecular O–H···OH and O–H···N hydrogen bonding interactions. It has been shown that the competing nature of these interactions, along with the different length and functionality of the ligand auxiliaries, affects the resulting motifs of the porphyrin–ligand supramolecular assembly.

The structural study reported by Fromm addresses the relationship between solution and solid state structures of a series of alkaline earth metal halide adducts.²² It is argued that, even though the alkaline earth metal iodides are known to behave ionically in water, their bonding situation is not that clear in tetrahydrofuran (thf) where they behave more like the MX₂ molecules known from the gas phase. Some alkaline earth metal iodide adducts, *i.e.* [MI₂(thf)₅] (M = Sr and Ba), [CaI₂(L)₄] (L = thf, H₂O), [Ba(OH)I(H₂O)₄] and [CaI₂(dme)(diglyme)] (dme = dimethoxyethane; diglyme = diethylene glycol dimethyl ether) have been investigated in detail. It has been shown that, excluding water, ether and polyether ligands apparently lead to solvate alkaline earth metal iodides that

behave as neutral molecules. In the case of water, which is capable of separating the ions and solvating them, the final outcome depends on the number of water molecules in the structure.

Hydrogen bonding, synthon robustness and applications

Hydrogen bonding is the key theme in this selection of short papers, and indeed the interaction is of major importance to the whole subject.²³ The paper by Le Questel and co-workers examines the relative hydrogen bond acceptor abilities of amino nitrogen and carbonyl oxygen in various chemical environments that probe both steric and electronic factors.²⁴ Both CSD²⁵ and *ab initio* theoretical methods are used. An acceptor like a tertiary amine is not so good if it is sterically hindered. All this brings to mind that solid state acidity and basicity depend not only on electronic but also on steric factors – unlike gas phase and solution measurements. This also allows one to recapitulate the so-called ‘Etter rules’ that imply a hierarchy of donor with acceptor matching in terms of strength.²⁶ How does one assess solid state donor and acceptor capabilities taking into account steric factors in addition to the electronic ones? Even if one could get a reliable scale of solid state donor and acceptor strengths, does crystallization proceed in this modular way? This is surely a question of major importance.

Hierarchy is implied in the design strategy of Nangia and co-workers²⁷ who substitute a carboxamido group, CONH₂, for a carboxyl group, CO₂H, in the expectation that the dimer synthon will be conserved. This expectation is realised and the extra H atom from the amide is ‘free’ to hydrogen bond to an adjacent phenyl ring, also conserved from the acid structure. The aim of the game is to specifically design an interaction, in this case the relatively exotic N–H⋯π hydrogen bond. The rather elaborate hydrogen bond network in the original 4-tritylbenzoic acid does not come tumbling down simply because an ‘extra’ hydrogen bond donor is present. Rather, this extra hydrogen atom seeks out the nearest available acceptor, in this case the multi-atom phenyl ring, without disturbing the overall packing. Structural repetition is ensured by the isolation of a second structure that shows the same interaction.

Hydrogen bonds can be put together to form supramolecular synthons, and then naturally comes the question of synthon robustness. Podesta and Orpen discuss the robustness of a hydrogen bonded synthon constructed with 4,4′-bipyridinium and a nickel dithiooxalate tecton.²⁸ A number of manipulations are carried out within the molecular framework but the synthon robustness is, happily, unaffected. Similar observations are reported by Aakerøy *et al.* who have studied hydrogen bonding in a family of oxime coordination compounds with Ag(I).²⁹ In both these examples, it is gratifying to note that hydrogen bond robustness can co-exist or at least not contradict the ligand-to-metal coordination bonds. The combination of coordination bonds and hydrogen bonds has much to offer the crystal engineer and clearly these present studies hint at more general studies in the future. On the flip side, lack of sufficient acidity in the selected donors and the consequent weakness of the desired N–H⋯N interactions is the probable reason why Pedireddi did not succeed in obtaining molecular complexes of malonamide, glutaramide and other amides with heterocyclic compounds like 4,4′-bipyridyl while the corresponding carboxylic acids readily furnished the corresponding adducts.³⁰ His experiment is somewhat similar to that of Nangia and co-workers²⁷ but the donor–acceptor mismatch proves to be the villain in his case. The building block concept is all very well in the elementary teaching and popularisation of crystal engineering but, in the end, it must be remembered that the analogy between crystal engineering and Lego block-type modularity can only be taken so far. Chemistry is not geometry.

These methodology-type papers culminate in the Highlight provided by Coppens *et al.*³¹ on the use of calixarene-based crystals in spectroscopy and time-resolved crystallography. The

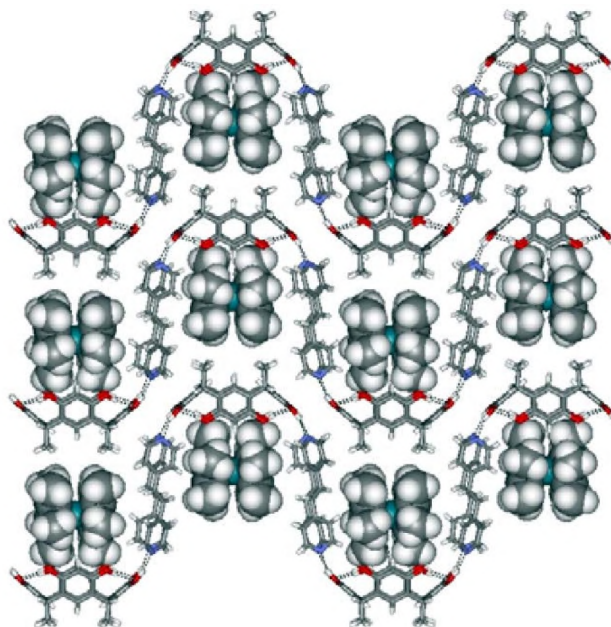


Fig. 4 Wavelike structure of [CMCR·2bpe]·DMR [bpe = *trans*-1,2-bis(4-pyridyl)ethylene; DMR = decamethylruthenocene] reported by Coppens *et al.*³¹

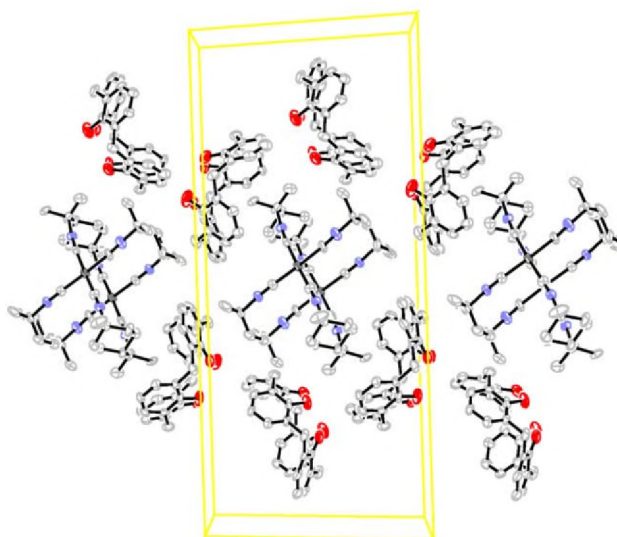


Fig. 5 Structure of the [Rh₂(dimen)₄]·(calix[4]arene-H)₂ salt reported by Coppens *et al.*³¹

Coppens paper consists of two parts: (i) the design of calixarene host–guest compounds with benzophenone (see Fig. 4), benzil, decamethylruthenocene and a binuclear Rh cationic complex (Fig. 5); and (ii) photochemical and photophysical measurements. Spectroscopists have used dilution in amorphous matrices to isolate photoactive molecules from each other and the authors argue convincingly that this can be done in supramolecular solids, that are crystals, without sacrificing three-dimensional periodicity. A number of structural and mechanistic issues are presented in this sophisticated study. Topological arguments are also used wherein hydrogen bonds are used to construct motifs such as a brick wall, more familiar in the coordination polymer area. It is heartening to note the nice conjunction between structure and properties. This work allows one to recollect the pioneering contributions of Gerhard Schmidt who gave the subject of crystal engineering its very name.⁴ Schmidt’s work revealed two important features about crystal engineering: (1) that both structure and function are

important, as is their inter-relationship; and (2) that both chemistry and crystallography come together in crystal engineering so that neither subject is subservient to the other in this synergy. The present paper of Coppens is but a natural extension of these philosophies, and practitioners of the subject would do well to note the many fine nuances that have been brought out here.³¹

Modelling crystals

A theory is tested by the accuracy of its predictions. Thus, we cannot really claim to understand crystal structures until we can reliably predict them. Ten years of experience starting from the simplest theory of crystal structures, essentially searching for the global minimum in the lattice energy, has shown that this is rarely sufficient. In his Highlight, Gavezzotti³² has identified the issues of accurately quantifying the relative thermodynamic stability of different crystal structures (see the energy of computed structures of dichlorobenzenes in Fig. 6), and then being able to establish how kinetic factors determine the existence of metastable polymorphs. Breaking this down further, Gavezzotti discusses how we will need to be able to accurately quantify inter- and intra-molecular forces, and develop sufficiently reliable theories to predict how these determine not only the thermodynamics of the different crystal structures but also the kinetics of their formation. The rates of nucleation and growth, and the barriers to transformations, all influence which metastable polymorphs could be observed.

The subtlety of polymorphism, which will make predicting it such a challenge, is nicely illustrated by the two polymorphs of a hydrogen malonate salt of a quinoline derivative, reported by Tedesco and co-workers.³³ The two polymorphs co-crystallize, and have very similar physicochemical properties, being only distinguishable by X-ray diffraction. The main packing motif of hydrogen bonding between the anions and cations shows an 'incredible similarity', and it is only the relative arrangement of these complex chain motifs that leads to the two structures being approximately related by a doubling of the unit cell in one direction. The new fingerprinting method introduced by Spackman and McKinnon would demonstrate this similarity very clearly.³⁴ The differences in the Hirshfeld 3D surfaces would show whereabouts the differences in packing were, and the similarity of the new form of 2D plot would emphasise the subtlety of the changes in the interatomic distances. This, like the co-crystallization, warns us that the energy differences between the two polymorphs must be negligible, and predicting such polymorphism will be too difficult to attempt in the near future. In the more usual range of crystal structures, the new 2D fingerprinting technique does give a graphic way of showing up the similarities and differences of crystal packings of

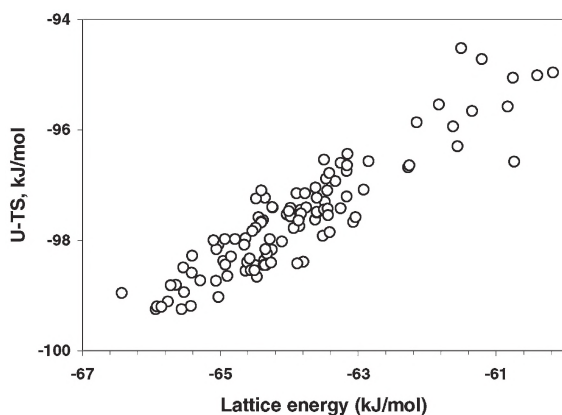


Fig. 6 Lattice energies, U , reported by Gavezzotti³² of many computer-generated crystal structures of dichlorobenzenes, bare and corrected with the lattice vibrational entropy term. Note the restricted energy range. (Lattice energy, $U/\text{kJ mol}^{-1}$ on lower axis would be better.)

molecules of very different sizes. The paper clearly shows its usefulness in discussing the variations in the crystal structures within, and between, families of molecules. It could have the potential for use in a more automated, quantitative fashion, possibly even in a more knowledge-based method of crystal structure prediction.

Gavezzotti's proposed solution to the problems of modelling the intermolecular interactions sufficiently accurately for polymorph prediction, by using the electronic wavefunction to evaluate the electrostatic and polarisation contributions to the lattice energies, and eventually the repulsion and dispersion terms, will require both developments in theory and computational power. The traditional isotropic atom-atom model of intermolecular interactions has brought us a long way, but the loss of its interpretability and transferability is a price that we will have to pay in the search for accuracy. Most intermolecular interactions are diffuse, and cannot be quantitatively associated with individual close contacts. We will need very molecule-specific models for interactions such as the $\text{H}\cdots\text{H}$ interaction in organometallic solid state structures. The investigation of this interaction in $\text{HMn}(\text{CO})_5$, by Calhorda and Costa,³⁵ illustrates the challenge involved in Gavezzotti's proposal of aiming for high accuracy in the electrostatic, induction, repulsion and dispersion terms for specific molecules. Even this will not be adequate when the division between inter- and intra-molecular forces becomes indistinct, as in the case of tetracyanoethylene anion dimers, investigated by Novoa *et al.*³⁶ The interaction within the dimer (at least) has sufficient characteristics of a bond that it would have to be modelled *ab initio* as an intra-molecular-type force, even though the dimer would not exist in isolation. In the debate about whether or not we should identify and classify interactions, we have to be aware that the divisions into types of bonding are not exact, but are for our convenience in discussion and to guide the choice of theoretical model. There are many interactions that fall in the grey regions between different prototypes, which will be particularly challenging to model to a level of high accuracy.

However, even in the region of weak intermolecular interactions, where we can have moderate confidence in relative lattice energies, the kinetic problem remains. This is illustrated by the attempt to rationalise the complex ($Z' = 4$) crystal structure of pyridine by Anghel and co-workers.³⁷ A significant number of simpler crystal structures are predicted to be more thermodynamically stable than the observed complex structure. The discovery of another polymorph with a simpler crystal structure by the Boese group is a nice illustration of the value of experimental/theoretical collaborations, although the new polymorph was essentially no more stable than the original form and not predicted. However, there is a tentative rationalisation of the occurrence of these two forms for this low melting point solid, in that simple estimates suggest the observed crystallites will grow faster.

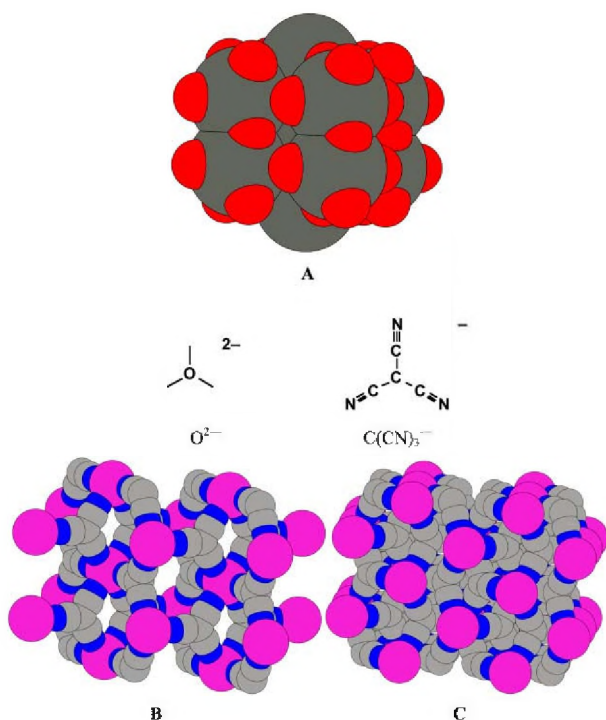
The problems of growing suitable single crystals for X-ray diffraction make the recent advances in solving molecular crystal structures from powder diffraction by Harris *et al.* particularly welcome.³⁸ The addition of lattice energy terms to help in guiding a Genetic Algorithm to finding the best fit to the laboratory powder diffraction data is clearly demonstrated on crystal structures with considerable conformational flexibility. The rapid development of this field is also illustrated by Tedesco and co-workers who obtained the structure of Terbinafine HCl from high resolution synchrotron data.³³ Undoubtedly, new powder diffraction techniques will provide the structures of many 'hard to grow' crystals. This, plus increased diligence in looking for polymorphs with more sensitive techniques, could well increase the challenge of polymorph prediction. There may well be some correlation with the difficulty in growing the crystal with the importance of kinetics in determining which of the energetically feasible

structures are seen. In chasing a full understanding of crystal structures and an ability to predict them, we may be chasing an ever-advancing target. All of these papers show that even current modelling methods have considerable practical use, and it is possible to predict some crystal structures. There is just so much more that needs to be done before we have a theory that can be adequately implemented to reliably predict crystal structures.

Coordination networks and properties

The eventual use of the new materials is discussed in several contributions with the key anticipated areas being as ion-exchange materials – as being the driving force of the paper reported by Schröder's group³⁹ – and the development of the means to study 1-D magnetic interactions – which typically cannot be disentangled from 2- and 3-D interactions, by the clever use host-guest interaction chemistry as described by Hulliger's group.⁴⁰ The development of porous materials for sorption, separations, and catalysis was briefly touched on in the paper from Yaghi's group.⁴¹ These and other applications are expected to draw further attention and study in the future.

Construction of 1-, 2- and 3-D structures primarily utilizing coordinate covalent interactions is one of several thrusts in this section of papers. While important examples of such structures, *e.g.* 2-D Hoffmann clathrates^{42a} and 3-D Prussian blues,^{42b} are well entrenched as part of the history of inorganic coordination chemistry, extension to new examples *via* the utilization of ligands capable of binding to more than one metal in a selective and controllable manner has led to a variety of solids with fascinating structural motifs. For example, the rutile TiO₂ possesses a planar tricoordinate oxide that bridges to three different Ti(IV) ions and as a consequence forms this important basic solid state structure **A**. Substitution of the tricoordinate oxide with the tricoordinate tricyanomethanide C(CN)₃[−] likewise, with, *e.g.* Mn(II), forms the same rutile motif, **B**. However, the larger size of C(CN)₃[−] with respect to O^{2−} mandates that the metal ions are substantially further apart [5.38 Å for Mn(II) *vs.* 2.96 Å for Ti(IV)] and this lengthening provides open space within the structural framework that in this situation enables a second, interpenetrating, lattice (**C**) to coexist.^{42c}



Yaghi *et al.*⁴¹ provided a short introduction to basic concepts and common structural motifs observed depending on the

coordination number of the metal ion and shape and number of metal ions that can be bound to the ligand. In general, a problem faced by those interested in creating network structures is that of network interpenetration. When interpenetration does not occur, however, the architecture may collapse upon removal of the solvent or guest molecules. A goal is, therefore, that of preparing highly porous materials that can withstand exchange of the guests. Yaghi showed that not only is this possible but also that the network functionality can be changed by varying the type and size of the spacers ('expansion and decoration of basic nets'). The use of metal carboxylate clusters as bridges provided the required rigid geometry that aids in directing the construction of open framework structures. For example, 'paddle wheel' clusters M(O₂CR)₄ have been used to produce low density structures (see Fig. 7). Similar building blocks were used by others to generate high density interpenetrating structures (see Fig. 8).^{42d} These compounds can take up very large amounts of guest molecules.

Proserpio and co-workers⁴³ explore the structures obtained from the employment of linear dinitriles of NCC_nH_{2n}CN (*n* = 2, 3, ..., 7) composition with Ag⁺ ions. In this system both 2-D (4.4) and 3-D diamond-like motifs are reported, with the latter only observed for even values of *n*. As *n* increases the separation between the Ag⁺ ions increases and the degree of interpenetration (parallel and inclined) increases and as many as six interpenetrating lattices is reported for *n* = 7.

Hosseini's group uses bis-amidinium dication to bridge two metal ion sites *via* hydrogen bonding.⁴⁴ Using d⁸ square planar (D_{4h}) [M(CN)₄]^{2−}, 1-D structures form, but 2-D structural motifs arise from octahedral (O_h) [M(CN)₆][−]. The details of the nature of the 2-D structure vary as *z* = 4− or 3− due to charge balance considerations. In the latter case the tris-chelate nature of the interaction leads to supramolecular chirality.

The use of weak Au⋯Au interactions enabled Raithby and co-workers⁴⁵ to identify (Ph₃P)Au(C=C(C₄H₂S)₂C=C)Au(PPh₃) among a series of five related compounds to form a 1-D polymeric structure in the solid state. They note that a monogold analogue possesses stronger Au⋯S and π⋯π interactions that are not evident in the several di-gold complexes they report. Nonetheless, the presence of Au⋯Au interactions depends on many features of the system, and Pt⋯Pt interactions are not observed for the related family of Pt(II) compounds.

Ruiz-Pérez and co-workers⁴⁶ manipulate the Cu^{II}(mal)₄ (H₂mal = malonic acid) building blocks with ancillary ligands, *e.g.* 4,4'-bipyridyl, capable of bridging two additional metal sites to form paramagnetic materials in which the magnetic behaviour is dominated by intra-tetramer spin interactions.

Schröder's group³⁹ studied the transformation Ag(4,4'-bipyridyl)NO₃ + BF₄[−] = Ag(4,4'-bipyridyl)BF₄ + NO₃[−] by several techniques as, owing to their low solubility, they are used as ion-exchange materials. The studies led to the conclusion that a solvent-mediated mechanism is operative. Both polymers are structurally characterized.

In another theme, exploitation of host-guest interaction chemistry enables Hulliger and colleagues⁴⁰ to study 1-D spin interactions. For example, perhydrotriphenylene forms 1-D chains with holes 1.5 nm in diameter. These channels are filled with paramagnetic 1,3,5-trithia-2,4,6-triazapentalenyl (*S* = 1/2) radicals, which corresponds to a 1:5 ratio. Using a Markov-like theory the average chain length of extended magnetic interactions of nine molecules is predicted and preliminary EPR data are reported.

Conclusions

The collection of papers reviewed in this joint Highlight demonstrates that crystal engineering has definitely expanded from its origins, which are rooted in the fields of inorganic and organic solid state chemistry and crystallography, to span

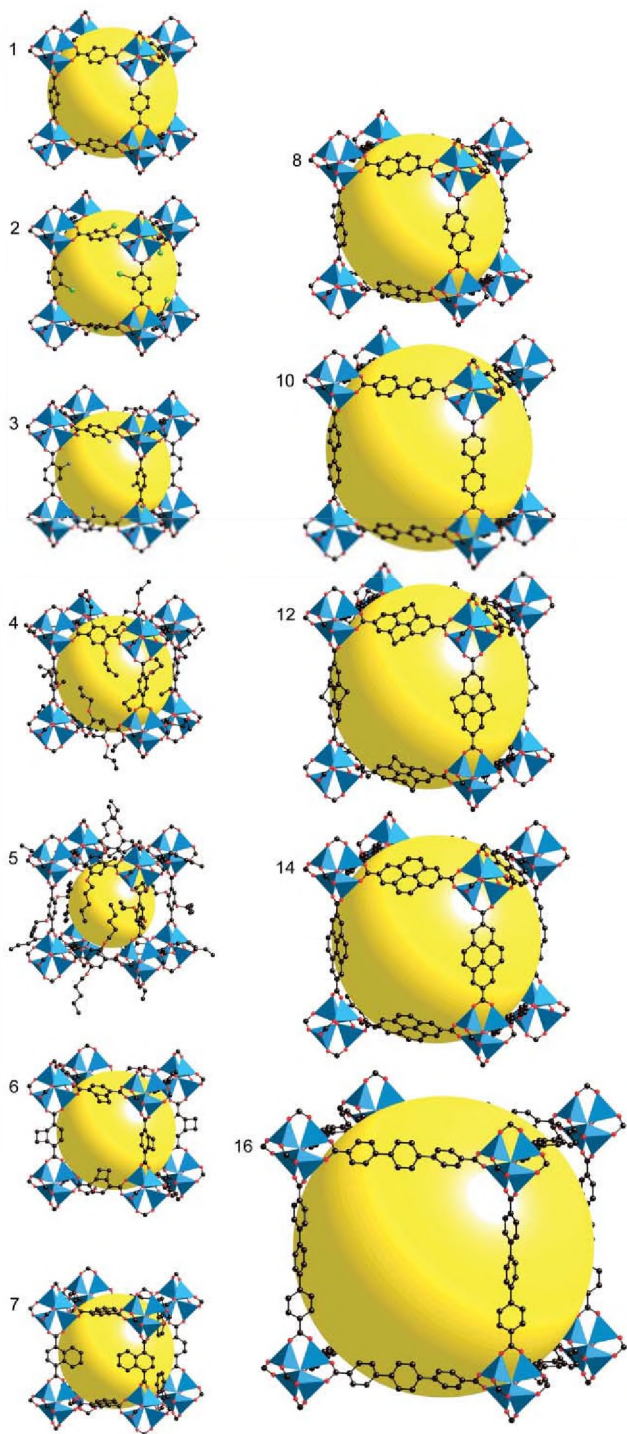


Fig. 7 Several structures having the same metal–organic framework topology have been synthesized by Yaghi *et al.*⁴¹ using exactly the same synthetic parameters except for the addition of the desired link.

many of the neighbouring areas in solid state and materials science. This development has not only provided a broader reference scheme to well established and productive research areas (such as, just to mention two ‘extremes’, the investigation of solid state reactivity and the design of molecule-based magnets and electrical conductors), but has also allowed the *cross fertilization* between distant research areas. This is true, for example, for network coordination chemistry *versus* the exploitation of weak non-covalent interactions, for the investigation of bulk properties *versus* the bottom-up control of crystal growth, for studies of polymorphism *versus* those of solid–gas reactivity and solvate formation, *etc.*

As pointed out in the Introduction, the evolution of crystal

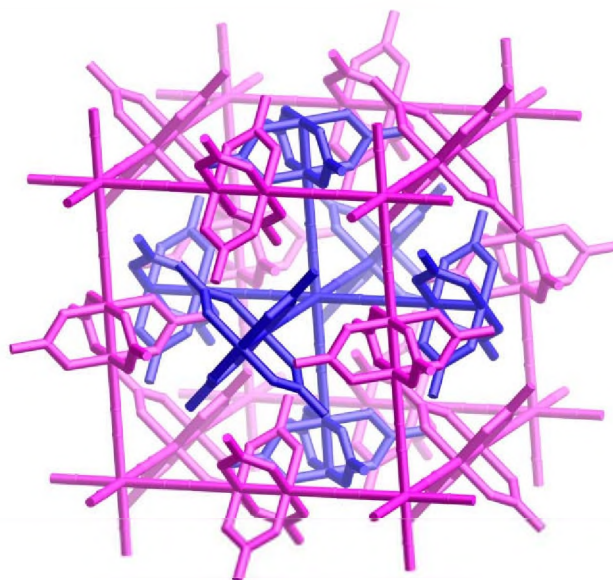


Fig. 8 Interpenetrating structure of $[\text{Ru}^{\text{III}}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}^{\text{III}}(\text{CN})_6]_3\text{M}(\text{O}_2\text{CR})_4$ containing $\text{M}(\text{O}_2\text{CR})_4$ ‘paddle wheels’.^{42d}

engineering is most likely the result of the cultural *hybridization* of supramolecular chemistry, *e.g.* the chemistry of extramolecular bonding, with the chemistry of molecular materials, *e.g.* the utilitarian, application-oriented side of molecular aggregation. It goes without saying that *crystal engineering* belongs to chemistry, as the chemist knows how to synthesize, isolate and characterize molecules and to assemble molecules in a bottom-up approach to larger and more complex aggregates. Crystal engineering shares with supramolecular chemistry the idea that the collective properties of the (solid) aggregates will depend upon the choice of intermolecular and inter-ion interactions between components and are attained *via* processes of self-recognition and assembly (although crystallization is often under kinetic control). Crystal engineering shares with materials chemistry the goal of preparing functionalised crystalline materials in order to obtain novel or improved physico-chemical properties. The applications can be diverse, for instance in non-linear optical technology, optoelectronics and photonics, in conductivity and magnetism, as well applications in catalysis, molecular traps, reservoirs, and sieves, solid state reactivity, and mechanics. The offspring of the hybridization process is this broad, burgeoning, boiling, albeit poorly defined, idea of ‘making crystals with a purpose’, with the epithet ‘making’ also encompassing the theoretical crystal structure generation and computational approach to polymorphism.

What is crystal engineering, or, more pointedly, what is crystal engineering in 2002? The question was asked several times during the Discussion. To some extent, it is a rhetorical question, since the field is still tumultuously expanding. In the materials chemistry area, crystal engineering is perceived as a working strategy, a utilitarian method with relevant interdisciplinary interactions with biology, informatics and physics. In the supramolecular chemistry area, crystal engineering is perceived as a way to exploit non-covalent interactions to assemble molecules in solid supermolecules. In the area of solid state reactivity, crystal engineering is seen as the tool that allows topochemical control of reactivity and stereochemistry, as well as the understanding and exploitation of solvent-free, environmentally more friendly reactions, and/or heterogeneous reactions with potentials for sensing and trapping of molecules or for the preparation of otherwise elusive molecules. In the theoretical chemistry area, the challenge of crystal engineering is to predict the outcome of a crystallization process, hoping that this knowledge will then suggest methods of control. In

the area of biology and biotechnology, crystal engineering is the investigation of the interaction between biological matrices and crystalline phases. For crystallography, crystal engineering provides the push and additional motivation to improve methods of data collection, data storage, data mining and, most importantly, to develop friendly and portable methods for direct structure determination from powder diffraction data. In the field of polymorphism, crystal engineering is perceived as a conceptual (and practical) way to tackle the relationship between kinetics and thermodynamics, to generate polymorphs and pseudo-polymorphs *on purpose* by a judicious choice of the crystallization conditions, and to practise ways to *trick* Nature into doing what the researcher needs.

All of these aspects, and many others touched on in the course of many lively discussions, are touched on by the papers collected in the special issue. They demonstrate that, in the year 2002, crystal engineering has grown to an all-purpose mature discipline, a science without borders, where the motivations can well be utilitarian and economical, but also aesthetical (when not artistic) and/or fuelled by pure, quintessential, scientific curiosity. Nor could it be otherwise: the tree wherefrom the fruits of useful materials and practical applications can be picked up, feeds on basic knowledge and on the results of fundamental studies.

Acknowledgements

The authors wish to thank the local organising committee of the *CrystEngComm* Discussion on 'Innovation in Crystal Engineering'. It was a pleasure to collaborate with Dr J. Humphrey, managing editor of *CrystEngComm*, in the preparation of this meeting. We are grateful to P. Mohammed for her efforts towards a smooth organisation of the meeting. We thank the University of Bristol and its staff (notably Dr John Jeffery, Dr Jon Charmant, Dr Chris Adams and Dr Tim Podesta) for support in the local organisation of the meeting and for providing an excellent site for the conference. We would like to thank Dr Neil Champness and Professor Philip Coppens for joining the *CrystEngComm* editorial board and for chairing sessions at the meeting. Finally, we acknowledge the Royal Society of Chemistry for having recognised crystal engineering as a strategic field of research, which deserves investment and support. This foresight was witnessed by the launch of the *CrystEngComm* three years ago.

References

- G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; See, for a recent general entry in the area of inorganic crystal engineering: *J. Chem. Soc., Dalton Trans.*, 2000, 3705 (whole issue); D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.
- D. Braga, F. Grepioni and A. G. Orpen, *Crystal Engineering: From Molecules and Crystals to Materials*, Kluwer Academic Publishers, Dordrecht, 1999; *The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry*, G. R. Desiraju, ed., Wiley, Chichester, 1996, vol. 2, p. 107; M. D. Hollingsworth, *Science*, 2002, **295**, 2410.
- J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.
- G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.
- J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, J. Wiley, Chichester, UK, 2000.
- F. Toda, *CrystEngComm*, 2002, **4**(40), 215; see also: K. Tanaka and F. Toda, *Chem. Rev.*, 2000, **100**, 1025 and refs. cited therein.
- T. D. Hamilton, G. S. Papaefstathiou and L. R. MacGillivray, *CrystEngComm*, 2002, **4**(41), 223.
- R. Ahmad and M. J. Hardie, *CrystEngComm*, 2002, **4**(42), 227.
- J. M. Cole and S. Kreiling, *CrystEngComm*, 2002, **4**(43), 232.
- L. Brammer, M. D. Burgard, M. D. Eddleston, C. S. Rodger, N. P. Rath and H. Adams, *CrystEngComm*, 2002, **4**(44), 239.
- O. J. Dautel, M. Fourmigué and E. Faulques, *CrystEngComm*, 2002, **4**(45), 249.
- K. Claborn, B. Kahr and W. Kaminsky, *CrystEngComm*, 2002, **4**(46), 252.
- J. Bernstein, R. J. Davey and J.-O. Henck, *Angew. Chem., Int. Ed.*, 1999, **38**, 3440; J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press, Oxford, 2002.
- T. L. Threlfall, *Analyst*, 1995, **120**, 2435; D. Braga and F. Grepioni, *Chem. Soc. Rev.*, 2000, **4**, 229; N. Bladgen and R. J. Davey, *Chem. Br.*, 1999, **35**, 44.
- R. J. Davey, K. Allen, N. Bladgen, W. I. Cross, H. F. Lieberman, M. J. Quayle, S. Righini, L. Seton and G. J. T. Tiddy, *CrystEngComm*, 2002, **4**(47), 257.
- G. S. McGrady, M. Odlyha, P. D. Prince and J. W. Steed, *CrystEngComm*, 2002, **4**(49), 271.
- D. Braga, G. Cojazzi, D. Emiliani, L. Maini, M. Polito, R. Gobetto and F. Grepioni, *CrystEngComm*, 2002, **4**(50), 277.
- S. L. Childs and K. S. Hagen, *CrystEngComm*, 2002, **4**(48), 265.
- D. Volkmer, M. Fricke, C. Agena and J. Mattay, *CrystEngComm*, 2002, **4**(52), 288.
- A. M. Beatty, C. M. Schneider, A. E. Simpson and J. L. Zaber, *CrystEngComm*, 2002, **4**(51), 282.
- Y. Diskin-Posner, G. K. Patra and I. Goldberg, *CrystEngComm*, 2002, **4**(53), 296.
- K. Fromm, *CrystEngComm*, 2002, **4**(57), 318.
- G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999; C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397; S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357; G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin, 1991; L. Brammer, D. Zhao, F. T. Ladipo and J. Braddock-Wilking, *Acta Crystallogr., Sect. B*, 1995, **51**, 632; D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, **33**, 601; G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565.
- N. Ziao, C. Laurence and J.-Y. Le Questel, *CrystEngComm*, 2002, **4**(59), 326.
- F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 31.
- M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.
- C. M. Reddy, A. Nangia, C.-K. Lam and T. C. W. Mak, *CrystEngComm*, 2002, **4**(58), 323.
- T. J. Podesta and A. G. Orpen, *CrystEngComm*, 2002, **4**(60), 336.
- C. B. Aakeröy, A. M. Beatty and D. S. Leinen, *CrystEngComm*, 2002, **4**(55), 310.
- V. R. Pedireddi, *CrystEngComm*, 2002, **4**(56), 315.
- P. Coppens, B. Ma, O. Gerlits, Y. Zhang and P. Kulshrestha, *CrystEngComm*, 2002, **4**(54), 302.
- A. Gavezzotti, *CrystEngComm*, 2002, **4**(61), 343.
- E. Tedesco, D. Giron and S. Pfeffer, *CrystEngComm*, 2002, **4**(67), 393.
- M. A. Spackman and J. J. McKinnon, *CrystEngComm*, 2002, **4**(66), 378.
- M. J. Calhorda and P. J. Costa, *CrystEngComm*, 2002, **4**(64), 368.
- J. J. Novoa, P. Lafuente, R. E. Del Sesto and J. S. Miller, *CrystEngComm*, 2002, **4**(65), 373.
- A. T. Anghel, G. M. Day and S. L. Price, *CrystEngComm*, 2002, **4**(62), 348.
- K. D. M. Harris, R. L. Johnston, E. Y. Cheung, G. W. Turner, S. Habershon, D. Albesa-Jové, E. Tedesco and B. M. Kariuki, *CrystEngComm*, 2002, **4**(63), 356.
- A. N. Khlobystov, N. R. Champness, C. J. Roberts, S. J. B. Tendler, C. Thompson and M. Schröder, *CrystEngComm*, 2002, **4**(71), 426.
- H. I. Süss, T. Wuest, A. Sieber, R. Althaus, F. Budde, H.-P. Lüthi, G. D. McManus, J. Rawson and J. Hulliger, *CrystEngComm*, 2002, **4**(72), 432.
- N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *CrystEngComm*, 2002, **4**(68), 401.
- (a) T. Iwamoto, *Inclusion Compd.*, 1984, **1**, 28; (b) A. Ludi and H. U. Güdel, *Struct. Bonding*, 1973, **14**, 1; (c) J. L. Manson, C. Campana and J. S. Miller, *Chem. Commun.*, 1998, 251; (d) Y. Liao, W. W. Shum and J. S. Miller, *J. Am. Chem. Soc.*, 2002, **124**, 9336.
- L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *CrystEngComm*, 2002, **4**(70), 413.
- S. Ferlay, V. Bulach, O. Félix, M. W. Hosseini, J.-M. Planeix and N. Kyritsakas, *CrystEngComm*, 2002, **4**(74), 447.
- P. Li, B. Abrens, K.-H. Choi, M. S. Khan, P. R. Raithby, P. J. Wilson and W.-Y. Wong, *CrystEngComm*, 2002, **4**(69), 405.
- Y. Rodríguez-Martín, M. Hernández-Molina, F. S. Delgado, J. Pasán, C. Ruiz-Pérez, J. Sanchiz, F. Lloret and M. Julve, *CrystEngComm*, 2002, **4**(73), 440.