Crystal engineering of binary metal imidazolate and triazolate frameworks

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This article summarizes the recent advances in the crystal growth, structural control strategies and diverse structures of the binary metal imidazolate and triazolate frameworks, which are the simplest systems for crystal engineering of two-, three- and four-connected coordination polymers.

Introduction

Crystal engineering of metal–organic frameworks (MOFs) with structure-based properties is of great current interest but remains a distant prospect since we can hardly control over the extended structures or local coordination modes of individual components, even the chemical composition of the final products,[1–4] and the development of effective crystal growth and structural control strategies is one of current important topics in supramolecular chemistry. In fact, one of the main problems for understanding the crystal growth of MOFs is the complexity of one-pot assembly in multi-component systems and flexible coordination modes of common metal ions and ligands. Thus the simplest two-component metal–organic compound comprising of coordination-restricted metal ions and ligands represents the most reliable crystal engineering system for MOFs.
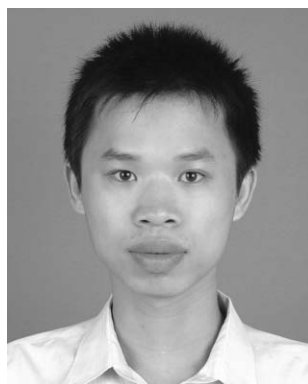
Five-membered heterocycles such as pyrazole (Hpz), imidazole (Him) and triazole (Htz) are some kinds of the smallest and simplest organic ligands. These heterocycles can be readily deprotonated to form corresponding azolate anions, in which each individual nitrogen atom is a very strong N-ligating

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donor for a d-metal ion.[5,6] Therefore, one may use only metal ions and azolates (or binary metal azolates) to establish a simple, two-component MOF system with predictable local coordination environments for crystal engineering. Binary metal pyrazolates were widely reported as simple discrete clusters (mainly triangles) and chain-like structures.[6] Meanwhile, it is rather complicated and difficult to predict the coordination behaviour of tetrazolate because of the high potential coordination number and steric hindrance between the attached metal ions. Moreover, only few binary metal tetrazolates have been reported to date.[7] Therefore, pyrazolate and tetrazolate compounds will not be discussed here.
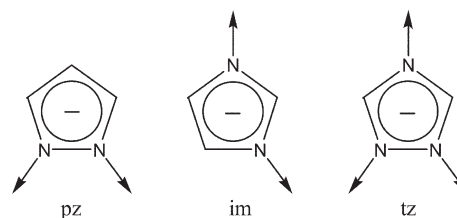
Binary metal imidazolates and triazolates, which may cover two-, three- and four-connected MOF systems as the most important and plausible targets for crystal engineering (Scheme 1), usually occur as highly insoluble and intractable polycrystalline powders due to the strong ligating ability of the anionic ligands and polymeric nature, affording relatively

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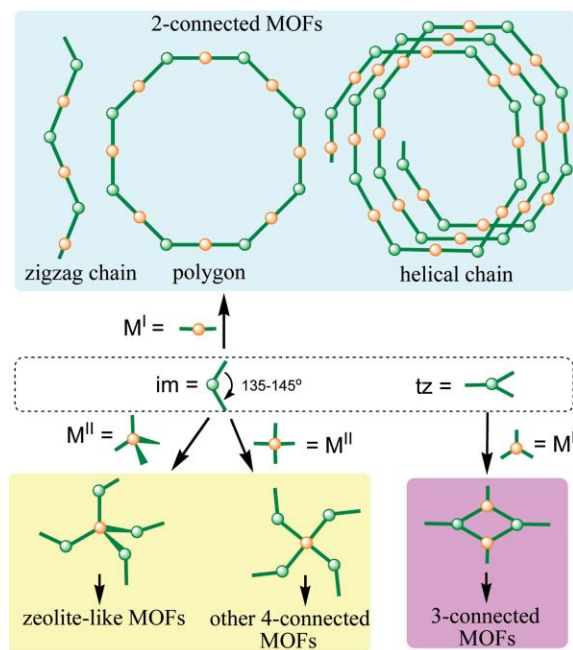

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simple and predictable chemical compositions, but hindering crystal-structural analysis. Although such polycrystalline coordination polymers can be structurally established by powder X-ray diffraction (PXRD),[6] it is usually very difficult to obtain large quantities of phase-pure samples for PXRD measurements. Fortunately, solvothermal (including hydrothermal) treatment and liquid diffusion provide viable routes to growing single crystals, and make single-crystal X-ray diffraction studies of such compounds possible. Meanwhile, a few new and important solvothermal strategies, including in-situ metal/ligand reaction, templating, ligand-structure directing, as well as reaction-condition tuning (temperature, pH, buffering additive, etc.), have been established for crystal engineering of these compounds. The crystal engineering approaches, along with the diverse structures will be summarized in this review.

Univalent metal imidazolates

Supramolecular isomerism is an essential element in the crystal engineering and understanding the structure–property relationship of MOFs.[3] The zero-dimensional (0D) ring, 1D zigzag and helical chains constructed by angular and linear building blocks with 1:1 stoichiometry are well known as the simplest isomerism system. The crystal engineering of these three isomers, especially the high-membered polygons, homochiral helices, or a complete set of these isomers still remain a great challenge.

Imidazolate is an angular two-connected building block with two nitrogen donors oriented at an angle of ca. 135–145°. Univalent metal centres such as Cu(I), Ag(I) and Au(I) ions can act as linear, two-coordinated linkers since the metal:ligand ratio is restricted to 1:1. Therefore, besides the zigzag and helical chains, metal–organic polygons with high numbers of sides for the univalent metal imidazolates are expected (Scheme 1). For example, the octagon, nonagon and decagon require angles of 135, 140 and 144°, respectively, being within the range of the possible im bridging geometry.

However, the very low solubilities of binary univalent metal imidazolates favour the kinetic products of infinite chain-like coordination polymers. The zigzag chain-like structure of univalent metal imidazolate, Ag(im) (**1**), was firstly established by Masciocchi et al. with PXRD, in which the chains are further attracted together by argentophilic interactions (3.16 Å) to generate a (10,3)-a net (Fig. 1) when im bridges and Ag···Ag interactions are regarded as linkers.[8]

Masciocchi et al. also prepared Cu(im) powders but failed to solved its structure since copper(I) complexes were generally unstable in the micro-crystalline state and good PXRD data could not be obtained.[6] Recently, You et al. have successfully obtained single crystals of Cu(im) (**2**) using copper(II) acetate as the copper source under solvothermal condition.[9] **2** possesses a zigzag chain structure, but its packing pattern is a 2D $8^2 10$ net bilayer structure consolidated by inter-chain ligand-unsupported cuprophilic interactions (2.78 Å). The im rings in **2** are disordered in two orientations, but the disorder is due to the superstructure rather than the rotation of the ligand or packing sequence of the layers, since a single-crystal analysis at 123(2) K revealed an ordered structure (hereafter designated as **2′**) similar to that of **2**, but the unit-cell volume was increased by four times.[10] As depicted in Fig. 2, there are two types of intermolecular Cu···Cu interactions in **2′**, i.e. N–Cu···Cu–N = 90° for Cu···Cu = 2.69 Å and N–Cu··· Cu–N = 51° for Cu···Cu = 2.78 Å, implying that the cuprophilic attractions (or the Cu···Cu distances) are influenced by the steric hindrance between the im ligands.[11] On the other hand, no helical or polygonal structure for Cu(im) or Ag(im) is known to date, although several supramolecular isomers of **1** and **2** have been prepared.[10a]

Obviously, synthesis of more structurally interesting M(I)– im polygons rather than the kinetically favoured infinite chains remained a challenge. It is important to reduce the crystallization speed of the infinite chain and/or increase the formation energy of the thermodynamically favourable polygon. In situ generation of Cu(I) ions from Cu(II) salts under solvothermal condition is a convenient approach to control the
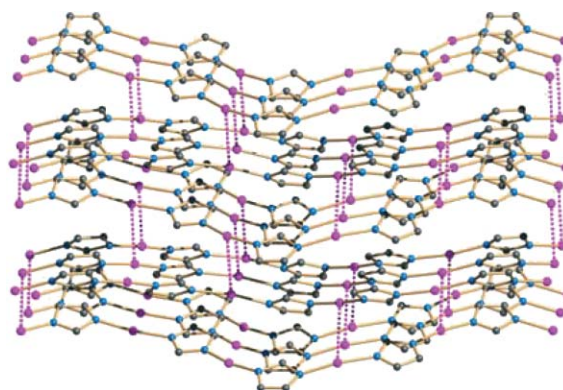

Scheme 1 Schematic presentations of the two-, three and four-connected MOFs constructed by binary metal imidazolates and triazolates.

Fig. 1 The 3D (10,3)-a packing structure of Ag(im) (**1**).
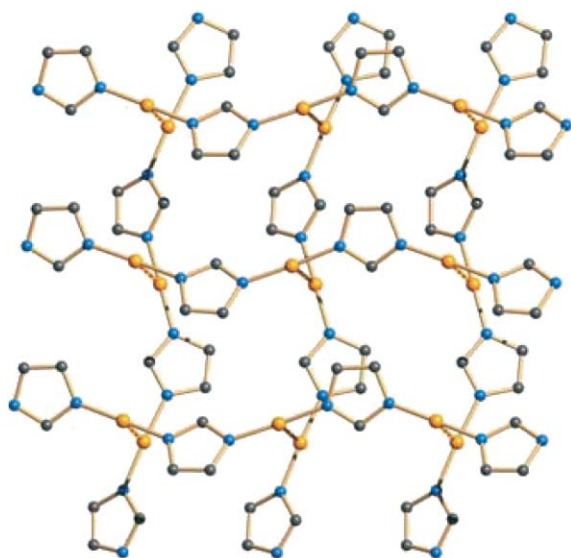
Fig. 2 The bilayer 8^210 packing structure of Cu(im) (**2′**).

Fig. 3 Space-filling view of $[Cu_8(mim)_8]\cdot$toluene (**3**).

formation of M(I)–im species. Another possible strategy is the use of aqueous ammonia, which functions not only as a base but also as a coordination competing or buffering agent to reduce the crystallization speed or increase the solubilities of some intermediate M(I)–im species. However, such a strategy seems inadequate to control the formation of M(I)–im polygons. An additional technique is the use of guest templates, which is helpful for inducing the formation of discrete polygonal species and offering additional supramolecular stabilization energy for the formation of crystals. Of course, such guest molecules should have appropriate sizes and supramolecular interactions with the targeted polygonal hosts. Unfortunately, the inner cavities of the targeted polygons are too large compared to common round-shape organic molecules such as benzene (*ca.* 6.7 Å). For example, the effective van der Waals diameter of the inner cavity of a $[Cu_8(im)_8]$ octagon is estimated to be *ca.* 8.6 Å. To reduce the inner cavity size, as well as to strengthen the supramolecular interaction between the polygon and guest molecule, a methyl group can be introduced to the 2-position of the im ligand.

In the absence of organic templates, we could only obtain an infinite zigzag chain structure for Cu(mim) (Hmim = 2-methylimidazole) from solvothermal reactions of copper(II) salts, aqueous ammonia and mim, whereas the presence of particular organic templates induced the formation of the targeted $[Cu_n(mim)_n]$ (*n* = 8 or 10) polygons.[12] A basically planar octagon $[Cu_8(mim)_8]$ (**3**) can be obtained by using small templates such as benzene, cyclohexane or toluene (Fig. 3). Large guest xylene or naphthalene induces the formation of a slightly undulated decagon $[Cu_{10}(mim)_{10}]$ (**4**) (Fig. 4), which is the highest-membered, uniform metal–organic molecular polygon reported so far. As shown in Fig. 3, the toluene guest is perfectly fitted inside the cavity of octagon in **3**, while the smaller benzene/cyclohexane guest can freely rotate inside the cavity. Although the guest molecules are not coplanar with the decagon in the crystal structure of **4**, the large guest molecules are expected to play a crucial role in the formation
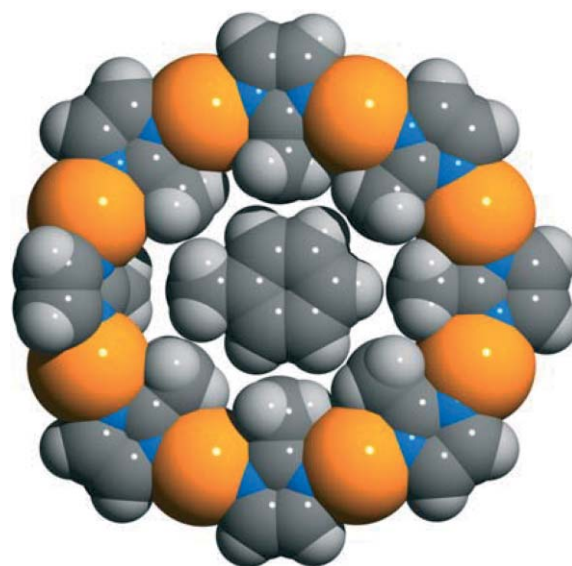
process in solution. In addition, intermolecular cuprophilic interactions (2.78–2.89 Å) are found in **3** and **4**.

When the 2-methyl group is replaced by a more bulky ethyl group, it is unlikely to induce a molecular polygon since the cavity is too small for the guest templates and the mutual repulsion between the adjacent ethyl groups should be very strong for a polygonal structure. Actually, upon variations of the reaction mediates and/or templates, we isolated a zigzag chain (**5a**) and a helical structure (**5b**) as two true supramolecular isomers for the Cu(eim) system (Heim = 2-ethylimidazole).[13] The infinite Cu(eim) chains in **5b** intertwined with each other to generate triple helices with all ethyl groups hidden within the Cu(im) tubular backbone. These triple helices further stack in an anti-parallel manner *via* strong cuprophilic interactions (2.834 and 3.034 Å) to produce a centric structure. It is interesting to note that **5a** was obtained in water–cyclohexane or water–benzene mixtures, while **5b** was obtained
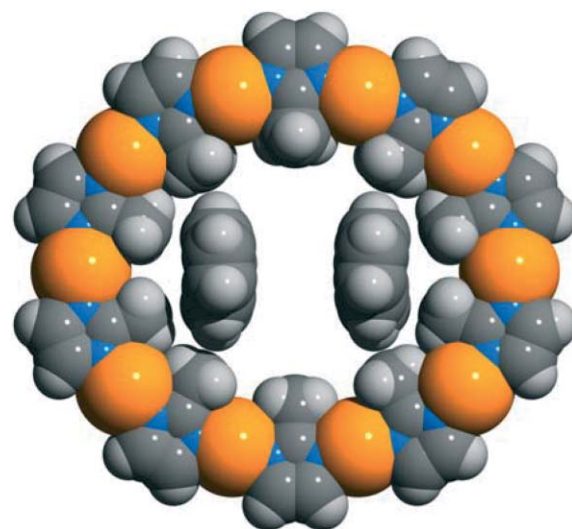

Fig. 4 Space-filling view of $[Cu_{10}(im)_{10}]\cdot$2naphthalene (**4**).

in pure water. This fact suggests that the hydrophobic ethyl group has a self-templating effect to form **5b** in the highly polar medium (Fig. 5), while the aggregation of the ethyl groups is weakened in the less polar media, leading to the simple zigzag chains in **5a**.

The univalent metal imidazolate MOFs did show predicted local coordination geometries and diverse superstructures. The potential supramolecular isomers of these imidazolates may be obtained by varying the reaction conditions, but the most interesting aspect is the fact that small alkyl groups can be rationally introduced to strengthen the supramolecular interactions between the host MOFs and templates or solvents, and synthesize the unusual triple stranded helix and polygons, respectively. These results demonstrate again the importance of supramolecular interactions in crystal engineering of MOF materials.[4]

Bivalent metal imidazolates

The bivalent metal imidazolates should be expected to be four-connected networks with $M^{II}(im)_2$ stoichiometry. By using a bivalent metal centre possessing a tetrahedral coordination geometry, it would be possible to generate neutral zeolite-like MOFs since the bent im bridge is somewhat similar to the oxygen atom in inorganic zeolites (Scheme 1). Therefore, tetrahedral metal ions can expected to use two coordination sites to ligate the im ligands into different possible cyclic rings, which can be further connected *via* the remaining metal coordination sites into 3D MOFs with zeolite topologies (Scheme 2).

The first structurally characterized bivalent metal imidazolate, $Cu(im)_2$ (**6**), possesses a dense PtS network structure.[14] Three new supramolecular isomers of **6** were later synthesized as polycrystals by Masciocchi *et al.*, which have a 3D sodalite (SOD), a 3D moganite, and a 2D four-connected net topologies, respectively.[15] As depicted in Fig. 6, the unusual 2D four-connected topology can be described as two honeycomb networks connected by additional tetrahedral nodes. $Cu(im)_2$ is a rare example of true supramolecular isomerism within 3D four-connected networks, as there is no guest molecule is incorporated in any one of these isomers. The rich MOF topologies of $Cu(im)_2$ should be attributed to the 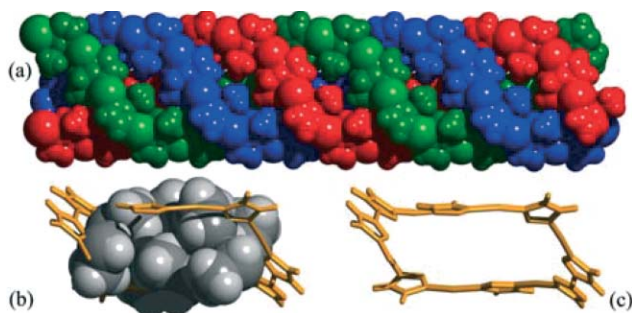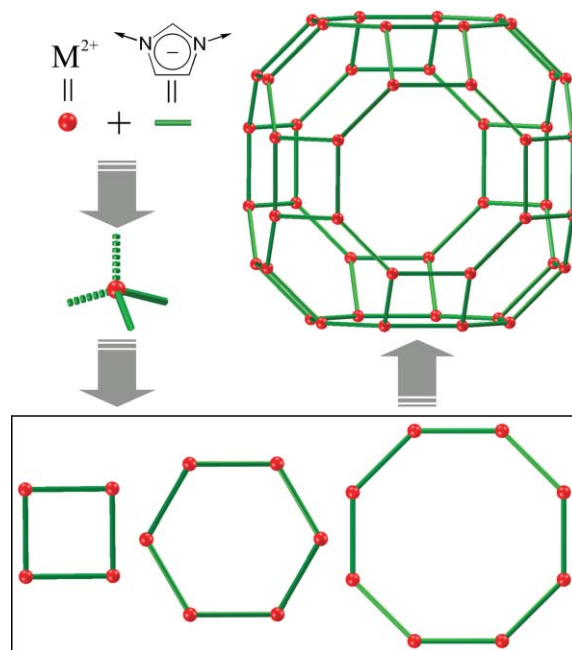various coordination environments (flattened tetrahedral and distorted square-planar) of Cu(II) ions. In contrast, only a simple 2D (4,4) network topology is known for $Ni(im)_2$.[16] It should also be noted that, structurally uncharacterized polycrystalline or amorphous samples of $Cu(im)_2$ and $Ni(im)_2$ were also prepared by Masciocchi *et al.*, implying the existence of other possible supramolecular isomers for these systems.[15,16]

PXRD has been demonstrated as an important tool for studying the polymorphic $Cu(im)_2$ structures, this method requires monophasic samples, which usually remains as a difficult challenge in polymorphic systems,[6] and has limitation for complicated structures, especially those containing guest molecules.
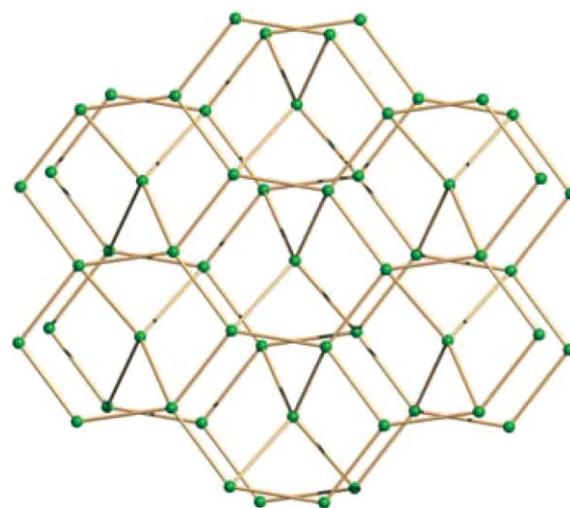

Scheme 2 Schematic presentation for the construction of zeolite-like MOFs with curved bidentate imidazolate ligands and tetrahedral metal ions.

Fig. 5 (a) Side view of the Cu(eim) triple helices in space filling mode, (b) top view of the Cu(eim) triple helices (ethyl groups are highlighted in space filling mode), and (c) top view of the Cu(im) triple helix backbone (ethyl groups are omitted for comparison) in **5b**.

Fig. 6 Topologic illustration of the 2D phase of $Cu(im)_2$ (**6**).

By virtue of guest inclusion, cobalt bisimidazolate $Co(im)_2$ MOFs are more structurally diverse. A dense, 3D tetranodal four-connected network structure of $Co(im)_2$ was reported in 1975.[17] Recently, You et al. have extended the $Co(im)_2$ MOFs to a 3D pentanodal four-connected net, a diamond and lonsdaleite related (6,4) net (Fig. 7), a banalsite net, a CrB_4 net, and a $CaGa_2O_4$ net, using different structural directing and/or templating agents.[18] The potential thermal stability and porosity, as well as magnetic properties of these $Co(im)_2$·guest supramolecular isomers were also found to be structurally dependent.

Many bivalent metal imidazolate MOFs incorporating paramagnetic transition metal ions have also been studied since azolate ligands transmit antiferromagnetic interactions between paramagnetic transition metal ions. Only a few of these compounds have been structurally characterized. Known examples include the CrB_4 network of $Fe(mim)_2$ and diamond-oid networks of isomorphic $Co(pim)_2$ and $Fe(pim)_2$ (Hpim = 4-azabenziimidazole).[19]

Most of the known group 12 metal bisimidazolates are nonporous. Isomorphous $Cd(im)_2$ and $Hg(im)_2$ are composed of two-fold interpenetrating diamond nets.[20] It was suggested that $Zn(im)_2$ can not be in this form since the diamondoid $Zn(im)_2$ network should be too small for accommodation of two-fold interpenetration.[6,20] Meanwhile, a single diamondoid $Zn(im)_2$ MOF was hitherto uncovered. Beside the long-known dense lonsdeite structure for $Zn(im)_2$,[21] $Zn(im)_2$·$0.25H_2O$ was
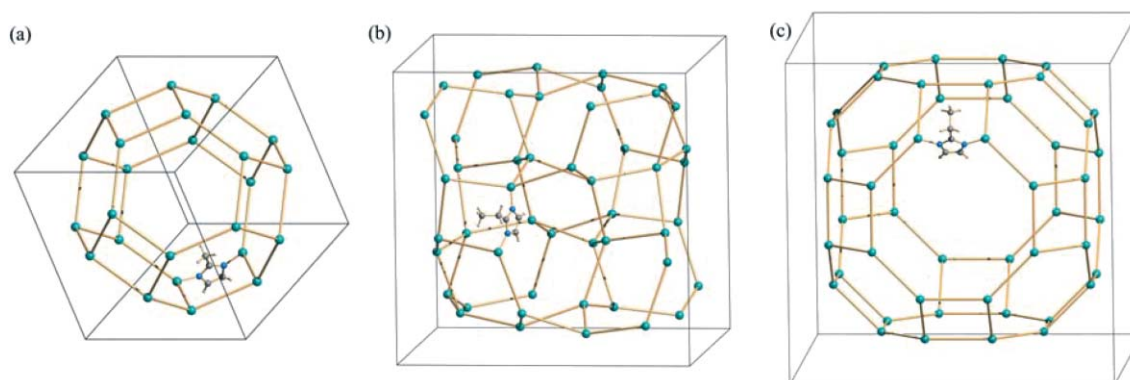
recently isolated and found to have very small cavities, which is isostructural with the dense phase of $Co(im)_2$.[18]

To avoid forming a dense MOF topology, different simple imidazole derivatives of bulky substituents have been used to modify the MOF structures. $Zn(bim)_2$·$5/3H_2O$ (7) (Hbim = benzoimidazole) was synthesized by liquid diffusion using aqueous ammonia as a coordination buffering agent, in which the MOF adopts a distorted SOD topology and has only ca. 18% guest accessible volume due to the network distortion and the presence of bulky benzyl group.[22] More interestingly, $Zn(mim)_2$·$3H_2O$ (8) and $Zn(eim)_2$·H_2O (9) can be also obtained using 2-alkylimidazolates.[23] The MOF of 8 features a regular SOD topology (Fig. 8(a)). There is ca. 47% guest accessible volume composed of spherical cavities (d = 12.5 Å) crosslinked by 3D intersected channels with effective van der Waals window opening diameters of ca. 3.3 Å. The MOF of 9 features a novel ANA (analcime) zeolite topology (Fig. 8(b)) in MOFs. Although the calculated guest accessible volume is comparable to that of 8, the 3D intersecting channels of 9 are very different to those of 8. Owing to the long ethyl groups, the diameter of the channels in 9 is diminished to ca. 2.2 Å. The guest-free MOFs of $Zn(mim)_2$ and $Zn(eim)_2$ are both stable up to 400 °C. Nitrogen adsorption experiments at 77 K revealed a BET surface of 1029 m^2 g^{-1} and N_2 sorption ability of 385 cm^3 g^{-1} for the MOF of 8, which are comparable to the most open zeolites. In contrast, 9 only exhibited the surface adsorption at 77 K due to its small window openings.

It is also worthy of note that a mixed-ligand MOF $Zn(eim/mim)_2$·H_2O (10) was isolated as a minor product upon attempting to replace part of the eim ligands of 9 by mim. The unprecedented MOF of 10 consists of octagonal prism-linked truncated cuboctahedral supercages, a typical feature of the rare RHO zeolite topology (Fig. 8(c)). The remarkable guest accessible volume, diameters of the supercages and the window openings of 10 are 57%, 18.1 Å and 7.4 Å, respectively.

Similar to inorganic zeolites, remarkable four-connected bivalent metal imidazolates, such as $Cu(im)_2$ and $Co(im)_2$, have been produced by variation of the reaction conditions and/or templating agents. Equivalently important, the successful syntheses of porous zinc imidazolates 8–10 with high symmetrical zeolite topologies suggest that introduction of small substituents to the imidazolate ligands is a powerful

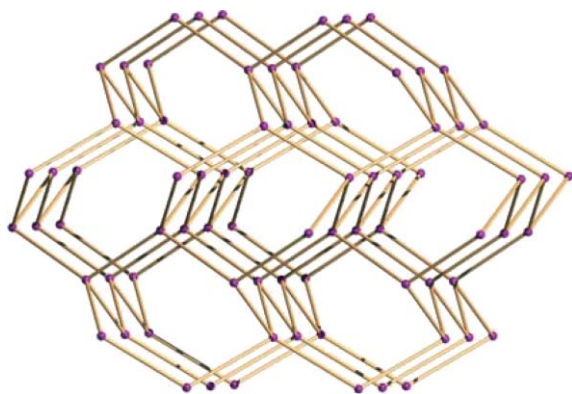**Fig. 7** The diamond-net related (6,4) topology of a $Co(im)_2$ supramolecular isomer.

Fig. 8 Topologic illustrations of the $Zn(mim)_2$ (7) (a), $Zn(eim)_2$ (8) (b) and $Zn(eim/mim)_2$ (9) (c) MOFs with their cubic crystal cells.

strategy for creating new zeolite-like topologies and porous materials. Moreover, these two strategies are compatible and may be combined for further studies.
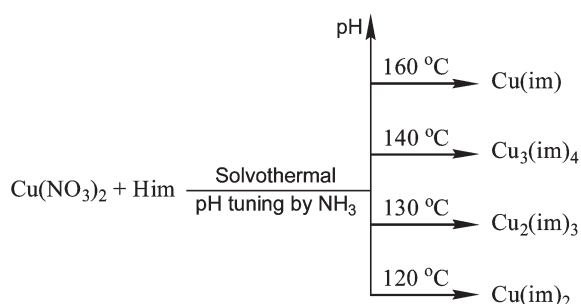
Mixed-valence metal imidazolates

In the known crystal structures of Cu(I) imidazolates, Cu(I) ions were all generated *in situ* by solvothermal reduction of Cu(II) ions (typically at 140–160 °C). On the other hand, we can also prepare single crystals of the SOD isomer of Cu(im)$_2$[15] by a similar method at a relatively low reaction temperature (120 °C).[24] As the reduction of Cu(II) is sensitive to the reaction temperature and pH, a metal-valence tuning approach is used to control the topological structures of copper(I,II) imidazolates (Scheme 3). In fact, the reactions of Cu(II) salts, imidazole and aqueous ammonia at 130–140 °C with specific stoichiometries generated two mixed-valence copper(I,II) imidazolate MOFs Cu^{I}Cu^{II}(im)$_3$ (**11**) and Cu$^I_2$Cu^{II}(im)$_4$ (**12**),[24] in which the Cu(I) and Cu(II) ions in are two- and four-coordinated, respectively. Regarding the Cu(II) ions as four-connected nodes, im and im–Cu^I–im as linkers, the topologies can be rationalized to be a self-interpenetrated uninodal four-connected net and a simple (4,4) net, respectively (Fig. 9).

The coordination environments of Cu(II) ions are usually distorted by network restriction in the 3D MOFs, while the Cu(II) ion in the 2D network of **12** features a typical square-planar geometry. These square-planar coordinated Cu(II) ions can be replaced by tetrahedrally coordinated metal ions such as Co(II) ions, giving rise to an isostructural Cu$^I_2$Co^{II}(im)$_4$ (**13**).[25] The linearly coordinated Cu(I) ions in **12** can also be replaced by Ag(I) ions. Since the inter-layer Cu^I⋯Cu^I separations in **12** and **13** are relatively long but still possibly acceptable as cuprophilic interactions, a complete set of isostructural M$^I_2$M^{II}(im)$_4$ (M^I = Cu^I or Ag^I, M^{II} = Zn^{II} or Cd^{II}) were also synthesized.[26] The Ag⋯Ag separations are shorter than the Cu⋯Cu ones in the M$^I_2$M^{II}(im)$_4$ compounds, suggesting that the metallophilic interaction is inhibited by inter-layer ligand repulsion, and argentophilic interaction is stronger than cuprophilic interaction.

Univalent metal triazolates

The three-connected nets are the simplest network topologies. Many three-connected nets have been theoretically predicted or evaluated from inorganic compounds,[27] but many of them have not been observed in MOFs. While all nitrogen donors
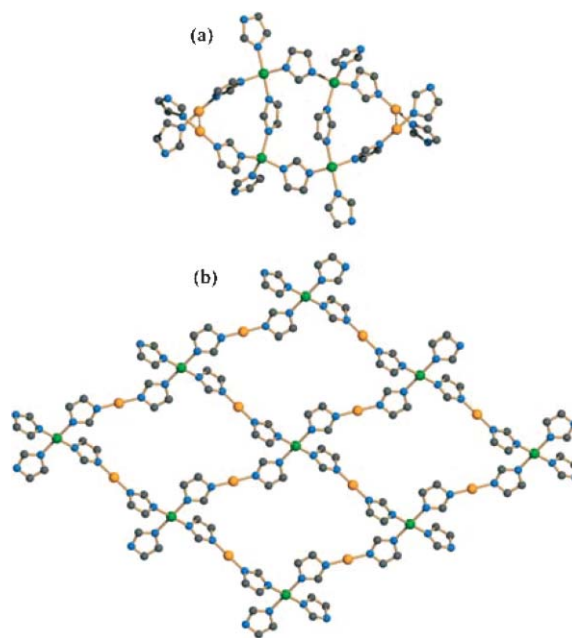

Fig. 9 Structures of Cu$_2$(im)$_3$ (**11**) (a) and Cu$_3$(im)$_4$ (**12**) (b).

involved in coordination, both the univalent metal centres and ligands of metal triazolates (Scheme 1) can serve as three-connected nodes, and we may construct unusual three-connected nets, as the triazolate three-connected node deviates from the ideal trigonal geometry.

As the first binary metal triazolate, Cu(mtz) (**14**; Hmtz = 3,5-dimethyl-1,2,4-triazole)[28] was discovered accidentally from a solvothermal reaction of 1,10-phenanthroline and copper(II) nitrate in a mixture of aqueous ammonia and acetonitrile.[29] Further experiments revealed that only Cu(II) ion, ammonia and acetonitrile was necessary for the generation of **14**. When acetonitrile was replaced by butyronitrile, Cu(ptz) (**15**; Hptz = 3,5-dipropyl-1,2,4-triazole) was obtained. Therefore, the 3,5-disubstituted 1,2,4-triazolate ligands should be generated from an oxidative cycloaddition between nitrile and ammonia molecules, in which Cu(II) serves as an oxidant and is converted to Cu(I) in the final products. In fact, other disubstituted triazolate ligands can also be prepared by the *in situ* solvothermal reaction, suggesting this *in situ* ligand reaction as a novel non-hydrazine-based synthetic route to these important heterocycles. By controlling the solvothermal reaction, a key intermediate of the reaction was isolated as a Cu(II) complex Cu(4-pytap)$_2$ (4-Hpytap = 2,4-di(4-pyridyl)-1,3,5-triazapentadiene) (Scheme 4). This intermediate could be further converted to the final triazolate ligand in the presence of Cu(II) ions at a higher temperature.[30]

The Cu(I) ions and triazolate ligands in **14** and **15** are all three-coordinated and both compounds have very similar dimeric Cu$_2$(tz)$_2$ units. The three-coordinated metal and ligand centres define a two-fold interpenetrated 4.8.10 net and a non-interpenetrated 4.12^2 net for **14** (Fig. 10) and **15** (Fig. 11), respectively. The three-connected 4.8.10 and 4.12^2 nets can be further simplified to be four-connected lvt (4^{2}8^4) and NbO (6^{4}8^2) nets when the dimeric Cu$_2$(tz)$_2$ units are regarded as four-connected nodes. These two 3D four-connected nets,

Scheme 3 Temperature- and pH-controlled reduction of Cu(II) ions.
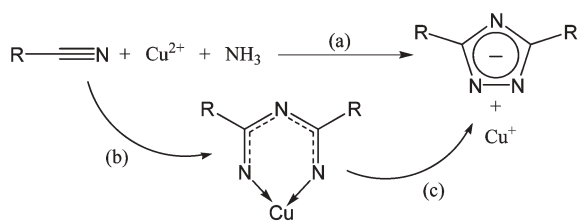
Scheme 4 Direct synthesis of copper(I) triazolates from organonitriles, ammonia and copper(II) salts (a), synthesis of the reaction intermediate at low temperature (b), and conversion of the intermediate to the final triazolate at higher temperature (c).

solely based on square-planar nodes, are very unusual in the MOFs since self-assembly of square-planar building blocks tends to form 2D (4,4) nets. The lvt (4.8.10) and NbO (4.12^2) copper(I) triazolate MOFs are highly porous, but the hollow spacings are filled by two-fold interpenetration and large, disordered propyl groups in **14** and **15**, respectively.[28]

The (4,4), lvt and NbO nets are all constructed solely by square-planar nodes, but the dihedral angles between adjacent nodes are different (Scheme 5). The formation of lvt and NbO network structures in **14** and **15** should be attributed to the steric repulsion of the alkyl groups. If the alkyl groups were replaced by hydrogen atoms, the (4,4) net, or corresponding 4.8^2 net would be obtained. We can also predict a porous structure for the ethyl-substituted triazolate. The ethyl groups would prevent interpenetration of the lvt net, but could not occupy all the space of the NbO net. On the other hand, there should be no related four-connected net for very bulky substituents such as the phenyl group, as the NbO copper(I) triazolate MOF is the most porous structure of these nets. Actually, Cu(phtz) (Hphtz = 3,5-diphenyl-1,2,4-triazole) was structurally characterized to be a 1D chain comprising pentanuclear clusters, in which only some of the triazolate ligands are three-coordinated.[30]
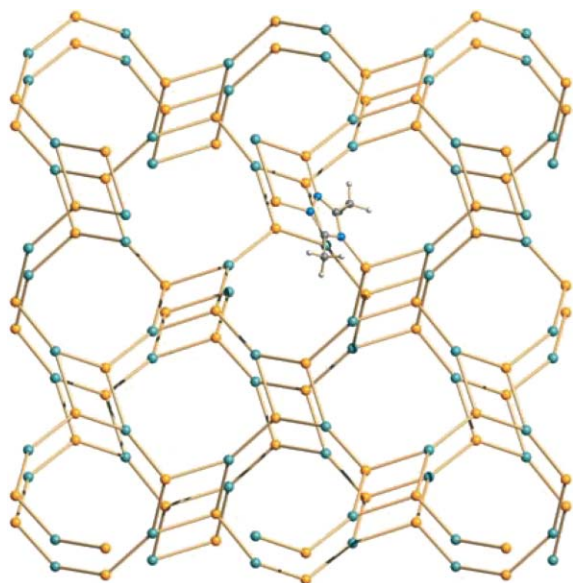

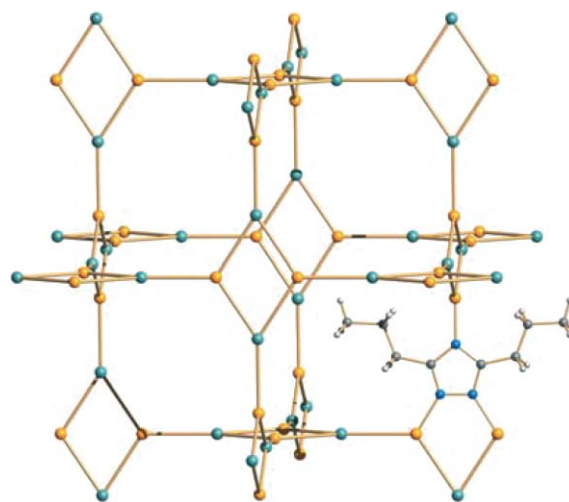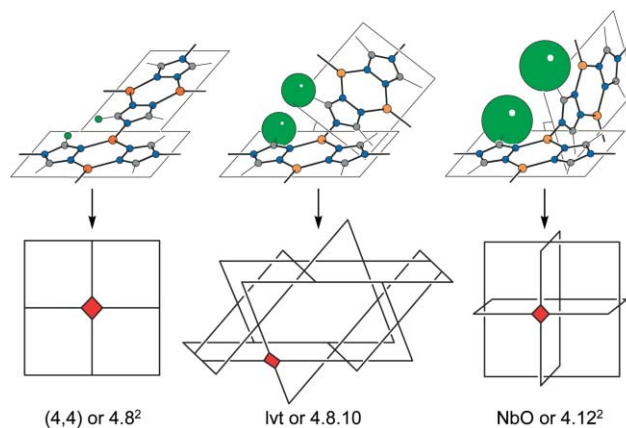Fig. 10 Topologic illustration of a single Cu(mtz) MOF in **14**.

Fig. 11 Topologic illustration of the Cu(ptz) MOF in **15**.

Scheme 5 Relationship of the dihedral angles and the substituents in Cu(tz) featuring Cu$_2$(tz)$_2$ building blocks with only different substituents (orange, Cu; blue, N; gray, C; only a pair of substituents are highlighted in green for clarity; red squares indicate the augmentation of three-connected nets from corresponding four-connected nets).

As expected, the MOF of Cu(etz)·H$_2$O (**16**; Hetz = 3,5-diethyl-1,2,4-triazole) is isoreticular to **15**,[30] having spherical cavities (d = ca. 9 Å) and a guest accessible volume ca. 35% (Fig. 12).

The non-substituted triazolate Cu(tz) (**17**)[30] was prepared by a 'direct' reaction using Cu(II) salt and triazole under similar conditions for the synthesis of the copper(I) imidazolates. **17** possesses the predicted planar (4,4) or 4.8^2 network structure (Fig. 13) having weak inter-layer Cu···Cu interactions. Similarly to **12** and **13**, Ag(tz) is isostructural to **17** and features shorter inter-layer metal···metal interactions and interesting photoluminescence properties.[30] Therefore, by making use of the similarity in the coordination mode of Ag(I) and Cu(I), crystal engineers may tune the physical/chemical properties of a particular imidazolate or triazolate architecture by simply replacing Cu(I) with Ag(I), or vice versa.

The structural prediction of these copper(I) triazolates is based on the formation of stable planar dimeric SBUs. Theoretically, other structural motifs should also be possible
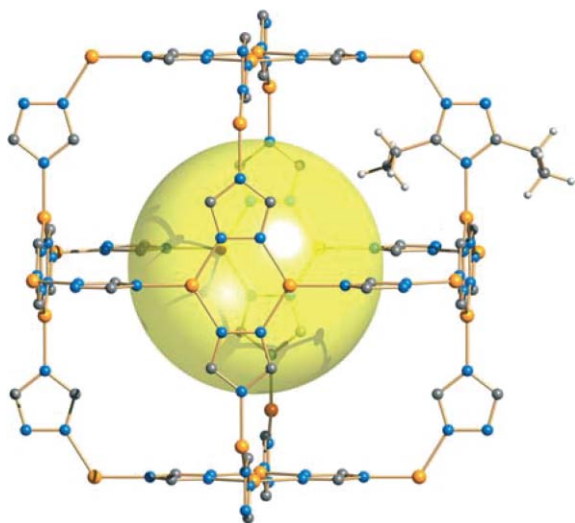
Fig. 12 Topologic illustration of the Cu(etz) MOF (**16**) (inner cavity are highlighted as a semitransparent yellow sphere, only a pair of ethyl groups are shown).
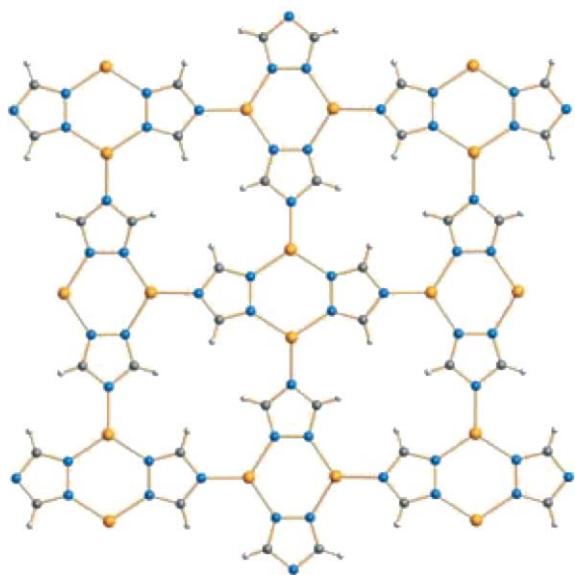

Fig. 13 2D 4.8^2 or (4,4) structure of Cu(tz) (**17**).

for copper(I) triazolates. The neutral compositions and strong coordination bonds of metal azolates imply that anions and/or some competing ligands may be used as buffering additives for the generation of different supramolecular isomers of slightly different local coordination geometries. This "buffering additive" strategy successfully led to the syntheses of two true supramolecular isomers of **14**, namely **14b** and **14c**, using 4,4'-bipyridine and nitrate as the additives, respectively.[31] **14b** and **14c** (containing no buffering additive in the structures) are both 3D three-connected structures, their topologies are uninodal $8^2 10$-a (Fig. 14(a)) and a new binodal 6.10^2 net (Fig. 14(b)), respectively. These isomers also displayed superstructure-related photoluminescence properties.[31] It deserves to note that true supramolecular isomers of 3D MOFs such as **6** or **14** are extremely rare since different 3D structures,

especially the three-connected ones, are usually highly porous and accompany with guest molecules.

When cyanopyridines were used to replace the alkyl nitriles, three pyridyl-substituted triazolate ligands 2-pytz, 3-pytz and 4-pytz (Hpytz = 3,5-dipyridyl-1,2,4-triazole) can be generated. The crystal engineering of binary metal complexes of these three ligands is rather different. It is difficult to fully ultilize all five nitrogen donors of these ligands since univalent metal ions such as Cu(I) usually have coordination numbers of two, three or four. Therefore, prediction of the superstructures or the local coordination environments of these systems seems to be very difficult. Indeed, several supramolecular isomers with unexpected structural features can be isolated for the Cu(4-pytz) system *via* the above-mentioned buffering additive strategy,[32] but no crystal of Cu(3-pytz) has been isolated so far.

However, the 2-pytz is quite different from 3-pytz and 4-pytz, since it contains bidentate chelating sites. We could readily predict two possible bis-bidentate chelating coordination modes for 2-pytz and four-coordinated Cu(I) centres in a Cu(2-pytz) (**18**) system as the tridentate mode is unlikely to be possible for Cu(I) (Scheme 6). Therefore, the Cu(2-pytz)
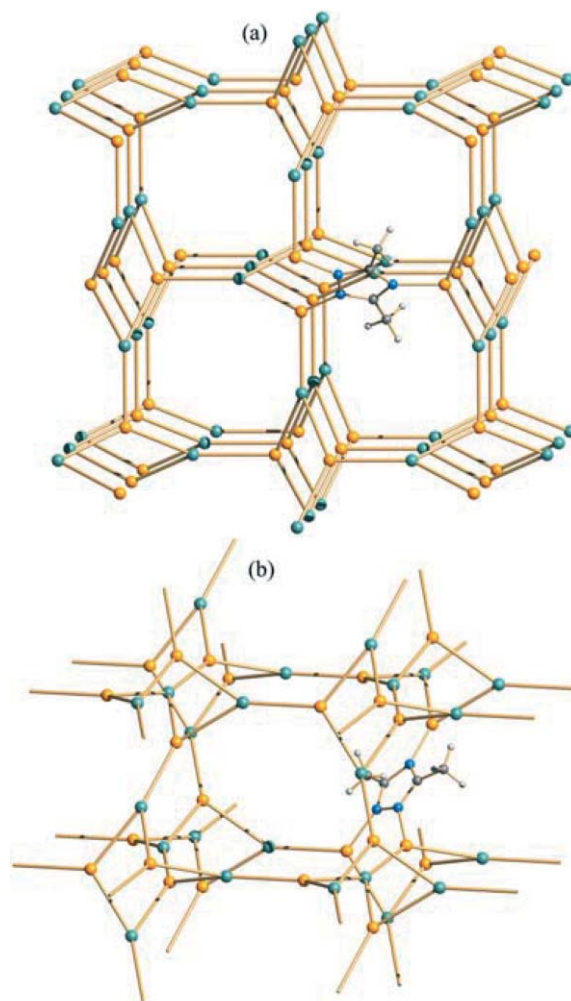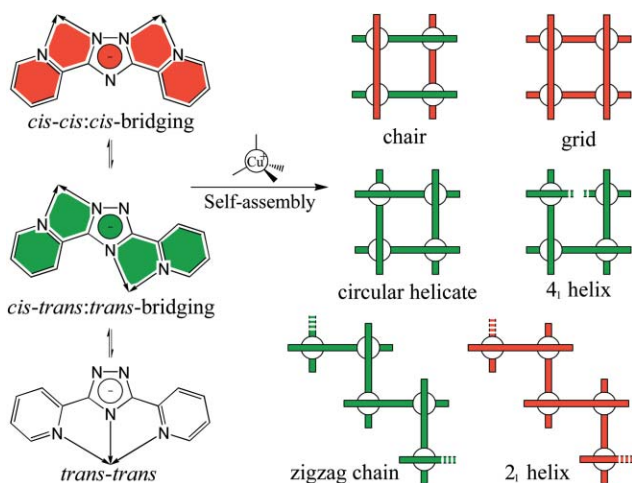

Fig. 14 Topologic illustrations of β-Cu(mtz) (**14b**) (a) and γ-Cu(mtz) (**14c**) (b).

Scheme 6 Some possible structures of Cu(2-pytz).

system may be used to synthesize a series of supramolecular isomers including 0D polygons, 1D zigzag chains, and 1D helical chains. Upon variation of the solvothermal conditions *via* the buffering additive strategy, a chair-like tetranuclear metallomacrocycle, a zigzag chain, a homochiral 4_1 helix, and an unexpected zipper-like double chain compound were isolated for **18** (Fig. 15).[33] The four isomers of **18** do possess the predicted local coordination modes and identical chemical compositions. Apart from the predictable local coordination geometries, the weak capability for hydrogen bonding to the MOF, the packing ability of the 2-pytz ligand, as well as the autogeneous high pressure of the solvothermal conditions are also crucial for the control of chemical composition.

Other metal triazolates

If all three nitrogen donors are coordinated in the binary divalent metal triazolates, more complex MOFs with mixed three- and six-connected nodes should be expected. However, crystal structures of binary divalent metal 1,2,4-triazolates remain unknown to date, only a magnetically active polymeric $Cu(tz)_2$ was obtained in a powder form.[19]

Ionic MOFs of binary metal imidazolate or triazolate are scarce compared with the neutral ones, as the neutral ones may be more energetically stable and crystallize at a faster speed. Two cationic binary metal triazolate MOFs, namely $[Ag_4(phtz)_3]^+$ (**19**)[34] and $[Ag_3(atz)_2]^+$ (**20**, Hatz = 3-amino-1,2,4-triazole)[35] have been reported recently. The 3D MOF of **19** was stable upon guest removal and showed both non-polar solvent adsorption and anion exchange properties.[34] The overall host framework of **20** comprises of closely interlocked five-fold interpenetrated $Ag_3(atz)_2$ networks, which are three-connected 4.14^2 or (dia-f) nets defined by the two-coordinated Ag(I) ions as linkers and three-coordinated atz ligands as nodes. Despite the five-fold interpenetration and the amino groups, **20** still contains large 1D columned channels with diameters of *ca.* 8.5 Å. **20** can reversibly transform between a tetragonal (at room temperature) and an orthorhombic (at 103 K) phases in a single-crystal-to-single-crystal fashion. More unusually, the five-fold interpenetrating $Ag_3(atz)_2$ host
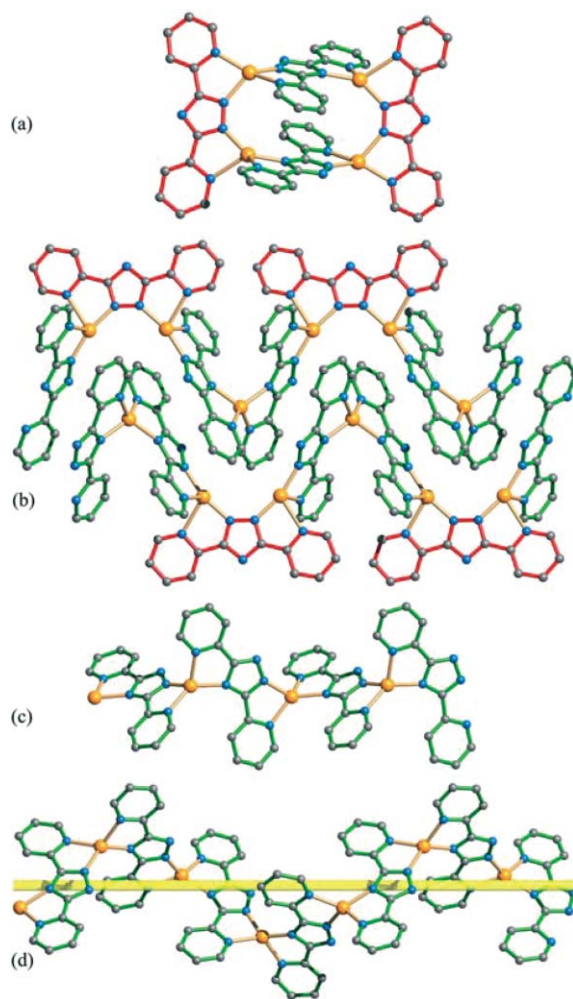

Fig. 15 Structures of Cu(2-pytz) isomers (**18**): (a) chair, (b) zipper, (c) zigzag and (d) helical chain (*cis*- and *trans*-bridged 2-pytz ligands are drawn in red and green, respectively).

MOF can reversibly rearrange into a six-fold interpenetrating network *via* guest removal/absorption in a single-crystal-to-single-crystal transformation fashion (Fig. 16).[35]

Summary and prospective

Similar to that in other systems, solvothermal and liquid diffusion methods are powerful for the crystal growth of these highly insoluble materials, and templating method is also very useful for crystal engineering of some porous MOFs and molecular polygons of binary metal imidazolates and triazolates.[12,18]

Meanwhile, the rapid expansion in the crystal engineering of binary metal imidazolate and triazolate MOFs is also facilitated by effective crystal engineering strategies. Among them, solvothermal *in situ* metal/ligand reaction is a powerful strategy for the crystal growth of Cu(I)/Cu(I,II) imidazolate and triazolate MOFs, in which Cu(I) ions can be generated from the reduction of Cu(II) ions by organic ligands under solvothermal conditions, and the Cu(II) to Cu(I) reduction degree/speed is readily controlled by simply varying the reaction conditions such as the temperature and/or pH value.[24]
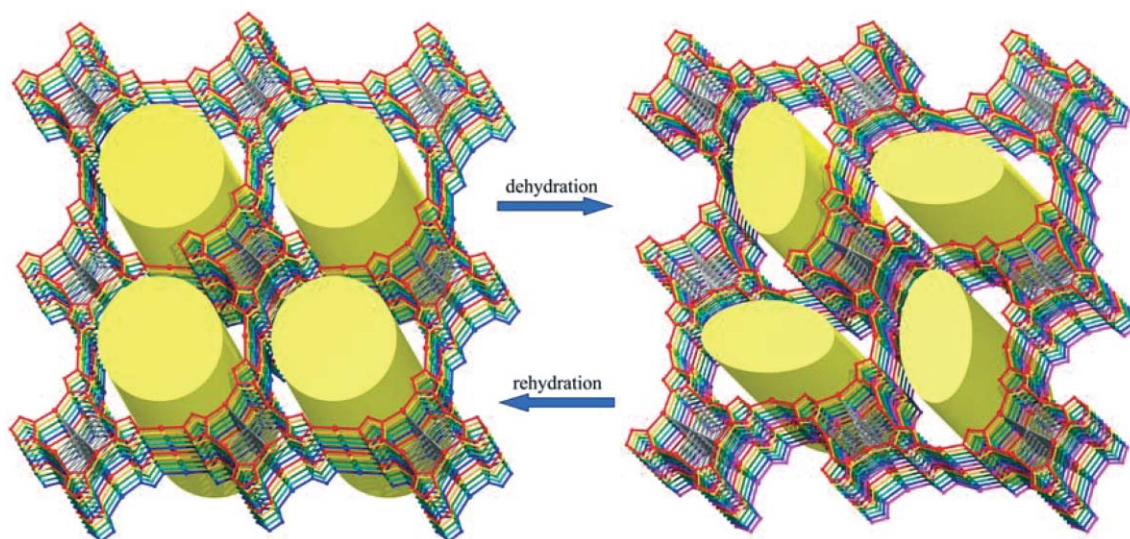
Fig. 16 Guest removal/adsorption induced single-crystal-to-single-crystal topological rearrangement of **20**.

The coordinatively unimportant alkyl groups of the imidazolate and triazolate ligands can also be rationally utilized to alter the MOF structures, implying that other related materials may be designed and synthesized by simply modifying the ligands. A buffering additive strategy can be used to fine-tune the local coordination structures for the formation of supramolecular isomers.[31–33]

Indeed, beautiful structural diversity and supramolecular isomerism have been obtained for the binary metal imidazolate and triazolate MOFs based on the above strategies. Moreover, the strategies could possibly be applied in crystal engineering of related MOFs. However, we are still unable to fully interpret the relationship between the reaction conditions and the resulting superstructures, especially for the true supramolecular isomers. These facts reflect the inherent difficulties of crystal engineering of MOFs, but on an optimistic point of view, supramolecular isomerism of these simple binary compounds also provides good opportunities for the study of structure–property relations and the controlled crystallization of individual supramolecular isomers.

To conclude, based on the established crystal engineering strategies, known structures and possible properties of the known binary metal imidazolate and triazolate MOFs, we can expect a bright future for crystal engineering of these kinds of simple compounds.

Acknowledgements

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