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## Structure modulation in two Cu<sup>II</sup>-based MOFs by synergistic assembly of mixed-ligand synthetic strategy and solvent effect

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Two Cu<sup>II</sup>-based MOFs have been constructed by synergistic assembly of mixed-ligand synthetic strategy and solvent effect. Compound **1** is a 3D structure and represents a *cds* topology, while compound **2** displays a rare structure built by three distinct {Cu<sub>4</sub>} clusters as SBUs. Moreover, the magnetic properties of **2** have been thoroughly investigated.

Metal–Organic Frameworks (MOFs), as a type of auspicious function material, have gained increasing interest due to their aptitudinal application in a variety of scientific fields like nanoscale magnetism,<sup>1</sup> catalysis,<sup>2</sup> gas storage and separation,<sup>3</sup> drug delivery,<sup>4</sup> and sensor devices.<sup>5</sup> From a synthetic point of view, the judicious selection of appropriate organic ligands and synthetic conditions are proved to be two of the most critical factors to manipulate the versatile structures of MOFs.<sup>6–10</sup> On one hand, among multitudinous organic ligands, dicarboxylate and diimidazole-containing ligands, in particular, have proven to be good candidates for the construction of novel MOFs due to their flexible and diverse coordination modes. To date, a large number of MOFs based on these two kinds of ligands have been constructed, respectively.<sup>7–10</sup> As known, the two famous systems represent the most reliable and typical building blocks which named by Metal Carboxylate Frameworks (MCFs) and Metal Azolate Frameworks (MAFs).<sup>7–10</sup> However, up to now the reports on the combination of two distinct kinds of mixed ligands system to prepare new MOFs have been far less explored. The results of previous studies show that polycarboxyl bridging ligands binding to various metal ions under different conditions will provide considerable structural complexity and diversity of MOFs.<sup>7,8</sup> Based on this consideration, the general nature of these polycarboxyl ligands are epitomized by fabrication of metal–carboxylate clusters or chains motifs as SBUs, e.g., the dimeric copper or zinc clusters, the trimeric zinc clusters, the tetrameric zinc or copper clusters, and the infinite rod-shaped SBUs.<sup>8</sup> Meanwhile, the rigid neutral bis(imidazole) ligands often exhibit the special ability to coordinate to various metal centers in two typical coordination fashions (cis-configuration and trans-configuration) through bonds rotation of the terminal imidazolyl rings, which can lead to novel structure modes.<sup>9,10</sup> Consequently, the incorporation of these two different ligands into one unique structure to construct Mixed-Ligand Metal–Organic Frameworks (ML-MOFs) might be advantageous. In this kind of materials, the two types of ligands can assume respective tasks or synergistic

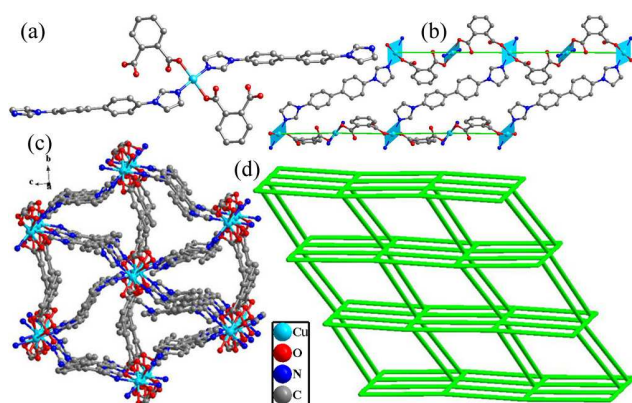
effects to construct ML-MOFs with structure diversities.<sup>10d,e</sup> On the other hand, a careful selection of the different external stimuli, such as solvent, template, counter-anions, pH value, pressure, and temperature, is a key step for the effective design of MOFs with specific structural modulation.<sup>11</sup> Undoubtedly, the most common external condition is solvent which can directly induce the potential structural transformations.<sup>11</sup> This aspect has been systematically reported in recent comprehensive reviews by Du and co-workers.<sup>11b</sup> Here, we draw lessons from this heuristic work and others using mixed solvents to generate two interesting Cu<sup>II</sup>-based 3D (three-dimensional) and 2D MOFs also involved in two mixed ligands. Remarkably, similar studies concerned with the mediation of the structures by synergistic assembly of mixed-ligand synthetic strategy and solvent effect are relatively scarce.

With these points in mind, we successfully implemented this synergistic assembly approach by introducing 4,4'-bis(imidazol-1-yl)biphenyl (here abbreviated as bibp) and 1,2-benzenedi carboxylic acid (here abbreviated as 1,2-H<sub>2</sub>bdc) mixed ligands into mixed solvent H<sub>2</sub>O/CH<sub>3</sub>OH and H<sub>2</sub>O/CH<sub>3</sub>CH<sub>2</sub>OH systems to elaborate two Cu<sup>II</sup>-based frameworks, namely, [Cu(bibp)(1,2-bdc)]<sub>n</sub> (**1**) and {[Cu<sub>4</sub>(OH)<sub>2</sub>(bibp)(1,2-bdc)<sub>3</sub>]·1.5H<sub>2</sub>O}<sub>n</sub> (**2**). Compound **1** shows 3D *cds* structural topology constructed from 1D Cu-chains further extended by the linear bibp ligands. While compound **2** represents 2D structural feature built from three distinct tetra-nuclear Cu-clusters {Cu<sub>4</sub>} as secondary building units (SBUs). Furthermore, the crystal structure, topological analyses of **1** and **2**, and magnetic properties of **2** have been investigated.

Block-like blue crystals of **1** and **2** were obtained *via* solvothermal reaction of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O with NaOH, bibp, and 1,2-H<sub>2</sub>bdc in H<sub>2</sub>O/CH<sub>3</sub>OH (for **1**) and H<sub>2</sub>O/CH<sub>3</sub>CH<sub>2</sub>OH (for **2**) mixed solution at 160 °C for 4 days.<sup>‡</sup> Phase purity of the bulky crystals was confirmed by the similarity between the experimental and simulated powder X-ray diffraction (PXRD) patterns (Fig. S1 and S2, ESI).

Single-crystal structural analysis reveals that **1** crystallizes in the monoclinic space group *P2<sub>1</sub>/c* and has a 3D framework abstracted as a *cds* topology. The basic structural unit of **1** contains one Cu<sup>2+</sup> ion, one bibp ligand, and one 1,2-bdc<sup>2-</sup> ligand. The asymmetric unit and coordination mode of Cu<sup>2+</sup> center is shown in Fig. 1a. The Cu<sup>2+</sup> ion is coordinated with two mono-coordinated oxygen atoms originating from two independent 1,2-bdc<sup>2-</sup> ligands and two mono-coordinated nitrogen atoms deriving

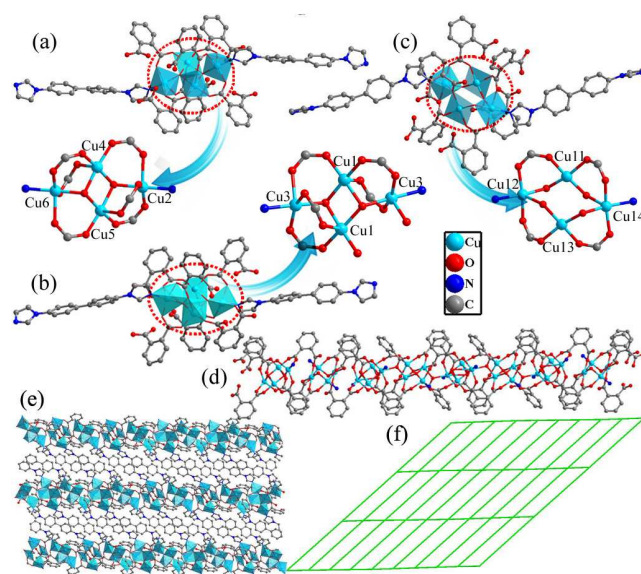
from two different bibp ligands to form a tetra-coordinated square-planar geometry. The bond lengths of Cu–O are in the range of 1.959(3)–1.986(3) Å and Cu–N are among 1.985(3)–2.015(3) Å. The selected bond lengths and angles are listed in Table S2 (ESI). The 1,2-bdc<sup>2-</sup> ligands using their two carboxyl mono-coordinated oxygen atoms “captures” two distinct Cu<sup>2+</sup> ions to generate a 1D Cu-chain as sub-SBU (Fig. 1b). The 1D Cu-chains further connected by bibp ligands to form a 2D layer (Fig. 1b). Furthermore, these 2D layers are linked by other imidazole groups form bridging bibp ligands, resulting a 3D framework (see Fig. 1c). From the topological point of view, the Cu<sup>2+</sup> ions can be abstracted as four-connected nodes which link with two bibp ligands and two 1,2-bdc<sup>2-</sup> ligands. While the bibp ligands and 1,2-bdc<sup>2-</sup> ligands only act as linear connection and not necessary to consider them in the topological analysis. Based on this simplification, the overall 3D network of **1** can be rationalized as a uninodal 4-connected **cds** topology with the Schläfli symbol of {6<sup>5</sup>.8} (Fig. 1d).



**Fig. 1** (a) The ball-and-stick view of the coordination environment of Cu<sup>2+</sup> in **1**; (b) the polyhedral view of 2D layer constructed by 1D Cu-chains and bibp ligands in **1**; (c) the ball-and-stick view of 3D structure of **1**; (d) schematic view of the **cds** topology for **1**. (The hydrogen atoms have been omitted for clarity)

The single-crystal X-ray diffraction study revealed that **2** crystallizes in the triclinic space group *P*-1. The basic structure of **2** contains a 2D layer constructed by 1D multinuclear Cu-chains bridging by bibp ligands. The asymmetric unit and coordination modes of Cu<sup>2+</sup> centers are shown in Fig. 2a-2c. There are three kinds of {Cu<sub>4</sub>}-clusters in **2** (see Fig. 2a-2c). In the first kind of {Cu<sub>4</sub>}-clusters, all Cu<sup>2+</sup> have penta-coordinated geometries but exhibit two different types of coordination environments, which are distorted quadrangular pyramid geometries for Cu4 and Cu5 centers, and distorted trigonal bipyramid geometries for Cu2 and Cu6 centers (see Fig. 2a). In the second kind of {Cu<sub>4</sub>}-clusters, the four Cu<sup>2+</sup> centers have the same penta-coordinated modes but different coordination environments, namely, distorted quadrangular pyramid geometries for Cu1 centers, and distorted trigonal bipyramid geometries for Cu3 centers (see Fig. 2b). The third kind of {Cu<sub>4</sub>}-clusters also contain two different Cu<sup>2+</sup> coordination modes with tetra-coordinated distorted square-planar geometries for Cu11 and Cu13 centers and penta-coordinated distorted trigonal bipyramid geometries for Cu12 and Cu14 centers (see Fig. 2c). The bond lengths of Cu–O are in the range of 1.883(5)–2.421(6) Å and Cu–N are among 1.948(7) – 2.006(7) Å. The selected bond lengths and angles are listed in

Table S3 (ESI). Remarkably, these three kinds of {Cu<sub>4</sub>}-clusters are connected through hand in hand together by carboxyl chelating of 1,2-bdc<sup>2-</sup> ligands to bring a 1D multinuclear Cu-chains (see Fig. 2d), and which are notably further-bridged by bibp ligands to give a 2D layer structure (see Fig. 2e). On the basis of the above structural feature, compound **2** represents a rare structural topology in the MOFs constructed from three distinct {Cu<sub>4</sub>} clusters as SBUs. From the topological point of view, all the {Cu<sub>4</sub>} clusters can be abstracted as four-connected nodes which link with two {Cu<sub>4</sub>} clusters by three 1,2-bdc<sup>2-</sup> ligands in the same 1D Cu-chain, and further link with other two {Cu<sub>4</sub>} clusters in the two-sided 1D Cu-chains through two bibp ligands. As compound **1**, the bibp ligands and 1,2-bdc<sup>2-</sup> ligands only act as linear connection and not necessary to consider them in the topological analysis. Based on this simplification, the overall 2D network of **2** can be rationalized as a uninodal 4-connected **sql** tetragonal plane net topology with the Schläfli symbol of {4<sup>4</sup>.6<sup>2</sup>} (Fig. 2f).

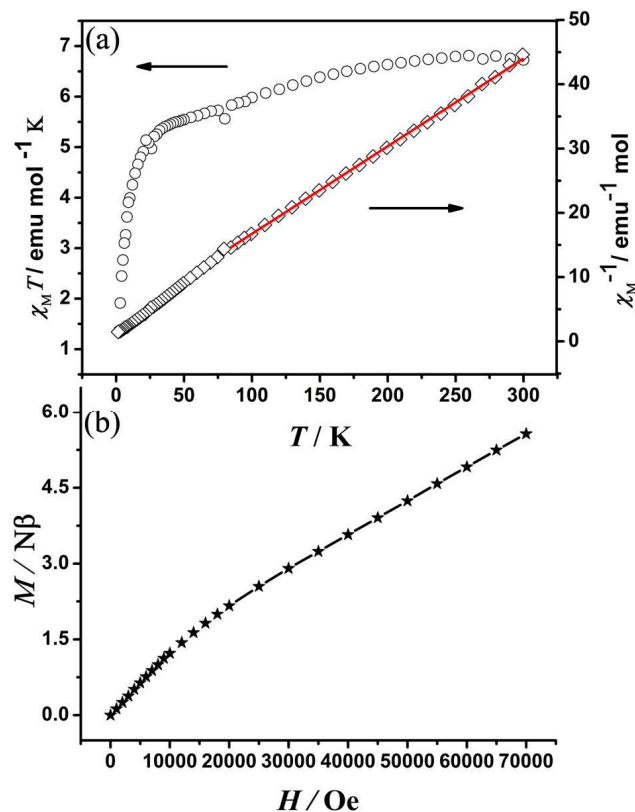


**Fig. 2** (a) (b) (c) The polyhedral view of three kinds of {Cu<sub>4</sub>}-clusters showing different coordination environments and the ball-and-stick view of four corresponding {Cu<sub>4</sub>} cores in **2**; (d) the ball-and-stick view of 1D multinuclear Cu-chains constructed by the above three kinds of {Cu<sub>4</sub>}-clusters in **2**; (e) the polyhedral view of 2D structure of **2** constructed by 1D multinuclear Cu-chains bridging by bibp ligands; (f) schematic view of the **sql** tetragonal plane net topology for **2**. (The hydrogen atoms have been omitted for clarity)

It is interesting to note that the organic solvents with different sizes, boiling points and polarity play important roles in inducing different structural aggregates of the two compounds, which not only dramatically influence the different dimensionality of the compounds, but also allow access to new structures and topologies through inducing the different coordination environments of Cu<sup>2+</sup> ions and linking modes of 1,2-bdc<sup>2-</sup> and bibp ligands. Due mainly to the employment of CH<sub>3</sub>CH<sub>2</sub>OH solvent with bigger steric hindrance, boiling points and polarity than that in CH<sub>3</sub>OH under similar synthetic conditions, distinct framework structures were obtained. As above discussion, compound **2** was formed in a 2D structure rather than a 3D structure in **1** by solvents impacting the assembly processes. The result shows that the choice of different solvents is clearly critical

in determining the molecular architectures of the MOFs and has a significant effect on the final structures.<sup>11</sup>

The magnetic properties of compound **2** were investigated by solid state magnetic susceptibility measurements in 2-300 K range at 1 kOe field and the isothermal field-dependent magnetizations  $M(H)$  at fields up to 70 kOe.<sup>12</sup> Magnetic measurements have been carried out on crystalline samples of **2** for its multinuclear structure, because compound **1** contains only single diamagnetic  $\text{Cu}^{2+}$  ion for the long distance of  $\text{Cu}^{2+}$  ions, it can be simplified as mononuclear copper from magnetic point of view, so magnetic properties of **1** were not investigated. The pure-phase has been confirmed by XRPD (see Fig. S1 and S2, ESI). According to the obtained data, antiferromagnetic couplings between  $\text{Cu}^{\text{II}}$  ions in **2** can be suggested, as discussed in more detail below.



**Fig. 3** (a) The  $M$  vs.  $H$  plots (★) at 2 K for **2**; (b) Plots of  $\chi_M T$  vs.  $T$  (○) and  $\chi_M^{-1}$  vs.  $T$  (◇) (red part for the Curie-Weiss fitting) for **2**.

The magnetic properties of **2** in the form of  $\chi_M T$  vs.  $T$  and  $M$  vs.  $H$  plots are shown in Fig. 3a and 3b. The  $\chi_M T$  value per  $\text{Cu}^{\text{II}}$  ion at 300 K is  $0.42 \text{ emu mol}^{-1} \text{ K}$ , slightly larger than the predicted  $0.375 \text{ emu mol}^{-1} \text{ K}$  for an isolated  $\text{Cu}^{\text{II}}$  ion. As the temperature decreases, the  $\chi_M T$  product slowly decreases, then more rapidly below 75 K to a minimum value of  $1.36 \text{ emu mol}^{-1} \text{ K}$  at 2 K, indicating antiferromagnetic coupling between the  $\text{Cu}^{\text{II}}$  ions in **2**. The susceptibility of **2** follows the Curie-Weiss law at temperatures above 85 K, with  $C = 7.33 \text{ emu mol}^{-1} \text{ K}$  and  $\theta = -22.06 \text{ K}$ , further indicating antiferromagnetic coupling in **2** (Fig. 3c). Magnetization rises very slowly as the field increases and tends to a value of  $5.57 \text{ N}\beta$  (far from a saturation value  $16 \text{ N}\beta$ ) at 70 kOe, suggesting antiferromagnetic coupling along the  $\text{Cu}^{\text{II}}$  chain (Fig. 3d).<sup>12,13</sup> It appears that antiferromagnetic coupling

would be expected for **2** for the *syn-syn* carboxylate bridge and the large angles for Cu-O-Cu. Notably, the long neutral ligands only provided negligible interchain antiferromagnetic interactions. In summary, MOF **2** exhibits antiferromagnetic behavior based on 1D  $\text{Cu}^{\text{II}}$  chains.<sup>12,13</sup>

In conclusion, two new  $\text{Cu}^{\text{II}}$ -based MOFs have been constructed by synergistic assembly of mixed-ligand synthetic strategy and solvent effect. Compound **1** is a 3D structure and represents a **cds** topology, while compound **2** displays a rare structural topology built by three distinct  $\{\text{Cu}_4\}$  clusters as SBUs. Moreover, the magnetic investigation show that compound **2** displays antiferromagnetic behaviour based on 1D multinuclear Cu-chains. The results further highlighted the importance of mixed ligands and solvents on tuning the material structures. Further investigations are underway, including the study of their other properties and an extension of the strategy into other systems, aiming at synthesizing novel compounds with diverse topological structures and various interesting functionalities.

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## Notes and references

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<sup>‡</sup>Synthesis of **1** and **2**: A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (121 mg, 0.5 mmol), NaOH ((40 mg, 1 mmol), bibp (143 mg, 0.5 mmol)<sup>10c,14</sup>, 1,2- $\text{H}_2\text{bdc}$  (83 mg, 0.5 mmol), and  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  (for **1**) or  $\text{H}_2\text{O}/\text{EtOH}$  (for **2**) (8 mL, V:V = 1:1) were sealed in a 23 mL Teflonlined stainless steel container, which was heated at 160 °C for 4 days and then cooled to room temperature at a rate of  $10 \text{ }^\circ\text{C}\cdot\text{h}^{-1}$ . Blue block shaped crystals of **1** and **2** were collected. Yield: 25% for **1** and 20% for **2** based on Cu. Elemental analysis (%) for **1**,  $\text{C}_{52}\text{H}_{36}\text{Cu}_2\text{N}_8\text{O}_8$  ( $M = 1027.98$ ): *Calcd.*: C, 60.76; H, 3.53; N, 10.90; *Found*: C, 60.98; H, 3.39; N, 10.77. For **2**,  $\text{C}_{168}\text{H}_{124}\text{Cu}_{16}\text{N}_{16}\text{O}_{62}$  ( $M = 4375.59$ ): *Calcd.*: C, 46.11; H, 2.86; N, 5.12; *Found*: C, 46.65; H, 2.57; N, 5.02.

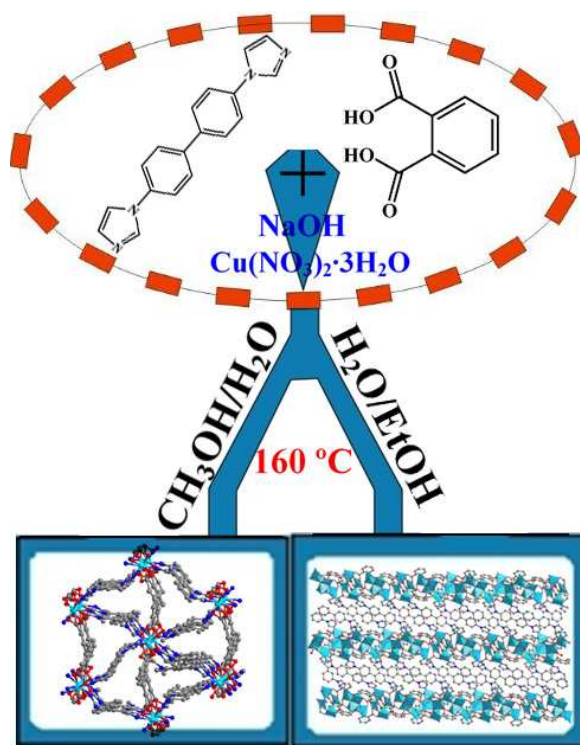
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## Graphic Abstract

**Structure modulation in two Cu<sup>II</sup>-based MOFs by synergistic assembly of mixed-ligand synthetic strategy and solvent effect**

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A synergistic assembly of mixed-ligand synthetic strategy and solvent effect was successfully applied to tune two Cu<sup>II</sup>-based MOFs. Compound **1** is a 3D structure and represents a **cds** topology, while compound **2** displays a rare 2D structure built by three distinct {Cu<sub>4</sub>} clusters as SBUs.