

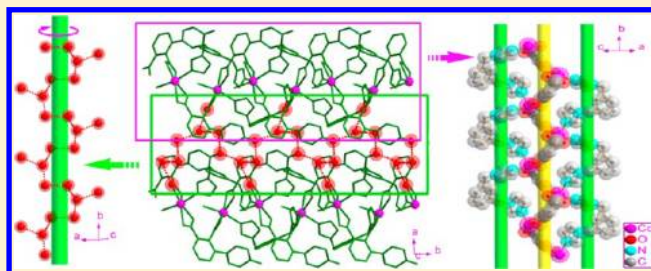
A Series of Cd(II) and Zn(II) Coordination Polymers with Helical Subunits Assembled from a Versatile 3-(4-hydroxypyridinium-1-yl) Phthalic Acid and N-Donor Ancillary Coligands

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S Supporting Information

ABSTRACT: A series of coordination polymers with various helical subunits, namely, $[\text{Cd}(\text{L})(\text{CH}_3\text{OH})(\text{H}_2\text{O})]_n$ (**2**), $\{[\text{Cd}(\text{L})(1,4\text{-bbi})] \cdot (\text{H}_2\text{O})\}_n$ (**3**), $\{[\text{Cd}(\text{L})(m\text{-bix}) \cdot (\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_2\}_n$ (**4**), $[\text{Zn}(\text{L})(4,4'\text{-bpy})_{0.5}]_n$ (**5**), and $[\text{Zn}(\text{L})(\text{bpp})]_n$ (**6**) (H_2L = 3-(4-hydroxypyridinium-1-yl) phthalic acid; PA = phthalic acid, a part of 3-(4-hydroxypyridinium-1-yl) phthalic acid)), have been hydro(solvo)thermally synthesized through the reaction of 3-(4-hydroxypyridinium-1-yl) phthalic acid with divalent zinc and cadmium salts in the presence or absence of N-donor ancillary coligands (1,4-bbi = 1,1'-(1,4-butanediyl)bis(imidazole), $m\text{-bix}$ = 1,3-bis(imidazol-1-ylmethyl)benzene, 4,4'-bpy = 4,4'-bipyridine, bpp = 1,3-bis(4-pyridyl)propane). As a result of various coordination modes of the versatile 3-(4-hydroxypyridinium-1-yl) phthalic acid and different coligands, these compounds exhibit structural diversity. Compound **2** displays a layered structure containing two kinds of $(\text{Cd}-\text{L})_n$ and $(\text{Cd}-\text{PA})_n$ helical chains. Compound **3** features a 3D supramolecular framework embodying a type of supramolecular helical chain. Compound **4** exhibits a metal–organic ribbon structure with two kinds of helical chains. Compound **5** features a 3D architecture in which a 1D lemniscate shape pseudo meso-helix chain is observed. Compound **6** exhibits a 2D achiral layer in which the 1D $(\text{Zn}-\text{bpp})_n$ helical chains are alternately arranged in a right- and left-handed sequence. These compounds have been characterized by powder X-ray diffractions (PXRD) and thermal gravimetric analyses (TGA). In addition, their photochemical properties have also been investigated.



■ INTRODUCTION

The rational design and synthesis of coordination polymers is currently of significant interest not merely due to the diverse network topology by the amalgamation of chemistry and geometry^{1–3} but mainly due to these extended systems playing a significant role in catalysis, chirality, luminescence, magnetism, nonlinear optics, adsorption, and separation.^{4,5} Among the known coordination polymers, helical structures have been attracting extensive attention in recent years owing to its potential applications and intriguing, fascinating architectures.^{6–8} Tactical selection of the organic ligand is a key factor for achieving this target. In general, helical structural motifs of these coordination polymers are closely related to the geometry and the number of coordination sites provided by organic ligands.

Since a carboxylate group can assume many types of bridging conformations to construct exciting networks, organic aromatic polycarboxylate ligands, as an important family of multidentate O-donor ligands, have been extensively employed in the preparation of such coordination polymers with helical structural motifs and interesting properties.⁹ Inspired by previous work, H_2L (3-(4-hydroxypyridinium-1-yl) phthalic acid) is chosen for the following reasons: (1) this organic ligand is a cation-type ligand, which has a good water-solubility and is beneficial to investigate the nature of this ligand in

hydro(solvo)thermal conditions; (2) the pyridine ring and phenyl ring are twisted across the C–N single bond, and the skew coordination orientation of the carboxyl groups provides the potential of the formation of helical segments; (3) the functional hydroxyl group on this ligand can act not only as a coordination site but also as a hydrogen-bond acceptor to give rise to supramolecular helical architecture; (4) only one coordination polymer constructed from H_2L has been reported,¹⁰ and much more work is still necessary to understand the coordination chemistry of H_2L .

Recently, a novel 3D supramolecular metal–organic framework $\{[\text{Cd}(\text{L})(\text{bix})] \cdot 1.75(\text{H}_2\text{O})\}_n$ (**1**) with a triple concentric helical system has been obtained by us through the reaction of Cd^{2+} metal center, H_2L , and bix (bix = 1,4-bis(imidazol-1-ylmethyl)benzene) based on hydro(solvo)thermal reactions.¹⁰ With the aim of further understanding the coordination chemistry of H_2L and preparing new materials with interesting architecture and excellent physical properties, we have recently engaged in the research of coordination polymers based on this ligand and d^{10} metal centers (Zn and Cd) in the presence or absence of N-donor ancillary coligands.

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Table 1. Crystal Data and Structure Refinement for Compounds 2–6^a

compound no.	2	3	4	5	6
formula	C ₁₄ H ₁₃ NO ₇ Cd	C ₂₃ H ₂₃ N ₅ O ₆ Cd	C ₂₇ H ₂₇ N ₅ O ₈ Cd	C ₁₈ H ₁₁ N ₂ O ₅ Zn	C ₂₆ H ₂₁ N ₃ O ₅ Zn
fw	419.65	577.86	661.94	400.66	520.83
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.1876(4)	17.459(2)	15.1589(9)	9.0309(10)	8.0033(5)
<i>b</i> (Å)	7.0215(3)	12.6894(18)	8.7394(6)	16.6234(18)	20.0585(11)
<i>c</i> (Å)	19.7798(7)	10.8705(11)	23.8358(17)	10.7100(12)	14.5833(9)
α (deg)	90	90	90	90	90
β (deg)	96.999(4)	90	120.386(5)	99.273(11)	101.315(7)
γ (deg)	90	90	90	90	90
<i>V</i> (Å ³)	1404.35(10)	2408.4(5)	2724(3)	1586.8(3)	2295.6(2)
<i>Z</i>	4	4	4	4	4
<i>D_c</i> (g·cm ^{−3})	1.985	1.594	1.614	1.677	1.507
<i>F</i> (000)	832	1168	1344	812	1072
reflns collected	2472	5261	11023	5923	9038
independent reflns	2464	3289	4791	2793	4031
<i>R</i> (int)	0.0292	0.0541	0.0323	0.0327	0.0268
GOF on <i>F</i> ²	1.057	1.001	1.061	1.107	1.026
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0363	0.8468	0.0524	0.0454	0.0323
<i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0888	0.8319	0.1190	0.1195	0.0751

^a*R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b*wR*₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

EXPERIMENTAL SECTION

Materials and Physical Measurements. All reagent and solvents employed in the present work were of analytical grade as obtained from commercial sources without further purification. Elemental analysis for C, H, and N were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range from 4000 to 400 cm^{−1} on a Nicolet NEXUS 470-FTIR spectrometer. Thermal analysis was performed on a SDT 2960 thermal analyzer from room temperature to 800 °C with a heating rate of 20 °C/min under nitrogen flow. Powder X-ray diffraction (PXRD) for 2–6 were measured at 293 K on a Rigaku D/max-3B diffractometer (Cu-Kα, λ = 1.5406 Å). The crushed single crystalline powder samples were prepared by crushing the crystals and scanned from 5 to 50 °C with a step of 0.1°/s. Solid UV–visible spectra were obtained in the 200–800 nm range on a JASCO UVDEC-660 spectrophotometer. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer.

Syntheses. 3-(4-Hydroxypyridinium-1-yl) phthalic acid was synthesized according to the literature.¹¹ Other starting materials were of reagent quality and obtained from commercial sources without further purification.

Synthesis of [Cd(L)(CH₃OH)(H₂O)]_n (2). A mixture of H₂L (0.0147 g, 0.05 mmol), Cd(NO₃)₂·4H₂O (0.0154 g, 0.05 mmol), KOH (0.0056 g, 0.1 mmol), 4 mL of water, and 1 mL of methanol was sealed in a 23 mL Teflon-lined stainless steel vessel and heated at 120 °C for three days. After the mixture was slowly cooled to room temperature, colorless crystals of 2 were obtained in 65% yield based on Cd(NO₃)₂·4H₂O. Anal. Calc. (%) for C₁₄H₁₃NO₇Cd (419.65): C 40.07, H 3.12, N 3.34. Found: C 39.29, H 2.85, N 3.10. IR/cm^{−1} (KBr): 3384(s, br), 3064(m), 1635(s), 1534(s), 1463(m), 1394(s), 1387(s), 1340(m), 1287(m), 1196(s), 1052(w), 1022 (w), 854(s), 774(s), 746 (w), 701(w).

Synthesis of [Cd(L)(1,4-bbi)]_n (3). Compound 3 was synthesized hydro(solvo) thermally in a 23 mL Teflon-lined autoclave by heating a mixture of H₂L (0.0147 g, 0.05 mmol), 1,4-bbi (0.0092 g, 0.05 mmol), Cd(NO₃)₂·4H₂O (0.05 mmol, 0.062 g), and KOH (0.0056 g, 0.1 mmol) at 120 °C in 4 mL of water and 1 mL of methanol for three days. Colorless needle-like crystals of 3 suitable for structure determination were picked out from the needle shaped crystals. Yield: about 67% (based on Cd(NO₃)₂·4H₂O). Anal. Calcd for C₂₃H₂₃N₅O₆Cd (577.87): C 47.81, H 4.01, N 12.12. Found: C 47.79, H 4.05, N 12.17. IR/cm^{−1} (KBr): 3483(m, br), 3116(m),

1631(s), 1560(s), 1561(m), 1453(w), 1388(m), 1344(w), 1286(w), 1197(w), 1096 (w), 855(w), 782(w).

Synthesis of [Cd(L)(bix)(H₂O)]_n (4). The procedure is similar to the synthesis of 3 except that bix (0.0119 g, 0.05 mmol) was used instead of 1,4-bbi. Colorless block-wise crystals of 4 were obtained in 58% yield based on Cd(NO₃)₂·4H₂O. Anal. Calcd for C₂₇H₂₇N₅O₈Cd (661.94): C 57.19, H 3.01, N 3.51. Found: C 57.12, H 2.98, N, 3.53. IR/cm^{−1} (KBr): 3373(s, br), 3117(m), 1634(s), 1556(s), 1523(w), 1393(s), 1352(w), 1283(w), 1190(s), 1060 (w), 1110(m), 854(s), 772(s), 728 (m), 663(w).

Synthesis of [Zn(L)(4,4'-bpy)_{0.5}]_n (5). The procedure is similar to the synthesis of 3 except that 4,4'-bpy (0.0078 g, 0.05 mmol) and Zn(NO₃)₂·6H₂O (0.014 g, 0.05 mmol) were used instead of 1, 4-bbi and Cd(NO₃)₂·4H₂O. Colorless block crystals of 5 were obtained in 73% yield based on Zn(NO₃)₂·6H₂O. Anal. Calcd for C₁₈H₁₁N₂O₅Zn (400.66): C 53.96, H 2.77, N 6.99. Found: C 53.92, H 2.79, N 6.95. IR/cm^{−1} (KBr): 3428(m, br), 3106(m), 1649(s), 1633(s), 1625(s), 1524(s), 1373(s), 1336(s), 1279(w), 1188(m), 1073 (w), 856(w), 836(w), 779(w).

Synthesis of [Zn(L)(bpp)]_n (6). The procedure is similar to the synthesis of 5 except that bpp (0.0094 g, 0.05 mmol) was used instead of bpy. Colorless block crystals of 6 were obtained in 61% yield based on Zn(NO₃)₂·6H₂O. Anal. Calcd for C₂₆H₂₁N₃O₅Zn (520.83): C 59.91, H 4.06, N 8.07. Found: C 59.87, H 4.11, N 8.13. IR/cm^{−1} (KBr): 3422(m, br), 3040(w), 1639(s), 1590(s), 1561(m), 1446(w), 1396(m), 1344(m), 1280(w), 1196(w), 1052 (w), 1022 (w), 848(w), 770(w).

X-ray Crystallography. Single-crystal X-ray diffraction data of compounds 2–6 were collected on a Bruker SMART APEX CCD diffractometer¹² equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature using the ω-scan technique. Empirical absorption corrections were applied to the intensities using the SADABS program.¹³ The structures were solved using the program SHELXS-97¹⁴ and refined with the program SHELXL-97.¹⁵ All nonhydrogen atoms were refined anisotropically. The hydrogen atoms of the coordination water molecules and ligands were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically. The hydrogen atoms of the solvent water molecules were located from the difference Fourier maps, then restrained at fixed positions and refined isotropically. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were

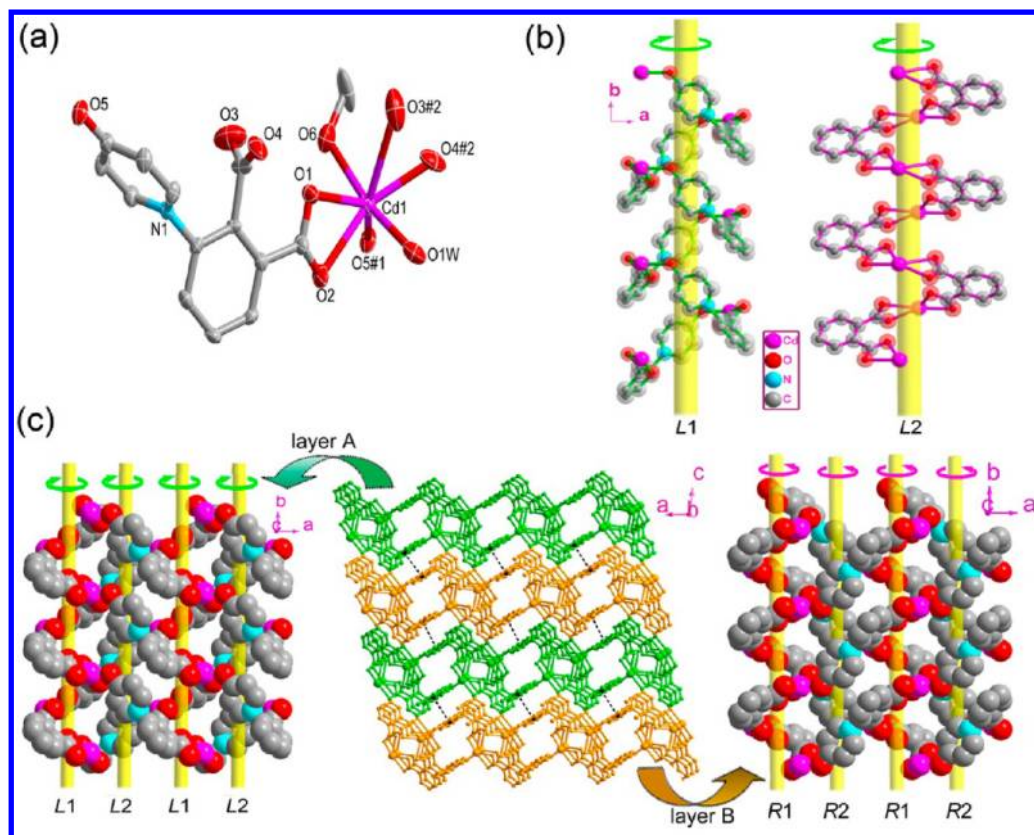


Figure 1. (a) View of the coordination environment of the Cd center in **2**. Symmetry codes: #1 $x - 1, y + 1, z$; #2 $-x, y + 1/2, -z + 1/2$. (b) Two adjacent homochiral helical chains (L1 for $(\text{Cd}-\text{L})_n$; L2 for $(\text{Cd}-\text{PA})_n$). (c) Layer A, left-handed layer; layer B, right-handed layer; and 3D supramolecular architecture of **2**.

incorporated. The crystallographic data, selected bond lengths, and angles for **2–6** are listed in Tables 1 and S1, Supporting Information.

RESULTS AND DISCUSSION

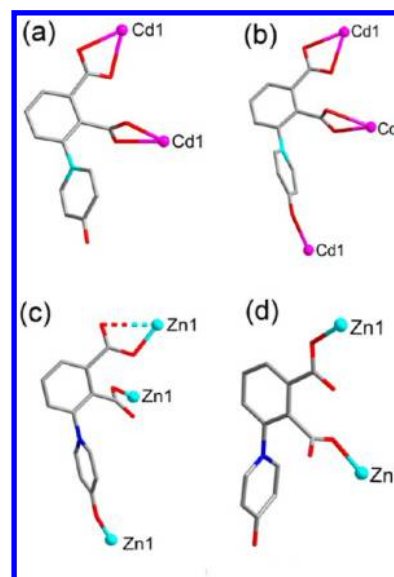
Syntheses. The successful isolation of **1** in our previous work prompted us to extend our study to other complexes based on H_2L . The result has proven that N-donor ancillary coligand is important in the construction of the resulting architecture. The common N-donor ancillary coligands are two kinds: rigid or flexible. In our investigation of the coordination chemistry of H_2L , we have selected one rigid N-donor ancillary coligand of 4,4'-bpy and three flexible N-donor ancillary coligands of 1,4-bbi, *m*-bix, and bpp.

Crystal Structure of $[\text{Cd}(\text{L})(\text{CH}_3\text{OH})(\text{H}_2\text{O})]_n$ (2**).** A single-crystal X-ray diffraction study reveals that **2** crystallizes in monoclinic system with $P2_1/c$ space group. As shown in Figure 1a, the asymmetric unit of **2** is composed of one Cd center, one L^{2-} anion, one coordinated water molecule, and one coordinated methanol molecule. The Cd center is seven-coordinated to form a pentagonal-bipyramidal geometry by O1, O2, O5#1, O3#1, and O4#2 from three distinct L^{2-} ligands, O6 from the coordinated methanol molecule and O1W from one coordinated water molecule. The range of Cd–O bond lengths fall in 2.219(4)–2.452(4) Å and all in the reasonable range.¹⁶ The L^{2-} ligand employs a twisted conformation, and the dihedral angle between pyridine ring and the phenyl ring is 43.1° , two carboxylate groups have a dihedral angle of 14.8 and 86.5° toward the plane of the corresponding linking phenyl rings, respectively. The bonding carboxylate groups of the L^{2-} ligand adopting chelating bidentate coordination mode and the

hydroxyl group in a monodentate mode coordinate to the Cd center (Scheme 1b).

The combination of the pyridine ring and phenyl ring are twisted across the C–N single bond and these twisted carboxylate groups result in the formation of $(\text{Cd}-\text{L})_n$ and $(\text{Cd}-\text{PA})_n$ helical chains. The cadmium cations are linked together by $\mu_3-\text{L}^{2-}$ to yield one type of $(\text{Cd}-\text{L})_n$ helical chain.

Scheme 1. Coordination Modes of the L^{2-} Anion, **a** in **1**, **3** and **4**; **b** in **2**; **c** in **5**; **d** in **6**



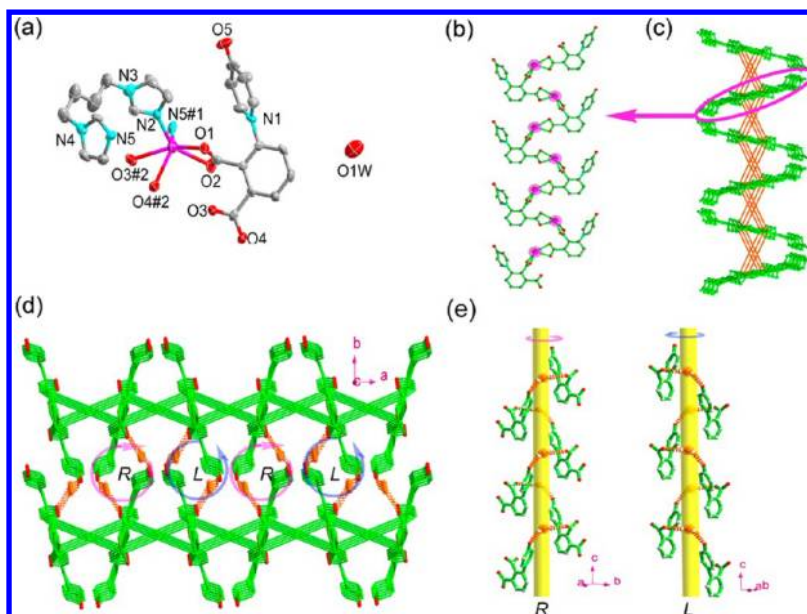


Figure 2. (a) View of the coordination environment of the Cd center in 3. Symmetry codes: #1 $x - 1/2, -y, z$; #2 $-x, -y, z - 1/2$ (all of the H atoms are omitted for clarity). (b) One-dimensional zigzag chain $[Cd(L)]_n$. (c) Two-dimensional layer of 3 ($[Cd(L)]_n$ is marked as green; 1,4-bbi ligand is marked as brown). (d) Three-dimensional supramolecular architecture of 3. (e) The right- and left-handed supramolecular helical chains.

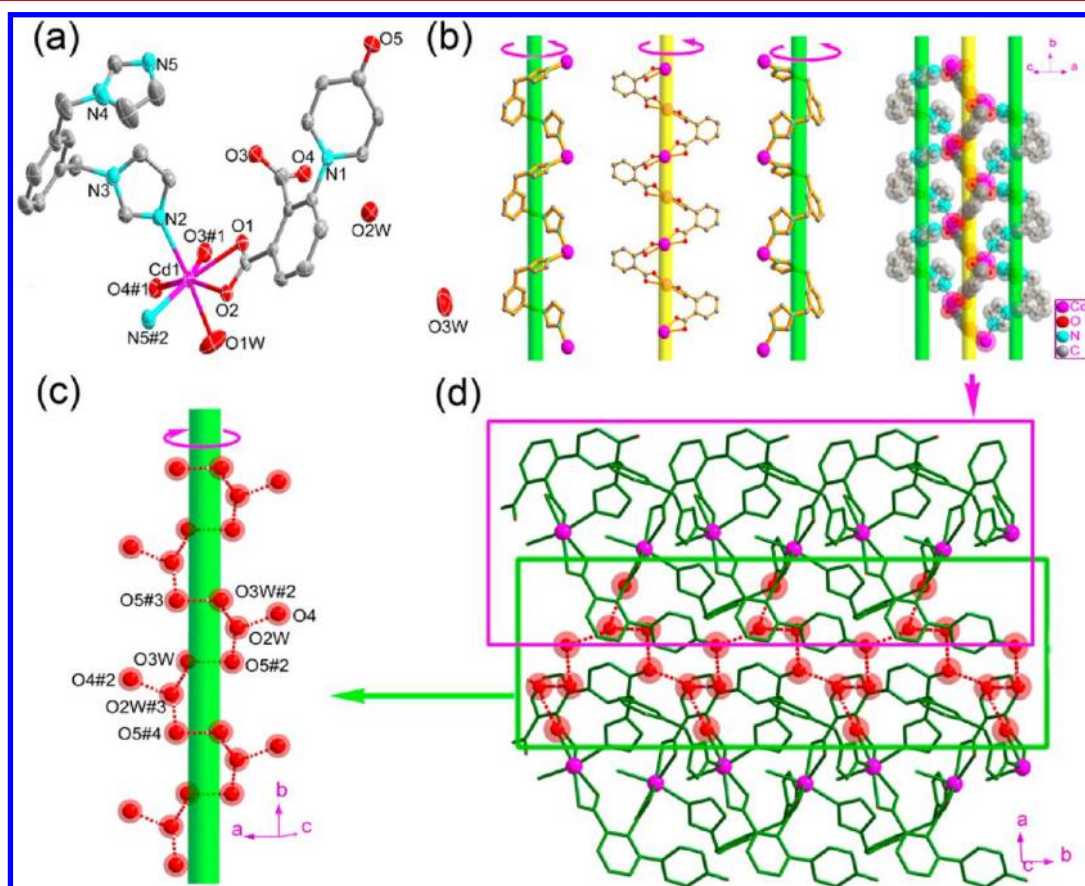


Figure 3. (a) View of the coordination environment of the Cd center in 4. Symmetry codes: #1 $-x, -1/2 + y, 3/2 - z$; #2 $x, -1 + y, z$. (b) A metal-organic ribbon structure. (c) Helical water chain. Symmetry codes: #2 $x, -1 + y, z$; #3 $1 - x, -1/2 + y, 3/2 - z$; #4 $1 - x, -3/2 + y, 3/2 - z$. (d) Two-dimensional supramolecular structure of 4.

More interest to us is that PA groups of L^{2-} ligands link Cd cations to generate another type of $(Cd-PA)_n$ helical chain with the same pitch as $(Cd-L)_n$ helical chain (Figures 1b and S1, Supporting Information). The screw axes of these helices

are all parallel to the b axis, and the pitch is $7.022(8) \text{ \AA}$. The $(Cd-L)_n$ and $(Cd-PA)_n$ helical chains with the same chirality are alternately arranged along the a axis to give rise to 2D homochiral helical structure by using Cd cations as hinges

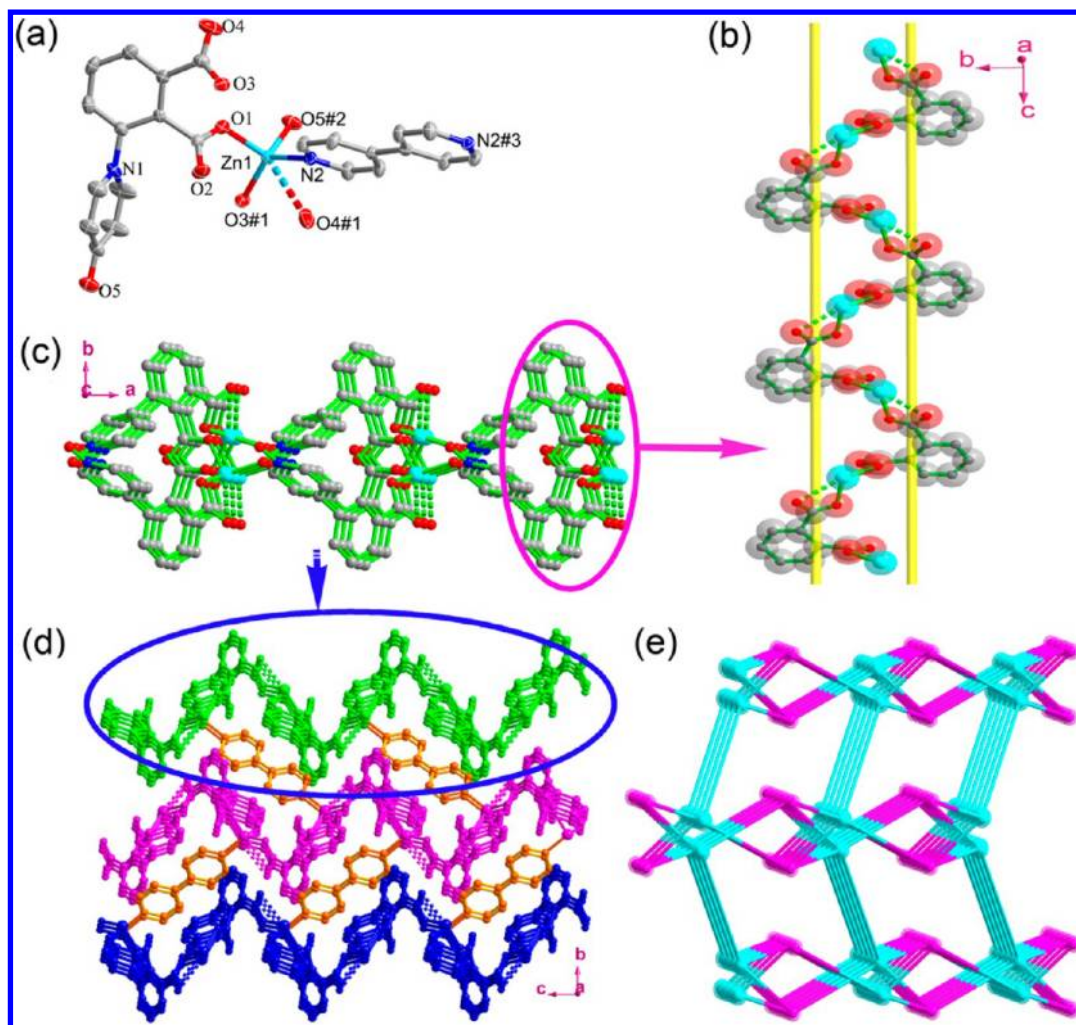


Figure 4. (a) View of the coordination environment of the Zn center in **5**. Symmetry code: #1 $x, -y + 3/2, z - 1/2$; #2 $x - 1, y, z$; #3 $x - 1, -y + 2, -z + 2$. (b) One-dimensional meso-helical chain $(\text{Zn-PA})_n$. (c) Side view of the two-dimensional network. (d) Three-dimensional network structure of **5**. (e) Schematic representation of **5**.

(layer A for the left-handed layer; layer B for the right-handed layer, Figure 1c). The chirality of each helical chain in one layer is opposite to that of the nearest ones of the same type in another layer along the c axis. Therefore, such 2D homochiral helical layers of the opposite chirality are alternatively packed into a mesomeric 3D supramolecular architecture by means of weak $\pi \cdots \pi$ interactions (separation 4.324 Å) (Figure 1c).¹⁷

Crystal Structure of $\{[\text{Cd}(\text{L})(1,4\text{-bbi})] \cdot (\text{H}_2\text{O})\}_n$ (3**).** A single-crystal X-ray diffraction analysis reveals that compound **3** belongs to the orthorhombic system with space group $Pca2_1$. As depicted in Figure 2a, the asymmetric unit of **3** contains one Cd center, one 1,4-bbi ligand, one L^{2-} anion, and one free water molecule. The Cd center adopts a distorted octahedral geometry by coordinating to two nitrogen atoms (N1 and N5#1) from neighboring 1,4-bbi ligands, and four oxygen atoms (O1, O2, O3#2, and O4#1) from two different L^{2-} anions. The nitrogen atom (N2) and oxygen atom (O2) occupy the axial positions, and the other nitrogen atom (N5#1) and oxygen atoms (O1, O3#2, and O4#2) comprise the equatorial plane. The Cd–O distances are 2.297(7), 2.384(6), 2.392(5), and 2.499(6) Å, respectively; and the Cd–N distances are 2.225(7) and 2.246(7) Å. As for the L^{2-} ligand, the dihedral angle between pyridine ring and the phenyl ring is 61.5°, and two carboxylate groups have 19.0 and 72.0° dihedral

angles, respectively, with the plane of the corresponding linking phenyl rings. Only two carboxylates in a bichelating fashion participate in coordination with Cd(II) ions (Scheme 1a). As shown in Figure 2b, Cd centers are linked together by L^{2-} anions, forming a 1D infinite zigzag chain $[\text{Cd}(\text{L})]_n$ along the c axis, and these chains are further connected by crossed 1,4-bbi ligands to produce a 2D layered structure in the ac plane (Figure 2c), leaving the uncoordinated hydroxyl group pointing up or down alternately from the layer (Figure 2d). Then, the lattice water molecules embed themselves between the 2D layers by forming hydrogen bonding interactions together with the coordinated carboxylate groups and uncoordinated hydroxyl groups (O1W–O2#3 2.897(9) Å and O1W–O5#4 2.684(9) Å) (Table S1, Supporting Information, and Figure 2e). Unexpectedly, a type of supramolecular helical chain with a helical pitch of 10.871(9) Å is generated by these hydrogen bonding interactions. Moreover, those supramolecular helical chains are arranged alternately with the opposite chirality between 2D sheets to give rise to a 3D racemic supramolecular network.

Crystal Structure of $\{[\text{Cd}(\text{L})(m\text{-bix})(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_2\}_n$ (4**).** A single-crystal X-ray diffraction study reveals that compound **4** crystallizes in monoclinic space group $P2_1/c$. As shown in Figure 3a, the asymmetric unit of **4** consists of one Cd center,

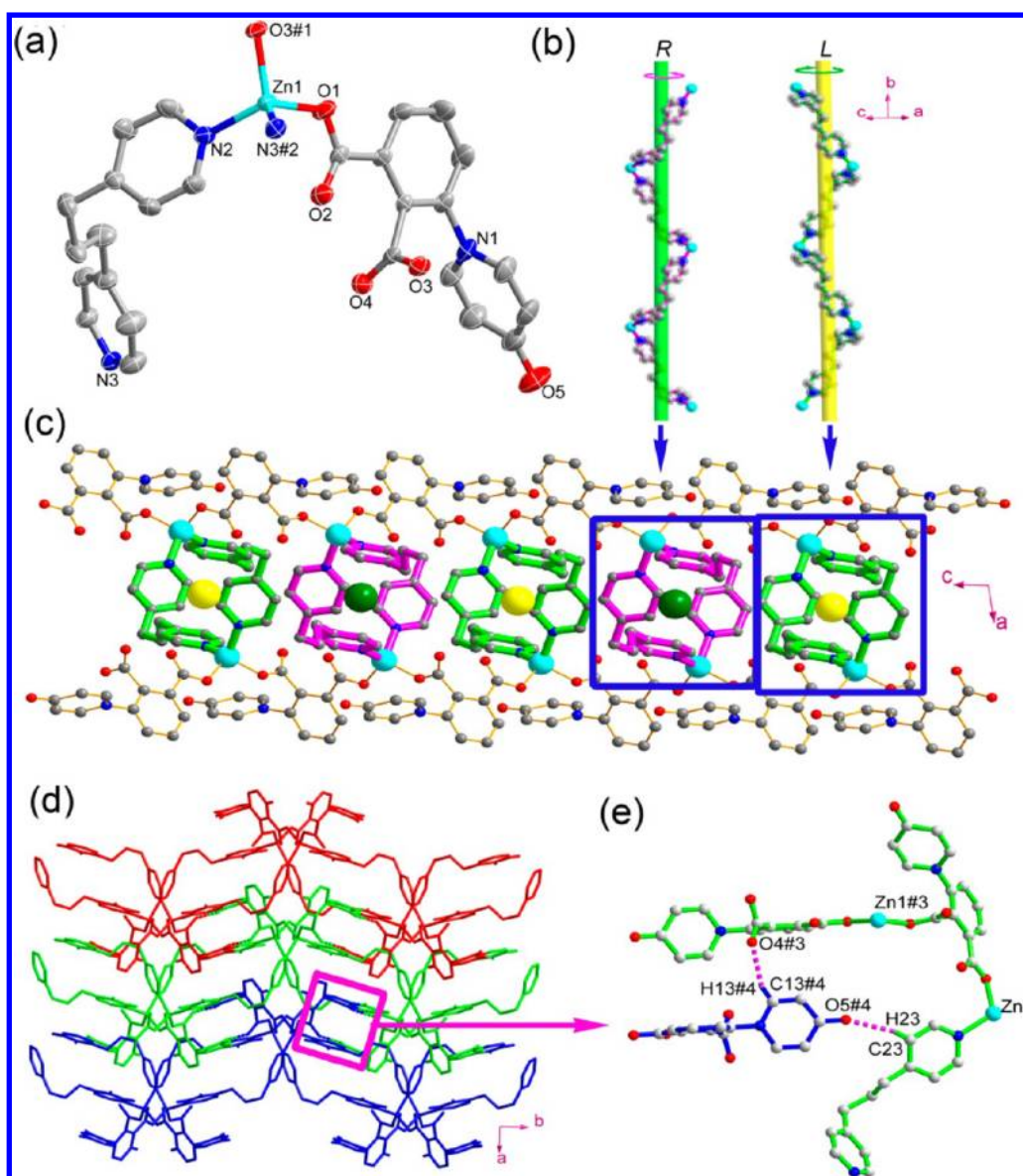


Figure 5. (a) View of the coordination environment of the Zn center in **6**. Symmetry codes: #1 $x, -y + 1/2, z - 1/2$; #2 $-x, y + 1/2, -z + 3/2$. (b) One-dimensional helical chains of $[\text{Zn}(\text{bpp})]_n$ with right- and left-handed chirality. (c) Top view of 2D layer structure. (d) Three-dimensional supramolecular structure. (e) C–H $\cdots$ O hydrogen bond interaction between adjacent 2D layers.

one L^{2-} anion, one *m*-bix ligand, one coordinated water molecule, and two solvent water molecules. The Cd center is seven-coordinated by four carboxylate O atoms from two L^{2-} anions, one water molecule, and two N atoms from two *m*-bix ligands, the metal environment is best described as a distorted pentagonal bipyramid geometry with one nitrogen (N1) and one water molecule oxygen (O1W) occupying the axial positions, with the other nitrogen (N5#2) and oxygens (O1, O2, O3#1, and O4#1) comprising the equatorial plane. The Cd–O distances are 2.332(4), 2.426(3), 2.434(3), 2.461(3), and 2.523(4) Å, respectively, and the Cd–N distances are 2.293(4) and 2.298(4) Å. The L^{2-} acts as a bis-chelating ligand (Scheme 1a), a visible twisting is observed between two carboxylate groups and the plane of the corresponding linking phenyl rings, with the dihedral angle between them being 17.9 and 79.6°. The hydroxyl group is not involved in the coordination with Cd ions, for the dihedral angle between pyridine ring and the phenyl ring is 57.8°. The coordination of

two bichelating carboxylate groups and Cd ions results in the formation of a right-handed $(\text{Cd}(\text{PA}))_n$ helical chain with the pitch of 8.739(8) Å. As described in Figure 3b, The winding axis corresponds to the *b*-axis. As for *m*-bix, it adopts the *cis*-conformation, with both imidazole groups on the same side of the central benzene ring, such a conformation plays a vital role in resulting a rare pseudo helical chain $(\text{Cd}-m\text{-bix})_n$. More interestingly, one right-handed $(\text{Cd}(\text{PA}))_n$ helical chain is just sandwiched between two $(\text{Cd}-m\text{-bix})_n$ pseudo helical chains to form a metal–organic ribbon structure (Figure 3b). These ribbons are held together by extensive hydrogen bonds, where two lattice water molecules form hydrogen bonds with the carboxylate oxygen atoms and hydroxyl oxygen atoms ($\text{O2W}\cdots\text{O5\#2}$ 2.861(6) Å; $\text{O2W}\cdots\text{O4}$ 2.791(6) Å; $\text{O3W}\cdots\text{O5\#2}$ 2.807(6) Å; and $\text{O3W}\cdots\text{O2W\#3}$ 2.838(7) Å) (Table S2, Supporting Information). It is noteworthy that a third kind of right-handed helical water chain extends the architecture of **4** from ribbon to 2D supramolecular layer

through hydrogen bonds (Figure 3d). Interestingly, along the *c* axis, these helical water chains are arranged alternately with the opposite chirality to give rise to a 3D racemic supramolecular network (Figure S2, Supporting Information). $\pi\cdots\pi$ interactions also exist between between parallel imidazole rings from neighboring layers with the centroid distance of 3.884 Å,¹⁸ these $\pi\cdots\pi$ interactions bring further stability of the structure of **4** (Figure S3, Supporting Information).

Crystal Structure of $[\text{Zn}(\text{L})(4,4'\text{-bpy})_{0.5}]_n$ (5**).** A single-crystal X-ray diffraction study reveals that compound **5** crystallizes in the monoclinic space group $P2_1/c$. As depicted in Figure 4a, the asymmetric unit of **5** consists of one Zn center, one L^{2-} ligand and half of a 4,4'-bpy molecule. The Zn center displays a distorted trigonal bipyramid configuration. At first glance, Zn1 should take a distorted tetrahedron geometry: three O atoms (O1, O3#1, and O5#2) from three different L^{2-} ligands and one N atom (N2) from 4,4'-bpy ligand. However, the distance of 2.709 Å between Zn1 and O(4#1) of the neighboring L^{2-} suggests a nonnegligible interaction between them. Thus, the Zn1 center can be regarded as a distorted trigonal bipyramid geometry. In compound **5**, the L^{2-} ligand employs a twisted conformation; the dihedral angles between the two carboxylate groups and their corresponding phenyl rings are 30.7 and 59.8°. The hydroxyl group is also coordinated with Zn ions, for the dihedral angle between pyridine ring and the phenyl ring is 82.7°. Two carboxylate groups show different coordination modes: one in a $\mu_2-\eta^1:\eta^1$ coordination fashion, and the other one shows a $\mu_1-\eta^1:\eta^0$ bridging mode (Scheme 1c). First, along the *c* direction, Zn1 centers are linked by PA group of L^{2-} to give rise to a 1D lemniscate shape pseudo meso-helical chain $[\text{Zn}(\text{PA})]_n$ (Figure 4b). Then, the adjacent $[\text{Zn}(\text{PA})]_n$ chains are joined together by the remaining hydroxyl groups to produce a 2D layered structure in the *ac* plane (Figure 4c). Such layers are further united together through 4,4'-bpy ligands to present a 3D framework (Figure 4d). From the topological view, Zn(II) atoms can be viewed as 4-connected nodes, L^{2-} anions can be viewed as 3-connected nodes, and the 4,4'-bpy ligands can be considered as linkers, so the overall 3D structure of **5** can be described as a (3,4)-connected framework with a Schläfli symbol of $\{6^3\}\{6^5.8\}$ (Figure 4e).

Crystal Structure of $[\text{Zn}(\text{L})(\text{bpp})]_n$ (6**).** A single-crystal X-ray diffraction study reveals that compound **6** belongs to the monoclinic system with space group $P2_1/c$. As is shown in Figure 5a, the asymmetric unit of **6** contains one Zn center, one bpp molecule, and one L^{2-} ligand. Each Zn center is surrounded by two oxygen atoms (Zn1–O1 1.935(2) Å; Zn1–O3#1 1.940(2) Å; and O1–Zn–O3#1 99.03(7)°) from two distinct L^{2-} anions, and two N atoms (Zn1–N2 2.015(2) Å; Zn–N3#2 2.030(2) Å; and N2–Zn–N3#2 105.01(8)°) from two different bpp ligands to furnish a slight distorted tetrahedron geometry. As for the L^{2-} ligand, the pyridine ring is almost perpendicular to the plane of corresponding linking phenyl ring, with the dihedral angle between them being 89.6°, one carboxylate group is almost parallel to the plane of corresponding linking phenyl ring, and the other carboxylate group is nearly perpendicular to the plane of corresponding linking phenyl ring, with the dihedral angle between them being 1.6° and 86.2°, respectively. The hydroxyl group does not participate in the coordination with Zn ions; as the carboxylate groups adopt $\mu_1-\eta^1:\eta^0$ (Scheme 1d) coordination mode, L^{2-} ligand acts as a linker to bridge Zn centers. For the bpp ligand, two pyridine rings rotate around the $(-\text{CH}_2-)_4$ spacer group with the dihedral angle between them being 56.3°, which

produces the bpp ligand in a twist conformation and results in the formation $[\text{Zn}(\text{bpp})]_n$ helical chains with right- and left-handed chirality. The screw axes of these helices are all parallel to the *b* axis, and the pitch is 20.059(12) Å. The adjacent helical chains with opposite chirality are arranged alternately via L^{2-} anions to give rise to a 2D achiral network (Figure 5b). Moreover, these achiral sheets are further extended via interlayer C–H $\cdots$ O hydrogen bonds into a 3D supramolecular structure (Figure 5d,e; Table S3, Supporting Information).

Comparison of the Structures. It is known that multicarboxylate ligands have been proved to be excellent structural constructors due to their various coordination modes.⁹ Therefore, comparison and comprehension of the coordination modes of the carboxylate ligand are a good and feasible method to predesign the MOFs. There are four kinds of coordination modes of L^{2-} in the complexes **1–6** described above (Scheme 1). In **1**, **3**, and **4**, each L^{2-} ligand adopts a μ_2 -bridging mode using its two carboxylate groups each with $\mu_2-\eta^1:\eta^1$ bis-chelating mode (Scheme 1a), the hydroxyl group does not play a part in the coordination with metal ions. In compound **2**, L^{2-} shows a similar coordination fashion as that in compounds **1**, **3**, and **4**, but the hydroxyl group participates in the coordination with metal ions (Scheme 1b), so a type of $[\text{Cd}(\text{L})]_n$ helical chain is obtained in **2**. In compounds **1**, **3**, and **4**, only $[\text{Cd}(\text{PA})]_n$ zigzag chain or helical chain formed from the PA group of L^{2-} ligand and the metal center, and the uncoordinated hydroxyl oxygen atom acts as a hydrogen-bond acceptor to give rise to supramolecular helical architecture. However, in compound **5**, two carboxylate groups show different coordination modes with one in a $\mu_2-\eta^1:\eta^1$ coordination fashion, and the other one shows a $\mu_1-\eta^1:\eta^0$ mode (Scheme 1c); the hydroxyl connects to another Zn(II) ion. A meso-helical chain $[\text{Zn}(\text{PA})]_n$ is obtained in **5**. Different from compounds **1–5**, in compound **6**, both carboxylate groups in L^{2-} ligand display $\mu_1-\eta^1:\eta^0$ coordination mode (Scheme 1d), and the hydroxyl group is not involved in the coordination with metal ions. The results indicate that the different coordination fashions of L^{2-} anions have a remarkable effect on the helical motifs of the coordination polymers.

The different structures of the polymers **1**, **3**, **4**, and **2** with the same metal center of Cd^{II} and L^{2-} ligand as **5** and **6** with the same Zn^{II} and L^{2-} ligand indicate that the N-donor ancillary coligands have great influence on the structures of the complexes due to their different structures and flexibility. The remarkable difference between **1**, **3**, **4**, and **2** is that no N-donor ancillary coligand participates in the formation of the 2D structure of **2**, while in **1**, **3**, and **4**, an N-donor ancillary coligand appeared. When the twist N-donor ancillary coligand is induced in **1**, **3**, and **4**, a 3D structure of **1**, 2D structure of **3**, and 1D structure of **4** are obtained as a result of the diversity of flexibility and distortion of bix, 1,4-bbi, and *m*-bix. The structural difference between **5** and **6** is obvious; when the rigid N-donor ancillary coligand 4,4'-bpy is used, a 3D structure of **5** is formed; while when the flexible bpp participates in the formation of 2D structure of **6**, $[\text{Zn}(\text{bpp})]_n$ helical chain is obtained, but no $[\text{Zn}(\text{PA})]_n$ or $[\text{Zn}(\text{L})]_n$ helical subunits are observed.

In brief, the different modes of the carboxylate groups lead to the formation of the polymers with varied structures, and at the same time, the N-donor ancillary coligands are versatile in construction of coordination polymers and make it difficult to predict the structures of the resulting polymers. In addition, the

different nature of the metal ions can also tune the final structures.

Thermal Analyses and PXRD Patterns. To characterize the compounds in terms of thermal stability, thermal gravimetric analysis (TGA) of 2–6 were carried out in nitrogen atmosphere (Figure 6). The TG curve for 2 shows the initial

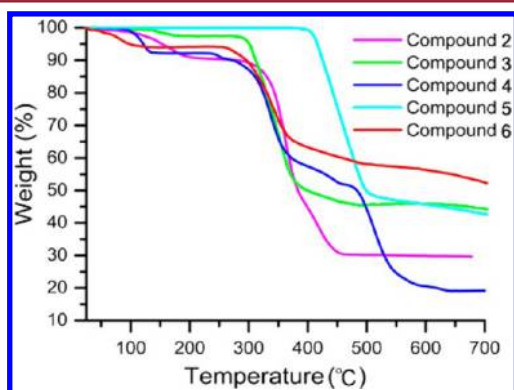


Figure 6. TG curves for compounds 2–6.

weight loss in the temperature range of 30–240 °C, which can be ascribed to the removal of lattice and coordinated water molecules (observed, 8.1%; calculated, 8.2%). Further weight loss indicates the decomposition of coordination framework. For compound 3, a gradual weight loss between 23 and 288 °C is attributed to the release of one lattice water molecule (observed, 3.05%; calculated, 3.12%), and then, the host framework started to decompose. The TG curve of 4 displays the first weight loss of 7.58% (calculated, 7.50%) from 30 to 265 °C, corresponding to the loss of two lattice water molecules per formula unit. A gradual weight loss from 270 °C dictates that the compound was decomposing continuously when the temperature was rising up. In the case of compound 5, no obvious weight loss was observed until the temperature reached 400 °C, where the framework of the structure began to collapse. For compound 6, the framework collapsed from 270 °C. It is obvious that only 5 has high thermal stability.

X-ray powder diffraction (XRD) was used to check the purity of compounds 2–6. As shown in Figures S4–S8, Supporting Information. The experimental PXRD patterns correspond well with the results simulated from the single crystal data,

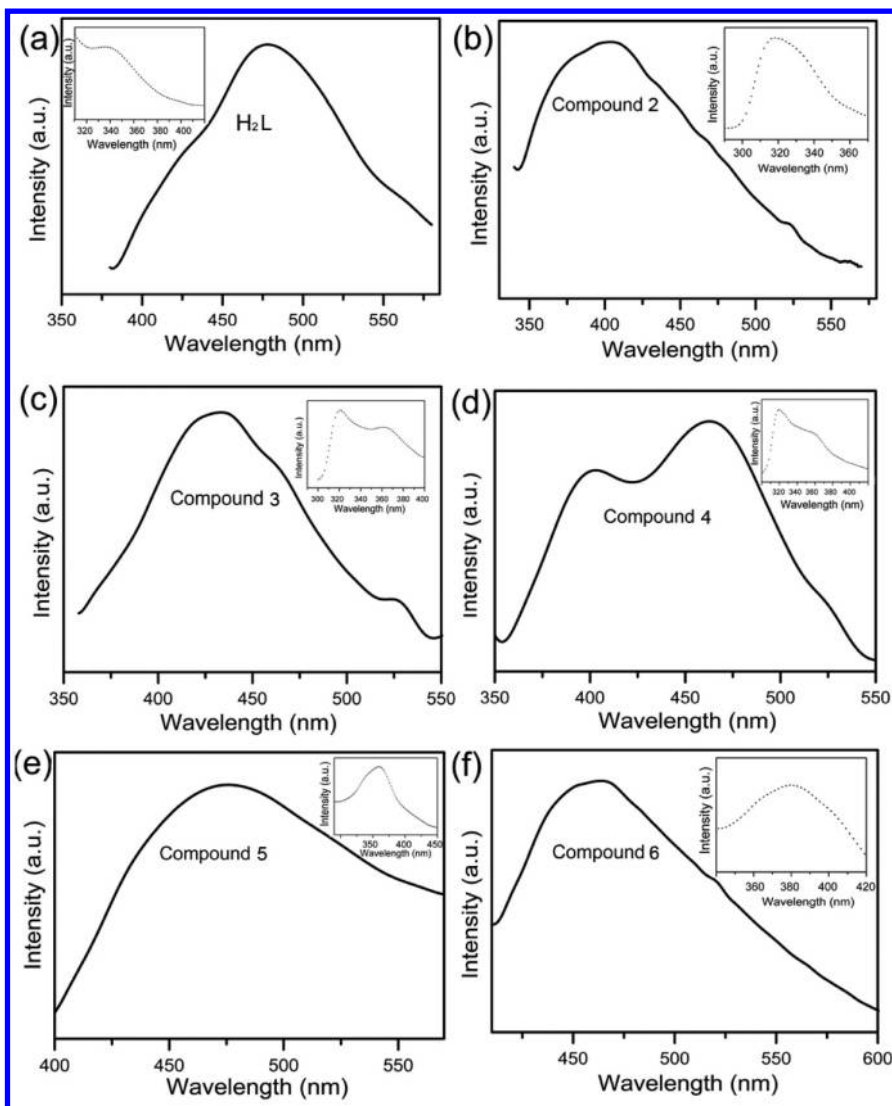


Figure 7. (a–f) Solid-state excitation (dotted line) and emission (solid line) spectra of H₂L and compounds 2–6 at room temperature.

indicating the high purity of the synthesized samples, and single phases of 2–6 are formed.

Photochemical Properties. All UV–vis absorption spectra for free ligands were recorded in reflectance mode in the solid state at room temperature (Figure S9, Supporting Information). The free ligands display absorption bands between 220–340 nm, arising from the π – π^* transitions of the aromatic rings.¹⁹

The solid-state emission spectra of compounds 2–6, the ligand H₂L, and the N-donor auxiliary ligands used in this work have been investigated at room temperature, and related data are listed in Table S4, Supporting Information. The emission spectra of H₂L and compounds 2–6 are shown in Figure 7a–f. Intense bands were observed at 467 nm ($\lambda_{\text{ex}} = 345$ nm) for H₂L, 410 nm ($\lambda_{\text{ex}} = 319$ nm) for 2, 439 nm ($\lambda_{\text{ex}} = 322$ nm) for 3, 397 and 464 nm ($\lambda_{\text{ex}} = 320$ nm) for 4, 475 nm ($\lambda_{\text{ex}} = 360$ nm) for 5, and 466 nm ($\lambda_{\text{ex}} = 384$ nm) for 6. Compared to the H₂L ligand, compound 2 results in a large blue shift of 57 nm, respectively. This indicates that the emission of 2 may be originated from charge transition between the ligand and the metal ions.²⁰ Two emission peaks were observed in compound 4, these bands of 4 are consistent with the emission wavelength of the free ligands (H₂L and *m*-bix), indicating the metal-perturbed intraligand charge transfers.²¹ The emissions of compounds 3 and 5–6 may be a mixture of characters of intraligand and ligand-to-ligand charge transition (LLCT), and the observed red or a little blue shift of the emission maximum between the compounds and the ligands was considered to mainly originate from the influence of the coordination of the ligand to metal atom.²² The different locations and profiles of their emission/excitation peaks of compounds 2–6 may result from different metal centers and conformational ligands as well as weak interactions in the network lattice, which may affect the rigidity of the whole network and further the energy transfer involved in the luminescence.²³ In addition, these compounds show blue luminescence, which may be considered as promising candidates for the exploration of fluorescent materials.

CONCLUSIONS

In summary, five new coordination polymers based on H₂L and different N-donor ligands have been successfully synthesized under hydro(solvo)thermally conditions. The results of our work have proven that H₂L is a good candidate in assembling of coordination polymers with various helical subunits, such as helix, pseudo helix, meso-helix, and supramolecular helix. In addition, N-donor ligand and metal ions can also slightly tune the final structural features.²⁴ Especially, the successful assembly of supramolecular helical water chain in compound 4 provides a better understanding of the process of water transport in biological systems. Moreover, polymers exhibit intense emissions, which appear to be potential photoactive materials of coordination polymers. Subsequent studies will be focused on the structures and properties of a series of coordination polymers constructed by the present ligand with a wide range of rare earth metals. Further investigations on this domain are underway.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format; hydrogen bond lengths (Å) and bond angles (deg) for 3, 4, and 6; XRD patterns of compounds 2–6; and some additional figures. This material is

available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data for the structures reported in this article have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 842166 and 869046–869049 for compounds 2–6.

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Notes

The authors declare no competing financial interest.

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