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# Hydrothermal Syntheses and Characterizations of Three Coordination Polymers Based on Mixed Organic Ligands

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Three new coordination polymers, namely $\{[Cu_2(bptc)(4,4'\text{-}bpy)(H_2O)_2]\cdot 2H_2O\}_n$ (**1**), $\{Cu_2(bptc)(bpe)(H_2O)_6\}_n$ (**2**), and $\{[Mn(H_2bptc)(H_2O)_4]\cdot 2bpe\}_n$ (**3**) [$H_4bptc$ = 3,3′,4,4′-biphenyltetracarboxylic acid, 4,4′-bpy = 4,4′-bipyridine, bpe = *trans*-1,2-bis(4-pyridyl)ethene], were rationally designed and hydrothermally synthesized at different pH values. Their structures were determined by X-ray diffraction on single crystals. Compound **1** exhibits a 3D network with 1D open channels that contain free solvent water molecules, and two kinds of chiral, helical, hydrogen-bonded chains exist in the neighboring holes. Both compounds **2** and **3** show a 3D supramolecular network that is connected through hydrogen bonds. Compound **2** also shows weak Cu···O semicoordinated interactions that are based on 1D chains. Importantly, bptc reveals three different coordination modes in these compounds: the four carboxylic groups combine with metal ions by bis(monodentate) and bis(chelate) fashions in **1**, whereas only two carboxylic groups are bis(monodentate) in **2** and **3**, respectively, and the 4,4′-carboxylic groups are protonated in **3**. The elemental analysis, IR spectra, UV/Vis spectra, and TG analysis for compounds **1**, **2**, and **3** are discussed. Additionally, the XRPD is also studied for compound **1**.

## Introduction

The design and construction of metal–organic coordination polymers is of current interest in the fields of supramolecular chemistry and crystal engineering.[1] Major reasons for this interest stem from their intriguing variety of topologies and structural diversity,[2] such as helixes[3]and diamondoid nets[4] and because of their potential applications as functional materials,[5] such as heterogeneous catalysis,[6] molecular recognition,[7] magnetism,[8] gas storage,[9] ion exchange,[10] nonlinear optics,[11] and electrical conductivity.[12] In order to build these molecular architectures, polycarboxylates are often employed as bridging ligands to construct coordination polymers owing to their versatile coordination modes and high structural stability.[13] These polymeric solids can be essentially regarded as a class of metal polycarboxylate salts. Hence, the structures of the resulting compounds are influenced by the degree of deprotonation, the coordination modes and capabilities, the size and shape of the polycarboxylic acids, as well as by the coordination spheres of the metal centers. Thus, it is possible to synthesize polymeric frameworks with interesting topologies through the appropriate choice of ligand, tailoring, and manipulation of the reaction conditions, including pH, temperature, stoichiometry, and the addition of templates or structure-directing agents. For resolving the poor solubility of reactants and products, the hydrothermal reaction technique offers a powerful synthetic route to prepare polymeric solids with better crystallinity[14] than traditional solution techniques such as evaporation, diffusion, and cooling etc. In most cases, water is not only a solvent but also acts as a competing ligand in these hydrothermal reactions. This phenomenon is observed in many coordination polymers that are constructed from polycarboxylate ligands where the water molecules usually act as terminal or bridging ligands in the coordination sphere of the metal; thus, the variety of the assembled structural topologies of the polymers increases.

According to the above strategy, 3,3′,4,4′-biphenyltetracarboxylic acid ($H_4bptc$, Scheme S1, Supporting Information), which has eight potential donor oxygen atoms, is undoubtedly a better choice as the ligand for the construction of novel metal–organic coordination polymers owing to its quadruple carboxylic dentate arms. However, to the best of our knowledge, polymers containing bptc have been scarcely studied so far.[15] With the aim to understand the coordination chemistry of bptc and to prepare new materials with interesting structures and excellent physical properties, we recently started to research this kind of coordination polymer. We also notice that the introduction of N-containing auxiliary ligands, such as 4,4′-bipyridine (4,4′-

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bpy) and *trans*-1,2-bis(4-pyridyl)ethene (bpe), into the {M-bptc}(M = transition metal) system may lead to the structural evolution of these metal–organic compounds and their structural motifs may ultimately be fine-tuned. Herein, we report three interesting coordination polymers with mixed organic ligands, $\{[Cu_2(bptc)(4,4'\text{-bpy})(H_2O)_2]\cdot 2H_2O\}_n$ (**1**), $\{Cu_2(bptc)(bpe)(H_2O)_6\}_n$ (**2**), and $\{[Mn(H_2bptc)(H_2O)_4]\cdot 2bpe\}_n$ (**3**). Our results demonstrate that bptc adopts various coordination modes in the three compounds (Scheme S2, Supporting Information). Interestingly, two kinds of hydrogen-bonded-directed chiral helices exist in 1D open channels of compound **1**.

## Results and Discussion

### General Synthesis

Because the mixing of metal salts and carboxylate solutions usually resulted in precipitation in traditional aqueous reactions, which makes the growth of crystals difficult, the hydrothermal method was adopted in these reactions. The use of hydrothermal conditions causes a reaction to shift from the kinetic to the thermodynamic domain. By performing parallel experiments, it was found that the pH values of the reaction solutions play an important role in the isolation of the three compounds, as is the case for some other metal polycarboxylate coordination polymers reported.[15b,16] The three compounds were prepared at different pH values: compound **1** at pH 6, compound **2** at pH 7, and compound **3** at pH 4. If the pH values of the reactions were lower or higher than those listed in the Experimental Section, no products could be obtained. Besides the pH, a suitable steric geometry of the reactants is also very important for the fabrication of the resulting coordination architectures. As described in the Experimental Section, although the synthetic conditions are very similar, only a small difference in the steric demands of the reactants, for example between 4,4′-bpy and bpe, results in the different coordination architectures of compounds **1** and **2**. However, we found that the above reactions were not sensitive to the reaction temperature. If the reaction temperature was set 10 °C above or below 145 °C, the intended crystals still formed.

### Description of the Structures

#### *$\{[Cu_2(bptc)(4,4'\text{-bpy})(H_2O)_2]\cdot 2H_2O\}_n$ (1)*

Single-crystal X-ray structural analysis showed that compound **1** crystallizes in the monoclinic space group $P2_1/c$, with two copper(II) atoms, one hexadentate bptc ligand, one 4,4′-bpy ligand, two coordinated waters, and two lattice water molecules in each crystallographic unit (Figure 1). Each copper atom has a distorted square-pyramidal environment (tetragonality parameter $\tau = 0.55$)[17] and binds equatorially to three oxygen atoms (O1, O3A and O4A) of two different bptc ligands and one nitrogen atom (N1) of 4,4′-bpy; a water molecule ($O_w5$) coordinates in the apical position. The equatorial plane of the copper atom is tetrahedrally distorted (maximum atomic deviation 0.046 Å), with the metal atom displaced by 0.207 Å from the best mean plane toward the apical ligand.

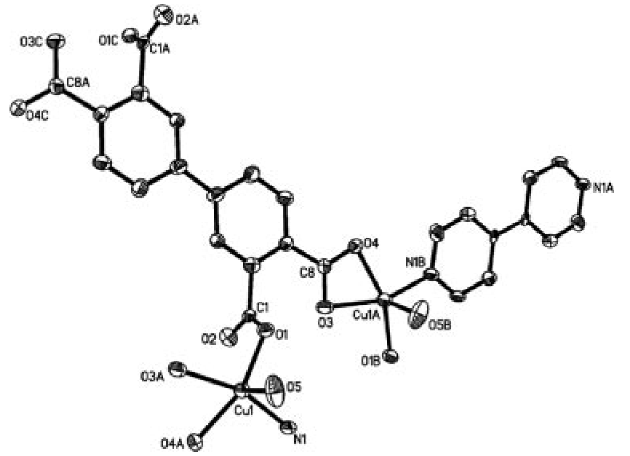

Figure 1. ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of compound **1**. Hydrogen atoms and the lattice waters are omitted for clarity.

Compound **1** exhibits an extended 3D framework involving 1D open channels when viewed along the crystallographic *c* axis (Figure 2). The approximate dimensions of these channels are 15.55 × 8.81 Å (calculated from the distance of the neighboring $Cu^{II}$ atoms),[18] which are large enough to encapsulate guest solvent water molecules. When viewed along the crystallographic *b* axis, the bptc and 4,4′-bpy ligands alternate one by one in each layer to form huge “infinite sandwiches”[19] (Figure S1, Supporting Information). The planes of the pyridyl rings and phenyl rings are offset between the adjacent layers with a face-to-face separation with a center-to-center distance of 3.844 Å and a dihedral angle of 8.43°. To the best of our knowledge, compound **1** represents the first example of a perfect molecular network building upon ligands bptc and 4,4′-bpy with copper in which the four carboxylate groups of bptc take part in coordination: the two carboxylate groups (3,3′-$COO^-$) adopt bis(monodentate) coordination with two different copper ions, the other carboxylate groups (4,4′-$COO^-$) are bis(chelated) with two dissimilar copper cations, and the 4,4′-bpy ligands are coordinatively bridged with them.

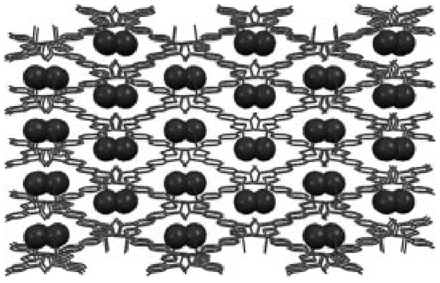

Figure 2. A perspective view of the 3D network of compound **1** containing 1D open channels encapsulating water molecules.

Multiple hydrogen bonds are known to cooperatively exert a dramatic influence on the control of molecular self-assembly in chemical and biological systems,[13b,20] and some examples of hydrogen-bonded helices have been reported.[21] The most fascinating structural feature of compound **1** is that chiral, helical, hydrogen-bonded (lengths and angles are listed in Table S1, Supporting Information) chains also exist in 1D open channels. Interestingly, when viewed along the crystallographic *a* axis, we found that the hydrogen-bonded chains, which are composed of coordinated water molecules (O5), carboxylate oxygen atoms (O2), and lattice water molecules (O6), show two different kinds of chiral helices (one is left-handed and the other is right-handed) in the neighboring holes (Figure 3) and that the winding axes are parallel to the *c* axis. The two parallel helices exist concurrently, and they are enchased in 1D channels by hydrogen bonds. So far, the examples that have two kinds of helices are still few.[3e,21c,22] Obviously, these strong hydrogen bonds undoubtedly steer the rotational direction of the helix.[23] It is worth noting that the use of hydrogen bonds as a steering force is becoming a very important strategy in crystal engineering.[24] To date, studies on this aspect are unprecedented with respect to the bptc ligand. Additionally, the O6 atom donates a hydrogen bond towards carboxyl oxygen atom O1 $[O_w6\cdots O_{COO^-}1 = 2.903(2)$ Å] that is situated on the bptc ligand of the host framework. This additional interaction has an important effect on the stability of the 1D chiral, helical, hydrogen-bonded chains.

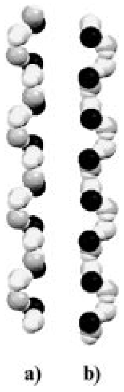

Figure 3. The right-handed (a) and left-handed (b) chiral helical hydrogen-bonded chains in the neighboring holes of compound **1** containing free solvent water molecules (light gray balls, O6), coordinated waters (dark gray balls, O5), and uncoordinated oxygen atoms (black balls,O2).

### *$\{Cu_2(bptc)(bpe)(H_2O)_6\}_n$ (2)*

The crystal structure of compound **2** consists of a neutral 1D zigzag chain based on alternating bptc and bpe ligands and crystallizes in the $P\bar{1}$ space group. As shown in Figure 4, in each asymmetry unit, compound **2** is composed of two copper(II) atoms, one bis(monodentate) bptc ligand, one bpe ligand, and six coordinated water molecules. The coordinated sphere of each copper atom is a distorted trigonal bipyramid with three water molecules in the equatorial plane, and a carboxylate oxygen atom (4,4′-$COO^-$) of bptc and a nitrogen atom of bpe occupy the apical positions.

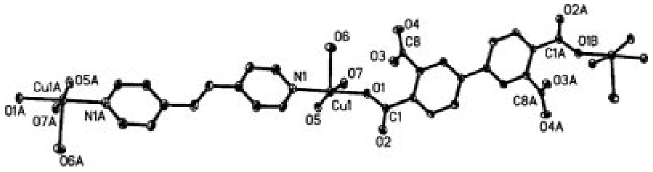

Figure 4. View of the 1D zigzag coordination polymer with alternating bptc and bpe ligands in compound **2** (30% thermal probability ellipsoids).

However, the copper atoms have a weak equatorial connection to semicoordinated centrosymmetrically related water molecules [Cu1···O5 = 2.896(4) Å, symmetry code: $1 - x, 1 - y, 1 - z$], resulting in a 5 + 1 coordination sphere for the copper atom (Figure 5). The equatorial plane of the copper atom has a moderate tetrahedral distortion (maximum atomic deviation 0.074 Å), the copper atom is displaced by only 0.073 Å from this plane towards the nitrogen atom. The dihedral angles between the equatorial plane and the planes of bptc and bpe are 87.62 and 73.18°, respectively. Furthermore, two pyridyl rings of bpe are parallel with each other at the distance of 0.528 Å.

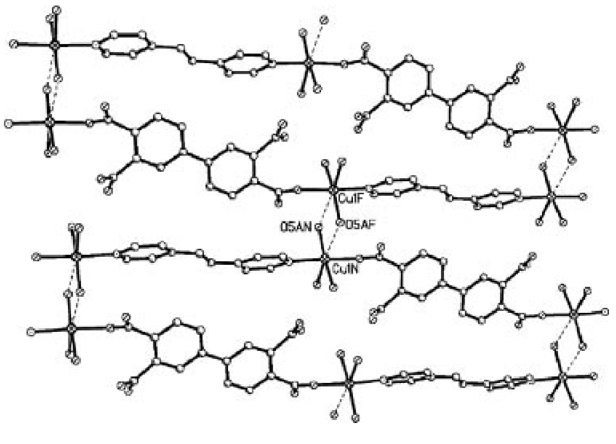

Figure 5. The 2D layer of compound **2** by $Cu\cdots O_w$ semicoordination and hydrogen bonds. Hydrogen bonds are deleted for clarity.

The shortest intermolecular metal···metal distance is Cu1F···Cu1N and measures 3.862 Å. It occurs between the pairs of 1D staggered chains (···ABAB··· fashion) that are connected through the semicoordination mentioned above and simultaneously the chains form a 2D network that including interlocking of hydrogen bonds. In other reported papers,[25] we found that only the lower dimensional architectures (1D chains or dimers) existed by weak Cu···O interactions. Because compound **2** possesses multiuncoordinated carboxylate oxygen atoms and coordinated water molecules, hydrogen bonds connect the 2D layers into a 3D supramolecular framework.

### $\{[Mn(H_2bptc)(H_2O)_4]\cdot 2bpe\}_n$ (3)

Compounds **3** and **2** have the same space group, $P\bar{1}$. The crystal structure of compound **3** also contains a neutral 1D chain, but here the chain is only based on bptc and the bpe ligands just exist as free solvent molecules in it. At the same time, different from **2**, two pyridyl rings of the bpe ligand are not parallel and have a dihedral angle of 2.72°. The manganese atoms are 4 + 2 six-coordinate in a slightly distorted octahedral coordination environment with four water molecules located in the equatorial plane and the two oxygen atoms (3,3′-COO) from the bptc ligand occupy the apical positions, as depicted in Figure 6. The best equatorial plane is defined by the O1, O2, O1A, and O2A atoms, which are perfectly planar (no deviation in the four atoms) and the manganese atom lies in this plane.

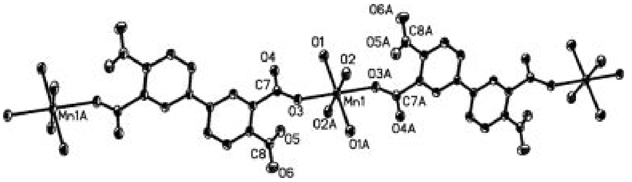

Figure 6. View of the coordination environment of $Mn^{II}$ in compound **3**. Hydrogen atoms and free bpe ligands are deleted for clarity.

According to the results of X-ray diffraction, there are two uncoordinated carboxylate groups of the bptc ligand that are protonated in compound **3**. This is dissimilar from compound **2** where two carboxylate groups do not take part in coordination even though they are deprotonated. The neighboring 1D chains are connected through hydrogen bonds between the coordinated water molecules and the oxygen atoms of the carboxylate groups [$O_w1\cdots O_{COO}6$ = 2.751(5) Å] (Figure S2, Supporting Information). The resulting wavelike 2D network contains almost rhombic holes in which the Mn···Mn distance through the bptc is 14.584 Å, whereas the distance through the water oxygen atoms of the bptc bridge is 7.970 Å, and there are no solvent molecules in the rhombic holes. The bpe ligands act as pillars, as in the case of the 4,4′-bpy ligand,[26] and link the 2D layers together to form a 3D network by using hydrogen-bonding recognition [$O_w2\cdots N1$ = 2.809(5) Å and $O_{COO}6\cdots N2$ = 2.560(4) Å] (Figure 7) as in compound **2**.

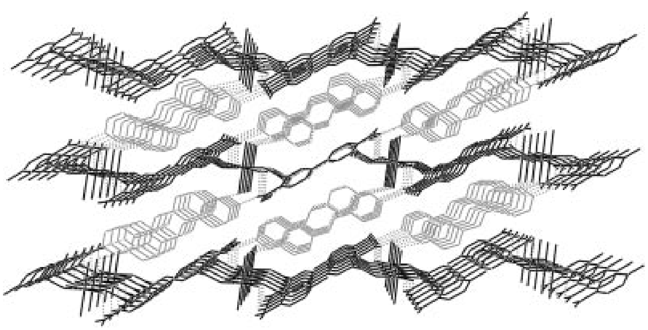

Figure 7. The 3D network of compound **3** constructed from 2D layers with bpe ligands as the pillars. The bpe ligands are represented in grey.

### Spectroscopic Characterization, Thermal Gravimetric Analysis, and XRPD Measurement

The IR spectra of the three compounds were performed as KBr pellets in the range 4000–400 cm$^{-1}$.These compounds show the characteristic bands of the carboxylate groups in the usual region[27] at 1630–1550 cm$^{-1}$ for the asymmetric vibration and at 1410–1360 cm$^{-1}$ for the symmetric, and the value $\Delta[\nu_{as}(COO^-) - \nu_s(COO^-)] > 200$ cm$^{-1}$ for the three compounds reveals that the carboxylate group is coordinated in a monodentate fashion,[28] which is consistent with the results of the X-ray analysis. Also observed were the bands for the 4,4′-bpy ligand at 1593, 1571, and 1494 cm$^{-1}$ for **1**, the bands of the bpe ligand at 1551 cm$^{-1}$ for **2** and 1574 cm$^{-1}$, 1506 cm$^{-1}$ for **3**. The splitting of $\nu_{as}(COO^-)$ in **1** confirms that the carboxylate groups have a variety of coordination fashions. These proposals are in accordance with the crystal structures. The UV/Vis spectra of the three compounds were recorded in *N*,*N*-dimethylformamide at room temperature and are characterized by several spectral regions (Figures S3, S4, and S5, Supporting Information). The maximum absorption band at 276 nm for the bptc ligand is ligand-centered (LC) due to π–π* transitions. The peaks at 286, 289, and 288 nm for compounds **1**, **2**, and **3**, respectively, are due to d–d transitions and the low-energy bands at 283, 299, and 298 nm, respectively, are assigned to metal-to-ligand charge-transfer transitions (MLCT).[29] This slight shift in absorption bands of the compounds relative to that of the bptc ligand is caused by the effect of metal-to-ligand charge-transfer transitions.

To examine the thermal stability of the three compounds, thermal gravimetric analyses (TGA) were carried out between 50–800 °C. As shown in Figure 8, for **1** a total weight loss of 11.58% occurred over the temperature range 67–158 °C, corresponding to the loss of four water molecules (calcd. 10.57%). When the temperature was increased to ca. 268 °C, the product began to lose the bptc and 4,4′-bpy ligands. Finally, the remaining weight of 19.10% corresponds to the percentage (calcd. 20.99%) of Cu and O components, indicating that the final product is $Cu_2O$. The TGA traces of **2** and **3** are much like that observed for **1**: compound **2** loses six water molecules between 74 and 171 °C (observed 15.61%, calcd. 14.54%), and compound

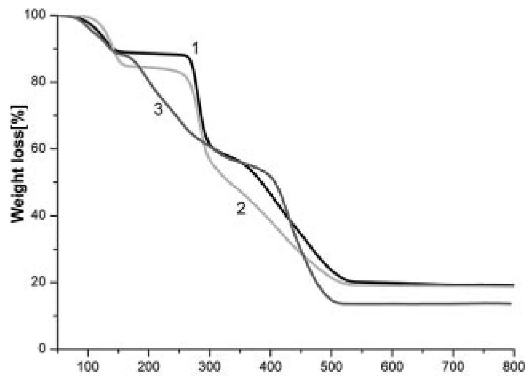

Figure 8. The TG curves of compounds **1**, **2**, and **3**.

**3** loses two bpe ligands and four water molecules between 79 and 384 °C (observed 46.27%, calcd. 46.90%), respectively. The remaining weight of 18.71% (calcd. 19.24%) for **2** (observed 13.33%, calcd. 12.55% for **3**) indicates that the final product is $Cu_2O$ ($MnO_3$). Additionally, to confirm the phase-pure and the stable framework of compound **1**, the original sample and dehydrated sample were characterized by X-ray powder diffraction (XRPD) at room temperature. The pattern that was simulated from the single-crystal X-ray data of compound **1** was in good agreement with those that were observed, thus compound **1** was obtained as a single phase. For compound **1**, after heating at 85 °C for 3 h, the guest water molecules were removed (the evacuated frameworks are defined as **1′**). The XRPD pattern of **1′** is similar to compound **1**, although minor differences can be seen in the positions, intensities, and widths of some peaks (Figure S6, Supporting Information), which indicates that the framework of compound **1** is retained after the removal of the guest molecules.

## Conclusions

As described above, we successfully designed and synthesized three coordination polymers constructed from bptc and N-containing auxiliary ligands (4,4′-bpy, bpe) at different pH values. Comparing the structure of compounds **1**, **2**, and **3**, it was found that the different coordination modes of the bptc ligand may have a significant effect on the formation and dimension of the resulting structures. The successful preparation of three compounds provides a valuable approach for the construction of many other coordination polymers with different dimensional structures by the introduction of another kind of organic ligand. More significantly, compound **1** contains 1D open channels that contain free water molecules and chiral hydrogen bonded helices exist.

## Experimental Section

**Materials:** All chemicals purchased were of reagent grade and used without further purification. The bptc ligand was obtained by hydrolyzing 4,4′-biphthalic anhydride that is bought from Alfa Aesar. All syntheses were carried out in 25-mL Teflon-lined autoclaves under autogenous pressure. The reaction vessels were filled to approximately 60% volume capacity. Distilled water was used in all reactions.

**$\{[Cu_2(bptc)(4,4'\text{-}bpy)(H_2O)_2]\cdot 2H_2O\}_n$ (1):** A mixture of $Cu(NO_3)_2\cdot 8H_2O$ (332 mg, 1.0 mmol), $H_4$bptc (165 mg, 0.5 mmol), 4,4′-bpy (78 mg, 0.5 mmol), and water (15 mL) was adjusted to pH 6 with a 1 M NaOH solution and then heated at 145 °C for 4 d. Well-shaped blue block crystals were obtained when the mixture was cooled to room temp. at 10 °C h$^{-1}$. Yield: 61.3%. IR (KBr): $\tilde{\nu}$ = 3472 (s), 3215 (m), 1613 (s), 1593 (s), 1571 (m), 1494 (m), 1423 (s), 1384 (s), 1221 (m), 1166 (w), 1096 (w), 1071 (m), 873 (s), 846 (s), 822 (s), 649 (m), 568 (m), 552 (w), 460 (w) cm$^{-1}$.$C_{26}H_{22}Cu_2N_2O_{12}$ (681.55): calcd. C 45.82, H 3.25, N 4.11; found C 45.69, H 3.22, N 4.20.

**$\{Cu_2(bptc)(bpe)(H_2O)_6\}_n$ (2):** A mixture of $Cu(OAc)_2\cdot H_2O$ (200 mg, 1.0 mmol), $H_4$bptc (165 mg, 0.5 mmol), bpe (91 mg, 0.5 mmol), and water (15 mL) was adjusted to pH 7 with a 1 M NaOH solution and then heated at 145 °C for 4 d. Blue-green crystals were obtained when the mixture was cooled to room temp. at 10 °C h$^{-1}$. Yield: 65.8%. IR (KBr): $\tilde{\nu}$ = 3397 (s), 3155 (m), 2921 (m), 1608 (s), 1551 (s), 1483 (m), 1370 (s), 1294 (m), 1159 (w), 1097 (w), 978 (m), 891 (w), 838 (m), 790 (m), 697 (w), 662 (m), 552 (m), 470 (m) cm$^{-1}$. $C_{28}H_{28}Cu_2N_2O_{14}$ (743.60): calcd. C 45.22, H 3.80, N 3.77; found C 45.35, H 3.62, N 3.64.

**$\{[Mn(H_2bptc)(H_2O)_4]\cdot 2bpe\}_n$ (3):** A mixture of $Mn(OAc)_2\cdot 4H_2O$ (123 mg, 0.5 mmol), $H_4$bptc (165 mg, 0.5 mmol), bpe (182 mg, 1.0 mmol), and water (15 mL) was adjusted to pH 4 with a 1 M NaOH solution and then heated at 145 °C for 4 d. Pale yellow crystals were obtained when the mixture was cooled to room temp. at 10 °C h$^{-1}$. Yield: 53.1%. IR (KBr): $\tilde{\nu}$ = 3333 (s), 3085 (m), 2225 (w), 1940 (w), 1626 (m), 1574 (s), 1506 (m), 1480 (m), 1403 (s), 1360 (m), 1250 (w), 1184 (w), 1094 (m), 944 (m), 899 (m), 868 (w), 793 (s), 694 (m), 636 (m), 544 (w), 450 (w) cm$^{-1}$. $C_{40}H_{36}MnN_4O_{12}$ (819.67): calcd. C 62.82, H 4.74, N 7.33; found C 62.73, H 4.89, N 7.21.

**Physical Measurements:** Elemental analyses (C, H, and N) were determined with a PE 2400 Elemental analyzer. Infrared spectra of KBr pellets were recorded with a BRUKER EQUINOX-55 spectrometer in the range of 4000–400 cm$^{-1}$. Thermal analyses were performed with a NETZSCH STA 449C microanalyzer with a heating rate of 10 °C min$^{-1}$ under a nitrogen atmosphere. Electronic spectra were recorded with a Cary 300 Bio UV/Vis spectrophotometer in the range 270–450 nm at ambient temperature. The XRPD pattern was recorded with a Pigaku D/Max 3III diffractometer.

**Crystal Data Collection and Refinement:** Diffraction experiments for **1**, **2**, and **3** were carried out with Mo-$K_\alpha$ radiation by using a BRUKER SMART APEX-CCD diffractometer at 291(2) (for **1**, **2**) and 296(2) (for **3**) K. A summary of the crystallographic data and structure refinement details are given in Table 1, and selected bond

Table 1. Crystallographic data and structure refinement details for compounds **1**, **2**, and **3**.

| Compound | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{26}H_{22}Cu_2N_2O_{12}$ | $C_{28}H_{28}Cu_2N_2O_{14}$ | $C_{40}H_{36}MnN_4O_{12}$ |
| Formula weight | 681.55 | 743.60 | 819.67 |
| Crystal system | monoclinic | triclinic | triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| Crystal size [mm] | 0.14×0.08×0.05 | 0.13×0.10×0.05 | 0.31×0.19×0.08 |
| $a$ [Å] | 6.696(7) | 7.541(2) | 7.9703(2) |
| $b$ [Å] | 17.504(1) | 8.345(2) | 9.6846(2) |
| $c$ [Å] | 11.322(2) | 11.793(3) | 12.6091(1) |
| $\alpha$ [°] | 90.00(1) | 106.204(4) | 87.237(2) |
| $\beta$ [°] | 95.445(1) | 90.862(4) | 87.197(2) |
| $\gamma$ [°] | 90.00(2) | 97.673(4) | 74.492(2) |
| $V$ [Å$^3$] | 1321(2) | 705.2(3) | 936.1(2) |
| $Z$ | 2 | 1 | 1 |
| $T$ [K] | 291(2) | 291(2) | 296(2) |
| $D_{\text{calcd.}}$ [g cm$^{-3}$] | 1.713 | 1.751 | 1.454 |
| $\mu$ [mm$^{-1}$] | 1.681 | 1.587 | 0.424 |
| $F(000)$ | 692 | 380 | 425 |
| Limiting indices | $-7\le h \le 7$ | $-9\le h \le 9$ | $-9\le h \le 8$ |
|  | $-20\le k \le 20$ | $-10\le k \le 10$ | $-11\le k \le 5$ |
|  | $-13\le l \le 13$ | $-14\le l \le 14$ | $-15\le l \le 15$ |
| $\lambda$ [Å] | 0.71073 | 0.71073 | 0.71073 |
| $\theta$ Range [°] | 2.95–25.10 | 2.57–25.50 | 1.62–25.10 |
| Reflections collected | 9257 | 5099 | 4804 |
| Goodness-of-fit on $F^2$ | 0.942 | 1.041 | 1.097 |
| $R_1$[a], $wR_2$[b] [$I>2\sigma(I)$] | 0.0737, 0.1413 | 0.0492, 0.0984 | 0.0584, 0.1292 |
| $R_1$[a], $wR_2$[b] [all data] | 0.1686, 0.1832 | 0.0793, 0.1128 | 0.1050, 0.1604 |

[a] $R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] of compounds **1**, **2**, and **3**.

| **1** | | **2** | | **3** | |
|---|---|---|---|---|---|
| Cu1–O1 | 1.948(6) | Cu1–O7 | 1.956(3) | Mn1–O1 | 2.176(3) |
| Cu1–N1 | 1.973(7) | Cu1–O5 | 1.962(3) | Mn1–O2 | 2.216(3) |
| Cu1–O4[a] | 1.990(6) | Cu1–O1 | 1.971(3) | Mn1–O3 | 2.150(2) |
| Cu1–O3[a] | 2.050(6) | Cu1–N1 | 2.019(4) | Mn1–O1[b] | 2.176(3) |
| Cu1–O5 | 2.216(7) | Cu1–O6 | 2.324(4) | Mn1–O2[b] | 2.216(3) |
| | | | | Mn1–O3[b] | 2.150(2) |
| O1–Cu1–N1 | 98.1(3) | O7–Cu1–O5 | 167.72(1) | O1–Mn1–O2 | 87.12(1) |
| O1–Cu1–O4[a] | 158.3(3) | O7–Cu1–O1 | 88.11(1) | O1–Mn1–O3 | 86.89(2) |
| N1–Cu1–O4[a] | 96.7(3) | O5–Cu1–O1 | 91.46(2) | O1–Mn1–O2[b] | 92.89(2) |
| O1–Cu1–O3[a] | 98.0(2) | O7–Cu1–N1 | 88.18(2) | O1–Mn1–O3[b] | 93.12(1) |
| N1–Cu1–O3[a] | 160.1(3) | O5–Cu1–N1 | 92.26(1) | O2–Mn1–O3 | 89.72(2) |
| O4[a]–Cu1–O3[a] | 64.8(2) | O1–Cu1–N1 | 176.26(2) | O2–Mn1–O1[b] | 92.89(2) |
| O1–Cu1–O5 | 94.9(3) | O7–Cu1–O6 | 92.94(2) | O2–Mn1–O3[b] | 90.28(2) |
| N1–Cu1–O5 | 97.6(3) | O5–Cu1–O6 | 99.32(1) | O3–Mn1–O1[b] | 93.12(1) |
| O4[a]–Cu1–O5 | 98.8(3) | O1–Cu1–O6 | 87.43(1) | O3–Mn1–O2[b] | 90.28(2) |
| O3[a]–Cu1–O5 | 92.7(3) | N1–Cu1–O6 | 92.46(2) | O1[b]–Mn1–O2[b] | 87.12(1) |

[a] Symmetry codes: $x$, $-y + 3/2$, $z + 1/2$. [b] Symmetry codes: $-x$, $1 - y$, $2 - z$.

lengths and angles are listed in Table 2. Both structures were solved by direct methods and refined with the full-matrix least-squares technique on $F^2$ by using SHELXS-97[30] and SHELXL-97.[31] All non-hydrogen atoms were refined anisotropically. The water H atoms were located in a different Fourier map and refined with restrained O–H bond lengths [0.82(2) Å] in **1**. CCDC-634976 (for **1**), -634977 (for **2**), and -634978 (for **3**) 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.

**Supporting Information** (see footnote on the first page of this article): Coordination modes of the bptc ligand, table of hydrogen bond lengths and angles, UV/Vis spectra for the three compounds, XRPD pattern for compound **1**, and additional plots of the structures.

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