Structural diversity and chemical trends in hybrid inorganic–organic framework materials

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Received (in Cambridge, UK) 18th July 2006, Accepted 20th October 2006
First published as an Advance Article on the web 7th November 2006
DOI: 10.1039/b610264f

Hybrid framework compounds, including both metal–organic coordination polymers and systems that contain extended inorganic connectivity (extended inorganic hybrids), have recently developed into an important new class of solid-state materials. We examine the diversity of this complex class of materials, propose a simple but systematic classification, and explore the chemical and geometrical factors that influence their formation. We also discuss the growing evidence that many hybrid frameworks tend to form under thermodynamic rather than kinetic control when the synthesis is carried out under hydrothermal conditions. Finally, we explore the potential applications of hybrid frameworks in areas such as gas separations and storage, heterogeneous catalysis, and photoluminescence.

1 Introduction

The purpose of this feature article is to give an overview of developments in the field of hybrid inorganic–organic framework structures over recent years, especially during the last decade. We have not attempted to be comprehensive because of the huge amount of activity in the area, but instead we have focused on placing these developments in a broader context. We shall illustrate the enormous chemical and structural diversity of these materials and discuss some of the systematic trends that are starting to appear in synthetic routes for hybrids. We shall also examine some of the emerging application for materials in this exciting area.

There is an extensive class of purely inorganic framework materials based upon extended arrays such as chains, sheets or 3-D networks. The silicate and aluminosilicate minerals, which were classified by Pauling almost 70 years ago, constitute the most versatile group. Indeed, their dimensionalities can range from 0, as in simple silicates such as zircon that are based upon isolated orthosilicate SiO_4^{4-} units, through 1-D silicate chains (*e.g.* pyroxenes), 2-D sheets (*e.g.* micas and clays) to 3-D arrays (*e.g.* quartz). Zeolites represent a particularly interesting sub-class of these aluminosilicate frameworks, since their architectures display nanoporosity that can be harnessed for applications in separations, catalysis and so on.[1] More recently it has been shown that a wide range of other inorganic families, especially phosphates, can form framework structures with varying dimensionalities. This is true, for example, of aluminium phosphates, tin(II) phosphates, zinc phosphates and so on.[2] Fig. 1 shows examples from the case of tin phosphates.

In the world of organic solids, by contrast, such structural diversity is less well represented. Molecular organics (*i.e.* 0-D) are ubiquitous, of course, but extended arrays are largely limited to 1-D chains, such as those found in polymer systems ranging from polyolefins to block copolymers and proteins. With the exception of covalent organic frameworks (COFs) that contain borate,[3] extended 2-D and 3-D organic arrays are essentially unknown, aside from cross-linked polymers and examples based upon molecular units that assemble into networks *via* hydrogen bonding rather than covalent bonding.[4] In the light of this basic distinction between inorganic and organic networks, it is interesting to examine the structural diversity of hybrid inorganic–organic frameworks.

We define hybrid inorganic–organic framework materials as compounds that contain both inorganic and organic moieties as integral parts of a network with infinite bonding connectivity in at least one dimension. This definition excludes systems that are molecular or oligomeric, such as the

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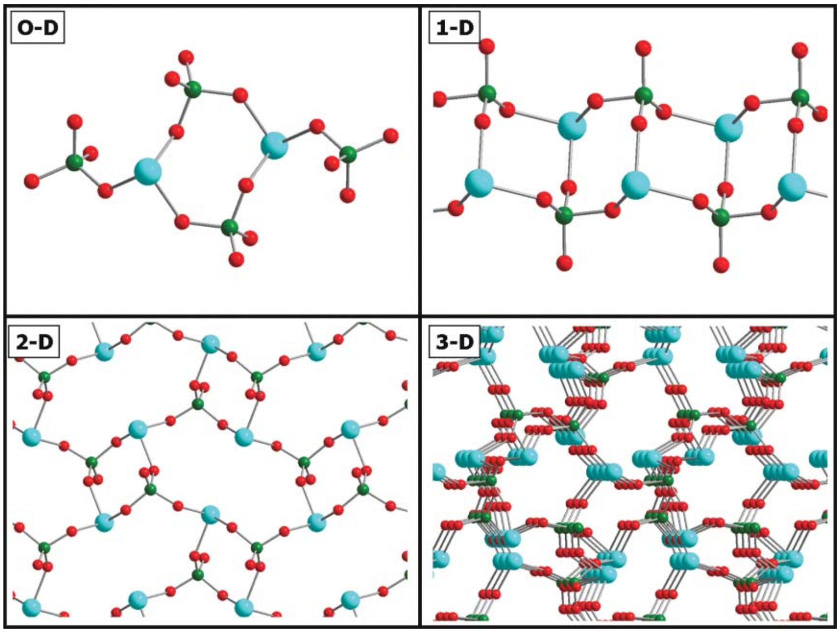

Fig. 1 Four tin phosphates, each containing the same $Sn_2P_2O_4$ motif, with monomeric, 1-D, 2-D, and 3-D structures. Blue spheres denote tin, green phosphorus, and red oxygen.

supramolecular assemblies described by Lehn, Hosseini, Stang, Fujita and many others. It also excludes systems in which the organic is merely a guest inside an inorganic cavity, as is often observed in zeolites and mesoporous materials, and hybrid composites, in which the inorganic and organic components are present as separate phases. Most of the known hybrid frameworks may conveniently be divided into two categories.[5] The *coordination polymers*, or metal organic frameworks (MOFs) as they are also known, can be defined as extended arrays composed of isolated metal atoms or clusters that are linked by polyfunctional organic ligands, L; these are based upon M–L–M connectivity. Second, there are systems that contain extended arrays of inorganic connectivity, which we shall refer to for convenience as *extended inorganic hybrids*. At present, the vast majority of known materials in this area are based upon oxygen bridges. These *hybrid metal oxides*, which often contain infinite metal–oxygen–metal (M–O–M) arrays as a part of their structures, represent a sub-group of a larger class in which there is extended M–X–M bonding *via* other atoms such as Cl, N or S, or *via* inorganic groups such as phosphate.

Examples of 1-D coordination polymers are relatively common in the early literature, even though they were not seen at the time as part of a vast and remarkable family of materials. Examples include porphyrin coordination polymers (Fig. 2) with interesting magnetic properties that were first discovered by Basolo and co-workers in the 1970s and characterized by X-ray diffraction at a later date.[6] Early examples in the 3-D coordination polymer area can be found in the work of Gravereau, Garnier and Hardy in the late 1970s, in which zeolitic materials with ion-exchange properties were made by linking hexacyanoferrate units with tetrahedrally coordinated Zn^{2+} cations.[7] There were also early examples of hybrid materials with extended inorganic connectivity, the most notable being the layered zirconium phosphonates such as the one shown in Fig. 3.[8]

Interest in the hybrid area began to accelerate in the 1990s, when several groups, particularly those of Robson, Hoffman and Yaghi, recognized that rigid, polyfunctional organic molecules could be used to bridge metal cations or clusters into extended arrays. Robson published a landmark paper in 1990,[9] laying the groundwork for an important part of the field of crystal engineering – the science of predicting basic

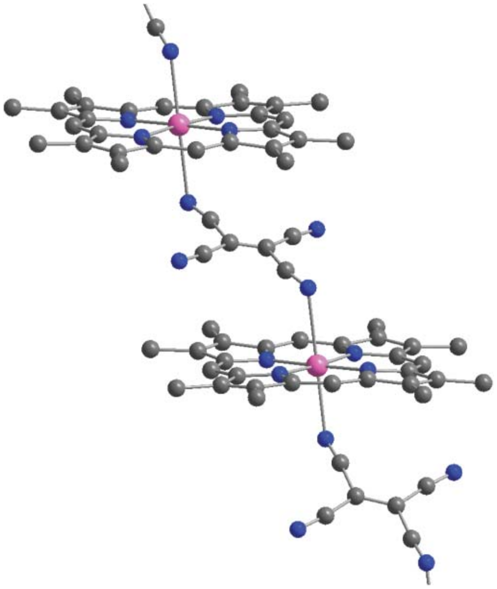

Fig. 2 The 1-D coordination polymer octaethylporphyrinatomanganese(III) tetracyanoethenide (ethyl groups omitted for clarity).[6] The two tetracyanoethenide anions are not crystallographically equivalent, but slightly tilted with respect to each other. Pink spheres denote manganese, blue nitrogen, and gray carbon.

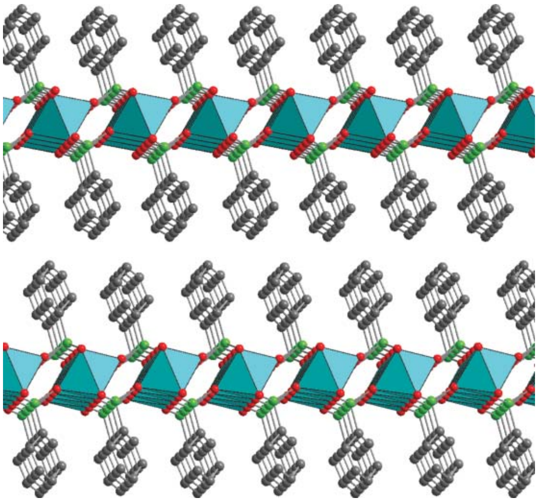

Fig. 3 A side view of the layered structure of zirconium bis(phenylphosphonate), with edge-to-edge interactions between phenyl rings on neighboring sheets.[8] Green spheres denote phosphorus, red oxygen, and gray carbon, with ZrO_6 octahedra in blue.

networks with potentially useful characteristics and then using appropriate molecular building blocks to synthesize them.[10] For the synthesis of *porous* materials, networks are often envisioned where rigid organic molecules and metal atoms or clusters replace bonds and atoms in classical inorganic structures.[11]

The purpose of our feature article is to discuss some of the emerging trends in this rapidly developing field rather than to provide a comprehensive review of hybrids. This is a very complex and diverse field, so we are suggesting a systematic classification of hybrid frameworks that places new and existing materials in a simple, rational context. We have also attempted to identify the structural and chemical trends that are beginning to emerge from the literature and to pinpoint some of the areas where there are important gaps and opportunities. Recent reviews of various aspects of hybrid materials include those of Clearfield, Rowsell and Yaghi, Rosseinsky, and Rao *et al.*[12]

2 Chemical and structural diversity

2.1 Chemical diversity

Hybrid frameworks are found for a wide range of metals and involve a diverse range of organic ligands. Most of the published work involves transition metals, including zinc, but there is a growing body of literature around rare-earth based systems, which are of interest for their optical properties. In addition, there has been a certain amount of effort with p-block elements, especially aluminium, gallium and tin, plus a recent growth of interest in magnesium, driven by the search for lightweight materials for hydrogen storage.

In terms of organic ligands, much of the recent focus has been on connectivity through oxygen atoms of carboxylic acid groups, and there has been a recent review of this field by Rao and colleagues.[12] Rigid dicarboxylic acids, such as benzene-1,4-dicarboxylic acid, have proved very versatile, as have the simple but more flexible aliphatic systems, such as succinic and glutaric acids. The simplest member of this family, oxalic acid, has been used extensively. As will be discussed later, monocarboxylic acids can also form hybrids, and there has been some recent effort with formic and acetic acids. Nor is the field limited to carboxylic acids, since phosphonic acids and phenolic acids can also form hybrid frameworks. Beyond network formation involving M–O linkages, there has been a reasonable amount of work with other types of ligands, such as pyridyls and imidazoles, as well as mixed ligands that offer the possibility of more than one type of connection, *e.g.* M–O plus M–N or M–S. Much remains to be explored in the area of these more complex linkages.

We shall aim to illustrate the diversity of chemical types in the choice of examples that will be given in subsequent sections. Clearly the structures are strongly influenced by the coordination preferences of the metals as well as by the variety of ways in which different ligands can coordinate to metals.

2.2 Coordination polymers

The term coordination polymer owes its origins to the analogy with coordination compounds, in which ligands, organic or otherwise, are coordinated to monomeric metal centers. Coordination compounds can be thought of loosely as the monomers of coordination polymers. Given the enormous volume of work on coordination compounds over the last century, starting with the pioneering work of Werner for which he was awarded the Nobel Prize in Chemistry in 1913, it is hardly surprising that the field of coordination polymers is turning out to be so rich and varied.

A vast range of coordination polymers or supramolecular architectures with different dimensionalities – 1-D, 2-D and 3-D – have been discovered in recent years. Fig. 4 illustrates an example of a 1-D chain system involving Ag–N bonding through a linear 4,4′-bipyridyl group.[13] Since the linkage through the silver is also linear, the chain, itself, is too. By

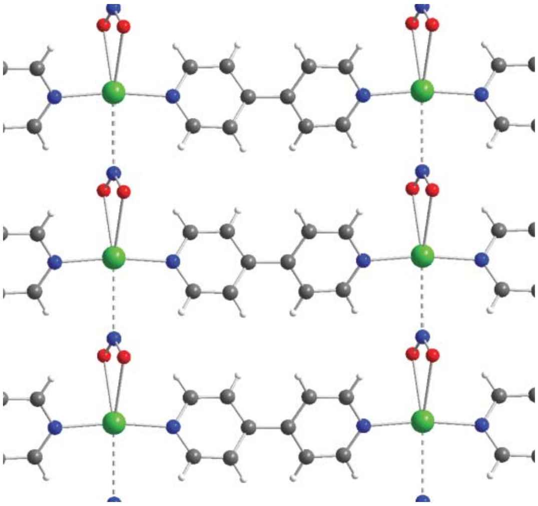

Fig. 4 A linear coordination polymer of silver with 4,4′-bipyridyl and bidentate nitrite anions,[13] There is a 3.0 Å contact between the silver and the nitrogen of the nitrite ion, shown as a dotted line. If this was a full covalent bond, the system would be two-dimensional. Gray spheres denote carbon, white hydrogen, dark blue nitrogen, red oxygen, and green silver.

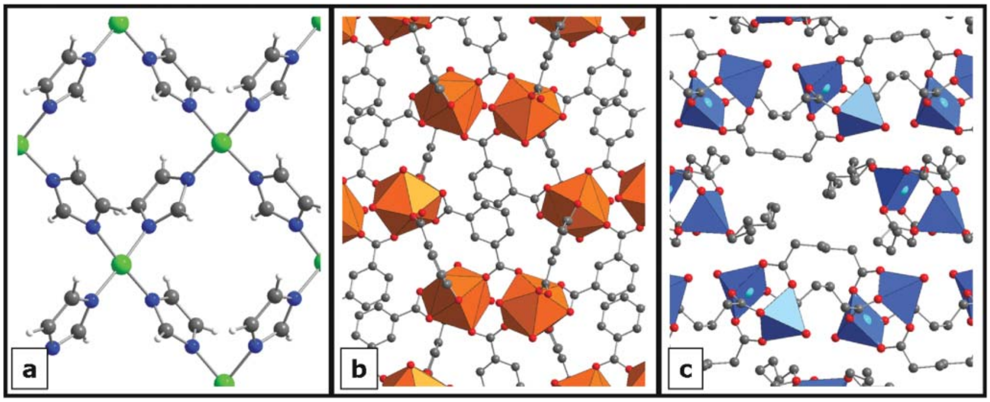

Fig. 5 Some 2-D coordination polymers: (a) nickel bis(imidazolate), containing neutral sheets of square planar metal centers,[16] (b) a plan view of the europium isophthalate structure,[17] showing nine-coordinate Eu^{3+}, and (c) copper adipate,[18] which consists of both chains and sheets, viewed along the chain axis. Gray spheres denote carbon, white hydrogen, blue nitrogen, red oxygen, and green nickel, with EuO_9 polyhedra in orange and CuO_5 square pyramids in blue.

contrast, when tetrahedrally coordinated zinc ions are connected through 4,4′-bipyridyl, this gives rise to a zigzag chain.[14] The metal center does not have to be mononuclear. For example, the common copper acetate dimer, with its paddle wheel geometry, can form linear chains through simple bidentate ligands.[15] The scope of these 1-D coordination polymers is enormous, since they may be neutral or charged (in which case they require compensating cations or anions) and they often contain solvent molecules in voids or channels.

Turning to 2-D systems, Fig. 5(a) shows a very simple example in which nickel ions are connected *via* square planar coordination by imidazolate anions to form a very simple neutral layered structure.[16] A more complex case based upon a combination of rare-earth ions with isophthalic acid is shown in Fig. 5(b); the thiophene derivatized version of the same ligand combined with Tb^{3+} yields a product with enhanced green luminescence.[17] As a final example to illustrate the versatility of this area, we show in Fig. 5(c) a 2-D coordination polymer based on the copper carboxylate dimer, linked through adipic acid, in which a 2-D layer alternates with 1-D chains that contain the same basic building blocks.[18] Here we note that the paddle wheels are linked *via* the dicarboxylic acid rather than by ligands in the axial position of the Jahn–Teller distorted copper coordination sphere.

Robson's early work yielded some elegant examples of crystal engineering in which 3-D networks of simple, known structure types, such as the diamondoid and ReO_3 structures, were built from suitable combinations of metal ions and rigid linkers. Fig. 6 shows a simple example based upon the PtS structure.[19] Others have exploited the same concept, including Carlucci *et al.*,[20] who reported some remarkable open-framework structures based upon silver in combination with ligands such as pyrazine (Fig. 7). Some of the most striking examples

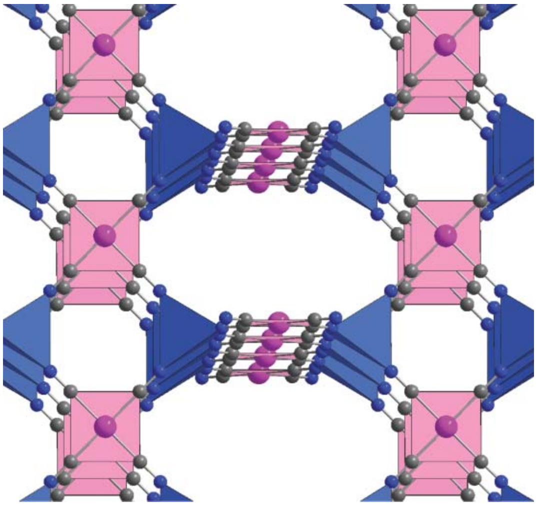

Fig. 6 A mixed copper–platinum tetracyanide, structurally analogous to PtS, with sulphur replaced by a bridging copper tetracyano complex.[19] Pink spheres denote platinum, gray carbon, and blue nitrogen, with PtC_4 square planes in pink and CuN_4 tetrahedra in blue. Reproduced with permission. Copyright 1990, Royal Society of Chemistry.

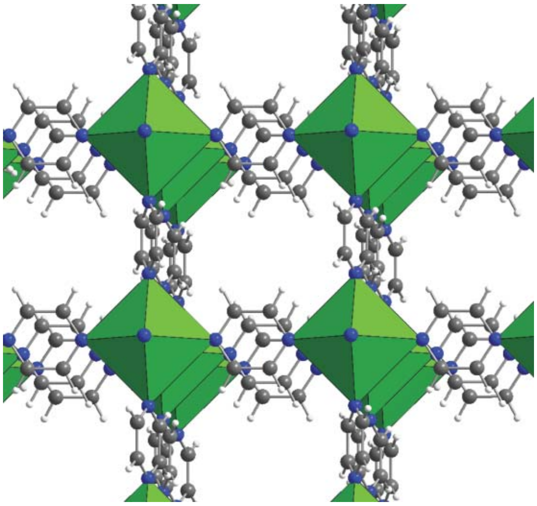

Fig. 7 Silver pyrazine hexafluoroantimonate,[20] a porous framework with an ReO_3-like structure (SbF_6^- groups omitted for clarity). Gray spheres denote carbon, blue nitrogen, and white hydrogen, with AgN_6 octahedra in green. Reproduced with permission. Copyright 1995, Wiley–VCH.

of porous 3-D coordination polymers can found in the work of Yaghi, O'Keeffe and co-workers, in which they have exploited bridging of simple Zn_4O groups *via* rigid aromatic dicarboxylates such as benzene-1,4-dicarboxylic acid to build networks with remarkably low densities and high porosity, such as MOF-5 (Fig. 8).[21] They have shown that large families based upon the same architecture can be created by altering the length or other chemical details of the organic linker.[22] In the case of the *reticular* family based upon MOF-5, for example, they have made as many as 16 derivatives with the same basic architecture. It should also be noted that in addition to architectures based upon the topologies of simple inorganic structures, there has also been success in building porous hybrids based upon known zeolite structures. These include zinc, cadmium and indium coordination polymers that adopt the ABW, BCT, MTN, RHO and SOD topologies.[23] Imidazole-based ligands are particularly effective for this purpose since they can mimic the Si–O–Si angles that are found in typical zeolites.

One of the complications that can arise when the structures are very open is that the networks can interpenetrate or interweave, thereby reducing or eliminating the porosity. There are some remarkable examples of such behavior, including cases where multiple interpenetration is observed.[24] Paradoxically, Yaghi has shown that interpenetration can be attractive for certain gas storage applications, since it can increase the available surface area per unit volume (see section 5.1).

A very recent and exciting example of a 3-D coordination polymers can found in the work of Férey *et al.*[25] on the use of trinuclear chromium clusters in combination with benzene-1,4-dicarboxylic acid. This reaction yields porous structures with unit cells volumes of up to 700 000 Å^3, *i.e.* similar to that of a small protein! In the absence of single crystals for structure determination, the structures were solved by the ingenious use of Monte Carlo simulations with simulated annealing.

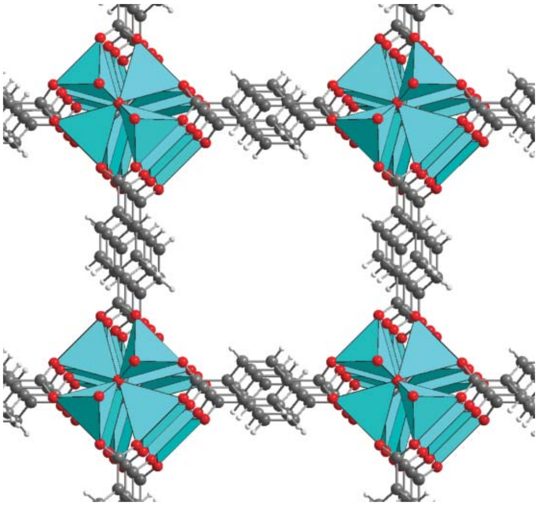

Fig. 8 MOF-5,[21] a porous cubic zinc terephthalate which is topologically analogous to ReO_3. Gray spheres denote carbon, red oxygen, and white hydrogen, with ZnO_4 tetrahedra in blue. Reproduced with permission. Copyright 1999, Macmillan Publishers Ltd.

Finally in this brief section on the exploding field of coordination polymers, we should mention that there growing body of work on systems that contain more than one metal or more than one ligand type, or both. For example, some beautiful open architectures can form when transition metals are combined with rare-earths in the presence of glycolate and water as ligands.[26] Assemblies that contain more than one metal can often be facilitated by the use of ligands with multiple N and O donor atoms, taking advantage of the different ligand affinities of transition metals and rare earths. Equally, the use of more than one ligand with a single metal can yield interesting results, as in the work mixed oxalate–diphosphonates and oxalate–dicarboxylates.[27] A variation on this theme involves a single metal with a carboxylate ligand such as oxalate in combination with phosphate as a second anion.[28] Materials of this type were initially made serendipitously when oxalate salts were being used as precursors in the synthesis of metal phosphate frameworks. These examples illustrate the huge scope of this burgeoning area, with its unlimited permutations of metals and ligands.

2.3 Extended inorganic hybrids

The area of coordination polymers is only one sub-field of the broader domain of hybrid framework materials, since far more structural permutations become accessible if we allow for the possibility of extended inorganic connectivity. This idea is illustrated schematically in Fig. 9, which compares 1-D and 2-D coordination polymers with a system that has inorganic connectivity in two dimensions and is connected in the third dimension by organic linkers. Such extended inorganic hybrid materials not only open up a vast area of new chemical and structural permutations, but they also provide a basis for creating materials with properties that are traditionally found in metal oxides. Thus we have the tantalizing possibility of making hybrid materials that are metallic, superconducting, or high temperature ferromagnets. In this section of the paper, we describe some of the progress that has already been made in this fascinating area.

Early examples of 1-D hybrid metal halides include the famous Wolfram's red salt, which contains $\{Pt(EtNH_2)_4\}$ units linked into infinite chains by Pt–Cl–Pt bridges (Fig. 10(a)).[29] In this, and other more recent examples such as the zinc phosphonate chain of Stucky and co-workers (Fig. 10(b)),[30] the organic ligands simply decorate the inorganic chains, rather than cross-linking them. However, 1-D inorganic chains can also be cross-linked to make a layered structure rather than a 1-D network, as in the case of the metal succinate $Ni_7(OH)_6(H_2O)_3(C_4H_4O_4)_4 \cdot 7H_2O$ (Fig. 11).[31] A beautiful example of a cross-linked inorganic chain is found in transition-metal gallates, which comprises chains of *trans*-corner-sharing MO_6 octahedra cross-linked into a 3-D network by the gallate ions (Fig. 12).[32] Note that all the oxygen atoms of the MO_6 octahedra are supplied by the gallate ligands; the resulting topology of the inorganic network looks like the chain found in Rb_2FeF_5,[33] thereby revealing the striking resemblance between this area and classical solid-state chemistry. Note, too, that the array contains channels that accommodate zeolitic water molecules.

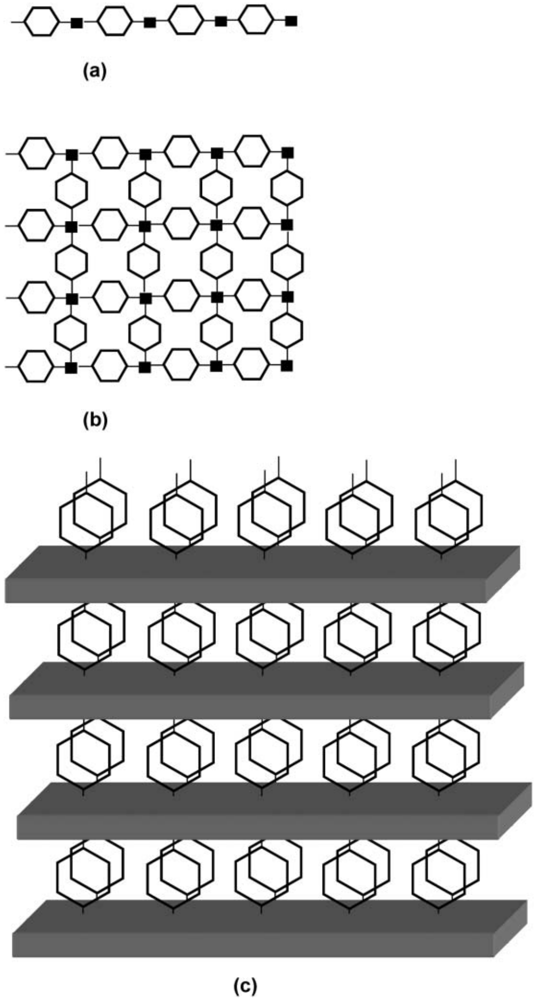

Fig. 9 Schematic representation of coordination polymers and extended inorganic hybrids; (a) and (b) show 1-D and 2-D coordination polymers, respectively, while (c) shows a system that has inorganic connectivity in two dimensions and is connected in the third dimension by organic linkers.

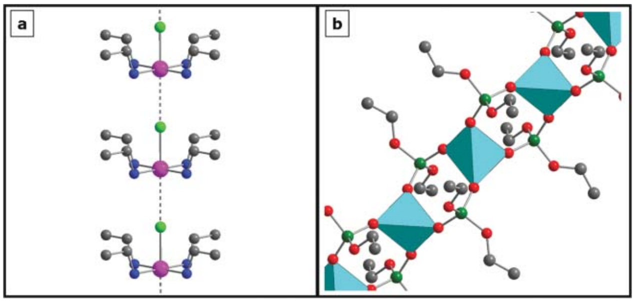

Fig. 10 Some 1-D extended inorganic hybrid materials: (a) Wolfram's Red salt, a 1-D platinum chloride polymer.[29] Controversy continues as to whether the coordination geometry is square pyramidal as shown here, or alternating octahedral and square planar; and (b) zinc diethylphosphate,[30] an inorganic chain decorated by organic groups. Light green spheres denote chlorine, gray carbon, dark blue nitrogen, pink platinum, red oxygen, and dark green phosphorus, with ZnO_4 tetrahedra in light blue.

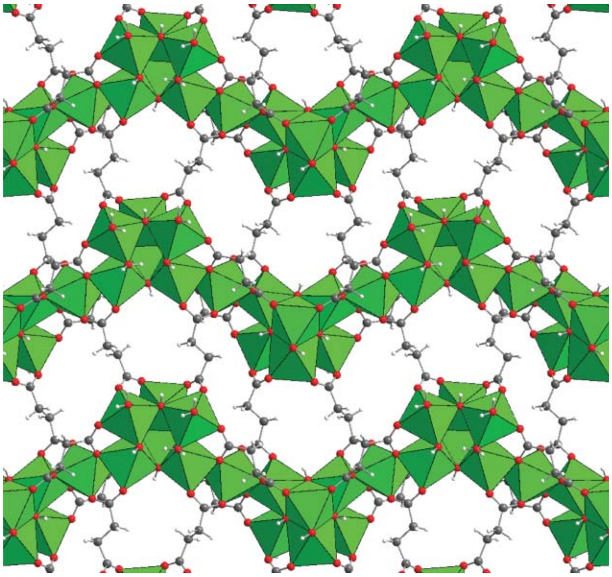

Fig. 11 A nickel succinate containing inorganic chains, bridged by organic groups along a second dimension to form sheets.[31] Gray spheres denote carbon, red oxygen, and white hydrogen, with NiO_6 octahedra in green. Reproduced with permission. Copyright 2003, Wiley–VCH.

Many nice examples of 2-D hybrid oxides can be derived from Clearfield's α-zirconium phosphate structure, which contains 2-D sheets of ZrO_6 octahedra sandwiched between phosphate layers.[34] Alberti *et al.*[8] was able to increase the interlayer spacing by taking advantage of monophosphonates, which acted as spacers between the layers, albeit with no bonding connection between them (Fig. 3). As with some of the examples in the previous paragraph, the organic groups are decorating the layers in the Alberti structures. In order to build three-dimensional frameworks, Dines *et al.* demonstrated that

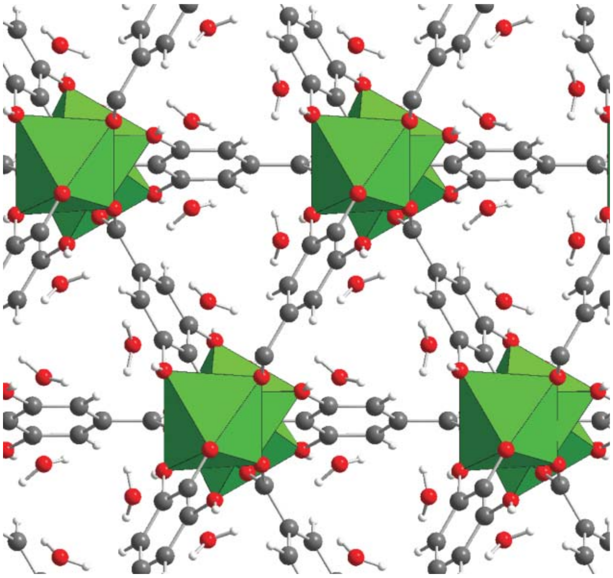

Fig. 12 Nickel gallate,[32] a framework containing inorganic chains bridged by organic groups into a 3-D network. Gray spheres denote carbon, red oxygen, and white hydrogen, with NiO_6 octahedra in green. Reproduced with permission. Copyright 2006, Elsevier Ltd.

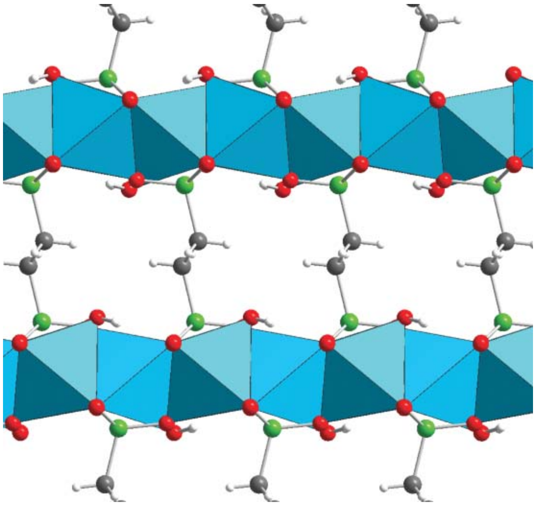

Fig. 13 A pillared cobalt(II) ethanediphosphonate with inorganic sheets connected in the third dimension by organic groups.[35] Gray spheres denote carbon, red oxygen, white hydrogen, and green phosphorus, with CoO_6 octahedra in blue. Reproduced with permission. Copyright 2005, American Chemical Society.

is possible to create connections between the inorganic layers by using diphosphonates (Fig. 13).[36] These materials are not porous, but porosity can be created by using a combination of diphosphonate linkers and shorter monophosphonate groups.[37] There has also been some work to add functionality to the zirconium-based materials through careful choice of the diphosphonate used in the synthesis. For example, Vermuelen and Thompson used viologens, rigid organic molecules of the formula $[H_2O_3PCH_2CH_2\text{–bipyridinium–}CH_2CH_2PO_3H_2]^{2+}$, to bridge zirconium phosphonate layers.[38]

In view of the existence of 1-D and 2-D inorganic connectivity in hybrid materials, there has been considerable interest in the possible existence of 3-D systems. A striking example was found in 2002 with the discovery of a nickel succinate with a 3-D network of corner- and edge-sharing NiO_6 octahedra (Fig. 14).[39] Additional examples have since been found in other systems, including cadmium malonate[40] and nickel glutarate.[41] In all of these systems, the frameworks are open with the organic groups lining the pores, as in Fig. 14, and the structures show enhanced thermal stability on account of the inertness of the inorganic skeleton. Nickel succinate, for example, is stable to 400 °C in air.

2.3 Classification of hybrid framework structures

The examples of hybrid materials presented in the previous two sections underline the enormous structural diversity of this exciting class of materials. For example, while we have focused on the dimensionality with respect to either M–ligand–M or extended inorganic connectivity, it is clear that many systems exhibit both types of linkages. For example, the cobalt diphosphonate shown in Fig. 13[35] is 2-D with respect to inorganic connectivity and 1-D with respect to M–ligand–M connectivity. Overall, therefore, the dimensionality of the network is 3-D. Table 1 shows the full range of possibilities in terms of M–ligand–M or extended inorganic dimensionalities.

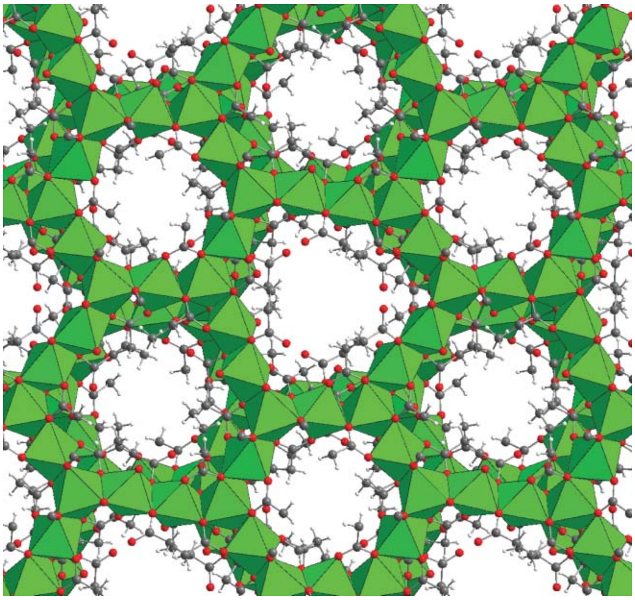

Fig. 14 A nickel succinate containing a channelled 3D nickel–oxygen network decorated by organic groups.[38] Gray spheres denote carbon, red oxygen, and white hydrogen, with NiO_6 octahedra in green. Reproduced with permission. Copyright 2002, Wiley–VCH.

It is interesting to reflect that virtually the whole of organometallic chemistry and much of classical coordination chemistry is contained within a single box in this table (*i.e.* both M–L–M and inorganic connectivity = 0). For conciseness, we refer to this type as I^0O^0 (I = inorganic and O = organic); note that the sum of the exponents gives the overall dimensionality of the structure. The 3-D nickel succinate (Fig. 14) falls in the box with M–L–M = 0 and inorganic connectivity = 3 (I^3O^0) while the MOF-5 structure (Fig. 8) has M–L–M = 3 and inorganic connectivity = 0 (I^0O^3). There are known examples of all of these classes of hybrid material. Wolfram's red salt (Fig. 10(a)), for example, would be I^1O^0, since there is no bonding between the chains, whereas the 1-D coordination polymers of Basolo (Fig. 2) would be I^0O^1. However, some classes, such as I^0O^3, are quite common, while other, such as I^1O^1, are relatively rare.

The question arises as to whether there are materials that can be classified within the empty boxes in the bottom right part of the table. For example, can we have materials in which the connectivity is 2-D with respect to both M–L–M and M–X–M. We currently know of no such materials, but the possibility exists that these may be found in materials that have not yet been discovered.

2.4 Dense and open frameworks

In the previous three sections, we have not attempted to differentiate between dense and open hybrid framework structures. As with inorganic silicates and aluminosilicates, there is no fundamental chemical difference between the dense and open hybrid structures, though their properties and applications are often quite distinct. There are also differences in the synthetic strategies that are needed to synthesize them, and in section 4 we shall discuss some of the reaction

Table 1 Proposed classification of hybrid materials, showing the dimensionality of different structures with respect to both organic connectivity between metal centers (O^n) and extended inorganic connectivity (I^n) (see text for explanation)

Dimensionality of inorganic connectivity, I^n (n = 0–3)

Metal–organic–metal connectivity, O^n (n = 0–3)

	0	1	2	3
0	Molecular complexes I^0O^0	Hybrid inorg. chains I^1O^0	Hybrid inorg. layers I^2O^0	3-D Inorg. hybrids I^3O^0
1	Chain coordination polymers I^0O^1	Mixed inorg.–organic layers I^1O^1	Mixed inorg.–organic 3-D framework I^2O^1	—
2	Layered coordination polymers I^0O^2	Mixed inorg.–organic 3-D framework I^1O^2	—	—
3	3-D Coordination polymers I^0O^3	—	—	—

conditions that are likely to favor the formation of open structures. One strategy that should be mentioned here concerns the use of organic template molecules in the creation of open hybrid structures. Template molecules or structure-directing agents, especially quaternary amines, have been extensively used in zeolite synthesis, but the strategy has not been widely adopted in the hybrid area. Exceptions include the use of amines and other templates in the synthesis of transition-metal diphosphonates, aluminium monophosphonates, and cobalt squarates.[42] In the latter instance, Dan *et al.* prepared $[C_6N_2H_{14}]_2[Co_2(C_4O_4)_3(H_2O)_4]$ and $[C_3N_2H_5]_2$-$[Co_2(C_4O_4)_3(H_2O)_4]$ under hydrothermal conditions in the presence of quaternary amines. Both compounds contain chains formed by cobalt dimers linked by the squarate units, the chains being connected through hydrogen bonding interactions *via* the amines. These materials would be classified as I^0O^1 in the classification shown in Table 1, since we do not include organic connectivity through hydrogen bonding. Finally we should mention a rather unusual example of *inorganic* templating, in which Rao and co-workers prepared an open-framework cadmium oxalate that formed around an alkali halide assembly.[43]

3 Chemical trends

We now turn to the intriguing question of what chemical factors influence whether a particular system will form coordination polymers rather than frameworks with extended inorganic connectivity, or low dimensional rather than high dimensional networks. The findings so far in this area are relatively sparse, but a few systematic trends are beginning to emerge and will be discussed in the following sub-sections.

3.1 Effects of ligand geometry and flexibility on dimensionality

A growing number of materials have been made recently that involve the use of 1,2- 1,3- or 1,4-cyclohexanedicarboxylates (CHDCs) or cyclohexenedicarboxylates.[44] In the case of the CHDCs, the structural trends for the hybrids formed by the three different isomers have been examined systematically with cadmium- and manganese-containing systems;[45] each of the organics can be found as both a *cis*- and a *trans*-isomer. Two-dimensional layered structures of all three of the 1,2-, 1,3- and 1,4-cyclohexanedicarboxylates were made, but infinite metal-oxygen-metal linkages were observed only in the case of the 1,2-dicarboxylate (Fig. 15), the remaining phases being coordination polymers. Only with the close proximity of the carboxylate groups that is found in the 1,2 compound can the metals be sufficiently close to sustain infinite inorganic connectivity, while the 1,3 and 1,4 ligands all provide excellent linkages for coordination polymers with varying dimensionalities. This conclusion is further corroborated by work on cobalt and manganese 4-cyclohexene-1,2-dicarboxylates.[46] We note that the geometry of the 1,2 compound is similar to that of succinic acid, which readily forms extended inorganic connectivity (Fig. 14).

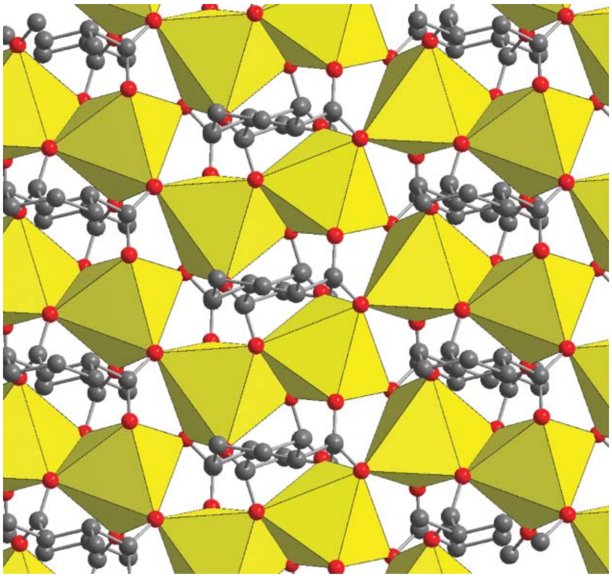

Fig. 15 A plan view of the inorganic sheet structure of cadmium cyclohexane-1,2-dicarboxylate.[45] Gray spheres denote carbon and red oxygen, with CdO_6 octahedra in yellow. Reproduced with permission. Copyright 2006, Royal Society of Chemistry.

Chirality offers another facet of ligand geometry that is very interesting. Many organic ligands, such as tartaric acid, can be obtained in an enantiomerically pure form (many occur naturally, of course), and there is much interest in the formation of chiral open frameworks that might be used as enantiomerically-selective catalysts (see section 5.2). One concern has been whether the chiral ligands are sufficiently robust to survive the reaction conditions that are required for hybrid framework formation without racemization, but this does not appear to be a general problem.[47] A considerable amount of work has been done with naturally occurring amino acids.[48] A nice example of the subtlety that can arise in this area is illustrated by a recent study with nickel aspartate.[49] The structure obtained with the L-aspartate contains a chiral helix based upon a chain of edge-sharing NiO_6 octahedra (space group $P2_12_12_1$), whereas the structure of the racemic analogue contains both left-handed and right-handed forms of the same chain (space group $I4_1/a$). In the more general case, it seems possible that the topologies of chiral structures might in some cases be quite different from those of their racemic analogues.

In addition to the geometry of the ligand, the degree of flexibility is also important in determining the type of structure that can be formed. In particular, ligands with greater flexibility are more likely to be able to adapt to the geometries found in extended inorganic hybrids, such as metal–oxygen–metal linkages. This has been seen in transition-metal diglycolates and iminodiacetates, where a range of hybrid metal oxides has been reported.[50] Furthermore, the use of monocarboxylates, which are clearly not ideal as linkers for coordination polymers, entirely eliminates the need for ligand flexibility, thereby facilitating the formation of frameworks with infinite inorganic connectivity. This is found, for example, in the case of transition-metal cyclopropane monocarboxylates[51] as well as in formates.[101] Lack of ligand flexibility is not only a disadvantage for forming extended inorganic hybrids, but there is also evidence that it may restrict the range of structures that may form in any particular system. Our recent work on transition-metal gallates illustrates this point, because in spite of many attempts to synthesize alternative hybrid frameworks, we have never succeeded in making anything other than the one shown in Fig. 12.[32] Other systems with more flexible ligands, such as the cobalt succinates, form large numbers of different structures (see section 4.1). We ascribe this difference to the limitations on the bonding options, which are very severe for the gallate ion compared with flexible ligands such as succinate.

3.3 Influence of metal ion properties

Turning to the role played by the metal ions in determining the types of structures that can form, a number of important factors are apparent. Most obviously, the preferred coordination number and geometry of the metal ion is a key issue, just as it is in classical coordination chemistry. Divalent and trivalent first-row transition metals, *e.g.* Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Mn^{3+}, Fe^{3+} and so on, all have well known coordination preferences that often depend upon the identity of the ligand environment. Mn^{2+} is typically octahedrally coordinated by oxygen, while Co^{2+} is more versatile and ranges from tetrahedral through pentacoordinated to octahedral. The optical properties change accordingly as the geometry influences the ligand field splitting. Cr^{3+} is always octahedral, while Ni^{2+} is usually octahedral when surrounded by oxygen, but may be square planar in nitrogen environments (this is apparent in the imidazole network shown in Fig. 5(a)). Zn^{2+}, which has been widely used in studies on hybrid frameworks, is very versatile and behaves somewhat like Co^{2+}. Isolated Cu^{2+}, by contrast, is relatively inflexible and is constrained by its need to accommodate the Jahn–Teller distortion that is characteristic of d^9 ions. The rare-earths ions, however, are entirely different from the transition metals, preferring coordination numbers greater than 6 and often 7, 8 or 9 with a wide variety of geometries (see Fig. 16 for a typical example[52]).

Another factor that is frequently apparent is that certain metal ions form well-defined and robust clusters that recur in many hybrid materials. Cu^{2+}, for example, is well known for forming a large number of molecular carboxylate clusters that contain the characteristic paddle wheel dimer shown for the case of copper acetate in Fig. 17(a), so it is not a surprise that this unit is ubiquitous in copper coordination polymers such as the highly porous 3-D Cu trimesate system described by Williams and co-workers[53] and the mixed 1-D and 2-D adipate illustrated in Fig. 5(c). Similarly, Yaghi and O'Keeffe have utilized the Zn_4O cluster (Fig. 17(b)) that is a found in basic zinc acetate, $Zn_4O(OCOCH_3)_6$, using this unit as the primary inorganic node in a huge range of zinc dicarboxylate coordination polymers,[21,22] of which MOF-5 is a prototypic example (Fig. 8). A third example of such a cluster is the trimeric Cr^{3+} cluster, Cr_3O (Fig. 17(c)), which was used in combination with terephthalic acid linkers to create the huge unit cells that are found in MIL-101 and related materials.[25] Silica clusters based upon silsesquioxanes have also been

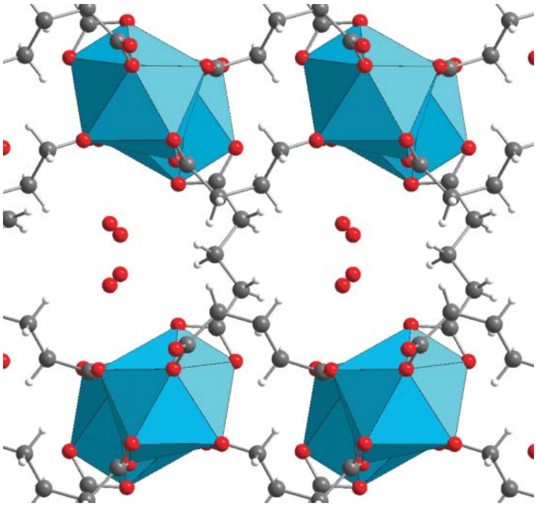

Fig. 16 Neodymium glutarate, a coordination polymer containing chains of edge-sharing NdO_9 polyhedra.[52] Gray spheres denote carbon, red oxygen, and white hydrogen, with NdO_9 polyhedra in blue. Reproduced with permission. Copyright 1998, Royal Society of Chemistry.

exploited, though many of the resulting hybrid frameworks are non-crystalline.[54]

A third point connected with the identity of the metal ions concerns their kinetic stability, or lack thereof. Most M^{2+} and M^{3+} aquo-coordination complexes show rapid ligand exchange with rate constants in the range 10^3 to 10^8 s^{-1}, but a small number of very inert ions have extremely slow ligand exchange rates. Cr^{3+} is the most common and striking example, with a rate constant of $\sim 10^{-5}$ s^{-1}, *i.e.* about eight orders of magnitude slower than Fe^{3+}! The origin of this huge difference lies in the large ligand field stabilization energy of the d^3 Cr^{3+} ion that is also responsible for its strong octahedral coordination preference. Clearly the Cr^{3+} ion provides an excellent basis for creating very stable hybrid frameworks, as has been demonstrated by the work on Férey on the MIL-101, though it can also pose synthetic challenges due to the inertness of the starting materials.

A final point concerning the nature of the metal ion relates to those cations, mainly d^{10}, that readily form linear complexes, *e.g.* Ag^+. As with certain types of ligands, these ions are only able to support the formation of 1-D coordination polymers when they have linear coordination (Fig. 4). This behavior was exploited in some of the very early work by Robson,[9] and continues to be a useful approach for creating low-dimensional structures, as the recent work of Abu-Youssef *et al.* on silver quinoxalines shows.[55]

4 Synthetic trends

4.1 Effect of reaction temperature and pH

It is reasonable to ask how over 100 years of effort in the field of coordination chemistry failed to uncover the existence of the whole world of hybrid framework materials until very recently. With the knowledge of hindsight, we can see that this extraordinary omission arose primarily because the classical coordination chemists did not explore the use of temperature as a variable during synthesis. The first clear insight into the influence of reaction temperature on hybrid formation arose from a series of experiments in which cobalt(II) hydroxide was reacted with succinic acid in a 1 : 1 molar ratio at five temperatures between 60 and 250 °C.[56] Remarkably, and perhaps serendipitously, this yielded a series of five different phases with clear trends in the structures and compositions. In particular, the phases became more dense and less hydrated with increasing temperature, transitioning from a hydrated 1-D coordination polymer at the lowest temperature to an anhydrous, 2-D hybrid metal oxide at the highest (Fig. 18). This showed for the first time that hybrid framework formation is strongly influenced by classical thermodynamic factors, such as condensation due to entropy-driven dehydration reactions at higher temperatures.

In a more comprehensive study of the cobalt succinate system by high throughput experimentation, the trends as a function of pH and time were also examined.[57] It was found that extended inorganic hybrid structures are also favored at high pH, where the formation of M-O-M linkages arise due to the elimination of water or hydroxide groups by condensation reactions. The evolution of reaction products as a function of time, however, showed relatively few changes, further supporting the idea that thermodynamic factors can be very important in hybrid synthesis. The work also lead to the discovery of new

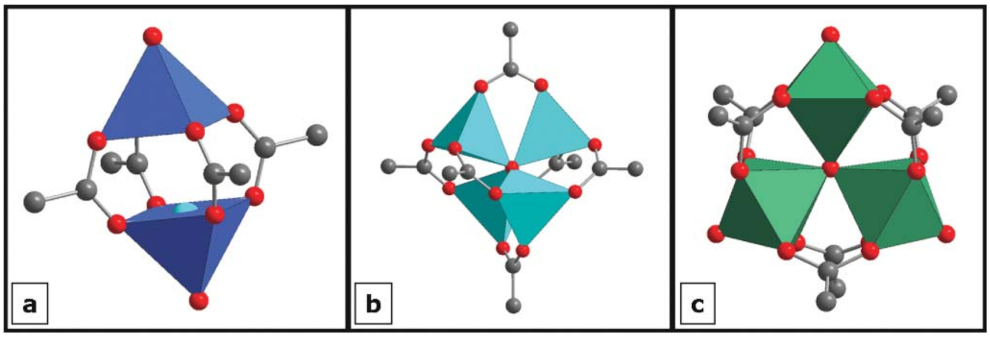

Fig. 17 Commonly recurring structural motifs: (a) the "paddlewheel" dimer of CuO_5 square pyramids, (b) the tetrahedron of ZnO_4 tetrahedra sharing a central oxygen, and (c) the trigonal planar trimer of CrO_6 octahedra sharing a central oxygen. Gray spheres denote carbon and red oxygen; CuO_5, ZnO_4 and CrO_6 polyhedra are shown in dark blue, pale blue and green, respectively.

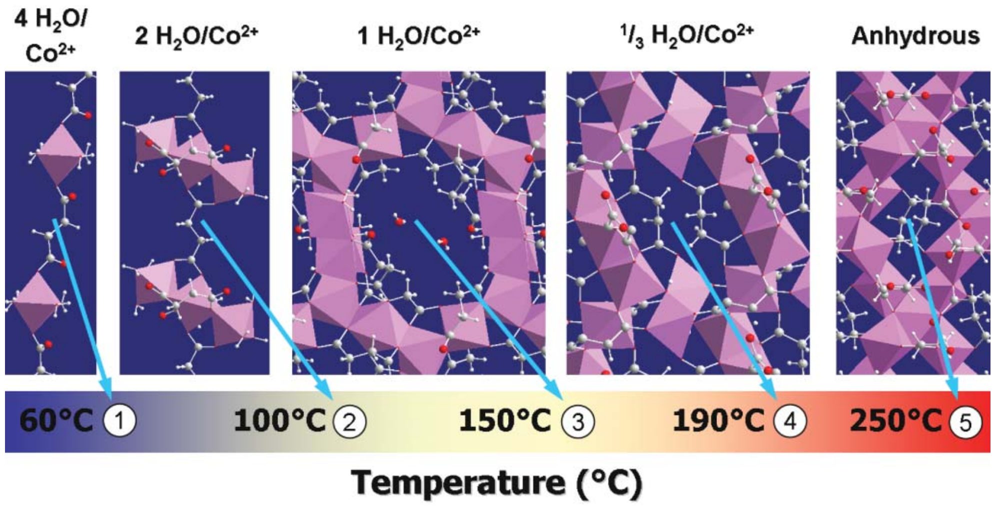

Fig. 18 Formation temperatures of five cobalt succinates, showing the trend toward greater inorganic connectivity and less hydration at higher temperatures.[56] Gray spheres denote carbon, white hydrogen, and red oxygen, with CoO_6 octahedra in pink.

phases,[58] underlining the power of high throughput methods in materials discovery.

Another interesting example of the influence of pH is apparent in the work of Stock and Bein on manganese with the phosphonocarboxylic acid, *p*-$H_2O_3PCH_2C_6H_4CO_2H$.[59] At low pH values, only one oxygen of the phosphonate group is deprotonated and the system is limited to forming a 1-D coordination polymer (Fig. 19). As the pH is raised, the second proton of the phosphonate group is released and the dimensionality increases to form a 2-D coordination polymer, while at the highest pH, the carboxylate becomes deprotonated and the dimensionality can increase to 3-D.

It is now becoming clear that the trends observed in the cobalt succinate and zinc phosphonocarboxylate systems are quite typical of hybrid materials synthesized under hydrothermal conditions. For example, looking back at work on the nickel(II) diphosphonates, $Ni_4(O_3PCH_2PO_3)_2{\cdot}nH_2O$ (n = 3, 2, 0), we see both an increase of dimensionality and multiple coordination changes during a temperature-driven quasi-topotactic dehydration reaction *in the solid state*.[60] With the knowledge of hindsight, we can also ascribe the increase in dimensionality with temperature in the system cobalt pyridine-3,4-dicarboxylate to the same effect.[61] However, we do not wish to imply that the synthesis of hybrid frameworks always proceeds under thermodynamic control; we shall return to this point in section 4.3.

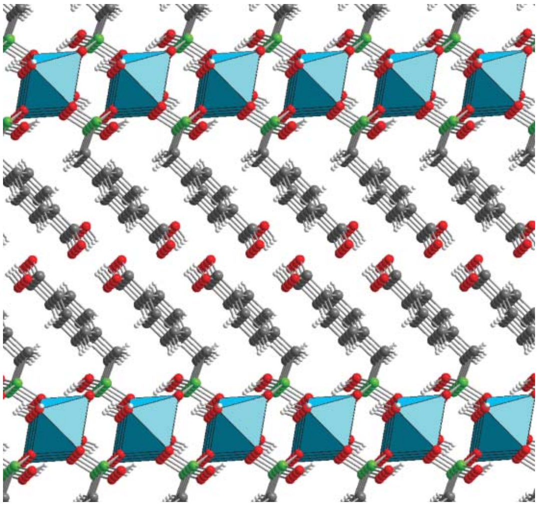

Fig. 19 The low-pH chain structure of manganese *p*-(phosphonomethyl)benzoate, with all carboxylate oxygens and half the phosphonate oxygens protonated.[59] Gray spheres denote carbon, red oxygen, white hydrogen, and green phosphorus, with MnO_6 octahedra in blue. Reproduced with permission. Copyright 2006, Royal Society of Chemistry.

4.2 Influence of solvent

The nature of the solvent is an important parameter in hybrid synthesis, especially as it can sometimes be problematic to identify a solvent that is suitable for both the inorganic and the organic reactants. Obviously, the use of non-aqueous or mixed solvents has been widely adopted, just as it has in the case of purely inorganic frameworks, and the use of immiscible biphasic solvents,[18] whereby the products form at the solvent interface, is an interesting strategy. Ionic liquids, which have been shown to be effective in the synthesis of inorganic framework materials,[62] are just starting to be applied to hybrid frameworks.[63]

4.3 Kinetic *vs*. thermodynamic factors

The emergence of clear trends in the synthesis of hybrid framework materials, as discussed in section 4.1, points to the likelihood that thermodynamic factors are more dominant than is found to be the case in zeolites and other inorganic framework materials. In the synthesis of aluminosilicate zeolites, it is well-known that hydrothermal crystallization often proceeds under kinetic control, with successive crystallization of increasingly stable phases as a function of time, according to the Ostwald step rule.[64] The high throughput work on cobalt succinates[57] reveals very little change as a function of time, aside from reactions that start with a large percentage of solid cobalt(II) hydroxide, in which case the kinetics of dissolution appear to be important. Other recent work also points towards the importance of thermodynamic control. A combined experimental and computational study of layered aluminium alkyldiphosphonates has shown that the stacking sequence is controlled by packing considerations that depend upon the number of carbon atoms in the alkyl chain; with even numbers the inorganic layers are more stable if they stack in an AAAA sequence, and with odd numbers the ABAB packing is more stable.[65] In a very recent study of zinc 4-cyclohexene-*cis*-1,2-dicarboxylates,[66] a similar combination of experimental and computational methods has shown that the temperature dependent behavior is controlled by thermodynamic considerations, with a hydrated phase being formed at temperatures below 100 °C and an anhydrous phase at higher temperatures. However, time-dependent effects are seen due to competition between the rate of product crystallization and the rate of isomerization of the *cis* ligand to the more stable *trans* form (Fig. 20).

The likelihood that thermodynamics play a strong role in hybrid framework formation is not very surprising with the knowledge of hindsight. In the case of aluminosilicate zeolites, crystallizations and transformations involve the making and breaking of very strong Si–O or Al–O bonds, whereas transition metal-ligand bonds, *e.g.* M–O, M–N *etc.* in hybrids are relatively weak. For example, M–OH_2 bonds for most divalent and trivalent transition metals give rates of water exchange that are in the range 10^3–10^8 s^{-1}, as mentioned in section 3.3, though a small number of very inert ions such as Cr^{3+} have extremely slow ligand exchange rates. We might therefore expect to see stronger kinetic control in systems containing these kinetically inert ions. Furthermore, it seems probable that very open frameworks such as MOF-5 and MIL-101, which are synthesized at relatively low temperatures, form under kinetic control, as is found with the zeolitic aluminosilicates. Further research is needed to clarify this question.

The use of microwave radiation in hybrid synthesis is a closely related issue that is beginning to attract attention, and in some cases the enhancement of the reaction rates is two–three orders of magnitude.[67] The reasons for this strong enhancement are not yet clear, and nor is it apparent whether the use of microwaves affects the overall outcome of the reaction in terms of which products are formed. Further work in this area should be very illuminating.

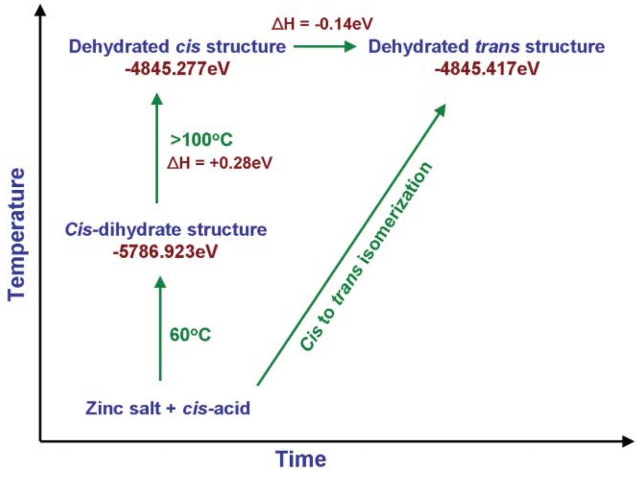

Fig. 20 The role of thermodynamics and kinetics in the zinc cyclohexene-1,2-dicarboxylate system as a function of temperature and time.[66]

4.4 Reaction pathways and building-up processes

Although a wide variety of hybrid framework materials with different dimensionalities have been synthesized and characterized in recent years, we do not yet know the mode of formation of these materials. In the case of inorganic open-framework structures, several workers have identified discrete secondary building units (SBUs), such as SBU-4 (formed by two metal oxygen polyhedra and two anionic polyhedra), which are believed to be involved in the building up process.[68–70] In the case of metal phosphates, for example, zero-dimensional units comprising four-membered rings can be transformed to chains, sheets and three-dimensional structures under relatively mild conditions. A recent study of zinc oxalates has shown that zero-dimensional dimeric units undergo transformations of this type as a function of temperature and time (Fig. 21).[71] Further evidence supporting such a mechanism has been found in the tin phosphonates, where the dimensionality can be controlled by blocking certain reaction pathways by means of using unreactive substituent

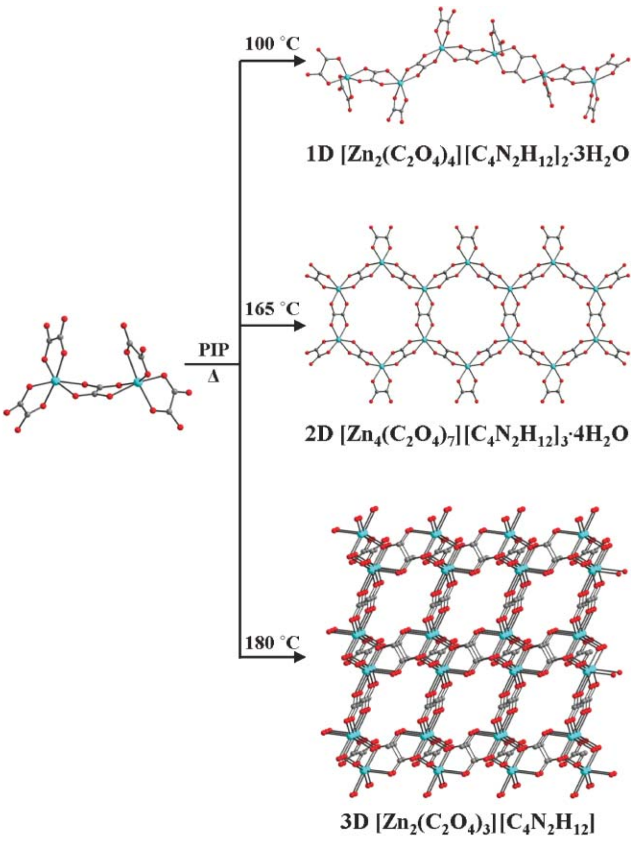

Fig. 21 Zero-dimensional dimeric zinc oxalate species transform progressively to chain, layered and 3-D structures with increasing temperature.[71] Reproduced with permission. Copyright 2005, Wiley–VCH.

groups.[72] Specially noteworthy is the transformation found in metal squarates, where it has been possible to form a sodalite structure from the assembly of six squarate units with divalent transition metals.[73] There is currently no *in situ* evidence for a building up process of the type that has been found in the purely inorganic systems, but a recent EXAFS study indicates that a trimeric iron oxide SBU remains intact during the crystallization of MIL-89.[74]

5 Properties and potential applications

5.1 Adsorption and separation processes

In comparison to the enormous number of commercial applications of the aluminosilicate zeolites and related inorganic materials in the fields of catalysis, separations, ion-exchange, and so on, the potential uses of hybrid frameworks are only gradually beginning to emerge. The most obvious possibilities concern highly porous hybrids, such as the MOF-5 and MIL-101 types of structures. In the case of MOF-5, which is a very low-density material, there is a good deal of data on gas storage capacities, including hydrogen and methane.[75] The locations of the hydrogen adsorption sites in MOF-5 have been determined at 4 K by single crystal neutron diffraction and inelastic neutron scattering.[76] The total hydrogen adsorption capacity of the MOF materials is not as high as was originally expected, no doubt because the pores are too large and molecules prefer to adsorb at surfaces. However, this problem can be alleviated and the capacity increased by using interpenetrating networks[77] or by using lightweight hybrid materials with smaller cavities, such as magnesium formate.[78] Another attractive strategy is to use hybrids that contain coordinatively unsaturated metal sites that are able to bind dihydrogen through a weak chemisorptive interaction.[79] Systems with smaller cavities are also of interest for adsorbing other molecules; for example, N_2 and CO_2 have been studied both experimentally and computationally in aluminium methylphosphonates.[80]

The system MIL-53, based upon trivalent ions, *e.g.* Cr(III), Fe(III), Sc(III) *etc*, in combination with benzene-1,4-dicarboxylate, is another highly porous materials with quite different properties.[81] The structure comprises parallel 1-D chains of corner-sharing MO_6 octahedra that are cross-linked to form a 3-D network by the benzene-1,4-dicarboxylate groups (Fig. 22). In terms of the classification in section 2.3, MIL-53 would be a (I^1O^2) system. The surface area of the dehydrated form of the first member of the MIL-53 family, the Cr(III) phase, is $\sim$1500 $m^2\ g^{-1}$ and it is stable to 500 °C. What is remarkable about the MIL-53 architecture is that it is sufficiently flexible that it can adapt its structure to accommodate sorbates of different sizes by means of a so-called "breathing effect".[81] The dehydrated structure is very open and actually contracts when water is adsorbed due to hydrogen bonding between the water molecules and the oxygen atoms of the benzene-1,4-dicarboxylate groups (Fig. 22). The case of MIL-88, which is an iron(III) fumarate structure, is similar in the sense that it can contract and expand with a considerable change in volume.[82] However, unlike MIL-53, it expands with the addition of solvent due to the unusual flexibility of the framework. For example, the cell volume of the anhydrous form is 1135 Å^3, while that of the fully hydrated form is 2110 Å^3.

As discussed in section 3.2, hybrid frameworks provide a unique opportunity to create interesting enantiomerically pure (homochiral), porous networks. One of the motivations for so doing is the possible applications of such networks in the area of chiral separations, which was first demonstrated in 2000 by Rosseinsky and co-workers.[83] In more recent work, a homochiral network based upon nickel benzene-1,3,5-tricarboxylate showed a modest enantiomeric excess (ee) of $\sim$8% for the adsorption of a simple naphthol derivative.[84] In general, it is found that the enantiomeric discrimination depends upon the relative sizes of the cavities and the sorbate molecules, with better selectivity being found when the size match is close. It also appears that ee values are higher for catalytic applications than chiral separations, as described in the following section.

5.2 Catalytic applications

It might seem likely that porous hybrid frameworks would be generally inferior to conventional zeolitic materials for applications in heterogeneous catalysis, given their relative instability, their lack of strong acidity, and their relatively costly synthesis. However, hybrids offer certain advantages

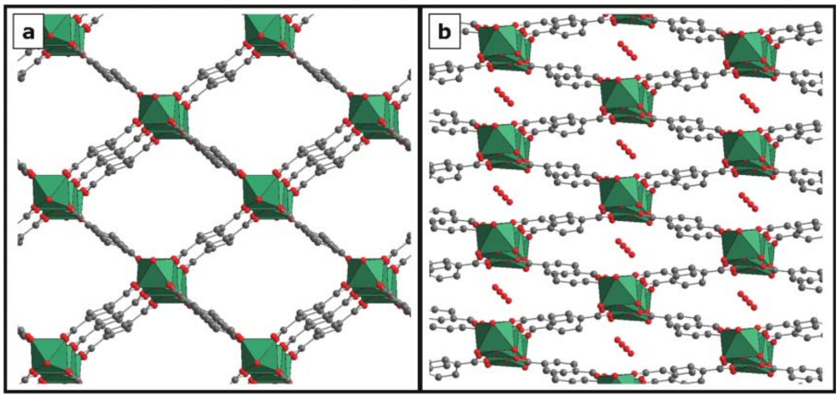

Fig. 22 Expanded (anhydrous) and contracted (hydrated) forms of the chromium terephthalate MIL-53, drawn to the same scale.[81] Gray spheres denote carbon and red oxygen, with CrO_6 octahedra in green. Reproduced with permission from Serre *et al*. Copyright 2002, American Chemical Society.

because of (i) the relative ease with which they can be functionalized, *post-synthesis*, (ii) the simplicity with which the pore size can be tuned over a wide range of sizes, and (iii) the manner in which *enatiomerically-pure* chiral frameworks can be created. The examples shown below will illustrate that many of these advantages are now beginning to be realized; further details are given in a recent review of the area.[85]

The first study of catalysis by a nanoporous coordination polymer used a simple lamellar coordination polymer of Cd and 4,4′-bipyridine in which several aldehydes were tested for cyanosilation with cyanotrimethylsilane.[86] Good yields were found for smaller molecules, with progressively poorer yields for larger ones, while control experiments using $Cd(NO_3)_2$ and 4,4′-bipyridine as catalysts resulted in no reaction, confirming the role of the coordination polymer's porosity in catalyzing the reaction.

Catalysis with organically pillared zirconium phosphate/phosphonate catalysts has recently been reviewed by Clearfield and Wang.[87] In one of the earlier demonstrations, a highly acidic catalyst was created by post-synthesis sulfonation of aromatic rings in zirconium phosphate-based systems,[88] though the acid groups are only stable up to ~130 °C, thereby limiting the utility of these systems. However, a sample saturated by acetone at room temperature produced the polymerization products mesityl oxide, isophorone, and 1,3,5-trimethoxybenzene as verified by *in situ* NMR,[89] confirming that the samples are indeed catalytic. Similarly, Pt- or Pd-containing viologen-bridged phosphonates are active catalysts for the photochemical production of H_2 gas from water[90] and for the production of H_2O_2 from streams of H_2 and O_2,[91] though there is uncertainty as to whether the reactions take place in the micropores of the catalysts.

One of the major limitations of aluminosilicate zeolites is their current inability to impart shape selectivity based on molecular handedness, primarily because it is extremely difficult to make enantiomerically pure materials. Because of the relative ease of synthesizing accessible chiral channels in hybrid materials, a significant amount of attention is now being devoted to developing materials with chiral pores and studying their catalytic activity. The area has recently been reviewed by Lin.[92] One potential problem is that chiral organics may not survive hydrothermal reaction conditions enantiomerically intact, but Williams and co-workers[47] have shown that this is not a general problem.

In the first demonstration of enantiomerically selective catalysis with hybrids, Kim and coworkers[93] demonstrated that a tartaric acid derivative of a well known oxo-bridged trinuclear zinc carboxylate cluster forms a chiral, layered phase, POST-1, which shows good activity toward transesterification. Tests on a racemic mixture of reactants resulted in a modest 8% enantiomeric excess of either *S* or *R* enantiomers depending on the chirality of the framework. Although a chiral catalyst is not always sufficient to promote a preference for a particular handedness in products, some of the recent results from Lin and co-workers are very impressive. For example, a cadmium-containing hybrid with large channels and over 50% void space gave 93% ee for the addition of diethyl zinc to 1-naphthaldehyde, rivaling the results obtained from homogeneous analogs.[94]

In an unexpected finding, it has been shown that the size of products is not necessarily limited by the size of molecules that are able to escape from the pores (in stark contract to the shape-selectivity found in zeolites). Li and coworkers generated a 3D porous structure from a known 1D cobalt biphenyldicarboxylate chain by replacing ligand water molecules with 4,4′-bipyridine under solvothermal conditions.[95] This 3D structure is very stable and porous, but decomposes back to the 1D hydrated chain when immersed in water. Treatment of the 1D chains with amine solvothermally regenerates the 3D structure. The ability to break and rebuild this phase reversibly leads to the name RPM-1, for Rutger's Recyclable Porous Material #1. Recognizing that the recyclable nature of the material might allow for the formation of larger molecules than the cavities would normally permit, Li and coworkers tested the material for photochemical catalysis of dibenzyl ketone. The reaction resulted in a significantly different mixture of products than is seen in zeolite hosts.

5.3 Other applications

Many applications beyond gas storage and catalysis have been proposed for hybrid systems. For example, several groups, particularly those of Ward[96] and Lin,[97] have developed strategies to engineer non-centrosymmetric frameworks for use as nonlinear optical materials. There has also been considerable interest in using hybrid systems to create porous magnets.[98] Although no hybrids currently display long-range ordering temperatures above 100 K,[99] several promising strategies have been proposed, such as using radical organic ligands to couple metal centers.[100] Other interesting observations include the modulation of the magnetic ordering temperature by guest molecules in porous manganese formate,[101] ferrimagnetic-ferromagnetic transformations in nickel cyclohexane-1,4-dicarboxylates,[102] and complex exchange interactions in trimetallic 4f–3d coordination polymers based upon Cu–Gd–Fe.[103]

There is also considerable interest in the optical properties of hybrid frameworks on account of their tunability and their capacity to incorporate a wide range of metal ion and organic ligand chromophors. There are a number of examples of photoluminescent behavior in rare-earth containing hybrids that could be of interest for applications as phosphors or fluorescent probes.[17,104] In the case of porous materials, the photoluminescent lifetimes of Eu^{3+}-doped gadolinium glutarates have been shown to depend on the degree of dehydration because the coordinating water molecules act as relaxation agents.[105] Other systems show fluorescent emissions due to charge transfer between metal ions and ligands or π to π^* transitions within the ligands.[106] For commercial applications, of course, it will be necessary for the materials to have sufficient chemical and optical stability.

Other interesting avenues are also being explored. For example, soluble 1-D coordination polymers based upon dendrimers in combination with palladium have been made;[107] such soluble, low-dimensional polymers are of interest for liquid crystalline behavior and use in nanocomposites. One- and two-dimensional coordination polymers have also been used as templates for the formation of zinc oxide nanorods and radial nanoneedles,[108] while silver-containing coordination polymers are being explored for their antimicrobial activity.[55] Finally, we would like to note that thin films of layered metal diphosphonates have been used as intercalation sensors for small molecules.[109]

6 Future prospects

The purpose of this brief overview has been to illustrate the progress that has been made in many aspects of the hybrid frameworks area in the last decade. The diversity of chemical and structural types is enormous and grows by the day, and a better understanding of the factors that influence hybrid formation is beginning to emerge. As this understanding improves, our ability to design new materials for specific uses will also improve, and this will be reflected in a greater range of applications than we see at present. This is most certainly an extraordinarily rich area that will be seen in the future as one of the most important developments in the history of materials chemistry. Many avenues still remain to be explored, including some that are mentioned in the above discussion, and we encourage the community to put further effort into this exciting field.

Acknowledgements

This work was supported by the National Science Foundation under Award No. DMR05-20415 to the MRSEC center at UCSB and Award No. DMR04-09848 to the International Center of Materials Research at UCSB.

References

1 A. Corma, *J. Catal.*, 2003, **216**, 298; M. E. Davis, *Nature*, 2002, **417**, 813; J. M. Thomas, *Sci. Am.*, 1992, **266**, 112.
2 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
3 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166.
4 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
5 A. K. Cheetham and P. M. Forster, in *Chemistry of Nanomaterials*, ed. C. N. R. Rao, A. Müller and A. K. Cheetham, Wiley–VCH, Weiheim, 2003, pp. 589–619.
6 D. A. Summerville, T. W. Cape, E. D. Johnson and F. Basolo, *Inorg. Chem.*, 1978, **17**, 3297; J. S. Miller, C. Vazquez, N. L. Jones, R. S. McLean and A. J. Epstein, *J. Mater. Chem.*, 1995, **5**, 707.
7 P. Gravereau, E. Garnier and A. Hardy, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, **35**, 2843.
8 G. Alberti, U. Constantino, S. Allulli and N. Tomassini, *Inorg. Nucl. Chem.*, 1978, **40**, 1113; M. D. Poojary, H.-L. Hu, F. Campbell, III and A. Clearfield, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1993, **49**, 996.
9 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.
10 R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; B. Moulton and M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 117.
11 M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.
12 A. Clearfield, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 495; J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3; M. J. Rosseinsky, *Microporous Mesoporous Mater.*, 2004, **73**, 15; C. N. R. Rao, S. Natarajan and R. Vaidhayanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466.
13 A. J. Blake, N. R. Champness, M. Crew and S. Parsons, *New J. Chem.*, 1999, 13.
14 J. T. Sampanthar and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 1999, 1993.
15 W. J. Belcher, C. A. Longstaff, M. R. Neckenig and J. W. Steed, *Chem. Commun.*, 2002, 1602.
16 N. Masciocchi, F. Castelli, P. M. Forster, M. M. Tafoya and A. K. Cheetham, *Inorg. Chem.*, 2003, **42**, 6147.
17 A. de Bettencourt-Dias, *Inorg. Chem.*, 2005, **44**, 2734.
18 P. M. Forster, P. Thomas and A. K. Cheetham, *Chem. Mater.*, 2002, **14**, 17.
19 R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 762.
20 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895.
21 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
22 N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *CrystEngComm*, 2002, **4**, 401.
23 Q. R. Fang, G. S. Zhu, J. Y. Sun, Y. Wei, S. L. Qiu and R. R. Xu, *Angew. Chem., Int. Ed.*, 2005, **44**, 3845; Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun and S. L. Qiu, *Dalton Trans.*, 2006, 2399; Y. L. Liu, V. C. Kravtsov, R. Larsen and M. Eddaoudi, *Chem. Commun.*, 2006, 1488; K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186.
24 L. Carlucci, G. Ciani, P. Macchi and D. M. Proserpio, *Chem. Commun.*, 1998, 1837.
25 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolake, *Science*, 2005, **309**, 2040; C. Mellot-Draznieks, J. Dutour and G. Férey, *Angew. Chem., Int. Ed.*, 2004, **43**, 6290.
26 A. C. Rizzi, R. Calvo, R. Baggio, M. T. Garland, O. Pena and M. Perec, *Inorg. Chem.*, 2002, **41**, 5609.
27 B. Adair, S. Natarajan and A. K. Cheetham, *J. Mater. Chem.*, 1998, **8**, 1477; N. Stock, G. D. Stucky and A. K. Cheetham, *Chem. Commun.*, 2000, 2277; M. Dan, G. Cotterau and C. N. R. Rao, *Solid State Sci.*, 2005, **7**, 437.
28 Y. F. Huang and K. H. Lii, *J. Chem. Soc., Dalton Trans.*, 1998, 4085; Z. A. D. Lethbridge and P. Lightfoot, *J. Solid State Chem.*, 1999, **143**, 58; A. Chowdhury, S. Natarajan and C. N. R. Rao, *Chem. Mater.*, 1999, **11**, 2316; J. Do, R. P. Bontchev and A. J. Jacobson, *Inorg. Chem.*, 2000, **39**, 3230.
29 B. M. Craven and D. Hall, *Acta Crystallogr.*, 1961, **14**, 475; S. Sato and K. Kobayashi, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1987, **43**, 1863.
30 W. T. A. Harrison, T. M. Nenoff, T. E. Gier and G. D. Stucky, *Inorg. Chem.*, 1992, **31**, 5395.
31 N. Guillou, C. Livage, W. van Beek, M. Nogues and G. Férey, *Angew. Chem., Int. Ed.*, 2003, **42**, 644.
32 R. K. Feller and A. K. Cheetham, *Solid State Sci.*, 2006, **8**, 1121; C. H. Wunderlich, R. Weber and G. Bergerhoff, *Z. Anorg. Allg. Chem.*, 1991, **598**, 371.
33 A. Tressaud, J. L. Soubeyroux, J. M. Dance, R. Sabatier and P. Hagenmuller, *Solid State Commun.*, 1981, **37**, 479.
34 A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 117.
35 C. A. Merrill and A. K. Cheetham, *Inorg. Chem.*, 2005, **44**, 5273.
36 M. B. Dines, P. M. DiGiacomo, K. P. Callahan, P. C. Griffith, R. H. Lane and R. E. Cooksey, in *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, ed. J. S. Miller, ACS Symposium Series 192, American Chemical Society, Washington, D. C., 1982, p. 223; G. Alberti, R. Viviani and S. Murcia Mascarós, *J. Mol. Struct.*, 1998, **470**, 81.
37 A. Clearfield, *Chem. Mater.*, 1998, **10**, 2801.
38 L. A. Vermeulen and M. E. Thompson, *Nature*, 1992, **358**, 656.
39 P. M. Forster and A. K. Cheetham, *Angew. Chem., Int. Ed.*, 2002, **41**, 457.
40 R. Vaidhayanathan, S. Natarajan and C. N. R. Rao, *Dalton Trans.*, 2003, 1459.
41 N. Guillou, C. Livage, M. Drillon and G. Férey, *Angew. Chem., Int. Ed.*, 2003, **42**, 5314.
42 V. Soghomonian, Q. Chen, R. C. Haushalter and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 223; V. J. Carter, P. A. Wright, J. D. Gale, R. E. Morris, E. Sastre and

J. Perez Pariente, *J. Mater. Chem.*, 1997, **7**, 2287; L. M. Zheng, H. H. Song, C. H. Lin, S. L. Wang, Z. Hu, Z. Yu and X. Q. Xin, *Inorg. Chem.*, 1999, **38**, 4618; L. M. Zheng, H. H. Song, C. Y. Duan and X. Q. Xin, *Inorg. Chem.*, 1999, **38**, 5061; H. H. Song, L. M. Zheng, Z. M. Wang, C. H. Yan and X. Q. Xin, *Inorg. Chem.*, 2001, **40**, 5025; M. Dan, K. Sivashanker, A. K. Cheetham and C. N. R. Rao, *J. Solid State Chem.*, 2003, **174**, 60.
43 R. Vaidhyanathan, S. Natarajan and C. N. R. Rao, *Chem. Mater.*, 2001, **13**, 3524.
44 Y. Kim and D. Y. Jung, *Chem. Commun.*, 2002, 908; M. Kurmoo, H. Kumagai, M. Akita-Tanaka, K. Inoue and S. Tagaki, *Inorg. Chem.*, 2006, **45**, 1627; J. Chen, M. Ohba, D. Zhao, W. Kaneko and S. Kitagawa, *Cryst. Growth Des.*, 2006, **6**, 664.
45 A. Thirumurugan, M. B. Avinash and C. N. R. Rao, *Dalton Trans.*, 2006, 221.
46 D. S. Kim, P. M. Forster, G. Diaz de Delgardo, S.-E. Park and A. K. Cheetham, *Dalton Trans.*, 2004, 3365.
47 S. Thushari, J. A. K. Cha, H. H.-Y. Sung, S. S.-Y. Chui, A. L.-F. Leung, Y.-F. Yen and I. D. Williams, *Chem. Commun.*, 2005, 5515.
48 J. B. Weng, M. C. Hong, Q. Shi, R. Cao and A. C. S. Chan, *Eur. J. Inorg. Chem.*, 2002, 2553.
49 E. V. Anohkhina and A. J. Jacobson, *J. Am. Chem. Soc.*, 2004, **126**, 3044.
50 P. M. Forster and A. K. Cheetham, *Microporous Mesoporous Mater.*, 2004, **73**, 57.
51 P. M. Forster and A. K. Cheetham, *Solid State Sci.*, 2003, **5**, 635.
52 F. Serpaggi and G. Férey, *J. Mater. Chem.*, 1998, **8**, 2737.
53 S. S. Y. Chui, S. M. F. Lo, J. P. H. Y. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
54 J. J. Morrison, C. J. Love, B. W. Manson, I. J. Shannon and R. E. Morris, *J. Mater. Chem.*, 2002, **12**, 3208; R. E. Morris, *J. Mater. Chem.*, 2005, **15**, 931.
55 M. A. M. Abu-Youssef, V. Langer and L. Öhrström, *Dalton Trans.*, 2006, 2542.
56 P. M. Forster, A. R. Burbank, C. Livage, G. Férey and A. K. Cheetham, *Chem. Commun.*, 2004, 368.
57 P. M. Forster, N. Stock and A. K. Cheetham, *Angew. Chem., Int. Ed.*, 2005, **44**, 7608.
58 P. M. Forster, A. R. Burbank, M. C. O'Sullivan, N. Guillou, C. Livage, G. Férey, N. Stock and A. K. Cheetham, *Solid State Sci.*, 2005, **7**, 1549.
59 N. Stock and T. Bein, *J. Mater. Chem.*, 2005, **15**, 1384.
60 Q. M. Gao, N. Guillou, M. Nogues, G. Férey and A. K. Cheetham, *Chem. Mater.*, 1999, **11**, 2937.
61 M.-L. Tong, S. Kitagawa, H.-C. Chang and M. Ohba, *Chem. Commun.*, 2004, 418.
62 E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature*, 2004, **430**, 1012.
63 J.-H. Liao, P.-C. Wu and Y.-H. Bai, *Inorg. Chem. Commun.*, 2005, **8**, 390; C.-Y. Sheu, S.-F. Lee and K.-H. Lii, *Inorg. Chem.*, 2006, **45**, 1891; Z. J. Lin, D. S. Wragg and R. E. Morris, *Chem. Commun.*, 2006, 2021.
64 R. A. van Santen, *J. Phys. Chem.*, 1984, **88**, 5768.
65 H. G. Harvey, B. Slater and M. P. Attfield, *Chem.–Eur. J.*, 2004, **10**, 3270.
66 C. Lee, C. Mellot-Draznieks, B. Slater, G. Wu, W. T. A. Harrison, C. N. R. Rao and A. K. Cheetham, *Chem. Commun.*, 2006, 2687.
67 S. H. Jhung, J.-H. Lee, P. M. Forster, G. Férey, A. K. Cheetham and J.-S. Chang, *Chem.–Eur. J.*, 2006, **12**, 7699.
68 G. Férey, *J. Solid State Chem.*, 2000, **152**, 37.
69 S. Oliver, A. Kuperman and G. A. Ozin, *Angew. Chem., Int. Ed.*, 1998, **37**, 46; C. N. R. Rao, S. Natarajan, A. Choudhury, S. Neeraj and A. A. Ayi, *Acc. Chem. Res.*, 2003, **34**, 80; A. J. Norquist and D. O'Hare, *J. Am. Chem. Soc.*, 2004, **126**, 6673.
70 R. Murugavel, M. G. Walawalkar, M. Dan, H. W. Roesky and C. N. R. Rao, *Acc. Chem. Res.*, 2004, **37**, 763.
71 M. Dan and C. N. R. Rao, *Angew. Chem., Int. Ed.*, 2005, **45**, 281.
72 B. A. Adair, S. Neeraj and A. K. Cheetham, *Chem. Mater.*, 2003, **15**, 1518.
73 S. Neeraj, M. L. Noy, C. N. R. Rao and A. K. Cheetham, *Solid State Sci.*, 2002, **4**, 1231.
74 S. Surble, F. Millange, C. Serre, G. Férey and R. I. Walton, *Chem. Commun.*, 2006, 1518.
75 J. L. C. Rowsell, A. R. Millward, K. S. Park and O. M. Yaghi, *J. Am. Chem. Soc.*, 2004, **126**, 5666; T. Duren, L. Sarkisov, O. M. Yaghi and R. Q. Snurr, *Langmuir*, 2004, **20**, 2683.
76 E. C. Spencer, J. A. K. Howard, G. J. McIntyre, J. L. C. Rowsell and O. M. Yaghi, *Chem. Commun.*, 2006, 278; J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard and O. M. Yaghi, *Science*, 2005, **309**, 1350.
77 J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670.
78 J. A. Rood, B. C. Noll and K. W. Henderson, *Inorg. Chem.*, 2006, **45**, 5521.
79 P. M. Forster, J. Eckert, B. Heiken, J. B. Parise, J. W. Yoon, S. H. Jhung, J.-S. Chang and A. K. Cheetham, *J. Am. Chem. Soc.*, in press.
80 C. Schumacher, J. Gonzalez, P. A. Wright and N. A. Seaton, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2351.
81 C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519; T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Férey, *Chem.–Eur. J.*, 2004, **10**, 1373; T. R. Whitfield, X. Q. Wang, L. M. Liu and A. J. Jacobsen, *Solid State Sci.*, 2005, **7**, 1096.
82 C. Mellot-Draznieks, C. Serre, S. Surble, N. Auderbrand and G. Férey, *J. Am. Chem. Soc.*, 2005, **127**, 16273.
83 C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158.
84 D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2004, **126**, 6106.
85 P. M. Forster and A. K. Cheetham, *Top. Catal.*, 2003, **24**, 79.
86 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
87 A. Clearfield and Z. K. Wang, *J. Chem. Soc., Dalton Trans.*, 2002, 2937.
88 C.-Y. Yang and A. Clearfield, *React. Polym.*, 1987, **5**, 13.
89 A. Clearfield, Z. Wang and P. Bellinghausen, *J. Solid State Chem.*, 2002, **167**, 376.
90 H. Byrd, A. Clearfield, D. Poojary, K. P. Reis and M. E. Thompson, *Chem. Mater.*, 1996, **8**, 2239.
91 A. Dokoutchaev, V. V. Krishnan, M. E. Thompson and M. Balasubramanian, *J. Mol. Struct.*, 1998, **470**, 191; K. P. Reis, V. K. Joshi and M. E. Thompson, *J. Catal.*, 1996, **161**, 62.
92 W. Lin, *J. Solid State Chem.*, 2005, **178**, 2486.
93 J. Soo Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982.
94 C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940.
95 L. Pan, N. Ching, X.-Y. Huang and J. Li, *Inorg. Chem.*, 2000, **39**, 5333.
96 K. T. Holman, A. M. Pivovar, J. A. Swift and M. D. Ward, *Acc. Chem. Res.*, 2001, **34**, 107.
97 O. R. Evans and W. B. Lin, *Acc. Chem. Res.*, 2002, **35**, 511.
98 G. Férey, *Chem. Mater.*, 2001, **13**, 3084.
99 K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem., Int. Ed.*, 2002, **41**, 281.
100 D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190.
101 Z. M. Wang, B. Zhang, H. Fujiwara, H. Kobayashi and M. Kurmoo, *Chem. Commun.*, 2004, 416.
102 M. Kurmoo, H. Kumagai, M. Akita-Tanake, K. Inoue and S. Takagi, *Inorg. Chem.*, 2006, **45**, 1627.
103 H. Z. Kou, B. C. Zhou and R. J. Wang, *Inorg. Chem.*, 2003, **42**, 7658.
104 X. D. Gou, G. S. Zhu, Q. R. Fang, M. Xue, G. Tian, J. Y. Sun, X. T. Li and S. L. Qiu, *Inorg. Chem.*, 2005, **44**, 3850.
105 F. Serpaggi, T. Luxbacher, G. Férey and A. K. Cheetham, *J. Solid State Chem.*, 1999, **145**, 580.
106 Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, F. X. Sun and S. L. Qiu, *Inorg. Chem.*, 2006, **45**, 3582; J. Lu, K. Zhao, Q. R. Fang, J. Q. Xu, J. H. Yu, X. Zhang, H. Y. Bie and T. G. Wang, *Cryst. Growth Des.*, 2005, **5**, 1091.
107 H. Tokuhisa and M. Kanesato, *Langmuir*, 2005, **21**, 9728.
108 Z. Li, Y. Xiong and Y. Xie, *Nanotechnology*, 2005, **16**, 2303.
109 T. E. Mallouk and J. A. Gavin, *Acc. Chem. Res.*, 1998, **31**, 209.