

# Direction of unusual mixed-ligand metal–organic frameworks: a new type of 3-D polythreading involving 1-D and 2-D structural motifs and a 2-fold interpenetrating porous network†

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The reaction of Cu<sup>II</sup> or Cd<sup>II</sup> acetate with mixed ligands terephthalic (tp) and 3,5-bis(4-pyridyl)-4-amino-1,2,4-triazole (bpt) under the same conditions affords two unusual metal–organic frameworks, in which **1** represents a new type of polythreaded supramolecular architecture consisting of distinct 1-D and 2-D coordination polymers within one crystal, however, **2** has an interpenetrating porous network with two similar laterally interlocking 2-D (4,4) layers.

Interest in assemblies of infinite metal–organic frameworks (MOFs) or coordination polymers has been rapidly expanded due to their intriguing supramolecular architectures and also potential applications as new functional solid materials.<sup>1</sup> So far, a variety of remarkable entangled systems of MOFs have been documented, which include polycatenane or polyrotaxane species, interweaved arrays of polymeric chains or helices, polythreaded networks and interlocking topologies of the same or different motifs and/or dimensionality.<sup>2</sup> It has been realized that metal ions coordinated by longer organic bridging spacers are relied upon to produce open MOFs possessing relatively larger voids, associated with a network occupied by one or more other independent nets, thus generating interpenetrating or entangled topologies. In this regard, the inherently rigid ditopic spacers, for instance, terephthalic acid (tp) and those containing *N*-heterocyclic groups, such as 4,4'-bipyridine (bipy) are most widely employed.<sup>1–3</sup> On the other aspect, there exist rare examples of MOFs involving two or more diverse coordination polymers that occur in the same crystal, affording unusual packing lattice such as interlocking, pseudo-polyrotaxane and others.<sup>4,5</sup>

Recently, we have initially explored the construction of novel MOFs of oxadiazole-containing bent dipyrindyl connectors.<sup>6</sup> During our continuous focus on this project, we extend this series of linkers to triazole-containing dipyrindyl compounds such as bis(4-pyridyl)-4-amino-1,2,4-triazole (bpt), which has a more bent backbone.<sup>7</sup> In this context, our synthetic strategy is to fabricate new topological frameworks by assembly of mixed ligands bpt and tp, with different metal ions, and we will describe herein the preparation, crystal/topology structures and properties of two new related MOFs  $\{[\text{Cu}(\text{tp})(\text{bpt})(\text{H}_2\text{O})_2][\text{Cu}(\text{bpt})_2(\text{tp})](\text{H}_2\text{O})_2\}_n$  (**1**) and  $\{[\text{Cd}(\text{tp})(\text{bpt})(\text{H}_2\text{O})_2](\text{DMF})_{1.5}(\text{H}_2\text{O})\}_n$  (**2**).

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† Electronic supplementary information (ESI) available: Additional experimental details, PXRD patterns, a figure of **1** and a table including the hydrogen-bonding parameters. See DOI: 10.1039/b509875k

Complexes **1** and **2** were obtained as blue or colorless crystalline materials by the reaction of bpt and tp with Cu<sup>II</sup> or Cd<sup>II</sup> acetate in ethanol/DMF/water medium in a molar ratio of 1 : 1 : 1.‡ The compositions were confirmed by elemental analysis and IR spectra, and the phase purities of the bulk samples were identified by powder X-ray diffraction (PXRD, see ESI).† It is noteworthy that the significant difference between **1** and **2** isolated under the same conditions must be ascribed to the nature of the metal centers.

Singe crystal X-ray diffraction study§ reveals that **1** is composed of two crystallographically independent and distinct polymeric motifs (see Fig. 1) and lattice water. One of the motifs with the composition of  $[\text{Cu}(\text{bpt})_2(\text{tp})]$  is an infinite tp-bridged 1-D array which is decorated by the terminal bpt ligands acting as 'side arms'. The Cu1 center lies on an inversion centre [at (0.5, 0.5, 0)] and displays a square-planar geometry, consisting of two carboxylate oxygens from a pair of tp dianions and two pyridyl nitrogens of the monodentate bpt ligands. The tp ligand binding to Cu1 also lies about another inversion centre [at (0, 0.5, 0)]. The combined effect of these two inversion operations is to generate a chain along [100]. The second motif  $[\text{Cu}(\text{bpt})(\text{tp})]$  consists of a planar 2-D (4,4) net, generated by a combination of *a*-axis translations (the 10.839(1) Å dimension) and *c*-glide operations [to give the 14.442(2) Å dimension of the almost rectangular grid]. The angles of the  $[\text{Cu}_4(\text{tp})_2(\text{bpt})_2]$  'rectangle' are 80.99(1) and 99.01(1)°. The unique Cu2 atom lies in a general position in the unit cell and has a slightly distorted square-pyramidal environment ( $\tau = 0.017$ ), with four equatorially bonded groups of two carboxylate and two pyridyl groups, as well as an axial aqua ligand.

As far as we know, it is quite rare to observe distinct coordination polymers,<sup>4,5</sup> especially with different dimensionality, within the same crystal, and in the limited examples of such MOFs,<sup>4a,Ac,Ad,4f,5d</sup> the different polymeric patterns in one crystal always align in the interpenetrating fashion as previously found in ref. 4a. So that a very fascinating structural feature of **1** is that

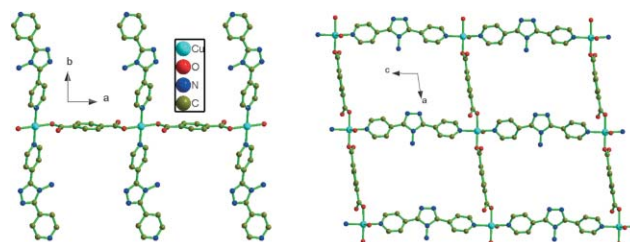
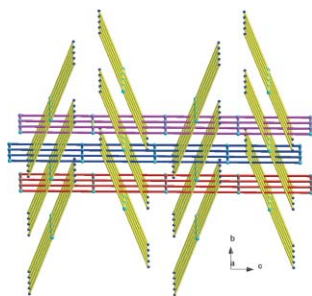


Fig. 1 Illustrations for the two coordination polymers observed in the crystal of **1**: left: 1-D polymeric chain; right: 2-D (4,4) sheet.

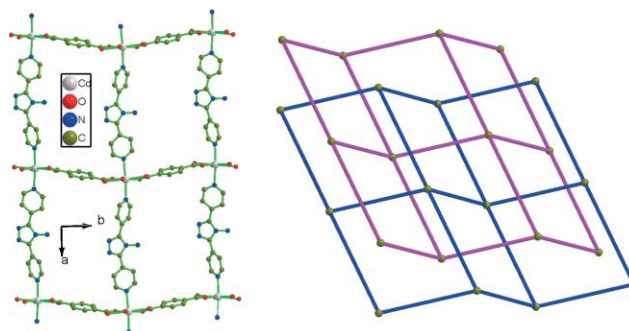


**Fig. 2** A schematic representation of **1** shows the interdigitated polythreading of the 1-D chains (yellow) and 2-D layers (purple, blue and red). The tp and bpt linkers are simplified only as the rods for clarity.

there are two individual coordination frameworks, 1-D polymeric chains and 2-D layers in the lattice. Also of further importance, analysis of the crystal packing of **1** reveals that it represents an unprecedented entanglement for such two motifs, that is, the side arms of the 1-D patterns intercalate the grids of the 2-D sheets in an inclined manner and adopt opposite directions alternately along [001] (Fig. 2). Clearly, the side arms of each 1-D array are involved in four adjacent 2-D motifs, and this fascinating supramolecular system could be considered as a new 3-D polythreaded architecture.<sup>2c</sup> Notably, polythreading with finite components is really unusual<sup>2c</sup> and the few known species include polythreaded 0-D rings with side arms that give 1-D<sup>8a</sup> or 2-D<sup>8b</sup> arrays, as well as molecular ladders with dangling arms, resulting in (1D → 2D)<sup>8c</sup> or (1D → 3D)<sup>8d</sup> polythreaded arrays. Very recently, one unique example of (2D → 3D) polythreaded network assembled from 2-D motifs has been reported.<sup>8e</sup> Remarkably, complex **1** represents the first 1-D + 2-D → 3-D polythreaded system with finite components. Additionally, though bpt is structurally similar to bipy,<sup>9</sup> its structural topology is greatly different: only 2-D double-layered motifs exist in the lattice, and each interpenetrates to another to give a 3-D net.

Additional investigation for this structure indicates that the 2-D sheets stack in an anti-parallel mode with slightly offset along [010]. Interlayer O–H...O hydrogen bonds can be detected between the carboxylate oxygens and aqua ligands, resulting in a 3-D supramolecular array together with weak C–H...O interactions, in which the large channels (Fig. S3) are accommodated by the side arms of the 1-D chains and aqua solvents. Furthermore, hydrogen-bonds also exist between two different motifs in **1**, involving the amido of bpt and triazole nitrogens/carboxylate oxygens, and between the lattice aqua and water ligand/carboxylates (see Table S1 for details), which further stabilize this framework.†

The Cd<sup>II</sup> MOF **2** with the same mixed-ligands, however, shows an interesting 2-fold interpenetrating network of 2-D sheets. The structure contains two crystallographically independent but similar Cd<sup>II</sup> centers that are in general positions; each one is hepta-coordinated and exhibits a pentagonal-dipyramid geometry, with five oxygen atoms from two chelating carboxylate groups and an aqua donor occupying the basal plane, and two pyridyl nitrogens at the apical sites. The most attractive structural point of **2** is the formation of a 2-fold parallel interpenetration network based on layered (4,4) topology, in which each Cd<sup>II</sup> ion provides the four-connected nodes and tp/bpt act as two-connectors (see Fig. 3 left). The 2-D CdI net is almost rectangular, and generated by a



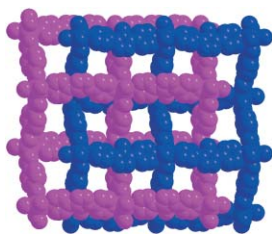
**Fig. 3** Left: the undulated 2-D network bridged by tp and bpt in **2**; right: schematic representation of the parallel interpenetrating (4,4) nets in **2**. The brown spheres represent the Cd centers, the tp and bpt linkers are simplified by showing only as the rods for clarity.

combination of *a*-cell translation [the 15.157(2) Å dimension] and 2-fold screw operation [the 11.173(1) Å dimension]. The angles of the ‘rectangle’ are 84.87(1) and 95.13(1)°. For the ‘rectangle’ involving Cd<sub>2</sub>, it also has a *a*-cell translation and 2-fold screw operations and the corresponding dimensions of the ‘rectangle’ are 15.157(2) and 11.333(1) Å, with angles of 83.73(1) and 96.27(1)°. Dissimilar to the 2-D motif in **1**, a pronounced bend at the two chelating carboxylate groups of tp provides the undulating character of each individual 2-D layer and the undulation of the two layers is out-of-phase, which makes the interpenetration possible. Additionally, the longer spacers tp and bpt lead to the generation of larger void space, which has been greatly exceeded to hold the guest molecules. Thus, the potential voids of the undulated layers are filled *via* mutual lateral catenation of two 2-D nets (Fig. 3 right), which are in *anti*-arrangement. The overall 2-fold layers then stack along [001] as ABABAB sequence.

A closely similar example of double 2-D interpenetrating net with mixed ligands is found in the structure of [Cu(tcm)(bipy)] (tcm = tricyanomethanide),<sup>10</sup> in which the tcm ligands act as bent two-connected units. The 2-D corrugated (4,4) sheet also consists of rectangular meshes with dimensions of 7.651(5) × 11.203(7) Å<sup>2</sup>. Interestingly, rod-like uncoordinated nitrile groups of tcm project like bristles from both sides of the composite paired-up sheets and interdigitate with adjoining composites with the formation of weak C–H...N interactions. As far as [Cd(tp)(4,4'-bipy)],<sup>3a</sup> it is also a 2-fold interpenetrated array, however, assembled from 3-D 6-connected  $\alpha$ -Po nets, which differs from **2**.

Significantly, the interpenetration of two (4,4) sheets leads to the partition of each large grid subunit into two identical halves, even though there are still enough voids left (run along [001], a computation of the voids suggests a value of 1500 Å<sup>3</sup>, corresponding to 28.8% of the unit-cell volume) to accommodate the lattice DMF/H<sub>2</sub>O as guest molecules (see Fig. 4). What is more, the parallel interlocking layers are interconnected *via* rich hydrogen bonds (see Table S1, ESI),† involving coordinated aqua molecules, carboxylate groups, triazole nitrogens, and lattice solvates, which extend the MOFs into a 3-D supramolecular network.

The porous MOF **2** is air stable and can retain the crystalline integrity at ambient conditions. The full occupancy for the guest solvates and thermal stability of **2** were examined by thermogravimetric analysis. All solvates are released from 86 to 280 °C indicated by a weight loss of 11.64% (calculated: 10.70%), and the



**Fig. 4** Space filling view of the interpenetration of two (4,4) layers in **2** showing the voids along *c* direction (the guest solvents located in the voids were omitted for clarity).

host MOF starts to decompose when heating beyond 340 °C. To further investigate the porosity of **2**, a freshly ground sample was placed inside a vacuum oven at 280 °C for 8 h. In the PXRD pattern of the evacuated solid with a weight loss of 11.55%, the main sharp diffraction peaks shift evidently compared with that of the original material (Fig. S4)† due to the release of the guest solvates, which also indicates the maintenance of the periodicity of this framework. Further adsorption study was carried out and confirmed by PXRD technique of the evacuated sample of **2** after soaking in DMF for 24 h. Interestingly, the PXRD pattern of the resultant solid remains essentially identical with that of **2**, which suggests that after this cycle process of desorption/adsorption, the framework integrity of the original solid is retained.

In conclusion, two interesting and distinct MOFs, including an unprecedented polythreaded system **1** consisting of both 1-D and 2-D coordination polymers, and a 2-fold interlocking porous network **2**, have been successfully assembled. Clearly, the different organization of the whole supramolecular arrays of such two MOFs is only controlled by the nature of the metal ions. This work also allows us to check and compare the mixed-ligand coordination polymers based on the linear bpy and the longer bent bpt building blocks, which are also significantly diverse in both framework topologies and properties. We are currently extending this design strategy by using bpt in connection with other carboxylate linkers and metal ions to construct new functional solid materials.

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## Notes and references

† Preparation of  $\{[\text{Cu}(\text{tp})(\text{bpt})(\text{H}_2\text{O})]_2[\text{Cu}(\text{bpt})_2(\text{tp})](\text{H}_2\text{O})_2\}_n$  (**1**). To a warming solution of bpt (25 mg, 0.1 mmol) in ethanol (20 mL) was added an aqueous solution of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (21 mg, 0.1 mmol), followed by slow addition of a DMF solution (10 mL) of tp (16 mg, 0.1 mmol) with vigorous stirring and heating at 80 °C for ca. 30 min. The resulting solution was filtered and allowed to stand at room temperature. Blue block-shaped crystals appeared over a period of 1 week in 75% yield (40 mg). *Anal.* Calcd for  $\text{C}_{72}\text{H}_{60}\text{Cu}_3\text{N}_{24}\text{O}_{16}$  ( $M_r = 1708.06$ ): C, 50.63; H, 3.54; N, 19.68%. Found: C, 50.30; H, 3.47; N, 19.19%. IR (KBr,  $\text{cm}^{-1}$ ): 3467 b, 3291 m, 3145 w, 2375 w, 2318 m, 1589 vs, 1503 w, 1459 m, 1443 m, 1406 s, 1358 w, 1217 m, 1064 m, 1006 m, 840 s, 751 s, 700 m, 596 m, 518 m.

$\{[\text{Cd}(\text{tp})(\text{bpt})(\text{H}_2\text{O})]_2(\text{DMF})_{1.5}(\text{H}_2\text{O})\}_n$  (**2**). The same synthetic method as for **1** was used except that  $\text{Cu}^{\text{II}}$  acetate was replaced by  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , affording colorless block single-crystals in 66% yield. *Anal.* Calcd for  $\text{C}_{44.5}\text{H}_{44.5}\text{Cd}_2\text{N}_{13.5}\text{O}_{12.5}$  ( $M_r = 1193.24$ ): C, 44.79; H, 3.76; N, 15.84%. Found: C, 44.43; H, 3.62; N, 15.31%. IR (KBr,  $\text{cm}^{-1}$ ): 3347 b, 1666 s, 1610 s, 1569 s, 1504 m, 1385 vs, 1224 w, 1096 w, 1067 w, 1013 w, 840 s, 746 s, 702 m, 665 m, 609 m, 516 m.

§ Crystal data for **1**:  $\text{C}_{72}\text{H}_{60}\text{Cu}_3\text{N}_{24}\text{O}_{16}$ , monoclinic,  $P2_1/c$ ,  $a = 10.8387(11)$ ,  $b = 11.6113(12)$ ,  $c = 28.883(3)$  Å,  $\beta = 99.010(2)^\circ$ ,  $V = 3590.1(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 0.969$  mm<sup>-1</sup>,  $S = 1.013$ ,  $R = 0.0393$  and  $wR = 0.0860$ . Crystal data for **2**:  $\text{C}_{44.5}\text{H}_{44.5}\text{Cd}_2\text{N}_{13.5}\text{O}_{12.5}$ , monoclinic,  $P2_1/n$ ,  $a = 15.1571(16)$ ,  $b = 20.483(2)$ ,  $c = 16.9026(19)$  Å,  $\beta = 96.1070(10)^\circ$ ,  $V = 5217.8(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 0.887$  mm<sup>-1</sup>,  $S = 1.069$ ,  $R = 0.0346$  and  $wR = 0.0999$ . X-ray diffraction data were collected on a Bruker Apex II CCD diffractometer at 293(2) K. In the structural refinement of **2**, the site occupation factor of one DMF guest (0.5) was adjusted to give reasonable thermal parameters, and 29 restraints were used for both DMF molecules. CCDC 277592 and 277593. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509875k

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