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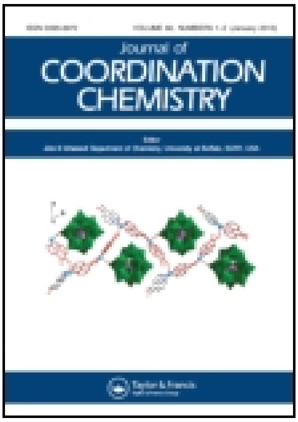

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Syntheses, crystal structures, and luminescent properties of two cadmium(II) complexes based on bis(imidazole) and dicarboxylate

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Syntheses, crystal structures, and luminescent properties of two cadmium(II) complexes based on bis(imidazole) and dicarboxylate

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Two complexes, $[Cd(ip–OH)(H_2biim)(H_2O)][Cd(ip–OH)(H_2biim)(H_2O)_3]\cdot 8(H_2O)$ (**1**) and $[Cd(Himdc)(H_2biim)]_n$ (**2**) ($H_2ip–OH$ = 5-hydroxylisophthalic acid, H_2biim = 2,2'-biimidazolate, H_3imdc = 4,5-imidazoledicarboxylic acid), have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. **1** is a 3-D supramolecular network constructed by 0-D and 1-D motifs through hydrogen bonds and $\pi\cdots\pi$ interactions. Complex **2** is a 1-D zigzag polymeric coordination chain and the chains are connected to form a 3-D supramolecular network by hydrogen bonds. The complexes were characterized by elemental and thermogravimetric analyses. Fluorescence was also investigated.

Keywords: Cadmium(II) complexes; 2,2'-Biimidazolate; 5-Hydroxylisophthalic acid; Supramolecular structure; Luminescent property

1. Introduction

Metal–organic coordination polymers have attention in supramolecular chemistry and crystal engineering for structural diversity and crystal packing motifs [1–3] and for potential applications as functional materials [4–6]. There are many studies using N-donor and multicarboxylates to build multidimensional frameworks with varied structures [7, 8]. Acting as auxiliary ligands or bridging ligands, various N-containing ligands, such as imidazole, 1,10'-phenanthroline, 4,4'-bipyridine, etc. generate many coordination polymers [9]. The rigid bridging N-donor, 2,2'-biimidazole (H_2biim), has also been used in constructing metal–organic complexes [10–12], and many H_2biim complexes with magnetism [13], inclusion phenomenon [14], and proton-coupled electron transfer [15] have been explored. H_2biim has useful structural features [16–18]. As a neutral ligand, the two imino moieties can chelate or bridge metal ions and the two amino moieties may be H-bond donors. When one amino group is deprotonated, H_2biim can be tridentate ($Hbiim^-$). And when both of the amino groups are deprotonated, tetradentate ($biim^{2-}$) can be formed.

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Additionally, $\pi \cdots \pi$ interaction may be another important noncovalent interactions because of the presence of the two imidazole rings. H_2biim is a good nitrogen donor with multicoordination and hydrogen bond, and $\pi \cdots \pi$ interactions.

Di- or multi-carboxylates including N-heterocyclic carboxylates [19–26] can coordinate with metal ions to form coordination polymers with diverse structures and properties.

Taking into account the factors above, we chose H_2biim with two different dicarboxylates, H_2ip–OH and H_3imdc, to react with cadmium salt giving [Cd(ip–OH)(H_2biim)(H_2O)] [Cd(ip–OH)(H_2biim)$(H_2O)_3$]·8(H_2O) (**1**) and [Cd(Himdc)(H_2biim)]$_n$ (**2**). In **1**, a 3-D supramolecular network is constructed by the 1-D chain [Cd(ip–OH)(H_2biim)(H_2O)] and the 0-D discrete [Cd(ip–OH)(H_2biim)$(H_2O)_3$] through hydrogen bonds and $\pi \cdots \pi$ interactions. In **2**, 1-D zigzag polymeric coordination chains are connected into a 3-D supramolecular network by hydrogen bonds. In this paper, we report syntheses, crystal structures, and thermogravimetric analyses (TGA) of the two complexes as well as their fluorescence properties.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were purchased commercially and used without purification. IR (KBr pellets) spectra were measured 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. The thermal behaviors were studied by TGA on a Perkin-Elmer Thermal Analyzer under N_2 with a heating rate of 5 °C min^{-1} for **1** and 10 °C min^{-1} for **2**. Luminescence spectra were measured on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier in solid state at room temperature.

2.2. *Synthesis of [Cd(ip–OH)(H_2biim)(H_2O)][Cd(ip–OH)(H_2biim)$(H_2O)_3$]·8(H_2O) (1)*

A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.10 mM, 0.02 g), H_2biim (0.05 mM, 0.007 g), H_2ip–OH (0.06 mM, 0.01 g), and H_2O (10 mL) was adjusted to pH 6.0 with 0.10 M L^{-1} NaOH solution, sealed in a 25 mL Teflon reactor and heated at 150 °C for 72 h. After the sample was cooled to room temperature at 3 °C h^{-1}, block colorless crystals were obtained. Yield: 51% based on Cd(II) salt. Anal. Calcd (%) for $C_{28}H_{44}Cd_2N_8O_{22}$: C, 31.45; H, 4.15; N, 10.48. Found: C, 31.47; H, 4.13; N, 10.49. IR (KBr, cm^{-1}): 3126 (s), 1683 (s), 1557 (s), 1374 (s), 1125 (m), 990 (m), 840 (m), 732 (s), 687 (s).

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

A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.13 mM, 0.03 g), H_3imdc (0.13 mM, 0.02 g), H_2biim (0.10 mM, 0.013 g), and H_2O (8 mL) was adjusted to pH 5–6 with NaOH solution, sealed in a 25 mL Teflon reactor and heated at 150 °C for 3 days. After being gradually cooled to room temperature at 3 °C h^{-1}, orange crystals of **1** were obtained (yield 54% based on Cd (II)). Elemental analyses Calcd (%) for $C_{11}H_7N_6O_4Cd$ (399.64): C, 33.06; H, 1.77; N, 21.03. Found: C, 33.08; H, 1.75; N, 21.05. IR (KBr, cm^{-1}): 3120 (s), 1681 (s), 1540 (s), 1508 (s), 1429 (w), 1393 (s), 1177 (m), 992 (s), 847 (m), 769 (s), 687 (s), 521 (m).

2.4. *X-ray crystallography*

Single-crystal X-ray diffraction data for **1** and **2** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were performed empirically. The crystal structures were solved by direct methods and refined employing full-matrix least squares on F^2 using SHELXTL-97. All nonhydrogen atoms were refined anisotropically; hydrogens of organic ligands and coordination waters were located geometrically. Hydrogens of free water were not located but were included in the formula of **1**. CCDC numbers of **1** and **2** are 895736 and 908293. The crystal data and structure refinements of **1** and **2** are summarized in table 1 and selected bond lengths and angles are listed in table 2, while O–H···O, N–H···O, C–H···O, and π···π interactions in **1** and **2** are listed in table S1.

3. Results and discussion

3.1. *Crystal structure of 1*

Structure analysis exhibits that **1** crystallizes in the triclinic space group $P\bar{1}$. The structure of **1** possesses [Cd(ip–OH)(H_2biim)(H_2O)$_3$] (unit A), [Cd(ip–OH)(H_2biim)(H_2O)] (unit B), and eight free waters (figure 1). In unit A, Cd1 is coordinated by two nitrogens (N1 and N3) from a H_2biim, one carboxylic oxygen (O1) from one ip–OH^{2-}, and three waters (O1, O2 and O3 W), showing a distorted octahedral coordination (figure 1). The distances of Cd–N [2.281(4)–2.366(4) Å] and Cd–O [2.253(4)–2.445(4) Å] in unit A are in the normal range of those observed in Cd(II) compounds [27]. The deprotonated ip–OH^{2-}

Table 1. Details of crystal data and structure refinement parameters for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{28}H_{44}N_8O_{22}Cd_2$	$C_{11}H_7N_6O_4Cd$
Formula weight	1069.40	399.64
Temperature (K)	293(2)	293(2)
Wavelength λ (Å)	0.71073	0.71073
Crystal system	$P\bar{1}$	$P2(1)/c$
Space group	Triclinic	Monoclinic
Unit cell dimensions (Å, °)		
a (Å)	10.1884(4)	10.2087(5)
b (Å)	10.5347(5)	9.7057(5)
c (Å)	19.6220(9)	14.0838(8)
α (°)	102.142(4)	90
β (°)	91.323(4)	97.517(5)
γ (°)	101.178(4)	90
Volume (Å^3)	2015.41(16)	1383.47(13)
Z	2	4
Calculated density (g cm^{-3})	1.736	1.919
Absorption coefficient (mm^{-1})	1.148	1.607
F (0 0 0)	1048.0	780.0
R_{int}	0.0319	0.0392
Goodness-of fit on F^2	1.021	1.000
R_1^{a} [$I > 2\sigma(I)$]	0.0467	0.0336
wR_2^{b} [$I > 2\sigma(I)$]	0.1141	0.0597

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $^bwR_2 = \sum\{[w(F_o^2 - F_c^2)^2]/\sum[w(F_0^2)]^2\}^{1/2}$.

Table 2. Bond lengths [å] and angles [°] for **1** and **2**.

[Cd(ip–OH)(H$_2$biim)(H$_2$O)][Cd(ip–OH)(H$_2$biim)(H$_2$O)$_3$]·8(H$_2$O) (**1**)			
Cd(2)–O(8)#1	2.438(4)	Cd(1)–O(1)	2.253(4)
Cd(2)–O(4 W)	2.318(4)	Cd(1)–N(1)	2.281(4)
Cd(2)–O(6)	2.254(3)	Cd(1)–O(2 W)	2.313(5)
Cd(2)–N(5)	2.286(5)	Cd(1)–N(3)	2.366(4)
Cd(2)–N(7)	2.331(4)	Cd(1)–O(3 W)	2.391(4)
Cd(2)–O(9)#1	2.407(5)	Cd(1)–O(1 W)	2.445(4)
O(1)–Cd(1)–N(1)	126.01(15)	O(3 W)–Cd(1)–O(1 W)	86.08(18)
O(1)–Cd(1)–O(2 W)	84.24(19)	O(6)–Cd(2)–N(5)	135.66(14)
N(1)–Cd(1)–O(2 W)	100.4(2)	O(6)–Cd(2)–O(4 W)	85.99(15)
O(1)–Cd(1)–N(3)	160.55(15)	N(5)–Cd(2)–O(4 W)	94.21(19)
N(1)–Cd(1)–N(3)	73.19(14)	O(6)–Cd(2)–N(7)	101.25(14)
O(2 W)–Cd(1)–N(3)	89.32(18)	N(5)–Cd(2)–N(7)	74.98(15)
O(1)–Cd(1)–O(3 W)	79.23(16)	O(4 W)–Cd(2)–N(7)	169.2(2)
N(1)–Cd(1)–O(3 W)	152.65(16)	O(6)–Cd(2)–O(9)#1	83.49(14)
O(2 W)–Cd(1)–O(3 W)	91.8(3)	N(5)–Cd(2)–O(9)#1	140.27(15)
N(3)–Cd(1)–O(3 W)	82.67(16)	O(4 W)–Cd(2)–O(9)#1	95.4(2)
O(1)–Cd(1)–O(1 W)	90.94(16)	N(7)–Cd(2)–O(9)#1	93.44(15)
N(1)–Cd(1)–O(1 W)	83.40(15)	O(6)–Cd(2)–O(8)#1	135.59(18)
O(2 W)–Cd(1)–O(1 W)	175.0(2)	N(5)–Cd(2)–O(8)#1	88.59(19)
N(3)–Cd(1)–O(1 W)	94.88(15)	O(4 W)–Cd(2)–O(8)#1	87.29(17)
N(7)–Cd(2)–O(8)#1	92.95(15)	O(9)#1–Cd(2)–O(8)#1	53.57(18)
[Cd(Himdc)(H$_2$biim)]$_n$ (**2**)			
Cd(1)–N(1)	2.240(3)	Cd(1)–N(2)#1	2.241(3)
Cd(1)–N(3)	2.316(3)	Cd(1)–N(5)	2.332(3)
Cd(1)–O(1)	2.457(3)	Cd(1)–O(4)#1	2.503(3)
N(1)–Cd(1)–N(2)#1	97.99(12)	N(3)–Cd(1)–N(5)	73.93(11)
N(1)–Cd(1)–N(3)	159.61(12)	N(1)–Cd(1)–O(1)	70.97(10)
N(2)#1–Cd(1)–N(3)	98.02(11)	N(2)#1–Cd(1)–O(1)	121.61(11)
N(1)–Cd(1)–N(5)	95.36(11)	N(3)–Cd(1)–O(1)	89.85(10)
N(2)#1–Cd(1)–N(5)	157.38(12)	N(5)–Cd(1)–O(1)	80.08(10)
N(1)–Cd(1)–O(4)#1	85.78(10)	N(5)–Cd(1)–O(4)#1	92.08(10)
N(2)#1–Cd(1)–O(4)#1	70.86(10)	O(1)–Cd(1)–O(4)#1	154.46(9)
N(3)–Cd(1)–O(4)#1	111.44(11)		

Symmetry codes: for **1**: #1 $x-1$, y, z; #2 $x+1$, y, z; for **2**: #1 $-x+1$, $y+1/2$, $-z+3/2$.

used only a single oxygen (O1) from its carboxylic group to bridge a Cd(II) site, a rare example of a multidentate ligand only adopting monodentate coordination. Owing to this type of coordination of ip–OH^{2-}, Cd1 cations are not linked into an infinite structure. In unit B, Cd2 is also six coordinate by two nitrogens (N5 and N7) from one H$_2$biim, three carboxylic oxygens (O6, O8#2 and O9#2) from two ip–OH^{2-}, and one water (O4 W), exhibiting a distorted octahedral coordination (figure 1). The Cd–N [2.286(5)–2.331(4) Å] and Cd–O [2.254(3)–2.438(4) Å] distances are in the normal range [28, 29]. The ip–OH^{2-} is μ_2-$\eta^1:\eta^1:\eta^1$ bridging in which two carboxylic groups are monodentate and bidentate chelating. The bridging μ_2-ip–OH^{2-} link Cd2 into a 1-D chain along the *a*-axis, while H$_2$biim as neutral ligands chelate Cd2 on opposite site of the chain. In **1**, unit A and unit B adopt ···BAABBA··· (figure 2). Noncovalent interactions such as hydrogen bond and $\pi\cdots\pi$ interactions play important roles in stabilization **1**. The crystal structure reveals that units A and B are stabilized by O–H···O interactions (O2 W···O3 2.832(8) Å, O5···O8 3.324(7) Å, O4 W···O9 2.800(6) Å), N–H···O interactions (N2···O7 2.839(7) Å, N4···O7 2.835(5) Å, N6···O3 2.734(5) Å, N8···O4 2.738(5) Å) to form 2-D supermolecular layers (figure 3(a), table S1). O–H···O interactions (O3 W···O4 2.780(7) Å) and

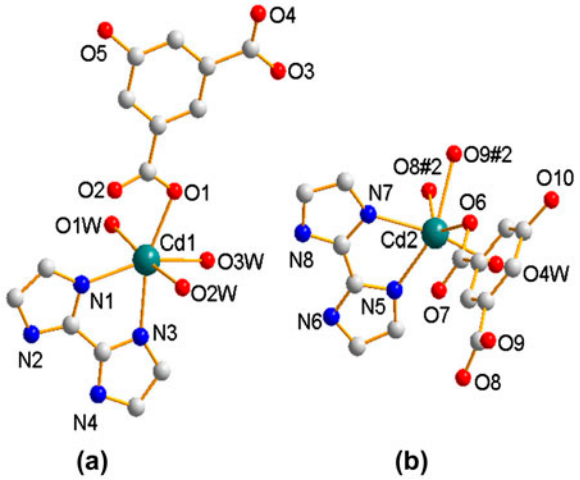

Figure 1. Coordination environments of Cd(II) in **1** (symmetry codes: #1: $x-1$, y, z; #2: $x+1$, y, z. All hydrogens and free waters are omitted for clarity).

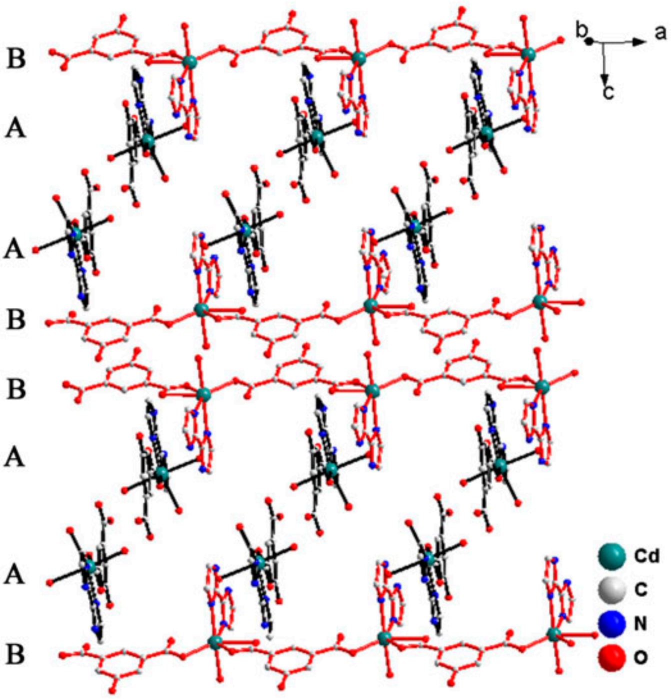

Figure 2. Ball and stick pattern of **1** (all hydrogens and free waters are omitted for clarity).

C–H$\cdots$O interactions (C3$\cdots$O10 3.358(7) Å) further connect A and B to form a 3-D supramolecular structure (figure 3(b), table S1). There exist four kinds of π$\cdots$π stacking

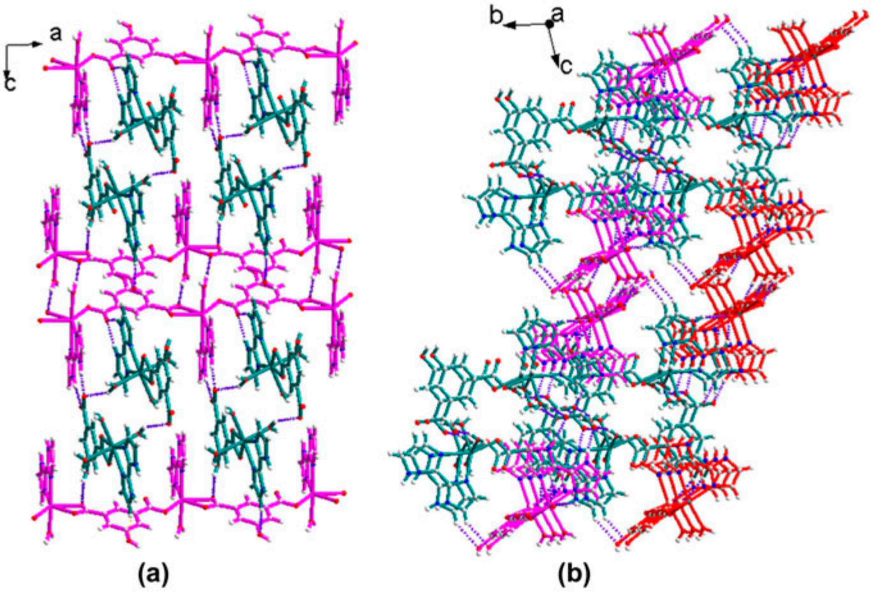

Figure 3. (a) Perspective view of the 2-D layer formed via hydrogen bond interactions. (b) Perspective view of the 3-D frameworks via hydrogen bond interactions. (All free waters are omitted for clarity).

interactions (figure 4(a)–(d), table S1), ip–OH^{2-}–ip–OH^{2-} with centroid-to-centroid distance of 3.464(3) Å, ip–OH^{2-}–H_2biim with centroid-to-centroid distances of 3.684(3) and 3.664(3) Å, and H_2biim–H_2biim with centroid-to-centroid distance of 3.795(3) Å. The hydrogen bonds and π···π interactions link the two parts of **1** into a stable 3-D supramolecular architecture.

3.2. *Crystal structure of 2*

The X-ray crystallographic analysis reveals that **2** crystallizes in the monoclinic space group *P*2(1)/*c*. The asymmetric unit of **2** consists of one Cd(II), one $Himdc^{2-}$, and one H_2biim, as shown in figure 5. Each Cd(II) is six-coordinate with a distorted octahedral geometry by two oxygens (Cd(1)–O(1) = 2.457(3) Å, Cd(1)–O(4)#1 = 2.503(3) Å, symmetry codes: #1 $-x+1$, $y+1/2$, $-z+3/2$) of two $Himdc^{2-}$, four nitrogens (Cd(1)–N(1) = 2.240 (3) Å, Cd(1)–N(2)#1 = 2.241(3) Å, Cd(1)–N(3) = 2.316(3) Å, Cd(1)–N(5) = 2.332(3) Å, symmetry codes: #1 $-x+1$, $y+1/2$, $-z+3/2$) of two $Himdc^{2-}$ and two H_2biim. In **2**, $Himdc^{2-}$ is a polydentate ligand connecting two Cd; N(1) and O(1) are bidentate chelating and N(2) and O(4) exhibit the same coordination to another Cd. In this way, Cd ions are linked by $Himdc^{2-}$ to form a 1-D wavy chain (figure 6(a)), and the dihedral angle of the two chelating rings around each cadmium (Cd–N–C–C–O) is 79.20(14)°. H_2biim are bidentate chelates arranging on both sides of the chain. The H_2biim give hydrogen bonds which play important roles in stabilization **2**. As shown in figure 6(b), neighboring chains are linked by C–H···O interactions (C1···O3 3.210(5) Å) to form a 2-D supermolecular structure along the *a*-axis, which further forms into a 3-D supramolecular network through

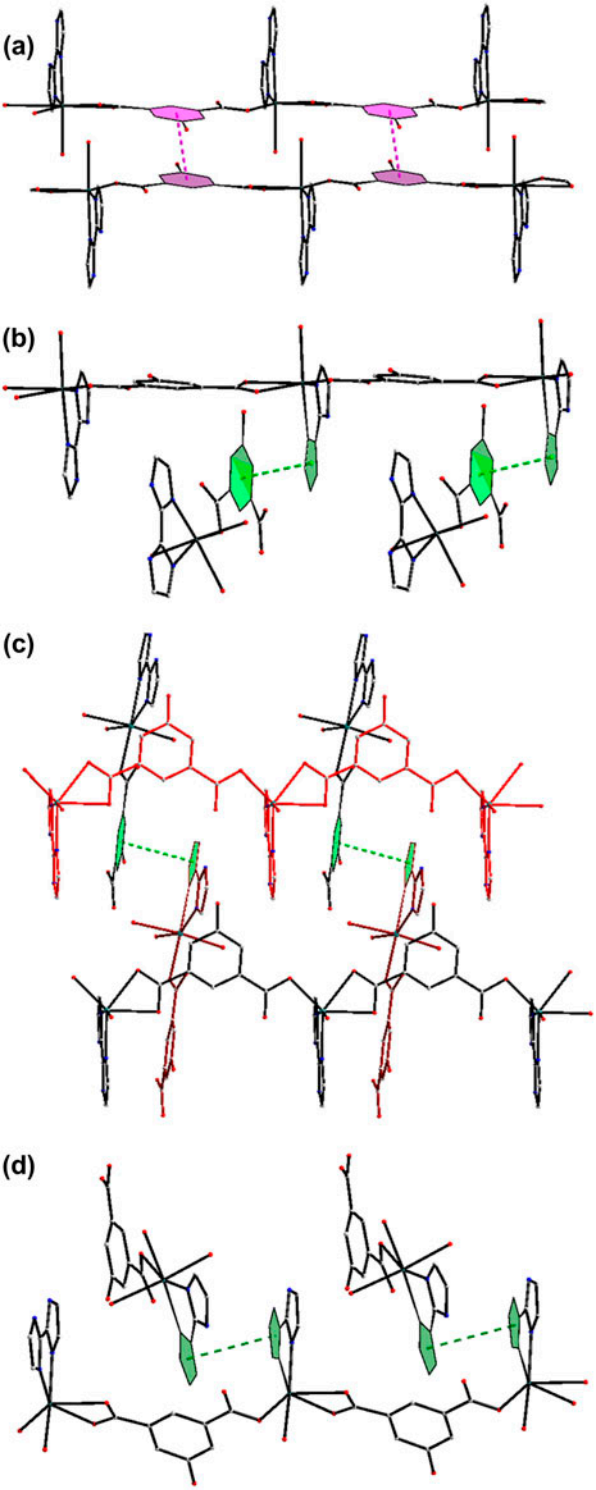

Figure 4. (a)–(d) Four kinds of π· · ·π interactions in **1**.

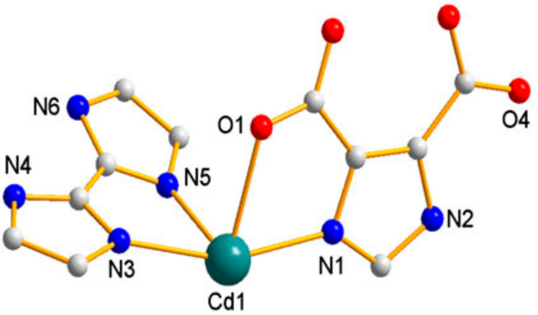

Figure 5. The asymmetric unit of **2** (all hydrogens are omitted for clarity).

C–H···O interactions (C8···O4 3.293(5) Å, C11···O4 3.316(5) Å) and N–H···O interactions (N4···O2 2.812(4) Å, N6···O1 2.771(4) Å).

3.3. *Photoluminescent properties*

Luminescent properties of compounds with d^{10} centers have potential applications in chemical sensors, photochemistry, and electroluminescent displays [30–32]. Solid state luminescent spectra of **1** and **2** are depicted in figure 7. Compound **1** exhibits blue light with one fluorescent emission band at $\lambda_{max} = 481$ nm upon photoexcitation at 360 nm, and **2** shows at $\lambda_{max} = 510$ nm ($\lambda_{ex} = 370$ nm). To further analyze the emission band, photoluminescent properties of H_2ip–OH, H_3imdc and H_2biim have also been investigated under the same experimental conditions. H_2ip–OH displays emission at 411 nm upon excitation at 360 nm (figure S1). H_3imdc displays emission at 449 nm upon excitation at 370 nm (figure S2). H_2biim displays emission peaks at 343 and 356 nm upon excitation at 280 nm (figure S3). The emissions of **1** and **2** are neither metal-to-ligand charge transfer nor ligand-to-metal transfer since Zn(II) and Cd(II) are difficult to oxidize or reduce [33, 34], but rather are assigned to intraligand emission [35]. Comparing with free ligands, emission bands of **1** and **2** are red-shifted. This may be assigned to coordination effectively increasing the rigidity of the ligands [36, 37].

3.4. *Thermal analyses*

Thermal behaviors of **1** and **2** were examined by TGA on polycrystalline sample (figure S4). **1** shows three weight loss steps. The first of 12.35% from 100 to 135 °C corresponds to loss of eight free waters (Calcd 13.47%). The second of 5.16% from 135 to 271 °C corresponds to loss of four coordination waters (Calcd 6.73%). The third weight loss of 57.61% from 271 to 546 °C is assigned to decomposition of ligands (Calcd 55.78%). The final decomposition product (24.88%) might be CdO (Calcd 24.02%). For **2**, a weight loss of 31.91% (Calcd 33.56%) was observed at 260–320 °C, corresponding to loss of H_2biim, and then loss of 36.57% (Calcd 38.30%) from 320 to 645 °C is attributed to the decomposition of H_3imdc ligands; the final decomposition product (31.52%) might be CdO (Calcd 32.13%).

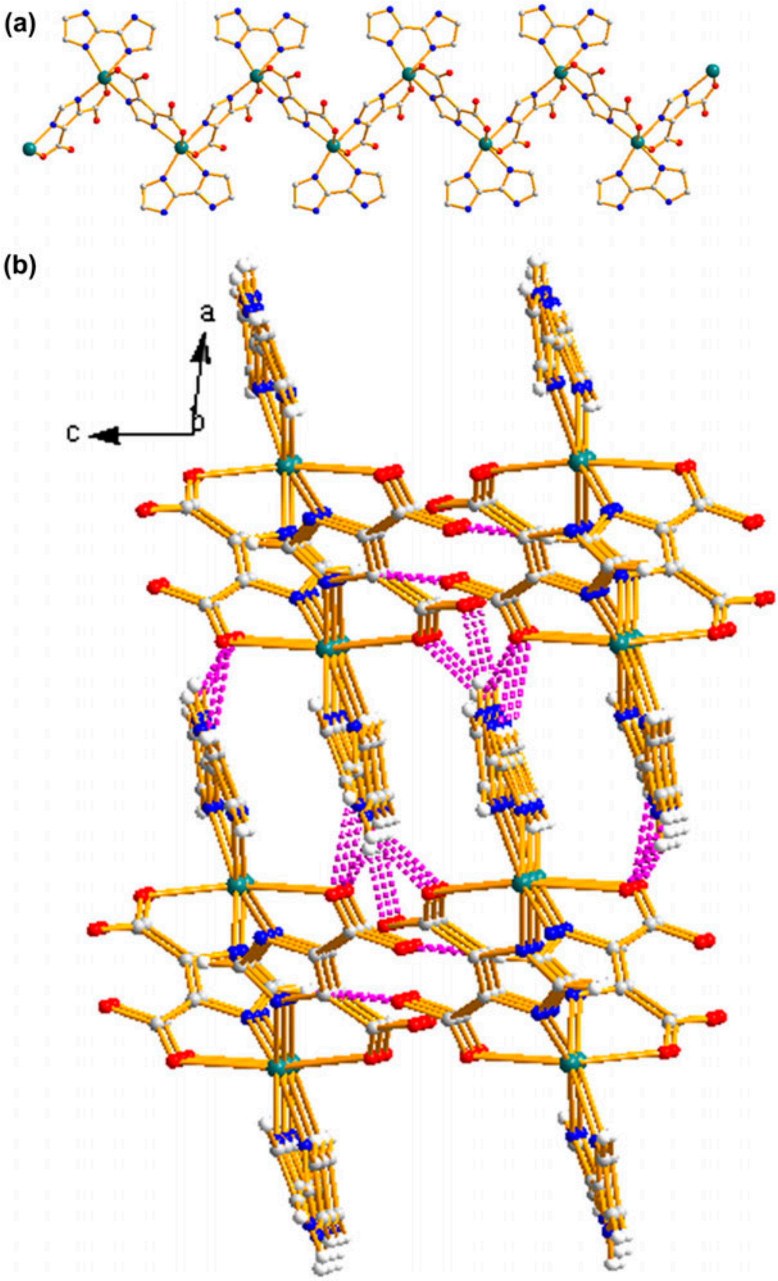

Figure 6. (a) The 1-D zigzag chain of **2**. (b) Perspective view of the 3-D frameworks via hydrogen bond interactions.

4. Conclusion

Two new coordination compounds, [Cd(ip–OH)(H_2biim)(H_2O)][Cd(ip–OH)(H_2biim)($H_2O)_3$]·8(H_2O) (**1**) and [Cd(Himdc)(H_2biim)]$_n$ (**2**), were synthesized and characterized.

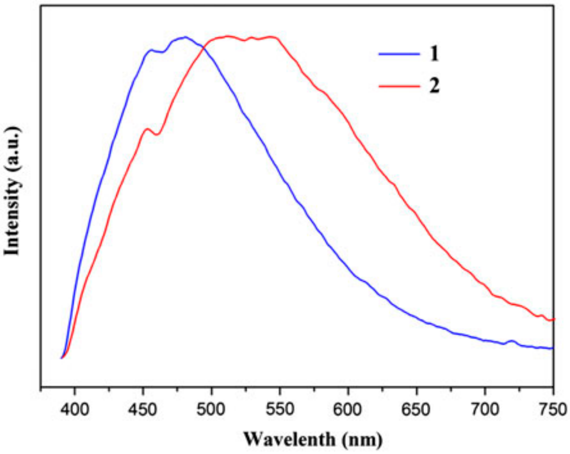

Figure 7. Solid state luminescent spectra of **1** ($\lambda_{ex} = 360$ nm) and **2** ($\lambda_{ex} = 370$ nm) at room temperature.

For **1**, the 3-D supramolecular network was formed from co-existing 0-D and 1-D motifs via hydrogen bonds and $\pi\cdots\pi$ interactions. **2** is a highly undulated chain, and neighboring chains are connected into a 3-D supramolecular network through hydrogen bonds. Luminescent properties indicated that **1** and **2** are candidates for hybrid inorganic-organic photo-active materials. Subsequent work will focus on the construction of complexes by reacting H_2biim with more metal ions to find new linking modes of H_2biim.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 895736 and 908293 for **1** and **2**. The data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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