Developments in inorganic crystal engineering

Lee Brammer

Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, UK S3 7HF.
E-mail: lee.brammer@sheffield.ac.uk

The design and synthesis of crystalline materials through the self-assembly of molecular building blocks and the pursuit of functional materials based upon this approach are usually classified under the banner *Crystal Engineering*. The field is interdisciplinary in nature involving synthetic, materials, structural and theoretical chemists. There are strong ties to modern crystallography which can offer rapid and accurate structure determination and, in particular, insight into molecular and intermolecular geometries. Illustrative examples that chart the development field and provide an assessment of the current state of the art will be reviewed with an emphasis on inorganic chemistry. Broadly speaking, two classes of compounds will be discussed: those based upon molecules or ions linked into networks *via* noncovalent interactions and those (coordination polymers) in which metal centres are linked using coordination bonds through bridging ligands into extended networks.

1 Introduction

Contemporary crystal engineering involves the design and synthesis of crystals.[1] The aim of this endeavour is the development of new crystalline materials with a variety of properties, functions and applications. Examples include porous materials for use in chemical separations and as highly selective reaction microenvironments, polar materials for non-linear optical applications including second harmonic generation, materials with tailored magnetic or photophysical (*e.g.* luminescent) properties that may be useful in electronics applications or as molecular sensors, *etc*. Inherent in this approach to materials design is the realisation that the properties of crystals are derived from their molecular components and the manner in which these components are aligned, and are linked or interact, in the crystalline state. The field of crystal engineering has strong ties to solid state chemistry, materials chemistry, and increasingly strong links with traditional synthetic chemistry which has much to contribute in advancing crystal synthesis. Crystal engineering, has connections to theoretical chemistry through the study of intermolecular interactions and crystal structure prediction, and must be linked to the study and application of the properties arising from newly designed functional materials. Since this review is presented within a special issue of *Chemical Society Reviews* devoted to crystallography, the links between crystal engineering and crystallography will be stressed. The scope of this review is not comprehensive, but rather provides some illustrative examples intended to convey the breadth of the field. The discussion of crystal syntheses and the properties arising from the crystalline products will focus on examples that are inorganic in nature, that is to say involving metal-containing building blocks.

Lee Brammer obtained his PhD in Inorganic Chemistry from the University of Bristol. Following a NATO postdoctoral fellowship at the University of New Orleans and further postdoctoral work at Brookhaven National Laboratory, he embarked on his independent academic career in the USA in 1990 at University of Missouri-St. Louis, returning to the UK in 2001 to take up an appointment at the University of Sheffield. He is a recipient of the S. S. Sidhu Award from the Pittsburgh Diffraction Society for contributions to the field of crystallography and diffraction and is currently a co-editor for Acta Crystallographica, Section B, chair

of the Editorial Board of the RSC journal of crystal engineering, CrystEngComm, and chair of the IUCr Commission on Structural Chemistry. His research interests within the field of crystal engineering include the study of intermolecular interactions, particularly hydrogen bonding, and the design and synthesis of metal-containing network solids through the application of non-covalent and/or coordination bonds.

2 Origins of crystal engineering and the role of crystallography

Crystallography as a discipline has its origins in the pre-diffraction era when the term referred to the study of the morphology of crystals. During the time since the first diffraction experiments some 90 years ago crystallography has become synonymous with accurate structural characterisation of natural and synthetic compounds in their crystalline forms. The power of this method of structure determination of compounds from the simplest inorganic salts to large complex biomolecules is evident from its prominent role in the award of over 25 Nobel Prizes during this period spanning the disciplines of Chemistry, Physics and Medicine.

Modern crystal structure determination is not only accurate and precise, but quite rapid, particularly for smaller chemical rather than large biological systems, permitting large numbers of crystal structures to be determined and systematic comparisons of intra- and intermolecular geometries to be made. Indeed, the Cambridge Structural Database (CSD),[2] which houses crystallographic data for compounds containing organic and metal–organic compounds, already contains data for over 300 000 crystal structures and is expanding at *ca.* 10% per year. These crystal structures provide a wealth of knowledge that can now be used to help design new crystalline materials from the bottom up. Thus, by selecting the right molecular building blocks, and armed with a detailed knowledge of the preferred

interactions likely to be undertaken by these molecules, it is in principle possible to synthesise new crystalline materials in a predictable way. This opens the possibility not only of tuning of the metrics and contents of crystals but by implication their chemical and physical properties. This is the essence of the field that is most commonly known as crystal engineering,[3] though the precision associated with the word 'engineering' is perhaps currently a more distant promise for most systems. Crystal engineering as it is generally viewed involves the study of interaction geometries and energies, most commonly by crystallographic or theoretical approaches, the synthesis of crystals (both exploratory and by design), and the study of the structures and properties of the crystalline products. It has been suggested that the synthetic endeavour at the heart of crystal engineering can be viewed an evolution of crystallography, formally the study of crystals, from an analytical method to one that also encompasses crystals as synthetic targets and the development of a suitable synthetic methodology. Indeed, the recently applied term 'synthetic crystallography'[4] nicely emphasises this development and provides a link between crystallography and crystal engineering.

The development of the field of crystal engineering is usually traced to work of Schmidt in the 1960s, work that was underpinned by keen crystallographic insight.[3a,5] Thus, Schmidt noted that chlorinated aromatic compounds frequently crystallised such that stacking of molecules at a separation of *ca.* 4 Å was observed. This observation was then put to use in some early examples of what became known as crystal engineering.[5a] A further crystallographic insight in studies of cinnamic acid derivatives led directly to a practical application in solid-state synthesis. Thus, it was established by crystallographic studies that in two of three polymorphs (α and β forms) molecules of *trans*-cinnamic acid derivatives stack in pairs within which the two alkene groups are aligned in a parallel manner at a separation of *ca.* 4 Å. In the third polymorph (γ form) a greater separation is observed (4.7–5.1 Å). Upon γ-irradiation stereospecific [2+2] cycloaddition reactions occur in crystals of the α and β forms to yield the corresponding substituted cyclobutane products as crystalline materials. These are known as topochemical reactions since the correct topology is required for the reaction to take place. Thus, no reaction occurs in the γ form upon similar irradiation (Fig. 1).[5b,c] These and related studies led to the topochemical principles outlined by Schmidt for this C–C bond forming reaction in the solid state, wherein the parallel alignment of alkenes at a distance of <4.2 Å is required for reaction to take place.[3a] In more recent work, Lauher and coworkers have made use of carefully designed hydrogen-bonded templates to align functionalised diyne and triyne molecules in crystals so as to permit their topochemical polymerisation to be undertaken.[6] MacGillivray has also further developed the original approach to alkene dimerisation pioneered by Schmidt through the application of contemporary crystal engineering ideas involving the use of specific intermolecular interactions to position molecules in the solid state. Specifically, an approach has been developed wherein the two reactant alkenes are held at the appropriate reaction geometry using template molecules that
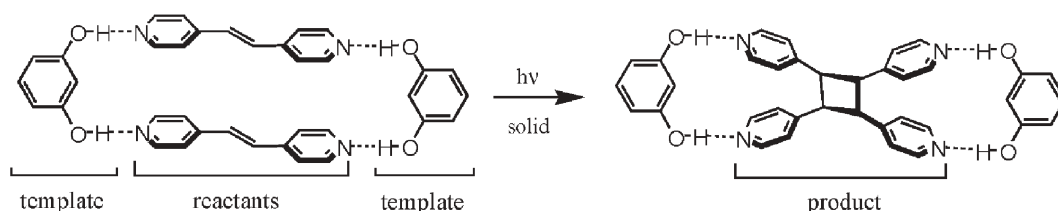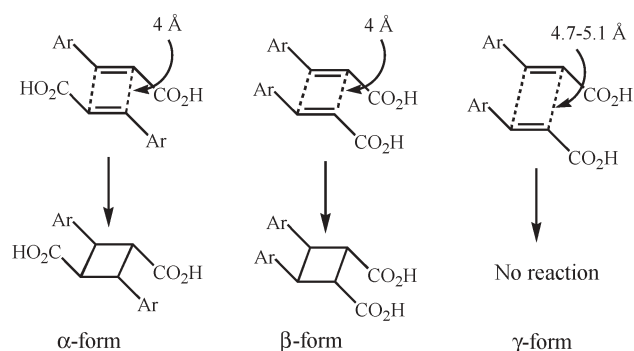
Fig. 1 Topochemical cycloaddition reactions of the polymorphic forms of cinnamic acid and its derivatives (Ar[1]† = unsubstituted, mono-and disubstituted phenyl).[5b,c]

interact with the substituents of the alkene through well-defined intermolecular forces, such as hydrogen bonds (Fig. 2).[7] This work not only involves crystal synthesis, but the use of crystals to perform chemical synthesis.

Focusing now on inorganic, that is to say metal-containing, systems, crystal engineering can be roughly divided into the study of crystals in which molecular (neutral and ionic) building blocks are linked *via* non-covalent interactions and crystals in which extended networks (coordination polymers) are propagated *via* metal–ligand coordination bonds. The former have a number of features in common with organic molecular crystals, in which the molecular building blocks are similarly linked, though in some respects this division is artificial since the crystal structures of low dimensional (1D and 2D) coordination polymers may be influenced strongly by intermolecular interactions.

3 Inorganic crystal engineering using hydrogen bonds and other non-covalent interactions

## 3.1 Crystal synthesis—what do we need to know to begin?

Priorities and patterns of interactions: developments arising from studies of organic molecular crystals. For molecular crystals, crystal engineering may be regarded as a solid-state branch of supramolecular chemistry. Dunitz has aptly captured this connection in his statement that "The crystal is, in a sense, the supermolecule *par excellence* …".[8] However, in order to understand how molecules come together in particular arrangements to form crystals and then to harness that understanding to design and synthesise new crystalline materials there are many steps to undertake. Firstly, one might ask, what interactions are involved? These include non-directional ionic forces and dispersion forces as well a number of directional interactions including π–π and other interactions

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† For many of the derivatives of *trans*-cinnamic acid not all three forms are known. For the parent *trans*-cinnamic acid only the α- and β-forms are known. The *ortho*-ethoxy derivative provides an example where all three forms are known. Typically the β-form is metastable and able to be converted to the more stable α-form. (See references 5b and 5c).

Fig. 2 Use of hydrogen-bonded templates to align substituted alkenes for topochemical 2+2 cycloaddition reactions. Adapted from ref. 5 with permission from the Royal Society of Chemistry.

between aromatic rings, and various types of donor–acceptor interactions, culminating in hydrogen bonds. A discussion of these different types of forces can be found in Desiraju's monograph on organic crystal engineering.[3c] Understanding and harnessing this cacophony of competing and collaborating forces to design and synthesise crystals may seem like a daunting task. Fortunately, significant progress can be and has been made by simplifying our treatment of this complex situation through focusing first and foremost on the stronger and more directional interactions. Here, moderately strong hydrogen bonds have found the greatest application. Such interactions have energies in the range *ca.* 15–60 kJ mol^{-1}, show marked directionality and are widely accessible particularly through a variety of organic functional groups incorporating nitrogen and oxygen atoms. Directional preferences for hydrogen bonds in crystals have been firmly established through systematic surveys of the CSD.[9] Thus, a preference for a linear three-centre arrangement is not only found for conventional hydrogen bonds, *e.g.* O–H⋯O, N–H⋯O, N–H⋯N, but persists in weaker hydrogen bonds, *e.g.* C–H⋯O, though deviations from linearity are necessarily far more prevalent for weaker hydrogen bonds due to the greater relative competition from other intermolecular forces within a given crystal. Preferences are also found in angles at the hydrogen bond acceptor, *e.g.* H⋯O=C[9] of *ca.* 120° and H⋯Cl–M of 90–130°.[10]

Among her seminal contributions to organic solid state chemistry, Etter proposed a set of rules for hydrogen bonding in organic crystals that are valuable when considering the synthesis of crystals comprising molecules linked by hydrogen bonds.[11] These are that:

(i) All good hydrogen bond donors and acceptors will be used in hydrogen bonding.

(ii) Six-membered ring intramolecular hydrogen bonds form in preference to intermolecular hydrogen bonds (Scheme 1).
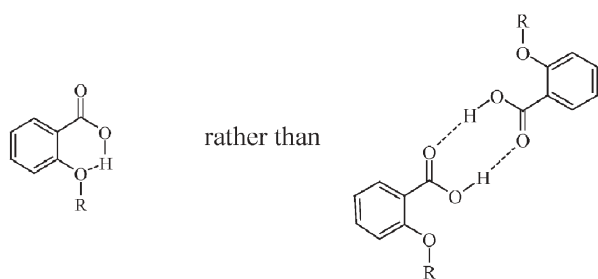
Scheme 1

(iii) The best proton donors and acceptors remaining after intramolecular hydrogen bond formation form intermolecular hydrogen bonds.

The third of these tenets was recently extended by Aakeröy and coworkers to include the assertion that following hydrogen bond formation between the best proton donors and acceptors, the next best donors and acceptors will form hydrogen bonds. An elegant application of this principle has been used in the design and synthesis of ternary supermolecules in the solid state (Fig. 3).[12]

Looking now more broadly at intermolecular interactions, by adaptation of Corey's concept of synthons in organic molecular synthesis into that of 'supramolecular synthons',
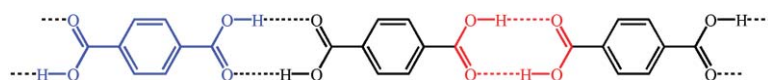

Fig. 3 Design of a ternary supermolecule using a hierarchy of hydrogen-bonding interactions.[12]

Desiraju introduced an important conceptual framework for the supramolecular synthesis of crystals[13] This concept is illustrated in Fig. 4 for a one-dimensional hydrogen-bonded network. Thus, the supramolecular synthon is an interaction motif that permits a range of building blocks (tectons[14]) to be linked in a well-defined and reproducible way. The concept does not simply apply to hydrogen-bonded interactions, but can include a variety of interaction types, both strong and relatively weak. Some examples of supramolecular synthons are shown in Scheme 2. However, if such synthons‡ are to be

Scheme 2 Examples of supramolecular synthons.

used in crystal syntheses the inevitable question is how reliable are they? This question has been answered for the 75 most commonly occurring hydrogen-bonded ring synthons found in

‡ Hereafter the term synthon is used to refer to supramolecular synthons.

Fig. 4 Hydrogen-bonded polymer of terephthalic acid with the molecular building block (tecton) shown in blue and the supramolecular synthon that propagates the network shown in red.
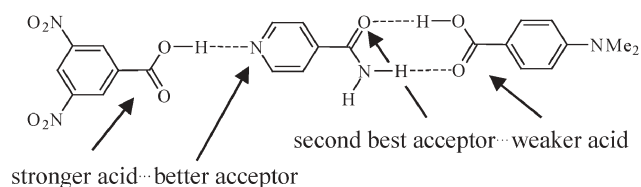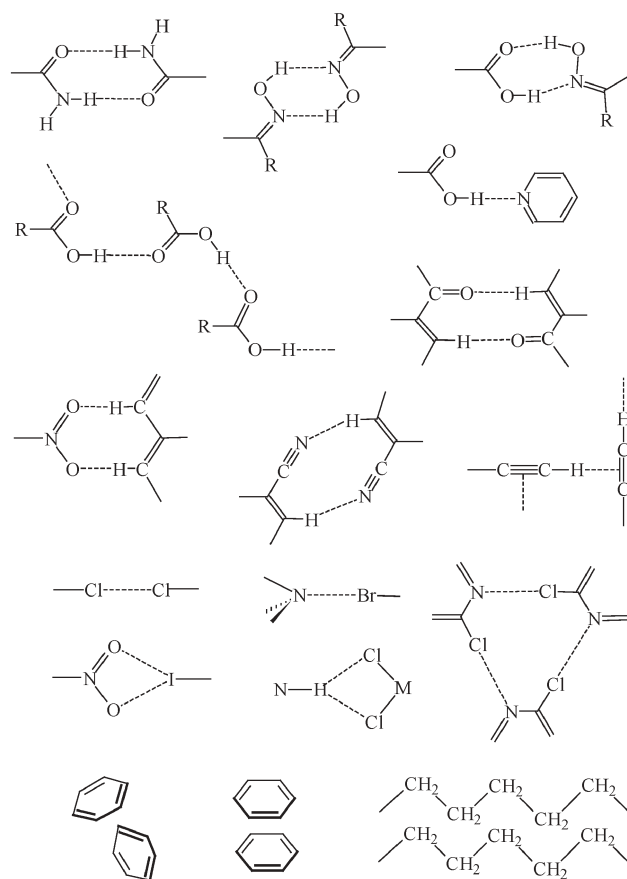
crystal structures present in the CSD. The probability of occurrence of these synthons in organic crystal structures was determined by considering the number of occurrences observed as a fraction of the maximum possible number of occurrences, given the presence of the appropriate function groups necessary to form the synthon.[15] Remarkably the often used carboxylic acid dimer synthon that is illustrated in Fig. 4 has a probability occurrence of only 0.33 across all structures containing carboxylic acid groups. This low value reflects the competition from other hydrogen bond donors and acceptors, particularly water molecules and carboxylate groups. In the absence of such competing groups the probability of the dimer synthon forming rises to 0.86 and is as high as 0.95 for crystal structures of monocarboxylic acids.

Similarities and differences between organic and inorganic molecular crystals. In the mid 1990s Braga, Grepioni, Desiraju and coworkers[16] conducted a series of studies using the CSD to examine the differences in hydrogen bonding geometries and patterns (*viz.* synthons) between functional groups such as –OH, –COOH and –$CONH_2$ found in crystal structures of organic compounds and these same functional groups when found as part of ligands in structures of transition metal complexes. The conclusions that these functional groups behave similarly in the different environments confirmed their applicability to inorganic crystal engineering (see Section 3.2). By contrast, CSD studies and theoretical calculations on hydrogen bonds in which halide ligands serve as hydrogen bond acceptors (D–H···X–M; D = C, N, O; X = F, Cl, Br, I) showed that these have pronounced directional character and lead to useful synthons, while the organic counterparts (D–H···X–C) exhibit less well-defined geometric behaviour due to far weaker interaction energies.[10b] The role of the metal centre in this case is crucial, giving rise to an M–X bond that is more polar than the corresponding C–X bond.

A key difference between the situation involving "organic" functional groups (amide, carboxyl, *etc.*) and that involving the halogens is their proximity to the metal, in each case, when present in inorganic building blocks. The former are typically well-separated from the metal centre and are influenced electronically by the metal to only a small extent while the latter are directly bonded to the metal centre and thus their properties are markedly influenced.[17] A further difference between organic crystal engineering and its molecular inorganic counterpart is that in the latter area charged building blocks are more common. While hydrogen-bonded networks based upon charged organic building blocks have been put to excellent use,[18] such an approach is more common with inorganic systems due to the vast choice particularly of cationic building blocks.[19]
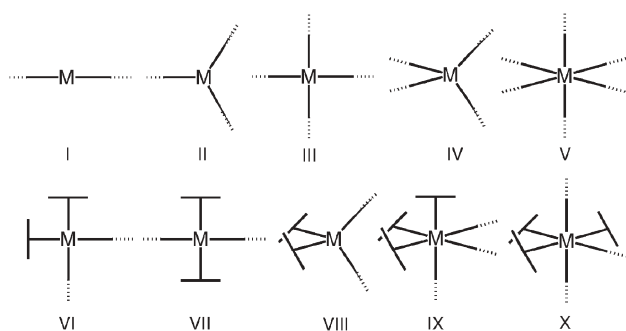
Scheme 3 Common coordination geometries of metal ions used in network synthesis. Dashed lines indicate the direction of propagation of the network *via* hydrogen bonds (Section 3) or coordination bonds (Section 4).

3.2 Design strategies employing hydrogen bonds

Building blocks comprising coordination compounds with ligands bearing "organic" hydrogen-bonding groups. Metal centres with well-defined coordination geometries can be used to orient hydrogen-bonding groups placed on rigid ligands (Scheme 3). This is an effective approach to the design of metal-containing hydrogen-bonded networks. The same general approach also underpins the design of coordination polymers, except that ligands capable of forming coordination bonds to neighbouring metal centres are used (Section 4). Linear hydrogen-bonded networks have been synthesised using two-coordinate Ag(I) centres (*cf.* **I**) in combination with pyridine-based ligands bearing amide, oxime or carboxyl§ groups that are able to form networks through self-recognition *via* hydrogen bonding.[1e,20] This strategy has been extended to include trigonal (**II**) and square planar (**III**) nodes, in the latter case leading to the synthesis of 2D square nets through the use of Pt(II) centres,[21] which have a strong preference for square planar coordination geometry (Fig. 5). Building blocks in which some of the metal coordination sites are blocked by ligands that do not actively propagate the network (*e.g.* **VI**[22] and **IX**[23]) have also been employed.

(a)

(b)
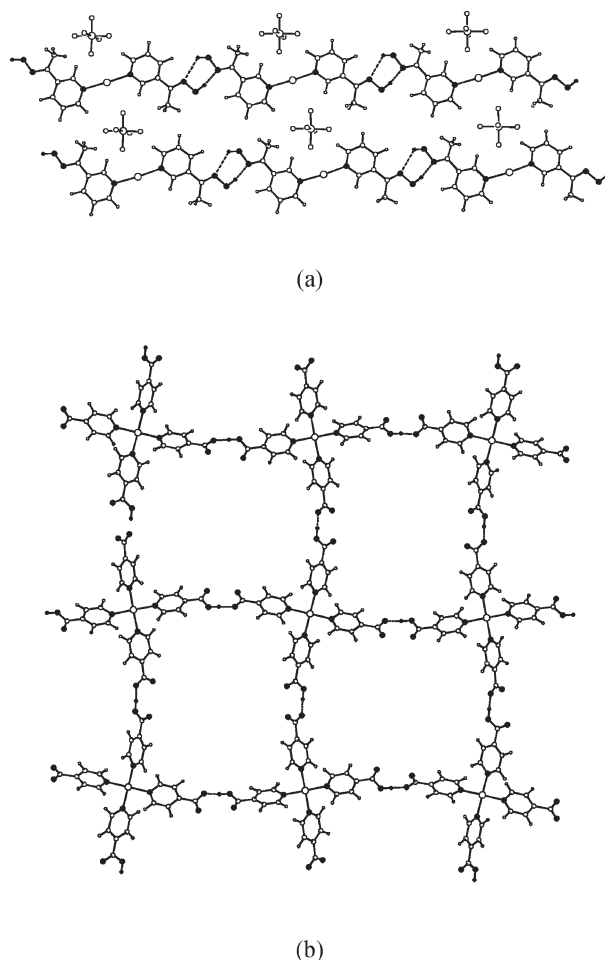
Fig. 5 (a) Linear oxime–oxime hydrogen-bonded network observed for [Ag(3-acetoximepyridine)$_2$]PF$_6$.[20b] (b) Section of one of the O–H···O$^-$ hydrogen-bonded square grids found in [Pt(L)$_2$(HL)$_2$]·2H$_2$O (L = isonicotinate).[21] Reproduced from ref. 1d with permission. Copyright John Wiley & Sons Limited.

§ There is a tendency for deprotonation of carboxyl groups to occur upon coordination of ligands such as nicotinic acid and isonicotinic acid.

Chelating ligands give rise to particularly robust coordination compounds. Thus, it should not be surprising that such complexes can provide effective building blocks for hydrogen-bonded networks. Indeed, early work by Mingos and coworkers exploited this approach through the design and use of bidentate ligands with peripheral functional groups capable of forming double or triple hydrogen bonds with neighbouring molecules[24] in a manner reminiscent of the hydrogen-bonded recognition between the DNA base pairs. Tadokoro has used the monoanionic 2,2′-biimidazolate (HBim$^-$) ligand in conjunction with dicationic octahedral metal centres, M(II), to prepare 2D honeycomb networks based upon M(Hbim)$_3^-$ building blocks linked by N–H···N hydrogen bonds[25] (Fig. 6).
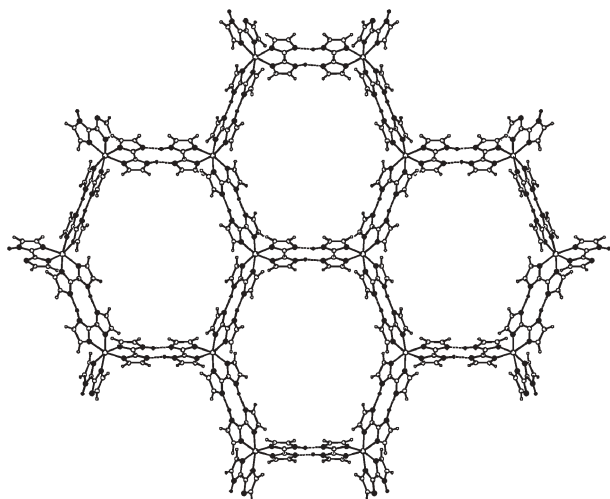
Fig. 6 Use of chelating ligands with hydrogen-bonding capability. 2D honeycomb network constructed from Ni(Hbim)$_3^-$ building blocks (HBim$^-$ = 2,2′-biimidazolate) linked *via* double N–H···N hydrogen bonds as seen in crystal structure of [K(dibenzo-18-crown-6)][Ni(Hbim)$_3$]·3CH$_3$OH·2H$_2$O.[25] Reproduced from ref. 1d with permission. Copyright John Wiley & Sons Limited.

The final structure can be either a layered arrangement or an interpenetrated network (*i.e.* self-catenating—see Section 4 for a more extensive description of this concept) depending upon the choice of cation. The M(Hbim)$_3^-$ building blocks are chiral, though the resulting honeycomb network is not since alternating *R* and *S* enantiomers are employed in its construction.

Organometallic compounds as building blocks. The use of hydrogen-bonded organometallic components in crystal engineering has involved two main strategies. The first resembles that described for coordination compounds in the previous section. Thus, organometallic compounds with peripheral hydrogen-bonding groups, predominantly carboxyl groups, have been employed as building blocks. These have consisted of sandwich or half-sandwich complexes in which arene or cyclopentadienyl ligands carry carboxyl substituents capable of mutual recognition *via* O–H···O hydrogen bonds. Braga, Grepioni and coworkers have extensively used the 1,1′-dicarboxyl derivatives of the sandwich complexes ferrocene, cobaltocene and bis(benzene)chromium for this purpose, as exemplified by the series of network arrangements shown in Fig. 7.[26] The utility of the cobaltocenium system in undergoing solid–solid and solid–gas reactions has also been exploited as noted in Section 3.4. Hydrogen-bonded networks constructed from related boronic acid derivatives of the metallocenes also have been recently reported.[27] Derivatives of the half-sandwich complex Cr(η^6-C$_6$H$_6$)(CO)$_3$ have been prepared
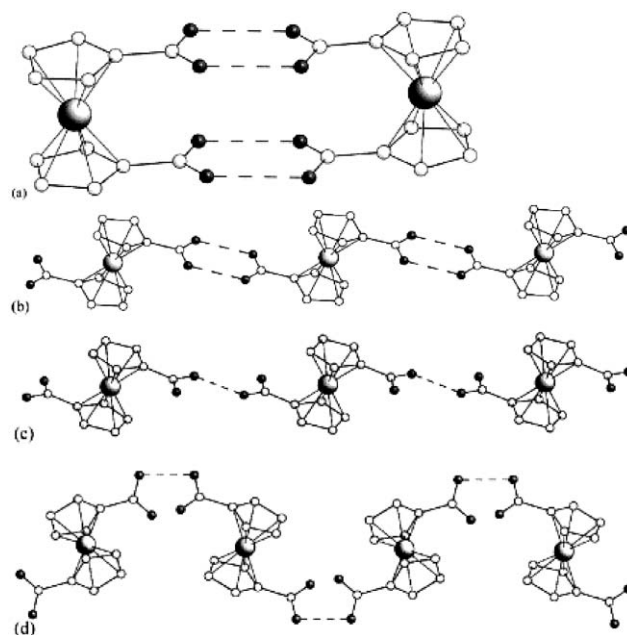
Fig. 7 Hydrogen-bonding patterns observed in structures involving (a) [Fe(η^5-C$_5$H$_4$COOH)$_2$], (b) [Co(η^5-C$_5$H$_4$COOH)$_2$]$^+$, (c) [Fe(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)]$^-$, and (d) [Co(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)]. Reproduced from ref. 26, copyright 2001, with permission from Elsevier.

with mono-, di- and tricarboxyl substitution on the benzene ring and their capacity to form hydrogen-bonded networks has been compared with their organic counterparts.[28] While the dicarboxyl systems were reported as solvates in which the hydrogen-bonded network is interrupted, the potential use of these systems as building blocks can be seen from the tricarboxyl building block, which forms an extended O–H···O hydrogen-bonded network (Fig. 8). A similar approach has
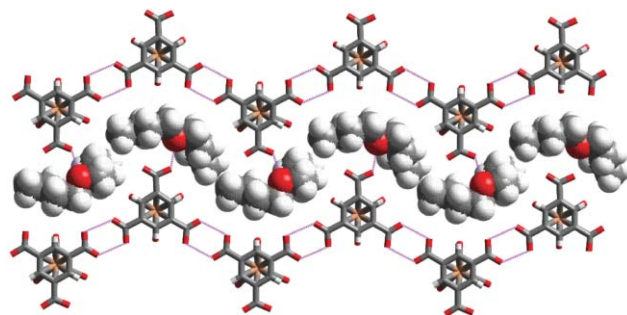

Fig. 8 Hydrogen-bonded network in crystal structure of [Cr{η^6-1,3,5-C$_6$H$_3$(CO$_2$H)$_3$}(CO)$_3$]·^{n}Bu$_2$O (encapsulated solvent molecules shown as large spheres).[28] Reproduced from ref. 1d with permission. Copyright John Wiley & Sons Limited.

also been successfully employed to prepare coordination polymers with organometallic linkers.[29] In an alternative approach, Braga, Grepioni and coworkers have also prepared an extensive series of compounds in which organometallic cations have been used to template polyanionic O–H···O hydrogen-bonded networks of (organic) carboxylic acids or alcohols to give hybrid organic–organometallic crystals.[30] The templating relies upon the formation of a large number of charge-assisted C–H···O hydrogen bonds between the organometallic cations and the organic network.

Use of simple ligands in which hydrogen bonding is strongly influenced by metal coordination. Focusing first on ligands that can serve as hydrogen bond acceptors, it has been noted (*vide*

supra) that coordination to metal centres as halide ligands effectively activates halogens as hydrogen bond acceptors.[10] Taking advantage of this behaviour and the pronounced directionality of the resulting hydrogen bond, as observed in the (N)H⋯X–M angle (particularly for X ≠ F), a strategy for designing inorganic–organic hybrid solids has been devised using organic cations with hydrogen bond donor groups and perhalometallate anions.[31] Specifically, studies of the distribution of N–H groups around perchlorometallate ions from crystal structure data (CSD) show accumulations corresponding very well with the sites of electrostatic potential minima obtained from theoretical calculations (*e.g.* Fig. 9). This
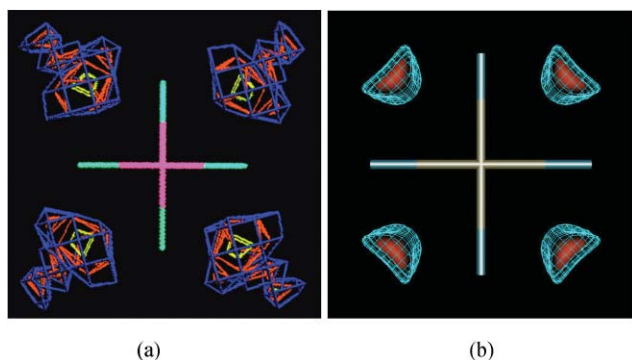

Fig. 9 (a) Experimental population density of hydrogen atoms from N–H groups in the vicinity of square planar $[MCl_4]^{n-}$ anions obtained from crystal structure (CSD) data. Contours: blue 35%, red 55%, yellow 80% of maximum population density. (b) Calculated negative electrostatic potential in the vicinity of the $[PdCl_4]^{2-}$ anion. Similar comparisons of experimental distribution with theoretical prediction for tetrahedral and octahedral anions are presented in ref. 31. Reproduced from ref. 31. Copyright 2002 National Academy of Sciences, USA.

suggests a preference for bifurcated $N–H⋯Cl_2M$ and trifurcated $N–H⋯Cl_3M$ hydrogen-bonding interactions, which occur at edge and face sites of polyhedra comprised of halide ligands in such anions and can be viewed as supramolecular synthons. Examples of simple 1D networks[32] that illustrate this approach are found in Fig. 10. A variety of 2D networks have also been reported and systematically classified by Orpen and coworkers.[33]
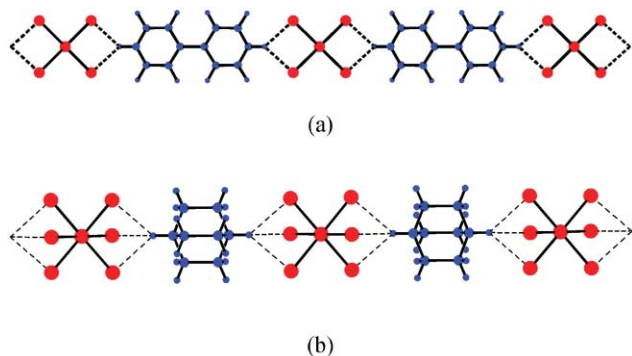
Fig. 10 One-dimensional hydrogen-bonded networks for (a) [(4,4'-bipy)H₂][PtCl₄][32a] and (b) [(DABCO)H₂][PtCl₆],[32b] using square planar and octahedral perchlorometallate ions and propagated *via* $N–H⋯Cl_2M$ and $D–H⋯Cl_3M$ hydrogen-bonded synthons, respectively.

In a related approach using cyanometallate ions, Hosseini and coworkers have prepared hydrogen-bonded networks in which the metal centres serve as chiral nodes due to chirality induced only upon formation of $N–H⋯NC–M$ hydrogen
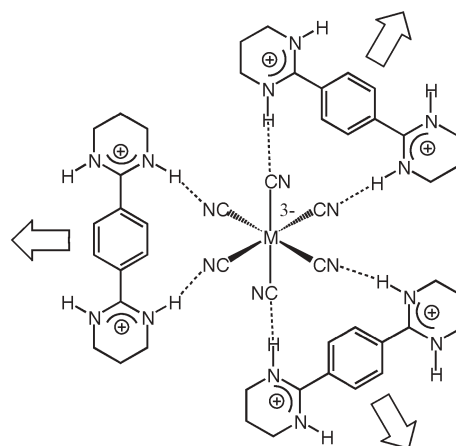
Fig. 11 Supramolecular chirality—a chiral network node generated through hydrogen bonding of achiral components. Adapted from ref. 34, copyright 2003, with permission of Elsevier.

bonds¶ between bisamidinium cations and the metallate anions (Fig. 11).[34] Thus, this is an example of supramolecular chirality arising from the assembly of achiral building blocks.

We now consider simple ligands that can serve as hydrogen bond donors, wherein coordination to a metal centre enhances hydrogen bond donor capability. The most prevalent examples involve OH_2 or NH_3 ligands though often control over the multiple hydrogen bonding possibilities is rather limited.[1d] A particularly elegant example involving hydroxide ligands is the diamondoid (M)O–H⋯N hydrogen-bonded network formed from the adduct between the tetrahedral manganese cluster and 4,4'-bipyridine in the crystal structure of $[Mn(\mu_3-OH)(CO)_3]_4·2(4,4'-bipy)·2CH_3CN$.[35]

3.3 Design strategies employing other non-covalent interactions

Halogen bonds. Although hydrogen bonds are the predominant type of non-covalent interaction used to design metal-containing crystalline materials, other types of interactions have been used effectively. Recently halogen bonds of the type M–X⋯X′–C (X = Cl, Br; X′ = Cl, Br, I) have been used in conjunction with $N–H⋯X(M)$ hydrogen bonds in the construction of networks involving perhalometallate anions and halopyridinium cations (Fig. 12).[36] The halogen–halogen separations are in many cases substantially below that expected for a simple van der Waals contact and the geometry of these interactions suggests formulation as a Lewis acid–Lewis base interaction. In simple orbital terms, M–X⋯X′ geometries lie close to 100° while C–X′⋯X geometries are approximately linear. Thus, the halide ligand can be envisaged as the base through use of a lone pair orbital, while the "organic" halogen can serve as a Lewis acid through use of its low lying empty C–X′ σ* orbital. Analogous halogen bonds can also be used to construct networks from neutral coordination complexes as exemplified by species of the type $MCl_2(halopyridine)_2$.[37]

Phenyl embraces and related interactions of aromatic rings. The importance of interactions between aromatic rings in crystal packing has long been recognised.[3c] These involve both edge–face and face–face interactions between the rings and the nature of these interactions has been carefully investigated for organic compounds[38] and for aromatic nitrogen-containing ligands.[39] In an extensive series of papers Dance and coworkers

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¶ The axial lone pair on the nitrogen atom of the cyano ligands leads to the formation of simple $N–H⋯NC–M$ hydrogen bonds rather than bifurcated interactions.
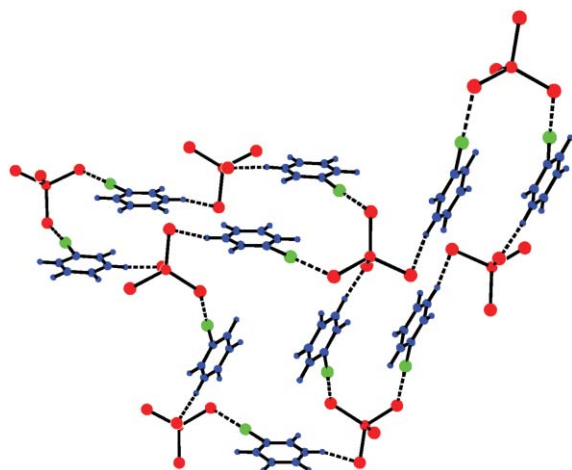
Fig. 12 Network propagated *via* Co–I···Cl–C halogen bonds and N–H···Cl–Co hydrogen bonds in the structure of (3-iodopyridinium)$_2$-[CoCl$_4$]. Reproduced from ref. 36*a* with permission from the Royal Society of Chemistry.

have demonstrated the pervasive nature of interactions between ligands and ions containing multiple phenyl or other aromatic groups. These interactions have been described as "embraces" in which multiple aromatic groups interact in a concerted manner as illustrated for PPh$_4^+$ cations,[40] for PPh$_3$ and similar ligands[41] and for terphenyl ligands (terpy) in [M(terpy)$_2$]$^{n+}$ salts.[42] Fig. 13 illustrates the sixfold phenyl embrace (6PE), *i.e.* involving all six phenyl rings, of two PPh$_3$ ligands from neighbouring molecules and its involvement in propagating networks. The importance of such interactions is evident from a CSD survey of crystal structures containing PPh$_3$ ligands in which *ca.* 90% were found to exhibit some type of phenyl–phenyl interaction, with the 6PE motif being found in 30% of these structures.[41]

3.4 Some synthetic challenges to be overcome

There are of course practical issues to be addressed in undertaking crystal syntheses, for example choice of solvents, mixing of solvents (or absence of solvent) when combining the building blocks to be used. Temperature and pressure can also be used to control crystallisation. When synthesising hydrogen-bonded networks the polarity of building blocks often dictates the use of polar solvents (for solution-phase synthesis). Such solvents (*e.g.* H$_2$O, alcohols, DMF, DMSO, *etc.*) are themselves very effective in hydrogen bond formation, which can lead to crystals containing solvent molecules that interact with the building blocks, disrupting the intended network.[28] There are some alternatives. Solvents such as nitromethane, for example, are very polar without exhibiting strong ability to form hydrogen bonds. A similar problem arises regarding the choice of counteranion in cases where the network is inherently cationic (*e.g.*, metal cations + neutral ligands) since most anions have some hydrogen bond acceptor capability. An elegant solution to the problem is to make these anions part of the network design.[43]

Polymorphism, the possibility of forming different crystal structures (different networks) from the same set of building blocks (same composition), is a perennial challenge in crystal synthesis and where this situation arises it may require extensive investigation of reaction conditions to establish synthetic routes to a single polymorph.

3.5 Applications

Although a number of open framework inorganic hydrogen-bonded networks have been reported, these are generally not
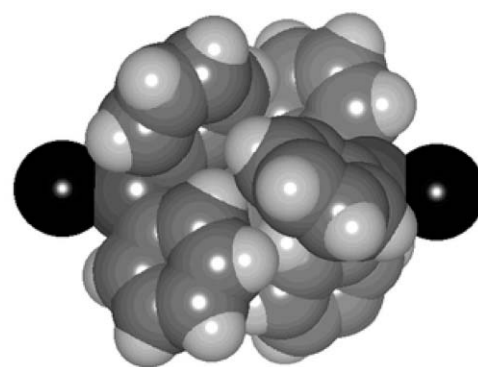

(a)
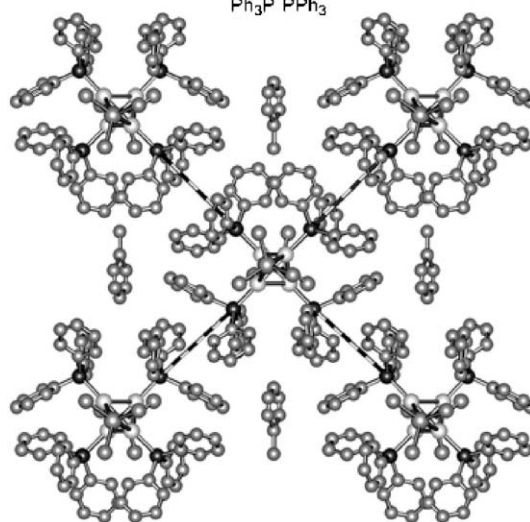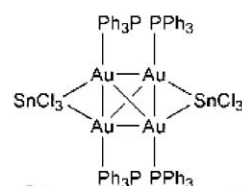
(b)

Fig. 13 (a) Sixfold phenyl embrace (6PE) between two between two MPPh$_3$ groups. (b) Square array of 6PEs formed by Cl$_3$Sn(AuPPh$_3$)$_4$SnCl$_3$. (Note the inclusion of the solvent toluene, which is in a position suitable for formation of several edge-to-face interactions). Reproduced from ref. 41 with permission of the Royal Society of Chemistry.

stable to guest removal or involve interpenetrated (self-catenating) networks with no available porosity.[44] However, robust organic hydrogen-bonding networks with host/guest properties suggest that this should be achievable.[14,45] Indeed there are some promising hybrid materials in which a combination of coordination networks and hydrogen-bonded networks have been employed, as illustrated in Fig. 14 for the entrapment of aromatic guest molecules.[46]

Mitzi has used hydrogen-bonding cations to link polyanionic perhalometallate layers in producing an extensive series of inorganic–organic hybrid perovskite materials with applications ranging from semi-conductors with high electron mobilities to novel optical and low-dimensional magnetic materials.[47]

Reactions of gases with crystals of hydrogen-bonded inorganic networks that result in incorporation of the gas molecules have been reported for SO$_2$[48] and for a series of simple acids and bases (*e.g.* HCl, NH$_3$).[49] These studies suggest the possibility for development of gas sensors.
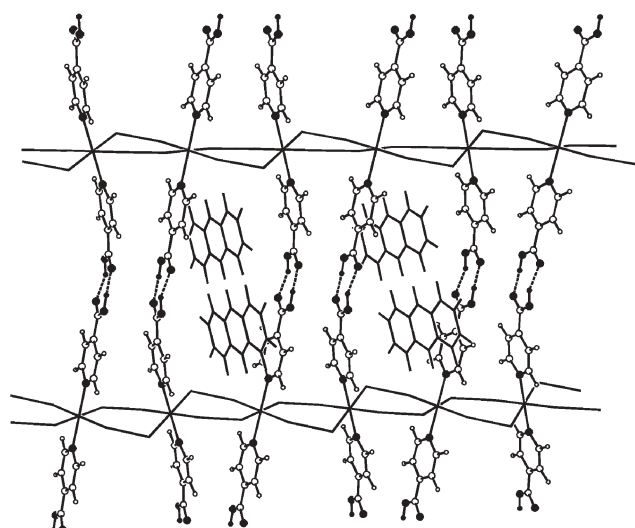
Fig. 14 Cross-linking of {Ni(μ-SCN)$_2$L$_2$}$_n$ coordination polymer *via* carboxyl–carboxyl hydrogen bonds between isonicotinic acid ligands (L) to give a sheet structure which stacks providing channels that accommodate polycyclic aromatic hydrocarbon (PAH) guest molecules, here anthracene.[44] Reproduced from ref. 1*d* with permission. Copyright John Wiley & Sons Limited.

Future potential in this area lies in harnessing the array of optical, electronic, magnetic, and catalytic properties that metal centres can provide within well-defined but geometrically flexible network solids that can be synthesised using non-covalent interactions.

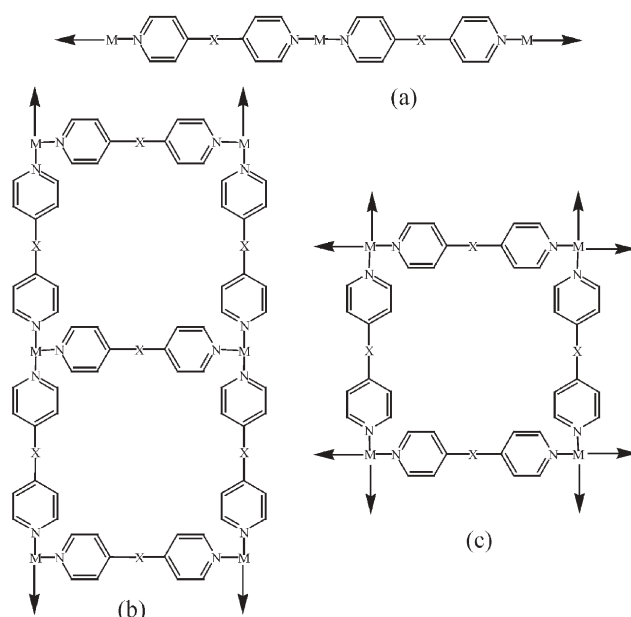# 4 Coordination networks

4.1 Strategies for crystal synthesis

Networks propagated through metal–ligand coordination bonds, known as coordination polymers or metal–organic frameworks (MOFs),[1a–c] comprise a large and diverse area of activity within inorganic crystal engineering. Such systems are based upon a combination of metal ions (usually transition metals) exhibiting well-defined preferences in coordination geometry (Scheme 3)[50] with ligands capable of bridging two or more metal centres. The connector ligands are typically rigid, comprising aromatic moieties and or other multiply-bonded components. The most commonly used ligands are those which bond to the metal centres through pyridyl, cyano or carboxylate groups (Scheme 4), though phosphorus- and sulfur-bonded ligands recently have been developed and used very effectively.[51]

The metal coordination geometries, metal–ligand bond lengths and dimensions of the connector ligands are mostly well established or can be estimated readily from existing crystallographic studies. This information provides an important quantitative foundation for the modular design of coordination networks. In its conceptually simplest form transition metal ions are used as nodes in a network that is completed through linking of pairs of metal centres by simple linear connector or spacer ligands (Fig. 15).[52] An extension of this approach involves the use of polydentate bridging ligands that can be viewed as additional network nodes. A well-developed literature describing mathematical nets and their use in the description of simple binary and ternary inorganic compounds has provided a valuable foundation upon which to develop a net-based approach to the synthesis of coordination polymers. Indeed, a vast literature of examples of 1D, 2D and 3D coordination networks has developed primarily since the early 1990s. Illustrative examples have been discussed by Robson, one of the pioneers of the net-based approach.[53] An
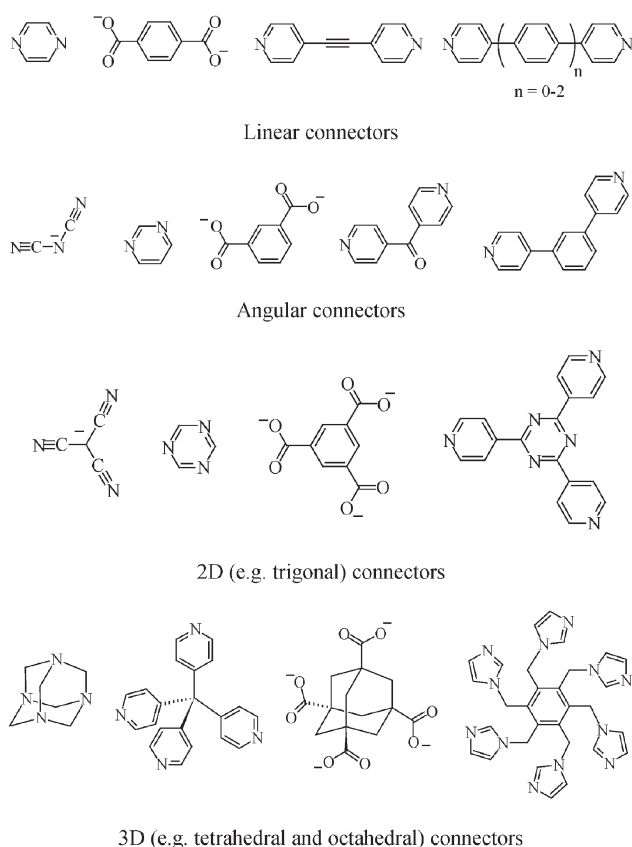
Scheme 4 Representative examples of connector ligands.

illustrative example is the combination of CuBF$_4$ and tetra(4-cyanophenyl)methane that leads to a diamondoid network in which Cu(I) centres and the central carbon atom of the ligand serve as tetrahedral nodes. Similarly, combination of square planar nodes and tetrahedral nodes (*e.g.* [Pt(CN)$_4$]$^{2-}$ with Cu(I) or, providing larger metrics, 5,10,15,20-tetra(4-pyridyl)porphyrin


Fig. 15 Three common network types found when using linear spacer ligands: (a) two spacer ligands coordinated to each metal centre leading to a linear chain (1D); (b) three spacer ligands leading to a ladder network (1D); (c) four spacer ligands leading to a square grid (2D). In each case the metal coordination sphere would be completed by other ligands that do not propagate the network.

with Cu(I)) can be used to construct a 3D network with the same topology as that of PtS.

Chelating ligands can impart additional stability to the linkages in a coordination network in the same manner that such ligands impart stability to isolated coordination compounds.[53] Metal-centred network nodes also need not be mononuclear. Indeed, dinuclear, trinuclear and tetranuclear nodes have been shown to be very effective in the construction of networks wherein the connector ligands carry carboxylate groups that bridge pairs of metal centres within the multinuclear node. Yaghi and coworkers have described such arrangements in terms of secondary building units (SBUs) as illustrated in Scheme 5.[54]
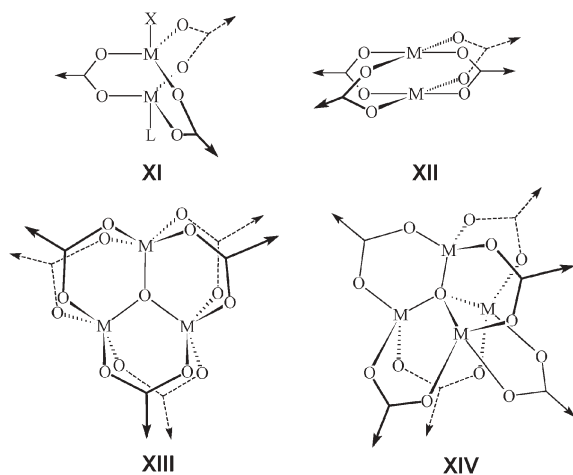

Scheme 5 Secondary building units (SBUs) comprising polynuclear metal carboxylate moieties.[54]

A practical point when undertaking synthesis of coordination polymers is realisation that growth of the network (indeed of the resulting crystals) occurs *via* a self-assembly process. Since there is a need for correction of 'mistakes' arising during the assembly process, as in all self-assembly mechanisms, choice of kinetically labile metal ions permits repeated metal–ligand bond formation and breaking leading to a thermodynamically driven product. Less labile metal centres can also be used, but there may be a need to work at elevated temperatures or pressure, for example using solvothermal methods.

4.2 Network isomerism and interpenetration

The net-based approach to synthesis of coordination polymers while effective can lead to specific surprises. Notably, some combinations of node geometry and spacer ligands do not necessarily have a unique network outcome. Zaworotko has highlighted this issue and coined the term 'supramolecular isomerism'.[55] The situation is exemplified by consideration of the simple combination of 3-connected T-shaped nodes (*e.g.* as often formed by $M^{II}(NO_3)_2$ moieties) with ditopic linear connector ligands wherein no fewer than six different network topologies have been observed (Fig. 16). These include 1D, 2D and 3D networks.

One of the principal motivations in designing coordination networks is the synthesis of porous solids whose channels and cavities can be tailored for applications in chemical separations, storage and even catalysis (see Section 4.3). However, the major challenge to overcome in the synthesis of such materials is interpenetration of the network. Thus, in many cases the desired vacant space can be occupied by a second (or multiple) copy(ies) of same network. This topic has been reviewed[56] and a number of strategies have been prescribed to avoid interpenetration. An illuminating account of these strategies can be
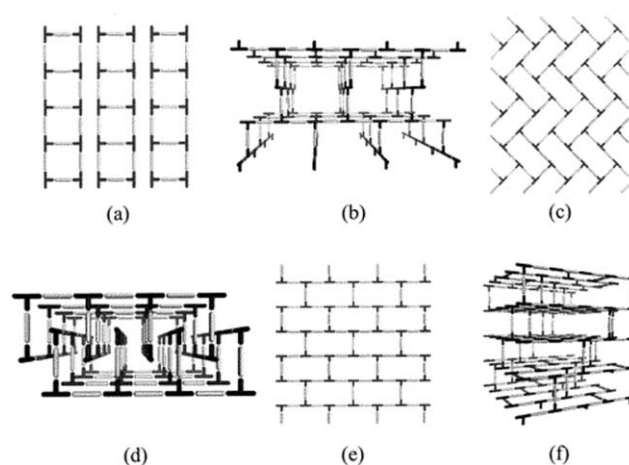
Fig. 16 Schematic representation of supramolecular isomers observed for T-shaped nodes linked by linear connector ligands: (a) 1D ladder, (b) 3D 'Lincoln logs', (c) 2D herringbone, (d) 2D bilayer, (e) 2D brick wall, (f) 3D frame. Reprinted with permission from ref. 55. Copyright 2001 American Chemical Society.

found in the recent review by James.[1b] A simple option is the design of a network that occupies slightly in excess of 50% of the available space in the crystal, but far larger free volumes have been achieved. Other approaches have included narrowing the apertures that define the entrance to the cavities (*i.e.* constriction of the network pores) through the use of bulky ligands. For some systems geometric relationships based upon the dimensions of the linker ligands have been developed to define the expected degree of interpenetration[57] or the limiting conditions under which it can be prevented.[51a] In the synthesis of crystals containing cubic networks (IRMOFs‖) in which SBU **XIV** is linked *via* linear dicarboxylate groups (Fig. 17), Yaghi and coworkers[58a] have established that interpenetration can be controlled by concentration effects. Thus, very dilute solutions of the building blocks were used to construct networks with free volumes reaching some 91% of the crystal volume.

4.3 Applications

Although still a relatively young field, the study of coordination polymers has yielded tangible applications in a number of areas and shows significant promise in others. The applications of coordination polymers have recently been reviewed.[1a] Some illustrative examples are presented here.

As alluded to above, the design of porous crystalline materials, whose pores can be tailored, not only in size but functionality, hold out tremendous promise for applications in a number of areas. One only has to look at the current use of zeolites to recognise some of the possibilities. Prominent among the applications being targeted are gas storage,[58] chemical (and chiral) separations and catalysis.[59]

Porous materials for gas storage. The neutral, highly porous framework materials reported by Yaghi (Fig. 17) have been found to be stable to temperatures of between 300 and 400 °C and maintain their crystallinity upon evacuation of the pores. These materials have therefore been examined for sorption of a variety of gases. IRMOF-6 (Fig. 17), which uses the cyclobutane-derivatised benzenedicarboxylate linker, was found to be particularly effective in the uptake of methane, with capacity exceeding that of zeolite 5A.[58a] This framework has also been investigated together with IRMOF-1 and

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‖ Isoreticular metal-organic frameworks. (Isoreticular means having the same network topology).
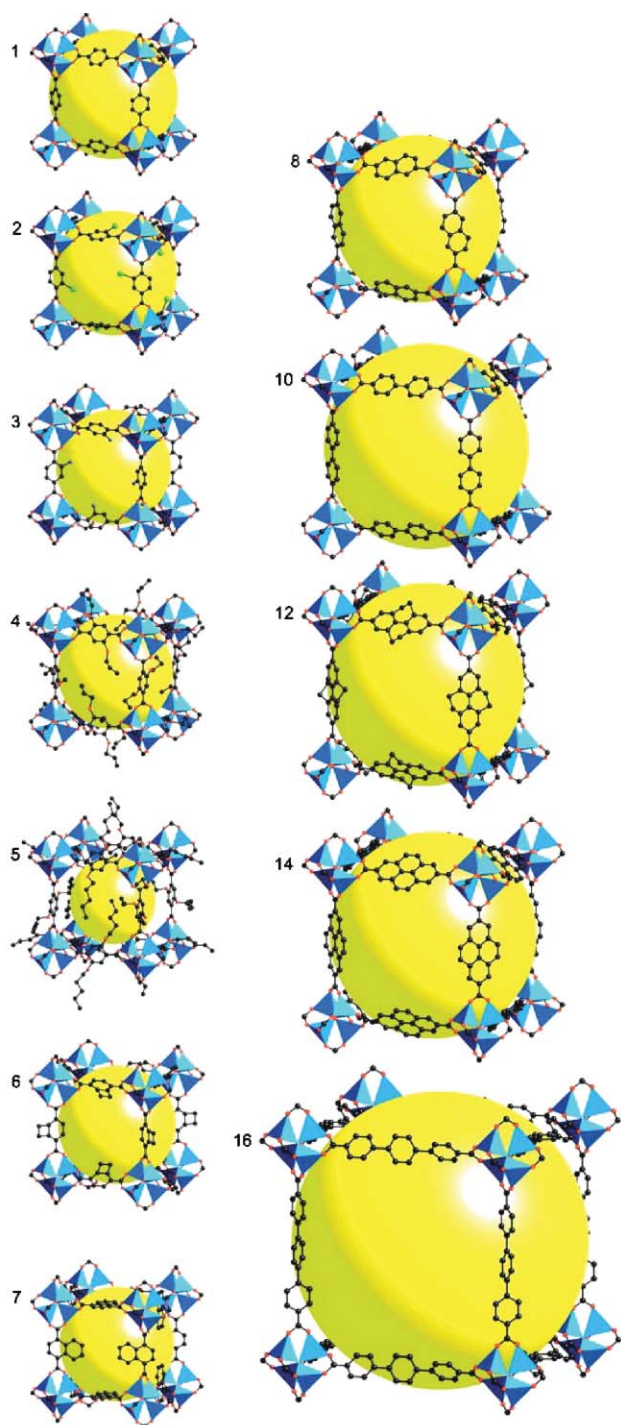
Fig. 17 The cubic repeat units of IRMOF[||] structures (numbered 1–16) in which series of dicarboxylate ligands are used to connect SBUs of type **XIV**. Reprinted with permission from ref. 58a. Copyright 2002 AAAS.

IRMOF-8 as a potential hydrogen storage medium, where future applications related to hydrogen fuel cells are sought.[58b] Uptake of hydrogen at room temperature and pressure (10 bar) was found to be as high as 2.0 wt% for IRMOF-8, already approaching the US Department of Energy target of 6.5 wt% for hydrogen storage materials to be used in automobile fuelling. The nature of the binding sites in IRMOF-1 has also been explored at different hydrogen gas loadings using inelastic neutron scattering (INS) spectroscopy.[58b]

Porous materials for use in catalysis. In contrast to molecular homogeneous catalysts, heterogeneous catalysts are often poorly understood both from a structural and mechanistic point of view. Porous materials such as zeolites offer the possibility of Lewis acid catalysis, but the promise of porous coordination polymers is that of structurally well-defined crystalline materials containing catalytic sites with activity comparable to homogeneous catalysts, but selectivity derived from geometrically and chemically tailored pores. One of the earliest examples of a porous coordination polymer exhibiting catalytic activity was reported by Fujita, wherein the 2D square grid framework $Cd(NO_3)_2(4,4'\text{-bipy})_2$ was found to catalyse the cyanosilylation of aldehydes when suspended in CH_2Cl_2.[60] Some shape (or size) selectivity was observed, with bulkier aldehydes giving lower yields. Importantly, no catalysis was observed in a solution of either $Cd(NO_3)_2$ or 4,4'-bipy alone or in the supernatant liquid of a suspension of $Cd(NO_3)_2(4,4'\text{-bipy})_2$ in CH_2Cl_2. Kim and coworkers subsequently reported a homochiral porous framework with 1D channels[61] (Fig. 18).

(a)

(b)
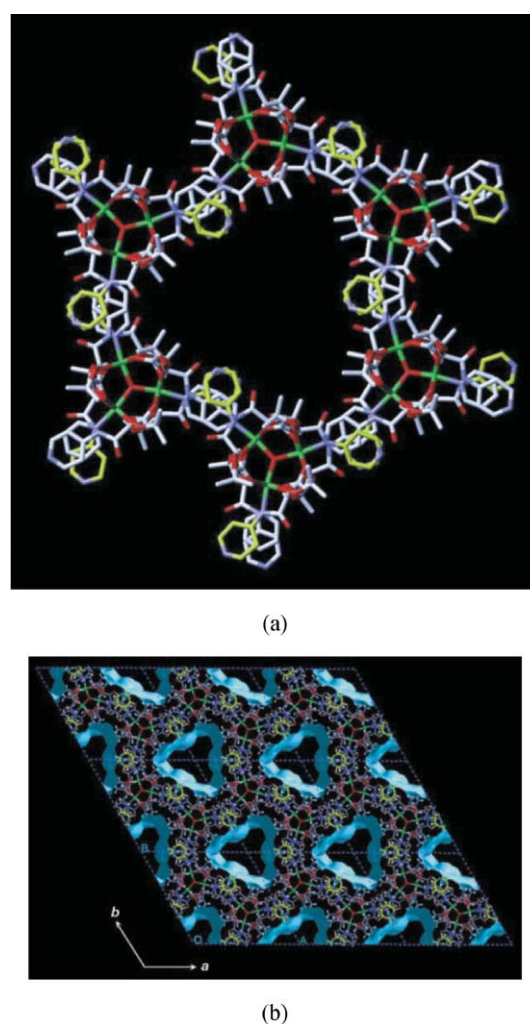
Fig. 18 Homochiral porous MOF[61] showing: (a) a close-up view of one channel (note the pyridinium groups shown in yellow that line the channels); (b) an extended view of the structure showing the arrangements of channels, which lie parallel to the crystallographic *c*-axis. Reproduced from *Nature* (http://www.nature.com), ref. 61, with permission of Macmillan Magazines Ltd.

The framework, based upon SBUs of type **XIII** which are linked *via* a chiral ligand containing pyridyl and carboxylate functions, showed activity in the catalysis of transesterification reactions of methyl 2,4-dinitrobenzoate with a variety of alcohols. Use of a racemic mixture of the chiral alcohol 1-phenyl-propan-2-ol resulted in a modest enantiomeric excess

of 8% in the product ester. Bulkier alcohols showed slower reaction rates consistent with the catalysis taking place within the channels.

Porous materials for separations. Lin and coworkers have reported a number of chiral coordination polymers using ligands that have been designed with 1,1'-binaphthyl moieties as the chiral element.[59] Functionalisation with phosphonic or carboxylic acid groups has permitted neutral coordination frameworks to be constructed using transition metals or lanthanide metals which are coordinated by phosphonate or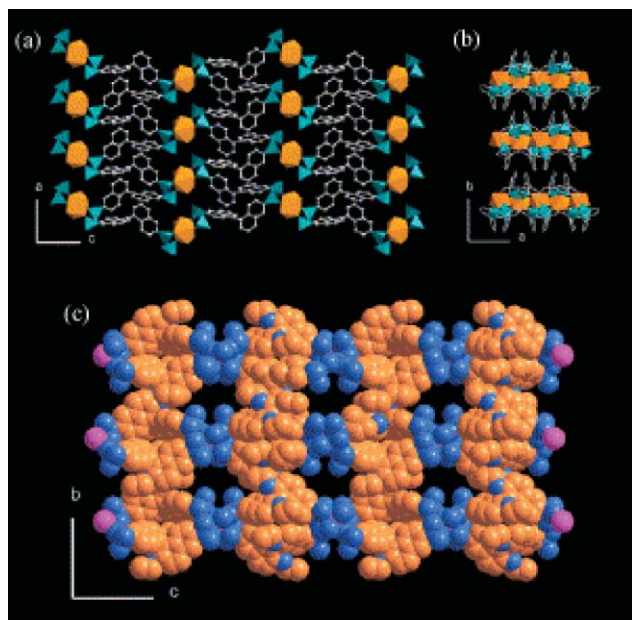 carboxylate groups. Of particular note here are a series of homochiral lamellar framework materials comprising lanthanide metals linked using 2,2'-diethoxy-l,1'-binaphthalene-6,6'-bisphosphonate ligands (Scheme 6, Fig. 19). Ammonia treated
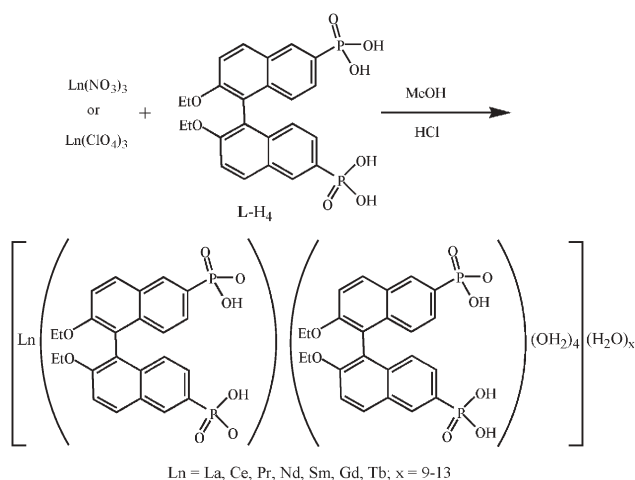
Scheme 6

Fig. 19 Crystal structure of [Gd(R-**L**-H$_2$)(R-**L**-H$_3$)(OH$_2$)$_4$]·12H$_2$O showing (a) one layer, (b) interdigitation of binaphthyl groups from adjacent layers, and (c) space filling view of one layer showing the chiral channels that run parallel to the crystallographic a-axis. Reproduced from ref. 59, copyright 2003, with permission of Elsevier.

samples of the samarium compound (R enantiomer) have demonstrated some selectivity in chiral separations. Thus, racemic 1,2-diaminocyclohexane as the substrate resulted in an

enantiomeric enrichment of 13.6% and 10% for the (S,S)-1,2- and (R,R)-1,2-diaminocyclohexane in the beginning and ending fractions, respectively.

Materials designed for their photophysical properties. A number of groups have exploited photophysical properties of transition metal and lanthanide coordination compounds to design coordination polymers that exhibit such properties, particularly luminescence.[1a] Examples include luminescence arising from ligand-to-metal charge-transfer (LMCT), from the ligand alone (though emission frequencies can be modified due to metal coordination), or metal based emissions (e.g. f→f emissions in lanthanide coordination polymers).

Another area in which crystal engineering may have an important role to play is in the design of materials that exhibit non-linear optical (NLO) properties. In particular there has been an interest in designing crystals that can be used in second harmonic generation (SHG), i.e. frequency doubling of light. The requirements of useful materials are that they contain a suitable chromophore and that the crystal structure is non-centrosymmetric. Within the context of coordination polymers, the use of conjugated organic ligands that connect an electron donating group with an electron acceptor is most desirable. Lin and coworkers have employed a deceptively simple but effective design strategy that clearly demonstrates the potential for applications of coordination polymers in this arena. Using conjugated monoanionic ligands with mutually opposed pyridyl and carboxylate groups, non-centrosymmetric diamondoid coordination networks have been prepared in which Zn(II) or Cd(II) metal centres are linked. Each metal centre serves as a tetrahedral node and is necessarily coordinated by two pyridyl and two carboxylate groups (Fig. 20).[62] Performance approaching that of the industry standard LiNbO$_3$ in terms of SHG intensities was observed in some of the materials prepared.

Materials designed for their magnetic properties. Coordination polymers designed with magnetic properties in mind generally involve the linking of metal centres with electron configurations involving one or more unpaired spins. The connector ligands typically have short spans and are conjugated to permit most readily the electronic communication between metal centres necessary for cooperative effects involved in ferro-, ferri- and antiferromagnets.[1a] Batten and Murray have recently reviewed the extensive range of coordination polymers formed using the archetypal anionic bridging ligands dicyanamide, N(CN)$_2$$^-$, and tricyanomethanide, C(CN)$_3$$^-$, and their magnetic behaviour.[63] A broader survey of examples can be found in the review by Janiak.[1a]

5 Future outlook for inorganic crystal engineering

The prospects for future development in inorganic crystal engineering are excellent. Much is already known about how to harness non-covalent interactions in linking metal-containing building blocks. These include interactions that behave analogously to those found in organic crystals, as well as entirely new interactions active only due to the involvement of metal centres. However, further fundamental studies continue to be needed to underpin developments in this area. These include theoretical modelling, which has been sparse to date, in addition to experimental (synthetic and crystallographic) studies. Stabilising porous networks using non-covalent interactions still presents a challenge, though the successes in organic crystal engineering point to definite prospects in this area, and the directionality combined with flexibility provided by hydrogen bonds and similar interactions clearly can be advantageous. Recently, inorganic analogues of Ward's highly

(a)

(b)
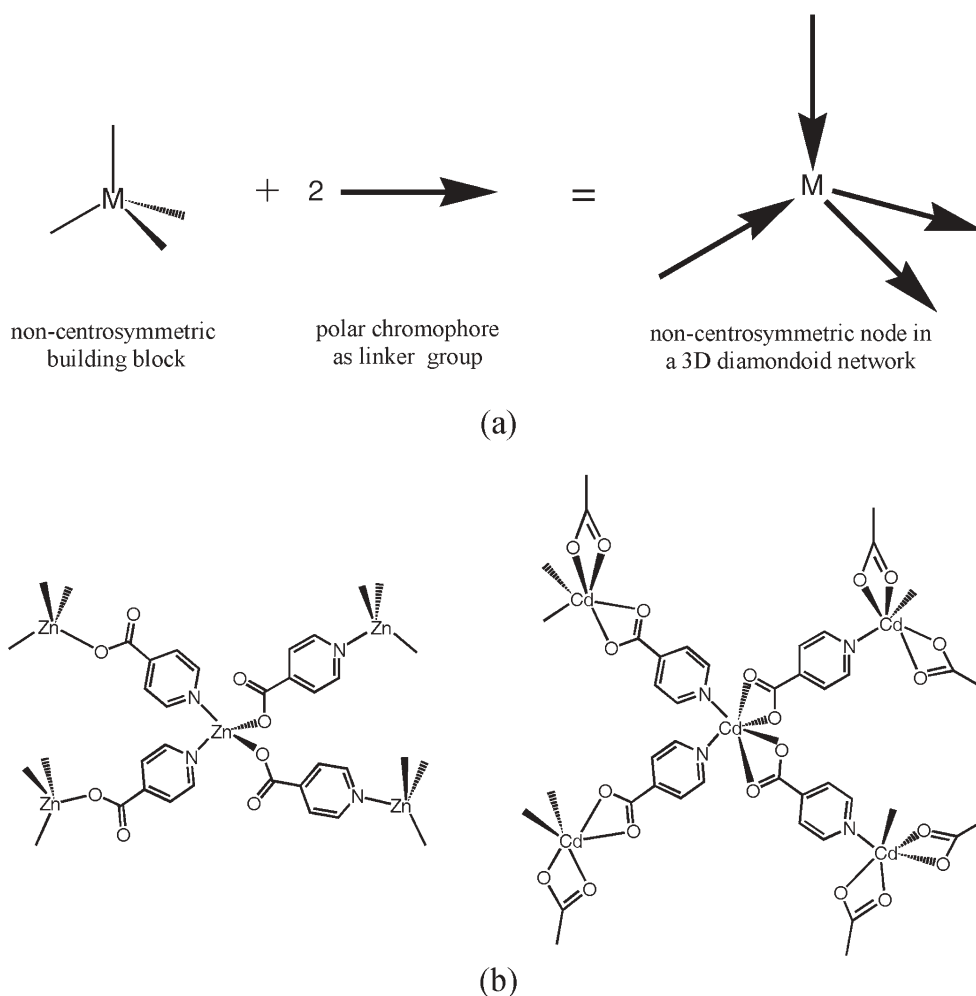
Fig. 20 (a) Schematic representation of the design strategy for noncentrosymmetric coordination networks for use in SHG. (b) Examples of such networks employing isonicotinate linker ligands. Fig. 20b is adapted from ref. 62 with permission. Copyright 2001 American Chemical Society.

successful guanidinium sulfonate host networks have been reported in which layers of $[Co(NH_3)_6]^{2+}$ cations are linked *via* organic disulfonates to give host networks capable of encapsulating small molecules.[64] The field of coordination polymers is more highly developed in terms of applications, but one can look to some of the advances realised therein to translate into corresponding advances in non-covalently assembled crystals. In particular, luminescent and NLO materials should be within the reach of non-covalent network compounds. However, magnetic materials can be expected to rely upon the stronger magnetic coupling provided through coordination bonds.

Great strides have been made not only in the structural design of coordination polymers, but also in developing applications. The diversity of metals available is vast and the prospects for design of new, highly tailored connector ligands is great given the well-developed fields of synthetic organic, organometallic and coordination chemistry whose contribution to crystal engineering is set to expand. Thus, one can anticipate major advances in coming years in well-characterised functional materials, particularly those taking advantage of porous frameworks whose interiors can be designed for a wide range of specific functions. As an indication of what may be to come in the area of catalysis, a recent report by Lin describes the incorporation of a highly active and selective (up to 99% ee) chiral catalysts into a porous zirconium phosphonate support.[65] This material is amorphous and so cannot be subjected to crystallographic characterisation, but already suggests what may soon also be possible using a crystal engineering approach.

But what about new areas? An interesting prospect is suggested by recent reports that show that a crystal engineering approach can be applied to the design of 2D networks not just within crystals but on surfaces. Thus, both hydrogen-bonded[66] and coordination[67] networks have been assembled in this manner and point the way towards the possibility of using this approach for patterning of surfaces and for molecular electronics.

6 Future role of crystallography in inorganic crystal engineering

Crystal engineering is a field that embodies both molecular and supramolecular synthesis, computational studies of intermolecular interactions and their role in dictating crystal packing arrangements, and a wide variety of techniques important in establishing and quantifying the chemical and physical properties (the function!) of newly synthesised crystalline materials. Crystallography pervades the discipline since it provides the principal means of accurate structural characterisation for the products of crystal engineering and provides the quantitative input regarding geometries that is so valuable for future design efforts. However, crystallography is not just about solving crystal structures and as the field of crystallography and its associated instrumentation advances it should continue to have much to offer in the further development of crystal engineering. This is evident from some of the other reviews in this issue of *Chemical Society Reviews*, in which research at the forefront of crystallography is described.[68] Thus, the rapidly growing

crystallographic databases,[68a] particularly the CSD, will continue to provide a means of analysing intermolecular interactions and coordination geometries to provide invaluable input into crystal engineering design strategies. Single crystal diffraction will obviously remain at the forefront of characterisation of crystalline compounds, but the greater accessibility of very low temperature studies[68b] is likely to permit novel studies of magnetic phenomena and to offer the potential for improved characterisation of the interior of pores in network materials. Coupled with the multiwavelength options and high flux available at synchrotron X-ray sources[69] accurate characterisation of a wider range of samples is inevitable. Charge density methods in which very accurate X-ray diffraction data are used to model the electron density and associated properties including the electrostatic potential, intermolecular interaction energies, dipole moments, *etc*. may also prove valuable. A recent charge density study of a zeolite by Lecomte and coworkers[70] suggests applications in the study of porous framework materials that are designed using crystal engineering.

Ab initio structure determination from powder X-ray diffraction has advanced greatly in recent years, and will most likely provide a method for rapid crystal structure determination that can be used not only in cases where single crystals are unavailable, but for monitoring dynamic processes in crystals such as phase changes, guest sorption/desorption, and chemical reactions. The technique has seen relatively limited use in inorganic crystal engineering to date, but early studies show clear potential for its efficacy.[71] Indeed, in a remarkable recent study using synchrotron X-ray powder diffraction, and aided by maximum entropy methods (MEM) of structure solution/refinement, Kitagawa, Takata and coworkers were able to determine the crystal structure of a new coordination framework material including identifying the positions of absorbed molecular oxygen within its channels![72]

Another recent advance in crystallographic studies has been the possibility to undertake time-resolved diffraction studies of short-lived excited state species (typically metal complexes) by coupling photo-excitation with rapid, high-flux synchrotron X-ray measurements.[68d] In connection with such studies, Coppens and coworkers have described crystal engineering strategies to control the distribution (positions and effective concentration) using designed host crystals.[73]

Thus, there are prospects for many areas in which crystallographic studies that go beyond single crystal structure determination may contribute to the future development of inorganic crystal engineering.

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