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Syntheses, Structures, and Photoluminescence of a Novel Class of d^{10} Metal Complexes Constructed from Pyridine-3,4-dicarboxylic Acid with Different Coordination Architectures

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Two novel d^{10} metal coordination polymers $[Zn(PDB)]_n$ (**1**) and $[Cd_3(PDB)_2(OH)_2(H_2O)_2]_n$ (**2**) (H_2PDB = pyridine-3,4-dicarboxylic acid) have been synthesized under hydrothermal conditions and characterized by elemental analysis, IR, TG analysis, and single-crystal X-ray diffraction. Crystal data for **1**: $C_7H_3NO_4Zn$, orthorhombic $Pna2_1$, a = 8.423(17) Å, b = 6.574(13) Å, c = 12.899(3) Å, Z = 4. Crystal data for **2**: $C_{14}H_{12}N_2O_{12}Cd_3$, monoclinic $C2/c$, a = 20.130(4) Å, b = 6.692(13) Å, c = 13.081(3) Å, β = 102.78(3)°, Z = 4. Both compounds exhibit novel three-dimensional frameworks. Compound **1** not only possesses a one-dimensional rectangular channel but also contains infinite double-stranded helical chains. Compound **2** has two different types of channels, one being built up from pyridine rings and $\{CdO_5N\}$ and $\{CdO_6\}$ building units and the other being constructed from pyridine rings and $\{CdO_5N\}$ building units. Furthermore, both compounds show strong photoluminescence properties at room temperature.

The rational design and synthesis of novel coordination polymers is of current interest in the field of supramolecular chemistry and crystal engineering, not only because of their intriguing structural motifs but also because of their potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, and molecular sensing.[1-3] Consequently, a variety of coordination polymers with interesting compositions and topologies have been prepared through taking certain factors into account, such as the coordination nature of the metal ion and the shape, functionality, flexibility, and symmetry of organic ligand,[4] of which many are derived from multicarboxylate ligands because of their interesting structural characteristics.[5] In particular, symmetrical multicarboxylate ligands, such as 1,3,5-benzenetricarboxylate, 1,2,4,5-benzenetetracarboxylate, and 1,4-benzenedicarboxylate, have been widely used by Yaghi, Williams, Férey, Chen, Hong,

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and their co-workers in the construction of high-dimensional structures with large pores or undulated layers.[6-10] In contrast, pyridine-3,4-dicarboxylic acid,[11] as a member of the multicarboxylate ligands containing N-donors, is rarely used. However, its two unique structure features inspire our research interest. In the first place, because of the steric hindrance between the two adjacent carboxyl groups, the conjugation interaction between the pyridine group and carboxyl group is markedly weakened; therefore, H_2PDB is likely to form high-dimensional frameworks with metal atoms.[12] In the second place, the steric orientation of the carboxyl groups is considerably flexible, which will cause the carboxyl groups to connect metal ions in different directions.[13] Such "skewing" of coordination sites in the carboxyl groups should favor the formation of a helical structure.[14]

On the other hand, polynuclear d^{10} metal (Cu^{I}, Ag^{I}, Au^{I}, Zn^{II}, or Cd^{II}) complexes have attracted extensive interest in recent years in that they not only exhibit appealing structures but also possess photoluminescent properties.[15] A series of d^{10} metal organic frameworks have been described recently.[5c,f,9b] However, to the best of our knowledge, there has been only one reported polymer constructed by a d^{10} metal and PDB ligand hitherto.[16]

On the basis of the aforementioned points, our aim is to synthesize novel high-dimensional coordination polymers through combining respective merits of pyridine-3,4-dicarboxylic acid and a d^{10} metal. In this paper, we report two novel d^{10} metal complexes $[Zn(PDB)]_n$ (**1**) and $[Cd_3(PDB)_2(OH)_2(H_2O)_2]_n$ (**2**). Compounds **1** and **2** both exhibit novel three-dimensional frameworks. Interestingly, the three-dimensional architecture of compound **1** not only possesses one-dimensional rectangular channels but also contains infinite double-stranded helical chains. Such structural features, to the best of our knowledge, have never been described before in the system of metal−carboxylate coordination polymers. And the three-dimensional structure of compound **2** has two different types of channels (9.6 × 4.0 Å and 5.7 × 3.6 Å), which is still rare so far.[17] Furthermore, both of them show intense photoluminescent properties at room temperature.

Experimental Section

General Methods. All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The contents of Zn and Cd were determined by a Leaman inductively coupled plasma (ICP) spectrameter. FTIR spectra were recorded in the range 400−4000 cm^{-1} on an Alpha Centaurt FTIR spectrophotometer using a KBr pellet. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Excitation and emission spectra were obtained on a Spex FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. Luminescence lifetimes were measured with a Spex 1934D phosphorimeter using a 7 W pulsed xenon lamp as the excitation source. All measurements were performed at room temperature.

Hydrothermal Syntheses. $[Zn(PDB)]_n$ (1). Compound **1** was synthesized from the reaction mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.5 mmol), H_2PDB (0.6 mmol), triethylamine (1.2 mmol), and water (10 mL) in a 23 mL Teflon reactor, under autogenous pressure at 160 °C for 5 days, and then cooled to room temperature at a rate of 10 °C/h. Light-yellow crystals of compound **1** were obtained (yield: 87% based on Zn). Anal. Found: C, 36.28; H, 1.26; N, 5.90; Zn, 27.95. Calcd: C, 36.45; H, 1.30; N, 6.07; Zn, 28.2. IR spectrum (cm^{-1}): 1653 (w), 1549 (s), 1493 (w), 1450 (s), 1418 (w), 1397 (s), 1286 (w), 1205 (m), 1172 (m), 1128 (m), 1074 (s), 946 (w), 890 (m), 856 (s), 818 (m), 775 (m), 734 (s), 687 (s), 611 (s), 575 (m), 479 (s), 422 (w).

$[Cd_3(PDB)_2(OH)_2(H_2O)_2]_n$ (2). Compound **2** was synthesized from the reaction mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.5 mmol), H_2PDB (0.6 mmol), triethylamine (1.5 mmol), and water (10 mL) in a 23 mL Teflon reactor, under autogenous pressure at 160 °C for 5 days, and then cooled to room temperature at a rate of 10 °C/h. Light-yellow crystals of compound **2** were obtained (yield: 36% based on Cd). Anal. Found: C, 22.64; H, 1.60; N, 3.72; Cd, 45.81. Calcd: C, 22.78; H, 1.63; N, 3.80; Cd, 45.72. IR spectrum (cm^{-1}): 1610 (s), 1593 (s), 1551 (w), 1483 (w), 1431 (s), 1403 (w), 1390 (w), 1287 (m), 1194 (w), 1164 (m), 1061 (s), 858 (s), 832 (m), 782 (w), 720 (s), 658 (s), 590 (m), 520 (w), 451 (m).

X-ray Crystallography. Single crystals of compounds **1** and **2** with dimensions 0.342 × 0.276 × 0.159 and 0.334 × 0.242 × 0.233 mm^3, respectively, were glued on a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα monochromated radiation ($\lambda = 0.710\ 73$ Å) at 293 K. An empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software

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Table 1. Crystal Data and Structure Refinement of **1** and **2**

molecular formula	$C_7H_3NO_4Zn$	$C_{14}H_{12}Cd_3N_2O_{12}$
M_r	230.47	737.46
T/K	293(2)	293(2)
λ/Å	0.710 73	0.710 73
cryst system	orthorhombic	monoclinic
space group	$Pna2_1$	$C2/c$
a/Å	8.4225(17)	20.130(4)
b/Å	6.5742(13)	6.6921(13)
c/Å	12.899(3)	13.081(3)
β/deg		102.78(3)
V/Å^3	714.2(2)	1718.5(6)
Z	4	4
F(000)	456	1400
reflcns collcd/ unique	1513/1513	3695/1961
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0263, wR2 = 0.0457	R1 = 0.0241, wR2 = 0.0666
R indices (all data)^a	R1 = 0.0308, wR2 = 0.0465	R1 = 0.0259, wR2 = 0.0681

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

Compound **1**			
Zn(1)−O(5)$^{\#1}$	1.968(2)	Zn(1)−O(1)$^{\#3}$	2.057(2)
Zn(1)−O(2)	1.9934(19)	Zn(1)−O(6)	2.209(2)
Zn(1)−N(1)$^{\#2}$	2.029(3)		
O(5)$^{\#1}$−Zn(1)−O(1)$^{\#3}$	100.19(11)	O(2)−Zn(1)−O(6)	84.29(9)
O(2)−Zn(1)−O(1)$^{\#3}$	83.86(8)	O(1)$^{\#3}$−Zn(1)−O(6)	168.06(8)
O(5)$^{\#1}$−Zn(1)−O(6)	89.34(11)	O(5)$^{\#1}$−Zn(1)−O(2)	135.41(17)
Compound **2**			
Cd(1)−O(1)	2.2295(18)	Cd(2)−O(1)$^{\#4}$	2.2362(19)
Cd(1)−O(1)$^{\#1}$	2.274(2)	Cd(2)−O(1)	2.2362(19)
Cd(1)−O(6)$^{\#2}$	2.297(2)	Cd(2)−O(4)$^{\#5}$	2.327(2)
Cd(1)−N(1)	2.319(2)	Cd(2)−O(4)$^{\#6}$	2.327(2)
Cd(1)−O(2)	2.415(2)	Cd(2)−O(5)$^{\#7}$	2.3846(19)
Cd(1)−O(3)$^{\#3}$	2.546(2)	Cd(2)−O(5)$^{\#8}$	2.3846(19)
Cd(1)···Cd(1)$^{\#1}$	3.3583(9)		
O(1)−Cd(1)−O(1)$^{\#1}$	83.58(7)	O(1)−Cd(1)−N(1)	102.20(7)
O(1)−Cd(1)−O(6)$^{\#2}$	162.37(8)	O(1)$^{\#1}$−Cd(1)−N(1)	153.82(7)
O(1)$^{\#1}$−Cd(1)−O(6)$^{\#2}$	85.78(7)	O(1)−Cd(1)−O(2)	104.84(8)
O(1)$^{\#1}$−Cd(1)−O(2)	78.40(8)	N(1)−Cd(1)−O(2)	123.35(8)
O(6)$^{\#2}$−Cd(1)−O(2)	86.66(9)	O(1)−Cd(1)−O(3)$^{\#3}$	77.28(7)
O(2)−Cd(1)−O(3)$^{\#3}$	155.80(7)	N(1)−Cd(1)−O(3)$^{\#3}$	78.55(8)
O(1)−Cd(2)−O(4)$^{\#6}$	77.36(7)	O(1)$^{\#4}$−Cd(2)−O(4)$^{\#5}$	77.36(7)
O(1)−Cd(2)−O(5)$^{\#7}$	86.30(7)	O(1)−Cd(2)−O(4)$^{\#5}$	104.88(7)
O(1)−Cd(2)−O(5)$^{\#8}$	90.88(7)	O(1)$^{\#4}$−Cd(2)−O(1)	176.19(9)

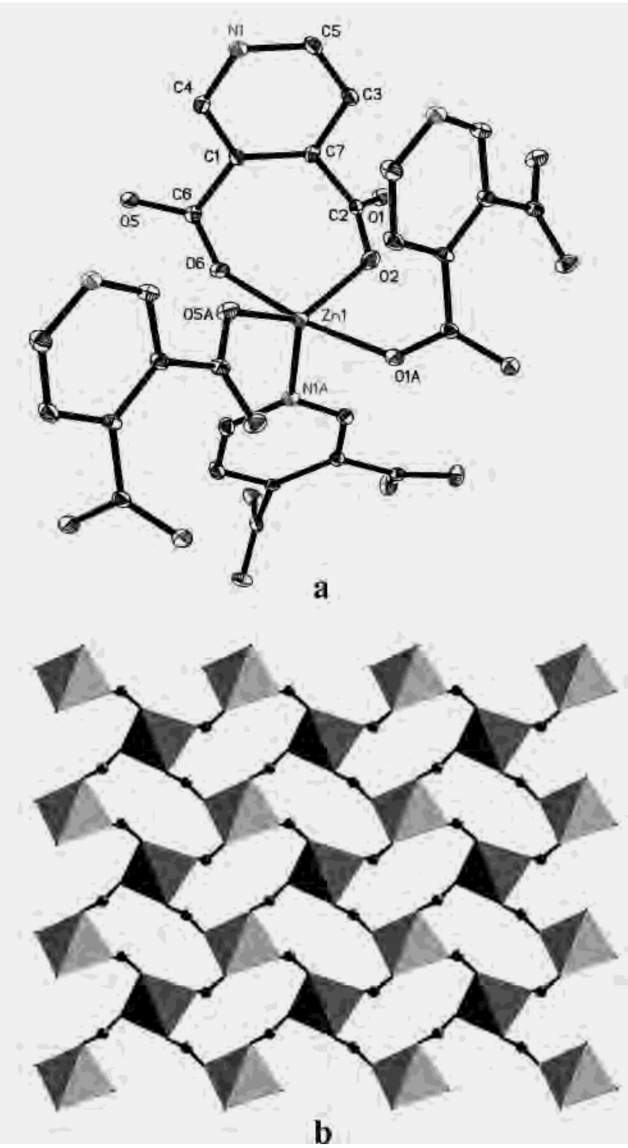

Figure 1. (a) Perspective view of the Zn(II) coordination environment including the asymmetric unit in **1**. (b) View of the two-dimensional Zn−O−C layer parallel to the *ac* plane showing the $\{Zn_4O_8C_4\}$ 16-numbered rings. (Pyridine rings are omitted for clarity.)

package.[18] Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. The crystal data and structure refinement of compounds **1** and **2** are summarized in Table 1. Selected bond lengths and angles of compounds **1** and **2** are listed in Table 2.

Results and Discussion

Crystal Structures. [Zn(PDB)]$_n$ (1). A single-crystal X-ray structural analysis shows that the structure of compound **1** is a unique three-dimensional framework in which the asymmetric unit contains 1 Zn atom and 1 PDB molecule. The zinc(II) atom exhibits a distorted hexahedral configuration[6c] coordinated by one nitrogen atom (Zn(1)−N(1A) 2.029(3) Å) of a PDB group and four oxygen atoms (Zn(1)−O(1A) 2.057(2) Å, Zn(1)−O(2) 1.993(19) Å, Zn(1)−O(5A) 1.968(2) Å, Zn(1)−O(6) 2.209(2) Å) of the carboxyl groups from three different PDB ligands, as shown in Figure 1a. The O−Zn−O bond angles range from 83.86(8) to 168.06 (8)°, and the O−Zn−N bond angles range from 87.36(13) to 118.92(11)° (see Table 2). Figure 1b shows that in the *ab* plane all the zinc atoms are connected with each other by carboxyl groups of PDB ligands, thus forming novel $\{Zn_4O_8C_4\}$ 16-membered rings. All the rings are further linked to form a two-dimensional Zn−O−C layer (Figure 1b). Meanwhile, in each $\{Zn_4O_8C_4\}$ ring there is a PDB ligand normal to the direction of the layer attaching to the ring, which connects three zinc atoms located in the ring via its two carboxyl groups in both chelate and bimonodentate coordination modes and links the fourth zinc atom situated in the adjacent layer via its N atom (Figure S1; Supporting Information). That is to say, each PDB ligand is connected with four zinc atoms (Chart 1a). On the basis of such a coordination mode, an interesting three-dimensional covalently bonded framework is formed. It is noteworthy that there exists a one-dimensional rectangular channel with

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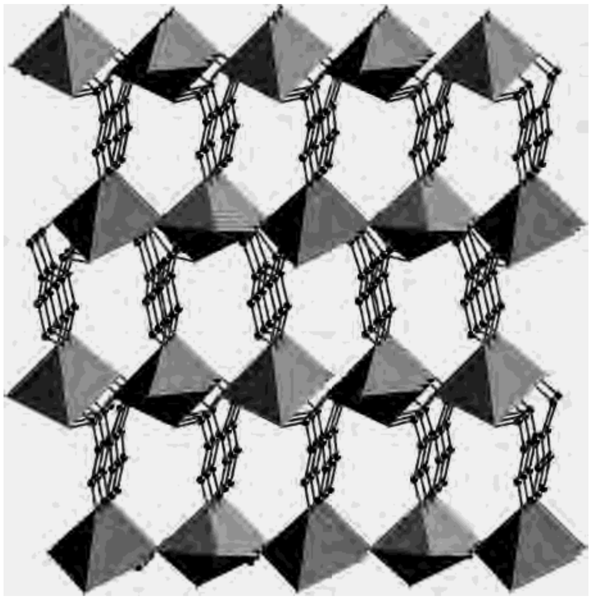
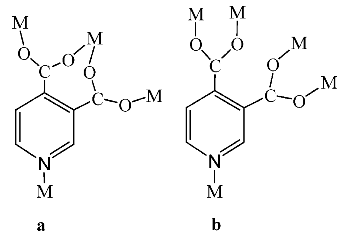


Figure 2. Molecular packing of **1** viewed along the *b* axis, showing the one-dimensional rectangular channels.

Chart 1. Coordination Modes of the PDB Ligand in Compounds (a) **1** and (b) **2**



pores open of 7.1 × 4.9 Å built up from pyridine ring and Zn−O−C layer building units running along the *b* axis (Figure 2).

The most striking feature of compound **1** is the interesting arrangement of PDB molecules and unusual coordination of zinc atoms forming a unique helical structure. As described in Figure 3, the PDB ligands bridge each pair of adjacent zinc atoms into a single-stranded helical chain running along a crystallographic 2_1 axis in the *c* direction with a long pitch of 12.90 Å. In addition, unlike the most double-helical complexes,[19] the adjacent helical chains in compound **1**, one exhibiting left-handedness and the other right-handedness, are not entangled together but bridged by common carboxyl oxygen atoms which are alternatively offered by two helical chains to generate a double-stranded helical chain (Figure 3b). To illustrate this clearly, the left- and right-handed helical chains are represented respectively in Figure 3a,c. These bridged double-stranded helical chains are further extended into the three-dimensional architecture in compound **1** (Figure S2). Because left-handed and right-handed helical chains coexist in the crystal structure, the whole crystal is mesomeric and does not exhibit chirality. As discussed above, the occurrence of helical structure in compound **1** may be attributable to the fact that the steric orientation of the carboxyl groups is remarkably flexible. As shown in Figure 2b, 3,4-sited carboxyl groups of PDB ligands in each single-stranded Zn−PDB chain chelate zinc atoms in different directions, sequentially causing a twist of the chain and finally resulting in the formation of the helical structure. To our knowledge, compound **1** constitutes the first example of a three-dimensional covalently bonded framework, with participation by a multicarboxylate ligand containing an N-donor, having both 1D rectangular channel and double-stranded helical structure.

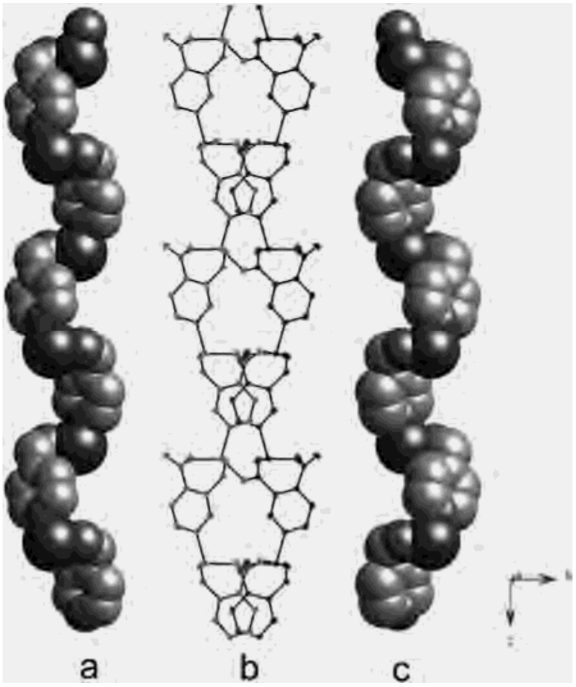


Figure 3. Space-filling plots of the (a) left-handed chain and (c) right-handed chain and the (b) ball-and-stick plot of the double helix bridged by common oxygen atoms in **1**.

$[\mathrm{Cd}_3(\mathrm{PDB})_2(\mathrm{OH})_2(\mathrm{H}_2\mathrm{O})_2]_n$ (2). X-ray crystallographic analysis reveals that compound **2** exhibits an interesting 3-D network. The fundamental unit is shown in Figure 4. There are two crystallographically unique Cd centers in the asymmetric unit, both displaying distorted octahedral coordination geometry. The Cd(1) center is coordinated by two oxygen atoms (Cd(1)−O(3C) 2.546(2) Å, Cd(1)−O(6B) 2.297(2) Å) of two different carboxylate groups, one nitrogen atom of a pyridine ring with Cd(1)−N(1) bond distance of 2.319 (2) Å, one terminal oxygen atom (Cd(1)−O(2) 2.415(2) Å), and two μ_3-oxygen atoms (Cd(1)−O(1) 2.230(18) Å, Cd(1)−O(1A) 2.274(2) Å). The terminal oxygen atom O(2) and the μ_3-oxygen atom O(1) have bond valence sums[20] of 0.251 and 1.190, respectively, suggesting that O(2) is a

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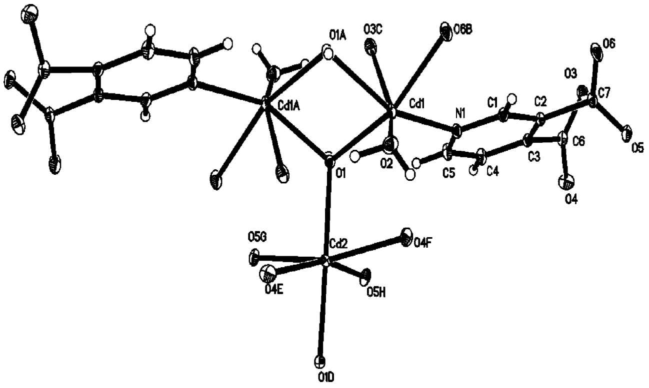
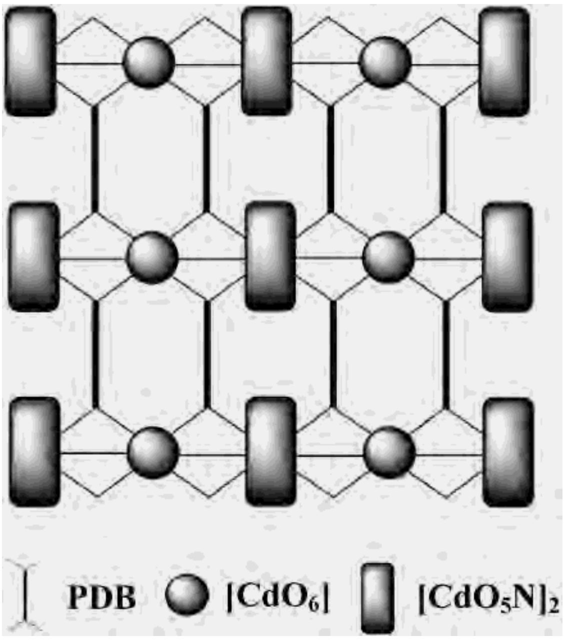


Figure 4. Perspective view of the coordination environment of the Cd(II) atoms in **2**.

Chart 2. Schematic Illustration of the Structure of the Two-Dimensional Layer in **2**



coordinated water molecule, while O(1) is a hydroxyl group. This result is consistent with the charge balance consideration. The O−Cd(1)−O bond angles range from 77.28(7) to 162.37(8)°, and O−Cd(1)−N bond angles range from 81.63(8) to 153.82(7)°. The Cd(2) center is defined by four oxygen atoms (Cd(2)−O(5G) 2.385(19) Å, Cd(2)−O(4F) 2.327(2) Å, Cd(2)−O(4E) 2.327(2) Å, Cd(2)−O(5H) 2.385(19) Å) of four different carboxylate groups and two μ_3-O atoms (Cd(2)−O(1) 2.236(19) Å, Cd(2)−O(1D) 2.236(19) Å). The O−Cd(2)−O band angles range from 77.36(7) to 176.19(9)° (shown in Table 2). The distance of Cd1···Cd1A bridged by two μ_3-O atoms is 3.358(9) Å. Unlike those in compound **1**, the two carboxyl groups of PDB ligand in compound **2** exhibit another kind of coordination mode with Cd atoms, as shown in Chart 1b. That is, all the carboxyl groups adopt a monodentate bridging mode to connect with four Cd atoms. The two $[CdO_5N]$ octahedra are first connected together via μ_3-O atoms in an edge-sharing mode to form a dinuclear Cd cluster, and then the dinuclear cluster is further connected by a $[CdO_6]$ octahedron in a corner-sharing fashion to generate a distinctive mono- and dinuclear mixed one-dimensional Cd−O−Cd chain along the *c* axis; the adjacent chains are linked via 3,4-sited carboxyl groups of PDB ligands in a bisbidentate fashion, thus forming a two-dimensional layer (Chart 2). Interestingly, each layer displays a beautiful sinusoidal-like wave with an amplitude of about 6.22 Å and a period of about 6.62 Å when viewed along the *b* axis. The layers are cross-linked by PDB ligands via their N and carboxyl groups, leading to the formation of a novel three-dimensional extended network (Figure 5a).

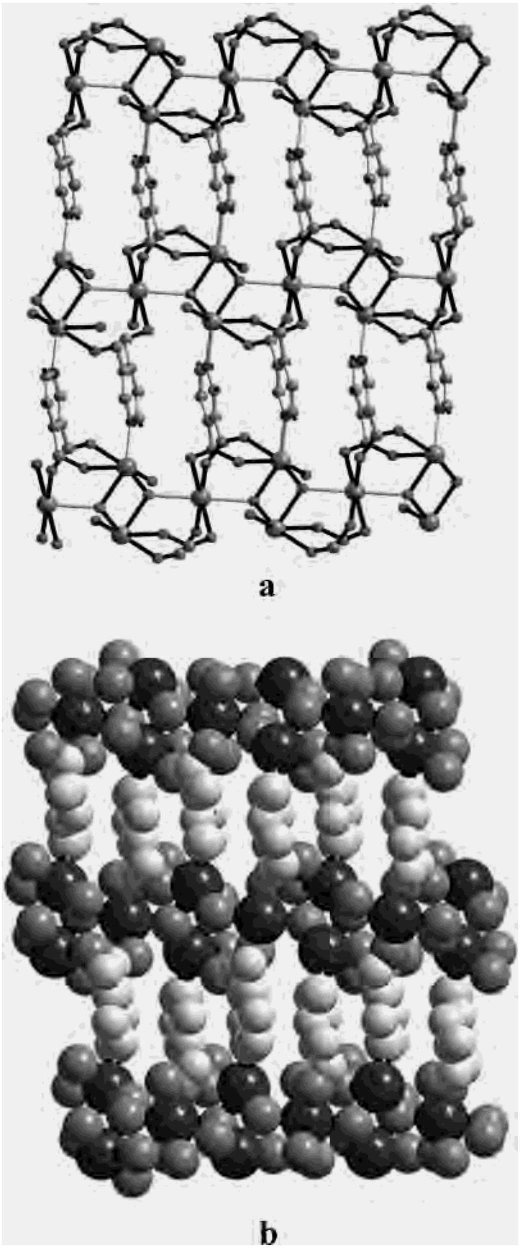


Figure 5. (a) Three-dimensional network of **2** viewed along *b* axis, showing the pseudosinusoidal wave layer. (b) Space-filling model of the crystal structure of **2**, highlighting the two types of channels.

The profound influences on the final structure of metal coordination geometries and coordination modes of organic ligand are revealed in the comparison of compound **2** with the related polymer $\{[Cd(pydc)(bpp)]\cdot 0.5H_2O\}_n$ (**2′**). In **2′**, pyridine-3,4-dicarboxylic acid acts as a tritopic subunit, each carboxyl group chelating a Cd^{II} ion, and as far as each Cd^{II} metal center is concerned, it has a slightly distorted $\{CdN_3O_4\}$ pentagonal bipyramid coordination sphere; thus, the Cd^{II} center provides the pentaconnecting trigonal bipyridine nodes and H_2PDB and 1,3-bis(4-pyridyl)propane act as triconnectors and diconnectors, respectively. While in **2**, H_2PDB acts as a pentatopic subunit, each carboxyl group adopting bisbidentate fashion; in addition, what is different from **2′** is that there are two kinds of coordination environmental Cd^{II} centers in **2**, i.e. $\{CdO_5N\}$ and $\{CdO_6\}$ octahedral. The above differences cause the distinctness of linking fashion of these subunits and finally result in the formation of two different three-dimensional frameworks.

It is also noteworthy that the arrangement of PDB groups between the layers in **2** is different from that of **1**. That is, all the PDB ligands adopt an AAAA arrangement in **1**, while in **2** they adopt an ABAB arrangement. The most interesting feature of **2** is that it possesses two different types of channels, which run parallel to the stacking direction, *b* (Figure 5b). One is constructed from pyridine rings and $\{CdO_5N\}$ building units with the size of ca. 5.7 × 3.6 Å, and the other is built up from pyridine rings and $\{CdO_5N\}$ and $\{CdO_6\}$ building units with the size of ca. 9.6 × 4.0 Å. Meanwhile, all the terminal water molecules protrude into the larger channel.

IR Spectra. The IR spectrum of compound **1** shows characteristic bands of carboxyl groups at 1549 cm^{-1} for the antisymmetric stretching and at 1440 and 1397 cm^{-1} for symmetric stretching. The separations (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ indicate the presence of chelating (99 cm^{-1}) and monodentate (152 cm^{-1}) coordination modes in compound **1**. The IR spectrum of compound **2** exhibits characteristic bands of carboxyl groups at 1610 and 1593 cm^{-1} for the antisymmetric stretching and at 1431 cm^{-1} for symmetric stretching. The separations (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ bands show that the carboxylate groups coordinate to the metal atoms in a bridging fashion.[21] The absence of the characteristic bands at around 1700 cm^{-1} in compounds **1** and **2** attributed to the protonated carboxylic group indicates that the complete deprotonation of PDB ligand upon reaction with Zn and Cd ions.[22] The IR spectra indicate that the carboxyl groups of PDB function in different coordination modes, consistent with the crystal structures of **1** and **2**.

Photoluminescence Properties. The emission spectra of compounds **1** and **2** in solid state at room temperature are depicted in Figure 6. It can be observed that intense emissions occur at 436 nm (Figure 6a, $\lambda_{ex} = 375$ nm) for **1** and 452 nm (Figure 6b, $\lambda_{ex} = 390$ nm) for **2**. To understand the nature of the two emission bands, we analyzed the photoluminescence properties of the H_2PDB ligand and found that the strongest emission peak for H_2PDB is at about 370 nm, which is attributable to the $\pi^* \rightarrow n$ transition.[23] Therefore, the two emissions may not be related to the $\pi^* \rightarrow n$ transition of the ligand. In addition, a similar emission band at about 430 nm has been observed previously for other zinc−organic polymers with either photoluminescent or nonphotoluminescent ligands, such as $[Zn(mpa)(phen)]_n$,[24] while the emission band at about 450 nm has also been observed in other polynuclear d^{10} metal polymers, such as $[Zn_4(OH)_2(fa)_3(4,4'\text{-bpy})_2]$[17a] and $Cd_3tma_2\cdot dabco\cdot 2H_2O$.[25] Thus according to the above literature, the two emission bands might be attributable to the ligand-to-metal charge transfer (LMCT). A bathochromic shift of emission occurs in **2**, compared with **1**, which is probably due to the differences of metal ions and coordination environment around them, because photoluminescence behavior is closely associated with the metalions and the ligands coordinated around them.[26] It should be pointed out that the lifetime of **2** is longer than that of **1** (Figure S4). The fact may be ascribed to the presence of the Cd_3O core, as the μ_3-oxo ligand may tighten the whole

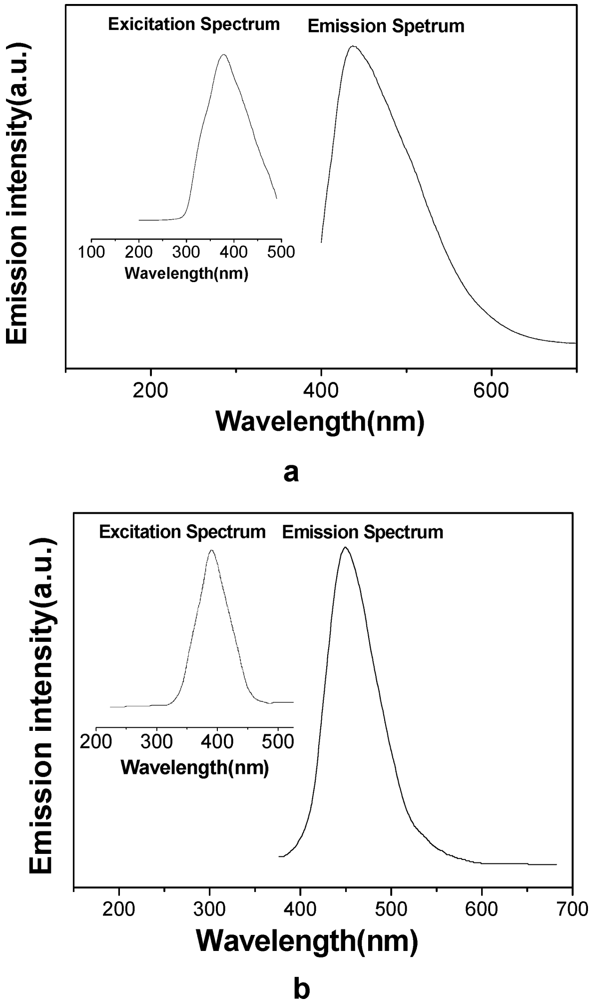


Figure 6. (a) Solid-state emission spectra of complexes at room temperature: (a) **1**; (b) **2**.

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skeleton, thus resulting in much weaker vibrations.[27] These observations indicate that compounds **1** and **2** maybe excellent candidates of blue-light-emitting diode devices, since these condensed materials are highly thermally stable and insoluble in common polar and nonpolar solvents.[17a]

Conclusion

In this paper, we successfully combined the merits of d^{10} metal and pyridine-3,4-dicarboxylic acid and synthesized two novel three-dimensional coordination polymers $[Zn(PDB)]_n$ (**1**) and $[Cd_3(PDB)_2(OH)_2(H_2O)_2]_n$ (**2**) with different coordination architectures. In a comparison of the structures of **1**, **2**, and related compounds, it has been found that the steric geometry of the ligand and coordination geometry of the central metal ion may have a very significant effect on the formation of the resulting structure. The successful preparation of compounds **1** and **2** provides a valuable approach for the construction of many other coordination polymers containing a helix or channel structure. Furthermore, the strong photoluminescence properties of compounds **1** and **2** may make them excellent candidates for potential photoactive materials.

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Supporting Information Available: Additional figures, TGA curves, crystallographic tables, and X-ray crystallographic information files (CIF) for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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