

Preparation, Crystal Structure, and Properties of Five Metal-Organic Complexes Based on a Triangular Nonplanar Carboxylate Ligand

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Keywords: Metal-organic frameworks / Hydrothermal synthesis / Ligand effects / Photoluminescence / Crystal growth

A nonplanar triangular carboxylate ligand has been synthesized and applied to assemble metal-organic frameworks under hydro- or solvothermal conditions. Five new metal-organic complexes, $[\text{H}_2\text{N}(\text{CH}_3)_2]_2[\text{Cd}(\text{HTMBTC})_2] \cdot 2\text{H}_2\text{O} \cdot \text{dmf}$ (**1**), $[\text{Cu}_3(\text{TMBTC})_2(2,2'\text{-bpy})_2] \cdot \text{H}_2\text{O}$ (**2**), $[\text{Zn}_3(\text{TMBTC})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**3**), $[\text{Cd}_3(\text{TMBTC})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (**4**), and $[\text{Cu}_3(\text{TMBTC})_2]$ (**5**), (dmf = dimethylformamide; TMBTC = 2,4,6-trimethylbenzene-1,3,5-tricarboxylic acid; bpy = bipyridine) were crystallized; they possess four different structural types. In **1**, the nonplanar carboxylate ligand connects the cadmium ion to give rise to a 2D (4,4) topological layer that contains two vertical left- and right-handed helical chains. In **2**, the carboxylate ligands first link the copper ions to generate a 1D tubular unit, which can be considered the basic building

block. The 1D tubular units are further connected by the ligand to form a 2D layer structure. Complexes **3** and **4** have similar structural types. The zinc and cadmium ions are connected by the ligand to form a bilayer framework that contains double (6,3) topological nets. Different from complexes **1–4**, complex **5** has a 3D framework. The copper ions are first connected by the ligand to generate a bilayer structure that contains double (6,3) nets, which are further connected by sharing the copper ion to form the final 3D framework. Photoluminescence measurements of **1**, **3**, and **4** in the solid state at room temperature show that all three coordination networks exhibit similar, strong luminescence, which can be assigned to an intraligand $\pi \rightarrow \pi^*$ transition.

Introduction

The rational assembly of metal-organic complexes from organic carboxylate ligands is currently of significant interest because the carboxylate ligand can not only provide a number of coordination sites to coordinate to metal ions through coordinative bonds, but also act as hydrogen-bonding acceptors or donors to further extend low-dimensional frameworks to high-dimensional architectures through hydrogen-bonding interactions.^[1–5] However, the rational design and synthesis of novel metal-organic frameworks (MOFs) with desired topologies based on carboxylate ligands is still a great challenge to chemists since many factors, such as ligand geometry, metal ion, and solvent, influence the final structure of an MOF.^[6,7]

Over the past decades, many metal-organic frameworks with desired topologies and interesting properties con-

structed from 1,4-benzenedicarboxylic acid (H_2BDC) and 1,3,5-benzenetricarboxylic acid (H_3BTC) have been designed and synthesized.^[8,9] Among these MOFs, the carboxylate groups and the central benzene rings in BDC and BTC almost locate in a plane, which make BDC and BTC planar ligands. As is commonly known, the organic ligand is one of the important factors in determining the ultimate structure and the planarity of the organic ligand and has a significant effect on the topologies of the final structure.^[10] For instance, nonplanar 4,4',4''-benzene-1,3,5-triyltribenzoate (BTB) and planar 4,4',4''-s-triazine-2,4,6-triyltribenzoic acid (TATB) are two similar tricarboxylate ligands, but they can result in two different structures with quite different gas-adsorption properties due to the different geometries of the organic ligands.^[11] Hence, novel metal-organic frameworks with interesting topologies could be constructed by applying nonplanar derivatives of BDC or BTC, for example, 2,3,5,6-tetramethylterephthalic acid (H_2TMBDC) or 2,4,6-trimethylbenzene-1,3,5-tricarboxylic acid (H_3TMBTC), which can be synthesized through the introduction of an organic group in the carbon atoms beside the carboxylate groups.^[12] The carboxylate groups in this nonplanar organic ligand can change the linking direction of the whole ligand when they coordinate to metal ions in bidentate bridging coordination mode. This change of ligand geometry may result in the formation of novel MOFs different from those constructed from the planar BTC ligand. In this

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejic.201000364>.

full paper, we report five metal-organic complexes, $[\text{H}_2\text{N}(\text{CH}_3)_2]_2[\text{Cd}(\text{HTMBTC})_2] \cdot 2\text{H}_2\text{O} \cdot \text{dmf}$ (**1**), $[\text{Cu}_3(\text{TMBTC})_2(2,2'\text{-bpy})_2] \cdot 2\text{H}_2\text{O}$ (**2**), $[\text{Zn}_3(\text{TMBTC})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**3**), $[\text{Cd}_3(\text{TMBTC})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (**4**), and $[\text{Cu}_3(\text{TMBTC})_2]$ (**5**) (dmf = dimethylformamide; TMBTC = 2,4,6-trimethylbenzene-1,3,5-tricarboxylic acid; bpy = bipyridine), which have been constructed from the triangular nonplanar TMBTC ligand.

Results and Discussion

Crystal Structure of $[\text{H}_2\text{N}(\text{CH}_3)_2]_2[\text{Cd}(\text{HTMBTC})_2] \cdot 2\text{H}_2\text{O} \cdot \text{dmf}$ (**1**)

X-ray single-crystal diffraction revealed that complex **1** has a two-dimensional layer structure. The asymmetric unit consists of half a cadmium ion, one TMBTC ligand, one protonated dimethylamine, one uncoordinated water molecule, and half of a dmf molecule. As shown in Figure 1, the central cadmium ion is coordinated by eight oxygen atoms from four different TMBTC ligands, with the average Cd–O distance being 2.426(6) Å. Two of the three carboxylate groups of the TMBTC ligand are deprotonated during the reaction and adopt a chelating coordination mode to coordinate to one cadmium ion. The third carboxylate group is protonated and does not take part in the coordination (Scheme 1), which is different from other complexes because of the drop of acid and the decomposition of the dmf solvent at high temperature (methanoic acid). As expected, the TMBTC ligand is nonplanar and the average dihedral angle between the carboxylate group and the benzene ring is 90.4°. Thus, the cadmium ions are connected by the monoprotonated TMBTC ligands to result in the formation of a two-dimensional anionic layer with the nearest Cd–Cd distance being 8.293 Å. The protonated carboxylate groups of TMBTC point out of the layer. Two protonated dimethylamine cations from the hydrolyzation of dmf locate in the lattice to balance the charge, as found in other complexes.^[13] If we consider the monoprotonated TMBTC ligand as a two-connected linker and the cadmium ion as a four-connected node, then the resulting two-dimensional layer possesses a (4,4) net (or 4⁴-sq).^[14,15]

There are several kinds of helical chains in the (4,4) topological layer along different directions. First, the TMBTC ligands connect the cadmium ions along the *a* axis to generate a 2₁ single right-handed helical chain with the nearest Cd–Cd distance being 9.338 Å. The 2₁ single right-handed helical chains connect each other by sharing cadmium ions to result in the two-dimensional layer. Every two adjacent 2₁ single right-handed helical chains constitute a 4₁ double helical chain by sharing the cadmium ions. The resulting 4₁ helical chain possesses the same chirality as the 2₁ right-handed helical one, as shown in parts a and b of Figure 2. Both the right-handed 2₁ single and 4₁ double helical chains are along the *a* axis and the helical axes sit in the *ab* plane. There exist similar left-handed 2₁ single and 4₁ double helical chains along the *b* axis, and the helical axes also sit in the *ab* plane (Figure 2, c and d). These two kinds of helical

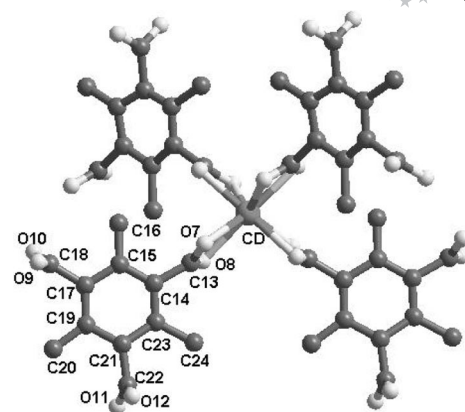
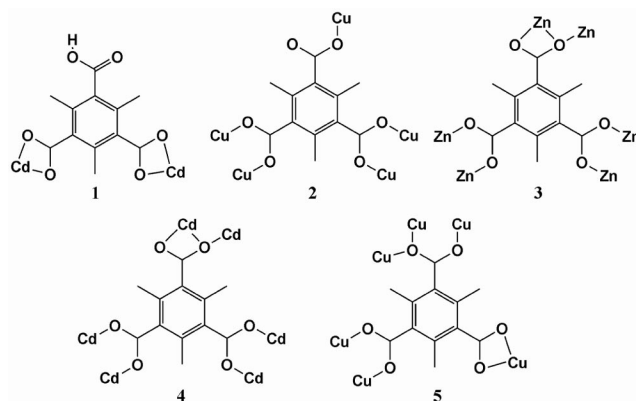


Figure 1. The coordination environment of the central cadmium ion in **1**.



Scheme 1. The coordination modes of TMBTC in **1–5**.

chains along different axes are vertical to each other, thus, the whole structure is achiral. To the best of our knowledge, complex **1** represents the first example of two kinds of left- and right-handed 2₁ single and 4₁ double helical chains running along different directions (*a* and *b* axis) to constitute the two-dimensional (4,4) topological layer (Figure 2, e).

Crystal Structure of $[\text{Cu}_3(\text{TMBTC})_2(2,2'\text{-bpy})_2] \cdot 2\text{H}_2\text{O}$ (**2**)

X-ray single-crystal diffraction revealed that **2** crystallizes in the triclinic $P\bar{1}$ space group and has a two-dimensional layer structure. There are two kinds of copper ions that possess different coordination environments in complex **2**. As shown in Figure 3, Cu1 is coordinated by one chelating 2,2'-bpy molecule and three oxygen atoms from different TMBTC ligands in a square-pyramidal geometry with the average Cu1–N and Cu1–O distances being 2.008(5) and 2.065(4) Å, respectively, whereas Cu2 is coordinated by four oxygen atoms from different TMBTC ligands in a square-planar geometry with the Cu2–O distance being 1.969(1) Å. These two kinds of copper ions play different roles in the formation of the layer structure. The

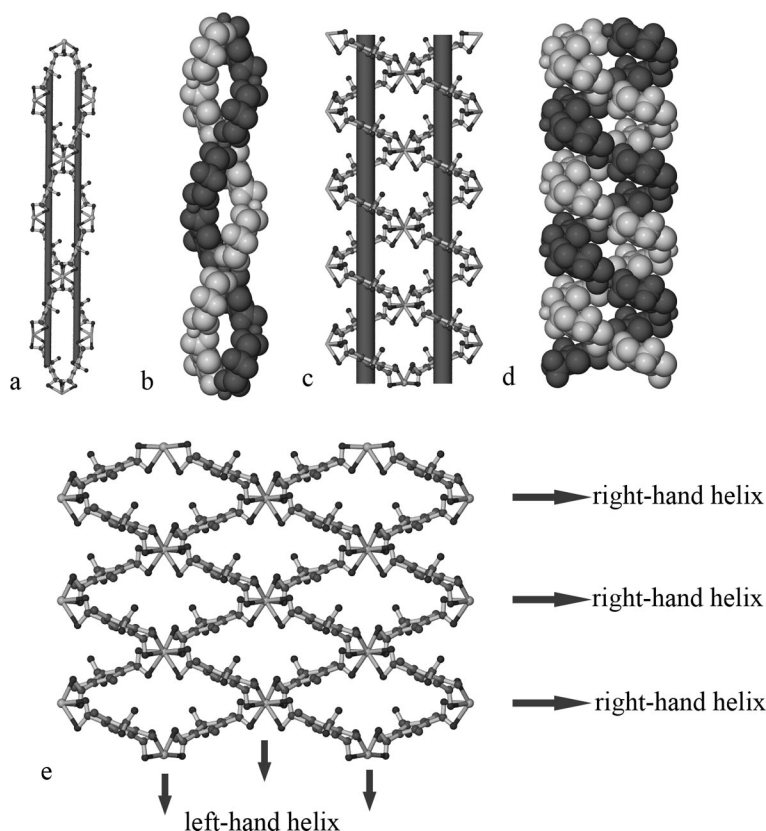


Figure 2. The right-handed (a) 2_1 single and (b) 4_1 double helical chains along the a axis; (c) and (d) along the b axis; and (e) the resulting (4,4) topological layer generated by these two kinds of vertical helical chains.

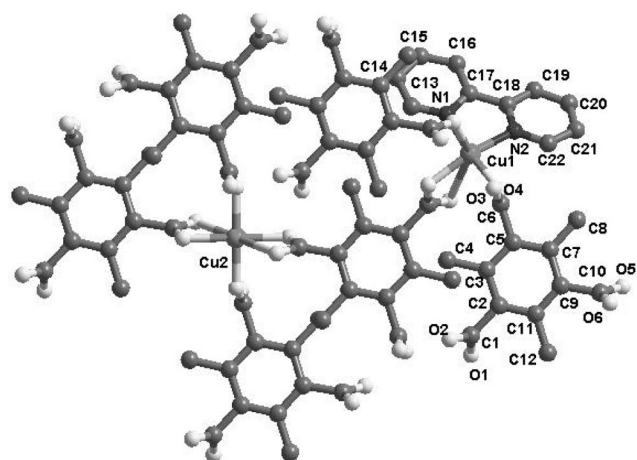


Figure 3. The coordination environment of copper ions in complex **2**.

Cu1 ions were first connected by the deprotonated TMBTC ligand to form a one-dimensional tubular building block with the dimensions of $7.0 \times 3.4 \text{ \AA}$, in which every carboxylate group of TMBTC adopts a monodentate coordination mode to coordinate to Cu1 ion (Scheme 1). The remaining coordination sites of the Cu1 ion are occupied by the chelating 2,2'-bpy ligand. The nearest Cu2–Cu2 distance is 8.361 \AA . The 1D tubular building blocks are further connected together by Cu1 and the bridging carboxylate groups of TMBTC, thus producing a two-dimensional framework with the Cu1–Cu2 distance being 3.90 \AA (Figure 4).

The TMBTC ligand is also nonplanar in **2**. The average dihedral angle between the carboxylate group and the benzene ring is 88.4° , which is slightly smaller than that in **1**. All the coordinated 2,2'-bpy ligands locate above or below the 2D layer, and the $\pi \cdots \pi$ stacking (3.50 \AA) between the coordinated 2,2'-bpy ligands in different layers further ex-

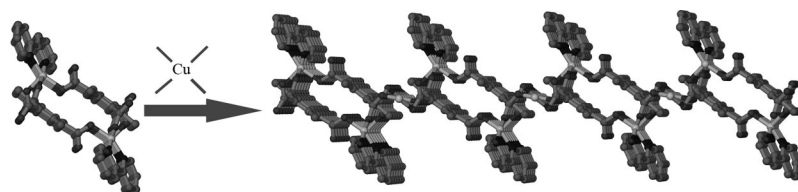


Figure 4. The 1D tubular building block (left) and the 2D layer (right) generated by sharing the four-coordinate Cu1 ion.

tends the 2D layer into a 3D supramolecular architecture with the distance between the layers being 10.217 Å (Figure 5).

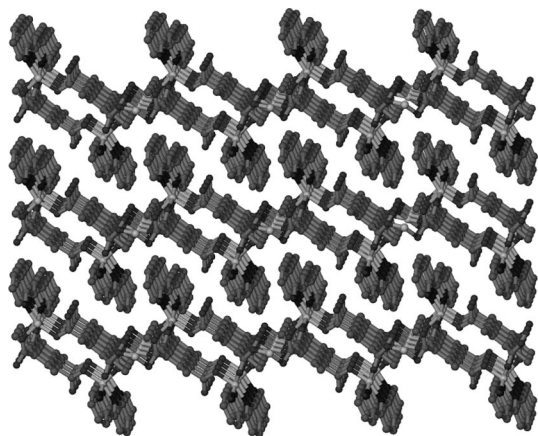


Figure 5. The 3D supramolecular architecture of **2** along the *a* axis.

Crystal Structure of $[\text{Zn}_3(\text{TMBTC})_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**3**) and $[\text{Cd}_3(\text{TMBTC})_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$ (**4**)

X-ray single-crystal diffraction revealed that complexes **3** and **4** have a similar two-dimensional framework with the trinuclear “hourglass” zinc or cadmium clusters as the secondary building unit. Complex **3** crystallizes in the monoclinic $C2/m$ space group, whereas complex **4** crystallizes in the triclinic $P\bar{1}$ space group. Figure 6 (a) shows the coordination environment of central zinc or cadmium ions in **3** and **4**. In complex **3**, Zn1 is coordinated by five oxygen atoms, four from three μ_2 -bridging carboxylate groups and one from a coordinated water molecule, in a distorted trigonal

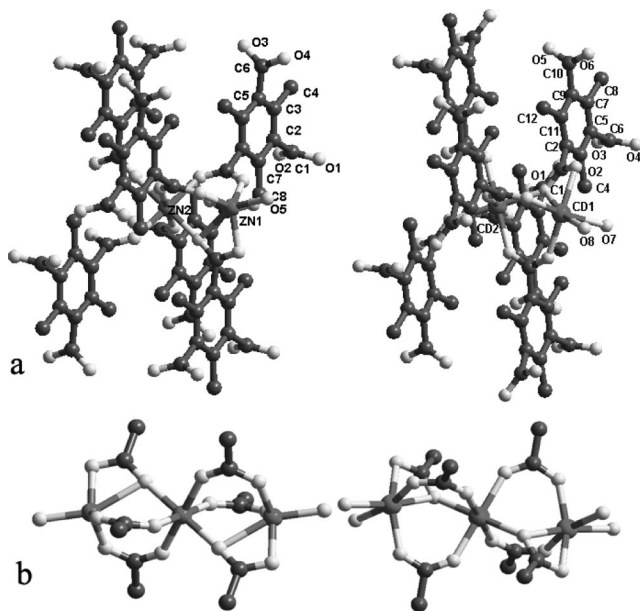


Figure 6. (a) The coordination environment of central ions in **3** and **4**; (b) the “hourglass” SBUs in **3** and **4** (omitting the ligands for clarity).

nal bipyramidal geometry with the average Zn–O distance being 2.095(7) Å. One oxygen atom of one μ_2 -bridging carboxylate group has a very weak coordination to the Zn1 ion with a Zn1–O distance of 2.444(7) Å. Zn2 is coordinated by six carboxyl oxygen atoms from different TMBTC ligands in an octahedral geometry with the average Zn–O distance being 2.075(6) Å. In complex **4**, Cd1 is coordinated by six oxygen atoms, four from three μ_2 -bridging carboxylate groups and two from two coordinated water molecules, in an octahedral geometry. The average Cd–O distance is 2.288(3) Å. Cd2 is coordinated by six carboxyl oxygen atoms from different TMBTC ligands in an octahedral geometry with the average Cd–O distance being 2.265(2) Å.

The whole TMBTC ligand acts as a μ_6 -bridge in **3** and **4** through two bidentate bridging carboxylates and one chelating-bridging carboxylate to link six zinc or cadmium ions (Scheme 1). The secondary building units (SBUs) for **3** and **4** are a trinuclear zinc or cadmium “hourglass” cluster (Figure 6, b), in which three zinc or cadmium ions are engaged by six carboxylate groups, four possessing bidentate bridging coordination modes and two possessing chelating-bridging coordination modes. The “hourglass” SBUs are connected by six TMBTC ligands to extend in the *ab* plane to give rise to a two-dimensional bilayer framework (Figure 7, a and b). The two layers are staggered with each other, thus there is no cavity in the bilayer. If we view the TMBTC as a three-connected linker and the Zn1 or Cd1 as a three-connected node, then the bilayer possesses double (6,3) nets and the two layers are connected to each other by sharing the Zn2 or Cd2 ion, as shown in Figure 7 (c, d).

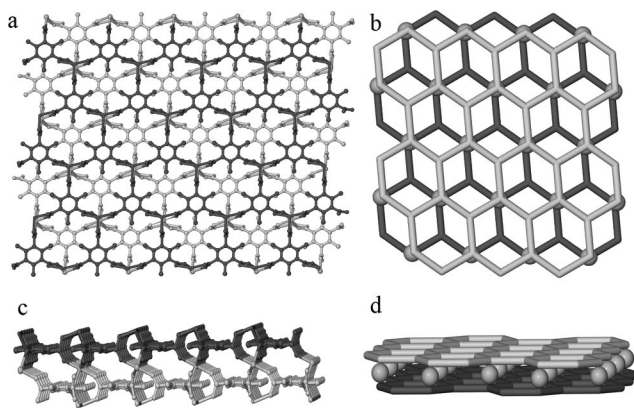


Figure 7. (a and b) The 2D bilayer framework of **3** or **4** (the coordinated water molecules in Zn1 or Cd1 were omitted for clarity). (c and d) Schematic representations of the double (6,3) nets of **3** and **4**.

Recently, many metal-organic frameworks that possess a two-dimensional bilayer structure or are constructed from “hourglass” SBUs have been designed and reported.^[10,14] Although a two-dimensional bilayer cobalt(II) metal-organic framework that possesses a double (4,4) net has been documented,^[16] no two-dimensional bilayer metal-organic framework that possesses double (6,3) nets has been reported. We believe that the key to connecting the “hourglass” cluster with a special shape to form the unique 2D

bilayer is the nonplanar characteristic of the TMBTC ligand. The three carboxylate groups of TMBTC in **3** and **4** are almost vertical with the central benzene ring, and the average dihedral angles between the carboxylate group and the benzene ring are 90.1 and 76.4° for **3** and **4**, respectively. To the best of our knowledge, complexes **3** and **4** are the first examples of a unique two-dimensional bilayer MOF that possesses double (6,3) nets constructed from “hour-glass” SBUs and a triangular carboxylate ligand.

In the 2D bilayer, all the coordinated water molecules in zinc or cadmium ions point out away from the layer and provide the hydrogen-bonding donors. The hydrogen-bonding interactions between the coordinated water molecules and the coordinated carboxyl oxygen atoms (O...O distance: 2.702 for **3**; 2.744 and 2.739 Å for **4**) in different layers further link the 2D bilayer into a 3D supramolecular architecture, as shown in Figure 8. The uncoordinated water molecules locate between the bilayers by forming hydrogen bonds with the coordinated carboxyl oxygen atom or coordinated water molecules (O...O distance: from 2.627 to 2.893 Å).

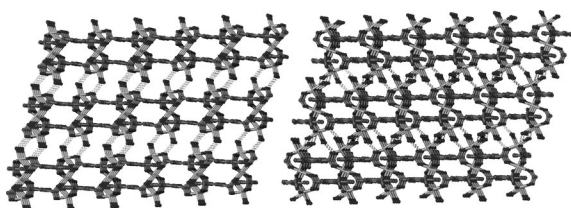


Figure 8. The 3D supermolecular architectures of **3** (left) and **4** (right) generated by the hydrogen-bonding interactions.

It is well known that temperature has a significant effect on the formation of the coordination polymer complexes with different structures.^[17] The reaction of the same ratio of starting materials at different temperatures may induce various complexes with different structural topologies. Like $[\text{Cd}_2(\text{H}_2\text{O})_5(\text{TMBTC})(4,4'\text{-bpy})_2]\cdot\text{NO}_3\cdot 3\text{H}_2\text{O}$ reported in our previous work,^[12b] complex **4** was obtained under the same conditions except the reaction temperatures were 140 °C and not 180 °C. As mentioned above, they have quite different structures: complex **4** is a 2D double (6,3) net without 4,4'-bpy ligands in the SBUs, whereas $[\text{Cd}_2(\text{H}_2\text{O})_5(\text{TMBTC})(4,4'\text{-bpy})_2]\cdot\text{NO}_3\cdot 3\text{H}_2\text{O}$ is a 3D framework with 1D Cd-4,4'-bpy chain SBUs. The structural difference between two complexes results from the different temperatures used in the synthesis. Complex **4** was synthesized at 140 °C and is controlled by kinetics to form the structure most easily; whereas $[\text{Cd}_2(\text{H}_2\text{O})_5(\text{TMBTC})(4,4'\text{-bpy})_2]\cdot\text{NO}_3\cdot 3\text{H}_2\text{O}$ was obtained at 180 °C and is mainly induced by thermodynamics to give rise to the most stable arrangement. As an N-donor ligand, 4,4'-bpy always exhibits excellent coordination ability. However, the TMBTC ligand displays much more competitive coordination ability than the 4,4'-bpy ligand at lower temperatures. As mentioned above, however, the 4,4'-bpy ligand proves its coordination competence at higher temperature.

Crystal Structure of $[\text{Cu}_3(\text{TMBTC})_2]$ (**5**)

Unlike complexes **1–4**, which possess 2D layers, complex **5** has a 3D framework. There are one-and-a-half copper ions and one TMBTC ligand in the asymmetric unit. Figure 9 shows the coordination environment of central copper ions (Cu1 and Cu2) in **5**. Cu1 is coordinated by four carboxyl oxygen atoms from different TMBTC ligands in a square-planar geometry with an average Cu1–O distance of 1.958(19) Å, and Cu2 is coordinated by five carboxyl oxygen atoms from four different TMBTC ligands in a square pyramidal geometry with an average Cu2–O distance of 2.008(19) Å, which is quite similar to those in complex **2**. All the carboxylate groups of TMBTC are protonated during the reaction with one carboxylate adopting bidentate chelating, one adopting bidentate bridging, and the remainder adopting μ_3 -bridging coordination modes (Scheme 1). Similar to that found in complexes **1–4**, the TMBTC is also nonplanar with the average dihedral angle between the carboxylate groups with the benzene ring of 84.9°.

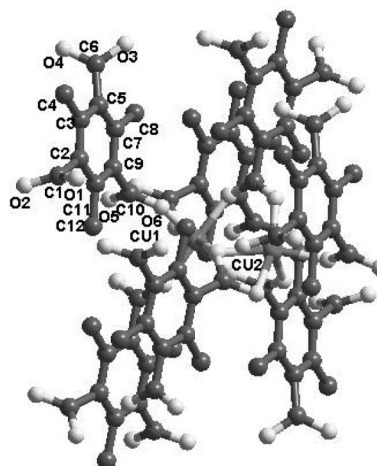


Figure 9. The coordination environment of copper ions in **5**.

The Cu2 ions are first connected by the deprotonated TMBTC ligand to form a one-dimensional tubular building block with dimensions of 5.0×3.9 Å (Figure 10), which is quite similar to that found in complex **2**. The one-dimensional tubular units are connected to each other infinitely by the μ_2 -carboxyl oxygen atom to complete the square pyramidal geometry of the Cu2 ions, thus producing a two-dimensional bilayer framework that contains a Cu_2O_2 four-membered ring, with the nearest Cu2–Cu2 distance being 3.166 Å. The 2D bilayer framework contains double (6,3) nets connected by a Cu2–O bond (Figure 11). The double (6,3) nets are slightly different from that in complex **3** and **4**, in which the two (6,3) nets are connected by sharing the coordinated metal ions. The 2D bilayers are further connected together by the combinations of four-coordinate Cu1 and the bridging carboxylate groups of TMBTC, thereby producing a three-dimensional framework that contains 1D infinite Cu–(OOC–R) chains (Figure 11, e) with the nearest Cu1–Cu2 distance being 3.37 Å (Figure 10).

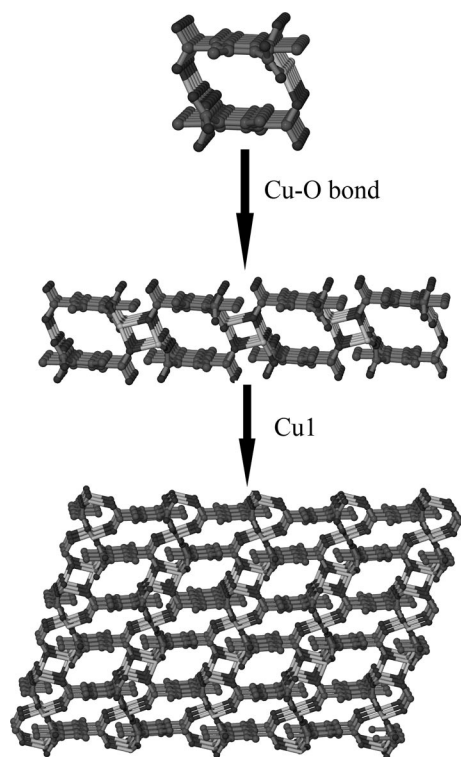


Figure 10. Hierarchical formation of the 3D framework of **5** from the tubular unit.

Meanwhile, coordination compounds with novel structures and/or characteristic properties can be created by adding auxiliary ligands.^[18] When the mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 4,4'-bpy, and H_3TMBTC was suspended in the solvent of H_2O and EtOH (1:1) and heated at 180 °C for one day, a 3D twofold interpenetrating framework $[\text{Cu}_{1.5}(\text{H}_2\text{O})(\text{TMBTC})(4,4'\text{-bpy})] \cdot 0.5\text{H}_2\text{O}$ was obtained.^[12b] When just 4,4'-bpy was removed from the whole reaction system, complex **5** could be produced. As a result of the absence of 4,4'-bpy in the SBUs, the final structure was totally changed. If 4,4'-bpy were replaced by 2,2'-bpy ligand under the same

conditions, complex **2** could be synthesized. But the reaction time and solvent might affect the purity and the yield of the final products.

Effect of Nonplanar Ligands on the Structures

As expected, the three carboxylate groups of TMBTC in the five complexes do not locate in a plane with the central benzene ring. The largest dihedral angle between the carboxylate group and the benzene ring is 89° 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°).^[19] In particular, with TMBTC bridging two metal ions, the location of the central benzene ring in the whole ligand greatly affects the arrangement of the atoms in final architectures.

Thermal Stability of Complexes 1–5

Thermogravimetric analysis (TGA) has been carried out on complexes **1–5**. A TGA study on an as-isolated crystalline sample of **1** shows a 2.1% weight loss from 50 to 150 °C, which corresponds to the loss of one uncoordinated water molecule (calcd. 2.3%). The second gradual weight loss of 21.4% from 180 to 300 °C corresponds to the loss of one uncoordinated water and two dmf molecules and two protonated dimethylamine molecules (calcd. 19.8%). Beyond 310 °C, **1** starts to decompose. For complex **2**, the weight loss of 1.5% from 50 to 170 °C corresponds to the loss of one uncoordinated water molecule (calcd. 1.78%). There is no further weight loss from 170 to 300 °C, and beyond that temperature, **2** starts to decompose. For complex **3**, the gradual weight loss of 7.5% from 50 to 240 °C is equal to the loss of one uncoordinated and two coordinated water molecules (calcd. 7.2%). There is no further loss from 250 to 450 °C, and beyond that temperature, **3** starts to decompose. For complex **4**, from 50 to 150 °C, there is a weight loss of 13.5%, which corresponds to the

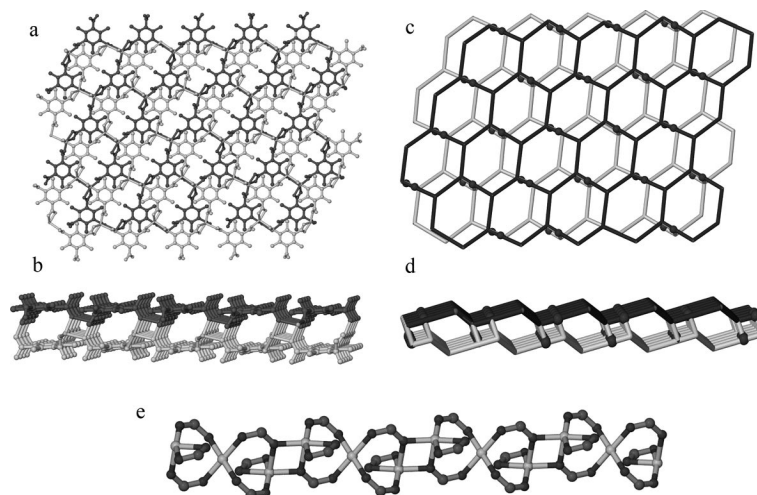


Figure 11. (a and b) The bilayer structure in **5** that possesses double (6,3) nets in light/dark colors. (c and d) Schematic representations of the double (6,3) nets. (e) The infinite Cu-(OOC-R) chain that exists in **5**.

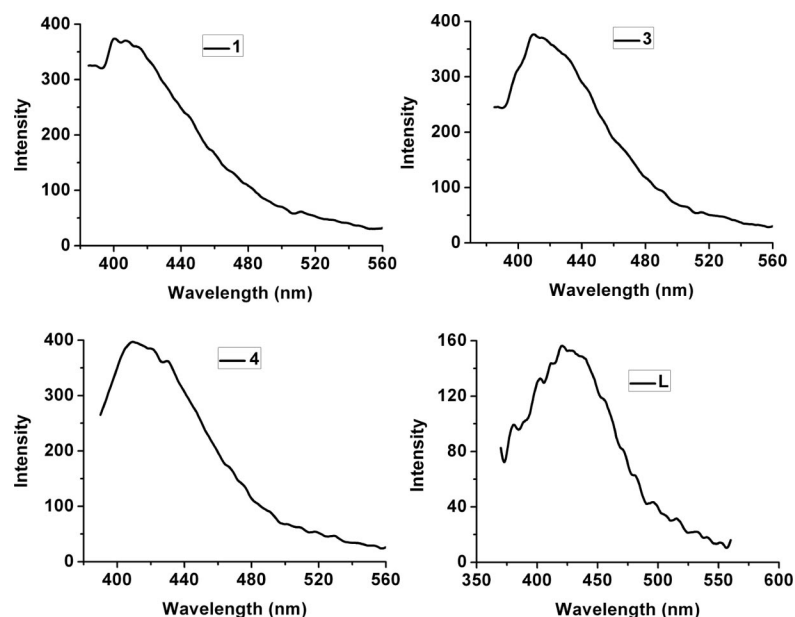


Figure 12. Solid-state emission spectra of free H_3TMBTC (L), **1**, **3**, and **4**.

loss of eight water molecules including four coordinated water molecules (calcd. 14.7%). There is no weight loss from 150 to 350 °C. For complex **5**, there is no weight loss from 50 to 370 °C, and beyond that temperature, **5** starts to decompose.

Photoluminescence Properties of **1**, **3**, and **4**

On the basis of current research on luminescent MOFs, the emission of coordination networks can be assigned to a ligand-to-metal charge transfer (LMCT),^[20] metal-to-ligand charge transfer (MLCT),^[21] or to an intraligand $\pi \rightarrow \pi^*$ transition. Metal coordination significantly influences fluorescence properties in MOFs (compared to organic ligands), an important property to consider when trying to synthesize new luminescent materials.

Photoluminescence measurements of **1**, **3**, and **4** in the solid state at room temperature show that all three coordination networks exhibit similar, strong luminescence at $\lambda_{\max} = 400$, 410, and 409 nm, respectively, upon excitation at 350 nm (Figure 12). These emissions can be assigned to an intraligand $\pi \rightarrow \pi^*$ transition, as free H_3TMBTC possesses similar emissions in the solid state ($\lambda_{\max} = 420$ nm), though about 2.5 times weaker than that of coordination networks. These observations suggest that the coordination of the TMBTC ligand with Zn^{2+} or Cd^{2+} ions has no influence on the emission mechanism of the metal-organic coordination polymers;^[22] the increase in the intensity of the intraligand fluorescent emission from the coordination of the TMBTC ligand to the metal ion is due to an increase in the rigidity of the ligand that reduces the nonradiative decay of the intraligand excited state.^[23]

Conclusion

By applying a triangular nonplanar carboxylate ligand, H_3TMBTC , to assemble with metal ions, five two- or three-

dimensional metal-organic complexes have been hydro- or solvothermally synthesized and characterized. All compounds possess different structural topologies from those constructed using planar 1,3,5-benzenetricarboxylic acid. We believe the special topologies in complexes **1–5** [for example, the double (4,4) net] derive from the ligand geometry of TMBTC, in which all the carboxylate groups are almost vertical with the central benzene ring. Our results further indicate that the organic ligand plays an important role in the construction of MOFs, and any change, even a subtle change of the ligand geometry, may result in the formation of novel MOFs.

Experimental Section

General: All chemicals used are as purchased without purification. Thermogravimetric experiments were performed with a TGA/SDTA851 instrument (heating rate of 10 °C min⁻¹, argon stream). Elemental analyses (C,H,N) were obtained with a Perkin–Elmer 240 elemental analyzer. Photoluminescence spectra were performed with a Perkin–Elmer LS 50B luminescence spectrometer.

Preparation

Synthesis of 1: A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (20 mg, 0.06 mmol), H_3TMBTC (10 mg, 0.05 mmol), and 1,3-bis(4-pyridyl)propane (10 mg, 0.05 mmol) was suspended in the mixed solvent of DMF (8 mL) and EtOH (4 mL) with 2 drops of HCl (10%), and heated in a Teflon[®]-lined steel bomb at 180 °C for 2 d. The resulting colorless crystals of **1** (25 mg) were collected and dried at 50 °C (yield 57%). Compound **1** (773.02): calcd. C 44.92, H 5.91, N 5.24; found C 45.25, H 5.48, N 5.07.

Synthesis of 2: A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (20 mg, 0.08 mmol), H_3TMBTC (10 mg, 0.05 mmol), and 2,2'-bpy (10 mg, 0.06 mmol) was suspended in H_2O (10 mL) and heated in a Teflon[®]-lined steel bomb at 180 °C for 200 min. The green crystals of **2** (19 mg) were collected, washed with water, and dried in the air (yield 47%). Compound **2** (1033.37): calcd. C 51.84, H 3.56, N 5.50; found C 48.78, H 3.30, N 5.04.

Synthesis of 3: A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (20 mg, 0.07 mmol), H_3TMBTC (10 mg, 0.05 mmol), and 4,4'-bpy (10 mg, 0.06 mmol) was suspended in the mixed solvent of H_2O (8 mL) and EtOH (8 mL), and heated in a Teflon[®]-lined steel bomb at 180 °C for 3 d. The resulting colorless crystals of **3** (28 mg) were collected, washed with water, and dried in the air (yield 44%). Compound **3** (807.63): calcd. C 38.51, H 3.23; found C 39.0, H 3.34.

Synthesis of 4: A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (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 solvent of H_2O (8 mL) and EtOH (8 mL), and heated in a Teflon-lined steel bomb at 140 °C for 3 d. The colorless crystals of **4** (14 mg) were collected, washed with water, and dried in the air (yield 51%). Compound **4** (927.68): calcd. C 29.42, H 3.50; found C 26.0, H 3.56.

Synthesis of 5: A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (20 mg, 0.08 mmol) and H_3TMBTC (10 mg, 0.05 mmol) was suspended in H_2O (15 mL), and heated in a Teflon[®]-lined steel bomb at 180 °C for 7 h. The green crystals of **5** (11 mg) were collected, washed with water, and dried in the air (yield 39%). Compound **5** (689.00): calcd. C 41.84, H 2.63; found C 42.2, H 2.55.

X-ray Structural Crystallography: Crystals of **1–5** mounted on glass fiber were studied with a Bruker SMART APEXII CCD Detector single-crystal X-ray diffractometer with a graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) source at 25 °C. 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. 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: $\text{C}_{28}\text{H}_{38}\text{CdN}_2\text{O}_{14}$; $M_r = 739.00$; monoclinic; space group $C2/c$; lattice constants $a = 16.7343(3) \text{ \AA}$, $b = 8.29270(10) \text{ \AA}$, $c = 25.2054(4) \text{ \AA}$; $\beta = 99.5090(10)^\circ$; $U = 3449.76(9) \text{ \AA}^3$; $Z = 4$; $D_c = 1.423 \text{ Mg m}^{-3}$; $\mu(\text{Mo-K}_\alpha) = 0.698 \text{ mm}^{-1}$; $T = 293 \text{ K}$; 20157 reflections collected. Refinement of 3858 reflections (205 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0728$ ($R1$ all data = 0.0818), $wR2 = 0.2014$ ($wR2$ all data = 0.2083), $\text{GoF} = 1.115$.

Crystal data for 2: $\text{C}_{44}\text{H}_{34}\text{Cu}_3\text{N}_4\text{O}_{14}$; $M_r = 1033.37$; triclinic; space group $P\bar{1}$; lattice constants $a = 8.7487(2) \text{ \AA}$, $b = 10.2172(2) \text{ \AA}$, $c = 11.8831(2) \text{ \AA}$; $\alpha = 88.3680(10)^\circ$, $\beta = 69.4470(10)^\circ$, $\gamma = 86.8800(10)^\circ$; $U = 993.06(3) \text{ \AA}^3$; $Z = 1$; $D_c = 1.728 \text{ Mg m}^{-3}$; $\mu(\text{Mo-K}_\alpha) = 1.672 \text{ mm}^{-1}$; $T = 293 \text{ K}$; 9179 reflections collected. Refinement of 4216 reflections (298 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0246$ ($R1$ all data = 0.0276), $wR2 = 0.0690$ ($wR2$ all data = 0.0712), $\text{GoF} = 0.882$.

Crystal data for 3: $\text{C}_{24}\text{H}_{35}\text{O}_{18}\text{Zn}_3$; $M_r = 807.63$; monoclinic; space group $C2/m$; lattice constants $a = 15.7546(5) \text{ \AA}$, $b = 9.1186(3) \text{ \AA}$, $c = 11.6314(4) \text{ \AA}$; $\beta = 105.653(2)^\circ$; $U = 1608.99(9) \text{ \AA}^3$; $Z = 2$; $D_c = 1.667 \text{ Mg m}^{-3}$; $\mu(\text{Mo-K}_\alpha) = 2.295 \text{ mm}^{-1}$; $T = 293 \text{ K}$; 10266 reflections collected. Refinement of 1982 reflections (116 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0519$ ($R1$ all data = 0.0832), $wR2 = 0.1490$ ($wR2$ all data = 0.1689), $\text{GoF} = 1.096$.

Crystal data for 4: $\text{C}_{24}\text{H}_{30}\text{Cd}_3\text{O}_{17}$; $M_r = 927.68$; triclinic; space group $P\bar{1}$; lattice constants $a = 9.05490(10) \text{ \AA}$, $b = 9.34590(10) \text{ \AA}$, $c = 11.54420(10) \text{ \AA}$; $\alpha = 88.7520(10)^\circ$, $\beta = 69.2450(10)^\circ$, $\gamma = 63.2570(10)^\circ$; $U = 804.660(14) \text{ \AA}^3$; $Z = 1$; $D_c = 1.914 \text{ Mg m}^{-3}$; $\mu(\text{Mo-K}_\alpha) = 2.037 \text{ mm}^{-1}$; $T = 293 \text{ K}$; 14636 reflections collected. Refinement of 3695 reflections (209 parameters) with $I > 1.5\sigma(I)$

converged at final $R1 = 0.0246$ ($R1$ all data = 0.0265), $wR2 = 0.0734$ ($wR2$ all data = 0.0748), $\text{GoF} = 1.123$.

Crystal data for 5: $\text{C}_{24}\text{H}_{18}\text{Cu}_3\text{O}_{12}$; $M_r = 689.00$; monoclinic; space group $P2_1/c$; lattice constants $a = 8.32500(10) \text{ \AA}$, $b = 9.36240(10) \text{ \AA}$, $c = 15.39170(10) \text{ \AA}$; $\beta = 105.24^\circ$; $U = 1157.45(2) \text{ \AA}^3$; $Z = 2$; $D_c = 1.977 \text{ Mg m}^{-3}$; $\mu(\text{Mo-K}_\alpha) = 2.802 \text{ mm}^{-1}$; $T = 293 \text{ K}$; 16167 reflections collected. Refinement of 2642 reflections (178 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0295$ ($R1$ all data = 0.0317), $wR2 = 0.0902$ ($wR2$ all data = 0.0918), $\text{GoF} = 1.061$.

Supporting Information (see also the footnote on the first page of this article): TGA curves and powder X-ray diffraction patterns for complexes **1–5**.

CCDC-705082 (for **1**), -705083 (for **2**), -705084 (for **3**), -705085 (for **4**), and -705086 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We gratefully thank the financial support of the National Science Foundation of China (90922014, 20701025), the National Science Foundation of Shandong Province (Y2008B01, BS2009CL007), and Shandong University.

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Received: April 1, 2010

Published Online: September 3, 2010