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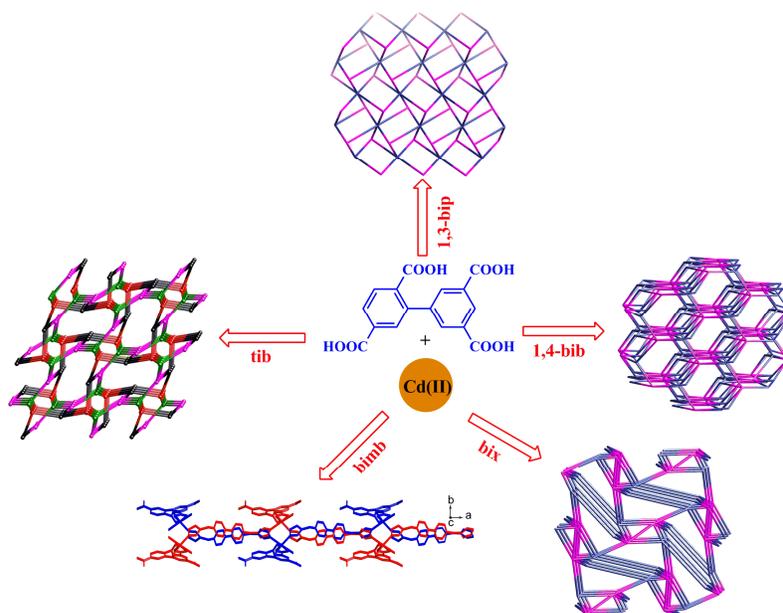
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Five Cd(II) coordination polymers based on 2,3',5,5'-biphenyl tetracarboxylic acid and different bis(imidazole) ligands have been synthesized under hydrothermal conditions. Structural analyses reveal that the backbone of H₄bptc plays an important role in governing the final structures of these coordination polymers.



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Five Cd(II) Coordination Polymers Based on 2,3',5,5'-Biphenyl Tetracarboxylic Acid and N-donor Coligands: Syntheses, Structures and Fluorescent Properties

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Five Cd(II) coordination polymers, $\{[\text{Cd}_2(\text{H}_4\text{bptc})_2(\text{H}_2\text{O})_2] \cdot (1,3\text{-H}_2\text{bip})\}_n$ (**1**), $[\text{Cd}_2(\text{bptc})(1,4\text{-bib})(\text{H}_2\text{O})_2]_n$ (**2**), $\{[\text{Cd}_2(\text{bptc})(\text{bix})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}\}_n$ (**3**), $\{[\text{Cd}(\text{H}_4\text{bptc})(\text{bimb})(\text{H}_2\text{O})]\}_n$ (**4**) and $\{[\text{Cd}_2(\text{bptc})(\text{tib})(\text{H}_2\text{O})]\}_n$ (**5**), where H_4bptc = 2,3',5,5'-biphenyl tetracarboxylic acid, 1,3-bip = 1,3-bis(imidazole)propane, 1,4-bib = 1,4-bis(imidazole)butane, bix = 1,4-bis(imidazol-1-ylmethyl) benzene, bimb = 4,4'-bis(imidazol-1-ylmethyl)biphenyl and tib = 1,3,5-tris(imidazol-1-yl)benzene, have been synthesized by using Cd(II) acetate with H_4bptc and different bis(imidazole) ligands under hydrothermal conditions. Their structures have been characterized by elemental analysis, IR spectroscopy, single-crystal X-ray crystallography and powder X-ray diffraction (PXRD) analysis. Complex **1** displays a (3,6)-connected CdI_2 topology, which further forms a 3D supramolecular framework by O–H...O hydrogen bonding interactions. Complex **2** features a 3D network with a (4,5,7)-connected $(3.4^3.5^2)(3.4^3.5^2.6^3.7)(3.4^6.5^4.6^8.7^2)$ topology. Complex **3** exhibits a 3D framework with a (3,4,5)-connected $(5.6.7)(4.5^2.6.7.8)(4.5^2.6^2.7^3.8^2)$ topology. Complex **4** has a 2-fold interpenetrated (4,4) net. Complex **5** possesses a 3D self-penetrating network with two **dia** nets. The results show that H_4bptc can act as a versatile building block for the construction of various metal organic frameworks (MOFs). Moreover, the fluorescent properties of **1–5** in the solid state have been investigated.

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Introduction

The rational design and synthesis of coordination polymers have attracted more and more interest from chemists, not only because of their fascinating topologies but also owing to their tremendous potential applications as functional materials.¹ Among various organic ligands, multicarboxylic acids have been proven to be excellent candidates for building highly connected, self-penetrating or helical coordination frameworks due to their versatile bridging fashions.² In the last two decades, aromatic multicarboxylate, such as 1,3-benzenedicarboxylate, 1,3,5-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate have been widely utilized to design and synthesis of MOFs.³ Compared to rigid 1,2,4,5-benzenetetracarboxylic acid, biphenyl tetracarboxylic acid is a flexible and longer ligand. Biphenyl tetracarboxylic acid ligand has four carboxylic groups that may be completely or partially deprotonated, inducing various coordination modes and allowing interesting structures with higher dimensionality, and can act as hydrogen-bond acceptor as well as donor, depending upon the degree of deprotonation. In addition, two sets of carboxylic groups separated by one phenyl ring can form different dihedral angles through the rotation of C–C single bonds, thus it may ligate metal centers in different orientations. These characters can lead to form cavities, interpenetration, helical structures, and other novel motifs with unique topologies.

To date, various biphenyl tetracarboxylic acid ligands, such as 2,2',3,3'-biphenyl tetracarboxylate,⁴ 2,2',4,4'-biphenyl tetracarboxylate,⁵ 2,2',5,5'-biphenyl tetracarboxylate,⁶ 2,2',6,6'-biphenyl tetracarboxylate,⁷ 3,3',4,4'-biphenyl tetracarboxylate,^{8,2f} and 3,3',5,5'-biphenyl tetracarboxylate,^{9,1n} have been widely used to construct coordination polymers. However, until now, there only one example based on 2,3',5,5'-biphenyl tetracarboxylic acid (H_4bptc) has been reported by our group.¹⁰ So it is necessary to construct new MOFs based on H_4bptc and investigate their physical properties.

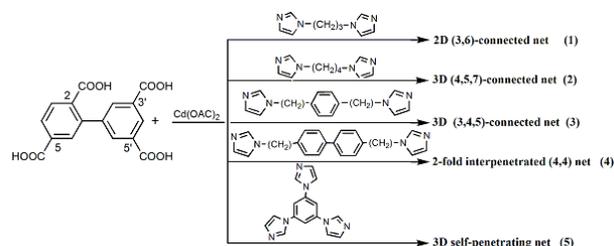
On the other hand, the mixed ligand assembly system has been widely used for the generation of new networks.¹¹ Herein, we report the syntheses and characterizations of five coordination polymers based on H_4bptc and different bis(imidazole) ligands, namely $\{[Cd_2(Hbptc)_2(H_2O)_2] \cdot (1,3-H_2bip)}\}_n$ (**1**), $[Cd_2(bptc)(1,4-bib)(H_2O)_2]_n$ (**2**), $\{[Cd_2(bptc)(bix)(H_2O)_2] \cdot 3H_2O\}_n$ (**3**), $\{[Cd(H_2bptc)(bimb)(H_2O)]_n$ (**4**) and $\{[Cd_2(bptc)(tib)(H_2O)]_n$ (**5**) (Scheme 1). These complexes exhibit a systematic variation of architectures from 2D layer to 3D frameworks. In addition, the fluorescent properties of **1–5** in the solid state were also investigated.

Experimental section

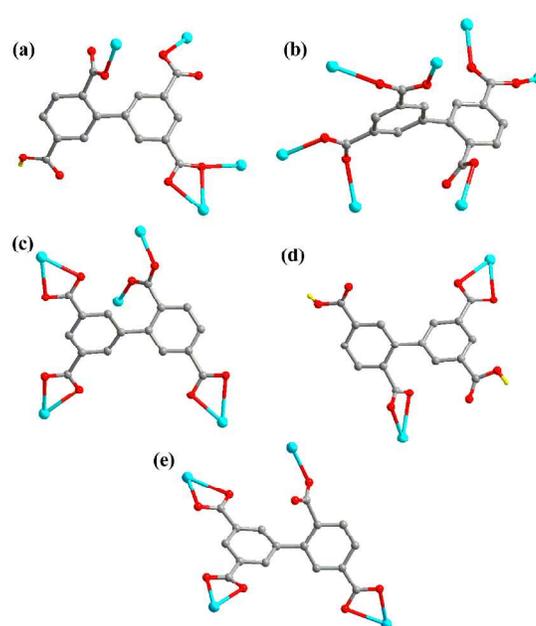
Materials and general methods

All chemicals purchased commercially were used as received without further purification. All the products were highly stable in air at ambient conditions. The infrared spectra (4000 ~ 600 cm^{-1}) were recorded on a NICOLET 6700 FT-IR spectrometer. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Vario EL III elemental analyzer. Powder

X-ray diffraction (PXRD) measurements for **1–5** were performed on a Bruker D8-ADVANCE X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and 2θ ranging from 5–50°. Fluorescent analysis for **1–5** was performed on a Hitachi F-4500 analyzer.



Scheme 1. Synthesis of complexes **1–5**



Scheme 2. Various coordination modes of H_4bptc

Synthesis of $\{[Cd_2(Hbptc)_2(H_2O)_2] \cdot (1,3-H_2bip)}\}_n$ (**1**)

A mixture of 2,3',5,5'-biphenyl tetracarboxylic acid (33.0 mg, 0.1 mmol), 1,3-bip (17.6 mg, 0.1 mmol), $Cd(OAc)_2 \cdot 2H_2O$ (26.6 mg, 0.1 mmol), and KOH (5.6 mg, 0.1 mmol) were added to water (12 mL) in a 25 mL Teflon-lined stainless steel vessel. The mixture was heated at 413 K for 3 days, and then slowly cooled down to room temperature. Colorless block crystals of **1** were obtained (yield: 48% based on cadmium). Anal. Calc. (%) for $C_{41}H_{32}Cd_2N_4O_{18}$: C, 45.03; H, 2.95; N, 5.12; found (%) C, 45.09; H, 3.02; N, 5.04. IR (cm^{-1}): 3064 m, 1700 m, 1547 s, 1397 m, 1362 m, 1228 m, 1149 s, 1111 m, 808 m, 727 m.

Synthesis of $[Cd_2(bptc)(1,4-bib)(H_2O)_2]_n$ (**2**)

The synthesis of **2** was similar to that of **1** except that 1,3-bip was replaced by 1,4-bib. Colorless block crystals of **2** were obtained (yield: 56% based on cadmium). Anal. Calc. (%) for

$C_{26}H_{24}Cd_2N_4O_{10}$: C, 40.17; H, 3.11; N, 7.21; found (%): C, 40.23; H, 3.03; N, 7.16. IR (cm^{-1}): 3119 m, 1606 m, 1556 s, 1435 m, 1308 m, 1235 m, 1113 s, 1081 s, 809 m, 720 m.

Synthesis of $\{[Cd_2(bptc)(bix)(H_2O)_2]\cdot 3H_2O\}_n$ (**3**)

The synthesis of **3** was similar to that of **1** except that 1,3-bip was replaced by bix. Yellow prismatic crystals of **3** were obtained (yield: 76% based on cadmium). Elemental analysis calcd (%) for $C_{22}H_{14}CdN_2O_8S_2$: C, 43.22; H, 2.29; N, 4.58. Found: C, 43.27; H, 2.32; N, 4.26. IR (cm^{-1}): 3390 m, 1701 s, 1617 m, 1542 m, 1467 m, 1394 s, 1225 w, 1141 w, 1107 w, 1068 w, 1044 w, 1014 w, 876 w, 850 w, 813 m, 719 w, 686 w, 630 w, 593 w, 536 w.

Synthesis of $\{[Cd(H_2bptc)(bimb)(H_2O)]_n$ (**4**)

The synthesis of **4** was similar to that of **1** except that 1,3-bip was replaced by bimb. Colorless block crystals of **4** were obtained (yield: 37% based on cadmium). Anal. Calc. (%) for $C_{36}H_{28}CdN_4O_9$: C, 55.93; H, 3.65; N, 7.25; found (%): C, 55.87; H, 3.70; N, 7.29. IR (cm^{-1}): 3117 w, 1697 m, 1539 s, 1517s, 1404 s, 1228 m, 1116 s, 1083 s, 804 m, 743 s.

Synthesis of $\{[Cd_2(bptc)(tib)(H_2O)]_n$ (**5**)

The synthesis of **5** was similar to that of **1** except that 1,3-bip was replaced by tib. Colorless block crystals of **5** were obtained (yield: 52% based on cadmium). Anal. Calc. (%) for $C_{31}H_{20}Cd_2N_6O_9$: C, 44.04; H, 2.38; N, 9.94; found (%): C, 44.09; H, 2.27; N, 10.03. IR (cm^{-1}): 3129 m, 1614 m, 1506 s, 1385 m, 1356 s, 1249 s, 1072 s, 837 m, 676 s.

X-ray crystallographic data collection and structural determination

The crystallographic diffraction data for complexes **1–5** were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K using the ϕ/ω scanning technique. All the structures were solved using direct methods and successive Fourier difference synthesis, and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms by SHELXS-97.¹² An empirical absorption correction was applied using the SADABS program. Basic information pertaining to crystal parameters and structure refinements are summarized in Table S1. Selected bond lengths and angles for **1–5** are listed in Table S2. Hydrogen bonding distance and angle data are listed in Table S3, shown in ESI†.

Results and discussions

Description of Crystal Structures

$\{[Cd_2(Hbptc)_2(H_2O)_2]\cdot(1,3-H_2bip)\}_n$ (**1**).

Single-crystal X-ray diffraction analysis shows that complex **1** crystallizes in the monoclinic system, $C2/c$ space group. The asymmetric unit of **1** consists of one crystallographically Cd(II) cation, one partly deprotonated $Hbptc^{3-}$ ion, one coordinated water molecule and half of a 1,3- H_2bip cation. As shown in Fig. 1a, each Cd(II) ion is six-coordinated with a distorted octahedral geometry by five carboxylic oxygen atoms from four separate $Hbptc^{3-}$ and one coordinated water molecule. The Cd-O bond lengths are in the range of 2.222(9)–2.526(8) Å.

$Hbptc^{3-}$ shows obvious torsion with the dihedral angle between the two benzene rings of 44.12°.

In **1**, 2-, 5- and 5'-COOH are deprotonated, scheme 2a shows the coordination mode of partly deprotonated $Hbptc^{3-}$, which connect Cd(II) ions to generate a 2D layer along ab plane with 5-COOH groups and corresponding phenyl rings decorating up and down sides (Fig. 1b). In the 2D layer, two 5'-COO⁻ groups link two Cd(II) ions to form a $[Cd_2O_2]$ dinuclear subunit, in which the two Cd(II) ions and two oxygen atoms are all coplanar with a parallelogram, and adjacent Cd...Cd distance is 3.77 Å. From the topological point of view, the 2D structure of **1** can be simplified to a binodal (3,6)-connected CdI_2 topology (Fig. 1c) with a Schläfli symbol of $(4^3)_2(4^6.6^6.8^3)$, in which, each $[Cd_2O_2]$ subunit links six $Hbptc^{3-}$ and $Hbptc^{3-}$ connects three $[Cd_2O_2]$ subunits. Furthermore, the adjacent 2D layers are extended into a 3D opening supramolecular framework by O5–H5...O3(I) hydrogen bonding between $Hbptc^{3-}$ with O...O distance of 2.731(13) Å. The guest 1,3- H_2bip cations are encapsulated in channels through $\pi\cdots\pi$ stacking interactions between benzene rings of $Hbptc^{3-}$ and imidazole rings of 1,3- H_2bip with the centroid-centroid distance of 3.677 Å (Fig. S1c, ESI).

Several binodal (3,6)-connected CdI_2 -type 2D MOFs were synthesized.¹³ For example, $\{[Mn(qptc)(phen)(H_2O)_2]\cdot 2H_2O\}_n$ exhibits a (3,6)-connected CdI_2 layered architecture incorporating left- and right-handed helical chains.^{13a} $[Zn_2(BTC)(OH)(2-PyBim)]$ has the similar 2D (3,6)-connected non-interpenetrating CdI_2 -type network with a $(4^3)_2(4^6.6^6.8^3)$ topology based on tetranuclear Zn_4 units.^{13d}

$[Cd_2(bptc)(1,4-bib)(H_2O)_2]_n$ (**2**).

The fundamental building unit of complex **2** consists of two crystallographically independent Cd(II) atoms, one $bptc^{4-}$, one 1,4-bib and two coordinated water molecules. As depicted in Fig. 2a, Cd1 center adopts a distorted trigonal bipyramidal coordination environment and is coordinated with one carboxylic oxygen atom (O4) from one $bptc^{4-}$ and one nitrogen atom (N1) from one 1,4-bib occupying the axial positions while three carboxylic oxygen atoms (O8#1, O6#2 and O2#3) from three different $bptc^{4-}$ lie in an equatorial plane. Cd2 center is coordinated by one nitrogen atom (N4#4) from 1,4-bib, three carboxylic oxygen atoms (O3, O5#2 and O7#5) from three different $bptc^{4-}$ and two coordinated water molecules (O9W and O10W), showing a distorted octahedral geometry. The Cd-O bond lengths are in the range of 2.203(3)–2.400(2) Å, and the Cd-N ones are 2.273(3) and 2.269(3) Å, respectively. The $bptc^{4-}$ shows obvious torsion with the dihedral angle between the two benzene rings of 80.83°. Coordination mode of the $bptc^{4-}$ ligand is displayed in scheme 2b, each $bptc^{4-}$ ligand links seven Cd(II) atoms to generate a 3D framework. Finally, 1,4-bib ligands are fixed in the channels of the 3D framework by Cd-N coordinated bonds (Fig. 2b).

From the topological perspective, each $bptc^{4-}$ can be considered as a 7-connected node and Cd1 center and Cd2 can be considered as 5-connected node and 4-connected node, respectively. The framework of **2** features an unprecedented trinodal (4,5,7)-connected network with a Schläfli symbol of $(3.4^3.5^2)(3.4^3.5^2.6^3.7)(3.4^6.5^4.6^8.7^2)$ topology (Fig. 2c).

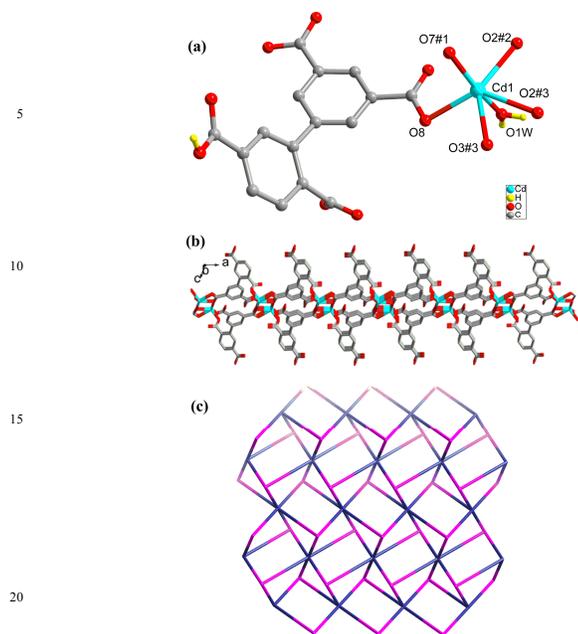


Fig. 1. (a) Coordination environments of the Cd(II) ion in **1**, hydrogen atoms and 1,3-H₂bip are omitted for clarity. Symmetry codes: #1: $x, y - 1, z$; #2: $-x + 1/2, -y - 1/2, -z$; #3: $x - 1/2, y - 1/2, z$. (b) Perspective view of the 2D layer in **1**. (c) Schematic view of the Cd₁₂ topology in **2** (blue nodes for 6-connected [Cd₂O₂] subunit and pink nodes for 3-connected bptc).

$\{[\text{Cd}_2(\text{bptc})(\text{bix})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}\}_n$ (**3**).

X-ray crystallography reveals that complex **3** crystallizes in a monoclinic system with space group $P2_1/n$ and displays a (3,4,5)-connected 3D framework. Complex **3** comprises two crystallographic independent Cd(II) atoms, one bptc⁴⁻, one bix, two coordinated water molecules and one free water molecule. As depicted in Fig. 3a, Cd1 is surrounded by one nitrogen atom from one bix and five carboxylate oxygen atoms from three different bptc⁴⁻, while Cd2 completed by one nitrogen atom from one bix, three carboxylate oxygen atoms from two bptc⁴⁻ and two oxygen atoms from two coordinated water molecules. The Cd-O bond lengths are in the range of 2.2106(19)-2.575(2) Å, and the Cd-N ones are 2.186(2) and 2.265(3) Å, respectively. The bptc⁴⁻ ligand shows obvious torsion with the dihedral angle between the two benzene rings of 40.17°. The bptc⁴⁻ ligand connects five Cd(II) atoms, and the coordination mode is exhibited in scheme 2c. Thus, the Cd(II) atoms are bridged by bptc⁴⁻ to form a 3D framework. The bix ligands are covalently filled in the voids of the framework of **3** via Cd-N coordination bonds to generate an overall 3D framework (Fig. 3b). There are also hydrogen bonding between water molecules (coordinated or uncoordinated) and carboxylate oxygen atoms to stabilize the structures (see Table S3, ESI).

From the topological perspective, each bptc⁴⁻ coordinates to five Cd(II) ions and therefore the ligand can be considered as 5-connected node. As Cd1 center and Cd2 can be considered as 4-connected node and 3-connected node, respectively. The network of **3** features a (3,4,5)-connected (5.6.7)(4.5².6.7.8) (4.5².6².7³.8²) topology (Fig. 3c).

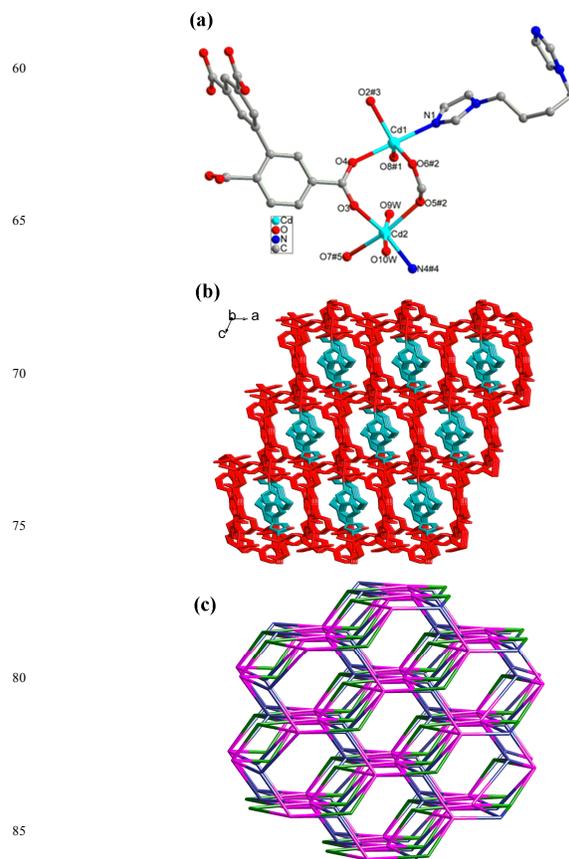


Fig. 2. (a) Coordination environments of the Cd(II) ion in **2**, hydrogen atoms are omitted for clarity. Symmetry codes: #1: $x, y, z - 1$; #2: $x - 1, y, z - 1$; #3: $-x + 2, y - 1/2, -z + 2$; #4: $x, y + 1, z$; #5: $-x + 2, y + 1/2, -z + 2$. (b) View of the 3D network constructed by Cd(II) ions and bptc⁴⁻ ligands (red part) along the b axis, with 1,4-bib ligands (green part) reside in. (c) Schematic view of the (4,5,7)-connected (3.4³.5²)(3.4³.5².6³.7)(3.4⁶.5⁴.6⁸.7²) topology in **2** (blue nodes for 5-connected Cd1 and green nodes for 4-connected Cd2; pink nodes for 7-connected bptc⁴⁻).

$\{[\text{Cd}(\text{H}_2\text{bptc})(\text{bimb})(\text{H}_2\text{O})]_n$ (**4**).

Single-crystal X-ray characterization indicates that complex **4** comprises one crystallographically Cd(II) atom, one partly deprotonated H₂bptc²⁻ ion, one bimb ligand and one coordinated water molecule. As shown in Fig.4a, each Cd(II) ion is seven-coordinated by four carboxylic oxygen atoms from two separate H₂bptc²⁻ ligands, two nitrogen atoms from two bimb ligands and one coordinated water molecule. The Cd-O bond lengths are in the range of 2.222(9)-2.526(8) Å. The H₂bptc²⁻ ligand shows obvious torsion with the dihedral angle between the two benzene rings of 44.48°. Both of deprotonated carboxylate groups (2- and 5'-COOH) of H₂bptc²⁻ adopt chelate coordination modes (Scheme 2d) joining Cd(II) atoms to form a chain along c direction, which is further extended to a 2D (4,4) net by bimb ligands (Fig. 4c). The Cd...Cd separation through the H₂bptc²⁻ dianions is 10.945 Å, which is shorter than that through the bridge ligand bimb (18.636 Å). A pair of networks are

interlocked in a parallel fashion forming a 2-fold interpenetrated network (Fig. 4c). Two kinds of hydrogen bonding are present: (a) hydrogen bonding between uncoordinated carboxylate oxygen atoms and coordinated carboxylate oxygen atoms with O...O distances of 2.541(3) (O(6)-H(6)...O(5)#5) and 2.645(3) (O(2)-H(2)...O(4)#6) Å, respectively; (b) hydrogen bonding between coordinated water molecules and uncoordinated carboxylate oxygen atoms with O...O distances of 2.923(3) (O(1)-H(2W)...O(7)#7) and 2.907(4) (O(1)-H(1W)...O(7)) Å (see Table S3, ESI). Such interpenetrated layers are further linked by hydrogen bonding interactions to generate an extended 3D supramolecular architecture.

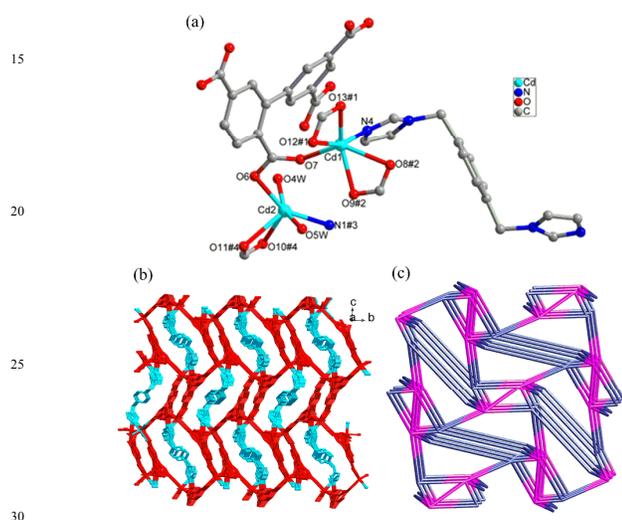


Fig. 3. (a) Coordination environments of the Cd(II) ion in **3**, hydrogen atoms and free water molecules are omitted for clarity. Symmetry codes: #1: $-x + 1, -y + 1, -z$; #2: $-x + 3/2, y - 1/2, -z + 1/2$; #3: $-x + 2, -y + 1, -z + 1$; #4: $x + 1, y, z$. (b) View of the 3D porous network constructed by Cd(II) ions and bptc⁴⁻ ligands (red part) along the *a* axis, with tib ligands (cyan part) reside in. (c) Schematic view of the (3,4,5)-connected (5.6.7)(4.52.6.7.8) (4.52.62.73.82) topology in **3** (blue nodes for 4-connected Cd1 and 3-connected Cd2; pink nodes for 5-connected bptc⁴⁻).

$\{[Cd_2(bptc)(tib)(H_2O)]_n\}$ (**5**).

The fundamental building unit of **5** consists of two crystallographically unique Cd(II) ions, one bptc⁴⁻, one tib and one coordinated water molecule. As illustrated in Fig. 5a, Cd1 is coordinated by four carboxylic oxygen atoms from two bptc⁴⁻ and two nitrogen atoms from two tib. Cd2 adopts a distorted square pyramidal coordination environment. Three carboxylic oxygen atoms from two different bptc⁴⁻ and one nitrogen atom from one tib form the equatorial plane and the apical position is occupied by one oxygen atom (O9W) from one coordinated water molecule. The Cd-O bond lengths are in the range of 2.219(6)-2.532(5) Å and the Cd-N ones are in the range of 2.234(6)-2.256(5) Å, respectively. The bptc⁴⁻ ligand shows obvious torsion with the dihedral angle between the two benzene rings of 55.10°. Four carboxylate groups of bptc⁴⁻ are deprotonated, and coordination mode is showed in scheme 2e.

The Cd(II) atoms are bridged by bptc⁴⁻ and tib ligands to form a complicated 3D framework (Fig. S3).

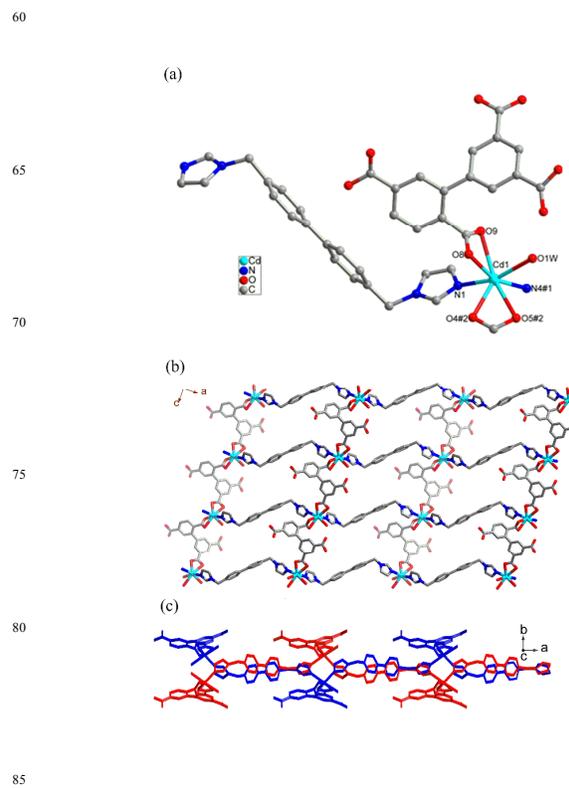


Fig. 4. (a) Coordination environments of the Cd(II) ion in **5**, hydrogen atoms are omitted for clarity. Symmetry codes: #1: $x + 1, -y + 3/2, -z - 1/2$; #2: $x, y, z - 1$. (b) View of 2D layer along the *ac* plane in **4**. (c) View of 2-fold interpenetrated (4,4) net in **4**.

Analysis of the network topology of **5** reveals that Cd1 center acts as a 4-connected node to connect two bptc⁴⁻ and two tib spacers. Cd2 center acts as a 3-connected node to two bptc⁴⁻ and one tib. While bptc⁴⁻ and tib ligands serve as 4- and 3-connected nodes, respectively. Thus the 3D network of complex **5** can be simplified as a (3,4)-connected (6².8)(6.8⁵) topology (Fig. 5b). To further understand this complicated structure, we break the N4-Cd2 bonds which bridges a pair of adjacent networks. Thus both Cd2 and tib serve as 2-connected node. The 2-connected Cd2 and tib are not ascribed to any node. So the topology of the 2-fold interpenetrated network becomes a binodal 4-connected **dia** nets (Fig. 5c). Therefore, the framework of **5** is clearly a self-penetrating net and can be considered as derived from cross-linking of 2-fold interpenetrated **dia** nets *via* N4-Cd2 bonds (Fig. 5d and 5e).

Influence of imidazole-containing ligands on the structures of the complexes.

Compounds **1-5** are prepared in single crystalline through the hydrothermal reaction of cadmium nitrate, H₄bptc, and five imidazole-containing ligands. From the structural descriptions above, it can be seen that the neutral imidazole-containing ligands have an influence on the frameworks of the complexes. As shown

in Scheme 2, H₄bptc in **1–5** displays different bridging coordination modes in the presence of different imidazole-containing ligands. These results show that both the imidazole-containing ligands and different coordination modes of H₄bptc have an effect on the final structures of metal organic frameworks.

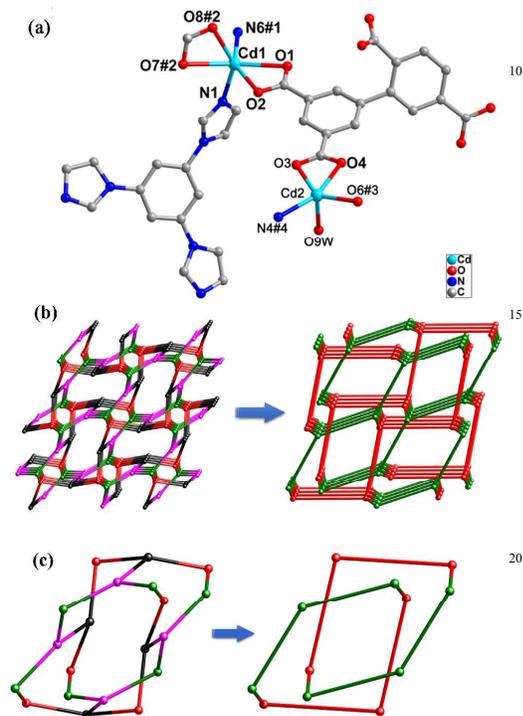


Fig. 5. (a) Coordination environments of the Cd(II) ion in **6**, hydrogen atoms are omitted for clarity. Symmetry codes: #1: $x, -y + 3/2, z - 1/2$; #2: $x + 1, y, z - 1$; #3: $x, -y + 1/2, z + 1/2$; #4: $-x + 1, y - 1/2, -z + 3/2$. (b) View of 3D framework with tetranodal (3,4)-connected topology (black: 3-connected tib node; pink: 3-connected Cd2 node; green: 4-connected bptc; red: 4-connected Cd1 node). (c) The 2-fold interpenetrated bimodal 4-connected **dia** network by breaking N4-Cd2 bonds. (d) View of the details of self-interpenetration by tridentate tib ligand *via* N4-Cd2 bond. (e) Formation of the interpenetration by breaking N4-Cd2 bonds.

PXRD Results and Photoluminescent properties

In order to check the phase purity of the complexes, powder X-ray diffraction (PXRD) patterns of **1–5** were recorded at room temperature. As shown in Fig. S4, ESI, the peak positions of the simulated and experimental PXRD patterns are in agreement with each other, which confirm their phase purity. The difference in intensity of some diffraction peaks may be attributed to the preferred orientation of the crystalline powder samples.

Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry and electroluminescent display.¹⁴ To examine the luminescent properties of these d¹⁰ metal complexes, the luminescence spectra of **1–5** (Fig. 6) have been measured. Complexes **1–5** display emission peaks at 447, 424, 446, 456 and 425 nm upon excitation at $\lambda = 348, 321, 370, 378$ and 363 nm, respectively. In order to

understand the nature of such emission bands, the fluorescence properties of the free H₄bptc ligand was also measured, upon excitation at *ca.* 417 nm, which shows the emission at *ca.* 466 nm. Compared with the emission spectrum of H₄bptc, blue shifts of emission bands for **1–5** have been observed. These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature, since Cd^{II} ions are difficult oxidize or reduce due to their d¹⁰ configuration.¹⁵ These shifts of the emission bands are attributed to both the deprotonated effect of H₄bptc and the coordination interactions of the organic ligands to Cd^{II} ions.¹⁶

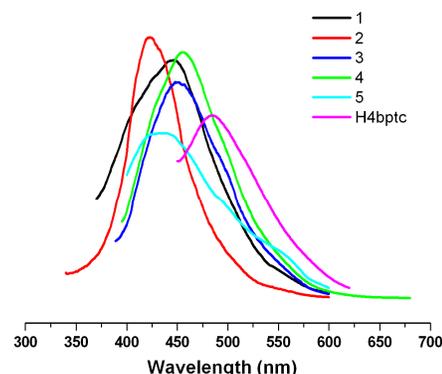


Fig. 6. Solid-state emission spectra of complexes **1–5** and H₄bptc ligand at room temperature.

Conclusions

In summary, five Cd(II) coordination polymers based on 2,3',5,5'-biphenyl tetracarboxylic acid and different bis(imidazole) ligands have been synthesized under hydrothermal conditions. Structural analyses reveal that the backbone of H₄bptc plays an important role in governing the final structures of these metal-organic coordination polymers. Our research demonstrates for the first time that H₄bptc could be a potential building block to construct novel coordination polymers with unusual architectures and interesting physical properties. Further experiments exploring the design and synthesis such crystalline materials with H₄bptc and other N-donor building blocks are underway in our laboratory.

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Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format for **1–5**, selected bond lengths, bond angles, and hydrogen-bonding geometries for **1–5**.

CCDC 978916-978920 contain the supplementary crystallographic data for 1–5. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Notes and references

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