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Article

# Metal-Organic Frameworks Constructed from 2,4,6-Tris(4-pyridyl)-1,3,5-triazine

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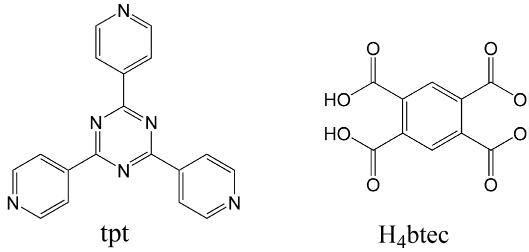
Five new metal-organic frameworks based on 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) ligand have been hydrothermally synthesized. Reaction of tpt and $AgNO_3$ in an acidic solution at 180 °C yields $\{[Ag(Htpt)(NO_3)]NO_3 \cdot 4H_2O\}_n$ (**1**). Ag(I) is trigonally coordinated by two pyridyl nitrogen and one nitrato oxygen to form a 1D zigzag chain. Reaction of tpt with $CuSO_4$ affords $\{[Cu_2(tpt)_2(SO_4)_2(H_2O)_2] \cdot 4H_2O\}_n$ (**2**). Copper(II) is bonded to two pyridyl nitrogen, two sulfato oxygen, and two water oxygen atoms to form an elongated octahedral geometry. Each $H_2O$ ligand bridges two copper(II), whereas sulfate bridges copper(II) via $\mu$-1,3 and $\mu$-1,1 fashions. The copper(II)−sulfate−$H_2O$ 2D layers are linked by bidentate tpt to form a 3D polymeric structure. Reaction of $Cu(SO_4)_2$, tpt, and 1,2,4,5-benzenetetracarboxylic acid ($H_4$btec) in the presence of piperidine gives $[Cu(tpt)(H_2btec)_{1/2}]_n$ (**3**). Copper(I) is located in a trigonal-pyramidal coordination environment and coordinated by three pyridyl nitrogen of tpt in a plane, whereas a carboxylate oxygen is coordinated to the copper(I) axially. The tpt−Cu forms a layer, and the layers are linked through $H_2btec^{2-}$ to form a 2D double-layered coordination polymer. Replacing $CuSO_4$ with $ZnI_2$ in the synthesis gives $\{[Zn(tpt)(btec)_{1/2}] \cdot H_2O\}_n$ (**4**). Zinc(II) is in a distorted tetrahedral geometry and linked through bidentate tpt and exotetradentate $btec^{4-}$ to form a 2D coordination grid. Reaction of tpt with CuCN leads to the assembly of a 3D metal-organic framework $[Cu_3(CN)_3(tpt)]_n$ (**5**). Copper(I) is trigonally coordinated by one pyridyl nitrogen and two cyanides to form an intriguing honeycomb architecture. Luminescence study shows that **1**, **3**, **4**, and **5** have blue fluorescence, which can be assigned to be ligand-centered emissions. Thermal analysis shows that all of these complexes are quite stable, and especially for **4**, the framework is stable up to 430 °C.

## Introduction

Metal-organic frameworks are of great interest due to their intriguing structural motifs and potentials for development of magnetic, luminescent, porous, and catalytic materials.[1] Much effort has been focused on the design and controlled synthesis of metal-organic frameworks. Multipyridyl and polycarboxylate ligands have received considerable attention, owing to the variety of their coordination modes and structural features.[2] Analogous to the well-known 4,4′-bipyridine ligand, the trigonal 3-connector 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt, Scheme 1) is of special interest in recent years, as this essentially planar ligand has afforded

**Scheme 1**



tpt H$_4$btec

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a number of unusual and highly symmetrical polynuclear complexes and metal-organic frameworks.[3] Its rigidity and trigonal geometry can lead to the formation of nanosized cages[4] and porous frameworks enclosing cavities,[5] chambers,[6] and channels.[7] Because tpt is an exotridentate ligand, the nitrogen atoms of three pyridyl groups tend to bind different metal atoms. For example, by using tridentate tpt ligand to link a linear coordination polymer such as 1D CuCN chain, nanoporous framework may be expected.[8] Although tpt is an excellent organic ligand and much work has been done on metal−tpt binary frameworks, the metal−tpt ternary frameworks containing other organic ligands are still less reported.

Tpt can form not only polymeric metal-organic frameworks,[9] but also structurally peculiar small supramolecular systems. The supramolecules, which can be squares, helices, cages, or rectangles, are of particular interest because of their potential applications in host−guest interaction, molecular recognition, and molecular sensors.[10] Complexes of Pd(en)($NO_3$)$_2$/Pd(bpy)($NO_3$)$_2$ with tpt in a ratio of 6:4 have been shown to strongly bind a variety of neutral guests in their aggregate forms.[4b,5b,c,11] Drug−host system, drug-delivery device, or encapsulation and controlled release in supramolecular assemblies are also very interesting applications of host−guest chemistry.[12] Previously, we have reported the host−guest interactions of a tpt cage complex with several guest molecules.[13] Herein, we present the synthesis and structures of five tpt metal-organic frameworks as well as their thermal stabilities and luminescent properties.

## Experimental Section

**General.** Tpt was prepared according to a previously published method with some modifications.[14] Other chemicals were of reagent grade and used without further purification. Elemental analyses (carbon, hydrogen, and nitrogen) were carried out on a Vario EL III elemental analyzer. Metal analyses were performed on an Oxford INCA-2000 energy dispersive spectroscopy (EDS), which was fixed on a JEOL JSM-6700F scanning electron microscope. Infrared spectra (KBr pellets) were recorded on a Nicolet A370 FTIR spectrophotometer. Thermal analyses were performed on a Netzsch STA 449C thermal analyzer from 20 to 800 °C at a heating rate of 10 °C $min^{-1}$ in air. Fluorescent spectra of crystalline samples were recorded on a Shimadzu RF-5301 PC spectrophotometer.

**Synthesis of tpt.** 18-crown-6 (1.0 g, 3.8 mmol) and KOH (0.225 g, 4.0 mmol) were dissolved in 10 mL ethanol and stirred for 10 min. The solution was concentrated to remove solvent under reduced pressure to give an oil product. To this oil, 10 g of 4-cyanopyridine was added. The mixture was heated at 220 °C. The color changed to red within a short period of time. After stirring at this temperature for 4 h, the mixture was cooled to room temperature, and then 30 mL pyridine was added. Stirring the mixture for several minutes gave the fine crystal compound that was filtrated off and washed with pyridine (25 mL twice) and toluene (25 mL). The pale-red crystals were dissolved in 2 mol $L^{-1}$ HCl (60 mL). After removing small amount solid by filtration, adjusting the solution to slight alkaline using concentrated $NH_3$ aqueous gave a pale-white powder that was filtrated, washed with water, and dried in air to afford 6.1 g of tpt in 61% yield. A simplified procedure for synthesis of tpt is as follows: 18-crown-6 (1.0 g, 3.8 mmol) and KOH (0.225 g, 4.0 mmol) were dissolved in 5 mL methanol with stirring for 10 min. The solution was concentrated to remove methanol in a hood. To this oil, 10 g of 4-cyanopyridine was added. The mixture was transferred into a 25 mL Teflon-lined stainless steel reactor and heated at 200 °C for 7 h. After cooling to room temperature, the solid was washed with water and dried in air to afford 6.5 g of tpt in 65% yield.

**Synthesis of $\{[Ag(Htpt)(NO_3)]NO_3\cdot 4H_2O\}_n$ (1).** A mixture of tpt (0.10 mmol), $AgNO_3$ (0.30 mmol), and 2 drops concentrated $HNO_3$ in 8 mL water was sealed in a 15 mL Teflon-lined stainless steel reactor. The reactor was held at 180 °C for 48 h to produce colorless needle crystals. The crude product was washed with water to give product **1** in 43% yield based on tpt. Anal. Calcd for $C_{18}H_{21}AgN_8O_{10}$: C, 35.02; H, 3.43; N, 18.15; Ag, 17.47%. Found: C, 35.39; H, 3.31; N, 17.73; Ag, 16.57%. IR: 3445br, 3037w. 1576m, 1518s, 1382s, 1375s, 1315m, 1059w, 796s, 642m $cm^{-1}$.

**Synthesis of $\{[Cu_2(tpt)_2(SO_4)_2(H_2O)_2]\cdot 4H_2O\}_n$ (2).** A mixture of $CuSO_4\cdot 5H_2O$ (0.20 mmol), tpt (0.20 mmol), and water (10 mL) was sealed in a 15 mL Teflon-lined stainless steel reactor. The reactor was held at 140 °C for 72 h. Dark-green block crystals were obtained in 45% yield. Anal. Calcd for $C_{36}H_{36}Cu_2N_{12}O_{14}S_2$: C, 41.10; H, 3.45; N, 15.98; Cu, 12.08%. Found: C, 39.19; H, 3.31; N, 14.73; Cu, 13.56%. IR: 3427m, 1518s, 1375s, 1151m, 1114m, 1059m, 806s, 642m $cm^{-1}$.

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**Table 1.** Crystallographic Data for **1**−**5**

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| formula | $C_{18}H_{21}AgN_8O_{10}$ | $C_{36}H_{36}Cu_2N_{12}O_{14}S_2$ | $C_{23}H_{14}CuN_6O_4$ | $C_{23}H_{15}N_6O_5Zn$ | $C_{21}H_{12}Cu_3N_9$ |
| fw | 617.30 | 1051.97 | 501.94 | 520.78 | 581.02 |
| cryst syst | monoclinic | orthorhombic | monoclinic | triclinic | orthorhombic |
| space group | $P2_1/n$ | *Pnma* | *C*2/*c* | $P\bar{1}$ | *Pbcn* |
| *a* (Å) | 8.9909(5) | 27.422(2) | 22.7672(17) | 9.6431(9) | 6.8270 (1) |
| *b* (Å) | 25.4622(13) | 26.560(2) | 13.1972(10) | 10.7674(10) | 14.9985(3) |
| *c* (Å) | 10.3609(6) | 11.1115(10) | 13.3665(10) | 11.9459(18) | 21.8388(6) |
| α (deg) | 90 | 90 | 90 | 101.312(2) | 90 |
| *β* (deg) | 92.792(4) | 90 | 100.020(1) | 107.147(2) | 90 |
| *γ* (deg) | 90 | 90 | 90 | 112.500(1) | 90 |
| *V* ($Å^3$) | 2369.1(2) | 8092.9(12) | 3954.9(5) | 1025.7(2) | 2236.18(8) |
| *Z* | 4 | 8 | 8 | 2 | 4 |
| $D_c$ ($g\ cm^{-3}$) | 1.731 | 1.727 | 1.686 | 1.686 | 1.720 |
| $\mu$ ($mm^{-1}$) | 0.922 | 1.241 | 1.153 | 1.251 | 2.854 |
| reflns collected | 15 222 | 40 576 | 10 101 | 5342 | 14 683 |
| unique reflns | 4153 | 7302 | 3507 | 3562 | 1970 |
| GOF | 1.066 | 1.039 | 1.077 | 1.059 | 1.000 |
| R1 ($I > 2\sigma(I)$) | 0.0750 | 0.0453 | 0.0354 | 0.0404 | 0.0373 |
| R2 (all data) | 0.2126 | 0.1119 | 0.0891 | 0.1131 | 0.0944 |
| $\Delta\rho_{max}$ ($e\cdot Å^{-3}$) | 1.161 | 0.874 | 0.279 | 0.438 | 0.379 |
| $\Delta\rho_{min}$ ($e\cdot Å^{-3}$) | −0.584 | −0.775 | −0.391 | −0.810 | −0.295 |

**Synthesis of $[Cu(tpt)(H_2btec)_{1/2}]_n$ (3).** A mixture of $CuSO_4\cdot 5H_2O$ (0.20 mmol), tpt (0.20 mmol), $H_4$btec (0.10 mmol), piperidine (0.40 mmol), and water (10 mL) was sealed in a 15 mL Teflon-lined stainless steel reactor. The reactor was held at 160 °C for 72 h. Dark-red block crystals were obtained in 48% yield. Anal. Calcd for $C_{23}H_{14}N_6O_4Cu$: C, 55.04; H, 2.81; N, 16.74; Cu, 12.66%. Found: C, 54.67; H, 2.90; N, 16.90; Cu, 12.92%. IR: 3056w, 1685w, 1574m, 1514s, 1373s, 1338m, 1053w, 802s, 650m $cm^{-1}$.

**Synthesis of $\{[Zn(tpt)(btec)_{1/2}]\cdot H_2O\}_n$ (4).** Following the procedure described for the preparation of **3**, reaction of $ZnI_2$ (0.20 mmol), tpt (0.20 mmol), $H_4$btec (0.10 mmol), piperidine (0.40 mmol), and water (10 mL) at 110 °C afforded light-yellow block crystals of **4** in 53% yield. Anal. Calcd for $C_{23}H_{15}N_6O_5Zn$: C, 53.05; H, 2.90; N, 16.14; Zn, 12.56%. Found: C, 53.18; H, 2.81; N, 15.77; Zn, 10.47%. IR: 1606s, 1578m, 1518s, 1375s, 1344s, 1057w, 804s, 642m $cm^{-1}$.

**Synthesis of $[Cu_3(CN)_3(tpt)]_n$ (5).** A mixture of CuCN (0.30 mmol), tpt (0.10 mmol), $K_3[Fe(CN)_6]$ (0.30 mmol), and water (8 mL) was sealed in a 15 mL Teflon-lined stainless steel reactor. The reactor was held at 160 °C for 72 h. Orange rhombus crystals were obtained in 50% yield. Anal. Calcd for $C_{21}H_{12}Cu_3N_9$: C, 43.41; H, 2.08; N, 21.69; Cu, 32.81%. Found: C, 43.71; H, 2.35; N, 20.81, Cu, 31.57%. IR: 3039w, 2131m, 1572w, 1516s, 1373s, 1057w, 802s, 652m $cm^{-1}$.

**X-ray Crystallography.** Suitable single crystals of **1**−**5** were selected for X-ray diffraction study. Data collections were performed with graphite-monochromatic Mo Kα radiation ($\lambda$ = 0.71073 Å) on a Bruker Smart Apex-II CCD diffractometer at $T$ = 293(2) K. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and absorption correction were applied. The structures were solved by the direct method and refined by full-matrix least-squares on $F^2$ with *SHELX-97*.[15] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated positions. The crystal data and structural refinement results are summarized in Table 1. The selected bond distances and angles are listed in Table 2.

## Results and Discussion

**Syntheses.** Ligand tpt was synthesized according to the method reported by Anderson[14] but no solvent was added. Excessive 4-cyanopyridine acted as a solvent. At the end of the reaction, some tpt precipitated on the wall of the reactor, which may cause uneven boiling. To prevent this from happening, the reaction can be carried in a Teflon-lined stainless steel reactor. This is a more convenient method to synthesize tpt.

**1**−**5** have been successfully prepared by hydrothermal reactions. Piperidine was used as an organic base in preparing **3** and **4**. It should be mentioned that copper(II) salt was used in the synthetic process for **2** and **3**. There was no redox taking place and it is still copper(II) in **2**. However, in the presence of $H_4$btec, copper(II) was reduced into copper(I) in **3**. Similar redox reactions have been reported. For example, solvothermal reduction of copper(II) in presence of tpt and butylmethyl-imidazolium tetrafluoroborate at 170 °C has been observed.[16] Hydrothermal reduction of copper(II) has also been reported in other systems.[17] **1**−**5** were characterized by IR spectra and elemental analysis, and their structures were confirmed by single-crystal X-ray diffraction analysis.

**Structure of $\{[Ag(Htpt)(NO_3)]NO_3\cdot 4H_2O\}_n$ (1).** In **1**, silver(I) is coordinated by two pyridyl nitrogen and one nitrato oxygen to form a trigonal environment (part a of Figure 1). Two nitrogen atoms coordinate to silver at 2.175(6) and 2.213(6) Å and are stronger than oxygen at 2.486(8) Å. All of the atoms are coplanar. The N4−Ag1−N6 has the largest angle of 145.9(2)°, whereas O1−Ag1−N6 has the smallest angle of 87.2(2)°. This difference may be attributed to the larger bulk of tpt compared with nitrate.

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**Table 2.** Selected Bond Distances (Angstroms) and Angles (Degrees) for **1**−**5**

| | | |
|---|---|---|
| | **1** | |
| Ag(1)−N(4) 2.175(6) | Ag(1)−N(6) 2.213(6) | Ag(1)−O(1) 2.486(8) |
| N(4)−Ag(1)−N(6) 145.9(2) | N(4)−Ag(1)−O(1) 126.7(2) | O(1)−Ag(1)−N(6) 87.2(2) |
| | **2** | |
| Cu(1)−O(1) 1.973(3) | Cu(1)−O(5) 1.984(4) | Cu(1)−N(1) 2.040(3) |
| Cu(1)−N(4) 2.045(3) | Cu(1)−O(11) 2.442(4) | Cu(1)−O(1A) 2.664(3) |
| Cu(2)−N(8) 2.013(3) | Cu(2)−N(12) 2.015(3) | Cu(2)−O(7A) 2.483(3) |
| Cu(2)−O(11) 2.758(4) | Cu(2)−O(10) 1.951(3) | Cu(2)−O(6) 1.988(3) |
| O(1)−Cu(1)−O(5) 165.81(15) | O(1)−Cu(1)−N(1) 89.46(12) | O(5)−Cu(1)−N(1) 91.34(14) |
| O(1)−Cu(1)−N(4) 92.04(12) | O(5)−Cu(1)−N(4) 87.38(14) | N(1)−Cu(1)−N(4) 178.32(13) |
| O(10)−Cu(2)−O(6) 168.44(14) | O(10)−Cu(2)−N(8) 89.77(14) | O(6)−Cu(2)−N(8) 87.49(12) |
| O(10)−Cu(2)−N(12) 89.86(14) | O(6)−Cu(2)−N(12) 93.60(12) | N(8)−Cu(2)−N(12) 176.18(14) |
| O(11)−Cu(1)−O(1) 176.2(1) | O(11)−Cu(2)−O(7A) 168.48(11) | |
| | **3** | |
| Cu(1)−N(4A) 2.027(2) | Cu(1)−N(5A) 2.041(2) | Cu(1)−O(1) 2.350(2) |
| Cu(1)−N(6) 2.058(2) | | |
| N(4A)−Cu(1)−N(5A) 120.77(9) | N(4A)−Cu(1)−N(6) 119.59(8) | N(5A)−Cu(1)−N(6) 115.01(9) |
| N(4A)−Cu(1)−O(1) 98.27(9) | N(6)−Cu(1)−O(1) 93.75(8) | N(5A)−Cu(1)−O(1) 99.40(9) |
| | **4** | |
| Zn(1)−O(3) 1.925(2) | Zn(1)−O(1) 1.955(2) | Zn(1)−N(4) 2.037(3) |
| Zn(1)−N(6) 2.087(3) | O(3)−Zn(1)−O(1) 116.20(10) | O(3)−Zn(1)−N(4) 119.11(11) |
| O(1)−Zn(1)−N(4) 108.88(10) | O(3)−Zn(1)−N(6) 96.61(11) | O(1)−Zn(1)−N(6) 103.23(11) |
| N(4)−Zn(1)−N(6) 110.84(11) | | |
| | **5** | |
| Cu(1)−C(1) 1.825(4) | Cu(1)−C(1A) 1.825(4) | Cu(1)−N(5) 2.146(5) |
| Cu(2)−C(12) 1.905(4) | Cu(2)−N(1C) 1.910(5) | Cu(2)−N(2) 2.057(3) |
| C(1)−Cu(1)−C(1A) 151.1(3) | C(1A)−Cu(1)−N(5) 104.44(13) | C(1)−Cu(1)−N(5) 104.43(13) |
| C(12)−Cu(2)−N(1C) 135.48(18) | C(12)−Cu(2)−N(2) 102.84(17) | N(1C)−Cu(2)−N(2) 121.62(15) |

There is an uncoordinated pyridyl group, which is protonated in each building block tpt. Thus, tpt acts as a bidentate ligand to link silver to form a 1D zigzag chain polymer (part b of Figure 1). The Ag···Ag distance in the 1D chain is 13.367 Å, whereas the Ag···Ag distance between adjacent chains in the same plane is 10.950 Å. The shortest Ag···Ag distance is 4.801 Å in adjacent coordination planes. The distance between adjacent layers is 3.169 Å (Figure S1 in the Supporting Information). This distance is slightly smaller than the $\pi-\pi$ stacking distances of 3.33−3.53 Å reported elsewhere.[18] The shortest $\pi-\pi$ stacking distance reported is 3.27 Å.[19] In this complex, two adjacent tpt layers are quite offset. This gives the reason why the layers separate only about 3.17 Å. Although offset exists in $\pi-\pi$ stacking,[18,19b,20] this short distance should not be considered as the $\pi-\pi$ distance. In this complex, the nearest Ag1···C16 distance of 3.317(9) Å is in the range of the d−$\pi$ interaction of 3.4 Å reported previously.[21] So, we may attribute the very short tpt layer distance to $\pi-\pi$ stacking and d−$\pi$ interactions. The self-assembly of coordination networks from the reaction of 2,4,6-trimesityl-1,3,5-triazine and silver(I) trifluoroacetate reported by Bosch shows Ag−C nonbonding contacts of 3.102 and 3.332 Å. These distances are less than the sum of the van der Waals radii of approximately 3.42 Å. Clearly, these contacts are intermediate in nature.[22] The nonbonding Ag1···C16 distance in **1** is even shorter.

Steel reported a similar complex, a ribbonlike coordination polymer from the reaction of $AgNO_3$ with 1,4-bis(2-pyridyl)buta-1,3-diyne, in which silver(I) is coordinated to two pyridyl nitrogens and one chelating nitrate to form a four-coordinated complex.[23] Two oxygen atoms of the nitrate chelate to silver(I) at 2.570 and 2.642 Å, respectively. In **1**, Ag1−O1 2.486(8) Å is slightly shorter than literature data.[23] However, the Ag1···O2 distance 3.101(8) Å is obviously longer than the normal Ag−O bond distance. Thus, O2 is not coordinated to silver(I). Similar to the complex with the Ag···O (nitrate), the distance of 2.739 Å is considered uncoordinated.[24] For the coordination environment of **1**, the bond distances and angles are similar to that of a trigonal silver(I) complex with two pyridines and a carboxylate oxygen coordination.[24,25] However, the difference is obvious. In **1**, all of the atoms are essentially coplanar, whereas in all its analogues, two pyridines are far away from coplanar.[24–26] In addition, there exists a strong hydrogen-bonding interaction between pyridyl N5 and nitrate O6 with a N5···O6 distance of 2.691(8) Å.

**Structure of $\{[Cu_2(tpt)_2(SO_4)_2(H_2O)_2]\cdot 4H_2O\}_n$ (2).** **2** is a 3D coordination polymer using tpt, sulfate, and $H_2O$ as bridging ligands (part a of Figure 2). Both Cu1 and Cu2 centers are in a typical elongated octahedral coordination environment and coordinate to two pyridyl nitrogens, one

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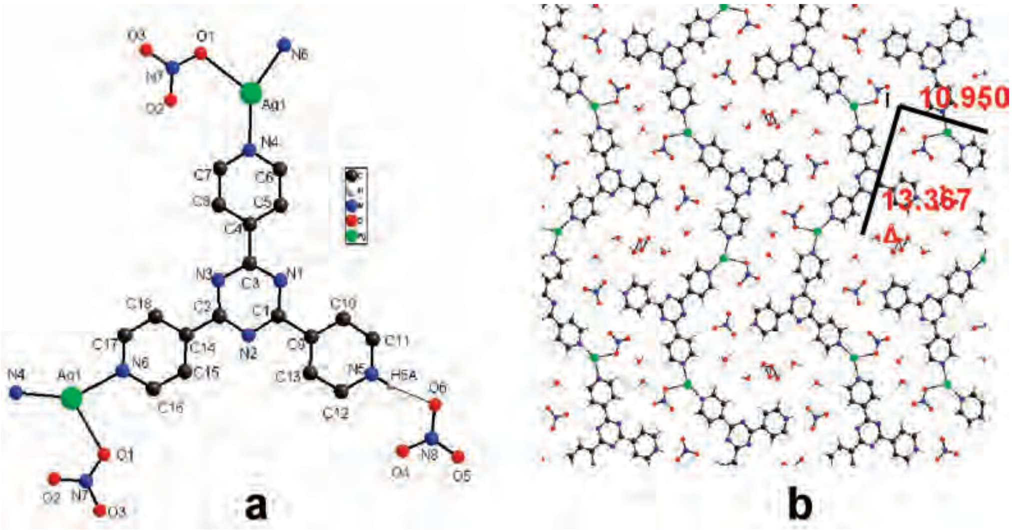

**Figure 1.** (a) Crystal structure of **1**, (b) view of tpt−Ag zigzag chains.

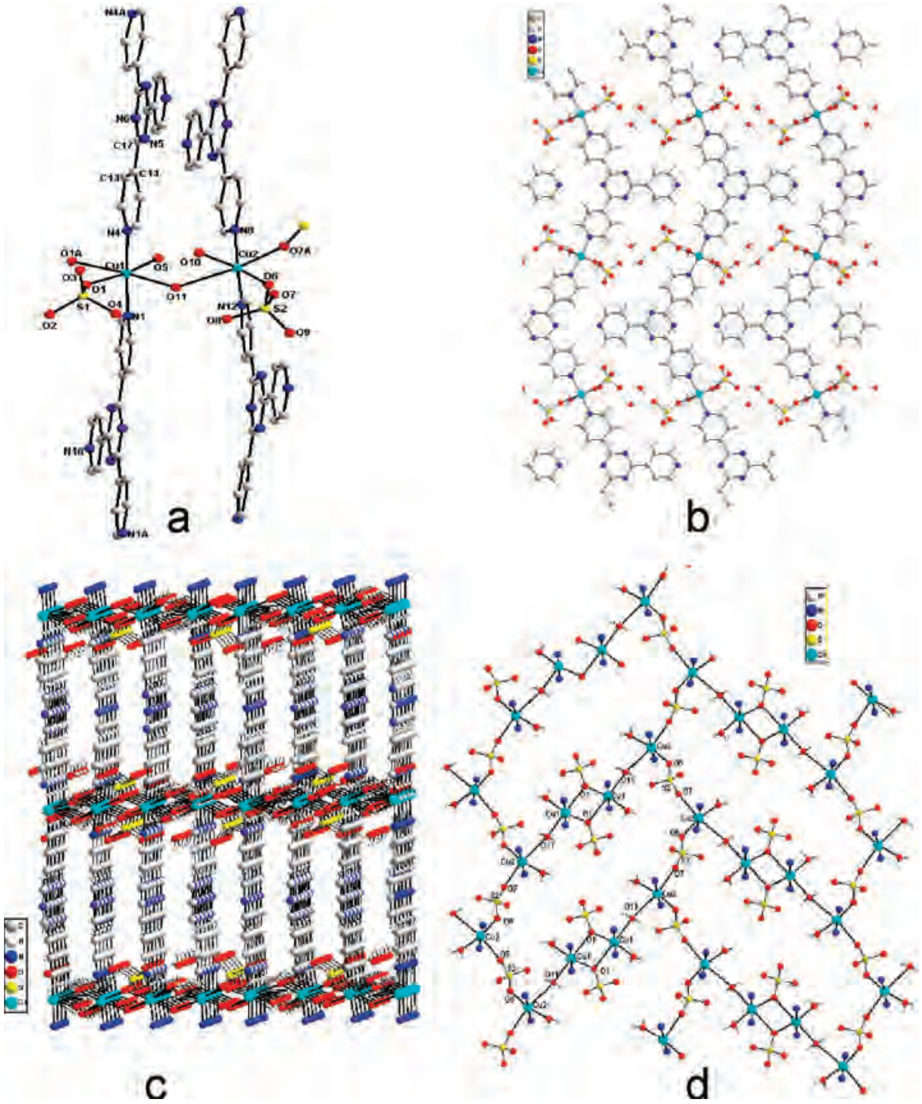

**Figure 2.** (a) Crystal structure of **2**, (b) view of tpt−Cu zigzag chains, (c) view of 3D coordination polymer, and (d) view of sulfate−Cu−$H_2O$ coordination layer.

water oxygen, and one sulfate oxygen in equatorial positions. Bond distances of Cu1−O1 1.973(3) and Cu1−O5 1.984(4) Å show water and sulfate oxygen coordinated to Cu1 stronger than pyridyl nitrogen (Cu1−N1 2.040(3), Cu1−N4 2.045(3) Å). The bond angles of N1−Cu1−N4 and O1−Cu1−O5 are 178.32(13), 165.81(15)°,

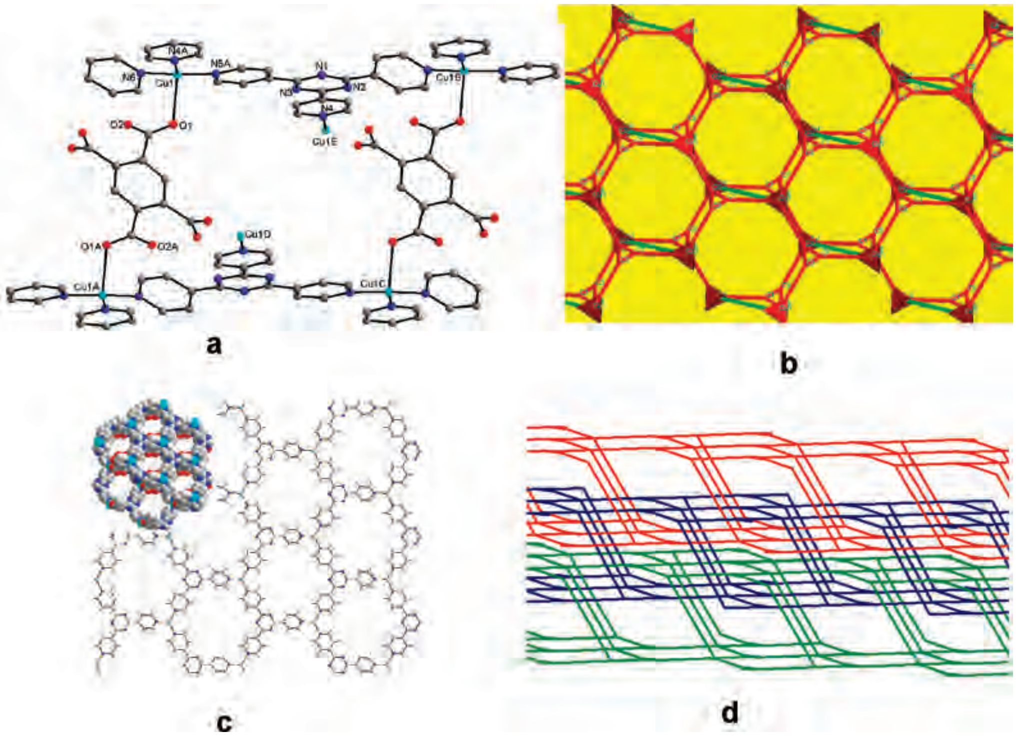

**Figure 3.** (a) Crystal structure of **3**; (b) view of 2D double-layer topologic structure; (c) view of tpt−Cu layer; (d) 2D double-layers interpenetrate into 3D structure (each color represents a double-layered piece).

respectively. Water O11 and sulfate O1A coordinate to Cu1 axially with bond distances of Cu1−O11 2.442(4) and Cu1−O1A 2.664(3) Å and bond angle of O11−Cu1−O1A 176.2(1)°. Water O11 and sulfate O7A coordinate to Cu2 axially with Cu2−O11 2.758(4) and Cu2−O7A 2.483(3) Å. Obviously, water O11 coordinates to Cu1 stronger than Cu2.

Four N-heterocycles of tpt are essentially coplanar, with a maximum torsion angle C13−C14−C17−N6 5.43(55)°. There is still an uncoordinated pyridyl nitrogen in tpt. Tpt acts as a bidentate ligand to link copper to form a zigzag chain as shown in part b of Figure 2. The tpt layers pack together in a way shown in part c of Figure 2. The distance between the layers is 3.43 Å, which is quite normal for a $\pi-\pi$ stacking distance. It can be seen that tpt layers pack not only by $\pi-\pi$ stacking but also in coordination bonds through sulfate and $H_2O$ ligands. The coordination domain forms layers perpendicular to the tpt layers. The coordination layer of sulfate−Cu−$H_2O$ is shown in part d of Figure 2. Cu1 and Cu1 bridged via sulfate O1 forms a diamond core. Cu1···Cu1 distance is 3.539(1) Å. Cu2 and Cu2 are bridged via sulfate O6 and O7; the Cu2···Cu2 distance is 6.517(1) Å.

Predominately, $H_2O$ acts as a monodentate ligand to coordinate metal ions. However, $H_2O$ as a bridging ligand is also quite common. We ran a CCDC search and found 1274 $H_2O$-bridging complexes, of which 83 are copper(II) complexes. In these complexes,[27] the Cu−O bond distance may vary from 1.96 to 2.83 Å and is generally in the range of 2.30−2.52 Å.[28] The Cu−O distances in **2** are 2.442(4) and 2.758(4) Å, suggesting it is a $H_2O$-bridging complex. There are two different sulfates. One sulfate bridges two Cu2 via O6 and O7. The other sulfate bridges two Cu1 via O1. The former 1,3-bridge with a symmetric Cu−O distance 2.43 Å is common.[29] However, in **2**, the 1,3-bridging sulfate is asymmetric with distances of Cu2−O6 1.988(3) Å and Cu2−O7 2.483(3) Å. The 1,1-sulfate bridged complex is uncommon.[30] To our best knowledge, this is the first bis-$\mu$−1,1 coordinated sulfate copper(II) complex.

**Structure of $[Cu(tpt)(H_2btec)_{1/2}]_n$ (3).** The centrosymmetric 1,2,4,5-benzenetetracarboxylate is a good organic building block in constructing metal-organic frameworks. A series of interesting $btec^{4-}$ complexes were reported, such as double-chain $[Cd_4(btec)_2(phen)_4(H_2O)_4]_n$, ladder-like $[Cu_2(btec)(bpy)_2]_n$, and rectangular grid $\{[Cu_2(btec)(H_2O)_4]\cdot 2H_2O\}_n$.[31] $H_4btec$ has four carboxyl groups, which can be completely or partially deprotonated. This makes it very appealing for the design of metal-organic frameworks with interesting structures and properties.

The hydrothermal reaction of $CuSO_4$, tpt, $H_4btec$, and piperidine in a molar ratio of 2:2:1:4 afforded copper(I) complex **3**. As shown in part a of Figure 3, the copper atom is in a trigonal-pyramidal coordination environment and coordinates to three pyridyl nitrogen atoms (from 2.027(2)

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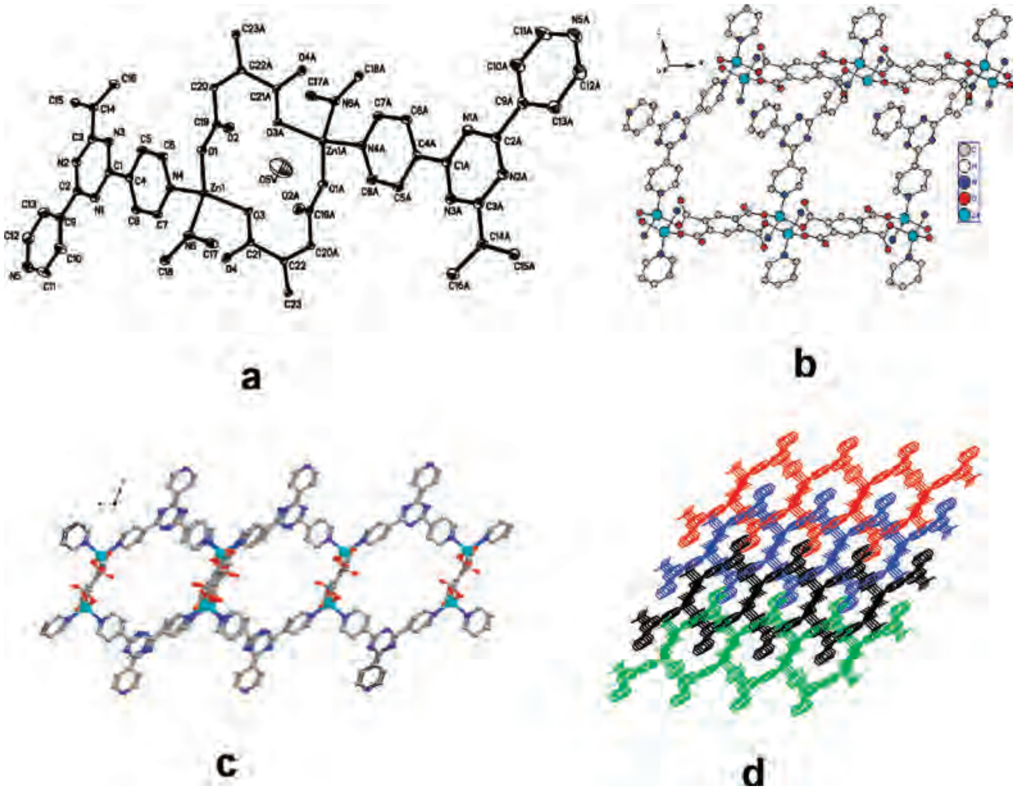

**Figure 4.** (a) Crystal structure of **4**; (b) view of 2D grid; (c) view of hexagonal cavity; (d) 2D coordination polymer packed into 3D structure.

to 2.058(2) Å) and a carboxyl oxygen atom of $H_2btec^{2-}$ at 2.350(2) Å. Each tpt acts as an exotridentate ligand binds to three copper(I) atoms. Two opposite carboxylate groups of $H_2btec^{2-}$ coordinate to two copper(I) atoms in a monodentate mode. The distance between Cu1 and Cu1A is 11.053(6) Å, whereas the distance between Cu1 and Cu1B is 13.197(1) Å. Although Cu−N bond distances are similar to other Cu(I)−tpt complexes, the coordination environments are quite different. All of the reported Cu(I)−tpt complexes are in a tetrahedral coordination environment.[3c,16] In most of the cuprous complexes, copper(I) atoms are in tetrahedral or trigonal coordination environment. Trigonal-pyramidal geometry of copper(I) center is quite rare.

The exotridentate tpt coordinates to copper(I) atoms to form a 2D sheet. Tpt ligands and copper(I) atoms are essentially coplanar with a maximum dihedral angle of 26.46° among pyridyl groups. Copper(I) and its adjacent three pyridyl nitrogen atoms are in the same plane. By occupying the apical position of trigonal-pyramidal geometry, $H_2btec^{2-}$ ligands link two sheets to form an interesting 2D double-layered piece, which is rarely observed in previous reports. This double layer overlaps itself, and the $H_2btec^{2-}$ links two layers in a way shown in part b of Figure 3. Two layers of tpt−Cu are linked by $H_2btec^{2-}$ (green line) via carboxylate oxygen. The small empty triangle is triazine of tpt, and the solid triangle is the copper(I) center. However, the two layers are different in direction as the triazine is arranged in a different way. Each layer forms a honeycomb structure (part c of Figure 3). The approximate diameter of the holes is 0.6 nm. Furthermore, these double layers interpenetrate each other to form a 3D metal-organic framework (part d of Figure 3). The distance between adjacent layers is 3.34 Å, which is slightly smaller than that in **2** (3.43 Å), indicating some $\pi-\pi$ stacking interaction as expected.

**Structure of $\{[Zn(tpt)(btec)_{1/2}]_n \cdot H_2O\}_n$ (4).** Several Zn(II)−tpt complexes have been reported. They are all in a tetrahedral coordination environment.[3a,6b,7a,32] In **4**, the asymmetric unit contains an independent zinc(II) atom, a bidentate tpt, and half of a tetradentate $btec^{4-}$ ligand (part a of Figure 4). Zn1 is in a distorted tetrahedral coordination environment and coordinates to two pyridyl nitrogen and two carboxylate oxygen atoms. The Zn−N bond distances are 2.037(3) and 2.087(3) Å, which are almost the same as the Cu−N distances in **3**. Whereas the Zn−O bond distances are 1.925(2) and 1.955(2) Å, which are clearly much shorter than the Cu−O distance in **3**, indicating the carboxylate oxygen atoms coordinate to zinc(II) much stronger. The coordinated bond angles are in the range of 96.61(11)−119.11(11)°. It should be mentioned that carboxylate O2 is close to Zn1. The Zn1−O2 distance of 2.740 Å shows some weak interaction between O2 and Zn1. Different from **3**, there is a lattice−water molecule in **4**. The distance of 2.790 Å between coordinated carboxylate O3 and water O5w shows some H-bonding interaction.

Similar to **1** and **2**, tpt in **4** acts as a bidentate bridging ligand. One pyridyl group of tpt is free. The uncoordinated pyridine is coplanar with the central triazine, while the coordinated pyridines have torsion angles of about 9° with triazine. Four carboxyl groups of $H_4btec$ are all deprotonated and coordinated to four zinc(II) atoms in a monodentate mode to form a 2D grid but not a double-layered structure

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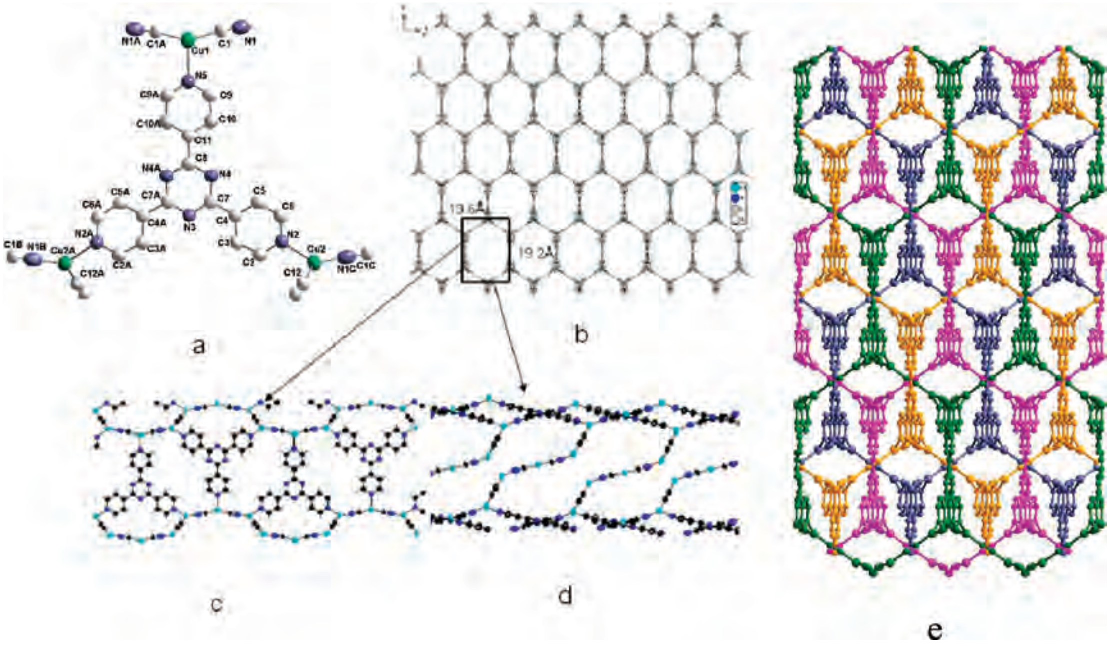

**Figure 5.** (a) Crystal structure of **5**; (b) view of honeycomb network along the *c* axis; (c) side view of the hexagon; (d) top view of the hexagon; (e) 4-fold interpenetrations of the networks (each color represents a honeycomb network).

as that in **3**. However, in **3**, it is exotridentate tpt that binds copper(I) to form 2D layer, and bidentate $H_2btec^{2-}$ links to tpt−Cu layers, whereas in **4** the bidentate tpt can only form a 1D chain with zinc(II). It is the exotetradentate $btec^{4-}$ that links tpt−Zn(II) chains to form a 2D grid (part b of Figure 4). Along the *a* axis, the framework exhibits large hexagonal cavities (part c of Figure 4). In each cavity, two of the six edges are ribbonlike Zn(II)−btec double chains, and the other four edges are built by bidentate tpt ligands. The approximate dimensions of the hexagonal cavity are 1.0 nm × 1.3 nm. The 2D coordination polymer is packed in a way shown in part d of Figure 4. Different from that in **3**, this packing is in a noninterpenetrate way. The tpt overlay each other between adjacent 2D polymeric layers. Tpt in **4** is a little bit away from coplanar compared with that in **1**−**3**. The average tpt layer distance is 3.43 Å, which is the same as that in **2**.

**Structure of $[Cu_3(CN)_3(tpt)]_n$ (5).** There has been a growing interest in copper(I) cyanide coordination polymers, because CuCN is a good molecular building block in constructing metal-organic frameworks.[33] Copper(I) favors trigonal or tetrahedral coordination with cyanide and N-heterocyclic ligands. This gives the possibility of promoting the formation of frameworks because of the strong coordination of these ligands and their ability to act as connectors between different copper centers. A series of copper(I) cyanide coordination polymers have been synthesized and structurally characterized.[34]

**5** is a 3D metal-organic framework, which contains a CuCN linear helix chain and tridentate linker tpt. As shown in part a of Figure 5, each exotridentate tpt binds to three CuCN helix chains through three pyridyl N-donors. Copper(I) atoms adopt a trigonal coordination geometry as cyanides occupy two sites and pyridyl nitrogen occupies the third one. Along the *c* axis, the complex shows intriguing honeycomb framework (part b of Figure 5). In each hexagon motif, two of the six edges are $\pi$ faces of planar tpt units, and the other four edges are the stacks of CuCN chains. The approximate dimensions of the hexagon are 1.9 nm × 1.4 nm. Further research found that the hexagonal honeycomb microporous network is 4-fold interpenetrated (part e of Figure 5), which leads to the formation of a 3D metal-organic framework.

**5** is the first example of mixed-ligand metal-organic frameworks of tpt with a cyanide group. Robson reported a cuprous metal-organic framework, $[Cu_3(tpt)_4](ClO_4)_3$, prepared by diffusion reaction of the copper(I) ion and tpt in acetonitrile.[3c] It has a larger octahedral chamber of 1.82 nm in diameter. Kim prepared a cuprous tpt 3D framework, $[Cu_3(tpt)_4](BF_4)_3\cdot(tpt)_{2/3}\cdot 5H_2O$, which has a middle-sized channel of 0.5 nm diameter filled with noncoordinating tpt, $H_2O$, and $BF_4^-$ anions.[16] In both coordination polymers, copper(I) centers are coordinated by four tpt-derived pyridyl nitrogen donors in a distorted tetrahedral arrangement. To our knowledge, no structurally characterized examples of a three-coordinated tpt−Cu(I) complex were documented.[35] Both of the above copper(I) complexes have relatively free counterions in the porous frameworks, whereas **5** is a neutral metal-organic framework with a perfect honeycomb motif.

**Infrared Spectra.** In the infrared spectra of **1**−**5**, the characteristic bands of the tpt ligand appear at 1576 v(C=C), 1518 v(*C*=N), 1375 (ring deformation mode C−C), and 802 $cm^{-1}$ (out-of-ring bend C−H) (Figure S8 in the Supporting Information). These assignments are similar to Kincaid's

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assignment of $[Ru(bpy)_3]^{2+}$ complexes.[36] The IR spectrum of **1** shows characteristic absorption of $NO_3^-$ at 1383 $cm^{-1}$. **2** displays characteristic peaks of $SO_4^{2-}$ at 1151, 1114 $cm^{-1}$ corresponding to sulfate bridging ligand. **3** and **4** contain $H_2btec^{2-}$ and $btec^{4-}$ ligands, respectively. The former has a $v_{as}(COOH)$ vibration absorption at 1685 $cm^{-1}$, whereas the latter shows $v_{as}(COO^-)$ absorption at 1606 $cm^{-1}$. Both carboxyl groups have $v_s$ vibration absorption near 1344 $cm^{-1}$. The IR spectrum of **5** shows characteristic absorption of cyanide at 2131 $cm^{-1}$. These IR spectra are in good agreement with the results of X-ray structural analysis.

**Photoluminescence.** Although many tpt complexes have been reported and there are some diamagnetic complexes, no fluorescence data is available yet. Tpt is a conjugated organic compound. When excited with 430 nm light, free tpt gives a strong fluorescent emission at 469 nm. It is well-known that paramagnetic ions can quench fluorescence emission. **2** does not emit because the copper(II) is a paramagnetic ion and quenches the ligand emission. Other four complexes likely show emission because they are $d^{10}$ metal centers and thus do not quench ligand emission. **1**, **3**, and **5** show blue fluorescent emissions in the range of 465−468 nm (Figure S9 in the Supporting Informaion), which are almost identical with the emission of tpt. We assign these emissions as ligand fluorescence. The emission of **4** shifted to higher wavelength of 478 nm. Because of charge transfer emission, whether an M−L or L−M emission, requires the metal center, it is oxidizable or reducible. The emission of **4** is not a charge transfer emission due to the fact that $Zn^{2+}$ is not an oxidizable ion. The energy of the fluorescence strongly suggests ligand-centered emission, especially because the emission of uncoordinated tpt occurs at nearly the same energy (wavelength).

**Thermal Gravity.** The TG curve of **1** indicates the complex lost lattice−water from 30 °C. A weight loss of 11.2% was found up to 110 °C, corresponding to four $H_2O$ (11.6%). Similar to a TG curve of free tpt (Figure S10 in the Supporting Information), this complex vigorously decomposed at a temperature higher than 335 °C. **2** is stable under 64 °C. In the range of 64−170 °C, it lost 9.58%, corresponding to the release of two coordinated $H_2O$ and four lattice $H_2O$ (10.27%). The framework vigorously decomposed at temperatures higher than 303 °C. **3** is stable under 230 °C. In the 230−300 °C range, it lost 20.58%, corresponding to lost $H_2btec^{2-}$ ligand (21.92%). It started to decompose tpt from 310 °C. **4** started weight loss from 100 °C. It lost 3.63% up to 210 °C, corresponding to the loss of lattice $H_2O$ (3.46%). The framework of **4**, $[Zn(tpt)(btec)_{1/2}]_n$, is stable up to 430 °C, which is much higher than the decomposed temperature of free tpt, indicating that tpt is stabilized in the framework. Compared with **3**, the nonoxidative zinc(II) complex **4** with fully deprotonated $btec^{4-}$ ligand is much more stable than the $H_2btec^{2-}$ copper(I) complex. **5** is stable up to 300 °C, which is more stable than the corresponding copper(I) complex **3**.

## Conclusions

Hydrothermal reactions of tpt with $AgNO_3$, $CuSO_4$, $ZnI_2$, and CuCN in the presence/absence of $H_4btec$ led to the assembly of a 1D $\{[Ag(Htpt)(NO_3)]NO_3 \cdot 4H_2O\}_n$ (**1**), 3D $\{[Cu_2(tpt)_2(SO_4)_2(H_2O)_2] \cdot 4H_2O\}_n$ (**2**), 2D $[Cu(tpt)(H_2btec)_{1/2}]_n$ (**3**), 2D $\{[Zn(tpt)(btec)_{1/2}] \cdot H_2O\}_n$ (**4**), and 3D $[Cu_3(CN)_3(tpt)]_n$ (**5**) coordination polymers. **5** possesses an intriguing honeycomb motif. All of the complexes are quite thermal stable, especially **4**, whose framework is stable up to 430 °C. Sulfate-bridge and $H_2O$-bridge coordination modes are observed in **2**. There are $\pi-\pi$ stacking interactions in **1**−**4**. The layer distance in **1** is 3.16 Å, which is possibly the shortest $\pi-\pi$ stacking distance. The complexes exhibit blue fluorescence, which can be assigned to be ligand-centered emissions.

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**Supporting Information Available:** Additional characterization data and crystallographic data for **1**, **2**, **3**, **4**, and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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