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## ARTICLE

## Bent Tritopic Carboxylates for Coordination Networks: Clues to the Origin of Self-penetration

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Jin-Xiang Chen,<sup>\*a</sup> Hai-Qing Zhao,<sup>a</sup> Huan-Huan Li,<sup>a</sup> Sheng-Li Huang,<sup>b</sup> Ni-Ni Ding,<sup>b</sup> Wen-Hua Chen,<sup>a</sup> David J. Young,<sup>bd</sup> Wen-Hua Zhang,<sup>\*be</sup> and T. S. Andy Hor<sup>\*bc</sup>

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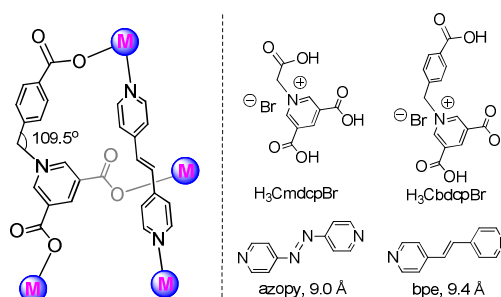
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We suggest in this paper that the combinative use of bent tritopic carboxylate, linear dipyridyl and adaptable Cu<sup>2+</sup> ion engenders higher probability of self-penetrated polymeric networks. This assertion is supported by four structures isolated herein, among which two are self-penetrated, highlighting the potential of controlled assembly of self-penetrating networks.

### Introduction

Interpenetration is common in the synthesis of porous coordination polymers (PCPs)/metal-organic frameworks (MOFs).<sup>1</sup> Interpenetration, wherein the pores of one net are occupied by identical framework bearing (usually) translational symmetry, is one of Nature's strategies for filling space, but can potentially limit porosity and therefore some applications. The opposite that interpenetration leads to increased porosity can also be true,<sup>2</sup> as exemplified by an early report from Yaghi and co-workers of an infinite periodic chain mail with large pores and prodigious adsorbing properties.<sup>3</sup> A less common and often more complicated sub-class of interpenetration is self-penetration,<sup>4</sup> defined as "single networks in which the smallest topological circuits are penetrated by themselves".<sup>1b, 4a, 4b</sup> Self-penetration requires a serendipitous harmony among the length, shape and

flexibility of ligands with the geometry of the metal centers during the network forming process. Self-penetration has been hard to predict, to classify or even to rationalize in hindsight. In this article, we suggest that the use of bent tritopic carboxylate ligands engender a higher probability of self-penetration in PCPs. The particular tritopic carboxylate ligands used in this work contains two moieties: i) an approximately co-planar pyridinium dicarboxylate (delineated as Part A), and ii) an N-alkyl carboxylate or benzoate (delineated as Part B) (Chart 1). The C-C-N angle of *ca.* 109.5° around the methylene linkage dictates the angle of Part A relative to the second rod-shaped dipyridyl ligand, precluding parallel and perpendicular alignment, but making an irregular angle through which the dipyridyl rod can thread (Chart 1).



**Chart 1** Self-penetration with a bent tritopic ligand and a linear ditopic ligand (left, M delineates for metal ion), and the ligands used in this study (right).

We herein report four polymeric complexes from Cu<sup>2+</sup> and the permutative combination of tritopic pyridinium carboxylates H<sub>3</sub>CmdepBr (H<sub>3</sub>CmdepBr = N-carboxymethyl-(3,5-dicarboxyl)pyridinium bromide), H<sub>3</sub>CbdepBr (H<sub>3</sub>CbdepBr = N-(4-carboxybenzyl)-(3,5-dicarboxyl)pyridinium bromide) and ancillary ligands azopy and bpe (azopy = 4,4'-azopyridine; bpe =

<sup>a</sup> School of Pharmaceutical Sciences, Southern Medical University, Guangzhou 510515, P. R. China

Email: jxchen@smu.edu.cn

<sup>b</sup> Institute of Materials Research and Engineering (IMRE), A\*STAR, 3 Research Link, 117602, Singapore

Email: zhangw@imre.a-star.edu.sg

<sup>c</sup> Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore

Email: andyhor@nus.edu.sg

<sup>d</sup> School of Science, Monash University, 46150 Bandar Sunway, Selangor D.E., Malaysia

<sup>e</sup> Present address: College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

Email: whzhang@suda.edu.cn

† Electronic Supplementary Information (ESI) available: X-Ray crystallographic files in CIF format, packing diagrams for **2** and **3**, entangled networks in **4**, TGA curves for **1–4**, powder XRD patterns for **1–4**. CCDC numbers 982017–982020. For ESI and crystallographic data in CIF see DOI: 10.1039/c000000x/

*trans*-1,2-bis(4-pyridyl)ethylene) with different size and shape (Chart 1). Improbably, two of the four isolated complexes exhibit self-penetrated structures, supporting our assertion.

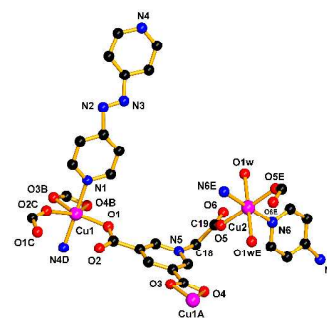
A number of groups have recently employed pyridinium carboxylate ligands in PCPs for gas adsorption, sensing and magnetic applications.<sup>5, 6</sup> The positively charged pyridinium center potentially enhances interaction with gas molecules such as CO<sub>2</sub>.<sup>7</sup> These viologen-like ligands also exhibit unique redox properties.<sup>5c, 8</sup> Some of us have investigated the interaction and cleavage of anionic DNA chains with cationic pyridinium carboxylate polymers of Cu(II) and Zn(II).<sup>9</sup>

Complexes  $\{[\text{Cu}_3(\text{Cmdep})_2(\text{azopy})_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2\}_n$  (**1**, 3D self-penetrating),  $\{[\text{Cu}(\text{Cmdep})(\text{bpe})(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}\}_n$  (**2**, 1D chain),  $\{[\text{Cu}_3(\text{HCbdep})_4(\text{azopy})_3(\text{H}_2\text{O})_2] \cdot \text{Cbdep}\}_n$  (**3**, 2D grid) and  $\{[\text{Cu}_3(\text{Cbdep})_2(\text{bpe})_3(\text{H}_2\text{O})_3] \cdot (\text{NO}_3)_2\}_n$  (**4**, 3D self-penetrating) were synthesized from the reactions of Cu(NO<sub>3</sub>)<sub>2</sub> with deprotonated pyridinium carboxylate in the presence of NaOH, followed by addition of the dipyridyl ancillary ligand.<sup>9</sup> Activated sample of **4** has a Brunauer-Emmett-Teller (BET) surface area of 129 m<sup>2</sup>·g<sup>-1</sup>.

## Results and discussion

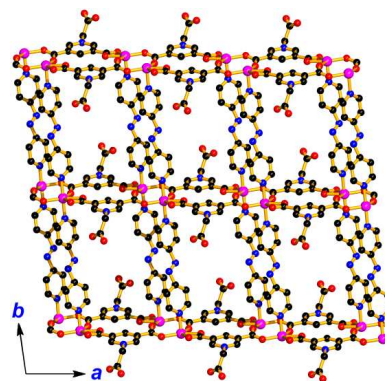
### Crystal structure of $\{[\text{Cu}_3(\text{Cmdep})_2(\text{azopy})_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2\}_n$ (**1**)

Compound **1** crystallizes in triclinic space group *P*-1. The asymmetric unit contains 1.5 Cu(II) centres: Cu1 is located on a general position whereas Cu2 on a centre-of-inversion. One disordered NO<sub>3</sub><sup>-</sup> anion is also present to balance the charge. Cu1 and Cu2 are bridged by one Cmdep ligand utilizing two monodentate carboxylates. Cu1 has triangular bipyramidal geometry with three monodentate carboxylates defining the equatorial plane. The axial position of Cu1 is occupied by two N atoms from a pair of disordered *trans* azopy ligands. The coordination geometry of Cu2 is octahedral, consisting of a pair of monodentate carboxylates, a pair of N atoms and a pair of H<sub>2</sub>O groups, all *trans* oriented. The angle around methylene ( $\angle\text{N5-C18-C19}$ ) is found to be 112.8(4)° (Table 2). The bond length of Cu(1)-O(1) (1.960(3) Å) is comparable to that of Cu(1)-O(3B) (2.027(3) Å) and Cu(2)-O(5) (1.990(3) Å), but shorter than Cu(1)-O(2C) (2.219(3) Å) and Cu(2)-O(1W) (2.413(4) Å), indicating weak Cu-aqua association of the later. The four Cu-N distances fall into a short range of 2.006(3) Å to 2.016(3) Å with an average distance of 2.009(3) Å (Table 2).



**Fig. 1** Asymmetric unit of **1** with labelling scheme showing the complete coordination sphere of Cu1 and Cu2. Symmetry codes: A  $x + 1, y, z$ ; B  $x - 1, y, z$ ; C  $-x + 2, -y + 1, -z + 1$ ; D  $x, y + 1, z$ ; E  $-x + 3, -y + 1, -z + 2$ .

Complex **1** features a 3D self-penetrating network. The structure of **1** can be better understood by initially detaching Cu2 and its coordinated azopy ligands from the framework. Cu1 forms a dimer cluster unit commonly found in Cu(II)-based MOFs.<sup>10</sup> The two Cu1 atoms in this dimer are linked by the *meta* oriented carboxylates and this octagonal ring propagates along the *a* axis. The remaining methyl carboxylate is tilted relative to the pyridinium dicarboxylate planes with a dihedral angle of 61.9°, orienting this coordinating functionality along the *b* axis. Each metal in the Cu1 dimer coordinates with two azopy ligands to extend the dimer in the *b* direction. Parallel 2D grids are thereby formed in the *ab* plane (Fig. 2).

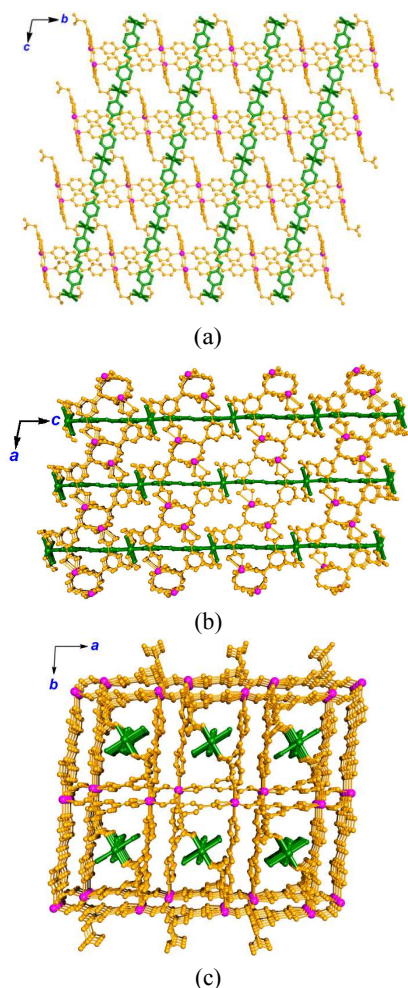


**Fig. 2** 2D network based on Cu1, azopy and Cmdep, the structure extended in the *ab* plane of complex **1**. All disordered domains and hydrogen atoms are omitted. Color codes: Cu (dark magenta), O (red), N (blue), C (black).

These adjacent 2D layers based on Cu1 have their associated methyl carboxylates oriented face-to-face and approximately 13.0 Å apart, ideal positioning for coordination to a pair of Cu atoms (Cu2) bridged by an azopy rods. This distance of 13.0 Å approximates the length of an azopy ligand (*ca.* 9.0 Å) plus two Cu-N bonds (*ca.* 2.0 Å for each).<sup>11</sup> The Cu2-azopy chain is aligned in the *c* direction and, because it is anchored between the

2D grid layers formed by Cu1, the overall result is a self-penetrated 3D network (Fig. 3).

Topologically, each Cmdcp ligand, Cu1-based dimer and Cu2 can be treated as 3-, 6- and 4-connecting nodes. Calculation by OLEX<sup>12</sup> indicates that the overall topology of **1** is  $(4^2 \cdot 6^2)(4^2 \cdot 6^8 \cdot 8^3 \cdot 10^2)(6^2 \cdot 8 \cdot 10^2 \cdot 11)$ .



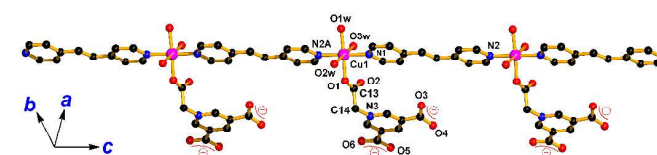
**Fig. 3** Parallel and perspective views of **1** looking along the *a* axis (a), *b* axis (b) and *c* axis (c). All disordered domains and hydrogen atoms are omitted. The 2D layers from Cu1 are presented in ball-and-stick model with golden-yellow color for atoms and bonds (except that the color for Cu atoms are in dark magenta) while the 1D chains of Cu2 are presented using wires-or-sticks model with green color for all the atoms and bonds.

#### Crystal structure of $\{[\text{Cu}(\text{Cmdcp})(\text{bpe})(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}\}_n$ (**2**)

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Compound **2** crystallizes in triclinic space group  $P\bar{1}$  and each Cu adopts octahedral geometry, associated by one Cmdcp ligand and one water molecule in the axial position with angle around methylene ( $\angle \text{N3-C14-C13}$ ) being  $110.30(15)^\circ$  (Table 2). Its equatorial plane is defined by a pair of coordinated water and two N atoms from a pair of bpe ligands, both *trans* located (Fig. 4). The bond length of Cu(1)-O(1) of  $2.0140(13)$  Å is comparable to that of Cu(1)-O(1W) ( $2.0199(15)$  Å), but significantly shorter than those of Cu(1)-O(2W) ( $2.3143(16)$  Å) and Cu(1)-O(3W) ( $2.529(2)$  Å), indicating weaker association for Cu(1)-O(2W) and Cu(1)-O(3W) (Table 2). The average length of the two Cu-N bond features  $2.004(13)$  Å, which is close to that found in compound **1**.

Complex **2** is a zwitterionic 1D chain structure propagated along the bpe direction and coincides with the crystallographic *c* direction. Detailed analysis indicates that the overall structure of **2** is stabilized by extensive inter-molecular hydrogen bonding interactions (Fig. S1).



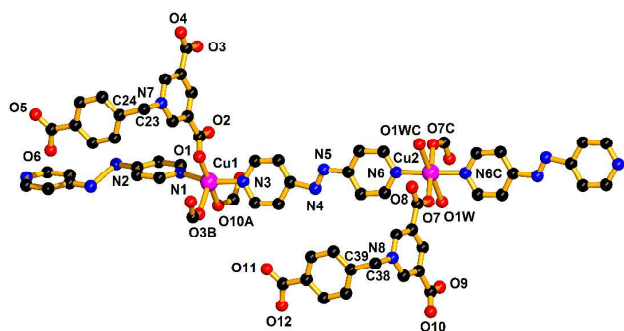
**Fig. 4** The structure of **2** showing a 1D zwitterionic chain propagated along the *c* direction. All aqua solvates and hydrogen atoms are omitted. Color codes: Cu (dark magenta), O (red), N (blue), C (black).

#### Crystal structure of $\{[\text{Cu}_3(\text{HCbdcp})_4(\text{azopy})_3(\text{H}_2\text{O})_2] \cdot \text{Cbdcp}\}_n$ (**3**)

Compound **3** crystallizes in triclinic space group  $P\bar{1}$ . The asymmetric unit contains 1.5 Cu(II) centres: Cu1 is located on a general position whereas Cu2 on a centre-of-inversion which is similar to that of compound **1**. Cu1 and Cu2 are bridged by one disordered azopy ligand (Fig. 5). Cu1 further associates with one N atom from one azopy ligand and three O atoms from three HCbdcp ligands to form square pyramidal geometry. Cu2 further associates with one additional *trans* located N atom from an azopy ligand, a pair of *trans* located O atoms from HCbdcp ligands and a pair of *trans* located  $\text{H}_2\text{O}$  to give an octahedral geometry. Notably, one uncoordinated and protonated benzoate is found in each HCbdcp ligand as estimated by the large discrepancy of the C–O distances ( $0.141$  Å) within these carboxyl groups. A dissociated Cbdcp ligand with half site occupancy was also found in the crystal lattice, this ligand is tentatively proposed as fully deprotonated based on the charge counting and the small

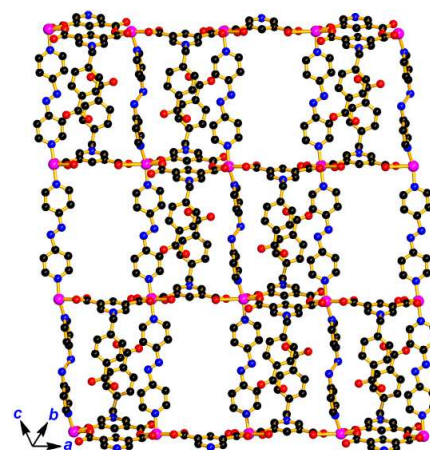
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discrepancy of the C–O distances (maximum 0.037 Å), with the latter diagnostic of conjugation.<sup>5c</sup> The angles around methylene groups ( $\angle\text{N7-C23-C24}$  110.3(3)° and  $\angle\text{N8-C38-C39}$  110.1(3)° for coordinated HCbdcp and  $\angle\text{N9-C53-C54}$  109.9(5)° for free Cbdcp) fall in a narrow range (Table 2). In compound **3**, the bond distances for Cu(1)–O(1) (1.969(2) Å), Cu(1)–O(10A) (1.994(2) Å) and Cu(2)–O(7) (1.962(2) Å) are similar and with an average distance of 1.975(2) Å, which is shorter than those of Cu(1)–O(3B) (2.183(3) Å) and Cu(2)–O(1W) (2.329(7) Å). The average bond length for four Cu–N distances of 1.962(9) Å is also comparable to those in **1** and **2** (Table 2).

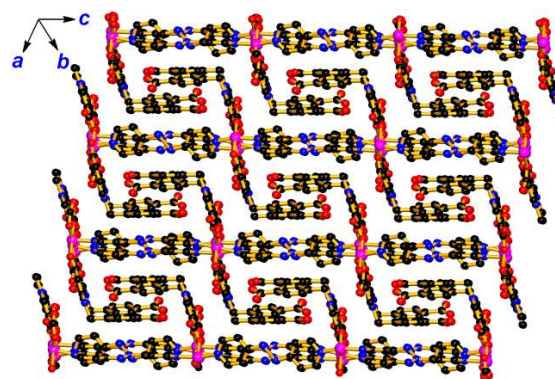


**Fig. 5** Asymmetric unit of **3** with labelling scheme showing the complete coordination sphere of Cu1 and Cu2. All disordered domains and hydrogen atoms are omitted. Symmetry codes: A  $x, y, z - 1$ ; B  $-x + 2, -y - 3, -z + 2$ ; C  $-x + 1, -y - 2, -z + 3$ .

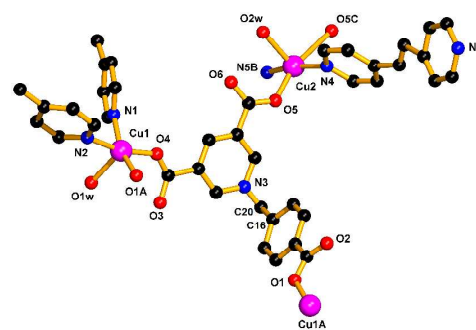
Complex **3** features a 2D grid structure. The Cu centers in the *a* direction are alternatively connected by Cbdcp bridging ligands in a  $-\text{[double-single-single]}_n-$  chain fashion (Fig. 6). These Cbdcp double bridges are aligned face-to-face with the two Cu centers joined as observed for **1**. Each Cu(II) center further coordinates with one additional monodentate carboxylate from the Cbdcp single bridges and a pair of *trans* azopy link in the *c* direction linking the corresponding  $-\text{[double-single-single]}_n-$  chains above and below, to form a 2D grid in the *ac* plane. The double and single bridge in a 1:2 ratio results in 2/3 of the cavities being covered with a free benzoic acid (Fig. 6). The open cavity is threaded by the disordered free Cbdcp ligands (Fig. S2). The packing diagram of **3** shows synergy among layers. The benzoic acids are perpendicular relative to the pyridinium dicarboxylate plane and hover over the 2D grids to generate free space (Fig. 7). This space is filled by the benzoic acid from an adjacent layer, interrelated by center-of-inversion, reminiscent of the Chinese ‘Yin-Yang’ symbol.



**Fig. 6** 2D grid structure of **3**. All disordered domains, solvates and hydrogen atoms are omitted. Color codes: Cu (dark magenta), O (red), N (blue), C (black).



**Fig. 7** Packing of the 2D structure of **3** showing the ‘Yin-Yang’ arrangements of the layers. All disordered domains, solvates and hydrogen atoms are omitted. Color codes: Cu (dark magenta), O (red), N (blue), C (black).



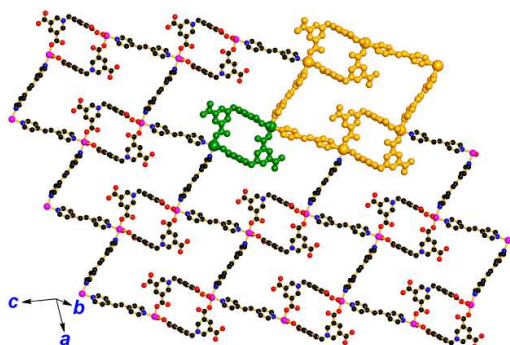
**Fig. 8** Labelling scheme of the asymmetric unit of **4** showing the complete coordination of Cu1 and Cu2. Symmetry codes: A  $-x - 0.5, -y - 0.5, -z + 2$ ; B  $x - 1, y - 1, z$ ; C  $-x - 1, y, -z + 1.5$ .

#### Crystal structure of $\{[\text{Cu}_3(\text{Cbdcp})_2(\text{bpe})_3(\text{H}_2\text{O})_3] \cdot (\text{NO}_3)_2\}_n$ (**4**)

Compound **4** crystallizes in monoclinic space group  $C2/c$  and its asymmetric unit contains one fully occupied Cu1 and one Cu2

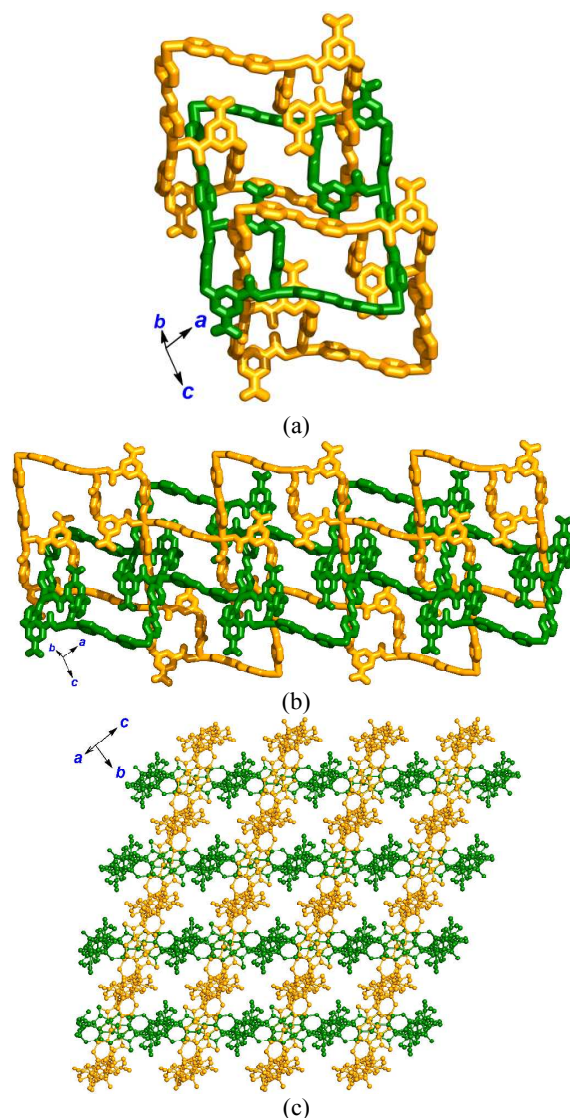
disordered with respect to the center of inversion (Fig. 8). One disordered  $\text{NO}_3^-$  anion is also present to balance the charge, similar to that observed in **1**. Cu1 and Cu2 are bridged by one disordered Cbdcp ligand via a pair of monodentate pyridinium carboxylates. The angles around the methylene (C16-C20-N3 and C16-C20-N3A) are  $109.8(7)^\circ$  and  $108.0(5)^\circ$ , respectively (Table 2). Cu1 further coordinates to two bpe ligands, one monodentate carboxylate from benzoate and one  $\text{H}_2\text{O}$  group while Cu2 associates with two disordered bpe ligands, one aqua molecule and the other one monodentate pyridinium carboxylates. Cu(1)-O(4) (1.845(19) Å) features the shortest Cu-O bond distance amongst all the four complexes. While the others of Cu(1)-O(1A) (1.931(3) Å), Cu(2)-O(5) (1.961(9) Å) are normal and comparable to those relevant distances in **1-3**. The Cu(1)-O(1W) (2.268(4) Å), Cu(2)-O(2W) (2.284(6) Å) distances are also comparably longer and similar to those observed in **1-3** (Table 2).

Complex **4** is a self-penetrating network and the analytical method used for **1** (*ie.* detaching the Cu2 atom first) can be invoked here. Cu1 and its coordinated Cbdcp and bpe ligands topologically form a (6, 3) net (Fig. 9). A pair of Cbdcp ligands juxtaposes a pair of Cu1 centers to form a small parallelogram (green circuit in Fig. 9) using one pyridinium carboxylate and the bent benzylcarboxylate in a head-to-tail fashion. The dinuclear Cu cycle can be considered as a secondary building unit (SBU), joining four of these SBUs with four bpe ligands, in two different bridging arrangements provides an enlarged parallelogram (golden-yellow circuit in Fig. 9) and finally a 2D layer with corner-overlapping large and small parallelograms.



**Fig. 9** A single 2D (6, 3) net of formed by Cu1 and its coordinated ligands in **4**. Color codes: Cu (dark magenta), O (red), N (blue), C (black).

A closer examination reveals inclined  $2\text{D} \rightarrow 3\text{D}$  interpenetration for these Cu1-based (6, 3) networks (Fig. 10 and Fig. S3) with the larger parallelograms of one net threading through the smaller parallelograms of an adjacent, inclined net.



**Fig. 10** Structure formed by Cu1 and its ligands in **4** showing (a) the entanglement of one parallelogram (green) with two parallel parallelograms (golden-yellow) in a wires-or-sticks model, (b) the consecutive entanglement of the parallelograms in a wires-or-sticks model, and (c) inclined 3D interpenetration in a ball-and-sticks model.

Although with complicated interpenetration, the inclined 2D nets arrange in such a way to still permit channels along the *b* direction and the free pyridinium carboxylate pairs are pointing towards this channel (Fig. 11). These carboxylates from interwoven, inclined networks are 13.8 Å apart which, as observed in complex **1**, is an ideal distance for coordination to a

second, independent Cu2 atom to form a self-penetrating 3D network (Fig. 11). Notably, a solvent accessible void of 1087.3 Å<sup>3</sup> (14.3% of the total cell volume) along the *b* direction can still be found in this condensed network.<sup>13</sup>

Topologically, each Cbdcp ligand, Cu1 and Cu2 can be treated as 3-, 4- and 4-connecting nodes. Structure analysis by OLEX<sup>12</sup> revealed a topology of (4·10<sup>2</sup>)(4·8<sup>5</sup>)(9<sup>2</sup>·10<sup>3</sup>·11) for complex 4.

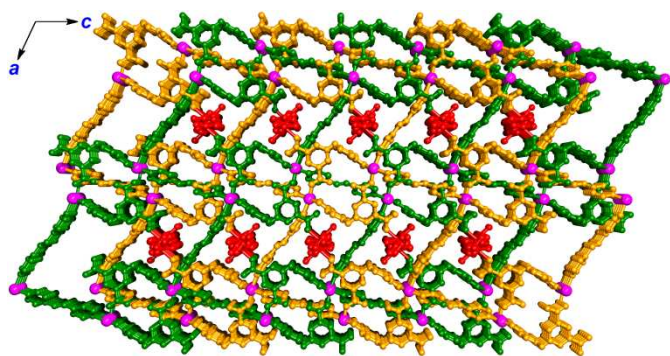


Fig. 11 Ball-and-stick representation of the 3D structure of 4 looking along the *b* direction showing the interpenetrated network from Cu1 (green and golden-yellow) anchoring a 1D chain from Cu2 and bpe (red)

### Gas sorption of complex 4

Thermogravimetric analysis (TGA) indicated that complex 4 is stable up to 230 °C (Fig. S4). Powder X-ray diffraction (PXRD) further indicated that the structure of 4 was maintained after activation at 130 °C for 48 h (Fig. S6). The degassed sample of 4 showed CO<sub>2</sub> uptake at 195 K (Fig. 12), but no uptake of the larger N<sub>2</sub> even at 77 K.<sup>5b, 14</sup> Estimation of CO<sub>2</sub> sorption data provided Brunauer-Emmett-Teller (BET) surface area of 129 m<sup>2</sup>·g<sup>-1</sup> for 4. Complex 4 shows a type I CO<sub>2</sub> profile with steep uptake at the low-pressure region, suggesting the presence of an open channel in the degassed phase.

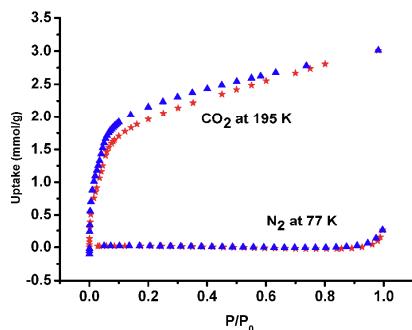


Fig. 12 N<sub>2</sub> (77 K) and CO<sub>2</sub> (195 K) sorption isotherms for complex 4. Five-point stars indicate adsorption and triangular shapes desorption. P<sub>0</sub> is the saturated vapour pressure of the sorbates at the measurement temperature.

### Conclusion

Comparing the self-penetrated 1 and 4 with the non-interpenetrated 2 and 3, it is clear that i) a match of the size and shape of the mixed ligands is required for self-penetration, ii) the bend provided by the pyridinium methylene increases the likelihood of this improbable event, and iii) the selection of Cu(II) (*d*<sup>9</sup>) with adaptable coordination geometry also assists self-penetration. Knowledge of these design features is a step towards creating self-penetrating networks for topological study in a controlled way and it is also useful for avoiding self-penetration to gain increased porosity.

### Experimental

#### Materials and methods

All reagents and solvents were obtained from commercial sources and used without further purification. IR spectra were recorded on a Nicolet MagNa-IR 550. Elemental analyses for C, H, and N were performed on an EA1112 CHNS elemental analyzer. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 10 °C/min under a nitrogen gas flow in an Al<sub>2</sub>O<sub>3</sub> pan. Powder X-ray diffraction (PXRD) spectra were recorded with a Bruker D8 GADDS (General Area Detector Diffraction System) micro-diffractometer equipped with a VANTEC-2000 area detector with  $\Phi$  rotation method. The X-ray generated from a sealed Cu tube was monochromated by a graphite crystal and collimated by a 0.5 mm MONOCAP ( $\lambda$  Cu-K $\alpha$  = 1.54178 Å). The tube voltage and current were 40 kV and 40 mA respectively.

#### Synthesis of ligands H<sub>3</sub>CmdcpBr and H<sub>3</sub>CbdcpBr

General procedure: To a solution of bromoacetic acid (2.76 g, 20 mmol) or 4-(bromomethyl)benzoic acid (4.3 g, 20 mmol) in DMF (20 mL) was added drop wise a solution of 3,5-pyridinedicarboxylic acid (3.34 g, 20 mmol) in DMF (40 mL). The resulting mixture was stirred at 80 °C for 6 h. The formed white precipitates were collected by filtration and washed with DMF (45 mL) and ether (15 mL) to afford H<sub>3</sub>CmdcpBr from bromoacetic acid and H<sub>3</sub>CbdcpBr from 4-(bromomethyl)benzoic acid.

**H<sub>3</sub>CmdcpBr**: white powder, 3.0 g (50%). Anal. Calcd. for C<sub>9</sub>H<sub>8</sub>NO<sub>6</sub>Br: C, 35.32; H, 2.63; N, 4.58; Found: C, 35.67; H, 2.37; N, 4.87 and IR bands (KBr disc, cm<sup>-1</sup>)  $\nu$  3564 (s), 3486 (s), 3322 (s), 3249 (s), 3053 (m), 2535 (w), 1746 (s), 1627 (m), 1449 (w), 1356 (s), 1281 (w), 1249 (s), 1217 (m), 1181 (w), 1034 (w), 988 (w), 912 (w), 891 (w), 768 (s), 756 (s), 716 (s), 694 (s), 507 (m), 460 (m).

**H<sub>3</sub>CbdcpBr**: white powder, 6.5 g (85%). Anal. Calcd. for C<sub>15</sub>H<sub>12</sub>NO<sub>6</sub>Br: C, 47.14; H, 3.16; N, 3.67; Found: C, 47.23; H, 3.34; N, 3.54 and IR bands (KBr disc, cm<sup>-1</sup>)  $\nu$  3426 (w), 3073 (s), 2626 (w), 1724 (s), 1645 (s), 1421 (m), 1398 (m), 1256 (s), 1211 (m), 1170 (w), 1020 (w), 943 (w), 928 (w), 910 (w), 866 (w), 788 (s), 748 (s), 695 (s), 637 (m), 589 (m), 537 (m), 449 (m).

#### Synthesis of complexes 1–4

General procedure: A solution of H<sub>3</sub>CmdcpBr (122.4 mg, 0.4 mmol) or H<sub>3</sub>CbdcpBr (152.8 mg, 0.4 mmol) was suspended in MeOH (5 mL), and the pH was adjusted to 7.0 with 0.1 M NaOH solution to give clear solution. Then, a solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (96.4 mg, 0.4 mmol) in MeOH (5 mL) was added. After stirring for 30 min, the green precipitates formed were collected by filtration and washed with MeOH (15 mL), then dissolved in H<sub>2</sub>O (100 mL) at 100 °C, then treated with bipyridine derivatives azopy (73.6 mg, 0.2 mmol) or bpe (72.8 mg, 0.2 mmol) in 2 mL DMF. It formed bright yellow solution for azopy and a great amount green precipitates for bpe, for both of H<sub>3</sub>CmdcpBr and H<sub>3</sub>CbdcpBr ligands. Then filtered and the filtrate was allowed to stand at ambient temperature for several days to produce the crystals of complexes 1–4.

{[Cu<sub>3</sub>(Cmdcp)<sub>2</sub>(azopy)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (**1**): Dark green crystals, 85 mg (51%). Anal. Calcd. for C<sub>48</sub>H<sub>34</sub>Cu<sub>3</sub>N<sub>14</sub>O<sub>14</sub>·4H<sub>2</sub>O: C, 44.57; H, 3.27; N, 15.16; Found: C, 44.60; H, 3.18; N, 15.15. IR (KBr disc, cm<sup>-1</sup>)  $\nu$  3394 (s), 1668 (s), 1617 (s), 1603 (s), 1494 (w), 1423 (w), 1384 (s), 1364 (s), 1229 (w), 1171 (w), 1060 (w), 1025 (w), 904 (w), 851 (m), 775 (m), 722 (m), 573 (m).

{[Cu(Cmdcp)(bpe)(H<sub>2</sub>O)<sub>3</sub>](H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**2**): Green crystals, 62 mg (27%). Anal. Calcd. for C<sub>21</sub>H<sub>27</sub>CuN<sub>3</sub>O<sub>12</sub>·3.5H<sub>2</sub>O: C, 49.08; H, 3.92; N, 8.18; Found: C, 49.40; H, 3.97; N, 8.07. IR (KBr disc, cm<sup>-1</sup>)  $\nu$  3402 (s), 1668 (s), 1615 (s), 1597 (s), 1433 (w), 1384 (s), 1367 (s), 1229 (w), 1172 (w), 1074 (w), 1028 (w), 904 (w), 833 (m), 775 (m), 722 (m), 552 (m).

{[Cu<sub>3</sub>(HCbdcp)<sub>4</sub>(azopy)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>](Cbdcp)]<sub>n</sub> (**3**): Dark green crystals, 193 mg (85%). Anal. Calcd. for C<sub>105</sub>H<sub>69</sub>Cu<sub>3</sub>N<sub>17</sub>O<sub>32</sub>·29H<sub>2</sub>O: C, 45.14; H, 4.58; N, 8.52; Found: C, 44.84; H, 3.98; N 8.02. IR (KBr disc, cm<sup>-1</sup>)  $\nu$  3314 (s), 1650 (s), 1605 (s), 1362 (s), 1294 (w), 1225 (w), 1158 (w), 1053 (w), 1019 (w), 923 (w), 849 (m), 767 (s), 722 (s), 603 (m), 573 (m).

{[Cu<sub>3</sub>(Cbdcp)<sub>2</sub>(bpe)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (**4**): Blue crystals, 85 mg (45%). Anal. Calcd. for C<sub>66</sub>H<sub>48</sub>Cu<sub>3</sub>N<sub>8</sub>O<sub>15</sub>·25H<sub>2</sub>O: C, 43.22; H, 5.39; N, 6.11; Found: C, 43.00; H, 5.46; N 6.37. IR (KBr disc, cm<sup>-1</sup>)  $\nu$  3434 (s), 1703 (m), 1649 (s), 1611(s), 1556 (s), 1508 (m), 1433 (s), 1383 (s), 1223 (m), 1207 (m), 1167 (m), 1115 (w), 1073 (m), 1027 (m), 982 (w), 833 (s), 769 (s), 724 (m), 728 (s), 551 (m).

#### X-ray crystallography for 1–4

Crystallographic measurements were made on a Bruker APEX II diffractometer by using graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) irradiation for 1–4. The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for

absorption effects with SADABS.<sup>15</sup> All crystal structures were solved by direct methods and refined on F<sup>2</sup> by full-matrix least-squares techniques with SHELXTL–97 program.<sup>16</sup> In the complex **1**, One azopy bridging ligand display conformational disorder with the relative ratios of 0.50/0.50 refined for the two components. NO<sub>3</sub><sup>-</sup> anions were found in two regions and their occupancy factors were fixed to 0.5 each to maintain the charge neutrality of the molecule. The hydrogen atoms on the coordinated water solvate were not located. In the complex **3**, two phenyl rings from two azopy ligands display rotational disorder and the relative ratio for (N1, N2, C1–C5)/(N1A, N2A, C1A–C5A) was refined to 0.45/0.55 and (N4, N5, N6, C11–C15)/(N4A, N5A, N6A, C11A–C15A) was refined to 0.47/0.53. One free Cbdcp ligand (O13–O18, N9, C46–C60) lies on a special position of higher symmetry than the molecule can possess. It is treated as spatial disorder by applying PART –1 and PART 0 in the *.ins* file with the site occupation factors changed to 0.50 for the atoms. The hydrogen atoms on the coordinated water as well as the carboxylic acid from Cbdcp ligands were not located. In complex **4**, one phenyl ring from one Cbdcp ligand displays positional disorder and the relative ratio for (O3–O6, N3, C21–C27)/(O3A–O6A, N3A, C21A–C27A) was refined to 0.52/0.48. The bpe ligand containing N4 and N5 lies on a special position of higher symmetry than the molecule can possess. They are treated as spatial disorder but applying PART –1 and PART 0 in the *.ins* file with the site occupation factors changed to 0.50 for the atoms. The NO<sub>3</sub><sup>-</sup> displayed conformational disorder with the relative ratios of 0.59/0.41 refined for the two components. The hydrogen atoms on the aqua molecule coordinated to Cu1 and Cu2 were not located. Otherwise, the solvent accessible void occupies a volume of 194.7 Å<sup>3</sup> (12.1% of the total cell volume) for **1**, 543.3 Å<sup>3</sup> (17.0% of the total cell volume) for **3**, 1087.3 Å<sup>3</sup> (14.3% of the total cell volume) for **4**, and are filled with disordered H<sub>2</sub>O based on the FT-IR spectra. Modelling the electron density failed to provide satisfactory results, the solvent contribution to the scattering factors was taken into account with PLATON/SQUEEZE.<sup>13</sup> Where relevant, the crystal data reported in this paper contained no contribution from the disordered solvent molecules. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). A summary of the key crystallographic data for 1–4 are listed in Table 1 and selected bond distances, angles and torsion angles in Table 2, respectively.



**Table 1.** Crystallographic data for complexes 1–4

Complex	1	2	3	4
Molecular formula	C <sub>48</sub> H <sub>34</sub> Cu <sub>3</sub> N <sub>14</sub> O <sub>14</sub>	C <sub>21</sub> H <sub>27</sub> CuNO <sub>12</sub>	C <sub>105</sub> H <sub>69</sub> Cu <sub>3</sub> N <sub>17</sub> O <sub>32</sub>	C <sub>66</sub> H <sub>48</sub> Cu <sub>3</sub> N <sub>8</sub> O <sub>15</sub>
Formula weight	1221.51	577.00	2271.39	1383.74
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
Color	dark-green	blue	blue	blue
<i>a</i> (Å)	10.0616(8)	7.1089(14)	13.9922(13)	30.925(3)
<i>b</i> (Å)	12.9846(11)	13.125(3)	15.9422(15)	13.2450(11)
<i>c</i> (Å)	13.0016(11)	13.376(3)	16.2434(15)	19.2577(15)
$\alpha$ (°)	75.440(2)	93.524(3)	70.832(2)	90.00
$\beta$ (°)	78.837(2)	93.563(3)	69.321(2)	106.047(2)
$\gamma$ (°)	83.287(2)	99.823(4)	88.235(2)	90.00
<i>V</i> (Å <sup>3</sup> )	1608.8(2)	1224.1(5)	3187.1(5)	7580.6(11)
<i>Z</i>	1	2	1	4
<i>T</i> /K	100(2)	296(2)	100(2)	153(2)
<i>D</i> <sub>calc</sub> (g·cm <sup>-3</sup> )	1.389	1.565	1.183	1.321
$\lambda$ (Mo-K) (Å)	0.71073	0.71073	0.71073	0.71073
$\mu$ (cm <sup>-1</sup> )	1.061	0.962	0.570	0.908
Total reflections	27691	20422	40207	40088
Unique reflections	7366	5784	12969	7974
No. observations	6459	5332	10041	5548
No. parameters	365	352	897	479
<i>R</i> <sup>a</sup>	0.0771	0.0335	0.0737	0.0787
<i>wR</i> <sup>b</sup>	0.2283	0.090	0.2108	0.2443
GOF <sup>c</sup>	1.104	1.030	1.065	1.062
$\Delta\rho_{\max}$ (e·Å <sup>-3</sup> )	4.346	0.658	2.263	1.058
$\Delta\rho_{\min}$ (e·Å <sup>-3</sup> )	-0.905	-0.488	-1.174	-0.970

<sup>a</sup>  $R = \sum |F_o| - |F_c| / \sum |F_o|$ . <sup>b</sup>  $wR = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$ . <sup>c</sup>  $GOF = \{\sum [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$ , where *n* = number of reflections and *p* = total numbers of parameters refined.

**Table 2** Selected bond lengths (Å), angles (°) and torsion angles (°) for complexes 1–4

<b>Compound 1</b>							
Cu(1)-O(1)	1.960(3)	Cu(1)-N(4)#1	2.008(3)	Cu(1)-N(1)	2.016(3)	Cu(1)-O(3)#2	2.027(3)
Cu(1)-O(2)#3	2.219(3)	Cu(2)-O(5)#4	1.990(3)	Cu(2)-O(5)	1.990(3)	Cu(2)-N(6)#4	2.006(3)
Cu(2)-N(6)	2.006(3)	Cu(2)-O(1W)#4	2.413(4)	Cu(2)-O(1W)	2.413(4)		
O(1)-Cu(1)-N(4)#1	91.29(15)	O(1)-Cu(1)-N(1)	89.03(16)	N(4)#1-Cu(1)-N(1)	177.72(16)		
O(1)-Cu(1)-O(3)#2	147.63(14)	N(4)#1-Cu(1)-O(3)#2	91.36(13)	N(1)-Cu(1)-O(3)#2	89.57(13)		
O(1)-Cu(1)-O(2)#3	122.87(13)	N(4)#1-Cu(1)-O(2)#3	90.02(15)	N(1)-Cu(1)-O(2)#3	87.91(15)		
O(3)#2-Cu(1)-O(2)#3	89.38(12)	O(5)#4-Cu(2)-O(5)	180.000(1)	O(5)#4-Cu(2)-N(6)#4	91.17(16)		
O(5)-Cu(2)-N(6)#4	88.83(16)	O(5)#4-Cu(2)-N(6)	88.83(16)	N(6)#4-Cu(2)-N(6)	180.000(1)		
O(5)#4-Cu(2)-O(1W)#4	92.44(16)	O(5)-Cu(2)-O(1W)#4	87.56(16)	N(6)#4-Cu(2)-O(1W)#4	88.21(18)		
N(6)-Cu(2)-O(1W)#4	91.79(18)	O(5)#4-Cu(2)-O(1W)	87.56(16)	O(5)-Cu(2)-O(1W)	92.44(16)		
N(6)#4-Cu(2)-O(1W)	91.79(18)	N(6)-Cu(2)-O(1W)	88.21(18)	O(1W)#4-Cu(2)-O(1W)	180.000(1)		
N(5)-C(18)-C(19)	112.8(4)						
C(15)-N(5)-C(18)-C(19)	108.7(5)	C(14)-N(5)-C(18)-C(19)	-69.0(6)	N(5)-C(18)-C(19)-O(6)	-154.6(5)		
N(5)-C(18)-C(19)-O(5)	28.9(6)						
<b>Compound 2</b>							
Cu(1)-N(2)#1	1.9992(14)	Cu(1)-N(1)	2.0090(14)	Cu(1)-O(1)	2.0140(13)	Cu(1)-O(1W)	2.0199(15)
Cu(1)-O(2W)	2.3143(16)						
N(2)#1-Cu(1)-N(1)	178.58(6)	N(2)#1-Cu(1)-O(1)	88.07(6)	N(1)-Cu(1)-O(1)	92.65(6)		
N(2)#1-Cu(1)-O(1W)	89.02(6)	N(1)-Cu(1)-O(1W)	90.24(6)	O(1)-Cu(1)-O(1W)	177.03(5)		
N(2)#1-Cu(1)-O(2W)	89.41(6)	N(1)-Cu(1)-O(2W)	89.45(6)	O(1)-Cu(1)-O(2W)	83.98(6)		
O(1W)-Cu(1)-O(2W)	95.36(6)	N(3)-C(14)-C(13)	110.30(15)				
C(19)-N(3)-C(14)-C(13)	-96.12(19)	C(15)-N(3)-C(14)-C(13)	79.7(2)	O(2)-C(13)-C(14)-N(3)	18.8(2)		
O(1)-C(13)-C(14)-N(3)	-160.71(15)						
<b>Compound 3</b>							
Cu(1)-N(1)	1.953(9)	Cu(1)-O(1)	1.969(2)	Cu(1)-O(10)#1	1.994(2)	Cu(1)-N(3)	2.000(3)
Cu(1)-N(1A)	2.076(8)	Cu(1)-O(3)#2	2.183(3)	Cu(2)-N(6)#3	1.949(10)	Cu(2)-N(6)	1.949(10)
Cu(2)-O(7)	1.962(2)	Cu(2)-O(7)#3	1.962(2)	Cu(2)-N(6A)#3	2.118(10)	Cu(2)-N(6A)	2.118(10)
Cu(2)-O(1W)	2.329(7)	Cu(2)-O(1W)#3	2.329(7)	O(3)-Cu(1)#2	2.183(3)	O(10)-Cu(1)#4	1.994(2)
N(1)-Cu(1)-O(1)	90.9(3)	N(1)-Cu(1)-O(10)#1	85.6(3)	O(1)-Cu(1)-O(10)#1	175.11(10)		
N(1)-Cu(1)-N(3)	159.5(3)	O(1)-Cu(1)-N(3)	89.67(11)	O(10)#1-Cu(1)-N(3)	92.42(11)		
O(10)#1-Cu(1)-O(3)#2	99.13(10)	N(1)-Cu(1)-O(3)#2	105.6(3)	O(1)-Cu(1)-O(3)#2	85.09(10)		
N(6)#3-Cu(2)-N(6)	179.998(2)	N(3)-Cu(1)-O(3)#2	94.83(11)	N(6)#3-Cu(2)-O(7)	88.1(3)		
N(6)#3-Cu(2)-O(7)#3	91.9(3)	N(6)-Cu(2)-O(7)#3	88.1(3)	O(7)-Cu(2)-O(7)#3	179.997(2)		
N(6)-Cu(2)-O(7)	91.9(3)	N(6)#3-Cu(2)-O(1W)	99.9(3)	N(6)-Cu(2)-O(1W)	80.1(3)		
O(7)-Cu(2)-O(1W)	97.98(15)	O(7)#3-Cu(2)-O(1W)	82.02(15)	O(1W)-Cu(2)-O(1W)#3	179.999(2)		
N(6)#3-Cu(2)-O(1W)#3	80.1(3)	N(6)-Cu(2)-O(1W)#3	99.9(3)	O(7)-Cu(2)-O(1W)#3	82.02(15)		
O(7)#3-Cu(2)-O(1W)#3	97.98(15)	N(7)-C(23)-C(24)	110.3(3)	N(8)-C(38)-C(39)	110.1(3)		
N(9)-C(53)-C(54)	109.9(5)						
C(20)-N(7)-C(23)-C(24)	-101.5(4)	C(21)-N(7)-C(23)-C(24)	77.3(4)	N(7)-C(23)-C(24)-C(25)	-95.1(4)		
N(7)-C(23)-C(24)-C(29)	85.3(4)	C(35)-N(8)-C(38)-C(39)	-83.2(4)	C(36)-N(8)-C(38)-C(39)	96.9(4)		
N(8)-C(38)-C(39)-C(40)	84.0(4)	N(8)-C(38)-C(39)-C(44)	-95.1(4)				
<b>Compound 4</b>							
Cu(1)-O(4)	1.845(19)	Cu(1)-O(1)#1	1.931(3)	Cu(1)-N(2)	2.005(5)	Cu(1)-N(1)	2.006(4)
Cu(1)-O(3A)	2.08(2)	Cu(1)-O(1W)	2.268(4)	Cu(2)-N(4)	1.989(3)	Cu(2)-O(2W)	2.284(6)
O(4)-Cu(1)-O(1)#1	92.5(9)	O(4)-Cu(1)-N(2)	167.8(7)	O(1)#1-Cu(1)-N(2)	89.73(16)		
O(4)-Cu(1)-N(1)	85.6(8)	O(1)#1-Cu(1)-N(1)	160.7(2)	N(2)-Cu(1)-N(1)	88.30(18)		
O(4)-Cu(1)-O(3A)	4.3(14)	O(1)#1-Cu(1)-O(3A)	89.2(11)	N(2)-Cu(1)-O(3A)	170.6(7)		
N(1)-Cu(1)-O(3A)	89.6(9)	O(4)-Cu(1)-O(1W)	98.5(8)	O(1)#1-Cu(1)-O(1W)	100.90(17)		
N(2)-Cu(1)-O(1W)	92.84(18)	N(1)-Cu(1)-O(1W)	98.34(19)	O(3A)-Cu(1)-O(1W)	96.5(7)		
C(16)-C(20)-N(3)	109.8(7)	C(16)-C(20)-N(3A)	108.0(5)				
C(16)-C(20)-N(3)-C(21)	100.4(6)	C(16)-C(20)-N(3)-C(25)	-72.8(8)	C(15)-C(16)-C(20)-N(3)	-69.2(10)		
C(17)-C(16)-C(20)-N(3)	112.2(9)						

Symmetry codes to generate equivalent atoms: #1  $x, y + 1, z$ ; #2  $x - 1, y, z$ ; #3  $-x + 2, -y + 2, -z + 1$ ; #4  $-x + 3, -y + 1, -z + 2$ ; #5  $x + 1, y, z$ ; #6  $x, y - 1, z$ ; #7  $-x + 1, -y + 3, -z + 1$  (compound 1); #1  $x, y, z - 1$ ; #2  $x, y, z + 1$  (compound 2); #1  $x, y, z - 1$ ; #2  $-x + 2, -y - 3, -z + 2$ ; #3  $-x + 1, -y - 2, -z + 3$ ; #4  $x, y, z + 1$ ; #5  $-x + 2, -y - 3, -z + 1$  (compound 3); #1  $-x - 1/2, -y - 1/2, -z + 1$ ; #2  $-x - 1/2, -y - 3/2, -z + 2$ ; #3  $-x, -y - 1, -z + 2$  (compound 4).

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## Pictogram of Graphical Abstract

**Bent Tritopic Carboxylates for Coordination Networks:  
Clues to the Origin of Self-penetration**

Jin-Xiang Chen,\* Hai-Qing Zhao, Sheng-Li Huang, Ni-Ni Ding, Huan-Huan Li, Wen-Hua Chen,

David J. Young, Wen-Hua Zhang,\* and T. S. Andy Hor\*

