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ARTICLE

Eight Zn(II) and Cd(II) complexes based on the aromatic C-centered triangular multicarboxylate and N-donor mixed ligands

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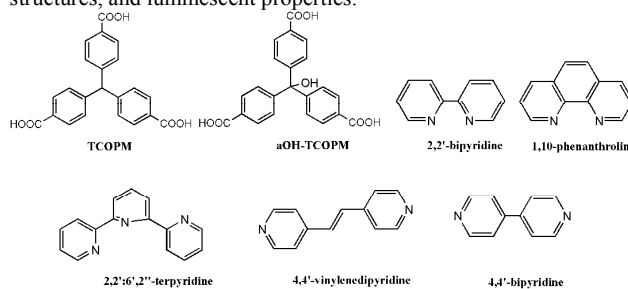
Eight new Zn(II) and Cd(II) complexes based on the aromatic multicarboxylate and N-donor mixed ligands, namely $Zn_2(TCOPM)(2,2'-bipy)(OH) \cdot 1.25DMF$ (TCOPM = tris(*p*-carboxyphenyl)methane; 2,2'-bipy = 2,2'-bipyridine; DMF = *N,N'*-dimethylformamide) (1), $Zn_2(\alpha OH-TCOPM)(phen)(OH) \cdot DMF$ ($\alpha OH-TCOPM$ = tris(*p*-carboxyphenyl)methanol; phen = 1,10-phenanthroline) (2), $Zn_2(\alpha OH-TCOPM)(tpy)(OH)(H_2O)$ (tpy = 2,2':6',2''-terpyridine) (3), $Zn_3(\alpha OH-TCOPM)_2(dpe) \cdot 2H_2O$ (dpe = 4,4'-vinylenedipyridine) (4), $Cd_3(TCOPM)_2(DMF)_2(H_2O)_2$ (5), $Cd_3(TCOPM)_2(4,4'-bipy)$ (6), $Cd_3(TCOPM)_2(dpe)$ (7), and $Cd_3(\alpha OH-TCOPM)_2(2,2'-bipy)_2 \cdot 2DMF$ (8) were synthesized through the solvothermal reaction. The $\alpha OH-TCOPM$ ligand is generated in-situ by the nucleophilic addition of TCOPM ligand. X-ray crystallographic analysis reveals that complexes 1-3, 5, and 8 exhibit a two-dimensional (2D) layered structure, while 4, 6, and 7 possess a 3D open framework. The coordination mode of TCOPM and the type of N-donors ligands have obvious effects on the final structures. Luminescent properties in the solid state of 1-4, 7, and 8 were also investigated.

1. Introduction

Recently, metal-organic frameworks (MOFs) have attracted a great deal of academic and commercial interest because of their intriguing structures and potential applications in gas storage and separation, catalysis, luminescence, electrochemical and magnetic fields.¹⁻¹¹ Rapid development in the self-assembly of transition metal ions and multitopic organic ligands has yielded a wide variety of one-, two- and three-dimensional MOFs with interesting architectures and specific properties.¹²⁻¹⁴ Among them, aromatic carboxylic-based ligands have attracted much attention for their abilities to construct open-framework networks with a wide diversity of topologies, and pore shapes and sizes.^{15,16} On the other hand, the employment of mixed ligands such as aromatic multicarboxylate and N-donor ligands is the most efficient family to be an effective method for the fabrication of coordination polymers because of their various and flexible connection modes.¹⁷⁻²¹ It is well known that Zn(II) and Cd(II) with a 3d¹⁰ configuration not only exhibit appealing structural geometries varying from tetrahedron, trigonal-bipyramid and square-pyramid to octahedron, but also possess luminescence properties because of their low-energy charge-transfer excited states. So, Zn(II) and Cd(II) complexes are important criteria for luminescent properties to be used as biological imaging probes, sensors and electrochemistry.²²⁻²⁴

Taking above comments into account, the 3-connecting open-shell ligand based on a triscarboxylic group tris(*p*-carboxyphenyl)methane (TCOPM) was selected by our group because this ligand can generate diverse coordination polymers because of the flexible C-centered atom and various coordination modes. Unfortunately, metal-TCOPM complexes have been documented limitedly to date.²⁵⁻²⁷ With the purpose of understanding the coordination chemistry of TCOPM ligand and constructing novel

complexes with intriguing structures and functionalities, we used in this work the C-centered triangular flexible TCOPM as O-donor ligand, and 2,2'-bipyridine (2,2'-bipy), 1,10-phenanthroline (phen), 2,2':6',2''-terpyridine (tpy), 4,4'-vinylenedipyridine (dpe), or 4,4'-bipyridine as N-donor ligands (Scheme 1) to react with transition-metal ions Zn(II) and Cd(II) through the solvothermal reaction, isolating eight new complexes, namely $Zn_2(TCOPM)(2,2'-bipy)(OH) \cdot 1.25DMF$ (1), $Zn_2(\alpha OH-TCOPM)(phen)(OH) \cdot DMF$ ($\alpha OH-TCOPM$ = tris(*p*-carboxyphenyl)methanol) (2), $Zn_2(\alpha OH-TCOPM)(tpy)(OH)(H_2O)$ (3), $Zn_3(\alpha OH-TCOPM)_2(dpe) \cdot 2H_2O$ (4), $Cd_3(TCOPM)_2(DMF)_2(H_2O)_2$ (5), $Cd_3(TCOPM)_2(4,4'-bipy)$ (6), $Cd_3(TCOPM)_2(dpe)$ (7), and $Cd_3(\alpha OH-TCOPM)_2(2,2'-bipy)_2 \cdot 2DMF$ (8). Here we reported their syntheses, crystal structures, and luminescent properties.



Scheme 1 The ligands in this work.

2. Experimental

2.1. Materials and physical measurements

All chemicals used in the syntheses were obtained from J&K CHEMICA in a reagent grade and were used without further purification. Tris(*p*-carboxyphenyl)methane (TCOPM) was prepared

according to a literature procedure.²⁸ Infrared spectra as KBr pellets were recorded in the range of 4000 to 400 cm^{-1} on a Nicolet FT-1703X FT-IR spectrophotometer. Powder X-ray diffraction (XRD) measurements were taken on a Shimadzu XRD-6000 diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406$ nm). Luminescent spectra in solid state were carried out with an Edinburgh Instruments FS5 spectrophotometer at room temperature.

2.2. Syntheses

2.2.1. Preparation of $\text{Zn}_2(\text{TCOPM})(2,2'\text{-bipy})(\text{OH})\cdot 1.25\text{DMF}$ (1)

$\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (33.4 mg, 0.1 mmol), TCOPM (37.6 mg, 0.1 mmol), and 2,2'-bipy (15.6 mg, 0.1 mmol) were dissolved in a solvent mixture of DMF/ H_2O (9 mL/3 mL). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) and heated to 85 $^\circ\text{C}$ for 48 h. Colorless crystals were collected and washed with DMF (Yield: 78% based on Zn salt). Anal. Calcd for $\text{C}_{143}\text{H}_{123}\text{O}_{33}\text{N}_{13}\text{Zn}_8$: C, 55.86; H, 4.03; N, 5.92. Found: C, 55.82; H, 4.09; N, 5.87. IR (KBr, cm^{-1}): 3450(vs), 2927(w), 1674(s), 1596(s), 1554(m), 1490(w), 1380(s), 1253(w), 1174(w), 1097(vs), 1016(w), 831(w), 775(m), 663(w), 572(w).

2.2.2. Preparation of $\text{Zn}_2(\alpha\text{OH-TCOPM})(\text{phen})(\text{OH})\cdot \text{DMF}$ (2)

The preparation of **2** was similar to that of **1** except phen (18.0 mg, 0.1 mmol) was used instead of 2,2'-bipy. Colorless crystals were collected and washed with DMF (Yield: 74% based on Zn salt). Anal. Calcd for $\text{C}_{37}\text{H}_{29}\text{N}_3\text{O}_9\text{Zn}_2$: C, 56.22; H, 3.70; N, 5.32. Found: C, 56.19; H, 3.76; N, 5.51. IR (KBr, cm^{-1}): 3425(m), 3058(w), 2931(w), 1932(w), 1668(s), 1598(s), 1564(s), 1514(m), 1392(s), 1249(w), 1087(m), 1016(vs), 848(m), 781(s), 729(m), 659(vs), 580(w), 526(w).

2.2.3. Preparation of $\text{Zn}_2(\alpha\text{OH-TCOPM})(\text{tpy})(\text{OH})(\text{H}_2\text{O})$ (3)

The preparation of **3** was similar to that of **1** except tpy (23.3 mg, 0.1 mmol) was used instead of 2,2'-bipy. Yellowish crystals were collected and washed with DMF (Yield: 81% based on Zn salt). Anal. Calcd for $\text{C}_{37}\text{H}_{27}\text{N}_3\text{O}_9\text{Zn}_2$: C, 56.37; H, 3.45; N, 5.33. Found: C, 56.29; H, 3.62; N, 5.45. IR (KBr, cm^{-1}): 3402(vs), 3080(w), 2922(w), 1676(s), 1587(s), 15629(m), 1475(vs), 1450(m), 1375(s), 1247(m), 1166(w), 1097(w), 1014(vs), 829(w), 774(s), 665(w), 570(w), 516(w).

2.2.4. Preparation of $\text{Zn}_3(\alpha\text{OH-TCOPM})_2(\text{dpe})\cdot 2\text{H}_2\text{O}$ (4)

The preparation of **4** was similar to that of **1** except dpe (18.2 mg, 0.1 mmol) was used instead of 2,2'-bipy. Yellowish crystals were collected and washed with DMF (Yield: 72% based on Zn salt). Anal. Calcd for $\text{C}_{56}\text{H}_{40}\text{N}_2\text{O}_{16}\text{Zn}_3$: C, 56.37; H, 3.38; N, 2.35. Found: C, 56.29; H, 3.52; N, 2.45. IR (KBr, cm^{-1}): 3408(w), 3049(w), 3923(w), 1614(s), 1562(vs), 1409(s), 1257(w), 1220(w), 1174(w), 1066(w), 1016(w), 829(w), 779(vs), 721(w), 657(w), 549(w).

2.2.5. Preparation of $\text{Cd}_3(\text{TCOPM})_2(\text{DMF})_2(\text{H}_2\text{O})_2$ (5)

The preparation of **5** was similar to that of **1** except $\text{Cd}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (33.4 mg, 0.1 mmol) was used instead of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 2,2'-bipy was removed. Colorless crystals were collected and washed with DMF (Yield: 68% based on Cd salt). Anal. Calcd for $\text{C}_{50}\text{H}_{44}\text{Cd}_3\text{N}_2\text{O}_{16}$: C, 47.43; H, 3.50; N, 2.21. Found: C, 47.51; H, 3.48; N, 2.20. IR (KBr, cm^{-1}): 3400(m), 3064(w), 2935(w), 1656(s), 1587(s), 1537(s), 1396(s), 1249(w), 1184(w), 1099(vs), 1016(w), 835(w), 779(m), 715(w), 667(w), 522(w).

2.2.6. Preparation of $\text{Cd}_3(\text{TCOPM})_2(4,4'\text{-bipy})$ (6)

The preparation of **6** was similar to that of **5** except adding 4,4'-bipy (15.6 mg, 0.1 mmol). Colorless crystals were collected and washed

with DMF (Yield: 64% based on Cd salt). Anal. Calcd for $\text{C}_{54}\text{H}_{34}\text{Cd}_3\text{N}_2\text{O}_{12}$: C, 52.30; H, 2.76; N, 2.26. Found: C, 52.35; H, 2.74; N, 2.20. IR (KBr, cm^{-1}): 3406(vs), 3057(w), 2962(w), 1604(m), 1537(m), 1398(s), 1220(w), 1182(w), 1014(w), 846(w), 778(vs), 713(w), 630(w).

2.2.7. Preparation of $\text{Cd}_3(\text{TCOPM})_2(\text{dpe})$ (7)

The preparation of **7** was similar to that of **5** except adding dpe (18.2 mg, 0.1 mmol). Colorless crystals were collected and washed with DMF (Yield: 55% based on Cd salt). Anal. Calcd for $\text{C}_{56}\text{H}_{36}\text{Cd}_3\text{N}_2\text{O}_{12}$: C, 53.12; H, 2.87; N, 2.21. Found: C, 53.07; H, 2.84; N, 2.20. IR (KBr, cm^{-1}): 3438(vs), 3055(w), 2925(w), 1674(w), 1610(m), 1548(m), 1494(m), 1392(s), 1180(w), 1014(vs), 837(vs), 779(m), 711(w), 663(w), 553(w), 524(w).

2.2.8. Preparation of $\text{Cd}_3(\alpha\text{OH-TCOPM})_2(2,2'\text{-bipy})_2\cdot 2\text{DMF}$ (8)

The preparation of **8** was similar to that of **5** except adding 2,2'-bipy (15.6 mg, 0.1 mmol). Colorless crystals were collected and washed with DMF (Yield: 72% based on Cd salt). Anal. Calcd for $\text{C}_{70}\text{H}_{56}\text{Cd}_3\text{N}_6\text{O}_{16}$: C, 53.40; H, 3.56; N, 5.34. Found: C, 53.25; H, 3.60; N, 5.28. IR (KBr, cm^{-1}): 3415(vs), 3003(w), 2683(w), 1683(s), 1610(m), 1415(w), 1294(w), 1176(vs), 1114(vs), 1016(w), 875(w), 763(w), 551(w).

2.3. X-ray crystallographic analysis

Single-crystal X-ray diffraction data for **1-8** were collected on a Bruker Smart APEX II detector diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) at 291(2) K. All diffraction data analysis and reduction were carried out within *SMART* and *SAINIT*.²⁹ Correction for Lorentz, polarization, and absorption effects were performed within *SADABS*.³⁰ Structures were solved using Patterson method within *SHELXS-97* and refined using *SHELXL-97*.³¹⁻³³ All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of TCOPM and N-donor ligands, and DMF molecules were positioned with an idealized geometry and refined using a riding model. The hydrogen atoms of coordinated and crystallized water molecules were located from difference Fourier maps and refined as riding model. CCDC numbers: 1444094-1444101 for **1-8**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data and structural refinement details for **1-8** are listed in Table S1. Selected bond distances and bond angles are given in Tables S2.

3. Results and discussion

3.1. Crystal structures

X-ray crystallography analysis reveals that complex **1** crystallizes in the monoclinic $P2_1/c$ space group (Table S1, Fig. 1).

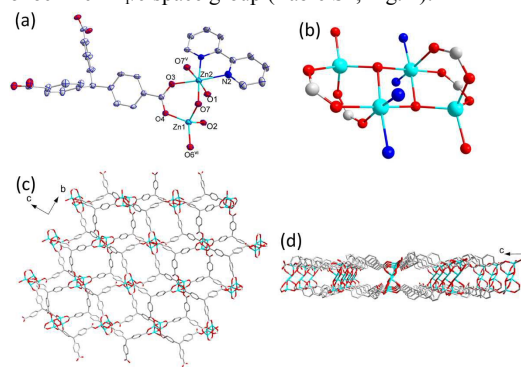


Fig. 1 (a) The coordination environment of Zn centers in **1**. Symmetry codes: (v) $-x + 1, -y, -z + 1$; (vi) $x, y - 1, z$. (b) The Zn_4 cluster. (c, d) Views of the 2D layered structure. All hydrogen atoms, DMF molecules, and 2,2'-bipy ligands were omitted for clarity.

As show in Fig. 1a, Zn1 is four-coordinated by three carboxylic oxygen atoms from three TCOPM ligands and one hydroxyl oxygen atom, adopting a tetrahedral geometry. The Zn1-O distance is in the range of 1.935(3)-2.199(2) Å. The Zn2 atom adopts a six-coordinated distortedly octahedral environment with two carboxylic oxygen atoms from two TCOPM ligands, two hydroxyl oxygen atoms and two nitrogen atoms from one 2,2'-bipy ligand. The Zn2-O and Zn2-N distances are in the range of 2.077(3)-2.134(3) Å and 2.122(3)-2.151(3) Å, respectively. Zn1 and Zn2 centers are bridged by hydroxyl group to form a Zn_4 cluster (Fig. 1b), and these clusters as 4-connected nodes are further linked by TCOPM ligands as 3-connected nodes, generating a 2D layer (Figs 1c, Fig. 1d).

Complex **2** was obtained when phen was utilized instead of 2,2'-bipy under the synthetic condition similar to **1**. Single-crystal structural analysis reveals that the space group and coordination environments of Zn atoms are the same as those for **1** (Fig. 2). The slight difference is that the hydrogen atom from center-carbon of TCOPM is substituted by hydroxy group through an in-situ reaction by the nucleophilic addition. Such phenomenon can be frequently observed in hydro(solvo)thermal reactions, resulting in unpredictable products with fascinating topological structures and appealing properties.³⁴ The Zn_4 clusters are connected through α_{OH} -TCOPM ligands to form a 2D layered structure. It should be mentioned that the thickness of layer for **2** is larger than that found in **1**. Complex **3** was isolated when tpy with much larger steric hindrance was used instead of 2,2'-bipy. Similar to **1** and **2**, complex **3** has also a 2D structure (Fig. 3). Notably, complex **3** adopts a monolayer, which is different to those found in **1** and **2**.

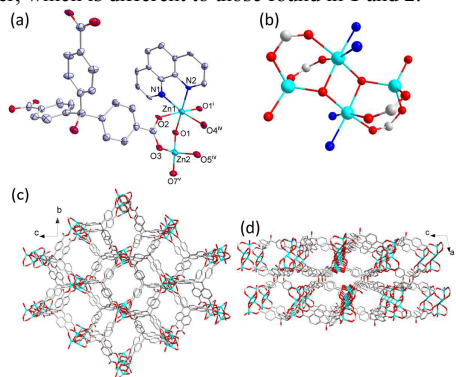


Fig. 2 (a) The coordination environment of Zn centers in **2**. Symmetry codes: (i) $-x, -y, -z$; (iv) $x, -y + 1/2, z - 1/2$; (v) $x, y - 1, z$. (b) The Zn_4 cluster. (c, d) Views of the 2D layered structure. All hydrogen atoms, DMF molecules, and phen ligands were omitted for clarity.

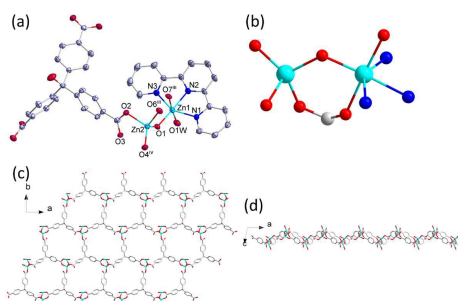


Fig. 3 (a) The coordination environment of Zn centers in **3**. Symmetry codes: (iii) $x - 1, y, z$; (iv) $-x + 1, y - 1/2, -z + 3/2$. (b) The Zn_2 cluster. (c, d) Views of the 2D layered structure. All hydrogen atoms and tpy ligands were omitted for clarity.

To construct the assemblies with high dimensionalities and open frameworks, the pillar ligand dpe was selected instead of chelate ligands. Fortunately, the 3D complex **4** was isolated, which crystallizes in the triclinic $P-1$ space group. The Zn1 atom is six-coordinated with five carboxylic oxygen atoms from four α_{OH} -TCOPM ligands and one nitrogen atom from one dpe ligand, whereas Zn2 has an six-coordinated octahedral geometry with six carboxylic oxygen atoms from six α_{OH} -TCOPM ligands (Fig. 4a). Zn1 and Zn2 centers are bridged by carboxylate oxygen atoms to generate a 1D rod structure (Fig. 4b). These rods are further connected by α_{OH} -TCOPM and dpe ligands for form a 3D open framework with 1D channels (Fig. 4c).

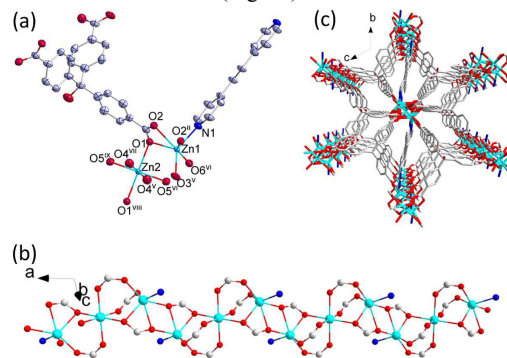


Fig. 4 (a) The coordination environment of Zn centers in **4**. (ii) $-x + 1, -y, -z$; (v) $x, y, z - 1$; (vi) $x, y - 1, z - 1$; (vii) $-x + 2, -y, -z + 1$; (viii) $-x + 2, -y, -z$; (ix) $-x + 2, -y + 1, -z + 1$. (b) The 1D rod structure. (c) View of the 3D open framework. All hydrogen atoms and water molecules were omitted for clarity.

The same synthesis strategy was employed to construct the Cd(II)-TCOPM system. Complex **5** was obtained in the absence of N-donor ligands, which crystallizes in the monoclinic $P2_1/n$ space group and features a 2D layered structure. Both Cd1 and Cd3 atoms have a distortedly octahedral geometry, coordinated by six carboxylic oxygen atoms from TCOPM ligands (Fig. 5a). Cd2 and Cd4 atoms are six-coordinated by four carboxylic oxygen atoms from three TCOPM ligands, one oxygen atom from one DMF molecule, and one water molecule. Cd centers are bridged by carboxylic oxygen atoms to form a Cd_3 cluster (Fig. 5b), which are further connected by TCOPM ligands to generate a 2D layered structure (Fig. 5c, Fig. 5d).

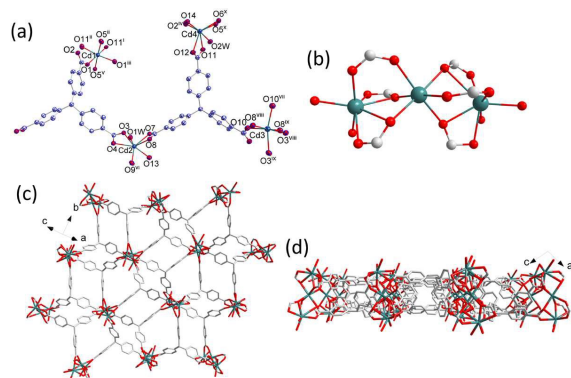


Fig. 5 (a) The coordination environment of Cd centers in **5**. Symmetry codes: (i) $-x, -y + 2, -z + 1$; (ii) $x + 1/2, -y + 2, z - 1/2$; (iii) $-x + 1/2, y, -z + 1/2$; (iv) $x - 1/2, -y + 2, z + 1/2$; (v) $-x + 1, -y + 2, -z$; (vi) $x + 1/2, -y + 1, z - 1/2$; (vii) $-x - 1/2, y, -z + 3/2$; (viii) $-x, -y + 1, -z + 1$; (ix) $x - 1/2, -y + 1, z + 1/2$; (x) $x - 1, y, z + 1$. (b) The Cd_3 cluster. (c, d) Views of the 2D layered structure. All hydrogen atoms and DMF molecules were omitted for clarity.

Complexes **6** and **7** were obtained in the presence of pillar ligands 4,4'-bipy and dpe, respectively. Complex **6** crystallizes in the monoclinic $P2_1/n$ space group, featuring a 3D structure. Cd1 is seven-coordinated by six carboxylic oxygen atoms from four TCOPM ligands and one nitrogen atom from one 4,4'-bipy ligand, while Cd2 is six-coordinated octahedral by six carboxylic oxygen atoms from six TCOPM ligands (Fig. 6a). For **7**, the Cd1 center is six coordinated with five carboxylic oxygen atoms from four TCOPM ligands, and one nitrogen atom of one dpe ligand, Cd2 is six-coordinated octahedral with six carboxylic oxygen atoms from six TCOPM ligands (Fig. 7a). Similar to **4**, Cd1 and Cd2 centers in **6** and **7** are bridged by carboxylic oxygen atoms to form a rod structure (Fig. 6b, Fig. 7b), and these rods are further linked by TCOPM and 4,4'-bipy or dpe ligands to generate a 3D open framework with 1D channels (Fig. 6c, Fig. 7c).

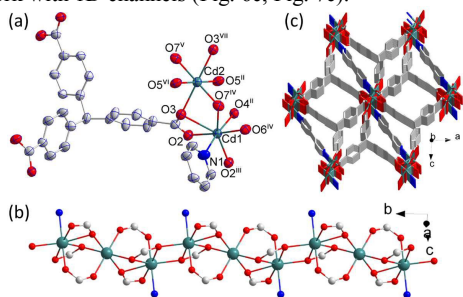


Fig. 6 (a) The coordination environment of Zn centers in **6**. Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x + 2, -y + 1, -z + 1$; (iv) $x + 1/2, -y, z - 1/2$; (v) $-x + 3/2, y, -z + 3/2$; (vi) $-x + 1, -y, -z + 1$; (vii) $-x + 2, -y, -z + 1$. (b) The 1D rod structure. (c) View of the 3D open framework. All hydrogen atoms were omitted for clarity.

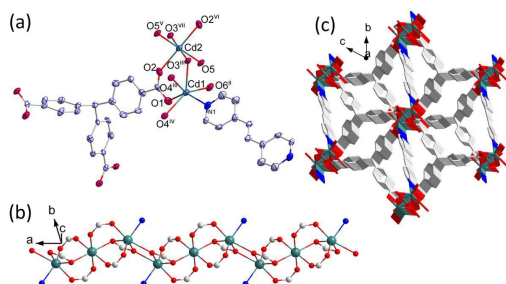


Fig. 7 (a) The coordination environment of Cd centers in **7**. Symmetry codes: (ii)

$x, y - 1, z$; (iii) $x, y, z - 1$; (iv) $-x + 1, -y, -z + 1$; (v) $-x, -y + 1, -z$; (vi) $-x, -y, -z$; (vii) $-x, -y, -z + 1$. (b) The 1D rod structure. (c) View of the 3D open framework. All hydrogen atoms were omitted for clarity.

The use of chelate ligand 2,2'-bipy has afforded the formation of **8**, which crystallizes in the triclinic $P-1$ space group. Cd1 is octahedrally coordinated, bound to six oxygen atoms from six $\alpha_{\text{OH}}\text{-TCOPM}$ ligands (Fig. 8a), whereas Cd2 is seven-coordinated with five carboxylic oxygen atoms from three $\alpha_{\text{OH}}\text{-TCOPM}$ ligands, and two nitrogen atoms of one 2,2'-bipy ligand. As show in Fig. 8b, Cd1 and Cd2 centers are bridged by carboxylic oxygen atoms to form a Cd_3 cluster. These clusters are connected by $\alpha_{\text{OH}}\text{-TCOPM}$ ligands to form a 2D layer (Fig. 8c, Fig. 8d), similar to complexes **1-3** and **5**, where chelate ligands were also used.

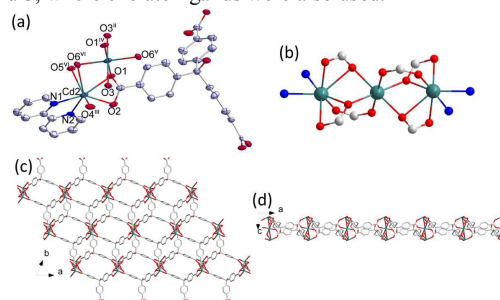
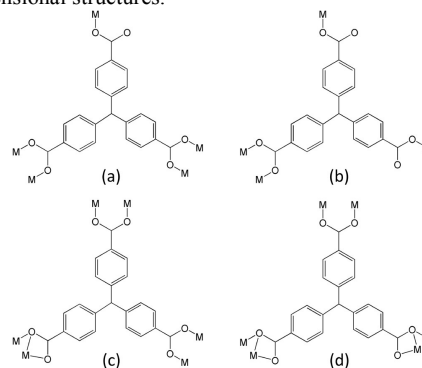


Fig. 8 (a) The coordination environment of Cd centers in **8**. Symmetry codes: (iii) $x + 1, y, z$; (iv) $-x + 1, -y + 2, -z + 1$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $x, y + 1, z$. (b) The $[\text{Cd}_3\text{O}_{12}\text{Na}]$ cluster. (c, d) Views of the 2D layered structure. All hydrogen atoms and 2,2'-bipy ligands were omitted for clarity.

It can be seen from above structural analysis that the coordination modes of the tricarboxylic acid ligands and the type of N-donor ligands have significant effects on the final structures of **1-8**. On one hand, the tricarboxylic acid ligands in **1-8** have displayed different coordination modes (Scheme 2). Tricarboxylic acid ligands in **1** and **2** exhibits two bis(monodentate) and one monodentate modes to bridge to adjacent metal centers (Scheme 2a), while one bis(monodentate) and one monodentate mode was observed in **3** (Scheme 2b). Tricarboxylic acid ligands in **4**, **5**, and **7** possess two bis(monodentate) and a bidentate chelating modes (Scheme 2c), whereas one bis(monodentate) and two tridentate chelating modes were found in **6** and **8** (Scheme 2d). On the other hand, complexes **1-3**, **5**, and **8** exhibit a 2D layered structure, where chelate N-donor ligands (2,2'-bipy, phen, tpy) were used. Additionally, the type of chelate ligands has also an influence on the thickness of 2D layer. For **4**, **6**, and **7**, a 3D open structure was observed, where pillar N-donor ligands (dpe, 4,4'-bipy) were employed. This result further confirms that pillar ligands facilitate the formation of high-dimensional structures.^{35,36}



Scheme 2 The coordination modes of the tricarboxylic acid ligands in **1-8**. The hydroxy groups of α_{OH} -TCOPM ligands were omitted for clarity.

3.2. Powder XRD and IR spectra analysis

Powder XRD patterns of *ay*-synthesized **1-8** are in accordance with those simulated from single-crystal XRD data (Figs. S1-S8), confirming high purities of final products. IR spectra of **1-8** are similar and exhibit broad absorption band at 3400 cm^{-1} , $1666\text{-}1620\text{ cm}^{-1}$ (Fig. S9), which are typical of -COO^- vibration bands. The red-shift in contrast to that for the free TCOPM (1701 cm^{-1}) is attributed to the coordination of TCOPM to metal atoms. The absorption bands at $1398\text{-}1598\text{ cm}^{-1}$ and $1429\text{-}1355\text{ cm}^{-1}$ indicate the asymmetric vibrations and symmetric vibrations of the aromatic ring skeletal vibrations.

3.3. Luminescent properties

The luminescent properties in the solid state of **1-4**, **7**, **8** and the free TCOPM ligand were investigated at room temperature (Fig. 9, Figs. S10-S16). Upon excitation at 344 nm , a maximum emission peak at 446 nm for the TCOPM ligand is observed, which can be attributed to the $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ electronic transition. For **1-4**, **7**, and **8**, the emission peaks are observed at 348 nm ($\lambda_{\text{ex}} = 324\text{ nm}$), 364 nm ($\lambda_{\text{ex}} = 270\text{ nm}$), 357 nm ($\lambda_{\text{ex}} = 298\text{ nm}$), 398 nm ($\lambda_{\text{ex}} = 343\text{ nm}$), 374 nm ($\lambda_{\text{ex}} = 270\text{ nm}$), and 378 nm ($\lambda_{\text{ex}} = 341\text{ nm}$), respectively. These emissions are neither ligand-to-metal charge transfer (LMCT) nor metal-to-ligand charge transfer (MLCT) in nature because Zn and Cd atoms are difficult to be oxidized or reduced.³⁷ The enhancement of luminescence intensities compared to the free TCOPM observed in these complexes, especially in **4** and **8**, is perhaps a result of the intraligand $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ fluorescent emission of the free TCOPM ligand. Furthermore, the emission bands of these complexes are similar to that of the free TCOPM but the maximum values of emission show blue shifts by $68\text{-}98\text{ nm}$, which may be caused by a change in the HOMO and LUMO energy levels of the ligands coordination to metal centers and a charge-transfer transition between ligands and metal centers. The emission decay lifetimes (τ) of complexes **1-4**, **7** and **8** are investigated, and the curves are best fitted by mono-exponentials in the solid, that is, complex **1** ($\tau = 1.13\text{ ns}$, $\chi^2 = 1.092$, Fig. S17), complex **2** ($\tau = 1.96\text{ ns}$, $\chi^2 = 1.057$, Fig. S18), complex **3** ($\tau = 1.63\text{ ns}$, $\chi^2 = 1.100$, Fig. S19), complex **4**, ($\tau = 1.22\text{ ns}$, $\chi^2 = 1.087$, Fig. S20), complex **7**, ($\tau = 0.98\text{ ns}$, $\chi^2 = 1.075$, Fig. S21) and complex **8**, ($\tau = 1.23\text{ ns}$, $\chi^2 = 1.046$, Fig. S22). In addition, all the complexes show a lower absolute fluorescence quantum efficiency (Φ), that is, complex **1** ($\Phi = 0.08$), complex **1** ($\Phi = 0.11$), complex **1** ($\Phi = 0.07$), complex **1** ($\Phi = 0.03$), complex **1** ($\Phi = 0.09$) and complex **1** ($\Phi = 0.05$), which can be attribute to excited-state distortion and vibrational quenching.³⁸

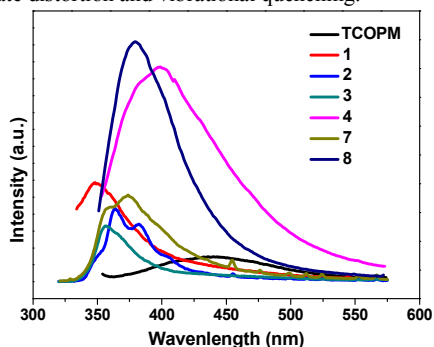


Fig. 9 The solid-state photoinduced emission spectra of TCOPM, **1-4**, **7**, and **8** at room temperature.

4. Conclusions

In summary, eight Zn(II) and Cd(II) complexes (**1-8**) constructed from the flexible C-centered triangular multicarboxylate TCOPM and different N-donor ligands have been successfully designed and prepared through the solvothermal reaction. The coordination modes of the tricarboxylic acid ligands and the type of N-donor ligands have significant effects on the structures of final products. In our case, **1-3**, **5** and **8** exhibit a 2D layered structure, while **4** and **6-7** possess a 3D open framework. Luminescent studies show that the emissions are significantly enhanced for **1-4**, **7** and **8** compared to the free TCOPM. The present contribution provides a useful strategy to construct assemblies with different topologies by employing aromatic multicarboxylate and N-donor mixed ligands.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [X-ray crystallographic files in CIF format, selected bond lengths and angles, powder XRD patterns, IR and luminescence spectra]. See DOI: 10.1039/b000000x/.

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Graphical Abstract

Eight Zn(II) and Cd(II) complexes based on the C-centered triangular multicarboxylate and N-donor mixed ligands were synthesized, which exhibit two-dimensional (2D) layered or 3D open structures. The coordination mode of ligands have obvious effects on the final structures. Luminescent properties were also investigated.

