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Tuning Structural Topologies of Three Photoluminescent Metal–Organic Frameworks via Isomeric Biphenyldicarboxylates

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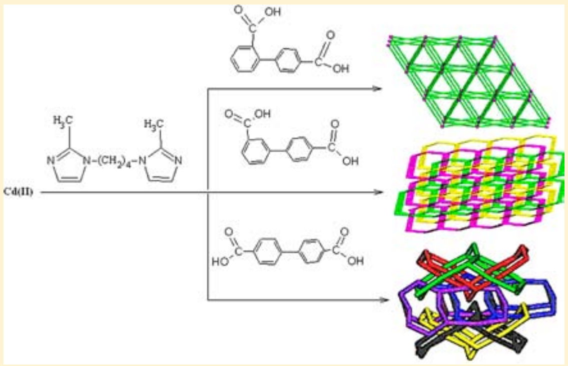
Supporting Information

ABSTRACT: Three new cadmium compounds, [Cd(2,4′-bpdc)(bib)$_{0.5}$] (**1**; 2,4′-bpdc = biphenyl-2,4′-dicarboxylate and bib = 1,4-bis(2-methyl-imidazol-1-yl)butane), {[Cd$_2$(3,4′-bpdc)$_2$(bib)$_{1.5}$(H$_2$O)]$_n$·H$_2$O}$_n$ (**2**; 3,4′-bpdc = biphenyl-3,4′-dicarboxylate), and [Cd (4,4′-bpdc)(bib)] (**3**; 4,4′-bpdc = biphenyl-4,4′-dicarboxylate), have been successfully synthesized by the assembly of Cd^{2+} ions, bib ligands, and isomeric bpdc ligands, respectively. This paper presents a comparative study on the tuning of structural topologies using three isomers of biphenyldicarboxylates as bridging ligands. Compound **1** based on 2,4′-bpdc features a three-dimensional (3D) framework with 6-connected **mab** topology. Compound **2** based on 3,4′-bpdc is another 3D framework, but it possesses a rare 3-fold interpenetrating 4,6-connected **fsh** net, while compound **3** based on linear 4,4′-bpdc shows unusual 2D → 3D parallel polycatenation of (4,4) layers. Furthermore, the luminescent properties of three compounds are investigated in the solid state.



INTRODUCTION

Novel functional coordination polymers (CPs) are currently of great interest because of their diverse structural topologies and potential applications in gas storage, magnetism, catalysis, and luminescence.[1−5] Although rapid progress in CPs has been made, it is also a great challenge to rationally prepare and control the structures and composition of target products in crystal engineering. It has been recognized that the construction of CPs is influenced by both structural and experimental factors, such as organic ligands, pH values, temperature, solvents, and so on.[6] The most effective and facile method to construct novel CPs is the appropriate choice of the well-designed organic ligands containing modifiable backbones. Biphenyldicarboxylates have proven to be good candidates for the construction of new CPs, such as biphenyl-2,2′-dicarboxylic acid, biphenyl-3,3′-dicarboxylic acid, and biphenyl-4,4′-dicarboxylic acid.[7,8] However, the investigation of unsymmetrical biphenyldicarboxylates, such as biphenyl-2,4′-dicarboxylic acid and biphenyl-3,4′-dicarboxylic acid, remains rarely explored.[9,10]

In this work, we perform a comparative study on the tuning of structural topologies using three isomers of biphenyldicarboxylates as bridging ligands. Three isomers of biphenyldicarboxylate (e.g., biphenyl-2,4′-dicarboxylic acid = 2,4′-H$_2$bpdc, biphenyl-3,4′-dicarboxylic acid = 3,4′-H$_2$bpdc, and biphenyl-4,4′-dicarboxylic acid = 4,4′-H$_2$bpdc) are employed to assemble with 1,4-bis(2-methylimidazol-1-yl)butane (bib) and Cd^{II} centers, respectively. Three new cadmium compounds with distinct structural topologies, [Cd(2,4′-bpdc)(bib)$_{0.5}$] (**1**), {[Cd$_2$(3,4′-bpdc)$_2$(bib)$_{1.5}$(H$_2$O)]$_n$·H$_2$O}$_n$ (**2**), and [Cd (4,4′-bpdc)(bib)] (**3**) have been successfully synthesized and structurally characterized. Compound **1** based on 2,4′-bpdc features a three-dimensional (3D) framework with 6-connected **mab** topology. Compound **2** based on 3,4′-bpdc possesses a rare 3-fold interpenetrating 4,6-connected **fsh** net, while compound **3** based on linear 4,4′-bpdc shows unusual 2D → 3D parallel polycatenation of (4,4) layers. Furthermore, the luminescent properties of these compounds were investigated in the solid state at room temperature.

EXPERIMENTAL SECTION

Materials and Physical Measurements. All reagents and solvents employed were commercially available and were used as received without further purification. Elemental analysis was carried out on a Carlo Erba 1106 fully automatic trace organic elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as dry KBr pellets in the 400−4000 cm^{-1} range. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA449C thermal analyzer under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Solid-state fluorescence spectra were recorded on a Hitachi F-4600 spectrometer equipped with a xenon lamp and a quartz carrier at room temperature (slit width = 3 nm and scan rate = 15 nm s^{-1}).

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Synthesis of [Cd(2,4′-bpdc)(bib)$_{0.5}$]$_n$(1). A mixture of Cd(CH$_3$COO)$_2$·2H$_2$O (0.267 g, 1 mmol), 2,4′-H$_2$bpdc (0.242 g, 1 mmol), bib (0.218 g, 1 mmol), NaOH (0.08 g, 2 mmol), and deionized water (18 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 96 h. After cooling to room temperature, the colorless block crystals were obtained and washed with alcohol several times (yield: 42% based on Cd). Elem anal. Calcd for $C_{20}H_{17}CdN_2O_4$: C, 52.02; H, 3.71; N, 6.07. Found: C, 51.88; H, 3.73; N, 6.15. IR (cm^{-1}): 3111 m, 1616 s, 1527 s, 1504 s, 1495 s, 1385 m, 1120 w, 894 m, 728 m.

Synthesis of {[Cd$_2$(3,4′-bpdc)$_2$(bib)$_{1.5}$(H$_2$O)]$_n$·H$_2$O}$_n$ (2). Compound **2** was obtained by the same hydrothermal procedure as that for the preparation of compound **1** only using the 3,4′-H$_2$bpdc (1 mmol) ligand instead of the 2,4′-H$_2$bpdc ligand. Colorless block crystals of **2** were collected in 40% yield based on Cd after washing with ethanol several times. Elem anal. Calcd for $C_{46}H_{47}Cd_2N_6O_{10}$: C, 53.29; H, 4.57; N, 8.11. Found: C, 53.07; H, 4.50; N, 8.04. IR (cm^{-1}): 3211 m, 1674 s, 1504 s, 1469 s, 1318 m, 1234 w, 1141 m, 938 m, 867 w, 775 m.

Synthesis of [Cd(4,4′-bpdc)(bib)]$_n$ (3). Compound **3** was prepared in the same manner as that of **1**, using 4,4′-H$_2$bpdc (1 mmol) instead of 2,4′- H$_2$bpdc. Colorless crystals of **3** were obtained in 52% yield based on Cd. Elem anal. Calcd for $C_{26}H_{26}CdN_4O_4$: C, 54.70; H, 4.59; N, 9.81. Found: C, 55.13; H, 4.62; N, 9.90. IR (cm^{-1}): 3012 m, 1635 s, 1526 s, 1507 m, 1441 s, 1376 m, 1223 w, 1108 m, 927 m, 864 w, 622 w.

X-ray Crystallography Study. Diffraction intensity data of single crystals of three compounds were collected on a Bruker SMART APEXII CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by using a ω-scan mode. An empirical absorption correction was applied using the *SADABS* programs.[11] All of the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program *SHEXL 97*.[12] All non-H atoms were refined anisotropically. The H atoms were located by geometrical calculations, and their positions and thermal parameters were fixed during structure refinement. Several C atoms (C48A, C48B, C49A, C49B, C50A, C50B, C52A, and C52B) and N atoms (N8A and N8B) are disordered in two positions for the bib ligand in the asymmetric unit of **1**. Several O atoms (O1, O1B,O2, O2B O3, O3B, O4, and O4B) are disordered in two positions for the 4,4′-bpdc ligand in the asymmetric unit of **3**. The crystallographic data are summarized in Table 1.

Table 1. Crystallographic Data and Structure Refinement Summary for Compounds 1−3

	1	2	3
empirical formula	$C_{20}H_{17}CdN_2O_4$	$C_{46}H_{47}Cd_2N_6O_{10}$	$C_{26}H_{26}CdN_4O_4$
fw	305.62	1068.70	570.41
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\overline{1}$	$P2_1/c$
a/Å	9.176(5)	8.604(5)	19.344(5)
b/Å	10.880(6)	15.769(5)	16.594(5)
c/Å	18.261(10)	17.344(5)	15.392(4)
α/deg	90	87.030(5)	90
β/deg	98.608(5)	80.751(5)	94.319(4)
γ/deg	90	80.751(5)	90
V/Å^3	1822.08(17)	2308.1(17)	4927(2)
Z	4	2	4
D_c/g cm^{-3}	1.683	1.887	1.539
indep reflns [$I > 2\sigma(I)$]	3781	6505	10427
F(000)	924	1288	2320
θ range for data collection	2.18−26.55	1.31−25.00	1.62−26.75
GOF	1.045	1.057	1.078
R1^a, wR2^b [$I > 2\sigma$(I)]	0.0194, 0.0490	0.0.0465, 0.1248	0.0504, 0.0891
R1^a, wR2^b (all data)	0.0216, 0.0504	0.0587, 0.1329	0.1128, 0.1050

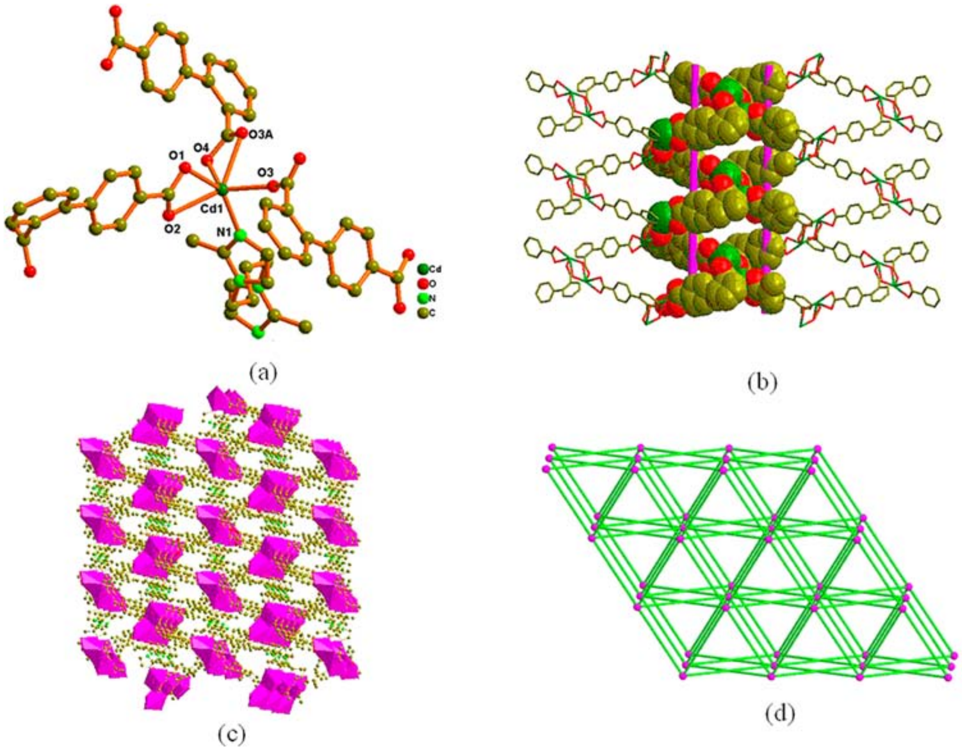
^{a}R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b}wR2 = $[\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)]^{1/2}$.

RESULTS AND DISCUSSION

Compound **1** reported here presents the first 3D CP constructed from the 2,4′-bpdc ligand. It features a pillared-layer structure with unusual 6-connected **mab** topology. In the asymmetric unit of **1**, there are one crystallographically independent Cd^{II} atom, one 2,4′-bpdc ligand, and half of a bib ligand. Each Cd^{II} atom is six-coordinated by five O atoms from three 2,4′-bpdc ligands [Cd−O bond lengths varying from 2.212(2) to 2.497(11) Å] and one N atom from one bib ligand [d_{Cd-N} = 2.2107(14) Å], showing highly distorted octahedral geometry (Figure 1a). Each 2,4′-bpdc ligand acts as a μ_3-linker and bridges three Cd^{II} atoms, where two carboxylate groups adopt bidentate chelating and bidentate chelating/bridging modes, respectively (type I, Scheme 1). Two carboxylate groups from two symmetry-related 2,4′-bpdc ligands connect two Cd^{II} atoms to a dinuclear Cd^{II} subunit, and the Cd···Cd distance is 3.7909 Å. It is interesting to note that the 2,4′-bpdc ligands link the Cd^{II} atoms to left- or right-handed helical 2$_1$ chains along a crystallographic b axis (Figure 1b). The resulting left- or right-handed helices with a pitch of 10.88 Å are alternately arranged in an equal ratio, generating an achiral neutral layer parallel to the bc plane. Finally, the μ_2-bib ligands act as pillars and further link the neutral layers into a 3D framework (Figure 1c). The Cd···Cd distance separated by the bib ligand is 12.455 Å.

From the viewpoint of structural topology, each dinuclear Cd^{II} unit can be viewed as a 6-connected node; thus, the whole framework of **1** can be topologically represented as a rare 6-connected **mab** net with the vertex symbol of 4^4.6^{10}.8 (Figure 1d). For 6-connected frameworks, the **pcu** net is a well-known one and the **mab** net is relatively rare. The structure of **1** adopting such an unusual **mab** net is mainly due to the presence of flexible bib ligands.

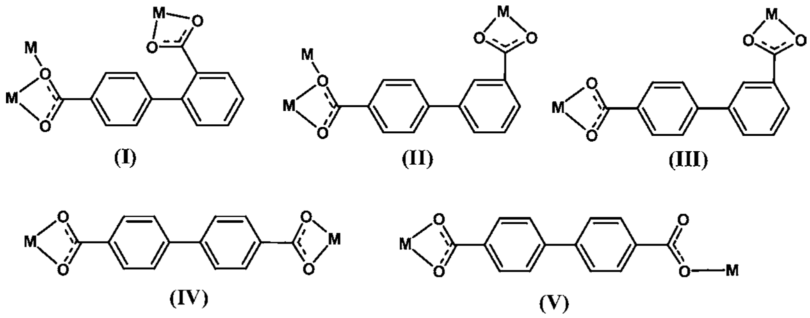
With the 3,4′-bpdc ligand instead of the 2,4′-bpdc ligand, new compound **2** with a distinct 3D framework structure was obtained. Compound **2** has two kinds of coordination nodes and is viewed as a 3-fold interpenetrating 4,6-connected **fsh** net. X-ray crystallography reveals that it crystallizes in triclinic space group $P\overline{1}$. Although two independent Cd^{II} atoms (Cd1 and Cd2) in the asymmetric unit show similar distorted octahedral coordination geometry, their coordination environments are totally different. As shown in Figure 2a, the Cd1 atom is coordinated by four O atoms from two carboxylate groups of two 3,4′-bpdc ligands and two N atoms from two bib ligands, while the Cd2 atom is surrounded by five O atoms from three different 3,4′-bpdc ligands, one coordinated water molecule, and one N atom from one bib ligand. Two independent 3,4′-bpdc ligands in the asymmetric unit of **2** have two different coordination modes (types II and III in Scheme 1): one is a μ_3-bridging ligand and another is only a μ_2-bridging ligand. Two symmetry-related Cd2 atoms are bridged by two carboxylate groups to a dinuclear unit with a short Cd···Cd distance of 4.145 Å. Without considering the bib ligands, the Cd^{II} atoms are interlinked by the 3,4′-bpdc ligands to form a 1D double chain (Figure 2b). Such resulting chains are further connected by the bib ligands to a 3D framework with large free spaces (Figure 2c). Because of the absence of the guest molecules to fill the large void space during the assembly process, the potential voids are filled via mutual interpenetration of three identical 3D frameworks, which directly



(a) (b) (c) (d)

Figure 1. (a) Local coordination geometry of the central Cd^{II} atom in **1** (all H atoms are omitted for clarity). (b) View of the left- and right-handed helical chains in the *bc* plane. (c) 3D framework of **1**. (d) Topological representation of the 6-connected **mab** net.

Scheme 1. Coordination Modes of the Ligands in Compounds 1−3



leads to the formation of a 3-fold interpenetrated final framework.

For a simple framework, each Cd1 atom can be reduced to a 4-connected node and each dinuclear Cd2 unit is regarded as a 6-connected node, so the 3D framework can be simplified as a binodal 4,6-connected network with **fsh** topology (Figure 2d). The short vertex symbol of **fsh** net is $(4^3.6^3)_2(4^6.6^6.8^3)$. To the best of our knowledge, only one noninterpenetrating CP with this **fsh** topology has been reported.[13] The structure of **2** presented here is the first 3-fold interpenetrating **fsh** network.

When the 4,4′-bpdc ligand was used, the third compound **3** with a 2-fold interpenetrating layered structure was prepared. It crystallizes in monoclinic space group $P2_1/c$. The asymmetric unit of **3** consists of two crystallographically independent Cd^{II} atoms, two 4,4′-bpdc ligands, and four bib ligands. As depicted in Figure 3a, two independent Cd^{II} atoms show different coordination environments. The Cd1 atom has a distorted octahedral coordination geometry defined by two N atoms from two bib ligands [d_{Cd-N} = 2.252(5) and 2.306(14) Å] and four O atoms from two different 4,4′-bpdc ligands [d_{Cd-O} ranging from 2.333(5) to 2.410(4) Å], while the Cd2 atom is five-coordinated by three O atoms from two 4,4′-bpdc ligands [d_{Cd-O} ranging from 2.202(4) to 2.443(4) Å] and two N atoms from the bib ligands [d_{Cd-N} = 2.262(5) and 2.224(5) Å], exhibiting a square-pyramidal geometry. Both independent 4,4′-bpdc ligands are μ_2-linkers, and the carboxylate groups exhibit bidentate chelating and monodentate modes (types IV and V in Scheme 1). It is remarkable that four Cd^{II} centers are bridged together by four 4,4′-bpdc ligands to generate a [Cd$_4$(4,4′-bpdc)$_4$] square. Furthermore, each [Cd$_4$(4,4′-bpdc)$_4$] square is doubly connected to four adjacent squares by eight bib ligands. Such an assembly leads to a layer based on square grids. Two identical layers further interpenetrate each other to block the free spaces in the squares (Figure 3b).

Notably, such an interpenetration occurring here is very different from that of the common (4,4) layers and exhibits an unprecedented interpenetration fashion. In a simple layer of **3**, there are four kinds of squares with different dimensions. The biggest one is the [Cd$_4$(4,4′-bpdc)$_4$] square with dimensions of 15.12 Å × 15.48 Å, and another big one is a [Cd$_4$(4,4′-

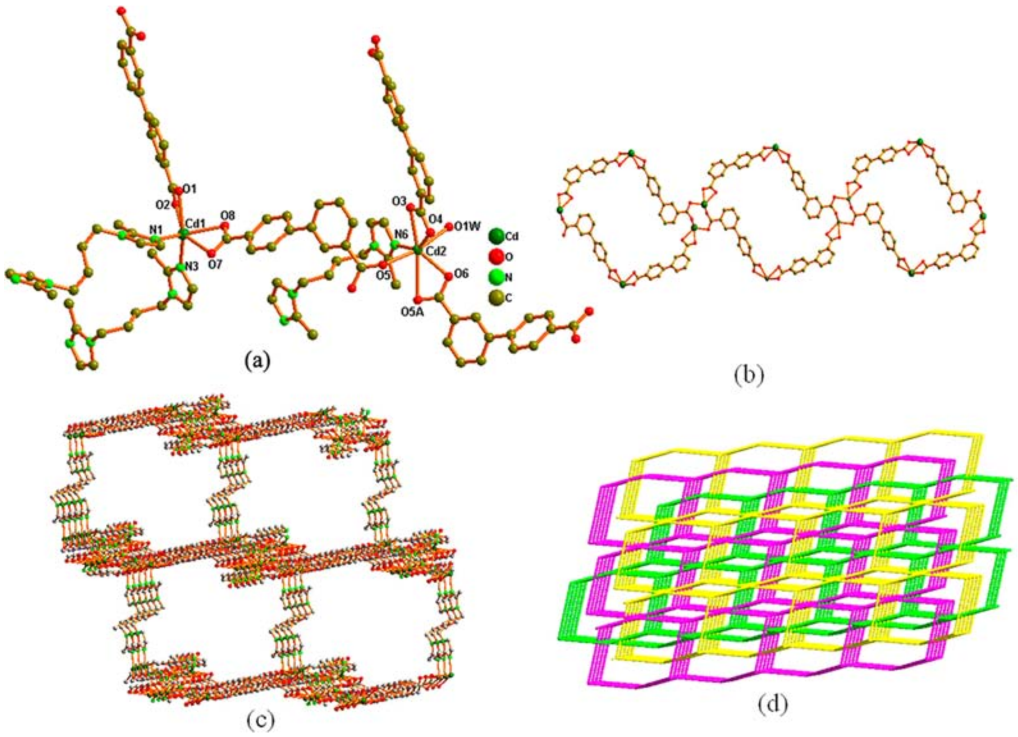


Figure 2. (a) Local coordination geometry of the central Cd^{II} atom in **2** (all H atoms are omitted for clarity). (b) Chain formed by the carboxylate ligands. (c) 3D framework of **2**. (d) Schematic representation of the 3-fold interpenetrating **fsh** net of **2**.

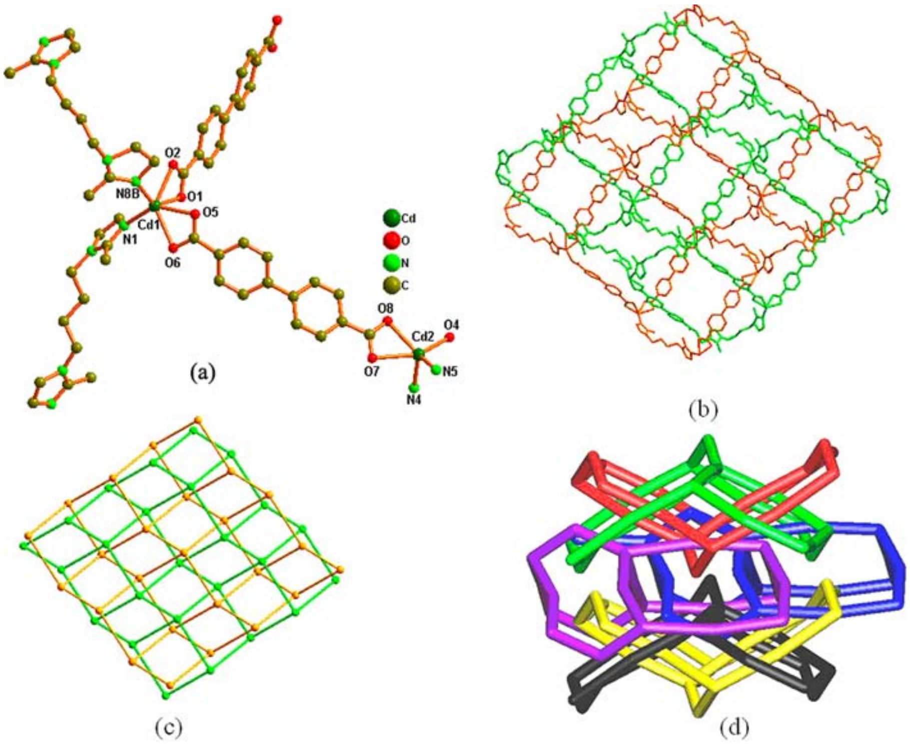


Figure 3. (a) Coordination environment of the Cd^{II} center in **3** (all H atoms are omitted for clarity). (b) 2D structure in **3**. (c) 2-fold interpenetrating **sql** net of **3**. (d) Parallel 2D → 3D polycatenation in **3**.

bpdc)$_2$(bib)$_2$] square with dimensions of 15.12 Å × 13.98 Å. Two small squares ([Cd$_4$(4,4′-bpdc)$_2$(bib)$_2$] and [Cd$_4$(bib)$_4$]) have dimensions of 15.48 Å × 11.01 Å and 13.98 Å × 11.01 Å, respectively. Unlike the common parallel interpenetration between (4,4) layers where each square is interpenetrated by another square, here the big squares are interpenetrated by the small squares and the small squares are not interpenetrated (Figure 3b).

More interesting is the unusual parallel 2D → 3D polycatenation that was observed in this complex structure.

The resulting 2-fold interpenetrating layers further catenate four adjacent layers (two above and two below; Figure 3d), extending into a 3D framework. Thus, each layer is actually catenated with five layers. To the best of our knowledge, such a polycatenation mode is unprecedented and is not known in other coordination frameworks.

TGA. To characterize the compounds more fully in terms of thermal stability, their thermal behaviors were studied (Figure 4).

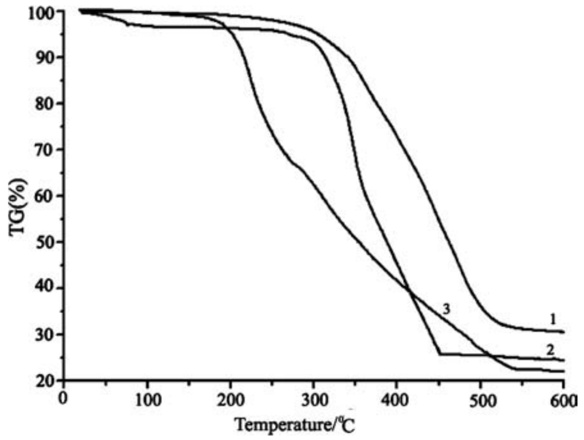


Figure 4. TGA curves of **1**−**3**.

No obviously weight loss was found for compounds **1** and **3** before decomposition of the frameworks occurred at about 300 and 200 °C, respectively. Compound **2** shows a weight loss of 3.28% in the temperature range of 40−130 °C, which is attributed to the release of the lattice and coordinated water molecules (calcd 3.36%), and decomposition of the backbone occurs at about 290 °C.

Luminescent Properties. The emission spectra of compounds **1**−**3** have been investigated in the solid state at room temperature. The emission peaks of the compounds are shown in Figure 5. The emission peaks at about 431 nm (λ_{ex} = 349 nm), 421 nm (λ_{ex} = 338 nm), and 414 nm (λ_{ex} = 353 nm) were observed for compounds **1**−**3**, respectively. Free 2,4′-bpdc, 3,4′-bpdc, 4,4′-bpdc, and bib ligands fluoresced in the solid state with their emission peaks at 354,[9a] 381,[10e] 396, and 465 nm,[14,15] respectively. In comparison to the free dicarboxylate ligands, the emission maxima of compounds **1**−**3** show obvious red shifts. The lifetimes for compounds **1**−**3** are 1.4, 2.1, and 2.7 ns, respectively. The nanosecond range of the lifetime in the solid state at room temperature shows that the emission is fluorescent in nature. Because each compound contains Cd^{II} ions, dicarboxylate ligands, and flexible bib ligands, it is truly difficult to assign its fluorescent emission as a ligand-to-metal charge-transfer or an intraligand charge-transfer transition.[16] Several factors might serve for the emissions, such as a change in the highest occupied and lowest unoccupied molecular orbital energy levels of deprotonated dicarboxylate anions and neutral ligands coordinating to metal centers, a charge-transfer transition between ligands and metal centers, and a joint contribution of the intraligand or charge-transfer transitions between the coordinated ligands and metal centers. However, because the Cd^{II} ions are difficult to oxidize or reduce, these bands should also be assigned to the intraligand fluorescent emissions that are tuned by the metal−ligand interactions and the deprotonated effect of the dicarboxyl ligands.[17]

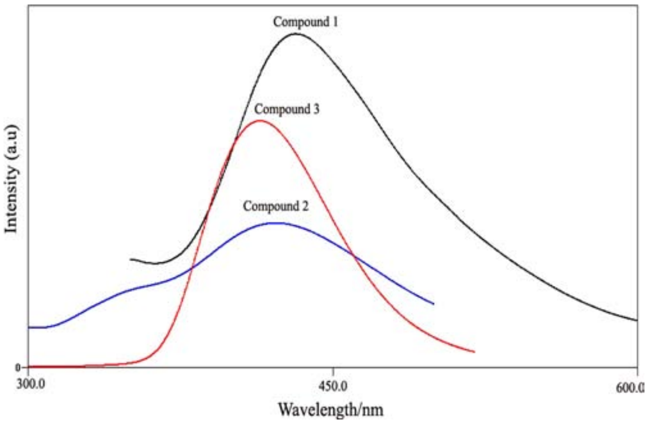


Figure 5. Solid-state emission spectra of **1**−**3** at room temperature.

CONCLUSION

Three new Cd^{II} CPs have been prepared and structurally characterized. Structural comparisons indicate that the positions of the carboxylate groups in the ligand backbone play an important role in governing the structural topologies of these compounds. The results reveal interesting 6-connected **mab** net, 4,6-connected **fsh** net, and unusual 2D → 3D parallel polycatenation of (4,4) layers. Moreover, all compounds display fluorescent properties.

ASSOCIATED CONTENT

Supporting Information

Xray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited with the Cambridge Crystallographic Data Center, as CCDC 819940, 860040, and 819941, and can be obtained free of charge at http://www.ccdc.cam.ac or Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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