Three Novel Cd(II) and Zn(II) Coordination Polymers with O-, N-donor Ligands: Syntheses, Structures, and Photoluminescence Properties

Yong-Hong Zhou

Abstract Three new multi-dimensional coordination polymers, namely, $[Cd(SIP)(HBPP)(BPP)_{0.5}(H_2O)\cdot H_2O]_n$ (**1**), $[Zn(L)(BIB)_{0.5}]_n$ (**2**), and $\{[Cd_2(L)_2(BIB)_2](H_2O)_7\}_n$ (**3**) (H_3SIP = 5-sulfo-1,3-benzenedicarboxylate, BPP = 1,3-bis (4-pyridyl)propane, H_2L = 4-oxyacetate-benzoic acid, and BIB = 1,4-bis(imidazol-1-yl)-butane), were hydrothermally synthesized by self-assembly of the flexible N-donor ligand and the polycarboxylate ligands. Single crystal X-ray analyses reveal that complexes **1**–**3** possess different structural features. The Cd(II) atom in complex **1** is seven-coordinated by two bidentate chelating carboxylate groups and two nitrogen atoms as well as one water molecule. The adjacent Cd(II) atoms are bridged by two carboxylate groups to form 1D chains running along different directions, which are connected by BPP ligands to generate 2D network. The resulting 2D networks are further linked by hydrogen-bond interactions, affording a 3D supramolecular architecture. In complex **2**, the $[Zn_2(COO)_4]$ units are bridged by L^{2-} ligands to generate 1D double chain structure and then linked by BIB ligands to give 2D grid framework. In complex **3**, the $[Cd(L_2)]_n$ and $[Cd(BIB)]_n$ helixes are alternately arranged, leading to the formation of a 2D bilayer structure.

Keywords Coordination polymer · N-donor ligand · Crystal structure · Luminescence · Cadmium(II) complex · Zinc(II) complex

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1 Introduction

Multidimensional coordination polymers (CPs) have attracted increasing interest because of their diverse structures, topologies, and promising applications in optics, catalysis, chemical separation, and molecular adsorption [1–4]. It has been postulated that the ultimate structures of target products are affected by many factors, in which the most crucial ones are the sharpness and functionality of the organic ligand and geometrical requirement of the central metal ions [5–8]. The structural geometries are controllable by the selection of suitable organic ligands and metal ions. In particular, organic polycarboxylate, such as benzene-, pyrazole-, pyridine- and imidazole-carboxylates, have been extensively involved in constructing CPs because of their various binding modes and high structural stability, and a great deal of CPs with elegant topologies and excellent properties have been synthesized [9–13]. In these regards, 5-sulfo-1,3-benzenedicarboxylate (H_3SIP) is an appropriate O-donor candidate for the preparation of novel multi-dimensional metal-organic frameworks owing to its two carboxylic and one soft sulfonic groups. The deprotonation of H_3SIP at different acidity level can afford multiple products including H_2SIP^-, $HSIP^{2-}$, and SIP^{3-}. Their potential O-donor atoms vary from one to seven, which are conducive to the formation of high-dimensional CPs. In recent years, H_3SIP has been already utilized in the self-assembly of CPs with Cd(II), Cu(II), Zn(II), Pb(II), Co(II), Ni(II), Ln(III), and Ag(I) salts [14–20], and the results reveal that H_3SIP exhibits versatile coordination modes and causes structural diversity.

As a multidentate ligand, 4-oxyacetate-benzoic acid (H_2L) contains one rigid aromatic carboxyl and one flexible aliphatic $-OCH_2-COO-$ groups. The H_2L ligand combines the characteristic coordination chemistry of both

the rigid carboxylate and flexible carboxylate system involved in the self-assembly process. Compared to the rigid or flexible carboxylate ligands, the incorporation of flexible –OCH$_2$–COO– group to aromatic carboxylate ligand may offer new opportunities to construct frameworks with unique structural features and tailorable properties [21–23].

To get further insight into the coordination chemistry of H$_3$SIP and H$_2$L, and to develop new materials with excellent properties and fascinating architectures, we start to explore new high-dimensional polymeric networks constructed from H$_3$SIP and H$_2$L. With the aid of two N-donor ligands, highly flexible 1,3-bis(4-pyridyl)propane (BPP) and 1,4-bis(imidazol-1-yl)-butane (BIB), three new CPs, namely, [Cd(SIP)(HBPP)(BPP)$_{0.5}$(H$_2$O)·H$_2$O]$_n$ (1), [Zn(L)(BIB)$_{0.5}$]$_n$ (2) and {[Cd$_2$(L)$_2$(BIB)$_2$](H$_2$O)$_7$}$_n$ (3) have been obtained. In this study, we report the synthesis, crystal structures and fluorescence properties of these complexes.

2 Experimental Section

2.1 Materials and Physical Measurements

All of the initial materials were commercially obtained (NaH$_2$SIP and BPP were purchased from Acros and other analytical-grade reagents were from Aladdin) and used without further purification. H$_2$L [24] and BIB [25] were synthesized using the literature methods. Elemental analyses (C, H, N and S) were carried out with a Vario EL III elemental analyzer. The FT-IR spectra were taken on a Nicolet 170SX FT-IR spectrophotometer from KBr pellets in the range of 4,000–400 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D2 PHASER diffractometer using Cu K$_\alpha$ radiation. Thermogravimetric analyses (TGA) were done in air with a heating rate of 10 °C min^{-1} using a Shimadzu DTG-60H analyzer. Solid-state fluorescent spectra were performed on a RF-5301PC fluorescence spectrometer at room temperature.

2.2 Synthesis of [Cd (SIP)(HBPP)(BPP)$_{0.5}$(H$_2$O)·H$_2$O]$_n$ (1)

The mixture of Cd(CH$_3$COOH)$_2$·2H$_2$O (53.3 mg, 0.2 mmol), 5-sulfoisophthalic acid monosodium salt (53.6 mg, 0.2 mmol), and BPP (39.6 mg, 0.2 mmol) was dissolved in deionized water (10.0 mL). The pH value was adjusted to 5.5 by addition of triethylamine. Consequently, the resulting mixture was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 96 h. After the mixture was slowly cooled to room temperature at a rate of 5 °C/h, colourless crystals of 1 suitable for X-ray analysis were isolated. Yield: 36%. Anal. Calcd for C$_{27.5}$H$_{29}$N$_3$O$_9$SCd: C 47.83, H

4.20, N 6.09, S 4.64%. Found: C 47.80, H 4.23, N 6.11, S 4.67%. IR (KBr, cm^{-1}): 3445 m, 2931 w, 1607 s, 1558 s, 1504 w, 1445 s, 1434 s, 1368 s, 1241 s, 1175 s, 1101 m, 1019 w, 804 w, 730 m, 627 m.

2.3 Synthesis of [Zn(L)(BIB)$_{0.5}$]$_n$ (2)

A mixture of Zn(CH$_3$COO)$_2$·2H$_2$O (21.9 mg, 0.1 mmol), H$_2$L (19.6 mg, 0.1 mmol), NaOH (4 mg, 0.1 mmol), BIB (19 mg, 0.1 mmol), and 10 mL H$_2$O was sealed in a 25 mL Teflon-lined stainless steel vessel and kept at 140 °C for 72 h. After being naturally cooled to room temperature, colourless crystals of 2 were collected. Yield: 52%. Anal. Calcd for C$_{14}$H$_{13}$N$_2$O$_5$Zn: C 47.37, H 3.66, N 7.90%. Found: C 47.40, H 3.62, N 7.87%. IR (KBr, cm^{-1}): 3446 m, 2934 w, 1634 vs, 1507 w, 1434 s, 1373 vs, 1277 s, 1183 m, 1071 m, 1035 w, 820 w, 731 w, 691 w.

2.4 Synthesis of {[Cd$_2$(L)$_2$(BIB)$_2$](H$_2$O)$_7$}$_n$ (3)

Complex 3 was synthesized in a procedure similar to that for 2 except Cd(CH$_3$COOH)$_2$·2H$_2$O was used instead. Yield: 52%. Anal. Calcd for C$_{38}$H$_{54}$N$_8$O$_{17}$Cd$_2$: C 40.72, H 4.82, N 10.00%. Found: C 40.75, H 4.85, N 9.97%. IR (KBr, cm^{-1}): 3455 m, 3118 w, 1604 vs, 1526 w, 1396 vs, 1228 s, 1108 m, 1089 m, 1015 w, 863 w, 726 w, 658 w.

2.5 X-Ray Data Structural Determination

Single-crystals of 1–3 were mounted on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K. Data reductions and empirical absorption corrections were carried out using SAINT and SADABS programs, respectively [26]. All the structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares methods using SHELXL-97 [26]. All the non-hydrogen atoms were refined anisotropically. Notably, three carbon atoms (C26, C27, and C28) in 1 are disordered over two positions with occupancy factors of 0.756/0.244. Further crystallographic data are shown in Table 1. Selected bond lengths and angles are given in Table 2. CCDC-1015299 (1), 1015300 (2), and 1015301 (3) contain the supplementary crystallographic data for this paper.

3 Results and Discussion

3.1 Structure of [Cd(SIP)(HBPP)(BPP)$_{0.5}$(H$_2$O)·H$_2$O]$_n$ (1)

Single-crystal X-ray diffraction study shows that 1 crystallizes in the monoclinic space group C2/c, and adopts a

Table 1 Crystal data and structure refinement details for complexes **1–3**

Compound	1	2	3
Formula	$C_{27.5}H_{29}N_3O_9SCd$	$C_{14}H_{13}N_2O_5Zn$	$C_{38}H_{54}N_8O_{17}Cd_2$
Formula weight	690	354.64	1,119.7
Crystal size (mm^3)	$0.32 \times 0.28 \times 0.15$	$0.43 \times 0.28 \times 0.12$	$0.28 \times 0.21 \times 0.15$
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	P2$_1$/c
Unit cell dimensions			
a(Å)	16.7896(15)	8.0660(6)	16.8299(14)
b(Å)	10.7481(9)	9.3519(7)	15.7099(12)
c(Å)	32.399(3)	9.7401(8)	18.6328(16)
α(°)	90	98.6750(10)	90
β(°)	100.298(2)	93.1010(10)	109.213(2)
γ(°)	90	110.287(2)	90
Volume/Å^3	5,752.4(9)	676.76(9)	4652.0(7)
Z	8	2	4
Density (calculated) (mg/mm^3)	1.593	1.740	1.599
Absorption coefficient (mm^{-1})	0.890	1.841	0.992
θ range for data collection/(°)	2.82–25.02	2.71–25.02	2.25–25.02
$F(000)$	2,808	362	2,280
Limiting indices	$-19 \leq h \leq 18, -12 \leq k \leq 12, -38 \leq l \leq 35$	$-9 \leq h \leq 9, -11 \leq k \leq 9, -10 \leq l \leq 11$	$-20 \leq h \leq 18, -10 \leq k \leq 18, -21 \leq l \leq 22$
Goodness-of-fit on F^2	1.048	1.050	1.058
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0431, wR_2 = 0.0825$	$R_1 = 0.0266, wR_2 = 0.0647$	$R_1 = 0.0476, wR_2 = 0.1108$

2D supermolecular structure. The asymmetric unit consists of one Cd(II) atom, one SIP^{3-} anion, one protonated HBPP, half of the BPP, one water ligand, and one solvent water molecule. As shown in Fig. 1, each Cd(II) atom lies in a distorted pentagonal bipyramidal coordination geometry, which is formed by four carboxylate oxygen atoms from two inequivalent SIP^{3-} ligands, two nitrogen atoms from two BPP ligands, as well as one water molecule.

The SIP^{3-} ligand acts as μ_2-bridge by two chelating carboxylate, whereas the sulfonate group remains idle. The adjacent Cd(II) atoms are connected by SIP^{3-} ligands to generate a 1D polymeric chain with Cd···Cd separation of 9.968 Å (Fig. 2). It should be pointed out that there exist two types of BPP ligands with *TT* and *GG'* (*T = trans* and *G = gauche*) conformations, respectively. The *TT* conformational HBPP ligand (containing N2 and N3), with a N···N distance of 9.570 Å and two pyridyl rings being twisted by 86.3°, possesses a monodentate coordination fashion with N3 uncoordinated. Similar coordination mode has been found in some related complexes containing BPP ligands [27, 28]. The *GG'* conformational BPP ligands, with a N···N distance of 6.734 Å and dihedral angle of 10.1° between two pyridyl rings, act as pillars, bridging

two Cd(II) centres of adjacent 1D chains. Thus, the 1D chains are linked by *GG'* BPP spacers, forming a 2D layer in which the Cd···Cd distance spanned by BPP is 9.462 Å. Notably, the water ligand (O8) of each layer is hydrogen bonded (O8–H8C···O5 = 2.783 Å) to the sulfonate group of the neighbouring layer, forming a 3D supramolecular framework (Fig. 3), which is also stabilized by hydrogen bonds between lattice water, carboxyl, sulfonate and protonated pyridyl groups (O9–H9C···O3 = 2.783 Å, O9–H9D···O6 = 2.772 Å, N3–H3···O9 = 2.643 Å).

3.2 Structure of [Zn(L)(BIB)$_{0.5}$]$_n$ (2)

When the reaction of H$_2$L, BIB with Zn(CH$_3$COO)$_2$·2H$_2$O was carried out, complex **2** was obtained. The asymmetry unit of complex **2** consists of one Zn(II) atom, one L^{2-} anion, and half BIB molecule. As shown in Fig. 4, the central Zn(II) atom is in a distorted square pyramidal coordination environment with four oxygen atoms (O1, O3, O2A, and O4A) from four different L^{2-} ligands with Zn–O distances ranging from 2.0415(17) to 2.0816(17) Å, and one nitrogen atom (N2) from BIB ligand with Zn–N distance of 2.004(2) Å. The Zn–O/N bond distances are

Table 2 Selected bond lengths (Å) and bond angles (°) for Complexes **1–3**

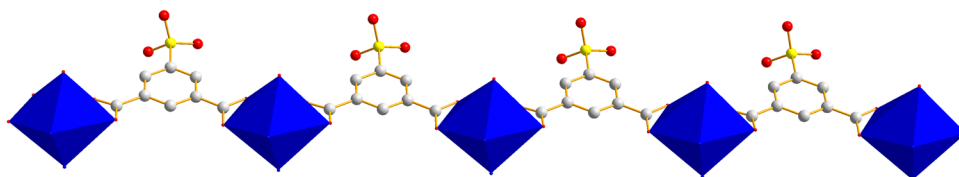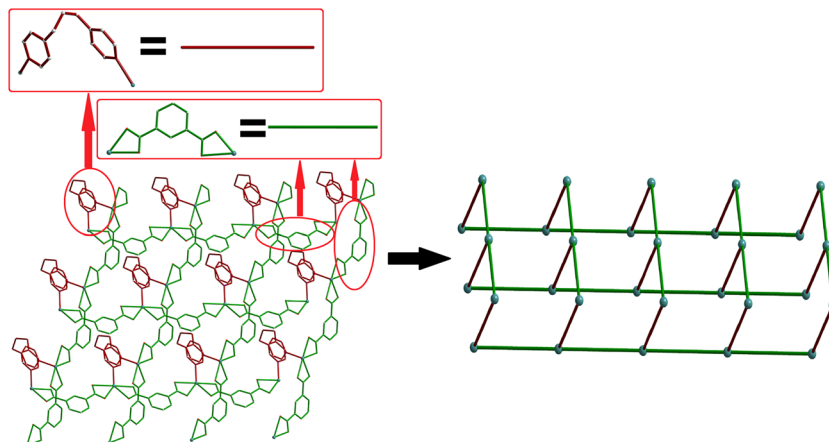|			
Complex 1			
Cd(1)–O(1)	2.241(3)	Cd(1)–O(2)	2.574(3)
Cd(1)–O(3)	2.361(3)	Cd(1)–O(4)	2.453(3)
Cd(1)–O(8)	2.336(3)	Cd(1)–N(1)	2.330(4)
Cd(1)–N(2)	2.384(4)		
O(1)–Cd(1)–N(1)	145.31(14)	O(1)–Cd(1)–O(8)	85.42(13)
N(1)–Cd(1)–O(8)	83.24(13)	O(1)–Cd(1)–O(3)	77.44(12)
N(1)–Cd(1)–O(3)	134.67(13)	O(8)–Cd(1)–O(3)	88.56(13)
O(1)–Cd(1)–N(2)	101.03(14)	N(1)–Cd(1)–N(2)	82.12(14)
O(8)–Cd(1)–N(2)	162.18(14)	O(3)–Cd(1)–N(2)	109.00(14)
O(1)–Cd(1)–O(4)	129.57(13)	N(1)– Cd(1)– O(4)	84.88(13)
O(8)–Cd(1)–O(4)	101.40(13)	O(3)–Cd(1)–O(4)	53.21(12)
N(2)–Cd(1)–O(4)	87.38(14)	O(1)–Cd(1)–O(2)	53.54(11)
N(1)–Cd(1)–O(2)	93.00(12)	O(8)–Cd(1)–O(2)	86.29(12)
O(3)–Cd(1)–O(2)	130.96(11)	N(2)–Cd(1)–O(2)	84.38(13)
O(4)–Cd(1)–O(2)	171.70(12)		
Complex 2			
Zn(1)–N(2)	2.004(2)	Zn(1)–O(1)	2.0415(17)
Zn(1)–O(3)	2.0612(17)	Zn(1)–O(4A)	2.0702(17)
Zn(1)–O(2A)	2.0816(17)		
N(2)–Zn(1)–O(1)	107.06(8)	N(2)–Zn(1)–O(3)	105.61(8)
O(1)–Zn(1)–O(3)	90.65(8)	N(2)–Zn(1)–O(4A)	96.63(8)
O(1)–Zn(1)–O(4A)	87.84(8)	O(3)–Zn(1)–O(4A)	157.14(7)
N(2)–Zn(1)–O(2A)	96.27(8)	O(1)–Zn(1)–O(2A)	156.31(8)
O(3)–Zn(1)–O(2A)	86.92(7)	O(4A)–Zn(1)–O(2A)	85.39(8)
Complex 3			
Cd(1)–N(2)	2.235(5)	Cd(1)–N(4)	2.250(6)
Cd(1)–O(4)	2.357(5)	Cd(1)–O(1)	2.362(5)
Cd(1)–O(2)	2.407(5)	Cd(1)–O(3)	2.458(5)
Cd(2)–N(6)	2.223(5)	Cd(2)–N(8)	2.244(6)
Cd(2)–O(7)	2.262(5)	Cd(2)–O(8)	2.419(5)
Cd(2)–O(9)	2.433(5)	Cd(2)–O(6)	2.553(5)
N(2)–Cd(1)–N(4)	109.4(2)	N(2)–Cd(1)–O(4)	132.02(19)
N(4)–Cd(1)–O(4)	84.65(19)	N(2)–Cd(1)–O(1)	111.3(2)
N(4)–Cd(1)–O(1)	123.84(19)	O(4)–Cd(1)–O(1)	95.20(19)
N(2)–Cd(1)–O(2)	94.0(2)	N(4)–Cd(1)–O(2)	86.1(2)
O(4)–Cd(1)–O(2)	133.40(19)	O(1)–Cd(1)–O(2)	54.41(18)
O(2)–Cd(1)–O(3)	142.97(18)	N(2)–Cd(1)–O(3)	84.94(18)
N(4)–Cd(1)–O(3)	129.15(19)	O(4)–Cd(1)–O(3)	54.06(16)
O(1)–Cd(1)–O(3)	91.51(17)	N(6)–Cd(2)–O(7)	112.61(19)
N(6)–Cd(2)–N(8)	112.5(2)	N(8)–Cd(2)–O(7)	116.8(2)
N(6)–Cd(2)–O(8)	86.00(18)	N(8)–Cd(2)–O(8)	133.08(19)
O(7)–Cd(2)–O(8)	91.64(18)	N(6)–Cd(2)–O(9)	128.09(18)
N(8)–Cd(2)–O(9)	83.49(19)	O(7)–Cd(2)–O(9)	100.84(18)
O(8)–Cd(2)–O(9)	53.53(16)	N(6)–Cd(2)–O(6)	89.66(18)
N(8)–Cd(2)–O(6)	84.86(19)	O(7)–Cd(2)–O(6)	53.94(17)
O(8)–Cd(2)–O(6)	140.10(17)	O(9)–Cd(2)–O(6)	142.07(17)

Symmetry Code: complex **2**: (A) −x + 1,−y + 1,−z + 1
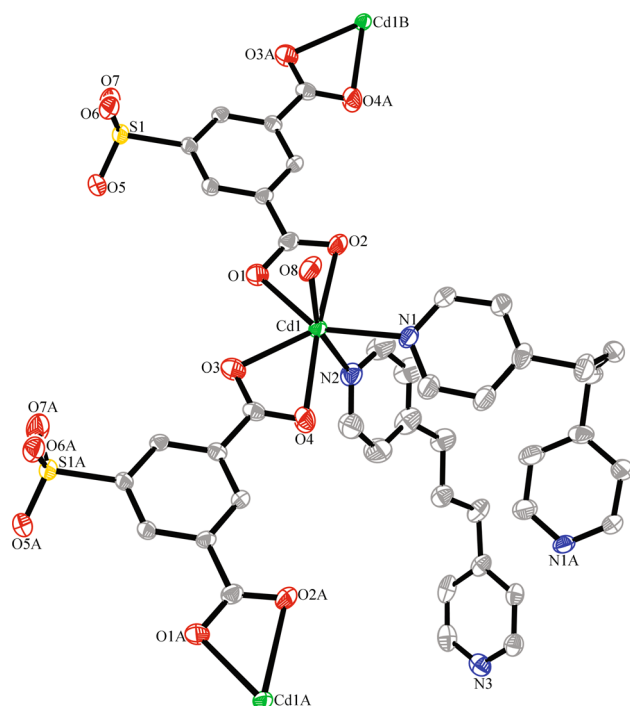
Fig. 1 The coordination environment for Cd(II) centers in **1**. Hydrogen atoms are omitted for clarity. Symmetry codes: (A) x + 1/2, y + 1/2, z; (B) x−1/2, y−1/2, z

within the normal range [29]. Two symmetry-related Zn(II) atoms are bridged by four carboxylate groups in the bidentate bridging fashion to give a paddle-wheel binuclear

$[Zn_2(COO)_4]$ motif, in which the Zn···Zn separation is 3.0574(6) Å (Fig. 5). Further, the $[Zn_2(COO)_4]$ units are bridged by L^{2-} ligands to generate 1D double-stranded chain along the c axis and then crosslinked by BIB ligands to give a 2D rhombic grid network (Figs. 6, 7).

Similar $[Zn_2(COO)_4]$ units are also found in $[Zn_7L_2 (OH)_2(H_2O)_9]\cdot12.25H_2O$ (H_6L = 5,5′,5″-(2,4,6-trimethyl-benzene-1,3,5-triyl) trismethylene-trisoxy-triisophthalic acid) (**I**) [30] and $[Zn_2(PBA)_2(BDC)(DMF)_3(H_2O)_4]$ (HPBA = 4-(4-pyridyl) benzoic acid, H_2BDC = 1,4-benzenedicarboxylic acid) (**II**) [31]. In **I**, the Zn(II) atom is four-coordinated by four carboxylate groups and locates in a tetrahedral environment, whereas each Zn(II) atom in complex **2** has a distorted square pyramidal configuration and five-coordinated by four carboxylate groups and one N atom. Though the Zn(II) atom in **II** are also five-coordinated with four O atoms and one N atom as that in **2**, the main difference is that the $[Zn_2(COO)_4]$ in **II** is bridged by the PBA anions to form a 2D square grid, then further linked by BDC ligands to form a 3D framework. However, in **2**, the 1D double-stranded chains are bridged by BIB ligands, forming a 2D network.

3.3 Structure of $\{[Cd_2(L)_2(BIB)_2](H_2O)_7\}_n$ (**3**)

Single-crystal X-ray diffraction investigation shows that complex **3** crystallizes in monoclinic system with space group $P2_1/c$. There are two Cd(II) centers, two BIB, two L^{2-} ligands and seven solvated water molecules in the

Fig. 2 The 1D chain structure constructed by SIP^{3-} ligands and Cd(II) ions in **1**

Fig. 3 View of the 2D network and its schematic representation for **1**. Hydrogen atoms and sulfonate group are omitted for clarity. SIP^{3-} and BPP ligands are simplified as solid lines

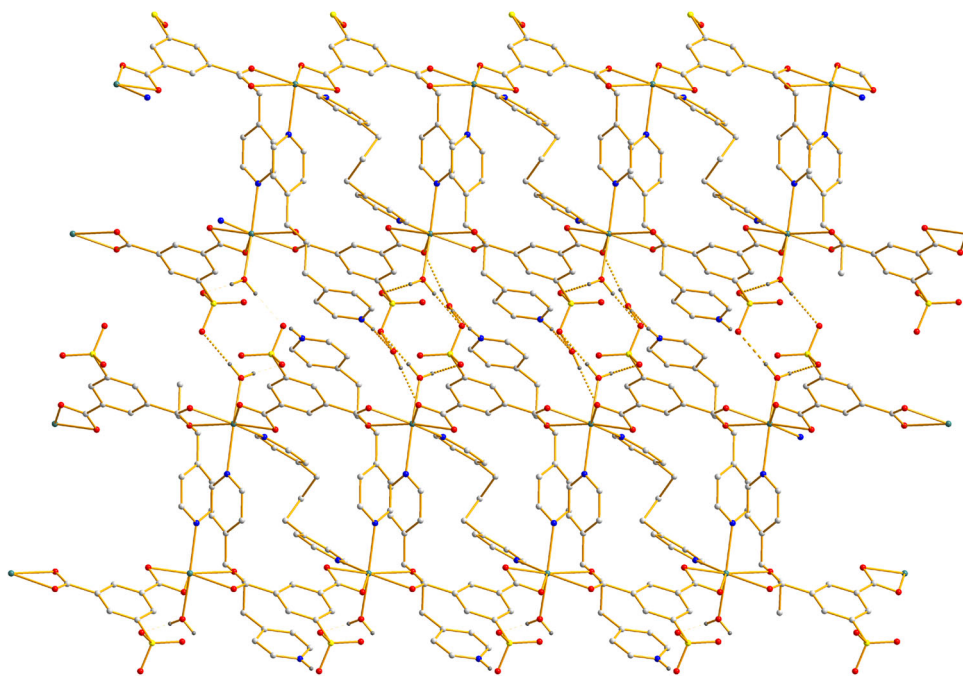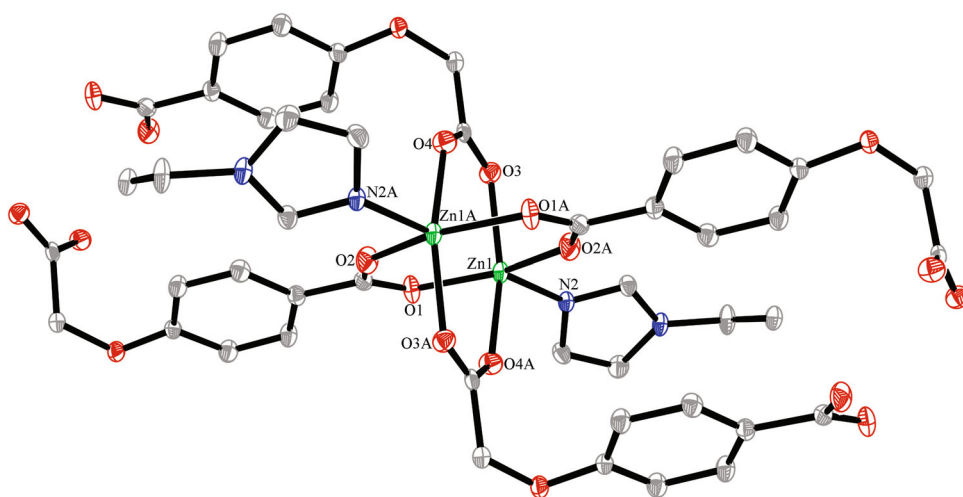**Fig. 4** View of the 3D framework formed by hydrogen bond interactions in **1**

Fig. 5 The coordination environment for Zn(II) centers in **2**. Hydrogen atoms are omitted for clarity. Symmetry code: (A) −x + 1,−y + 1, −z + 1


asymmetric unit. The coordination geometry of Cd1 and Cd2 ions are similar. Therefore, only Cd1 ion is described in detail. As depicted in Fig. 8, Cd1 atom is coordinated by four oxygen atoms from two different L^{2-} anions, and two N atoms from two BIB ligands, leading to a distorted octahedral geometry. The L^{2-} serves as a linker ligand, and the –OCH$_2$COO– group is obviously twisted out of the benzene ring with the C18–O10–C14–C15 torsion angle of −10.7(9)°, indicating the extraordinary conformational flexibility of H$_2$L as compared with rigid aromatic poly-carboxylate acid such as terephthalic acid [31]. The two carboxyl groups on a L^{2-} ligand possess chelating coor-dination mode, connecting symmetry-related Cd(II) atoms,

giving rise to the formation of an 1D [Cd(L)]$_n$ right-handed helical chain along the *b* axis.

Notably, BIB acts as bidentate bridging ligand and links Cd(II) atoms to form a right-handed [Cd(BIB)]$_n$ helical chain, which is also extended along the crystallographic *b* axis with the same pitch as [Cd(L)]$_n$ helix. Interestingly, [Cd(L)]$_n$ and [Cd(BIB)]$_n$ helixes are alternately arranged with Cd(II) atoms as hinges, forming a 2D grid with a window of about 10.7 × 12.5 Å^2 (Fig. 9). Moreover, two sheets based on Cd1 and Cd2, respectively, are parallelly interpenetrated, giving rise to a 2D bilayer framework (Fig. 10). Upon interpenetration, compound **3** has an effective volume of 40 Å^3, which is only about 1.0% of the

Fig. 6 The 1D double-stranded chain constructed by $[Zn_2(COO)_4]$ units and L^{2-} ligands in **2**
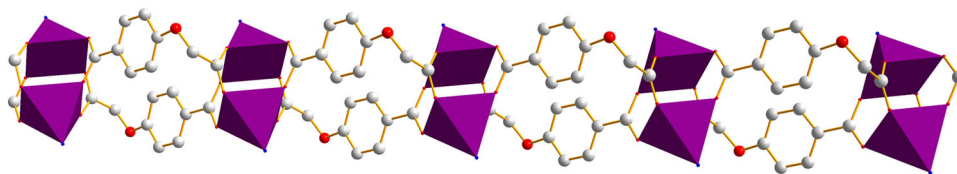
Fig. 7 View of the 2D grid network in **2**, also showing that each $[Zn_2(COO)_4]$ unit connects to four neighbouring ones
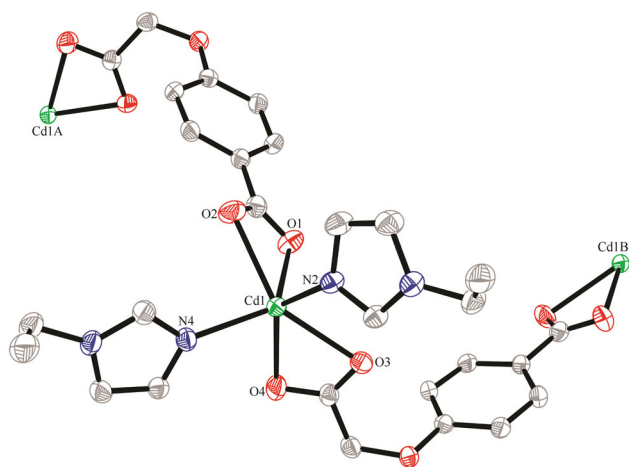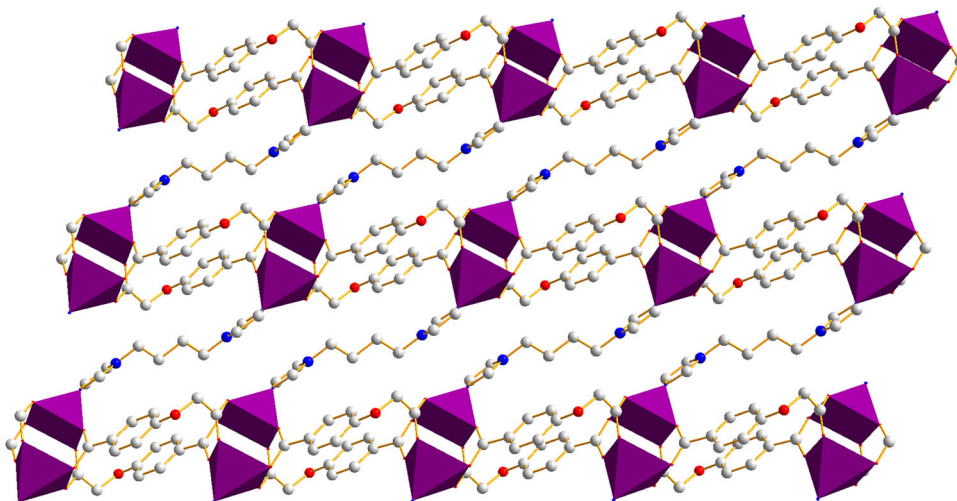
Fig. 8 The coordination environment for Cd(II) centers in **3**. Hydrogen atoms are omitted for clarity. Symmetry codes: (*A*) −x, y + 1/2, −z + 1/2; (*B*) −x, y−1/2, −z + 1/2

total crystal volume, although the single layer contains large windows as described above.

3.4 Powder X-ray Diffraction Patterns and Thermogravimetric Analyses

PXRD patterns were measured to check the purity of bulk samples of **1**–**3**. As shown in Fig. S1, all major peaks in the measured patterns are nearly identical to those simulated from the single crystal data, suggesting the homogeneity of the bulk samples.

Thermogravimetric analysis was carried out on crystalline samples from 30 to 700 °C with a heating rate of 10 °C/min (Fig. 11). For compound **1**, the first weight loss of 3.4% by 127 °C corresponds to the removal of the lattice water molecule (calcd. 2.6%). The second weight loss is 3.6% (calcd. 2.6%) in the range 160–229 °C, and can be assigned to the release of coordinated water molecule. The anhydrous compound is stable up to 290 °C, and then it decomposes gradually, giving rise to the formation of CdO as the residue (found 20.1%, calcd. 18.6%). For compound **2**, a total weight loss of 77.5% is observed in the temperature range 210–525 °C, which is attributed to the decomposition of the organic ligands, and the remaining weight corresponds to the formation of ZnO (found 22.5%. calcd. 23.0%). Compound **3** loses its free water molecules from room temperature to 156 °C (found 10.5%, calcd. 11.2%). The anhydrous $Cd_2(L)_2(BIB)_2$ is stable up to 275 °C, and the release of organic components occurs from 275 to 490 °C. The final residue may be CdO (found 22.1%. calcd. 22.9%).

3.5 Photoluminescence Properties

To investigate the fluorescent properties of **1**–**3**, their emission spectra were recorded in the solid state at room temperature (Fig. 12). Intense fluorescent emission at
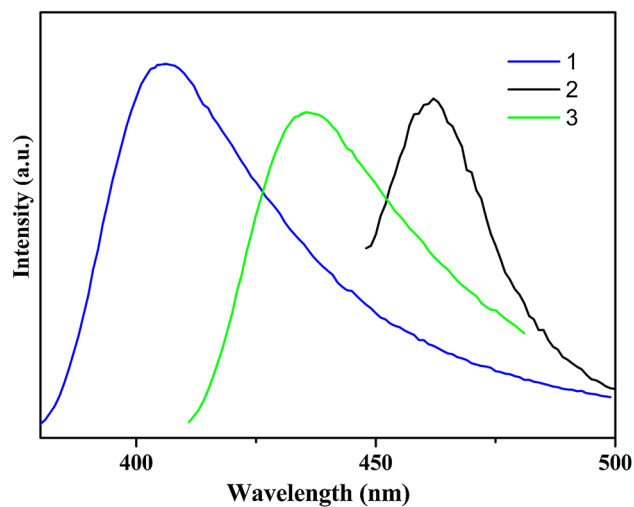
Fig. 9 Two types of helices are connected by Cd(II) atoms, forming a 2D helical layer in **3**
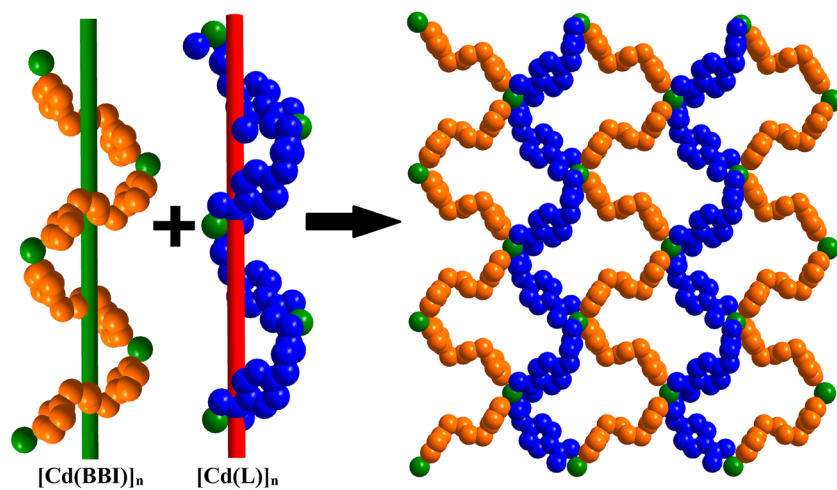
Fig. 10 a View of the twofold interpenetrated sheets, resulting in a 2D bilayer framework in **3**. **b** Schematic illustration of the twofold interpenetrated sheets, L^{2-} and BIB ligands are simplified as solid lines
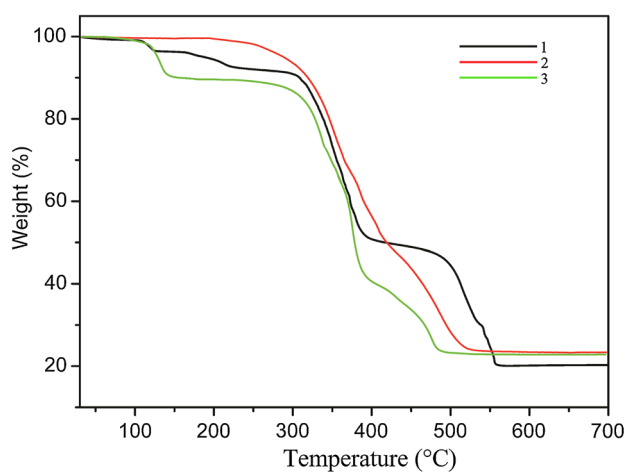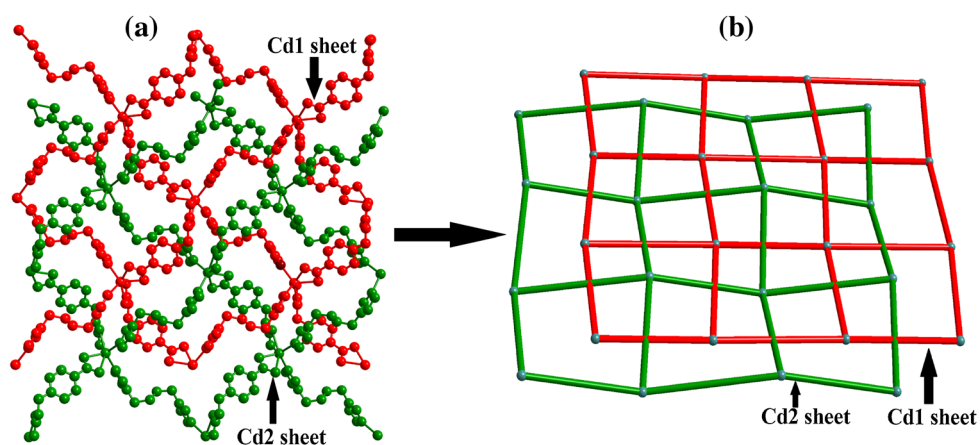
Fig. 11 TG curves for compounds **1–3**

Fig. 12 The fluorescent emission spectra of complexes **1–3** in the solid state at room temperature

405 nm ($\lambda_{ex} = 345$ nm) for **1** was observed. As reported previously, solid NaH$_2$SIP shows photoluminescent emission at 320 nm upon excitation at 286 nm [32]. Therefore, the emissions of **1** may be attributed to ligand-to-metal charge transfer (LMCT) [33].

Complexes **2** and **3** exhibit blue emissions with maxima at 461 nm ($\lambda_{ex} = 351$ nm) and 435 nm ($\lambda_{ex} = 343$ nm), respectively. Very different emission bands for **2** and **3** may be associated with their 2D structural motifs, even though they have the same mixed-ligand systems. According to the literature, the emission bands may be attributed to LMCT [34–36]. Similar LMCT has been observed in many CPs with mixed aromatic carboxylate/N-donor ligands [37]. The enhancement emission of **1**–**3** may be attributed to the ligand chelation to metal centers. The chelating coordination fashion enhances the rigidity of the ligands and decreases the loss of energy by radiationless pathway [38, 39].

4 Conclusions

In summary, three new Cd(II) and Zn(II) CPs based on H$_3$SIP, H$_2$L and different N-donor ligands were presented in this work. Our research demonstrates that H$_3$SIP and H$_2$L are good candidates to construct multi-dimensional CPs. The structural differences of polymers **1**–**3** highlight that flexibility of the polycarboxylate ligands, N-donor ligands, and metal centers play a vital role in defining the final structural features of these crystalline materials.

5 Supporting Information

Simulated and measured powder XRD patterns of **1**–**3**.

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