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Inverted metal–organic frameworks: solid-state hosts with modular functionality

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Contents

Abstract

Metal–organic frameworks (MOFs) are crystalline inorganic–organic hybrid materials that consist of metal ions and organic molecules connected in space to produce an infinite one-, two-, or three-dimensional framework. The modularity of MOFs, specifically, the ability to modify the organic and/or inorganic components, offers a ready means to modify and control properties of such materials (e.g. inclusion, magnetism). This review highlights the design and synthesis of cavity-containing and porous MOFs with emphasis on methods that enable the functionalization of interior void spaces with organic groups. A relatively new class of MOFs, known as inverted metal–organic frameworks (IMOFs), which enables organic functionalization using principles of supramolecular chemistry, is discussed. We also briefly outline methods to functionalize the interior spaces of mesoporous materials (MCMs) and zeolites, and suggest that MOFs offer a diverse space within which to place a wide range of organic functionalities.
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Keywords: Metal–organic framework; Modular functionality; Solid-state host

1. Introduction

Two decades ago the border between solid-state chemistry, which was largely orientated towards materials science, and molecular chemistry, which was largely orientated towards chemical reactivity and catalysis, was unambiguous. During the last two decades, a new field has developed, which bridges the gap between the solid-state chemistry and molecular chemistry, known as molecular materials science [1–3].

In contrast to solid-state inorganic materials, which are based on atoms, solid-state molecular materials are based

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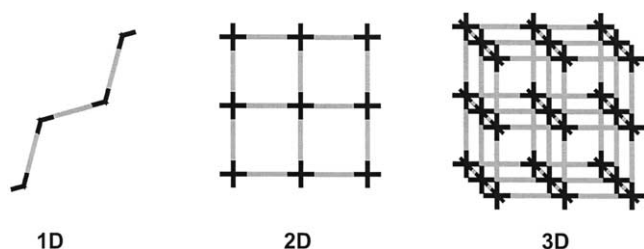*E-mail address:* len-macgillivray@uiowa.edu (L.R. MacGillivray).

Fig. 1. 1D, 2D, and 3D frameworks based on three different metal coordination geometries and a linear organic bridge (black connectors, metal; gray connectors, organic bridge).

on molecules. That such solids are based on molecules enables chemists to construct materials with diverse properties (e.g. chiral, magnetic). To this end, the development of synthetic strategies that grant control over the distribution of molecules within solid-state molecular materials is a challenge [4].

Metal–organic frameworks (MOFs) are crystalline molecular materials that consist of metal ions and organic molecules [5–14]. The synthesis of MOFs is achieved under mild conditions (e.g. solution chemistry, solvothermal synthesis) and, in the simplest case, involves reaction of a transition-metal-ion, which acts as a node, with an organic ligand, which acts as a linear bridge, to form an infinite one-(1D), two-(2D), or three-(3D) dimensional framework [15] (Fig. 1). Consequently, the components of MOFs are connected though coordination bonds, which are weaker in energy than the strong Si/Al–O bonds that sustain the structures of microporous zeolites and mesoporous molecular sieves (i.e. MCMs) [16]. Given the relative weakness and kinetic lability of coordination bonds, and the fact that MOFs consist of molecular components, one can readily apply concepts of supramolecular chemistry (e.g. self-assembly) to design MOFs.

A major driving force behind the syntheses of the first MOFs was the construction of topologically interesting structures [5,17,18]. Frameworks of increasing dimensionality (i.e. 2D to 3D) and complexity (e.g. interpenetration) dominated. The inorganic networks of Wells [19] emerged as tools to describe the diverse topologies of MOFs, while various forms isomerism were discovered [20–22]. Consequently, the field of MOFs was growing fast and a need for applications developed [23]. It was then that attention was turned to properties (e.g. magnetic [24–27], electronic [28], optic [29], host-guest [30]) that may be designed within such solids.

MOFs with cavities and pores [14,31] are potentially useful for applications in separations [32,33], storage [30], and catalysis [34], areas where zeolites and MCMs have encountered numerous applications [16]. Although the weaker coordination bonds that sustain the structures of MOFs lead to frameworks of general lower stability than zeolites and MCMs, the modular nature of MOFs has enabled a variety of MOFs to emerge as useful hosts of ions and molecules. The modular approach has provided a ready means to fine-tune

sizes, shapes, and functionalities of cavities and pores of MOFs by changing the organic bridge and/or metal node. In some cases, the modularity has made MOFs useful for which applications involving zeolites, for example, do not exist [35,36].

2. Overview

It is with these ideas in mind that we will provide here an account of a class of MOFs known as inverted metal–organic frameworks (IMOFs) [37]. IMOFs are constructed by employing an organic ligand as a node and a transition-metal-ion as a linear bridge such that the structural roles of the organic and metal components of a MOF, as compared with a more traditional MOF, are inverted. By inverting the structural roles of the components, IMOFs offer an ability to functionalize the walls of MOFs with terminal groups, in the form of molecules and/or anions, coordinated to the metal centers. Owing to the wide variety of molecules and anions (e.g. carboxylates) that may serve as terminal groups, and to the reversible nature of the interaction between a transition-metal-ion and ligand, IMOFs present a modular means to functionalize the cavities and pores of MOFs using principles of coordination supramolecular chemistry [2].

We will start by briefly describing methods to functionalize the walls of MCMs and zeolites, frameworks that have inspired the design and synthesis of host MOFs [22]. We will then describe a method to functionalize the cavities and pores of more traditional MOFs, and then outline the inverted approach.

3. Functionalization of MCMs and zeolites

The ability to functionalize a MCM or zeolite with organic groups provides a means to construct a hybrid inorganic–organic material with unique properties. In this context, two general methods to functionalize the walls of MCMs and zeolites with organic groups have been described. In the first approach, known as post-synthetic grafting [38], organic groups are covalently grafted onto the walls of a MCM or zeolite. The hexagonal pores of MCM-41, for example, have been recently grafted with coumarins [39]. In these solids, photocontrolled and reversible intermolecular dimerization of the coumarins was shown to affect the uptake, storage, and release of guest molecules. In the second approach, known as direct synthesis [38,40,41], the organic groups are designed within precursor building blocks of the host (e.g. organosiloxane) such that the organic groups, in a single synthetic step, are integrated within the framework. Phenethyl groups covalently tethered to silicon atoms, for example, have been incorporated into 1D and 2D zeolites and have been used for shape-selective catalysis [40]. An ultimate goal of both methods is to prepare, a priori, functionalized solids with targeted properties.

4. Functionalization of metal–organic frameworks

MOFs are highly promising frameworks for organic functionalization. For example, whereas the structures of MCMs are largely based on a single topology (i.e. 1D pores), the structures of MOFs are largely based on a variety of topologies (i.e. 1D, 2D, and 3D pores) [7,15,22]. Additionally, whereas the cavities and pores of zeolites are generally of a relatively narrow range of sizes (i.e. 2–14 Å), the cavities and pores of MOFs are generally of a wide range of sizes (i.e. 2–30 Å). The numerous frameworks, along with the variety of cavity and pore sizes, accessible using MOFs enables such materials to provide a diverse 'space' within which organic groups may be positioned to tailor specific properties of such host inorganic–organic solids [15].

4.1. Synthetic strategies

The most common strategy to synthesize a porous or cavity-containing MOF has been to propagate the coordination geometry of a transition-metal-ion using a linear organic bridge. Depending on the coordination preferences of the metal, the metal and organic components may assemble to form a 1D (e.g. linear), 2D (e.g. grid), or 3D (e.g. octahedral) structure. In such frameworks, the metal serves as a node and the organic serves as a spacer [21,22]. Consequently, the chemical functionality that defines the walls of such hosts is largely based on the chemical composition of the organic spacer.

The most common method to modify the walls of a host MOF based on a metal node and a linear organic bridge has been to modify the organic bridge [42–51]. Such modification has been achieved by covalently attaching functional groups, in a pre-framework synthesis, to the bridge such that the functionalized organic ligand is integrated within the MOF by a direct synthesis. In the ideal case, the functional groups are anticipated to project from the bridge to provide a means to systematically study and control the chemistry of the cavities and pores (e.g. recognition) [46]. Alternatively, the functional groups may interfere with the assembly process to produce a MOF with a different connectivity and/or topology [44]. Such interference may arise owing to structural influences of the functional groups on the coordination bonds and/or packing of the metal and organic components. Either a single metal ion [42–47] or a metal cluster [47–49], in the form of a secondary building unit (SBU) [11], may serve as the node.

4.1.1. Single metal ion as node

Early work of Kitagawa involving substituted pyrazines addressed the feasibility of modifying a linear organic bridge to functionalize MOFs with organic groups. With nodes based on copper(I), Kitagawa revealed that metal geometries and framework topologies were sensitive to substituents attached to the bridge. Reaction of 2,6-dimethylpyrazine

(2,6-dm-pyz) with $Cu(C_2H_4)(ClO_4)$, for example, produced a 2D planar sheet, $\{[Cu_2(2,6\text{-dm-pyz})_3](ClO_4)_{2.2}(acetone)_2\}_\infty$, composed of three-coordinate copper atoms linked by 2,6-dm-pyz molecules while reaction of 2-chloropyrazine (2-Cl-pyz) with $Cu(C_2H_4)(ClO_4)$ produced a 2D pleated sheet, $\{[Cu_2(2\text{-Cl-pyz})_{4.5}](ClO_4)_2\}_\infty$, composed of four-coordinate copper atoms (Fig. 2) [42]. In the former, guest acetone molecules resided within the MOF, sitting above and below hexagonal cavities lined by the methyl groups, while, in the latter, the components assembled to form a structure that prohibited inclusion of guests. The different coordination geometries of the metals, and different topologies of the MOFs, were ascribed to steric effects involving the metal centers and substituents of the pyrazine derivatives.

Recent studies by Zubieta involving substituted pyrazines have focused on copper(I) cyanides as building units [43]. Hydrothermal reactions of CuCN and KCN with alkylated pyrazines produced 2D networks and 3D frameworks with $[Cu(CN)]_\infty$ chains and/or $[Cu(CN)]_\infty$ rings as structural motifs. Reaction of CuCN, KCN, and 2,6-dm-pyz, for example, yielded the 3D network $[Cu_2(CN)_2(2,6\text{-dm-pyz})]_\infty$. The components of $[Cu_2(CN)_2(2,6\text{-dm-pyz})]_\infty$ assembled to produce doubled-stranded ribbons, involving three-coordinate copper atoms, linked to four adjacent ribbons to give the 3D framework. In a similar way to the MOFs described by Kitagawa, the coordination geometries of the metals were sensitive to substituents attached to the bridges.

A functionalization of a linear bridge that has enabled the coordination geometry of a metal to remain intact, yet has lead to a change in framework topology, has been reported by Fujita [44]. Specifically, reaction of $Cd(NO_3)_2$ with 1,4-bis(4-pyridylmethyl)benzene (bpmb) produced a 1D MOF, $[Cd(NO_3)_2(bpmb)_{1.5}]_\infty$, wherein the cadmium(II) ion, in a T-shaped geometry, was propagated by the bridge to form a ladder-like MOF with square cavities of dimensions $\sim 16.4 \times 16.6$ Å (Fig. 3). The ladders interpenetrated in the solid to give a 3D assembly of 1D networks wherein each ring of the ladder interlocked with four rings of adjacent ladders. The interpenetration enabled the bridging ligands to completely fill the square cavities, which prohibited the inclusion of guests.

Whereas reaction of $Cd(NO_3)_2$ with bpmb produced the 1D ladder framework $[Cd(NO_3)_2(bpmb)_{1.5}]_\infty$, reaction of $Cd(NO_3)_2$ with 1,4-bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene (bpmtfb) produced the 2D brick framework $[Cd(NO_3)_2(bpmtfb)_{1.5}]_\infty$. In this framework, the metal-ion, in a T-shaped geometry, was propagated by the linear bridge to produce a brick-like framework with large rectangular cavities of dimensions $\sim 16.3 \times 32.7$ Å. In a similar way to $[Cd(NO_3)_2(bpmb)_{1.5}]_\infty$, the bricks assembled to produce an interpenetrated 2D network, three independent bricks interpenetrating within the same plane. The interpenetration, similar to $[Cd(NO_3)_2(bpmb)_{1.5}]_\infty$, prohibited the inclusion of guest species.

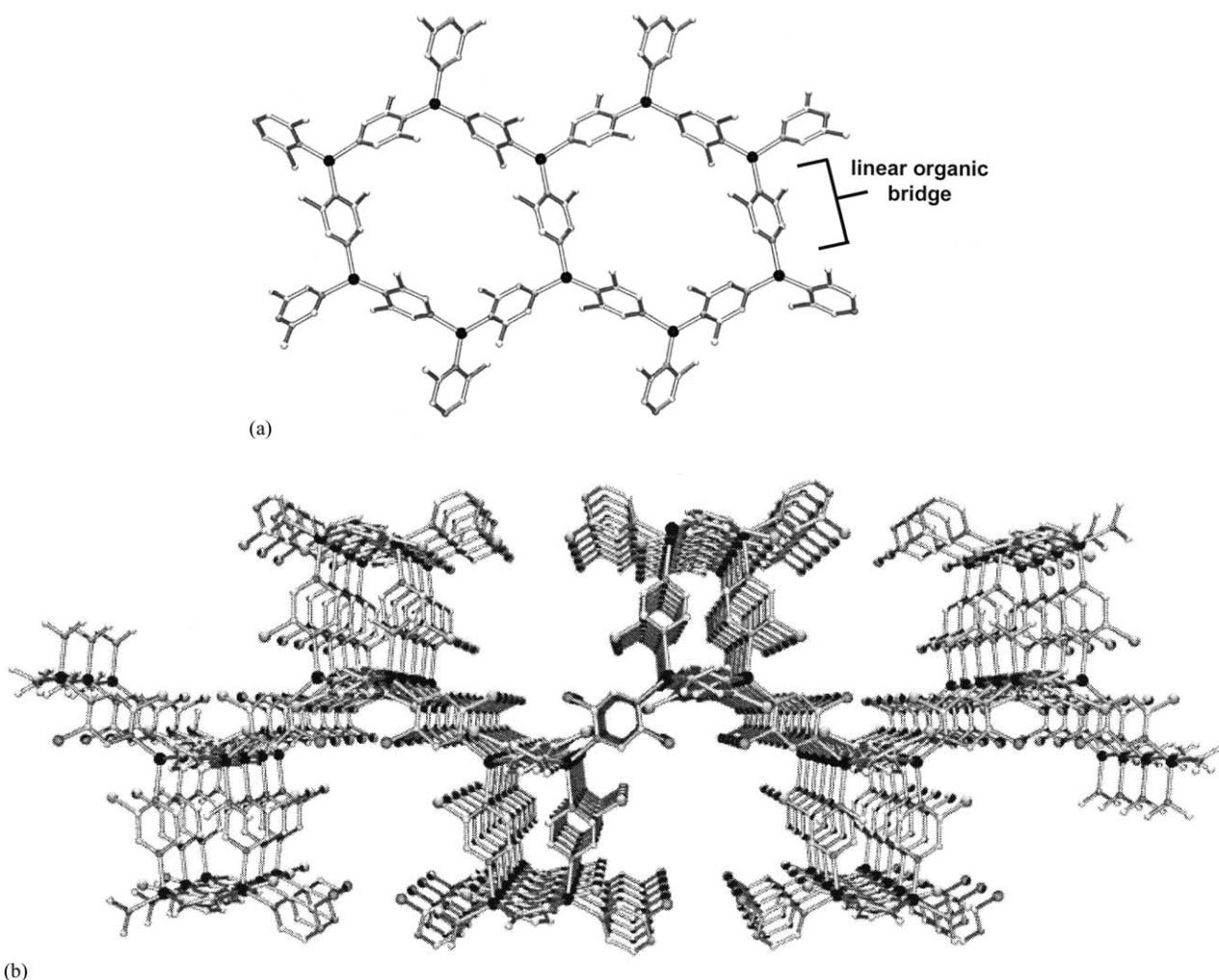Fig. 2. Perspective view of: (a) the hexagonal cavities of $\{[Cu_2(2,6\text{-dm-pyz})_3](ClO_4)_{2.2}(\text{acetone})_2\}_\infty$ and (b) the 2D pleated sheet of $\{[Cu_2(2\text{-Cl-pyz})_{4.5}](ClO_4)_2\}_\infty$.

Champness and Schröder have demonstrated that interpenetration of adamantoid networks can be affected by organic functionality added to a linear bridge. Specifically, copper(I) and 2,7-diazapyrene (2,7-dap) were shown to assemble to form a triply interpenetrated adamantoid lattice, $\{[Cu(2,7\text{-dap})_2](PF_6)\}_\infty$ [45], which contrasted the quadruply interpenetrated framework, $\{[Cu(4,4'\text{-bpy})_2](BF_4)\}_\infty$ (where $4,4'\text{-bpy} = 4,4'\text{-bipyridine}$). The decrease in the number of interpenetrating lattices was ascribed to a combination of $\pi\cdots\pi$ interactions and steric bulk, relative to $4,4'$-bpy, of the pyrene unit.

An organic functionalization that has enabled the metal coordination geometry and framework topology of a MOF to remain intact and, consequently, has been exploited for the construction of a chiral MOF, has been recently described by zur Loye and Bunz. In particular, reaction of $Cu(NO_3)_2$ with 9,9-diethyl-2,7-bis(4-pyridylethynyl)fluorine (depf) produced the 2D square-grid framework, $[Cu(\text{depf})_2]_\infty^{2+}$, with cavities of dimensions $\sim25 \times 25$ Å (Fig. 4) [46]. The central ethyl groups of the bridge projected at approximate

$90°$ angles parallel and perpendicular to the plane of the 2D host. As a result, the bridge lined the cavities of the MOF, which were filled by disordered anions and solvent molecules, with alkyl groups. Replacement of the alkyl groups with chiral groups was then shown to produce a chiral MOF. Specifically, chiral bipyridine 9,9-bis[(S)-2-methyl-butyl]-2,7-bis(4-pyridylethynyl)fluorine (S-mbpf) assembled with $Cu(NO_3)_2$ to form a chiral square-grid, $[Cu(S\text{-mbpf})_2]_\infty^{2+}$, with a topology virtually identical to the ethyl analog. In contrast to $[Cu(\text{depf})_2]_\infty^{2+}$, the fluorine groups of $[Cu(S\text{-mbpf})_2]_\infty^{2+}$ maintained the same orientation on the sides of the grids, which forced the chiral groups to project into the cavities. $[Cu(\text{depf})_2]_\infty^{2+}$ and $[Cu(S\text{-mbpf})_2]_\infty^{2+}$ also displayed different modes of packing, exhibiting ABAB and ABCABC stacking, respectively. Nevertheless, $[Cu(\text{depf})_2]_\infty^{2+}$ and $[Cu(S\text{-mbpf})_2]_\infty^{2+}$ demonstrated the feasibility of functionalizing, a priori, a linear organic bridge, and corresponding MOF, with chiral groups. Such functionalization may lead to MOFs that exhibit chiral selectivity of guests [47].
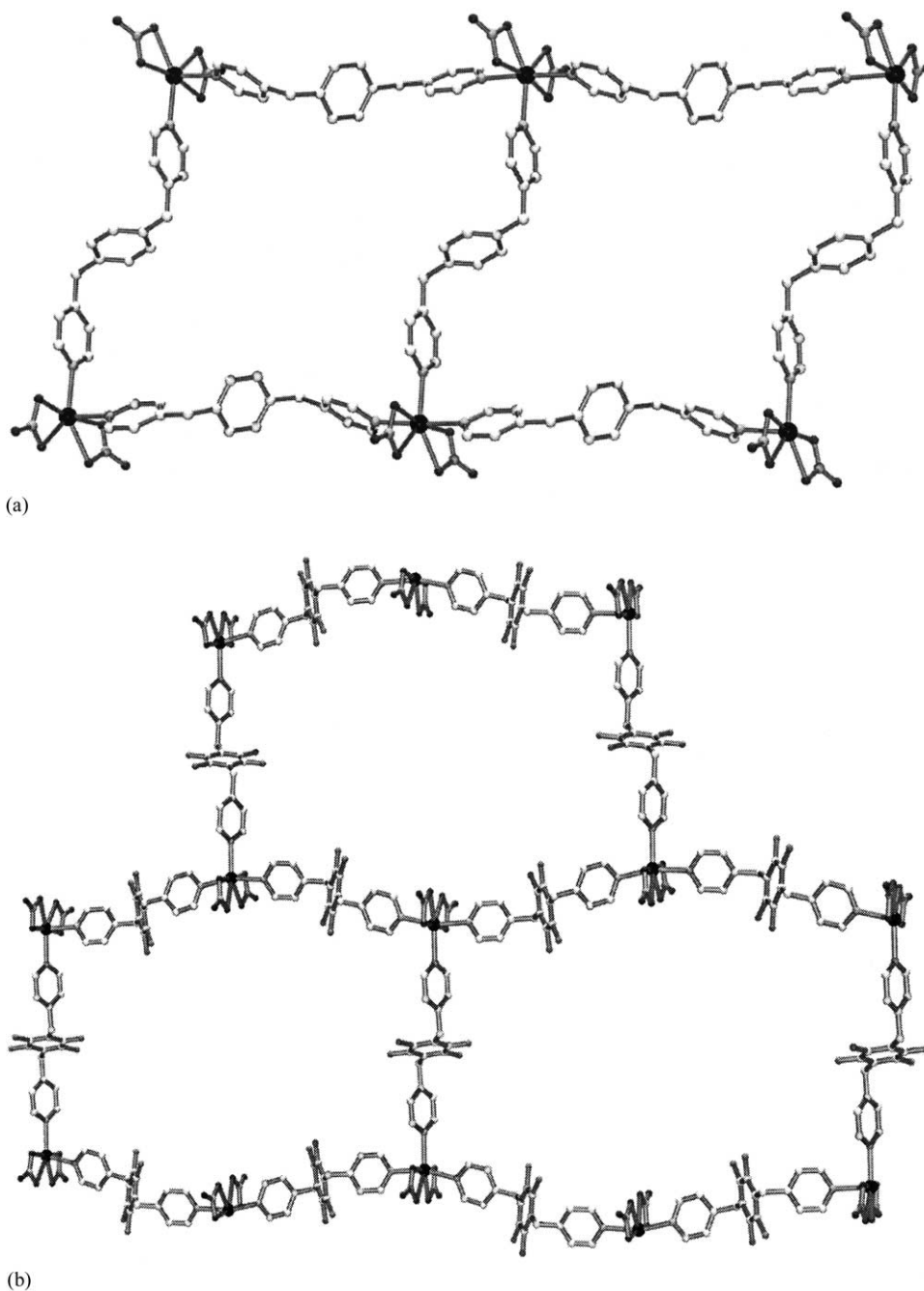
Fig. 3. Structures of: (a) 1D ladder framework $[Cd(NO_3)_2(bpmb)_{1.5}]_\infty$ and (b) the 2D brick framework $[Cd(NO_3)_2(bpmtfb)_{1.5}]_\infty$.

4.1.2. Secondary building unit as node

Transition-metal-ion clusters, in the form of oligonuclear metal carboxylates (Fig. 5) [48], have been successfully employed as nodes of host MOFs. In contrast to single metal ions, the clusters provide a means to fix the coordination geometry of a node by using rigid carboxylates to orient multiple metal ions, in the form of SBUs, into well-defined positions [11]. Consequently, the clusters impart rigidity upon the structures of MOFs, giving rise to highly stable cavity-containing and porous solids. In particular, clusters involving linear dicarboxylates have provided access to 2D

and 3D frameworks with walls readily amenable to organic functionalization.

Extensive work by Yaghi has demonstrated that the linear bridges of MOFs with SBUs as metal components can be functionalized with organic groups to produce isoreticular MOFs (IRMOFs) [49]. Reaction of the octahedral zinc cluster Zn_4O with substituted 1,4-benzenedicarboxylates, for example, has produced highly stable and porous 3D frameworks that adopt the topology of CaB_6 (Fig. 6). A variety of functional groups (e.g. bromo, amino, n-propoxy) have been attached, in pre-framework syntheses, to the linear
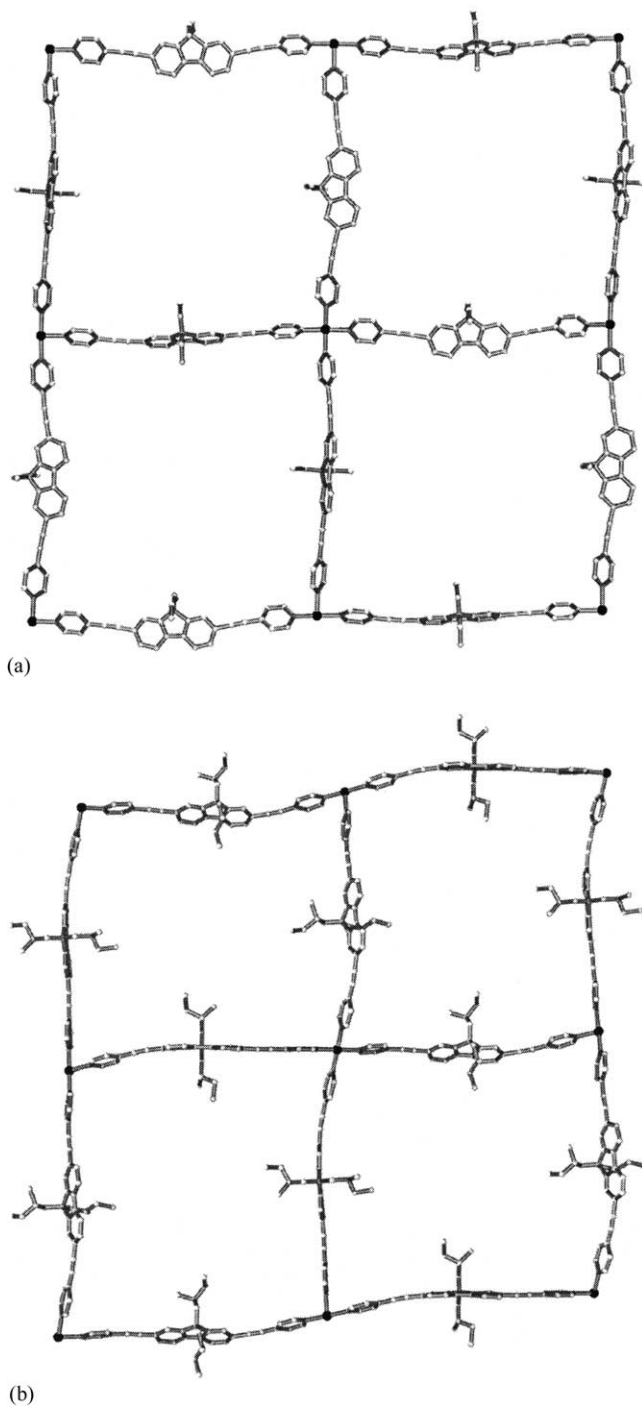
(a)

(b)

Fig. 4. Structure of two square-grids: (a) $[Cu(depf)_2]^{2+}_\infty$ and (b) $[Cu(S\text{-}mbpf)_2]^{2+}_\infty$.

spacer and have been shown to reticulate into the pores of the 3D structures by pointing into the voids. One IRMOF, with a cyclobutyl moiety as the organic group, was revealed to exhibit a high capacity for the uptake of methane (240 cm^3 at standard temperature and pressure per gram at 298 K and 36 atm). The exceptional uptake was ascribed to both the hydrophobic nature and ability of the functional group to provide an appropriately sized aperture for inclusion of the gas.

(a)

(b)
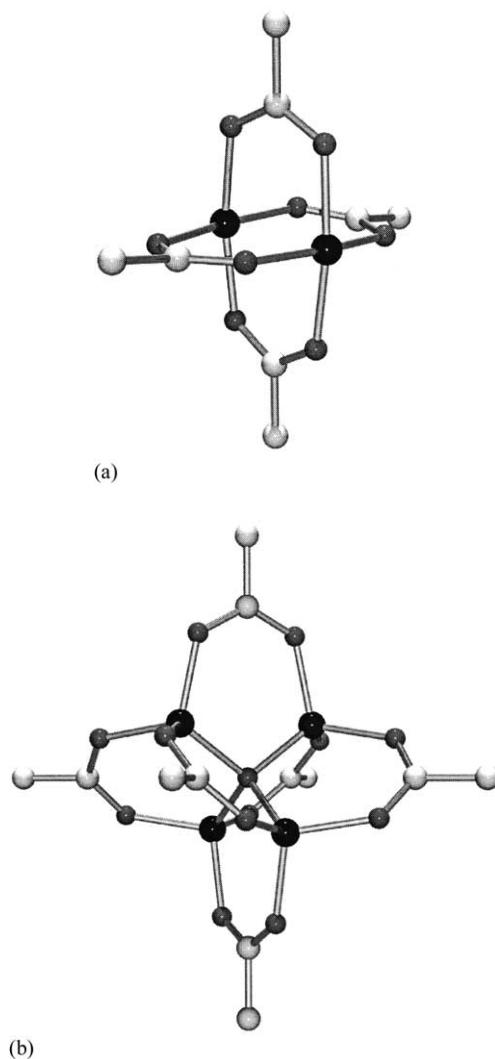
Fig. 5. Oligonuclear metal carboxylate clusters that provide fixed coordination geometries for the construction of MOFs: (a) M$_2$ paddle-wheel complex and (b) M$_4$ octahedral complex.

In addition to IRMOFs, Yaghi has revealed that a functional group attached to a linear bridge can be used to reticulate a square SBU into a 3D framework. Specifically, reaction of Cu(NO$_3$)$_2 \cdot 2.5$H$_2$O with *ortho*-bromoterephthalic acid produced a MOF, [Cu$_2$(*o*-Br-BDC)$_2$]$_\infty$ (where *o*-Br-BDC = *o*-bromo-benzene-1,4-dicarboxylate), wherein dinuclear copper paddle-wheel complexes were reticulated at right angles to form a 3D framework with a topology that conforms to the structure of NbO [50]. The bromine groups forced the carboxylate groups of the *o*-Br-BDC spacer to twist at right angles to each other and, thus, promote the SBUs to assemble into the 3D structure. The resulting MOF was both highly porous and stable, possessing cavities of volume ∼2309 Å^3 stable to exchange of solvent guests.

That a linear bridge of a metal carboxylate may be functionalized with chiral groups to produce a chiral MOF has been recently demonstrated by Lin. In particular, reaction
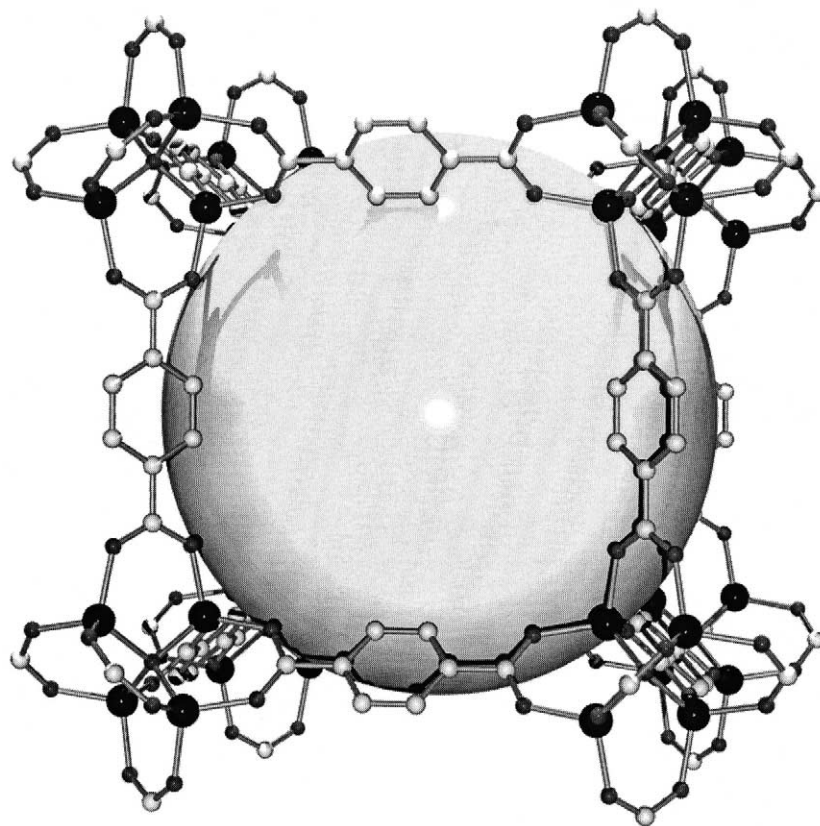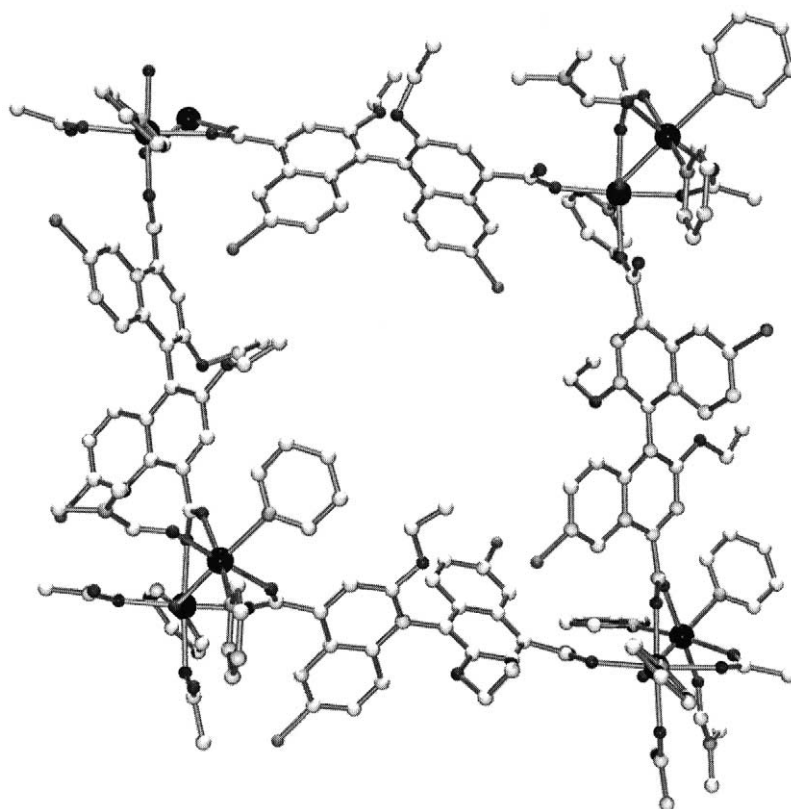
Fig. 6. A member of an isoreticular family of 3D MOFs.

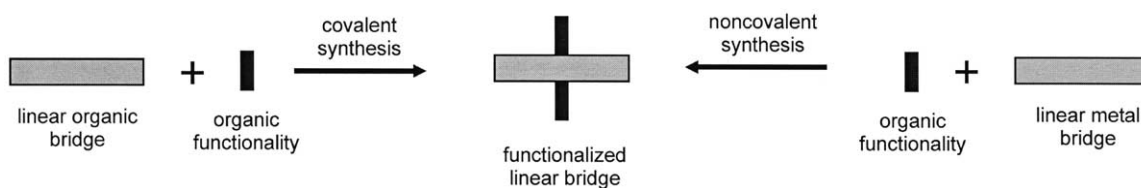Fig. 7. Structure of the chiral 2D MOF [Mn$_2$(μ-H$_2$O)(bda)$_2$(py)$_3$(dmf)]$_\infty$.

Fig. 8. Schematic representation of covalent and noncovalent approaches to functionalize a linear bridge.

of M(NO$_3$)$_2$ (M = Mn, Co, Ni) with the enantiopure atropisomeric 6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthalene-4,4′-dicarboxylic acid (H$_2$BDC) produced the homochiral MOF [M$_2$(μ-H$_2$O)(bda)$_2$(py)$_3$(dmf)]$_\infty$ (py = pyridine; dmf = dimethylformamide) (Fig. 7) [51]. The metal and organic components assembled to produce a 2D square grid, with cavities of dimensions ∼17.5 × 17.5 Å, involving paddle-wheel-like SBUs. The carboxylate groups located in the 4,4′-positions of the dicarboxylate served as linear links while a twisted 1,1′-binaphthalene unit provided the chirality. The ethoxy groups of the dicarboxylate pointed into the cavities of the framework while the grids stacked in a staggered arrangement such that SBUs from adjacent layers were positioned in the cavities of adjacent grids. The pointing of the functional groups into the cavities, coupled with the staggered stacking of the grids, resulted in a minimal void space. In a similar way to the chiral MOF reported by zur Loye and Bunz, the strategy may be used to design MOFs that display chiral selection of guests.

4.2. Pre-framework synthesis and covalent functionalization

A common feature of MOFs with metal ions or clusters as nodes and linear organic bridges as spacers is that the functionalization of the bridge has been performed by way of a covalent synthesis. Consequently, the functionalization has chiefly relied upon employing principles and methods of organic synthetic chemistry. Although such a covalent approach provides a means to functionalize a bridge with a virtually unlimited range of organic groups, the method can involve an elaborate, multi-step synthesis and/or produce the linear bridge in low yield. Indeed, an alternative and possibly more efficient means to functionalize a linear bridge is to employ a supramolecular approach [52,53]. In this design, reversible bonds are used to attach single and/or multiple organic groups to the bridge such that the bridge forms in a single step and high yield. By inverting the structural role of metal and organic components, an IMOF provides such an approach to functionalizing the interior of a MOF (Fig. 8).

5. Inverted metal organic frameworks

An IMOF is a MOF that consists of an organic bridge as a node and a single metal ion or SBU as a linear spacer [37]. Consequently, the structural roles of the metal and organic

components of an IMOF, as compared with a more traditional MOF, are inverted. In such a framework, the number of bonds used by a metal ion or cluster to support the MOF are minimized (i.e. two), which enables remaining coordination sites of the metals to be filled with terminal ligands that may be used to functionalize the interior of the framework. Thus, reaction of a linear metal bridge with organic ligands that serve as planar three-connected (vertex angle: 120°) and four-connected nodes (vertex angle: 90°) would generate MOFs with inverted hexagonal and square grid topologies, respectively (Fig. 9). In effect, such inversion of the structural role of the metal and organic components enable the coordination sphere of the metal-based bridge to line the cavities and pores of a MOF supramolecularly [52], where the terminal ligands may be tailored to define structural and recognition properties of the solid [53].

Although an IMOF offers an attractive means to line interior cavities and pores of a MOF with functional groups, the method has remained largely unexplored. To demonstrate the feasibility of the approach, we will discuss MOFs designed to date with structures that conform to the structure criteria of an IMOF [54–68]. We will then describe an example reported by our lab that employs the approach [37].

5.1. Single metal ion as linear bridge

To our knowledge, Robson reported the first MOF with a structure that conforms to an IMOF. Specifically, reaction of the tetrapyridyl metalloporphyrin (5,10,15,20-tetra-4-pyridyl-21H,23H-porphyrinato)palladium (Pd-py-porph) with Cd(NO$_3$)$_2$ · 4H$_2$O produced the infinite 3D host [Cd$_2$(NO$_3$)$_4$(Pd-py-porph)(H$_2$O)$_4$]$_\infty$ (Fig. 10) [54]. In this material, the porphyrin units served as planar four-connected nodes in which the four pyridyl units were bound to octahedral Cd(II) centers that served as either linear or bent connectors. Each Cd(II) ion was coordinated by two NO$_3^-$ ions, two H$_2$O molecules, and two pyridyl groups in either a *trans* or *cis* arrangement. The pyridyl groups in the *trans* and *cis* arrangements served as the linear and bent connectors, respectively. As a consequence of this arrangement, the connectors assembled with the porphyrin units to form 1D chains that passed over each other to produce the 3D network. The coordinated H$_2$O molecules and NO$_3^-$ ions lined voids of the solid, which were filled with H$_2$O molecules.

Robson has also described an IMOF based on a planar three-connected node. Specifically, reaction of 2,4,6-tris
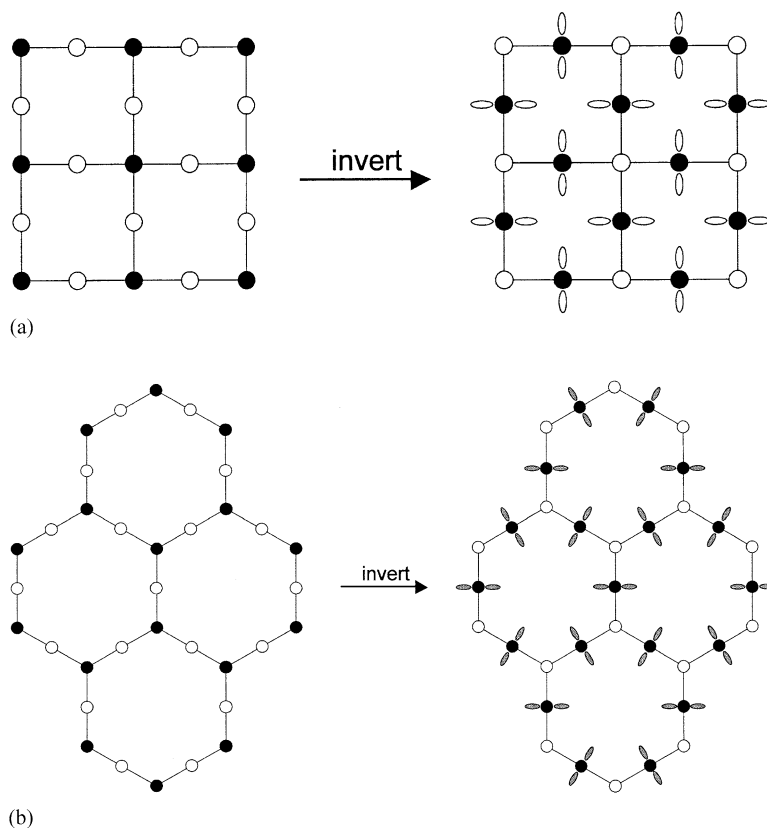
(a)

(b)

Fig. 9. Schematic of the inversion of: (a) square grid and (b) honeycomb network (black circle, metal; open circles, organic; ellipses, organic functionality).

(4-pyridyl)-1,3,5-triazine (tpt) with $ZnSiF_6$ produced $[Zn_3(SiF_6)_3(tpt)_2(H_2O)_6(MeOH)_3]_\infty$ [55] wherein the metal and organic components assembled to produce an eightfold interpenetrated 3D framework that involved an enantiomorphic (10,3)-a topology. Each Zn(II) center adopted an octahedral coordination geometry with two *trans* pyridyl units from two tpt ligands, while the remaining four sites were occupied by one MeOH molecule, two H_2O molecules, and one SiF_6^{2-} anion (Fig. 11). As a consequence of the assembly process, the components organized to form a (10,3)-a net with mutually perpendicular fourfold helices of the same handedness. The interpenetration of the (10,3)-a nets involved four networks of one handedness interpenetrating with four networks of the opposite handedness to give a 3D
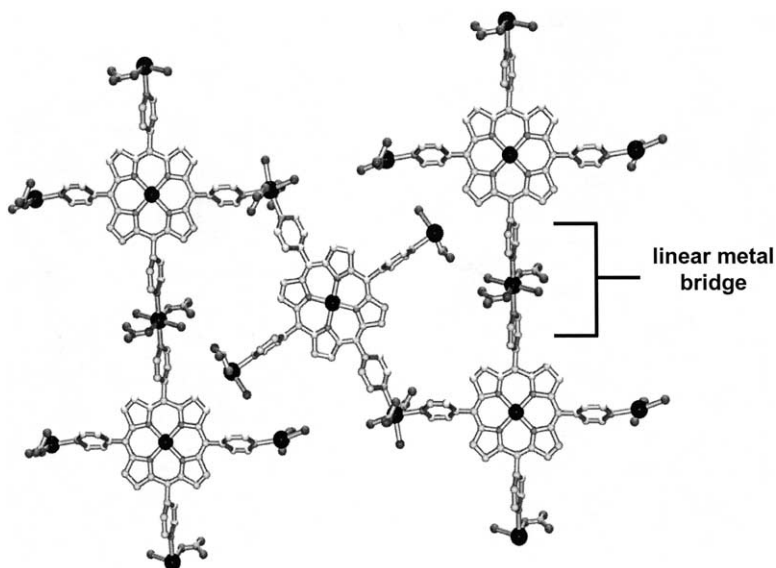

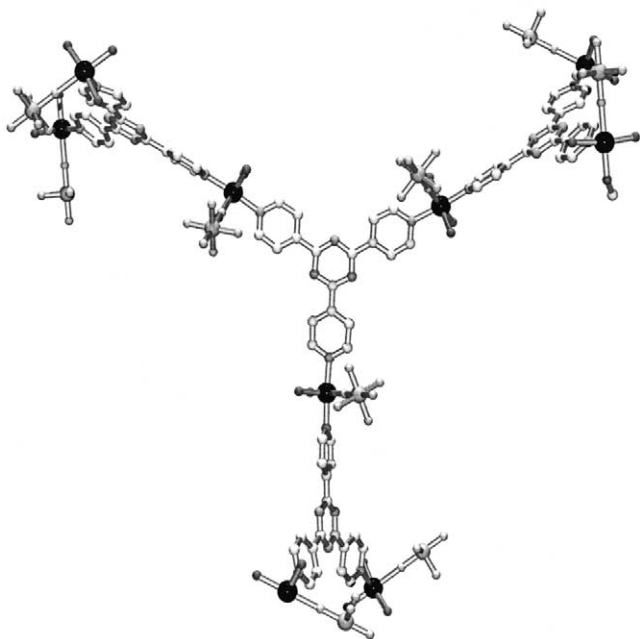Fig. 10. The linear and bent Cd(II) bridges of $[Cd_2(NO_3)_4(Pd–py–porph)(H_2O)_4]_\infty$.

Fig. 11. Structure of the 3D network $[Zn_3(SiF_6)_3(tpt)_2(H_2O)_6 (MeOH)_3]_\infty$ emphasizing the linear metal bridges between the tpt nodes.

racemate devoid of cavities and pores. The terminal ligands of the Zn(II) ions lined the interior of the 3D network.

Suh has described IMOFs based on a planar three-connected node, in the form of the 1,3,5-benzenetricarboxylate anion (BTC), and a linear bridge, in the form of a hydroxylated Ni(II) macrocycle. In particular, reaction of $NiL(ClO_4)_2$ ($L=C_{12}H_{30}N_6O_2$) with Na_2BTC produced two IMOFs of formula $[(NiL_3)(BTC)_2]_\infty$ which, depending on the nature of the guest, exhibited either a brick-wall

or honeycomb topology (Fig. 12) [56]. The honeycomb framework formed with dimethylformamide (DMF) and H_2O as the solvent while the brick-wall framework formed with DMF, H_2O, and pyridine. π–π interactions involving the BTC anions and included pyridine molecules were used to account for the formation of the brick-wall structure. In each case, the 2D framework assembled to produce 1D pores and the hydroxyl groups of the linear bridges served to connect adjacent layers by way of hydrogen bonds. Notably, each MOF was shown to lose crystallinity upon removal of solvent guest. A similar 2D honeycomb framework $[Ni(C_{20}H_{32}N_8)(C_6H_9(COO)_3]_\infty$, involving the *cis,cis*-1,3,5-cyclohexanetricarboxylate anion and a Ni(II) macrocycle with pendant pyridyl groups, has also been reported [57]. In a similar way to $[(NiL_3)(BTC)_2]_\infty$, the MOF was shown to lose crystallinity upon removal of the guest.

Rosseinsky has recently demonstrated that BTC may be used as a three-connected node to produce the 2D IMOF $[Ni_3(BTC)_2(pyridine)_9(H_2O)_3]_\infty$ [58]. The components assembled to produce a framework that exhibited a nearly planar (6,3) net composed of hexagons with side lengths of approximately 11.3 Å. The carboxylate groups of the anions adopted *trans* positions in the coordination sphere of each nickel atom. The coordination sphere of each metal was completed by three pyridines and one H_2O molecule. The pyridines pointed into the hexagonal cavities while the coordinated H_2O molecules participated in O–H···O hydrogen bonds with the carboxylate groups (Fig. 13). A similar 2D IMOF $[Ni_3(BTC)_2(pyridine)_6(n-butanol)_6]_\infty$ has also been reported wherein alkyl chains of coordinated alcohols pointed into hexagonal cavities. Each IMOF lost solvent guest upon standing in air and displayed an increase in crystallinity upon being exposed to pyridine vapor.
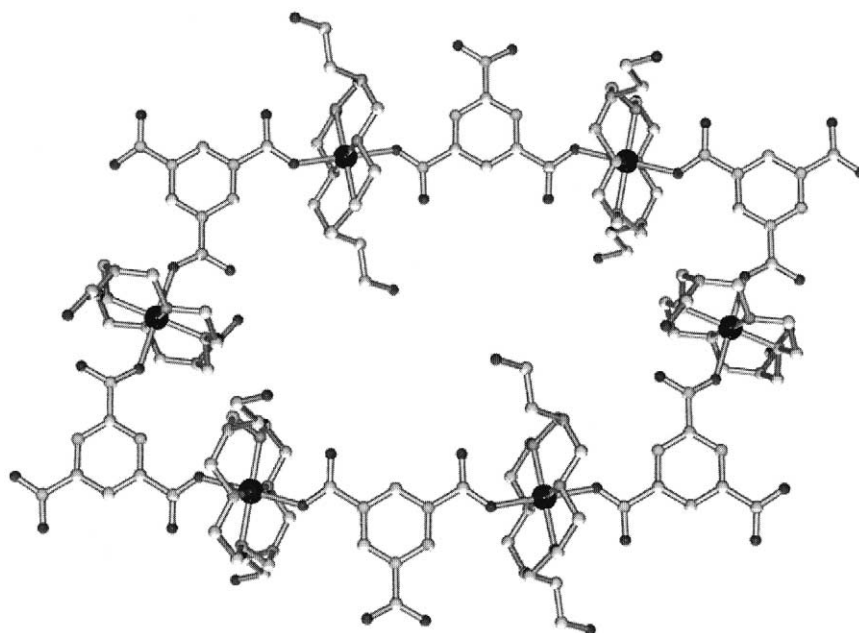

Fig. 12. The hexagonal grid $[(NiL_3)(BTC)_2]_\infty$.

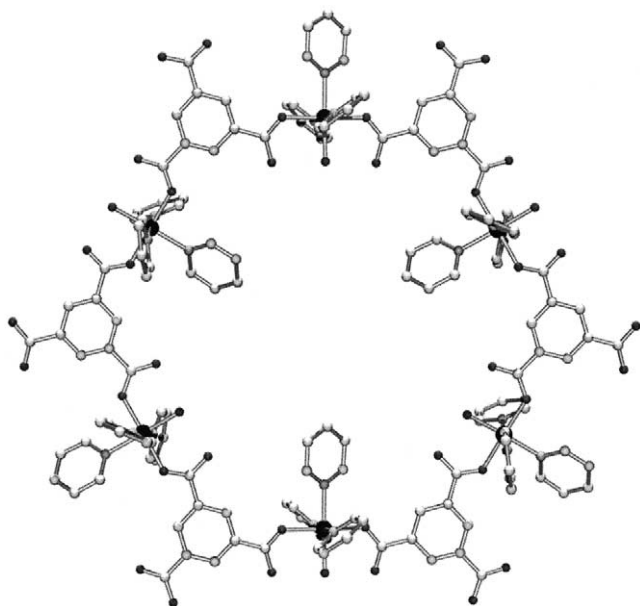Fig. 13. Structure of the 2D IMOF [Ni$_3$(BTC)$_2$(pyridine)$_9$(H$_2$O)$_3$]$_\infty$.

Fig. 14. The inverted square grid framework [Ag$_2$(Tos)$_2$(μ_4-hmt)]$_\infty$ (single atoms bonded to Ag from coordinated Tos anion: gray sphere, oxygen; white sphere, carbon).

It is well-established that the Ag(I) cation is able to adopt a linear, or bent, coordination geometry. Consequently, reaction of the Ag(I) cation with a polydentate ligand may, in principle, generate an IMOF. This has been the case when various Ag(I) salts have been reacted with hexamethylenetetramine (hmt), a tetrafunctional molecule with four nitrogen atoms located at the vertices of a tetrahedron. Specifically, four IMOFs based on the Ag(I) ion have been reported [59,61–63]. Three frameworks exhibit a square grid network while the fourth exhibits a hexagonal grid topology.

Reaction of Ag(Tos) (where Tos = p-CH$_3$C$_6$H$_4$SO$_3$) with hmt produced, as described by Ciani, the square grid framework [Ag$_2$(Tos)$_2$(μ_4-hmt)]$_\infty$ (Fig. 14) [59]. In this framework, the Ag(I) cation served as a bent bridge, being coordinated by two hmt molecules, a Tos anion, and an aromatic ring. The coordinated hmt molecule served as a four-connected node. As a consequence of this arrangement, the metal and organic components assembled to produce a 2D square grid with metal–metal separations of ∼6.4 × 6.4 Å. The bulkiness of the hmt ligand and relative short length of the metal bridge precluded formation of a cavity which, in effect, forced the aromatic groups of the anions to point above and below the plane of the 2D framework. A similar 2D grid involving Hg(II) as a bent spacer in [HgCl$_2$(hmt)] has been recently reported by Batten [60].

Similar to [Ag$_2$(Tos)$_2$(μ_4-hmt)]$_\infty$, reaction of Ag(NO$_2$) with hmt produced the 2D square grid [Ag$_2$(NO$_2$)$_2$(μ_4-hmt)]$_\infty$, as independently reported by Chen [61] and Liu [62]. In contrast to [Ag$_2$(Tos)$_2$(μ_4-hmt)]$_\infty$, the Ag(I) ion of [Ag$_2$(NO$_2$)$_2$(hmt)]$_\infty$ adopted two different coordination geometries. Specifically, half of the Ag(I) ions assumed a linear geometry, bridging two hmt molecules, while the remaining cations adopted an octahedral geometry, being chelated by two NO$_2^-$ anions and coordi-
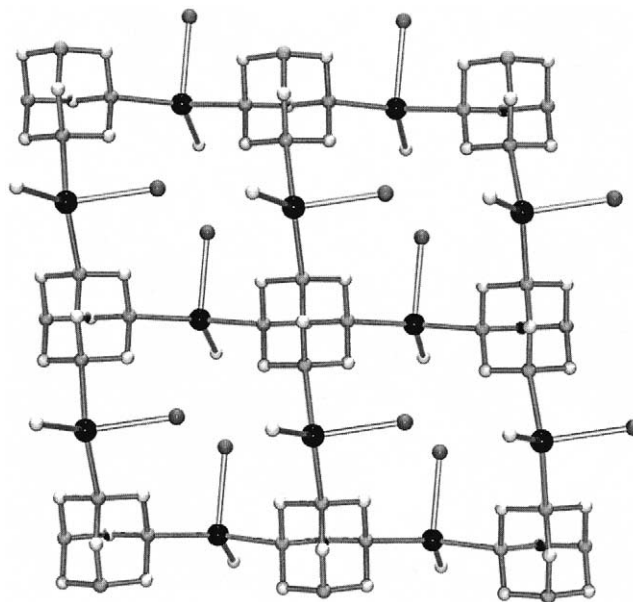
nated by two *trans* hmt molecules. The grid displayed metal–metal separations of ∼6.2 × 10.9 Å. In a similar way to [Ag$_2$(Tos)$_2$(μ_4-hmt)]$_\infty$, the NO$_2^-$ anions pointed above and below the plane of the framework.

Chen has revealed that reaction of Ag$_2$(SO$_4$) with hmt produced the square grid [Ag$_2$(SO$_4$)(μ_4-hmt)(H$_2$O)]$_\infty$ in which the Ag(I) cation, similar to Ag(NO$_2$), adopted two different coordination geometries [61]. In addition to serving as a linear spacer by bridging two hmt molecules, each ion was coordinated by either a SO$_4^{2-}$ anion or a H$_2$O molecule. The coordinated SO$_4^{2-}$ anions H$_2$O molecules pointed above and below the plane of each grid (metal–metal separations ∼6.3 × 10.4 Å), while adjacent grids were connected through hydrogen bonds that involved the coordinated H$_2$O molecules and SO$_4^{2-}$ anions. The hydrogen bonds involving the H$_2$O molecules and SO$_4^{2-}$ anions produced a 3D network with irregular pentagonal channels that included H$_2$O molecules as guests.

Whereas the metal and organic components of [Ag$_2$(Tos)$_2$(μ_4-hmt)]$_\infty$, [Ag$_2$(NO$_2$)$_2$(μ_4-hmt)]$_\infty$, and [Ag$_2$(SO$_4$)(μ_4-hmt)(H$_2$O)]$_\infty$ have assembled to form a MOF with a square grid topology, the components of {[Ag$_3$(μ_3-hmt)$_2$(H$_2$O)$_4$](PF$_6$)$_3$}$_\infty$ have assembled to form a MOF with a hexagonal grid topology. In particular, Ciani has revealed that the Ag(I) cation of the framework, similar to [Ag$_2$(SO$_4$)(μ_4-hmt)(H$_2$O)]$_\infty$, assembled in two different coordination geometries. Specifically, one third of the Ag(I) ions assumed a linear geometry, bridging two hmt molecules, while the remaining cations adopted a bent geometry, being coordinated by two hmt molecules and two H$_2$O molecules [59]. Hydrogen bonds involving the coordinated H$_2$O molecules formed between the layers to produce elongated hexagonal
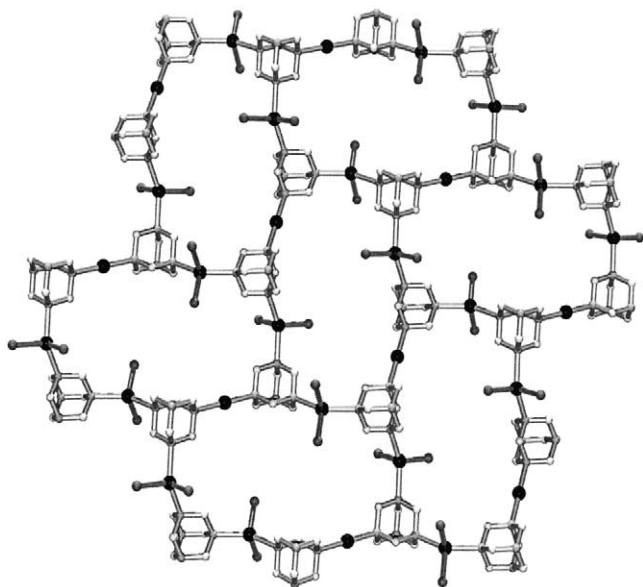
Fig. 15. Hexagonal grids of $\{[Ag_3(\mu_3\text{-hmt})_2(H_2O)_4](PF_6)_3\}_\infty$.

cavities (metal–metal separations $\sim 7.8 \times 14.9$ Å) filled by PF_6^- counter ions (Fig. 15).

5.2. Secondary building unit as linear bridge

In addition to serving as a node of a MOF, a metal carboxylate cluster, or SBU [11], may serve as a linear bridge of

an IMOF. Such a SBU would be expected to fix metals and organic functionalities of a linear bridge into well-defined geometries such that the cluster supports a robust IMOF with well-positioned organic groups. In this context, the dinuclear carboxylate paddle-wheel complex $M_2(RCO_2)_4$ (M = Cu, Rh, Ru, Mo; R = alkyl) has been used as a linear bridge to construct IMOFs [64–68].

The first IMOF based on a dinuclear paddle-wheel complex was reported by Cotton [64]. Specifically, reaction of $[Rh_2(O_2CCF_3)_4]$ with TCNE (where TCNE = tetracyanoethylene) produced the 2D square grid $[(Rh_2(O_2CCF_3)_4)_2 (TCNE)]_\infty$. The grid was composed of planar four-connected TCNE molecules and linear $[Rh_2(O_2CCF_3)_4]$ bridges that formed square cavities. The –CF_3 moieties of the carboxylates pointed into the cavities of the framework, lining the walls with disordered fluorine groups. The grids stacked at a separation distance of 9.5 Å to produce voids filled with solvent benzene molecules. Notably, Dunbar has recently reported a 2D IMOF $[(M_2(O_2CCF_3)_4)_2(TCNQ)]_\infty$ (where M = Ru, Rh; TCNQ = 7,7,8,8-tetracyano-quinodimethane) with a structure similar to $[(Rh_2(O_2CCF_3)_4)_2 (TCNE)]_\infty$ [65] (Fig. 16). The metal and organic components, owing to the presence of the aromatic ring of the TCNQ molecule, assembled to form a 2D cavity-containing framework with a square grid topology. The cavities hosted toluene molecules as guests. In a similar way to $[(Rh_2 (O_2CCF_3)_4)_2(TCNE)]_\infty$, the carboxylates lined the walls of the host with –CF_3 groups.
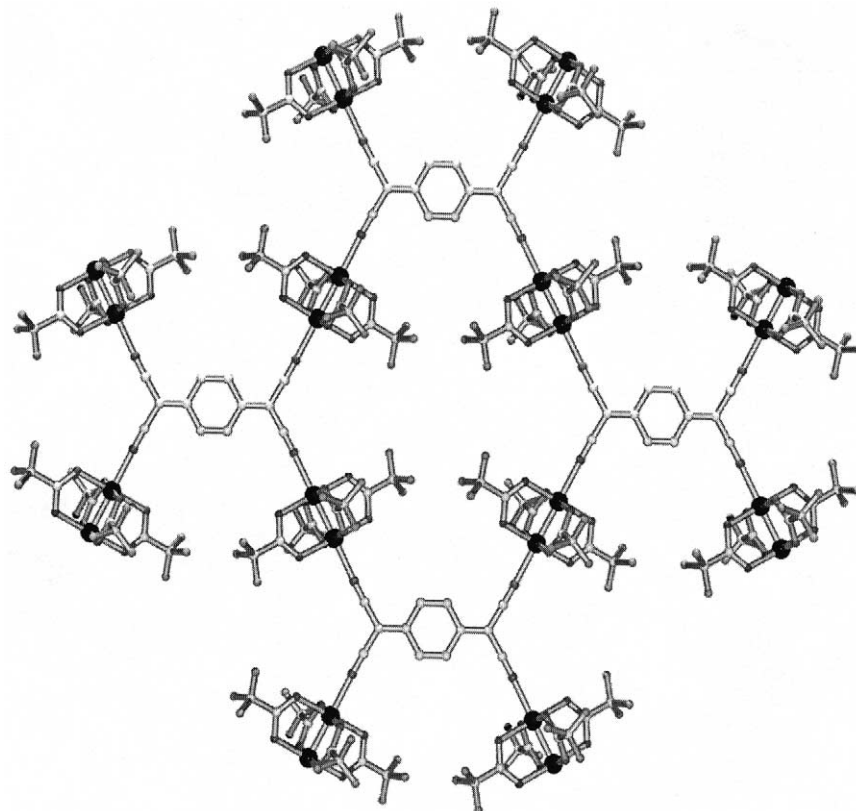

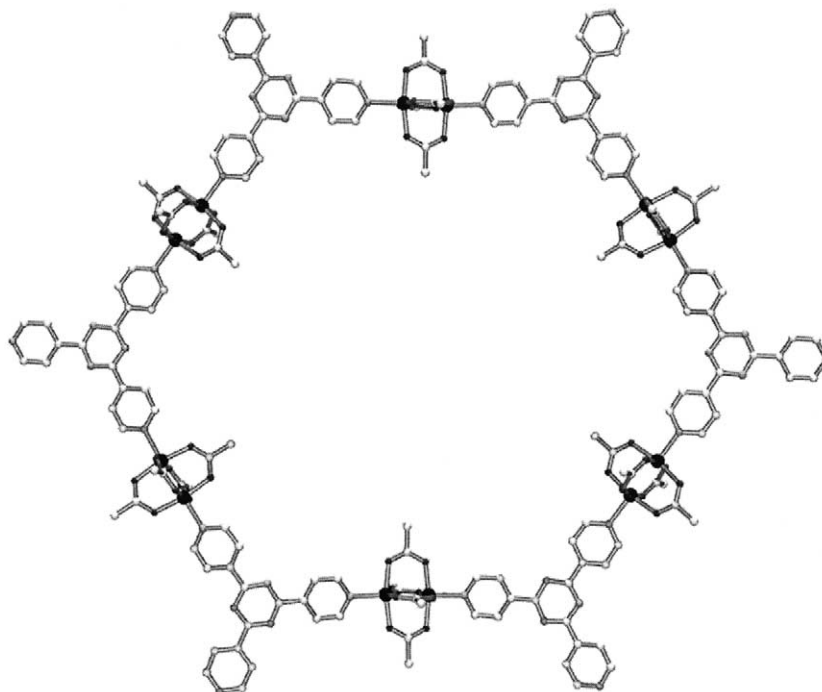Fig. 16. View of the distorted hexagonal network of $[(M_2(O_2CCF_3)_4)_2(TCNQ)]_\infty$, (M = Ru(II) or Rh(II)).

Fig. 17. The crystal structure of the inverted hexagonal framework [(Cu$_2$(O$_2$CCH$_3$)$_4$)$_3$(tpt)$_2$]$_\infty$.

Robson has shown that reaction of [Cu$_2$(O$_2$CCH$_3$)$_4$] with tpt produced the 2D IMOF [(Cu$_2$(O$_2$CCH$_3$)$_4$)$_3$(tpt)$_2$]$_\infty$. The framework consisted of (6,3) sheets wherein tpt molecules served as planar three-connected nodes and copper paddle-wheel complexes served as linear bridges (Fig. 17) [66]. As a consequence of this arrangement, the metal and organic components produced very large hexagonal cavities with ring diagonals of dimensions ∼35 Å. The grids adopted an *ABC* stacking pattern such that half of the organic nodes of one grid assembled above or below the cavities of the other. Consequently, π–π interactions between tpt units of sheets *X* and *X* + 2, within cavities of sheet *X* + 1, formed to produce a 3D framework devoid of cavities for inclusion. The –CH$_3$ groups of the SBU bridges pointed into the hexagonal cavities of the framework.

Work by Zaworotko has shown that hmt may be used as a node to produce a 2D IMOF with a SBU as a bridge. Specifically, reaction of [Cu$_2$(O$_2$CCH$_2$CH$_3$)$_4$] with hmt produced a 2D grid, [(Cu$_2$(O$_2$CCH$_2$CH$_3$)$_4$)$_5$(hmt)$_3$]$_\infty$, that displayed novel tiling of pentagons (Fig. 18) [67]. The hmt molecules of the framework served as both three- and four-connected nodes to produce non-planar grid with cyclopentanoid cavities of dimensions ∼10 × 15 Å. The ethyl groups of the carboxylates pointed into the cavities, which mitigated against inclusion of guest solvent molecules.

In addition to a 2D IMOF, hmt has been shown to generate a 3D IMOF. In particular, Dehnicke has shown that reaction of the silylated phosphaneimine Me$_3$SiNPEt$_3$ with [Mo$_2$(O$_2$CCH$_3$)$_4$] produced [(Mo$_2$(O$_2$CCH$_3$)$_4$)$_2$(hmt)]$_\infty$ which involved a 3D framework with a topology that con-

formed to a superdiamondoid lattice. The hmt molecules served as four-connected nodes while the dinuclear Mo clusters served as linear bridges [68]. Solvent CH$_2$Cl$_2$ molecules were included within cavities of the framework. The carboxylates of the linear bridges lined the cavities with –CH$_3$ groups.

5.3. Our approach

During the last 2 years, we have developed an approach for controlling reactivity in the organic solid state that employs bifunctional molecules that serve as linear hydrogen bond templates [69]. The method has enabled us to enforce topochemical alignment of olefins in organic solids such that the double bonds undergo an intermolecular [2 + 2] photocycloaddition reaction. Thus, co-crystallization of 1,3-dihydroxybenzene (resorcinol) with *trans*-1,2-bis(4-pyridyl)ethylene (4,4′-bpe) produced a four-component molecular assembly (Fig. 19), 2(resorcinol) · 2(4,4′-bpe), held together by four O–H⋯N hydrogen bonds wherein two double bonds were organized for a photodimerization [70]. Ultraviolet irradiation of the solid produced *rctt*-tetrakis(4-pyridyl)cyclobutane (4,4′-tpcb), stereospecifically (yield: 100%).

An attractive feature of the template approach has been the nature of the products. That hydrogen bond donors have been used to assemble the reactants has meant that the cyclobutane units have been lined with hydrogen bond acceptor sites in the form of pyridyl groups. Owing to the ubiquity of pyridyl groups in coordination chemistry, and the fact that
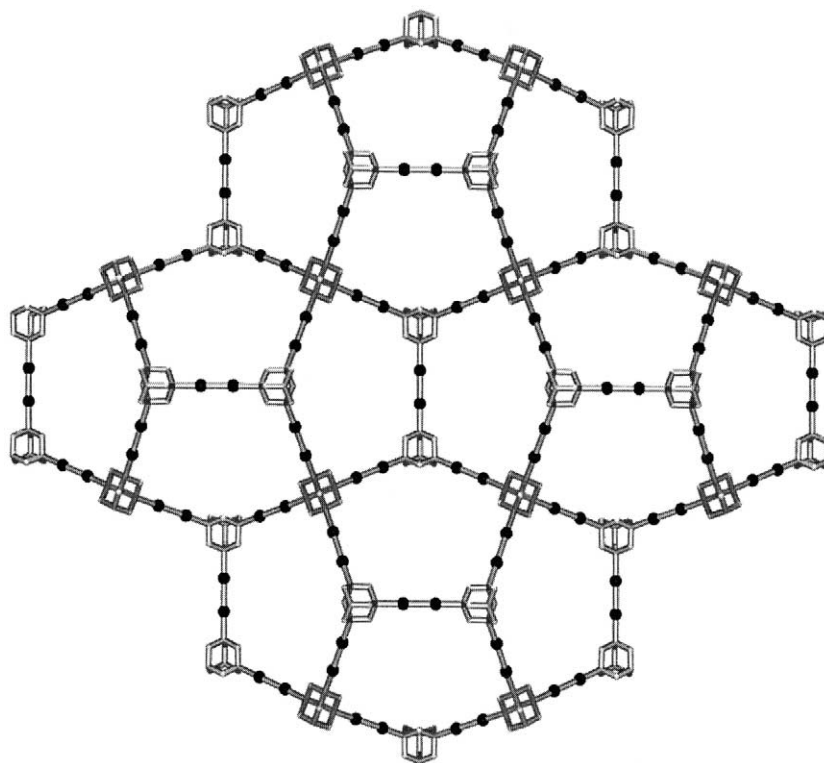
Fig. 18. The (5_4^3) network $[(Cu_2(O_2CCH_2CH_3)_4)_5(hmt)_3]_\infty$. Carboxylates have been omitted for clarity and the paddle-wheel complexes are shown as a single line with black spheres.

multiple and divergent pyridyl groups were attached to the cyclobutane unit, we anticipated that products of our linear templates could serve as nodes of IMOFs.

Our first result has involved the application of 4,4′-tpcb as a node for the construction of a 2D IMOF [37]. Specifically, reaction of copper paddle-wheel complex $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ with 4,4′-tpcb was shown to give $[(Cu_2(O_2CCH_3)_4)_2(4,4′-tpcb)]_\infty$ (Fig. 20). In this framework, each 4,4′-tpcb unit was surrounded by four paddle-wheel complexes such that the cyclobutane units served as four-connected nodes and the paddle-wheel complexes served as linear bridges. As a consequence of the assembly process, a 2D IMOF with rhombic cavities of dimensions $\sim17.2 \times 17.2$ Å and corner angles of ~75 and $105°$ formed.

The –CH_3 groups of the linear bridges of $[(Cu_2(O_2 CCH_3)_4)_2(4,4′-tpcb)]_\infty$ pointed into the cavities of the IMOF. In particular, four –CH_3 groups were directed into each cavity such that the alkyl groups subdivided each cavity into three compartments. The largest compartment, which defined a large rectangular box of dimensions $\sim20.0 \times 9.5$ Å, was located along the diagonal of the obtuse corner angles of the cavities and was occupied by solvent benzene guests. The two smaller compartments, which defined moderately-sized square boxes of dimensions $\sim7.0 \times 7.0$ Å, were located in the remaining corners and were filled by –CH_3 groups directed above and below each cavity (Fig. 21). The inclusion of the –CH_3 into the square-shaped compartments resulted in oblique stacking of the grids, which produced a 3D MOF with isolated 1D channels of dimensions
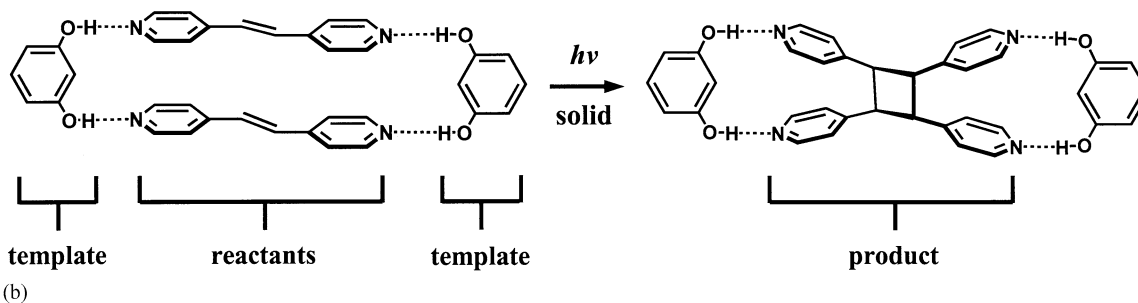

Fig. 19. Construction of 4,4′-tpcb in the solid state using a linear template.
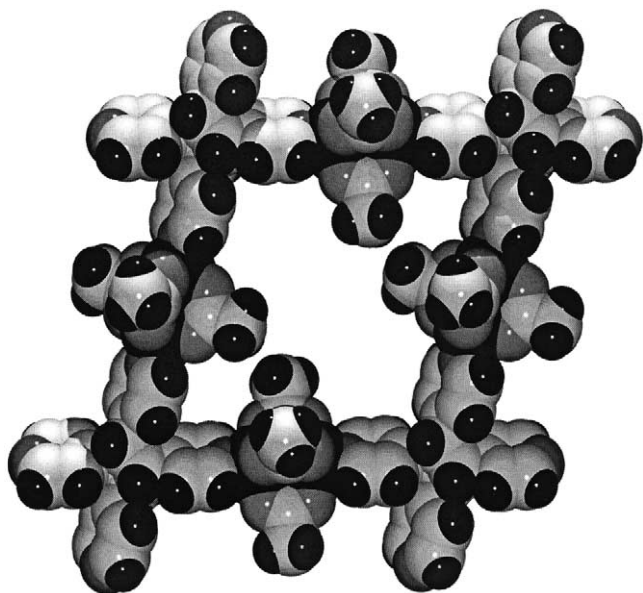
Fig. 20. Space filling model of the 2D IMOF [(Cu$_2$(O$_2$CCH$_3$)$_4$)$_2$ (4,4′-tpcb)]$_\infty$.

$\sim$12 × 10 Å. The channels were occupied by ordered and disordered benzene molecules, which represented about the 40% of the volume of the unit cell. Thus, the organic functional groups of the SBU accommodated the –CH$_3$ group as "pegs" in lining up the layers and preorganizing the grids to form the channels. To our knowledge, such molecular compartmentalization had not been observed within a MOF [37]. Preliminary guest-exchange experiments revealed that single-crystals of [(Cu$_2$(O$_2$CCH$_3$)$_4$)$_2$(4,4′-tpcb)]$_\infty$ were stable to removal of the benzene guest.

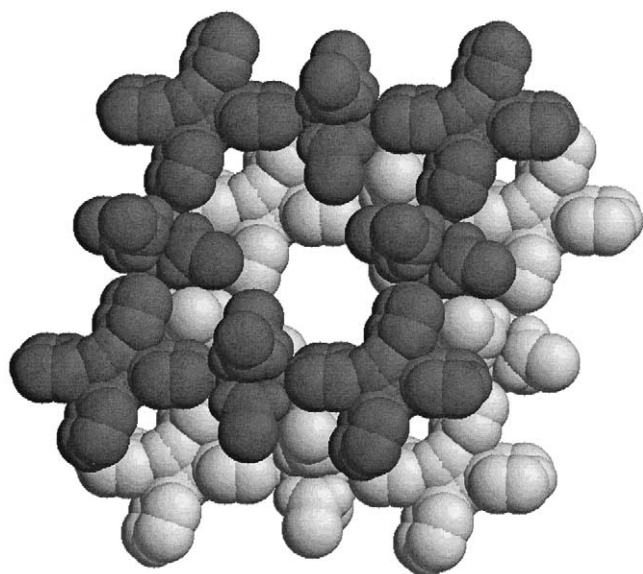

Fig. 21. Space filling view of two adjacent grids of [(Cu$_2$(O$_2$CCH$_3$)$_4$)$_2$ (4,4-tpcb)]$_\infty$ that illustrates the inclusion of methyl groups of adjacent grids.

6. Summary and outlook

In this article, we have described methods to functionalize the interiors of crystalline inorganic–organic hybrid materials [38–41], with focus on MOFs [42–68]. We have shown that MOFs offer a diverse space within which to place functional groups to affect and, in some cases, control properties of metal–organic solids (e.g. recognition). Cavity-containing and porous MOFs have been highlighted, where it has been demonstrated that IMOFs [37,54–68] offer an attractive means to functionalize the interiors of host MOFs with organic groups using principles of supramolecular chemistry [52]. Indeed, much of the efforts to functionalizing the interiors of MOFs are at a beginning and we anticipate a further understanding of those factors that dictate assembly processes in molecular crystalline solids will enable the ability to line and fine-tune the interiors of host MOFs to be further realized.

Acknowledgements

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