Coordination polymers of the bis(imidazole) ligand modulated by dicarboxylate ligands: from 2D layer to 3D framework

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Abstract: Three new coordination polymers, $[\text{Zn}(\text{H}_2\text{biim})(\text{pzdc})]_n$ (**1**), $[\text{Cd}(\text{H}_2\text{biim})(\text{pzdc})]_n$ (**2**) and $[\text{Cd}(\text{H}_2\text{biim})_{0.5}(\text{ip-OH})]_n$ (**3**) (H_2biim = 2,2'-biimidazolate, H_2pzdc = 2,3-pyrazinedicarboxylic acid, $\text{H}_2\text{ip-OH}$ = 5-hydroxyisophthalic acid), have been hydrothermally synthesized and characterized by elemental analysis, infrared spectra and X-ray single-crystal diffraction. Complexes **1** and **2** are isostructural and display two-dimensional (2D) undulated layers with 3-connected (4.8^2) topologies, which are further extended into three-dimensional (3D) supramolecular structures through hydrogen-bonding and $\text{C-H}\cdots\pi$ interactions. Complex **3** is a relatively rare 3D compound, featuring a binodal (4,5)-connected ($4^4.6^2$)($4^4.6^6$) topology. A comparison of all the complexes demonstrates that the structural characteristics of the dicarboxylate ligands play a great role in the modulation of the coordination structures. Moreover, their luminescent properties and thermal stabilities were also investigated.

Keywords: Transitional metal complexes; Bis(imidazole) ligand; Carboxylate ligands; Luminescence

1. Introduction

Generally speaking, coordination polymers (CPs) are constructed from inorganic nodes (single metal ions, polynuclear metal cluster, SBUs) and organic linkers (polycarboxylate, N-donors, phosphonate and so on) through coordination interactions. They have received considerable attention, not only because of their topological diversities but also for their potential applications in the following fields: catalysis, luminescence, gas adsorption, magnetism [1-10]. Up until now, a variety of

remarkable CPs have been documented, which include 1D chains or ladders, 2D grids and 3D porous motifs. However, the modulation of the coordination structure, which is closely related to the chemical environment, is still a significant challenge in the area of crystal engineering. So far, mixed-ligand coordination polymers involving rigid N-donor ligands have been widely constructed [11-15]. Among these rigid N-donor ligands, the 2,2'-biimidazole (H_2biim) ligand arouses our interest [16-19]. Firstly, as a neutral ligand, the two nitrogen atoms of the imino moieties have a high affinity for coordinating to metals in the chelating or bridging coordination modes. Secondly, the H_2biim ligand can be partly (Hbiim^-) or fully (biim^{2-}) deprotonated. Therefore, it can act as a bridging ligand and form up to four bonds. Thirdly, under the existence of different torsional angles between the imidazole rings, H_2biim may display different conformations, which provide rich structural diversities. Additionally, due to the existence of imidazole rings, the H_2biim ligand can form weak interactions such as hydrogen-bonding, $\pi \cdots \pi$ and $\text{C-H} \cdots \pi$ interactions. To our best knowledge, the use of H_2biim as a μ_2 -bridging ligand to construct 3D frameworks is comparatively rare. Only two examples have been reported for polyoxometallates (POMs) [20-21]. On the other hand, multidentate organic carboxylate ligands have been extensively employed in the construction of CPs with diverse structures and excellent properties, not only because of their many types of bridging coordination modes, but also because of their potential function as hydrogen-bonding acceptors and donors [22-25].

In order to explore the influence of dicarboxylate ligands on the tuning of coordination structures, two kinds of dicarboxylate ligands, namely H_2pzdc

(2,3-pyrazinedicarboxylic acid) and H₂ip-OH (5-hydroxyisophthalic acid), were introduced into the Cd/Zn-H₂biim system. Three interesting coordination polymers, [Zn(H₂biim)(pzdc)]_n (**1**), [Cd(H₂biim)(pzdc)]_n (**2**) and [Cd(H₂biim)_{0.5}(ip-OH)]_n (**3**) (H₂biim = 2,2'-biimidazolate), have been successfully synthesized under hydrothermal conditions. Although the three complexes were prepared in a similar way, we found that the different dicarboxylate ligands greatly influence the final structures produced. The structures display a 2D layer to 3D framework transition. In this paper, we report the syntheses, crystal structures, fluorescence properties and thermal stabilities of the three compounds.

2. Experimental

2.1. Materials and physical measurements

The reagents were purchased commercially and were used without further purification. The ligand H₂biim was prepared according to the literature procedures [26]. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu-K α radiation (λ = 0.15418 nm), 2θ ranging from 5 to 50° with an increment of 0.02° and a scanning rate of 5° min⁻¹. IR (KBr pellets) spectra were obtained from 4000 to 400 cm⁻¹ using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric (TG) analyses were recorded on a Perkin-Elmer Thermal Analyzer at a heating rate of 10 °C min⁻¹ and a flow rate of 100 cm³ min⁻¹ (N₂). Luminescent spectra were performed on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp

and quartz carrier in the solid state at room temperature.

<Insert Scheme 1>

*2.2. Synthesis of $[Zn(H_2biim)(pzdc)]_n$ (**1**)*

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 30 mg), H_2biim (0.1 mmol, 13 mg), H_2pzdc (0.1 mmol, 20 mg) and H_2O (8 mL) was adjusted to pH 5.0 with 0.05 mol L⁻¹ NaOH solution. It was then sealed in a 25 mL Teflon reactor and heated at 150 °C for 72 h. Finally the mixture was cooled to room temperature at a cooling rate of 3 °C h⁻¹ and block colorless crystals of **1** were obtained by filtration. **1** was washed with distilled water and dried in air. Yield: 47% based on the Zn(II) salt. Anal. calcd for $C_{12}H_8N_6O_4Zn$: C, 39.42; H, 2.21; N, 22.99. Found: C, 39.40; H, 2.20; N, 22.91%. IR (KBr, cm⁻¹): 3088 (w), 2993 (w), 2897 (w), 2777 (s), 1608 (s), 1564 (s), 1536 (s), 1457 (s), 1442 (s), 1359 (m), 1322 (m), 1231 (m), 1204 (s), 1170 (s), 1121 (m), 1107 (m), 1064 (s), 993 (s), 946 (m), 859 (s), 833 (m), 772 (m), 740 (s), 693 (s), 665 (s).

*2.3. Synthesis of $[Cd(H_2biim)(pzdc)]_n$ (**2**)*

The preparation of **2** was similar to that of **1** except that $CdCl_2 \cdot 2.5H_2O$ (0.1 mmol, 30 mg) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$. Block colorless crystals of **2** were obtained. Yield: 57% based on the Cd(II) salt. Anal. calcd for $C_{12}H_8N_6O_4Cd$: C, 34.93; H, 1.95; N, 20.37. Found: C, 34.91; H, 1.96; N, 20.38%. IR (KBr, cm⁻¹): 3082 (w), 2986 (w), 2909 (w), 2799 (w), 1588 (s), 1561 (s), 1530 (s), 1454 (s), 1437 (s), 1390 (s), 1358 (m), 1317 (m), 1231 (m), 1196 (s), 1166 (s), 1118 (s), 1105 (m), 1063 (s), 989 (s), 920 (m), 889 (s), 833 (m), 770 (m), 742 (s), 691 (s), 661 (s).

*2.4. Synthesis of $[Cd(H_2biim)_{0.5}(ip-OH)]_n$ (**3**)*

A mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.1 mmol, 30 mg), H_2biim (0.1 mmol, 10 mg) and $\text{H}_2\text{ip-OH}$ (0.1 mmol, 20 mg) and H_2O (8 mL) was adjusted to pH 5.0 with 0.05 mol L^{-1} NaOH solution. It was then sealed in a 25 mL Teflon reactor and heated at 150 °C for 72 h. The mixture was cooled to room temperature after 40 h. Slightly purple crystals were obtained. Yield: 42% based on the Cd(II) salt. Anal. calcd for $\text{C}_{11}\text{H}_7\text{N}_2\text{O}_5\text{Cd}$: C, 36.70; H, 1.95; N, 7.79. Found: C, 36.76; H, 1.95; N, 7.80%. IR (KBr, cm^{-1}): 3461 (m), 3058 (w), 2930 (w), 2866 (w), 1630 (s), 1583 (s), 1508 (m), 1397 (s), 1333 (s), 1291 (s), 1208 (m), 1165 (w), 1098 (w), 1014 (w), 859 (s), 750 (s), 661 (m), 428 (w).

2.5. X-ray crystallography

Single-crystal X-ray diffraction data for complexes **1-3** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Empirical absorption corrections were applied using the multiscan technique. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were located geometrically. The crystal data and structure refinements of **1-3** are summarized in Table 1. Selected bond lengths and angles are listed in Table S1, while hydrogen-bonding, C-H $\cdots\pi$ and $\pi\cdots\pi$ interactions in **1-3** are listed in Table S2, Table S3 and Table S4, respectively.

Table 1. Crystal data and structure refinements for compounds **1-3**.

Compound	1	2	3
Empirical Formula	C ₁₂ H ₈ N ₆ O ₄ Zn	C ₁₂ H ₈ N ₆ O ₄ Cd	C ₁₁ H ₇ N ₂ O ₅ Cd
Formula Weight	365.63	412.65	359.60
<i>T</i> (K)	293(2)	293(2)	293(2)
Wavelength λ (Å)	0.71073	0.71073	0.71073
Crystal system	<i>Pbca</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$
Space group	Orthorhombic	Orthorhombic	Triclinic
<i>a</i> (Å)	10.5585(2)	10.7029(4)	8.2763(8)
<i>b</i> (Å)	14.3946(3)	14.6422(6)	8.3342(8)
<i>c</i> (Å)	17.4888(3)	17.8357(8)	8.8041(14)
α (°)	90	90	107.567(2)
β (°)	90	90	107.865(2)
γ (°)	90	90	102.6640(10)
<i>V</i> (Å ³)	2658.04(9)	2795.1(2)	517.48(11)
<i>Z</i>	8	8	2
<i>D</i> _{calc} (g cm ⁻³)	1.827	1.961	2.308
<i>F</i> (000)	1472	1616	350
<i>R</i> _{int}	0.0219	0.0400	0.0176
GOF on <i>F</i> ²	1.027	1.013	1.094
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0233, 0.0616	0.0278, 0.0538	0.0297, 0.0778
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0279, 0.0639	0.0459, 0.0595	0.0347, 0.0932

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|.$$

$$^b wR_2 = \sum \{w(F_o^2 - F_c^2)^2\} / \sum [w(F_o^2)]^2\}^{1/2}.$$

3. Results and discussion

3.1. Synthesis

Three new Cd(II)/Zn(II) coordination polymers with a 2D layer or 3D framework have been synthesized under hydrothermal conditions. In order to investigate the

effect of the dicarboxylate ligands on the coordination structures, we carried out some parallel experiments by altering the dicarboxylate ligands. Reactions of H₂biim, H₂pzdc or H₂ip-OH and CdCl₂ in 8 mL H₂O at 150 °C produce crystals of **2** and **3**. When CdCl₂ was replaced with Zn(NO₃)₂ under the same reaction conditions, only crystals of **1** were obtained, the structure of which is isostructural with **2**. The pH value plays an important role in the formation of the three complexes. Using HCl and NaOH solutions to adjust the pH, higher-quality crystals can be obtained at a pH value of 5. However, much precipitation or a clear solution for compounds **1-3** comes into being at other pH values. In addition, we also performed a series of parallel experiments to change the reaction temperatures, and to vary the solvent types and ratios. Unfortunately, the other experiments gave powder forms or very small crystals, which were not suitable for X-ray diffraction studies.

< Insert Scheme 2 >

3.2. Description of the crystal structures

*3.2.1. Crystal structures of [Zn(H₂biim)(pzdc)]_n (**1**) and [Cd(H₂biim)(pzdc)]_n (**2**)*

Complexes **1** and **2** are isostructural, and hence only the structure of **1** is discussed here. There exists one Zn(II) ion, one pzdc²⁻ ligand and one H₂biim ligand in the asymmetric unit of **1**. Each Zn(II) ion is surrounded by three oxygen atoms (O1, O2#1, O4#2) of three distinct pzdc²⁻ ligands, two nitrogen atoms (N2, N4) of one H₂biim ligand and one nitrogen atom (N5#2) of one pzdc²⁻ ligand, displaying a octahedral geometry (Figure. 1(a)). The Zn-N and Zn-O bond distances are in the ranges 2.0824(16)-2.3796(17) and 2.0516(13)-2.1638(13) Å (Table S1), respectively, which

are comparable to similar zinc compounds [27]. In **1**, the H₂biim ligands, acting as neutral chelating ligands, are located on opposite sides of the layer (Scheme 3(a), Figure. 2(c)). Each pzdc²⁻ ligand employ its carboxylate groups and one pyrazine nitrogen atom to coordinate to three Zn(II) ions. The two carboxylate groups adopt bis-mondentate and monodentate coordination modes. Therefore, the pzdc²⁻ ligand shows a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$ coordination mode. The two carboxylate groups are out of the plane of the linking pyrazine ring, with the dihedral angles being 10.503 and 68.776°. Interestingly, two carboxylate groups from two different pzdc²⁻ ligands bridge two Zn(II) ions to form a binuclear unit, Zn₂(pzdc)₄(H₂biim)₂ (Figure. 1(b)). The binuclear unit is an 8-membered [Zn₂C₂O₄] ring with a Zn...Zn distance of 4.514 Å. The binuclear units are further linked by sharing pzdc²⁻ ligands to form a 24-membered [Zn₄C₁₂O₄N₄] macrocyclic ring with diagonal distances of 10.204 × 10.987 Å. The rings A and B are arranged on the ab plane to form a highly ordered 2D layer in an ABAB sequence (Figure. 1(c)). Topologically, both the pzdc²⁻ ligands and the Zn(II) ions are viewed as 3-connected nodes. Thus, the 2D layer of **1** has a 3-connected (4.8²) topology (Figure. 1(d)). The neighboring layers are linked together through hydrogen-bonding (N1...O3, 2.716(2) Å; N3...O4, 2.787(2) Å) and C-H... π (C7...Cg(5), 3.782(2) Å) interactions, resulting in a 3D supramolecular structure (Figure. 2(c), Tables S2 and S3).

< Insert Figs. 1 and 2 >

3.2.2. Crystal structure of [Cd(H₂biim)_{0.5}(ip-OH)]_n (**3**)

Single-crystal X-ray structural analysis shows that the asymmetric unit of complex

3 contains one Cd(II) ion, one ip-OH²⁻ ligand and half of a H₂biim ligand. As shown in Figure. 3(a), the Cd(II) ion is five-coordinated by four carboxylate oxygen atoms (O1, O3#1, O9#3, O10#2) from four different ip-OH²⁻ ligands and one nitrogen atom (N1) from one H₂biim ligand in a distorted trigonal bipyramidal coordination environment. The Cd-N bond length is 2.298(5) Å and the Cd-O bond lengths range from 2.153(4) Å to 2.504(4) Å (Table S1); they are all in the normal range of bond distances [28-29]. In the structure of **3**, all the carboxylate groups are deprotonated. The ip-OH²⁻ ligands, adopting a $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$ coordination mode, link the Cd(II) ions into a 2D undulated layer along the bc plane (Figure. 3(b)). Two carboxylate groups have a dihedral angles of 11.994° and 25.747° toward the plane of the corresponding linking phenyl rings. It is interesting that there exist two kinds of 8-membered [Cd₂C₂O₄] rings (ring A, ring B) and two kinds of 16-membered [Cd₂C₁₀O₄] rings (ring C, ring D) in the layer, where the Cd...Cd distances vary from 4.329 to 9.714 Å in the rings. The H₂biim ligands, adopting the μ_2 -bridging mode, link neighboring 2D layers into a 3D framework (Scheme 3(b), Figure. 3(c)). It is noteworthy that most H₂biim ligands adopt the bidentate chelating coordination mode to form coordination polymers and the μ_2 -bridging coordination mode is rare for the H₂biim ligand. As far as we know, only two examples involved the μ_2 -bridging coordination mode of the H₂biim ligand have been reported in polyoxometallates (POMs) to date [20-21]. Topologically, the Cd(II) ions and ip-OH²⁻ ligands are viewed as 5-connected and 4-connected nodes, respectively, and H₂biim ligands can be viewed as linkers. Therefore, the framework of complex **3** can be described as having a binodal

(4,5)-connected (4⁴.6²)(4⁴.6⁶) topology (Figure. 3(d)). In addition, hydrogen-bonding (O2...O1, 2.771(6) Å; N2...O10, 2.818(7) Å; C2...O9, 3.269(8) Å; C10...O2, 3.389(8) Å) and $\pi\cdots\pi$ interactions (Cg(1)-Cg(2), 3.708(4) Å) further stabilize the 3D framework of **3** (Tables S2 and S4).

< Insert Fig. 3 >

3.3. Effects of the carboxylate ligands on the structures

In **1** and **2**, the Zn(II) or Cd(II) ion is six-coordinated by three pzdc²⁻ ligands and one H₂biim ligand, while in **3**, each Cd(II) ion is five-coordinated by four ip-OH²⁻ ligands and one H₂biim ligand. Compared with the H₂pzdc ligand, the H₂ip-OH ligand has an extra hydroxyl group on each phenyl ring. Obviously, the extra hydroxyl groups of the H₂ip-OH ligand will increase the steric hindrance when coordinated with the metal atoms. In addition, in **1-3** the carboxylate ligands take different kinds of coordination modes. In **1** and **2**, the pzdc²⁻ ligands adopts a μ_3 -bridging mode with one carboxylate group in a $\mu_2\text{-}\eta^1\text{:}\eta^1$ coordination mode and the other in a $\mu_1\text{-}\eta^1\text{:}\eta^0$ coordination mode. Moreover, one nitrogen atom of the pyrazine ring participates in the coordination as well. The pzdc²⁻ ligands link three neighboring Zn(II) or Cd(II) ions to form a 2D layer with two kinds of rings. In **3**, the ip-OH²⁻ ligand takes a μ_4 -bridging mode to link four Cd(II) ions with two carboxylate groups in the $\mu_2\text{-}\eta^1\text{:}\eta^1$ coordination mode. Therefore, a 2D layer containing four kinds of rings is formed. Clearly, the different coordination modes of the organic dicarboxylate ligands have an obvious effect on the structures. Taking the H₂biim ligand into consideration, a bidentate chelating coordination mode was found in **1** and **2**, which

has no contribution to the dimensions of the structures. In contrast, the H₂biim ligand adopts a μ_2 -bridging mode to link 2D layers into a 3D framework in **3**. This result indicates that dicarboxylate ligands play an important role in altering the coordination modes of H₂biim ligands [30-31]. Also, the H₂biim ligands display different dihedral angles between the imidazole rings: 11.796° for **1** and **2**, and 0° for **3**, indicating the conformation of H₂biim ligands is adjusted on introducing the dicarboxylate ligands. The differences in dihedral angles may arise mainly from the influence of weak interactions between the H₂biim and dicarboxylate ligands. In conclusion, the introduction of suitable dicarboxylate ligands is a feasible route for tuning coordination structures.

3.4. Photoluminescent properties

In consideration of the excellent luminescent properties of coordination polymers with d¹⁰ transitional metals, solid state luminescent studies of the free organic ligands and complexes **1-3** were performed (Figs. S1 and S2) [32-35]. The free organic ligands emit strong fluorescence centered at 343 and 356 nm ($\lambda_{\text{ex}} = 280$ nm) for H₂biim, 411 nm ($\lambda_{\text{ex}} = 360$ nm) for H₂ip-OH and 409 nm ($\lambda_{\text{ex}} = 300$ nm) for H₂pzdc. Usually, the emission peaks may be assigned to $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transitions, as previously reported [36]. For complexes **1-3**, their corresponding emission peaks were observed at 496 nm ($\lambda_{\text{ex}} = 360$ nm), 473 nm ($\lambda_{\text{ex}} = 370$ nm) and 449 nm ($\lambda_{\text{ex}} = 360$ nm). In terms of the nature of the Cd(II) or Zn(II) ions being difficult to oxidize or reduce, the emissions of these compounds are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) [37-39]. For complex **3**, a

similar emission is observed compared to the free H₂ip-OH ligand, which may be attributed to intraligand transitions of the H₂ip-OH ligands [40]. For complexes **1** and **2**, the emissions are highly red-shifted relative to the organic ligands, which can probably be assigned to intraligand transitions, admixing with ligand-to-ligand charge transitions (LLCT) [41]. The observed red shift of the emission maximum with respect to the free ligands may largely originate from the coordination of the ligands to the metal ions [42].

3.5. Thermal analyses

Thermogravimetric analysis was carried out for complexes **1-3** in order to investigate their thermal stability (Fig. S3). The thermogravimetric curves of complexes **1-3** are similar, which indicate they have similar weight loss processes. The complexes are thermally stable up to 248 °C for **1**, 348 °C for **2**, and 326 °C for **3**. Further weight loss indicates the decomposition of the coordination framework. The majority of weight loss is 80.26% (calc. 82.05%) for **1** between 248 and 695 °C, 70.83% (calc. 72.70%) for **2** between 348 and 667 °C, and 66.39% (calc. 68.68%) for **3** between 326 and 682 °C, which can be attributed to the decomposition of the organic components. The weights of the remaining products are 19.74% (calc. 22.15%) for **1**, 29.17% (calc. 31.11%) for **2** and 33.61% (calc. 35.59%) for **3**. These results are consistent with formation of ZnO or CdO as the final residue.

3.6. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) has been used to check the phase purity of these complexes in the solid state (Fig. S4). The peak positions of the measured

PXRD patterns are in good agreement with the simulated patterns, which testify the synthesized materials and the measured single crystals are the same.

4. Conclusion

In summary, three coordination polymers based on the H_2biim and organic dicarboxylate ligands have been synthesized under hydrothermal conditions. They were formed under similar reaction conditions but with different dicarboxylate ligands. These complexes show a structural transition from 2D layer to 3D framework with different topologies. The results indicate that carboxylate ligands have an important effect on tuning coordination structures. The fluorescent properties of the complexes imply that they may be good candidates for optical materials. Further studies on modulating the structures of coordination polymers are underway.

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Scheme 1. Schematic representation of the organic ligands.

Scheme 2. Syntheses of compounds **1-3**.

Scheme 3. Coordination modes of the H₂biim ligand found in compounds **1-3**.

Fig. 1 (a) Coordination environment of the Zn(II) ion in **1** (Symmetry codes: #1: $-x+1, -y+1, -z+1$; #2: $x+1/2, -y+1/2, -z+1$. All hydrogen atoms are omitted for clarity). (b) View of the binuclear unit of **1** (c) The 2D layer of **1** with two types of rings (ring A, ring B). (d) Schematic view of the 3-connected (4.8²) topology of **1**.

Fig. 2 (a) A partial schematic view of the hydrogen bonding interactions in **1**. (b) A partial schematic view of the C-H... π interactions in **1**. (c) The 3D supramolecular framework constructed by hydrogen-bonding and C-H... π interactions in **1**.

Fig. 3 (a) Coordination environment of the Cd(II) ion in **3** (Symmetry codes: #1: $-x, -y, -z+1$; #2: $-x, -y+1, -z+2$; #3: $x, y, z+1$; #5: $-x+1, -y+1, -z+3$. All hydrogen atoms are omitted for clarity). (b) (top) The 2D layer with four types of rings (ring A, ring B, ring C, ring D) formed by ip-OH²⁻ ligands and metal centers and (bottom) the H₂biim ligand acting as a linker. (c) The 3D framework of **3** formed by Cd(II) ions, ip-OH²⁻ and H₂biim ligands. (d) Schematic view of the 3D binodal (4,5)-connected (4⁴.6²)(4⁴.6⁶) topology of **3**.