## Structural Investigation of Coordination Polymers Constructed from a Conformational Bis-triazole Ligand and V-Shaped Bridging Carboxylate Anions: Hydrothermal Syntheses, Crystal Structures, and Property Studies

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The conformational bis-triazole ligand 4,4'-bis[(1,2,4-triazol-1-yl)methyl]biphenyl (btmb, 1), was successfully synthesized, and seven new coordination polymers, namely {M(oba)-(btmb)}<sub>n</sub> [M = Cd<sup>2+</sup> (2), Co<sup>2+</sup> (3), Ni<sup>2+</sup> (4), and Zn<sup>2+</sup> (5)], {M(sdba)(btmb)}<sub>n</sub> [M = Co<sup>2+</sup> (6) and Cd<sup>2+</sup> (7)], and {[Cu(H<sub>2</sub>odpa)(btmb)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub> (8), (H<sub>2</sub>oba = 4,4'-oxydibenzoic acid, H<sub>2</sub>sdba = 4,4'-sulfonyldibenzoic acid, and H<sub>4</sub>odpa = 4,4'-oxydiphthalic acid), have been synthesized by utilizing the btmb ligand and the polymers have been characterized in detail. Complexes 2–4 are isostructural exhibiting 2D-layer structures and can be described as (3,4)-connected networks with (4<sup>2</sup>.6<sup>3</sup>.8)(4<sup>2</sup>.6) topological notation. Complex 5 shows 2D layers with left- and right-handed helical chains and has a (3,4)-connected net with (4.5<sup>2</sup>)(4.5<sup>3</sup>.7<sup>2</sup>) topology. Complexes 6 and 7 are isostructural and display 2D

## Introduction

Coordination polymers are currently of interest in the field of supramolecular chemistry and crystal engineering, not only because of their potential applications as functional solid materials for microelectronics, fluorescence, magnetic materials, nonlinear optics, ion exchange, catalysis, and sorption,<sup>[1–2]</sup> but also because of their intriguing aesthetic structures and topologies.<sup>[3–4]</sup> The coordination polymeric frameworks can be rationally designed by careful control of many factors such as the solvent system, temperature, pH value, the metal-to-ligand ratio, geometric requirements of metal ions, and second building-block ligands.<sup>[5–6]</sup>

Up to now, a number of pyridyl-containing ligands have been widely employed to construct coordination polymers with a variety of novel structural motifs and desirable physical properties.<sup>[7–9]</sup> According to the reported studies, the Ndonor imidazole and triazole ligands,<sup>[10–11]</sup> especially based undulating networks with (4,4) sheets that are further packed through van der Waals interactions to generate a 3D supramolecular structure. Complex **8** also represents a 2D network with a 4<sup>4</sup>-sql net, which is extended into a 3D supramolecular framework by hydrogen-bonding interactions. The structural differences of these complexes demonstrate that the conformation of the btmb ligand and flexible aromatic polycarboxylate anions play critical roles in the formation of the resulting frameworks. Furthermore, their thermal properties have been studied by thermogravimetric analysis (TGA) and the TGA results reveal that the triazole-based frameworks have a high thermal stability, which suggests they are good candidates for the construction of more stable complexes. The photoluminescent properties of complexes **2**, **5**, and **7** have also been studied.

on conformational bis-imidazole/triazole ligands such as 1,4-bis(imidazol-1-ylmethyl)benzene, 1,4-bis(imidazolyl)-2-1,1'-(1,4-butanediyl)-bis(imidazole), butyne, 1,4-bis(triazole-1-ylmethyl)benzene, and 9,10-bis(triazol-1-ylmethyl)anthracene,<sup>[12–15]</sup> are highly attractive because of their coordinating tendency to produce entangled frameworks. Therefore, the 4,4'-bis[(1,2,4-triazol-1-yl)methyl]biphenyl (btmb) ligand is a good candidate for the construction of coordination polymers for the following reasons: (i) compared with the bis-imidazole (bimb) ligand [bimb = 4,4'-bis(imidazol-1-ylmethyl)biphenyl],<sup>[16]</sup> the 1,2,4-triazole group of btmb exhibits a strong and typical coordination capacity and can provide more potential coordination sites; (ii) two 1,2,4-triazole groups can freely twist around two -CH<sub>2</sub>- groups with different angles to generate different conformations and coordination modes. In addition, two phenyl rings can also twist around the C-C single bond with different torsion angles to meet the requirements of the coordination geometries; (iii) it is noteworthy that self-assembly of coordination polymers based on trizazole ligands have high energy and good thermal stability.<sup>[1d,11a,17]</sup> Especially, the high thermal stability is required for coordination polymers to be practical for potential applications as functional solid materials.[18]

On the other hand, a mixed-ligand strategy is presently a good choice for the construction of coordination poly-

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mers. The V-shaped organic aromatic multicarboxylate species have been extensively employed as building blocks to construct coordination polymeric frameworks,<sup>[16a,19]</sup> because they show various coordination modes with metal ions, which give rise to a great variety of multidimensional structures and fascinating topologies. So far, to the best of our knowledge, only a few coordination polymers with the btmb ligand have been reported.<sup>[20]</sup>

Herein, we have successfully synthesized a series of new coordination polymers containing the conformational btmb ligand, namely {M(oba)(btmb)}<sub>n</sub> [M = Cd<sup>2+</sup> (**2**), Co<sup>2+</sup> (**3**), Ni<sup>2+</sup> (**4**), and Zn<sup>2+</sup> (**5**)], {M(sdba)(btmb)}<sub>n</sub> [M = Co<sup>2+</sup> (**6**) and Cd<sup>2+</sup> (**7**)], and {[Cu(H<sub>2</sub>odpa)(btmb)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub> (**8**), (H<sub>2</sub>oba = 4,4'-oxydibenzoic acid, H<sub>2</sub>sdba = 4,4'-sulfonyldibenzoic acid, and H<sub>4</sub>odpa = 4,4'-oxydiphthalic acid). The results indicate that the structural diversities of the complexes **2–8** result from employing the different organic carboxylate ligands and the conformational btmb ligand. In addition, the elemental analyses, infrared spectroscopy (IR), X-ray diffraction (XRD) patterns, thermogravimetric analyses (TGA), and the photoluminescent properties of complexes **2**, **5**, and **7** have been investigated (Scheme 1).



Scheme 1. The coordination modes and conformations of the btmb ligands in complexes 2–8.

## **Results and Discussion**

#### Syntheses

In this work, the 4,4'-bis[(1,2,4-triazol-1-yl)methyl]biphenyl (btmb) ligand was synthesized with the aim of understanding the coordination of btmb. As we know, hydrothermal synthetic methods have been demonstrated to be an effective and powerful technique for growing crystals of coordination polymers with interesting structures and special properties. We carried out the reaction of btmb with V-shaped organic acids (Scheme 2) and transition-metal salts in an aqueous medium in a molar ratio of 1:1:1, respectively. The results show that single-crystal products suitable for X-ray anyalyses were successfully obtained at 160 °C (Scheme 3). All complexes are highly stable in air at ambient temperature and insoluble in common organic solvents and water.



4,4'-sulfonyldibenzoic acid (H<sub>2</sub>sdba)



4,4'-oxydiphthalic acid (H<sub>4</sub>odpa)

Scheme 2. Structures of the organic acid ligands (H<sub>2</sub>sdba, H<sub>2</sub>oba, and H<sub>4</sub>odpa).

#### **Description of Crystal Structures**

**4,4'-Bis**[(1,2,4-triazol-1-yl)methyl]biphenyl (btmb) (1). The single crystal of btmb has been isolated recently by Xu.<sup>[21]</sup> The free btmb ligand displays *anti*-conformational features that extend into a 1D chain through weak C–H···N hydrogen-bond interactions (C···N 3.381 Å) (Figure S1, Supporting Information).

 ${M(oba)(btmb)}_n$  [M = Cd<sup>2+</sup> (2), Co<sup>2+</sup> (3), and Ni<sup>2+</sup> (4)]. The three complexes  $\{M(btmb)(oba)\}_n [M = Cd^{2+}(2), Co^{2+}(2)]$ (3), and  $Ni^{2+}$  (4)] are isostructural with the same monoclinic space group,  $P2_1/c$ , and distorted octahedral environments of the center ions. The structure of 2 will be described in detail herein. As shown in Figure 1 (a), the Cd atom is coordinated by four oxygen atoms from three different oba<sup>2-</sup> anions [Cd(1)-O 2.231(2)-2.403(2) Å] and two nitrogen atoms from two independent btmb ligands [Cd(1)-N 2.314(2)-2.319(3) Å]. Each oba<sup>2-</sup> anion adopts a bismonodentate/chelating coordination mode and the cadmium centers are bridged by the oba<sup>2-</sup> anions to form a 1D channel-like looped chain (Figure 1, b), which contains two kinds of rings (8- and 28-membered). The flexible btmb ligand has a cis-conformational coordination mode and links two Cd<sup>II</sup> atoms to form a 34-membered loop [Cd···Cd 16.148(1) Å] (part a of Figure S2, Supporting Information). Then, the adjacent but independent 1D looped chains are connected together by the btmb ligand to form a 2D planar motif (Figure 1, c, left). To further understand the topological structure of complex 2, if the  $oba^{2-}$  ligand is regarded as a 3-connected node, the btmb ligand is considered as a



Scheme 3. Hydrothermal syntheses of complexes 2-8.

linear linker and the metal center can be treated as a 4connector. The resulting structure of **2** affords a (3,4)-connected 2D network with a  $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$  topology (Figure 1, c, right).<sup>[13e]</sup> In addition, the 3D supramolecular structure is formed by the linking of 2D layers through van der Waals interactions (C30···C15 3.357 Å) (Figure 1, d).<sup>[22]</sup>

 $\{Zn(oba)(btmb)\}_n$  (5). Single-crystal X-ray structural analysis reveals that 5 crystallizes in the orthorhombic space group Pbca and exhibits a 2D planar layer structure. Each Zn<sup>II</sup> atom shows a distorted trigonal bipyramidal configuration, which is defined by three oxygen atoms of carboxyl groups of oba<sup>2-</sup> anions and two nitrogen atoms of two distinct btmb ligands (Figure 2, a). The distances of Zn1–O [1.962(5)–2.227(5) Å] and Zn1–N [2.023(7)– 2.057(6) Å] are in the normal range. In the structure of 5, as shown in Figure 2 (b), it is of interest that the Zn<sup>II</sup> ions are linked by oba<sup>2-</sup> ligands to form an infinite 2D network including left- and right-handed helical chains with a pitch of 11.206 Å along the a axis. The dihedral angle between the two phenyl rings of the oba<sup>2–</sup> ligand is 64.76°. The btmb ligand exhibits a *cis* conformation to link two Zn<sup>II</sup> ions to form the 0D loop with a distance of 15.639(1) Å, which is the same as for complex 2. From a topological view, the oba<sup>2-</sup> anions are considered as 3-connected nodes, and the Zn<sup>II</sup> ion is viewed to be a 4-connected node, then the btmb ligand is simplified as a linker connecting the metal centers. Thus, the structure of 5 can be simplified to a unique (3,4)connected framework with a  $(4.5^2)(4.5^3 \cdot 7^2)$  topology (Figure 2, c).<sup>[13e]</sup>

Additionally, the adjacent 2D layers are held together by van der Waals forces (C17···C32 3.564 Å) to afford a 3D supramolecular network along the *b* axis (Figure 2, d).

 $\{M(sdba)(btmb)\}_n$  [M = Co<sup>2+</sup> (6) and Cd<sup>2+</sup> (7)]. The structures of 6 and 7 are isostructural and the only differ-

ence in the coordination modes of the sdba2- anions are due to coordinative preferences of the metal centers (Figure 3, a, Figure S3, a). The structure of 6 will be described in detail herein. As shown in part a of Figure 3, each Co<sup>II</sup> ion exhibits a distorted tetrahedron environment, composed of two carboxylic oxygen atoms from two sdba2- anions [Co(1)–O(1) 2.002(5) Å, Co(1)–O(3) 1.963(5) Å] and two nitrogen atoms from two triazole rings [Co(1)–N(1) 2.036(7) Å; Co(1)–N(4) 2.002(8) Å]. Each sdba<sup>2–</sup> anion bridges cobalt atoms in a monodentate/monodentate coordination mode to form a 1D infinite zigzag chain with a Co-Co distance of 14.445(0) Å (Figure S3, b). Interestingly, the adjacent Co<sup>2+</sup> ions are linked by anti-conformational btmb ligands in a Z-shaped fashion, which results from a 1D sine wave-like chain with a Co--Co distance of 16.871(7) Å (Figure S3, c). Four Co<sup>II</sup> atoms are interlinked by btmb and sdba<sup>2-</sup> ligands to afford a square grid with a large window  $(14.445(0) \times 16.871(7) \text{ Å})$ . These are further connected together into a 2D undulating network with a (4,4) sheet by considering the [CoN<sub>2</sub>O<sub>2</sub>] units as the network nodes (Figure 3, b). In addition, the 3D supramolecular framework is stabilized by the linking of a 2D undulating network through van der Waals interactions (C16···C17 3.484 Å) (Figure 3, c).

{[Cu(H<sub>2</sub>odpa)(btmb)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>*n*</sub> (8). The single-crystal X-ray structural analysis reveals that complex 8 crystallizes in the triclinic space group  $P\bar{1}$ , and that there are two types of coordination environments around the Cu<sup>II</sup> ions in the crystal structure (Figure 4, a). The Cu1 atom has a distorted oblate octahedral geometry because of the Jahn–Teller effect, which is defined by two carboxylic oxygen atoms of two H<sub>2</sub>odpa<sup>2–</sup> ligands [Cu1–O1 1.980(2) Å] and two nitrogen atoms of two triazole rings from the *anti* conformation of the btmb ligands [Cu1–N1 1.974(2) Å] oc-















Figure 1. (a) ORTEP diagram showing the coordination environments for  $Cd^{II}$  ions in **2**. All H atoms are omitted for clarity. (b) Chain of  $oba^{2-}$  anions and  $Cd^{II}$  atoms forming a 1D channel. (c) View of the 2D-layer structure of complex **2** along the *b* axis and a schematic representation of the (3,4)-connected 2D network with  $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$  topological notation. The long rod represents the btmb ligand. (d) Overall view of the 3D supramolecular framework, formed by the linking of 2D layers through van der Waals interactions.

cupying the equatorial plane, while two carboxylic oxygen atoms of two H<sub>2</sub>odpa<sup>2–</sup> ligands [Cu1–O2 2.627(1) Å] are arranged in the *trans*-axial direction. However, the distance between the carboxylic oxygen (O2) atom and the Cu1 atom is in unusual and regarded as a non-negligible weak interaction.<sup>[23]</sup> Compared with the Cu1 atom, the Cu2 atom also occupies the center of a distorted elongated octahedral geometry that is six-coordinate. It is coordinated by two nitrogen atoms from the btmb ligands [Cu2–N4 1.977(4) Å], two oxygen atoms from the carboxylic groups of  $H_2odpa^{2-}$  [Cu2–O3 1.963(3) Å], and two coordination water molecules. The distance between Cu2–O12 also suggests a very weak interaction [Cu2–O12 2.772(4) Å].<sup>[23]</sup> These weak interactions (Cu1–O2 and Cu2–O12) may play an important role in fixing the metal centers in a definite conformation in **8**. Similar to complex **6**, Cu1 and Cu2 [Cu···Cu 6.152(0) Å] are linked by carboxylic groups of the  $H_2odpa^{2-}$ ligand to form a 1D zigzag chain in a monodentate/chelat-









(b)



(c)



Figure 2. (a) ORTEP diagram showing the coordination environments of the  $Zn^{II}$  atoms in **5**. All H atoms are omitted for clarity. (b) 2D network of  $Zn^{II}$  atoms and  $oba^{2-}$  anions containing left- and right-handed helical chains along the *a* axis. (c) Schematic description of the (3,4)-connected 2D framework built on the 3-connected  $oba^{2-}$  anions and 4-connected  $Zn^{II}$  centers (long linkers showing btmb ligands). (d) Weak van der Waals interactions between the 2D nets in **5**.



Figure 3. (a) ORTEP diagram showing the coordination environments for  $Co^{II}$  atoms in **6**. All H atoms are omitted for clarity. (b) Showing a 2D undulating network with (4,4) sheet in **6**. (c) A view of the packing by weak van der Waals interactions between the 2D layers in **6** and **7**.

ing coordination mode. A 1D infinite single-stranded polymeric chain is also formed by *anti*-conformational btmb ligands with a Cu···Cu separation of 16.359(0) Å

(Figure S4, a and b).<sup>[16b]</sup> These 1D chains are interlinked together to generate a 2D network with  $4^4$ -sql nets [6.151(8)×16.591(0) Å]; the H<sub>2</sub>odpa<sup>2-</sup> ligand is simplified



as a rod (Figure 4, b). Furthermore, the adjacent planar layers are packed together with weak hydrogen-bonding interactions [O···O 2.716(4)–2.933(1) Å] to generate a 3D supramolecular network (Figure 4, c).







Figure 4. (a) ORTEP diagram showing the coordination environments for Cu<sup>II</sup> atoms in **8**. All H atoms and lattice water molecules and disordered atoms are omitted for clarity. (b) The 2D structure with a 4-connected topology  $[6.151(8) \times 16.591(0) \text{ Å}]$  in **8**. (c) The 3D supramolecular structure was formed through hydrogen-bonding interactions (dotted lines) [O···O 2.716(4)–2.933(1) Å] in **8**.

### Discussion

From the structural descriptions above (Scheme 3) the conformation of the btmb ligand has an important effect on the constructuction of different structures in the selfassembly process. As illustrated in Scheme 1, generally, the long flexible btmb ligand shows two types of conformations (cis and anti) depending on the rotation of the two trizole rings,<sup>[16,19]</sup> which have formed distinct motifs with different configurations. For example, metal ions were bridged by btmb ligands with a cis conformation to form 0D loops in 2-5, whereas the 1D infinite chains based on an anti configuration were formed in 6-8. The different conformations of btmb ligands may be attributed to the introduction of organic anions.<sup>[12j]</sup> In addition, although the structures of 2 and 5 display 2D networks with the same (3,4)-connected notation, their topological structures are quite different. The Cd<sup>II</sup> ion is six-coordinate and can be described as having a distorted octahedral geometry in 2, but the Zn<sup>II</sup> ion is five-coordinate and has a distorted trigonal-bipyramidal geometry. The different coordination numbers may be substantially attributed to the distinct radii of the Cd<sup>II</sup> (2) and  $Zn^{II}$  (5) metal ions. The disparate radii of the metal ions induce the change of the binding mode of the O/N atoms to from different structures and topologies. It is suggested that metal ions are responsible for the different formations of the resulting structures.

#### X-ray Powder Diffraction and Thermal Properties

In order to characterize the phase purity of these complexes, X-ray powder diffraction (XRD) patterns of complexes 2–8 were performed at room temperature (Figure S5). Minor differences can be seen in the positions, intensities, and widths of some peaks, which indicates that these complexes were synthesized as a single phase.

To estimate the thermal stability of coordination polymers 2–8, thermogravimetric analyses (TGA) were carried out under a N<sub>2</sub> atmosphere in the temperature range 30– 850 °C. As depicted in Figure 5, the TGA curves of these



Figure 5. TGA curves of complexes 2-8 under a N<sub>2</sub> atmosphere.

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complexes indicate that the overall frameworks of complexes 3 and 5 began to collapse from 285 °C, while 2 and 4 were more stable up to 350 °C for 2 and 395 °C for 4, where the decomposition of the framework starts. For 6, no weight losses were observed up to 338 °C. The framework of complex 7 is stable up to 316 °C and the rapid weight loss from 316 to 454 °C corresponds to the loss of the btmb ligand (calcd: 44.04%; found 43.13%), where the overall framework begins to decompose slowly. For 8, the weight loss (7.01%) is attributed to the release of lattice water and coordinated water molecules in the temperature range 80-170 °C, which is in good agreement with the calculated value (6.95%). The second step occurs over the range 170-464 °C, corresponding to the loss of btmb ligands (calcd: 40.65%; found 40.02%). To some extent, the results reveal that the triazole-based frameworks have a high thermal stability, which is suggested as a good candidate for the construction of more stable coordination polymers.

#### **Photoluminescent Properties**

The metal-organic coordination polymers, especially the d<sup>10</sup>-metal complexes, have been investigated for luminescent properties and for potential application as photoactive materials.<sup>[24]</sup> Therefore, in the present work, the luminescent properties of 2, 5, and 7 as well as the free ligands were investigated in the solid state at room temperature (Figure 6). The luminescent spectra of the free btmb ligand shows emission at  $\lambda_{\text{max}} = 352 \text{ nm}$  upon excitation at 280 nm,  $\lambda_{\text{max}}$  = 330 nm for H<sub>2</sub>oba and 347 nm for H<sub>2</sub>sdba  $(\lambda_{ex} = 280 \text{ nm})$ . Complexes 2 and 5 exhibit an intense luminescence emission peak at 328 nm for **2** and  $\lambda_{max} = 321$  nm for 5 ( $\lambda_{ex}$  = 280 nm). In comparison with the btmb ligand, the emission of **2** and **5** may be assigned to intraligand ( $\pi$ –  $\pi^*$ ) fluorescence.<sup>[25]</sup> However, the emission peak for 7 is redshifted relative to that of the free ligands and exhibits an intense luminescence emission at  $\lambda_{max} = 372$  nm upon excitation at 280 nm. The enhancement of luminescence may be



Figure 6. The solid-state photoluminescent spectra of 2, 5, 7, and the free ligands at room temperature.

attributed to sdba<sup>2–</sup> ligand chelation at the Cd<sup>II</sup> center and their rigidity. The emission peaks for **7** in nature are probably assigned to ligand-to-metal charge-transfer (LMCT) transitions.<sup>[25b,26]</sup> In comparison with **2**, **5**, and **7**, the different emission bands may be attributed to the metal–ligand coordinative behaviors and the different architectures featuring different ligands.

### Conclusions

In summary, we have successfully synthesized and characterized seven coordination polymers with a conformational btmb ligand and V-shaped polycarboxylate ligands. The structural diversities indicate that the conformation of the btmb ligand and flexible aromatic polycarboxylate anions play dominant roles in the assembly of the resulting framework. In addition, the TGA results reveal that the triazole-based frameworks have a high thermal stability, which is suggested as a good candidate for the construction of more stable coordination polymers. On the basis of this work, other coordination polymers with conformational bis-triazole ligands and aromatic organic carboxylate anions with interesting aesthetic structures as well as physical properties will be further explored in our laboratory.

### Experimental Section

Reagents and Physical Measurements: All reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were recorded with a Perkin-Elmer model 240C instrument. Mass spectra were determined with an AXIMA-CFR™plus MALDI-TOF mass spectrometer. IR spectra were recorded with a Perkin-Elmer Spectrum One spectrometer in the region 4000-400 cm<sup>-1</sup> using KBr pellets. Thermal analyses were performed with a NETZSCH STA 449C microanalyzer with a heating rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere. The X-ray powder diffraction (XRD) data were recorded with a Rigaku RU200 diffractometer at 60 kV, 300 mA, and Cu-K<sub>a</sub> radiation ( $\lambda = 1.5406$  Å), with a scan speed of 2° min<sup>-1</sup> and a step size of  $0.02^{\circ}$  in  $2\theta$ . Luminescence spectra for the solid samples were investigated with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. <sup>1</sup>H NMR spectra were recorded using INOVA 400 MHz (Varian).

**btmb (1):** The 4,4'-bis[(1,2,4-triazol-1-yl)methyl]biphenyl (btmb) ligand was synthesized from literature methods.<sup>[19,14d]</sup> Yield 63%; m.p. 168–170 °C. MS: m/z = 317.63 for [Hbtmb]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>OD):  $\delta = 5.468$  (4 H), 7.393 (2 H), 7.634 (2 H), 8.008 (2 H), 8.608 (2 H) ppm.

{**Cd(oba)(btmb)**}<sub>*n*</sub> (2): A mixture containing Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.1 mmol, 26.7 mg), btmb (0.1 mmol, 31.6 mg), H<sub>2</sub>oba (0.1 mmol, 25.8 mg), and NaOH (0.2 mmol, 8.0 mg) in H<sub>2</sub>O (10 mL) was sealed in a 23 mL Teflon<sup>®</sup>-lined autoclave and heated at 160 °C for 3 d. Colorless, block, single crystals suitable for X-ray diffraction were obtained in 46% yield (31.5 mg, based on Cd).  $C_{32}H_{24}CdN_6O_5$  (684.97): calcd. C 56.11, H 3.53, N 12.27; found C 56.32, H 3.38, N 12.62. IR (KBr):  $\tilde{v} = 3440$  (s), 3097 (m), 2926 (w), 1599 (s), 1564 (m), 1532 (m), 1500 (w), 1438 (w), 1383 (s), 1300 (w), 1281 (w), 1248 (s), 1184 (m), 1157 (w), 1137 (m), 1101 (w),



1009 (m), 985 (w), 878 (w), 860 (w), 827 (w), 809 (m), 786 (m), 716 (w), 676 (m), 650 (m), 620 (w), 539 (w), 504 (m) cm<sup>-1</sup>.

{**Co(oba)(btmb)**}<sub>*n*</sub> (3): The synthetic method was the same as that used for **2**, except that Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O was used instead of Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O. Yield 65% (41.0 mg, based on Co). C<sub>32</sub>H<sub>24</sub>CON<sub>6</sub>O<sub>5</sub> (631.50): calcd. C 60.86, H 3.83, N 13.31; found C 60.91, H 3.62, N 13.54. IR (KBr):  $\tilde{v} = 3424$  (s), 3099 (m), 2926 (w), 1915 (w), 1605 (s), 1566 (w), 1531 (m), 1499 (w), 1384 (s), 1280 (w), 1247 (m), 1180 (w), 1157 (w), 1135 (m), 1098 (w), 1011 (w), 903 (w), 879 (w), 852 (w), 810 (m), 785 (m), 760 (m), 714 (w), 683 (w), 653 (w), 619 (w), 543 (m), 507 (w) cm<sup>-1</sup>.

{Ni(oba)(btmb)}<sub>n</sub> (4): The procedure was the same as that used for 3, except that Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O was replaced by Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O. Green, suitable crystals for crystal structure determination of 4 were obtained in 57% yield (36.0 mg, based on Ni). C<sub>32</sub>H<sub>24</sub>N<sub>6</sub>NiO<sub>5</sub> (631.28): calcd. C 60.88, H 3.83, N 13.31; found C 60.86, H 3.61, N 13.03. IR (KBr):  $\tilde{v} = 3430$  (s), 2925 (w), 1599 (s), 1530 (w), 1497 (vw), 1383 (s), 1296 (w), 1246 (m), 1156 (w), 1129 (m), 1016 (w), 878 (m), 756 (m), 682 (w), 652 (w), 618 (w), 546 (w), 504 (w) cm<sup>-1</sup>.

{**Zn(oba)(btmb)**}<sub>*n*</sub> (5): The synthetic method was the same as that used for **2**, except that Zn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O was used instead of Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O. Yield 56% (35.7 mg, based on Zn). C<sub>32</sub>H<sub>24</sub>N<sub>6</sub>O<sub>5</sub>Zn (637.94): calcd. C 60.25, H 3.79, N 13.17; found C 60.48, H 3.67, N 13.45. IR (KBr):  $\tilde{v} = 3422$  (s), 3096 (w), 1928 (w), 1680 (m), 1596 (s), 1560 (w), 1501 (m), 1384 (s), 1318 (w), 1288 (w), 1250 (s), 1158 (m), 1126 (m), 1103 (w), 1003 (m), 934 (w), 877 (w), 855 (m), 828 (w), 764 (m), 693 (w), 673 (w), 650 (m), 618 (w), 544 (m) cm<sup>-1</sup>.

{**Co(sdba)(btmb)**}<sub>*n*</sub> (6): The synthetic method was the same as that used for 3, except that H<sub>2</sub>sdba (0.1 mmol, 27.1 mg) was used instead of H<sub>2</sub>oba. Yield 62% (42.1 mg, based on Co). C<sub>32</sub>H<sub>24</sub>CoN<sub>6</sub>O<sub>6</sub>S (679.56): calcd. C 56.56, H 3.56, N 12.37; found C 56.73, H 3.74, N 12.68. IR (KBr):  $\tilde{v} = 3425$  (s), 3098 (m), 2962 (w), 2852 (w), 2665 (m), 2541 (w), 1691 (s), 1606 (m), 1562 (w), 1493 (w), 1424 (m), 1401 (m), 1379 (w), 1330 (w), 1283 (s), 1213 (w), 1157 (s), 1121 (m), 1099 (m), 1068 (w), 1014 (m), 930 (m),

861 (m), 747 (s), 724 (w), 686 (w), 620 (m), 568 (m), 548 (w), 463 (w) cm<sup>-1</sup>.

{**Cd(sdba)(btmb)**}<sub>*n*</sub> (7): The synthetic method was the same as that used for **6**, except that Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O was used instead of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O. Colorless block crystals of 7 were obtained in 45% yield (33.0 mg, based on Cd). C<sub>32</sub>H<sub>24</sub>CdN<sub>6</sub>O<sub>6</sub>S (733.03): calcd. C 52.43, H 3.30, N 11.46; found C 52.72, H 3.52, N 11.73. IR (KBr):  $\tilde{v} = 3214$  (s), 3114 (s), 1815 (w), 1659 (w), 1590 (s), 1546 (s), 1490 (m), 1403 (s), 1326 (w), 1297 (m), 1215 (w), 1155 (m), 1130 (m), 1101 (w), 1070 (w), 1012 (m), 968 (w), 907 (w), 865 (s), 803 (w), 777 (m), 749 (s), 695 (w), 676 (w), 619 (m), 574 (w), 494 (w), 468 (m) cm<sup>-1</sup>.

{[Cu(H<sub>2</sub>odpa)(btmb)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub> (8): A mixture containing Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.1 mmol, 20.0 mg), btmb (0.1 mmol, 31.6 mg), H<sub>4</sub>odpa (0.1 mmol, 31.0 mg), and NaOH (0.2 mmol, 8.0 mg) in H<sub>2</sub>O (10 mL) was sealed in a 23 mL Teflon<sup>®</sup>-lined autoclave and heated at 160 °C for 3 d. Blue, block-shaped single crystals suitable for X-ray diffraction were obtained in 72% yield (56.0 mg, based on Cu). C<sub>34</sub>H<sub>30</sub>CuN<sub>6</sub>O<sub>12</sub> (778.18): calcd. C 52.48, H 3.89, N 10.80; found C 52.67, H 3.747, N 10.77. IR (KBr):  $\tilde{v} =$ 3424 (s), 3123 (s), 2924 (w), 2854 (w), 1698 (s), 1612 (m), 1581 (m), 1549 (m), 1388 (s), 1281 (m), 1253 (m), 1224 (m), 1193 (m), 1128 (s), 1078 (w), 1043 (w), 1002 (w), 962 (w), 938 (w), 879 (w), 839 (w), 799 (m), 753 (m), 674 (w), 630 (w), 553 (w), 502 (w), 461 (w) cm<sup>-1</sup>.

**X-ray Crystallography:** Single-crystal X-ray diffraction analyses of the seven complexes were carried out with a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) by using the  $\phi/\omega$  scan technique at room temperature. All structures were solved by direct methods and refined by full-matrix least-squares fittings on  $F^2$  by SHELX-97.<sup>[27]</sup> Absorption corrections were applied by using the multi-scan program SADABS.<sup>[28]</sup> All non-hydrogen atoms were refined anisotropically, the water hydrogen atoms were located from difference Fourier maps and refined with isotropic thermal parameters, 1.5 times those of their carrier atoms. Hydrogen atoms of the water molecules in **8** were located from the difference maps and then refined by a riding model. In **5**, some carbon atoms (C19, C20, C22, C23, C25, C26, C28, C29; C19', C20', C22', C23', C25',

Table 1. Crystal data and structure refinements for complexes 2–5.<sup>[a]</sup>

	2	3	4	5
Empirical formula	$C_{32}H_{24}CdN_6O_5$	C <sub>32</sub> H <sub>24</sub> CoN <sub>6</sub> O <sub>5</sub>	C <sub>32</sub> H <sub>24</sub> NiN <sub>6</sub> O <sub>5</sub>	$C_{32}H_{24}ZnN_6O_5$
$M_{\rm r}$ [gmol <sup>-1</sup> ]	684.97	631.50	631.28	637.94
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pbca
a [Å]	15.2965(10)	15.056(9)	15.0103(19)	16.6690(19)
b [Å]	16.9485(12)	16.747(11)	16.738(2)	11.1789(12)
c [Å]	11.0150(8)	10.838(7)	10.8576(14)	29.645(3)
	90	90	90	90
β[°]	102.6370(10)	102.255(8)	102.245(2)	90
γ [°]	90	90	90	90
V[Å <sup>3</sup> ]	2786.5(3)	2670	2665.8(6)	5524.1(10)
Z	4	4	4	8
$\rho_{\rm calcd}  [\rm g  cm^{-3}]$	1.633	1.571	1.573	1.534
$\mu [\mathrm{mm}^{-1}]$	0.839	0.700	0.785	0.945
F [000]	1384	1300	1304	2624
θ[°]	1.82-25.10	1.84-25.10	1.85-25.10	1.84-25.10
Reflections collected	13737	13054	13255	26061
Goodness-of-fit on $F^2$	1.071	1.075	0.995	1.115
Final $R^{[a]}$ indices $[I > 2\sigma(I)]$	$R_1 = 0.0292$	$R_1 = 0.0891$	$R_1 = 0.0552$	$R_1 = 0.0776$
	$wR_2 = 0.0761$	$wR_2 = 0.1969$	$wR_2 = 0.1386$	$wR_2 = 0.1931$

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

C26', C28', C29') of two phenyl rings of the btmb ligand are disordered and were refined using carbon atoms split into two sites with a 50% occupancy. In complex 8 there is one disordered carboxylic group, (C34, O7, O8) and (C34', O7', O8') were refined using O or C atoms split over two equivalent sites, with a total occupancy of 1. The crystallographic data and selected bond lengths and angles for 2-8 are listed in Tables 1, 2, and S1 (Supporting Information).

Table 2. Crystal data and structure refinements for complexes  $6\!\!-\!\!8.^{[a]}$ 

	6	7	8
Empirical formula	C32H24CoN6O6S	C32H24CdN6O6S	C <sub>34</sub> H <sub>30</sub> CuN <sub>6</sub> O <sub>12</sub>
$M_{\rm r} [{\rm g}{ m mol}^{-1}]$	679.56	733.03	778.18
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_{1}$	ΡĪ
a [Å]	6.1365(10)	6.2057(10)	9.7697(10)
b [Å]	16.580(3)	16.634(3)	11.5172(12)
<i>c</i> [Å]	14.445(2)	14.671(3)	17.0312(18)
a [°]	90	90	96.1170(10)
β [°]	99.139(2)	100.005(2)	103.6930(10)
γ [°]	90	90	109.9310(10)
V [Å <sup>3</sup> ]	1451.0(4)	1491.4(5)	1713.2(3)
Ζ	2	2	2
$\rho_{\rm calcd.}  [\rm g  cm^{-3}]$	1.555	1.632	1.509
$\mu [{\rm mm}^{-1}]$	0.722	0.859	0.712
F [000]	698	740	802
θ[°]	1.43-25.10	1.87-25.10	1.92-25.00
Reflections collected	7343	7520	8592
Goodness-of-fit on $F^2$	1.039	1.025	1.061
Final R <sup>[a]</sup> indices	$R_1 = 0.0554$	$R_1 = 0.0467$	$R_1 = 0.0610$
$[I > 2\sigma(I)]$	$wR_2 = 0.1314$	$wR_2 = 0.0807$	$wR_2 = 0.1820$
[a] $R_1 = \Sigma( F_2  -  F_2 )$	$\sum  F_2  : wR_2 = 1$	$\{\sum [w(F_{a}^{2} - F_{a}^{2})^{2}\}$	$/\Sigma[w(F_{2}^{2})^{2}]^{1/2}$

CCDC-771063 (for 2), -771064 (for 3), -771065 (for 4), -771066 (for 5), -771067 (for 6), -771068 (for 7), -771069 (for 8) 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 also the footnote on the first page of this article): Additional figures selected bond lengths and angles, XRD patterns.

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