Three novel 3D metal–organic frameworks with a 1D ladder, tube or chain as assembly units†

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Three novel metal–organic frameworks, $Cu_4(OH)_2(SO_4)(HBTC)_2(bpy) \cdot bpy$ (**1**), $Cu_{1.5}(H_2O)(TMBTC)(bpy) \cdot 1/2H_2O$ (**2**) and $Cd_2(H_2O)_5(TMBTC)(bpy)_2 \cdot NO_3 \cdot 3H_2O$ (**3**), constructed from mixed organic ligands, have been synthesized and characterized. Complex **1** crystallizes in monoclinic space group *C*2/*c* and possesses a 3D three-fold interpenetrating framework. The copper ions were first connected by HBTC and SO_4^{2-} to generate a 1D ladder, which was further linked by a 4,4′-bipyridine ligand to give rise to a 3D interpenetrating framework. Complex **2** crystallizes in monoclinic space group *P*2/*c* and possesses a 3D two-fold interpenetrating framework. Similar to **1**, the copper ions were first connected by TMBTC to generate a 1D tubular unit, which can be considered as the assembly block. The 1D tubular unit was further linked by 4,4′-bipyridine ligands to result in the formation of the 3D framework. Complex **3** crystallizes in monoclinic space group *Cc* and has a three-dimensional structure. Different from **1** and **2**, the cadmium ions were first connected by a 4,4′-bipyridine ligand to form a 1D chain as the assembly unit, which was further linked by TMBTC ligand to generate the final 3D framework. The photoluminescence measurement of **3** in the solid state at room temperature showed that complex **3** exhibits luminescence, which can be assigned to an intraligand $\pi \rightarrow \pi^*$ transition.

Introduction

The rational design and synthesis of functional MOFs[1–4] is a challenging subject for synthetic chemists because there are many factors that influence the final structure of MOF. The choice of a suitable ligand with certain features and metal precursors is the key in the construction of metal–organic framework with desired structural topology.[2a,5] It is known that the planarity of the organic ligand has effect on the final structure of a MOF.[6] We select benzene-1,3,5-tricarboxylic acid (H_3BTC), and its derivative, 2,4,6-trimethylbenzene-1,3,5-tricarboxylic acid (H_3TMBTC), as assembly ligands considering their following characteristics (Scheme 1): (1) benzene-1,3,5-tricarboxylic acid is a well-known organic ligand in the construction of porous or chiral MOFs,[7,8] and its three carboxylate groups are almost located in the same plane with the central benzene ring in the free ligand as well as in the MOFs. (2) Due to the space hindrance between the methyl groups with the carboxylate groups in H_3TMBTC, its three carboxylate groups would not be in a plane with the central benzene ring, which will result in MOFs with novel structural topologies different from those constructed from H_3BTC.
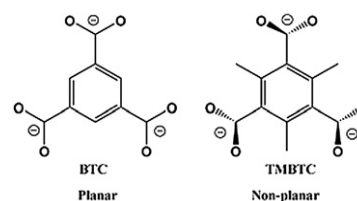
On the other hand, the construction of novel MOFs also depends on the novelty of the assembly units or SBU which are normally *in-situ* generated during the reaction.[9] In the past decade, a number of carboxylate-bridged metal clusters have been documented as assembly units to build extended MOFs.[10,11] The MOFs constructed from rod-shaped SBUs have also been reported by Yaghi and coworkers.[12] However, the reports on metal–organic frameworks based on a 1D ladder, tube or chain as the assembly units are somewhat rare in the literature.[13] In this paper, we report three novel 3D metal–organic frameworks with a 1D ladder, tube or chain as the assembly units.

Results and discussion

Crystal structure of $Cu_4(OH)_2(SO_4)(HBTC)_2(bpy) \cdot bpy$ (1)

Complex **1** crystallizes in the monoclinic *C*2/*c* space group. There are two crystallographically independent copper ions in **1**: Cu1 and Cu2. As shown in Fig. 1, Cu1 is coordinated by two carboxyl oxygen atoms from different HBTC, one nitrogen atom from bipy, one oxygen atom from SO_4^{2-} and one OH^- group with the average Cu1–O and Cu1–N distances of 2.074 and 2.018 Å, respectively. The Cu1 ion falls into a rough trigonal bipyramidal geometry,[14] in which the equatorial positions are occupied by

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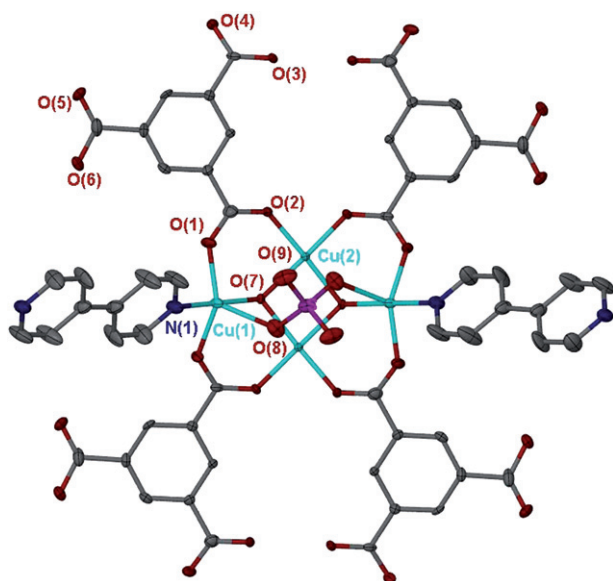

Scheme 1 Organic triangular carboxylate ligands, BTC and TMBTC.

Fig. 1 The coordination environment of the copper ions in **1** (thermal ellipsoids: 50%).

two carboxyl oxygen atoms and one oxygen atom of SO_4^{2-}, and the axial positions by one OH^- group and one nitrogen atom of bipy. Cu2 is coordinated by two carboxyl oxygen atoms from different HBTC and two OH^- groups in a square planar geometry with the average Cu2–O distance of 1.946 Å. Four copper ions are engaged by two μ_3-OH, one SO_4^{2-} group and four carboxylate groups of BTC to form a non-planar tetranuclear copper SBU, in which the SO_4^{2-} group sits above the four copper ions by connecting them through its two oxygen atoms. The sulfate atom of SO_4^{2-} group just lies on a twofold axis. The two carboxylate groups of HBTC are deprotonated and adopt bridging mode to connect two tetracopper SBUs. The remaining carboxylate group is protonated and does not take part in coordination, which provides hydrogen bonding donors. As expected, the HBTC ligand is almost planar with the average dihedral angle between the carboxylate group and the central benzene ring being 11.9°.

Thus, the tetracopper SBUs were connected by the planar HBTC to form a one-dimensional ladder structure (Fig. 2a and 2b), in which the HBTC plays the role of 1,3-benzenedicarboxylic acid as found in other compounds constructed from planar tetracopper SBUs.[15] The SO_4^{2-} groups alternatively appear above or below the 1D ladder and play two roles in the formation of **1**: connecting copper ions and balancing the charge.

The 1D ladder block can be considered as the assembly unit of the whole structure. The 1D ladder was further connected by 4,4′-bpy ligands in different directions to give rise to a three-dimensional porous framework with square or rectangle channels along [001] or [101] directions (Fig. 2c and d), respectively. The dimensions of the channels are 12 × 12 Å or 19 × 9.9 Å along [001] or [101] directions. All the protonated uncoordinated carboxylate groups of HBTC point toward the center of the square channels and the nearest O···O distance is 12.12 Å between the ladders (Fig. 2c). The distance between the protonated carboxylate groups (hydrogen bonding donor) just allows
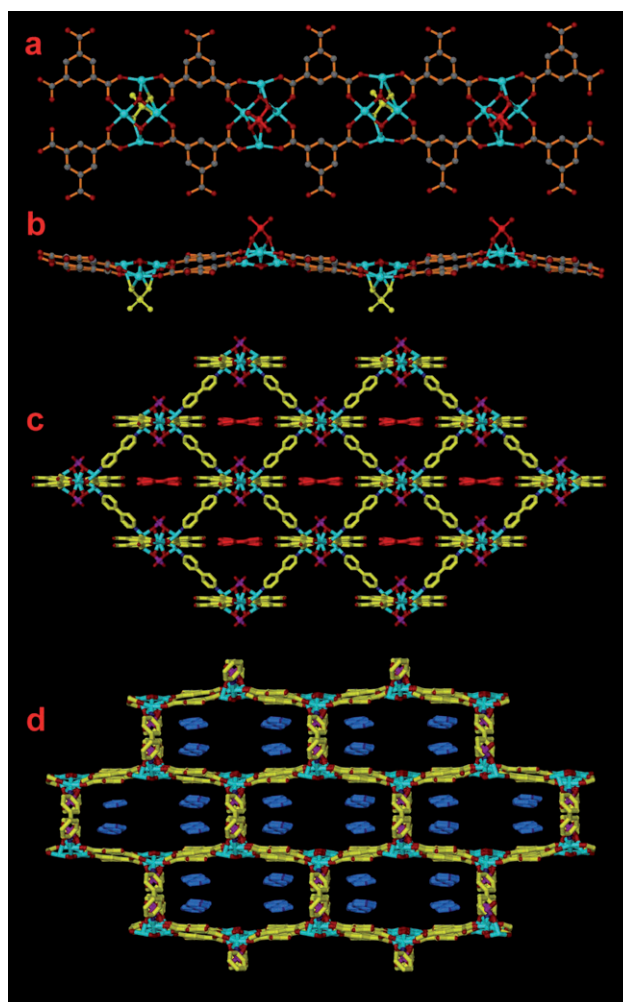

Fig. 2 (a) and (b) The 1D ladder unit generated by HBTC connecting tetracopper SBU showing the SO_4^{2-} groups locate above (red) or below (yellow) the ladder, (c) the 3D porous framework along [001] direction showing the free bpy ligands (in red colour) locate in the channels forming strong hydrogen bonds with the uncoordinated carboxylate groups and (d) the 3D porous framework along [101] direction showing the free bpy (in blue colour) of other net locate in the channels in **1**.

a free 4,4′-bpy (hydrogen bonding acceptor) to fill in. The free 4,4′-bpy ligands reside in the square channels by forming strong hydrogen bonds with the protonated uncoordinated carboxylate groups (O···N distance: 2.563 Å). Fig. 3 shows the linking direction of coordinated 4,4′-bpy and the location of uncoordinated bipy. Both coordinated and uncoordinated 4,4′-bpy
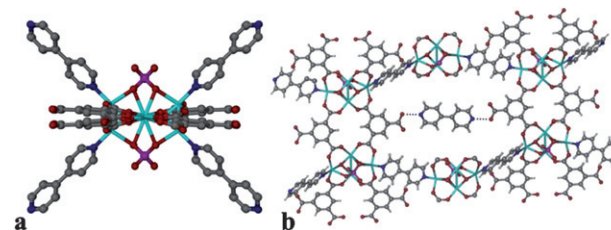

Fig. 3 The linking direction of coordinated 4,4′-bpy and the location of uncoordinated 4,4′-bpy in **1**.
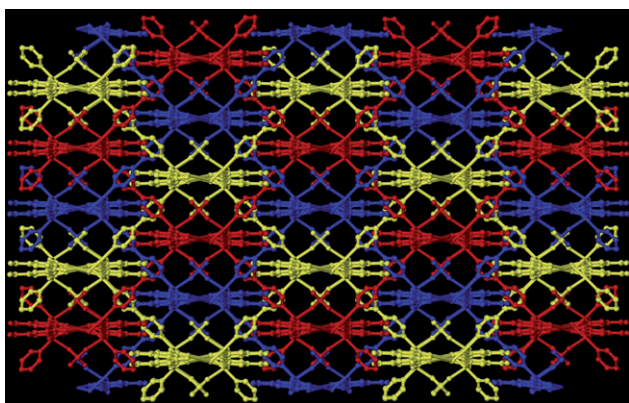
Fig. 4 The 3D three-fold interpenetrating framework of **1**.

ligands lie about independent inversion centres. To our best knowledge, this is the first example that bpy molecules reside in the channels acting as guest molecules to connect two carboxylate groups through strong hydrogen bonds, although some bpy-templated metal–organic frameworks have been reported.[7,16] Three such frameworks interpenetrate mutually to result in a three-fold interpenetrating 3D framework (Fig. 4). The solvent accessible volume after the removal of the uncoordinated 4,4′-bpy ligand is 19.9% calculated with PLATON/SOLV.[17] If we treat the Cu_4 cluster as a single node and the HBTC and 4,4′-bpy as linear linkers, then complex **1** possesses diamond topology,[18] as shown in Fig. 5.

Crystal structure of $Cu_{1.5}(H_2O)(TMBTC)(bpy)\cdot 1/2H_2O$ (2)

When H_3BTC was replaced by H_3TMBTC in the similar reaction, compound **2** was obtained as green prism crystals, which have a porous 3D interpenetrating framework. Complex **2** crystallizes in the monoclinic $P2/c$ space group. In the crystal structure, there are one and a half copper ions with different coordination environment: Cu1 lies on a twofold axis and is coordinated by two oxygen atoms from different TMBTC ligands and two nitrogen atoms from different bpy in a distorted square planar geometry; while Cu2 is in a general position and coordinated by three oxygen atoms from two TMBTC ligands, one nitrogen atom from bpy and one water molecule in a distorted square pyramidal environment, in which the axial oxygen atom (O6) has a very weak coordination to the metal ion with the
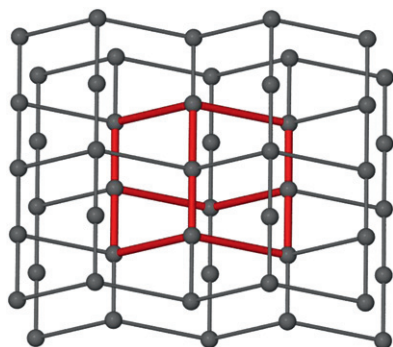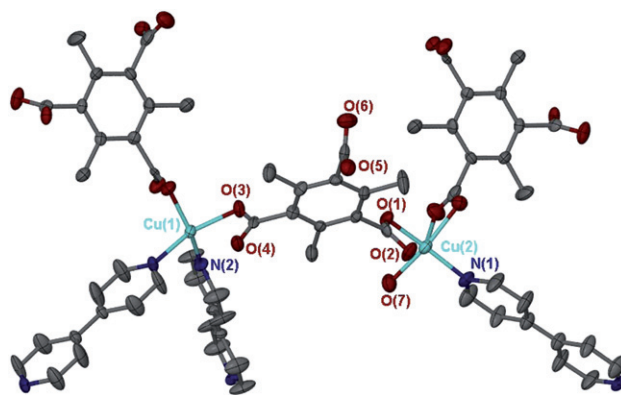

Fig. 6 The coordination environment of the copper ion in complex **2** (thermal ellipsoids: 50%).

Cu–O distance being 2.367 Å (Fig. 6). All the carboxylate groups of TMBTC are deprotonated during the reaction. Two carboxylate groups of TMBTC adopt a mono-dentate coordination mode to connect one copper ion, while the third carboxylate group adopts a chelating mode to chelate one copper ion and the whole ligand acts as a tri-dentate ligand to connect three copper ions. As expected, the three carboxylate groups of TMBTC do not locate in a plane with the central benzene ring. The largest dihedral angle between the carboxylate group and the benzene ring is 85.5° and the average dihedral angle is 75°, which is much larger than those found in MOFs constructed by benzene-1,3,5-tricarboxylic acid (normally 0–30°).

Thus, the copper ions are connected by the TMBTC to result in the formation of a one-dimensional tubular structure with dimensions 5.6 × 5.6 Å (Fig. 7b and c). All the copper ions locate outside of the tube (Fig. 6b) and the four- and five-coordinated copper ions are alternating in the resulting 32-membered ring,
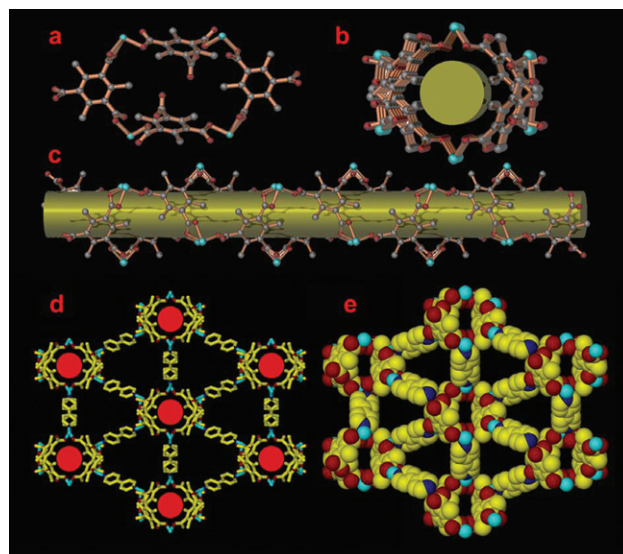

Fig. 7 (a) The 32-membered ring, (b) the 1D hydrophobic tubular structure along the *c* axis and (c) along the *a* axis in **2**. (d) The 3D porous framework along the *c* axis showing the 1D hydrophobic tubular unit was connected by two types of bpy ligands from different directions, (e) space-filling representation of **2** along the *c* axis.

Fig. 5 The diamond topological net of **1** after treating the Cu_4 cluster as a single node.

the nearest Cu–Cu distance being 8.982 Å (Fig. 7a). The methyl groups of the TMBTC ligands point toward the center of the tube which makes the inside of the tube a hydrophobic environment. The tube can be considered as the basic assembly unit, which is further connected by the 4,4′-bpy ligand to form a 3D framework (Fig. 7d and e).

As shown in Fig. 8, there are two types of 4,4′-bpy ligands lying about the inversion centres in the structure, which play different roles in the formation of **2**: one type of 4,4′-bpy (bipy1) connects two Cu2 ions to generate discrete dinuclear copper; while the other one (bipy2) connects the Cu(1) ion to form a 1D zigzag chain structure. Both types of 4,4′-bpy connect the 1D hydrophobic tubular unit from different directions to give rise to the 3D porous framework (Fig. 7d and e). The resulting 3D porous single net possesses 1D trigonal channels along the *c* axis with dimensions 7.6×8.4 Å. The final structure of **2** is a two-fold interpenetrating 3D porous framework, the dimensions along the *c* axis being 5.7×6.7 Å (Fig. 9). The 1D Cu(1)-bpy zigzag chain in one net was just located in the 1D hydrophobic tube of another net. The solvent accessible volume in the desolvated structure is 23.2% calculated from PLATON/SOLV.[17]

Crystal structure of Cd₂(H₂O)₅(TMBTC)(bipy)₂·NO₃·3H₂O (3)

Single crystal X-ray diffraction revealed that complex **3** is a three-dimensional framework. There are two crystallographically independent cadmium atoms (Cd1, Cd2) in the structure:
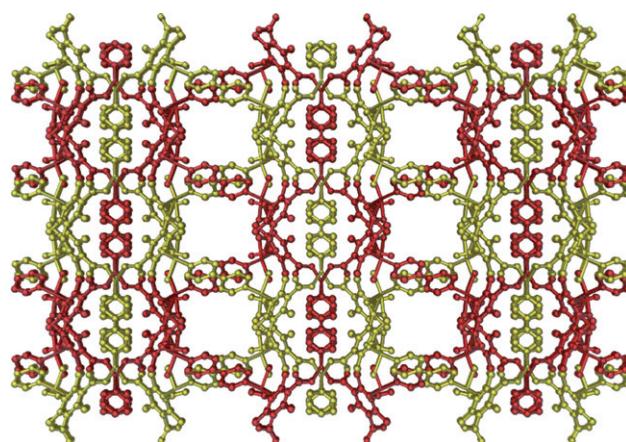

Fig. 9 The 3D two-fold interpenetrating framework of **2**.

Cd1 is coordinated by one carboxyl oxygen atom, two nitrogen atoms from 4,4′-bpy ligands and four coordinated water molecules with average Cd1–O and Cd1–N distances of 2.324 and 2.366 Å, respectively, in an octahedral geometry; Cd2 is coordinated by two carboxyl atoms from different TMBTC ligands, two nitrogen atoms and two coordinated water molecules with average Cd2–O and Cd2–N distances of 2.305 and 2.327 Å, respectively, in an octahedral geometry (Fig. 10). All the carboxylate groups of TMBTC are deprotonated during the reaction. One carboxylate group adopts a monodentate
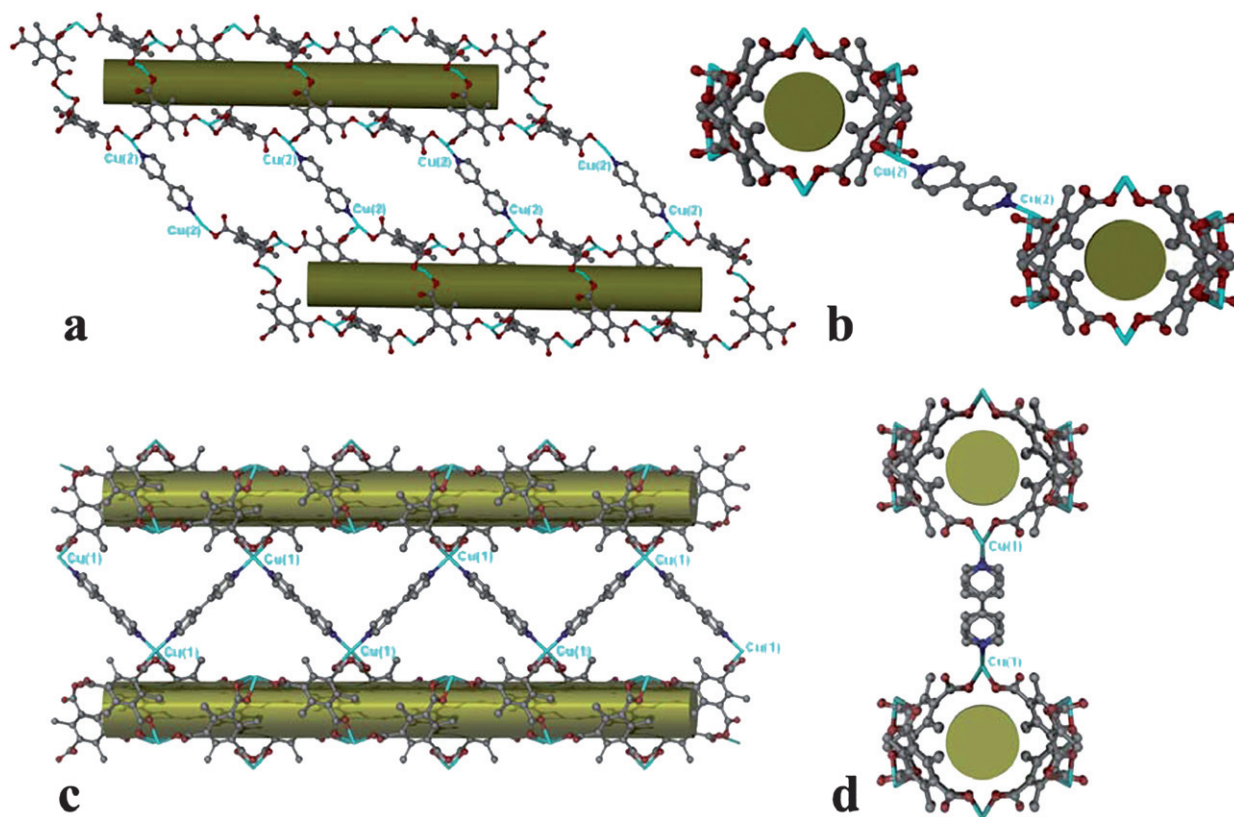

Fig. 8 Two hydrophobic tubular units were connected by bipy1 along the *b* axis (a) and the *c* axis (b) in **2** showing bipy1 connecting Cu(2) ions to form the discrete unit and two hydrophobic tubular units were connected by bipy2 along the *b* axis (c) and the *c* axis (d) in **2** showing bipy2 connecting Cu(1) ions to form an infinite zigzag chain.
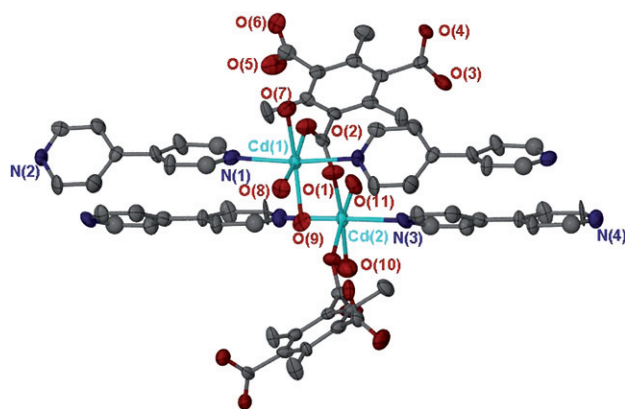
Fig. 10 The coordination environment of the cadmium ions in **3** (thermal ellipsoids: 50%).

coordination mode to connect one cadmium ion, the second one adopts a bidentate bridging coordination mode to bridge two cadmium ions and the third one does not take part in the coordination. As found in **2**, TMBTC is nonplanar, with an average dihedral angle between the carboxylate group and the benzene ring of 81.2°, which is slightly larger than that in **2**.

Thus, Cd1 and Cd2 are first connected by the 4,4′-bpy ligands to give rise to a one-dimensional chain, as shown in Fig. 11. The one-dimensional Cd-4,4′-bpy chain can be considered as the basic building unit of the whole structure, which is quite different from that in **1** and **2**, in which the copper ions are first connected by the carboxylate ligand to form a 1D ladder or tube as the assembly units. The Cd2−4,4′−bpy chains are further infinitely connected by TMBTC to generate a three-dimensional cationic porous framework, in which the Cd2−4,4′−bpy chains are vertical (Fig. 12a). The TMBTC ligand plays the role of 1,3-benzenedicarboxylic acid.

The Cd1−4,4′−bpy chains just locate in the channels fixed by Cd1–O bonds, as shown in Fig. 12b. The counterion ions of NO_3^- and uncoordinated water reside in the channels. The uncoordinated water molecules form strong hydrogen bonds with the uncoordinated carboxyl oxygen atoms with O⋯O distances of 2.568–2.832 Å.

Thermal stability of complexes 1, 2 and 3

The thermal stabilities of complexes **1**, **2** and **3** have been measured. Thermal gravimetric analysis (TGA) showed that **1**, **2** and **3** can be stable up to 300 °C. For complex **1**, there is no weight loss from 50 to 300 °C. We did not find the loss of free 4,4′-bpy before the complex decomposed at 310 °C. For complex **2**, there is a gradual weight loss of 4.9% from 40 to 250 °C, which corresponds to the loss of 0.5 uncoordinated and 1 coordinated water molecules (calcd: 5.1%). After 310 °C, **2** starts to
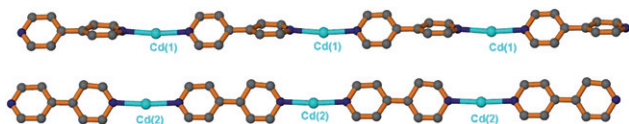

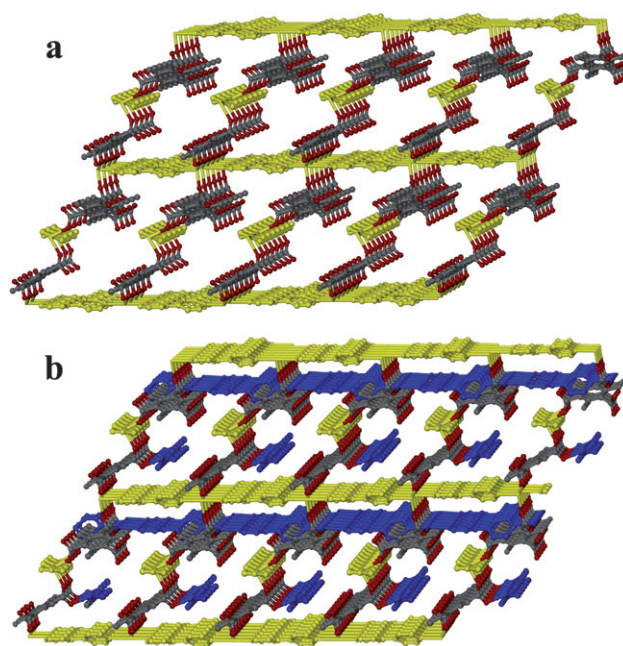**Fig. 11** The 1D Cd-4,4′-bpychains in **3**.

Fig. 12 (a) The 3D porous framework generated by TMBTC connecting Cd2−4,4′−bpy chains and (b) the final 3D framework of **3** showing the Cd1−4,4′−bpy chains locate in the channels. Cd2-bipy: yellow color, Cd1-bipy: blue color.

decompose. For complex **3**, the weight loss of 5.0% from 40 to 130 °C corresponds to the loss of 3 uncoordinated water molecules (calcd: 5.4%). We did not find the loss of coordinated water molecules from 150 to 320 °C, and after that, complex **3** starts to decompose.

Photoluminescence properties of 3

In general, metal coordination significantly influences fluorescence properties in MOFs (compared to organic ligands), an important property to consider when trying to synthesize new luminescent materials. The fluorescence properties **3** were measured at room temperature, and the fluorescent spectra are displayed in Fig. 13. Complex **3** exhibits luminescence at λ_{max} = 405 nm, upon excitation at 350 nm. The emissions **3** can probably
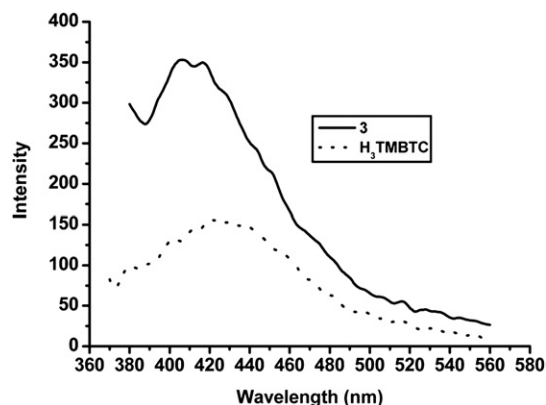

Fig. 13 Solid-state emission spectra of **3** and H_3TMBTC at room temperature.

be assigned to an intraligand $\pi \rightarrow \pi^*$ transition,[19] as free H_3TMBTC possesses similar emission in the solid state. These results imply that the coordination of the TMBTC ligand with cadmium ions has no influence on the emission mechanism of the metal–organic frameworks.[20]

Conclusions

In summary, three metal–organic frameworks have been synthesized and characterized based on H_3BTC and its derivative, H_3TMBTC. In complexes **1** and **2**, the different geometries of the carboxylate ligands (planarity and nonplanarity) induced two different assembly units (1D ladder and tube), which were further connected by 4,4′-bpy ligands in different directions to give rise to the final 3D frameworks. In complex **3**, the cadmium ions were first connected by 4,4′-bpy ligands to form a 1D infinite chain as the assembly unit, which was further linked by TMBTC to generate the 3D structure, quite different from that in **1** and **2**. Further studies on synthesizing other MOFs with this nonplanar carboxylate ligand are currently underway.

Experimental

Materials and physical measurements

All chemicals used are as purchased without purification. Thermogravimetric experiments were performed using a TGA/SDTA851 instrument (heating rate of 10 °C min^{-1}, nitrogen stream). Elemental analyses (C, H, N) were obtained on a Perkin-Elmer 240 elemetal analyzer. Photoluminescence spectra were performed on a Perkin Elmer LS 50B luminescence spectrometer.

Preparation

Synthesis of $Cu_4(OH)_2(SO_4)(HBTC)_2(bpy) \cdot bpy \cdot 3H_2O$ (1). A mixture of $CuSO_4 \cdot 5H_2O$ (20 mg, 0.08 mmol), H_3BTC (10 mg, 0.047 mmol) and 4,4′-bpy (10 mg, 0.06 mmol) was suspended in mixed solvents of EtOH (5 ml) and H_2O (5 ml), and heated in a Teflon-lined steel bomb at 180 °C for 12 h. The green crystalline precipitate formed was collected, washed with water and dried in the air (yield: 30%).

Synthesis of $Cu_{1.5}(H_2O)(TMBTC)(bpy) \cdot 1/2H_2O$ (2). A mixture of $CuSO_4 \cdot 5H_2O$ (20 mg, 0.08 mmol), H_3TMBTC (10 mg, 0.04 mmol) and 4,4′-bpy (10 mg, 0.06 mmol) was suspended in a mixed solution of EtOH (5 ml) and H_2O (5 ml), and heated in a Teflon-lined steel bomb at 180 °C for 12 h. The green crystalline precipitate formed was collected, washed with water and dried under air (yield: 35%). Elemental analysis calcd (%) for **2**: C 50.07, H 3.82, N 5.31; found: C 52.26, H 3.98, N 4.67%.

Synthesis of $Cd_2(H_2O)_5(TMBTC)(bipy)_2 \cdot NO_3 \cdot 3H_2O$ (3). A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (20 mg, 0.06 mmol), H_3TMBTC (10 mg, 0.05 mmol) and 4,4′-bpy (10 mg, 0.06 mmol) was suspended in the mixed solution of H_2O (8 ml) and EtOH (8 ml), and heated in a Teflon-lined steel bomb at 180 °C for 3 d. The colorless crystals of **3** were collected, washed with water and dried in the air (yield: 45%). Elemental analysis calcd (%) for **3**: C 38.72, H 4.16, N 7.06; found: C 37.53, H 4.64, N 7.59%.

Crystal structure determinations

Crystallographic data for **1–3** were collected on a Bruker Smart 1000 CCD diffractometer with Mo Kα ($\lambda = 0.71073$ Å) at room temperature. All structures were solved by the direct method using the SHELXS program of the SHELXTL package and refined by the full-matrix least-squares method with SHELXL.[21] The metal atoms in each complex were located from the E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The organic hydrogen atoms were generated geometrically (C-H 0.96 Å).

Crystal data for **1**: $C_{38}H_{26}Cu_4N_4O_{18}S$, $M = 1112.85$, monoclinic, space group $C2/c$, $a = 33.5656(8)$, $b = 6.6676(2)$, $c = 21.2236(5)$ Å, $\beta = 126.7420(10)°$, $U = 3806.26(17)$ Å^3, $Z = 4$, $D_c = 1.942$ mg m^{-3}, μ(Mo Kα) = 2.350 mm^{-1}, $T = 273$ K, 12823 reflections collected. Refinement of 2738 reflections (306 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0607$, $wR2 = 0.1577$, gof = 1.091. Crystal data for **2**: $C_{22}H_{18}Cu_{1.5}N_2O_{7.5}$, $M = 525.69$, monoclinic, space group $P2/c$, $a = 18.8020(17)$, $b = 8.5577(8)$, $c = 16.0542(16)$ Å, $\beta = 99.469(7)°$, $U = 2548.0(4)$ Å^3, $Z = 4$, $D_c = 1.370$ mg m^{-3}, μ(Mo Kα) = 1.313 mm^{-1}, $T = 273$ K, 20774 reflections collected. Refinement of 4349 reflections (307 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0935$, $wR2 = 0.2151$, gof = 1.009. Crystal data for **3**: $C_{32}H_{41}Cd_2N_5O_{17}$, $M = 992.50$, monoclinic, space group Cc, $a = 14.500(5)$, $b = 18.577(5)$, $c = 15.394(5)$ Å, $\beta = 103.97(3)°$, $U = 4024(2)$ Å^3, $Z = 4$, $D_c = 1.638$ mg m^{-3}, μ(Mo Kα) = 1.134 mm^{-1}, $T = 273$ K, 13780 reflections collected. Refinement of 6452 reflections (505 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0493$, $wR2 = 0.1270$, gof = 1.071. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: 675166 for **1**, 675167 for **2** and 687867 for **3**.

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