



Tuning structural topologies of five photoluminescent Cd(II) coordination polymers through modifying the substitute group of organic ligand

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ABSTRACT

Five new Cd(II) coordination polymers based on mixed 5-position substituted 1,3-benzenedicarboxylate ligands ($R = -NO_2/-OH/-CH_3$) and 1,4-bis(imidazol-1-yl)benzene (L_1) or 1,4-bis(1-imidazol-yl)-2,5-dimethyl benzene (L_2), namely $[Cd(5-NO_2-ip)(L_1) \cdot H_2O]$ (1), $[Cd(5-OH-ip)(L_1)]_n$ (2), $[Cd(5-NO_2-ip)(L_1)_{0.5}(H_2O)_2]_n$ (3), $\{[Cd(5-NO_2-ip)(L_2)_{0.5}(H_2O)] \cdot H_2O\}$ (4), $[Cd(5-CH_3-ip)(L_2)(H_2O)_2]_n$ (5), have been synthesized hydrothermally and structurally characterized. With different substituted groups in the organic ligands, five compounds exhibit five distinct framework structures. By changing the pH value, compound 1 with 2-fold interpenetrating (4,4)-layer structure and compound 3 with three-dimensional diamond-type framework are obtained, respectively, from the assembly of $Cd(NO_3)_2 \cdot 4H_2O$, 5- NO_2 -ip and L_1 ligand. The replacement of 5- NO_2 -ip with 5-OH-ip leads to a compound 2 which features a doubly pillared layered structure with pcu topology. Compounds 4 and 5 are constructed from L_2 ligand with 5- NO_2 -ip or 5- CH_3 -ip, respectively. Compound 4 has non-interpenetrating (4,4) layer, while compound 5 shows unusual 2D- > 3D polycatenation of bilayers. The results reveal a new approach toward tuning structural topologies of coordination polymers through modifying the substitute groups in organic ligands. Furthermore, the photoluminescent properties of compounds 1–5 have been studied in the solid state at room temperature.

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1. Introduction

Recently, the self-assembly of coordination polymers (CPs) have been given considerable attention not only for their potential applications in gas storage, luminescence, magnetism, catalysis and separation [1–10], but also for their structural diversities and intriguing topological net [11–14]. It has been recognized that the construction of CPs is influenced by many structural and experimental factors, such as the nature of the organic ligands, the metal centers, and the reaction conditions (pH value, template and solvents) [15–18]. The organic carboxylate and imidazole-containing ligands have been proven to be good candidates for the construction of CPs [19–25]. Among mentioned above, we selected the 5-position substituted 1,3-benzenedicarboxylate ligands ($R = -NO_2/-OH/-CH_3$) as organic anions, 1,4-bis(imidazol-1-yl) benzene and 1,4-bis(1-imidazol-yl)-2,5-dimethyl benzene as neutral ligands based on the following considerations: (I) The different electron-donating ($-OH/-CH_3$)/accepting ($-NO_2$) noncoordinating groups in 5-position groups might generate compounds with

different structures and properties [26–29]; (II) the rigid bis(imidazole) shows the good ability to coordinated to the metal center and can adopt two type coordination modes: *cis*-configuration and *trans*-configuration. Moreover, the rigid bis(imidazole) ligands are good framework pillars to sustain the structures [30–33]. Five new Cd(II) coordination polymers, $[Cd(5-NO_2-ip)(L_1) \cdot H_2O]$ (1), $[Cd(5-OH-ip)(L_1)]_n$ (2), $[Cd(5-NO_2-ip)(L_1)_{0.5}(H_2O)_2]_n$ (3), $\{[Cd(5-NO_2-ip)(L_2)_{0.5}(H_2O)] \cdot H_2O\}$ (4), $[Cd(5-CH_3-ip)(L_2)(H_2O)_2]_n$ (5), have been synthesized hydrothermally and structurally characterized. It is interesting that five compounds exhibit five distinct framework structures. The results reveal a new approach toward tuning structural topologies of coordination polymers through modifying the substitute groups in organic ligands. The luminescent properties of these compounds have been studied in the solid state at room temperature.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents employed were commercially available and used without further purification. Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic

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elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as a dry KBr pellet in the 400–4000 cm^{-1} range. Solid-state fluorescence spectra were recorded on a Hitachi F-4600 equipped with a xenon lamp and a quartz carrier at room temperature. The powder X-ray powder diffraction (XRPD) measurements were performed on a Bruker D8 diffractometer operated at 40 kV and 40 mA using Cu-K α radiation ($\lambda=0.15418$ nm).

2.2. Syntheses of complexes

[Cd(5-NO₂-ip)(L₁)·H₂O] (1): The mixtures of Cd(NO₃)₂·4 H₂O (0.5 mmol, 0.145 g), 5-NO₂-ip (0.5 mmol, 0.106 g), L₁ (0.5 mmol, 0.105 g) and 12 mL of water were placed in a 25 mL Teflon reactor, then the pH value was adjusted to 6.8 by addition of NaOH solution (1 mmol/4 mL), the mixtures were heated to 160 °C for 4 days, and then cooled to room-temperature. The colorless crystals were obtained in pure phase, washed with water and ethanol, and dried at room temperature (Yield: 53% based on Cd). Anal. Calc. for C₂₀H₁₇CdN₅O₈: C, 42.30; N, 12.33; H, 3.02. Found: C, 41.87; N, 12.26; H, 3.03. IR/cm⁻¹ (KBr): 3100 br, 1608 s, 1527 s, 1441 s, 1372 m, 1258 m, 1112 m, 1062 m, 961 m, 843 m, 787 m.

[Cd(5-OH-ip)(L₁)]_n (2): The mixtures of Cd(NO₃)₂·4 H₂O (0.5 mmol, 0.145 g), 5-OH-ip (0.5 mmol, 0.106 g), L₁ (0.5 mmol, 0.105 g) and 12 mL of water were placed in a 25 mL Teflon reactor. After pH was adjusted 5.1, the mixtures were heated to 160 °C for 4 days, and then cooled to room-temperature. The colorless crystals were obtained in pure phase, washed with water and ethanol, and dried at room temperature (Yield: 57% based on Cd). Anal. Calc. for C₂₀H₁₄CdN₄O₅: C, 47.78; H, 2.81; N, 11.14. Found: C, 47.69; N, 11.15; H, 2.80. IR/cm⁻¹ (KBr): 0.1559 s, 1383 m, 1273 m, 1126 m, 1061 m, 991 m, 832 m, 787 m, 649 m.

[Cd(5-NO₂-ip)(L₁)_{0.5}(H₂O)₂]_n (3): The compound 3 was obtained by the similar method as described for 2 by using of 5-NO₂-ip (0.5 mmol, 0.106 g) in place of 5-OH-ip (pH=4.8). The colorless crystals were obtained in pure phase, washed with water and ethanol, and dried at room temperature (Yield: 47% based on Cd). Anal. Calc. for C₁₄H₁₆CdN₃O₈: C, 36.34; H, 2.61; N, 9.08. Found: C, 36.41; H, 2.60; N, 9.06. IR/cm⁻¹ (KBr): 3138 br, 1612 s, 1530 s, 1446 m, 1348 m, 1256 m, 1063 m, 930 m, 842 m, 789 m, 649 m.

{[Cd(5-NO₂-ip)(L₂)_{0.5}(H₂O)]·H₂O} (4): The compound 4 was obtained by the similar method as described for 2 by using of 5-NO₂-ip (0.5 mmol, 0.106 g) and L₂ (0.5 mmol, 0.119 g) in place of 5-OH-ip and L₁, respectively (pH=4.5). The colorless crystals were obtained in pure phase, washed with water and ethanol, and dried at room temperature (Yield: 47% based on Cd). Anal. Calc. for C₁₅H₁₄CdN₃O₈: C, 37.79; H, 2.96; N, 8.82. Found: C, 37.70; H, 2.94; N, 8.86. IR/cm⁻¹ (KBr): 3438 br, 1621 s, 1533 s, 1430 m, 1310 m, 1230 m, 1153 m, 1023 m, 950 m, 836 m, 727 m, 660 m.

[Cd(5-CH₃-ip)(L₂)(H₂O)₂]_n (5): The mixtures of Cd(NO₃)₂·4 H₂O (0.5 mmol, 0.145 g), 5-CH₃-ip (0.5 mmol, 0.09 g), L₂ (0.5 mmol, 0.119 g) and 12 mL of water were placed in a 25 mL Teflon reactor. After pH was adjusted 6.8, the mixtures were heated to 160 °C for 4 days, and then cooled to room-temperature. The colorless crystals were obtained in pure phase, washed with water and ethanol, and dried at room temperature (Yield: 53% based on Cd). Anal. Calc. for C₃₀H₃₁CdN₆O₆: C, 52.68; H, 4.57; N, 12.28. Found: C, 52.73; N, 12.29; H, 4.58. IR/cm⁻¹ (KBr): 3268 br, 1625 m, 1533 m, 1428 s, 1375 s, 1110 m, 1060 m, 927 m, 832 m, 773 m, 654 m.

2.3. X-ray crystallography

Single crystal X-ray diffraction analyses of compounds 1–5 were carried out on a Bruker SMART APEX/CCD diffractometer

equipped with a graphite monochromated Mo-K α radiation ($\lambda=0.71073$ Å) by using a ω -scan mode. Empirical absorption correction was applied using the SADABS programs [34]. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97 [35]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table 1. Selected bond and angle parameters are listed in Table S1.

3. Results and discussion

3.1. Description of crystal structures

3.1.1. [Cd(5-NO₂-ip)(L₁)·H₂O]_n (1)

Compound 1 crystallizes in the triclinic space group $P\bar{1}$. As shown in Fig. 1a, each cadmium atom is coordinated by four oxygen atoms (Cd(1)–O, 2.257(2)–2.572(2) Å) and two nitrogen (Cd(1)–N(1)=2.366(2) and Cd(1)–N(3)=2.271(2) Å), exhibiting a distorted octahedral geometry. Three carboxylate oxygen atoms and one nitrogen atom construct equatorial plane and the axis positions are occupied by one water molecule and one nitrogen atoms. The structure of compound 1 is comprised of (4, 4) undulated layers. The size of the windows in the layer can be estimated as 10.173×14.031 Å from the distance of the Cd atoms. The undulated layers are associated in pairs to give (2D→2D) 2-fold interpenetrated sheets. The intermolecular interactions play a significant role in the packing of the layers. Firstly, the interpenetrated sheets are interacted via C–H... π bonds (C–H... $\pi=2.79$ Å, the angle of 170°) and the dihedral angle of two phenyl rings is 86.84° . Secondly, there are π ... π interactions between the phenyl rings of 5-NO₂-ip ligands with a centroid-to-centroid distance of $3.591(3)$ Å, and the interplane distance of 3.380 Å as well as the dihedral angles of 0° . Thirdly, the π ... π interactions also exist between the phenyl rings of 5-NO₂-ip and L₁ ligands with a centroid-to-centroid distance of $3.836(3)$ Å, and the shortest interplane distance of 3.558 Å as well as the dihedral angles of 7.775° . Such layer packing results in a 3D supramolecular structure. It is no doubted that the supramolecular interactions contribute to the stability of the structure.

3.1.2. [Cd(5-OH-ip)(L₁)]_n (2)

The replacement of 5-NO₂-ip with 5-OH-ip leads to a compound 2 which features a doubly pillared layered structure with pcu topology. Single-crystal X-ray diffraction analysis reveals that compound 2 crystallizes in the monoclinic space group $P2_1/n$. Each Cd (II) is coordinated by three oxygen atoms (Cd–O, 2.254(3)–2.252(3) Å) and two nitrogen atoms (Cd(1)–N(1)=2.293(3) Å and Cd(1)–N(4)=2.302(4) Å), showing a trigonal bipyramidal geometry. Two Cd (II) atoms, related by a twofold axis, are bridged by one pair of 5-OH-ip into a dinuclear unit with Cd...Cd distance of 4.078 Å. The dinuclear cadmium moieties are linked by four 5-OH-ip ligands to four adjacent dinuclear cadmium clusters, thus generating a (4,4) layer (Fig. 2b). The L₁ ligand bridges two metal centers and further connects adjacent layers into a 3D framework. From a topological view, the [Cd₂(CO₂)₃] dimeric unit can be treated as a 6-connected node, the 5-OH-ip and L₁ ligands are taken as linkers, the 3D structure can be classified as a pcu net (α -Po topology).

Table 1
Crystallographic Data and Structure Refinement Summary for Complexes 1–5.

Empirical formula	C ₂₀ H ₁₇ CdN ₅ O ₈	C ₂₀ H ₁₄ CdN ₄ O ₅	C ₁₄ H ₁₆ CdN ₃ O ₈	C ₁₅ H ₁₄ CdN ₃ O ₈	C ₃₀ H ₃₁ CdN ₆ O ₆
Formula weight	567.79	502.75	925.33	476.69	684.01
Crystal system, Space group	Triclinic, <i>P</i> –1	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>P</i> 2(1)/ <i>c</i>	Triclinic, <i>P</i> –1	Triclinic, <i>P</i> –1
Unit cell dimensions	<i>a</i> = 10.173 (7) Å <i>b</i> = 11.810 (8) Å <i>c</i> = 11.810 (8) Å α = 117.148 (7)° β = 104.809 (7)° γ = 99.441 (6)°	<i>a</i> = 9.866 (2) Å <i>b</i> = 14.137 (3) Å <i>c</i> = 13.808 (3) Å β = 94.019 (3)°	<i>a</i> = 9.616 (4) Å <i>b</i> = 28.514 (11) Å <i>c</i> = 12.458 (5) Å β = 106.009 (5)°	<i>a</i> = 7.843 (3) Å <i>b</i> = 10.053 (4) Å <i>c</i> = 11.639 (5) Å α = 90.144 (5)° β = 94.641 (5)° γ = 109.953 (4)°	<i>a</i> = 10.311 (6) Å <i>b</i> = 11.229 (6) Å <i>c</i> = 14.021 (8) Å α = 107.475 (7)° β = 96.101 (7)° γ = 96.513 (7)°
Volume(Å ³)	1063.67 (12)	1921.1 (7)	3283 (2)	859.3 (8)	1521.5 (11)
Z, Calculated density(mg/m ³)	2, 1.773	4, 1.738	4, 1.872	2, 1.842	2, 1.493
Independent reflections (<i>I</i> > 2 σ (<i>I</i>))	4322	3245	6288	3591	5870
<i>R</i> (0 0 0)	568	1000	1832	474	698
θ range for data collection	2.56–27.48	2.06–27.48	1.43–27.46	1.76–27.51	2.56–27.49
Limiting indices	–13 ≤ <i>h</i> ≤ 13 –12 ≤ <i>k</i> ≤ 14 –15 ≤ <i>l</i> ≤ 15	–12 ≤ <i>h</i> ≤ 12 –18 ≤ <i>k</i> ≤ 15 –17 ≤ <i>l</i> ≤ 17	–12 ≤ <i>h</i> ≤ 11 –36 ≤ <i>k</i> ≤ 28 –16 ≤ <i>l</i> ≤ 15	–10 ≤ <i>h</i> ≤ 6 –8 ≤ <i>k</i> ≤ 12 –14 ≤ <i>l</i> ≤ 14	–13 ≤ <i>h</i> ≤ 13 –14 ≤ <i>k</i> ≤ 11 –18 ≤ <i>l</i> ≤ 17
Goodness-of-fit on <i>F</i> ²	1.056	1.045	1.100	1.069	1.019
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0260, <i>wR</i> ₂ = 0.0653	<i>R</i> ₁ = 0.0413, <i>wR</i> ₂ = 0.0970	<i>R</i> ₁ = 0.0357, <i>wR</i> ₂ = 0.0704	<i>R</i> ₁ = 0.0217, <i>wR</i> ₂ = 0.0586	<i>R</i> ₁ = 0.0331, <i>wR</i> ₂ = 0.0760
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	<i>R</i> ₁ = 0.0292, <i>wR</i> ₂ = 0.0673	<i>R</i> ₁ = 0.0614, <i>wR</i> ₂ = 0.1067	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.0738	<i>R</i> ₁ = 0.0231, <i>wR</i> ₂ = 0.0596	<i>R</i> ₁ = 0.0405, <i>wR</i> ₂ = 0.0803
Largest diff. peak and hole (e/Å ³)	0.617 and –0.600	1.008 and –1.208	0.616 and –0.633	0.568 and –0.599	0.551 and –0.519

^a $R = \sum(|F_0| - |F_C|) / \sum |F_0|$.

^b $wR = [\sum w(|F_0|^2 - |F_C|^2)^2 / \sum w(F_0^2)]^{1/2}$.

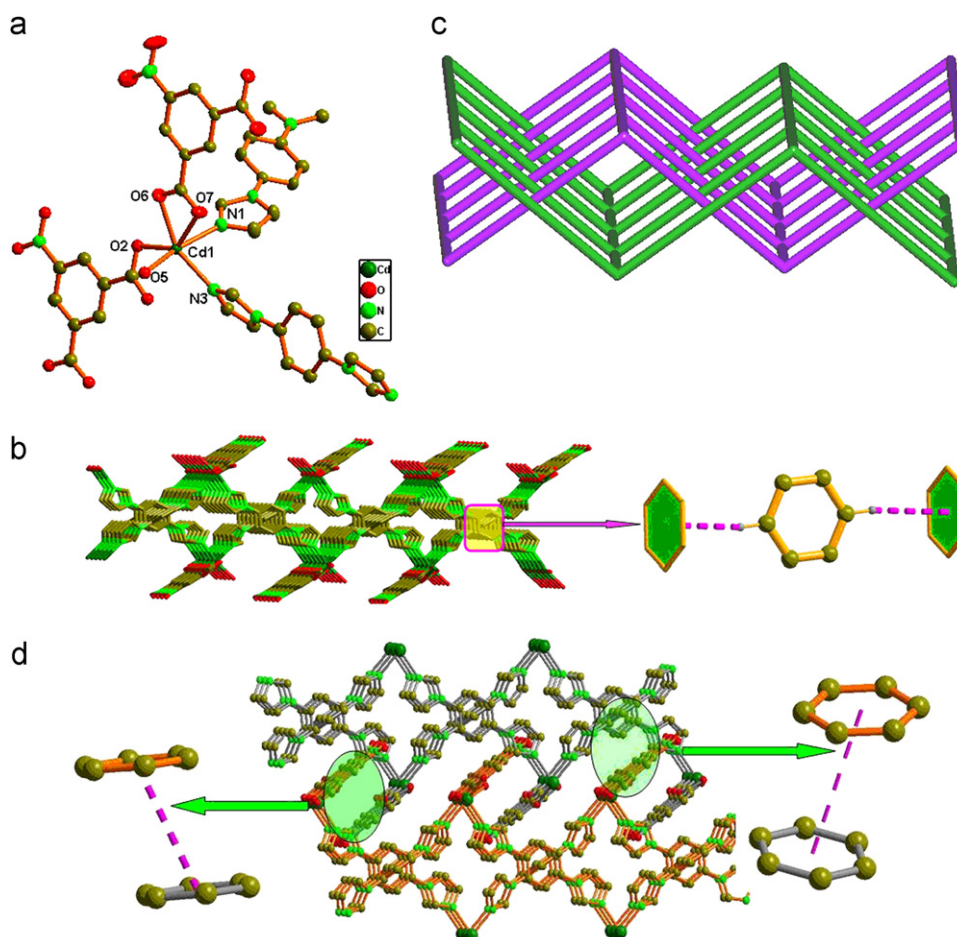


Fig. 1. (a) The coordination environment of Cd(II) atom in compound 1 (50% thermal ellipsoids); (b) the 2-fold interpenetrating layers (left) and the C–H... π interactions between phenyl rings; (c) the 2-fold interpenetrating topology for compound 1 and (d) the 3D supramolecular structure of compound 1 via π ... π interactions.

3.1.3. $[Cd(5\text{-NO}_2\text{-ip})(L_1)_{0.5}(H_2O)_2]_n$ (**3**)

Compared to **1**, the synthesis of **3** was performed under low pH value, which results in the formation of a new 3D structure with 4-connected dia topology. It is interesting that the structure of **3** is based on the dinuclear Cd_2 unit bonded by four 5- NO_2 -ip ligands and two L_1 ligands (Fig. 3a). In each dinuclear Cd_2 unit,

both Cd1 and Cd2 ions show similar coordination environment. Each Cd ion is coordinated by five oxygen atoms [Cd–O, ranging from 2.226 (2)–2.528(3) Å] and one nitrogen atoms [Cd(1)–N(4)=2.210(3) Å and Cd(2)–N(1)=2.233(3) Å], showing a distorted octahedral geometry. The two 5- NO_2 -ip anions adopting bridging/chelating-bidentate mode connect two adjacent Cd(II)

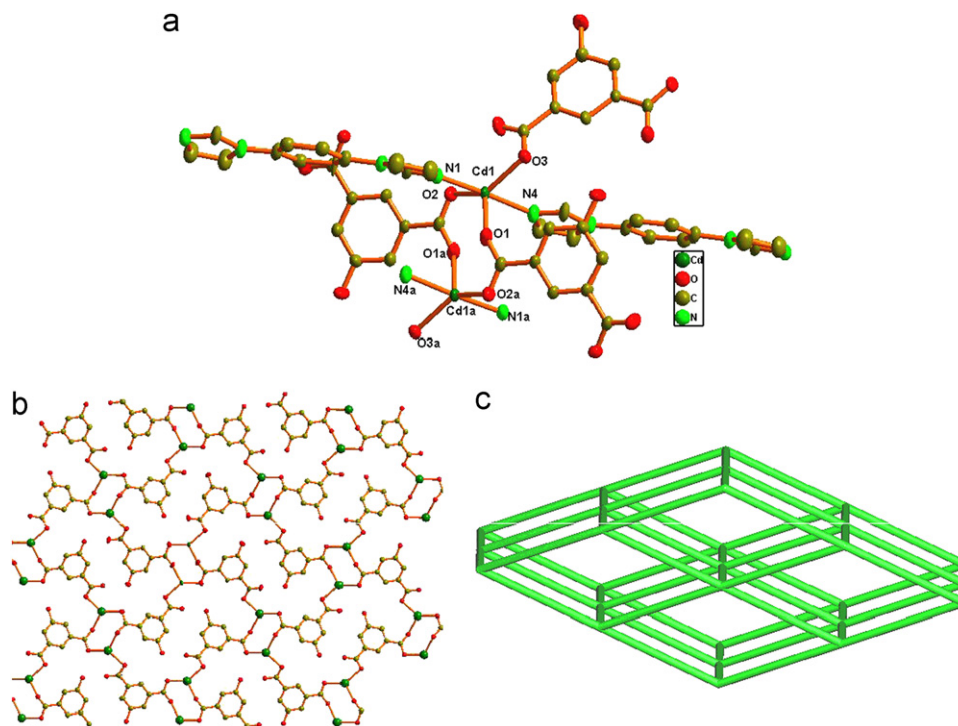


Fig. 2. (a) The coordination environment of Cd(II) atom in compound 2 (50% thermal ellipsoids); (b) The 2D layer structure formed by 5-OH-ip ligands and (c) the pcu topology of compound 2.

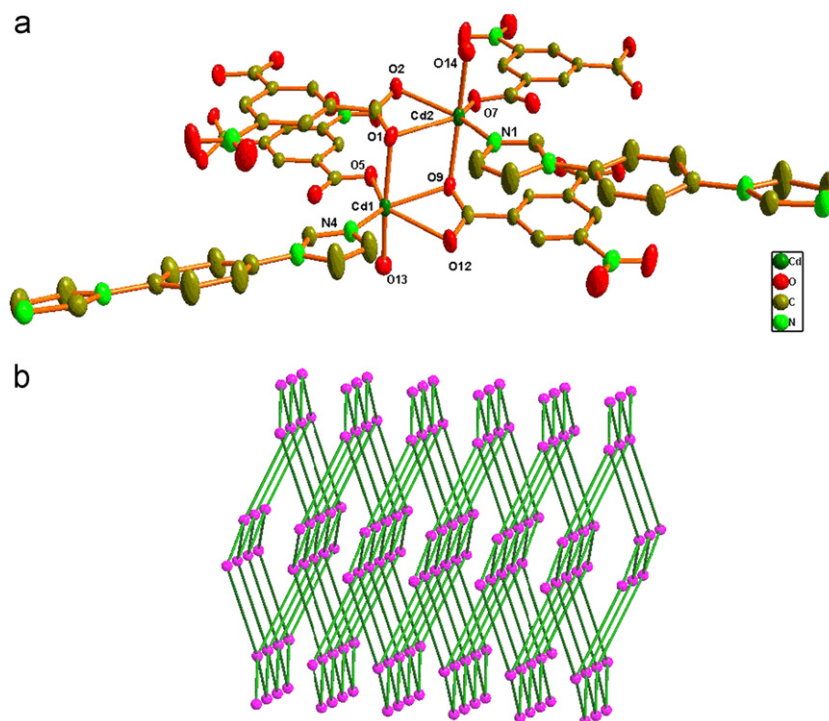


Fig. 3. (a) The coordination environment of Cd (II) atom in compound 3 (50% thermal ellipsoids) and (b) the dia topology for compound 3.

centers to form a dinuclear Cd_2 unit with a $\text{Cd}\cdots\text{Cd}$ distance of 3.881 Å (Scheme 1c). The resulting dinuclear Cd_2 unit further bonds to four adjacent ones through four 5- NO_2 -ip ligands and two L_1 ligands, leading to the formation of a 3D framework. Two adjacent dinuclear Cd_2 units are doubly linked by two 5- NO_2 -ip ligands. If each dinuclear Cd_2 unit is reduced into a 4-connected node, the 3D framework of 3 can be topologically simplified as a dia net (Fig. 3b).

3.1.4. $\{[\text{Cd}(5\text{-NO}_2\text{-ip})(L_2)_{0.5}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}$ (4)

In the structure of compound 4, each Cd (II) ion is six-coordinated by five oxygen atoms and one nitrogen atom to afford the CdNO_5 octahedral geometry (Fig. 4a). The Cd–O bond lengths are in the range of 2.211(2)–2.518 (2) Å. The carboxylate groups from two 5- NO_2 -ip ligands adopt *bis*-monodentate coordinate mode to connect two Cd(II) ions to form a dinuclear Cd(II) unit (Fig. 4b and Scheme 1a). The dinuclear Cd(II) units are further connected by the 5- NO_2 -ip ligands to form a ladder-like chain. The parallel chains are further connected by the L_2 ligand into a layer (Fig. 4c).

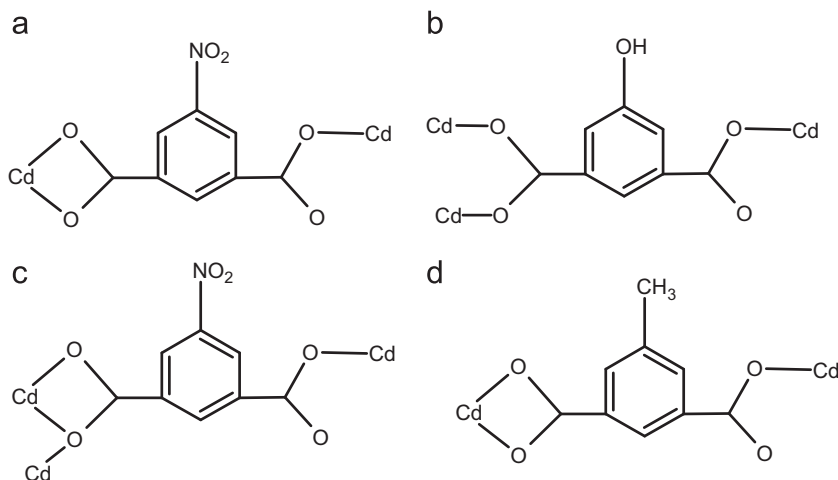
3.1.5. $[\text{Cd}(5\text{-CH}_3\text{-ip})(L_2)(\text{H}_2\text{O})_2]_n$ (5)

The replacement of 5- NO_2 -ip with 5- CH_3 -ip results in the generation of a new compound 5 with unusual 2D- > 3D

polycatenation of bilayers. Compound 5 crystallizes in triclinic space group $P\bar{1}$. In compound 5, the central Cd(II) ion coordinates with three oxygen atoms from two carboxylate groups (one monodentate: Cd (1)–O(1)=2.288(2) Å and one chelating bidentate: Cd (1)–O(3)=2.578(2) Å and Cd (1)–O(4)=2.344(2) Å) and three nitrogen atoms (Cd–N, 2.291(2)–2.317(2) Å) to form a distorted octahedron (Fig. 5a). The L_2 ligands link Cd (II) ions to form a ladder-like chain, and the chains are further connected by 5- CH_3 -ip to form a bilayer structure with the topological symbol of $(4^8.6^2)$. The Cd(II) ions are joined by 5- CH_3 -ip and L_2 ligands to give one-dimensional nanotube containing large cubelike box of approximate dimensions $10.311 \times 13.964 \times 14.021$ Å (Fig. 5b) in the bilayer. The adjacent bilayers are interlocked each other in a parallel fashion (along the b axis) to give rise to a 3D polycatenated structure (Fig. 5c).

3.2. Influence of organic ligands or reaction conditions on the structures

From the above descriptions, it is clear that different reaction conditions or organic ligands with different substitute groups may effectively tune the framework structures of the coordination polymers. By changing the pH value, compound 1 with 2-fold



Scheme 1. Coordination modes of carboxylate ligands in compounds 1–5: (a) for compounds 1 and 4; (b) for compound 2; (c) for compound 3 and (d) for compound 5.

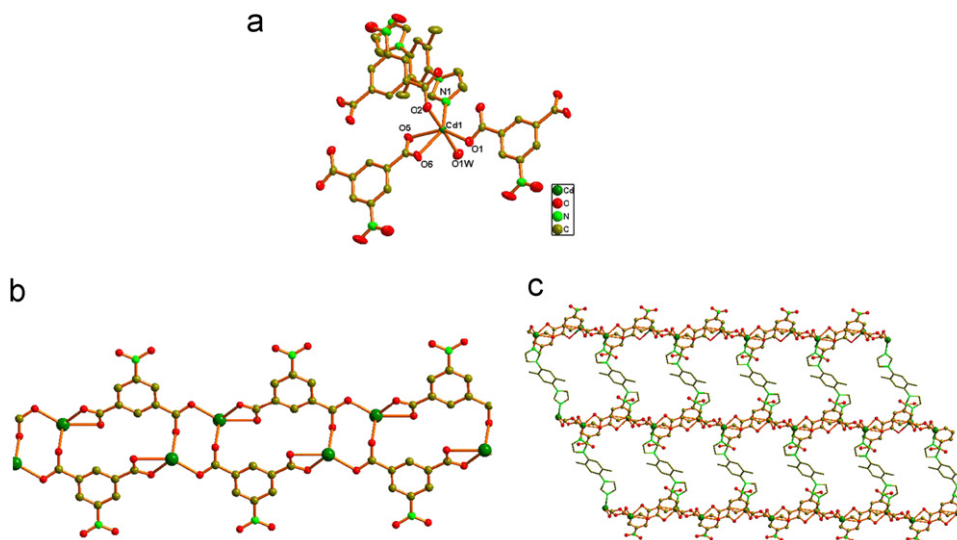


Fig. 4. (a) The coordination environment of Cd (II) atom in compound 4 (50% thermal ellipsoids); (b) The ladder-like chain via 5- NO_2 -ip ligands and (c) the layer structure for compound 4.

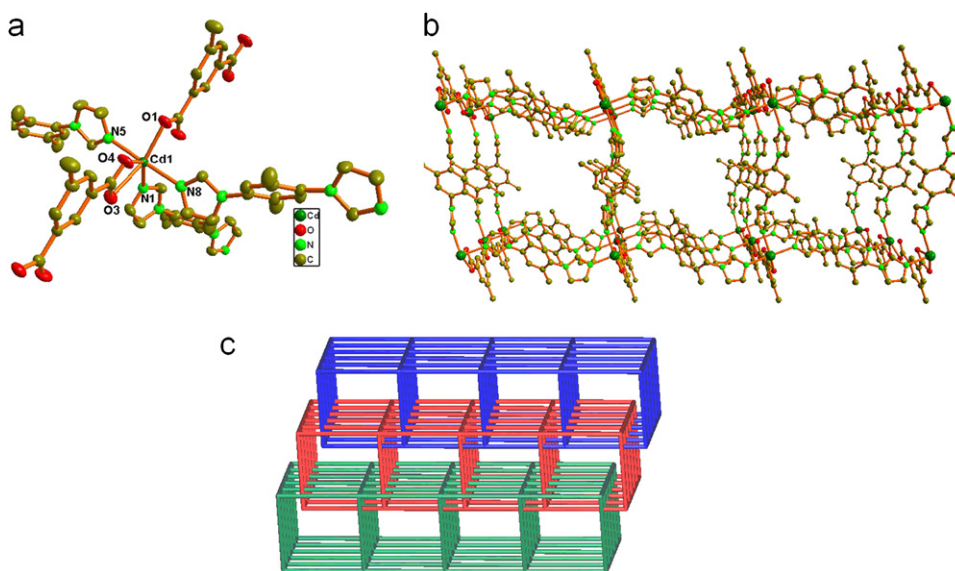


Fig. 5. (a) The coordination environment of Cd(II) atom in compound 5 (50% thermal ellipsoids); (b) the bilayer containing nanotubes paralleled to the *a* axis and (c) 3D polycatenated structure.

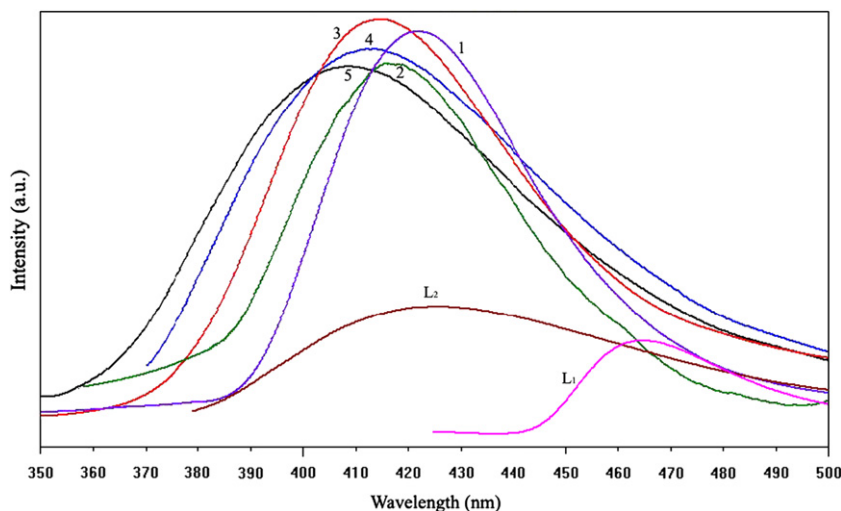


Fig. 6. The solid state emission spectra of complexes 1–5 at the room temperature.

interpenetrating (4,4)-layer structure and compound 3 with three-dimensional diamond-type framework are obtained, respectively, from the assembly of $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, 5- NO_2 -ip and L_1 ligand. The replacement of 5- NO_2 -ip with 5-OH-ip leads to a compound 2 which features a doubly pillared layered structure with pcu topology. Compounds 4 and 5 are constructed from L_2 ligand with 5- NO_2 -ip or 5- CH_3 -ip, respectively. Compound 4 has non-interpenetrating (4, 4) layer, while compound 5 shows unusual 2D- > 3D polycatenation of bilayers. From compound 3 to compound 4, inducing the CH_3 groups into 1,4-bis(imidazol-1-yl) benzene also dramatically changed the dia net in 3 to a (4,4) layer structure in 4. The preparation of compound 5 is similar to compound 1 except changing L_1 to L_2 with additional CH_3 groups, but their structures are also different.

3.3. Photoluminescent properties

The solid-state photoluminescent properties of compounds 1–5 have been investigated at room temperature. As shown in Fig. 6, complexes 1–5 exhibit luminescent emission peaks at 423 nm ($\lambda_{\text{ex}}=331$ nm) for 1, 415 nm ($\lambda_{\text{ex}}=334$ nm) for 2, 413 nm ($\lambda_{\text{ex}}=329$ nm) for 3, 410 nm ($\lambda_{\text{ex}}=354$ nm) for 4 and 408 nm ($\lambda_{\text{ex}}=357$ nm) for 5. Because the Cd(II) ion is difficult to oxidize or reduce because of

d^{10} configuration, the emission of these complex is neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer in nature. Compared with free L_1 and L_2 ligands [$\lambda_{\text{em}}=456$ nm ($\lambda_{\text{ex}}=341$ nm) for L_1 and $\lambda_{\text{em}}=421$ nm ($\lambda_{\text{ex}}=362$ nm) for L_2], the enhancement of luminescence intensity in the complexes 1–5 is in probably due to the coordination of the N-donors to the Cd(II) center, increasing the rigidity of the ligands, reducing the nonradiative decay of the intraligand ($\pi-\pi^*$) excited state [36,37]. The emission bands of the carboxylate ligands originated from the π^*-n transition are weak, and it was considered that the carboxylate ligands have no significant contribution to the luminescent emission peaks of complexes 1–5 in the presence of the N-donor ligands.

4. Conclusions

In summary, we presented here five new Cd(II) coordination polymers based on mixed 5-position substituted 1,3-benzenedicarboxylate ($R=-\text{NO}_2/-\text{OH}/-\text{CH}_3$) and N-donor ligands ($L_1=1,4$ -bis(imidazol-1-yl)benzene or $L_2=1,4$ -bis(1-imidazol-yl)-2,5-dimethyl benzene). With different substituted groups in the organic ligands, five compounds exhibit five distinct framework structures.

The results reveal that the adjustment of substituted groups in organic ligands can result in distinct framework topologies of coordination polymers. It also provides a new approach toward tuning structural topologies of coordination polymers through modifying the substitute groups in organic ligands.

Appendix A. Supporting information

Electronic supplementary information (ESI) available: X-ray crystallographic data, X-ray powder diffraction patterns for compounds 1–5 and the photoluminescence data for the free ligand L_1 and L_2 . CCDC reference 890905, 890906, 890907, 890908, and 890909 numbers for **1**, **2**, **3**, **4**, and **5**. For ESI and crystallographic data in CIF or other electronic format see Supporting Information.

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Appendix B. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jssc.2012.11.026>.

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