



Three new metal–organic frameworks based on 2-propyl-1*H*-imidazole-4,5-dicarboxylate: Synthesis, crystal structure and luminescent properties

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ARTICLE INFO

Article history:

Received 27 September 2011

Accepted 9 November 2011

Available online 22 November 2011

Keywords:

2-Propyl-1*H*-imidazole-4,5-dicarboxy acid

Crystal structure

Luminescence

ABSTRACT

Three new complexes $[\text{Cd}(\text{H}_3\text{pimda})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Zn}(\text{H}_2\text{pimda})_2(\text{H}_2\text{O})_2] \cdot 3.5\text{H}_2\text{O}$ (**2**) and $[\text{Cd}_2(\text{Hpimda})_2(\text{DMF})_2]_n$ (**3**) (H_3pimda = 2-propyl-1*H*-imidazole-4,5-dicarboxy acid, DMF = *N,N'*-dimethylformamide) have been synthesized under hydrothermal or solvothermal conditions, respectively. Crystal structures of complexes **1–3** were determined by single crystal X-ray diffraction. Crystallographic studies on **1** and **2** reveal that both complexes are six-coordinated, whose geometries can be best described as distorted octahedron. Complex **3** was synthesized based on that of complexes **1** and **2**. We change the coordination environment of H_3pimda during the synthesis process of complex **3** using organic acid and organic solvent, accordingly, result in different structures ranging from 0D molecule (for **1** and **2**) to infinite 2D network (for **3**). Complexes **1–3** have blue fluorescent emissions at room temperature in the dimethylsulfoxide (DMSO) solution, which indicate they are potential blue luminescence materials. The blue fluorescent emissions of complexes **1–3** are due to the $\pi^* \rightarrow \pi$ transitions of intra-ligand.

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1. Introduction

Recently, many novel complexes with unique structures have attracted considerable attention not only due to their intriguing variety of architectures and topologies, but also because of their potential applications in materials with luminescent and nonlinear optical properties [1–5]. The selections of metal source and organic ligands play important parts in the crystal engineering of metal–organic frameworks. Meanwhile, we also should pay more attention to the external factors that may affect the structure of metal–organic complex, such as temperature, pressure and pH value [6]. In previous investigations, imidazole-class ligands were successfully utilized to construct numbers of metal complexes, whose luminescence properties have been studied [7–10]. H_3pimda has been used to construct Ni(II) and Co(II) complexes which have magnetic properties [11]. The molecular structure of H_3pimda is shown in Scheme 1. H_3pimda acts as a kind of imidazole carboxylic acid ligand has the following advantages: firstly, H_3pimda contains N and O atoms which can coordinate to the metal ions to form metal complexes. Secondly, the NH site of the imidazole ring and the carboxyl group can serve as multiple proton donor and acceptor providing an opportunity to form hydrogen bonds. Finally, to our knowledge, H_3pimda exhibits blue-green fluorescence in the solid state when excited at room temperature, which is a good candidate for synthesizing fluorescence materials [12]. Based on above reasons, we choose H_3pimda as the studied candidate. As different anionic environment

results in different coordination modes of the ligand, we can vary the anionic environment by organic acid and amine. The NH site of the imidazole cannot coordinate to the metal center when the organic acid was used, which can make the solvent molecule coordinate to the metal center, accordingly, the ligand adopt different coordination modes, and result in structural variation in complexes [13–16]. In this paper, we report the syntheses, structures and luminescent properties of two new Cd(II) complexes and one Zn(II) complex. The crystal structures of these complexes and the systematic investigation of the effect of organic acid will be represented and discussed. The relevance between the structures and the luminescent properties of the complexes are discussed in detail.

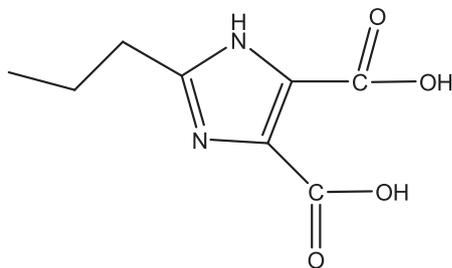
2. Experimental

2.1. Reagents and general techniques

All reagents and solvents were commercially available and used as received without further purification. Elemental analyses were performed on a Perkin-Elmer 240C element analyzer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer by KBr pellet in the 400–4000 cm^{-1} range. ^1H NMR spectra were recorded on a Bruker ACF 400 MHz spectrometer. ESI-MS spectra were recorded with Finnigan MATLCQTM mass spectrometer (USA) with a dual electrospray-ionization source. UV–Vis spectra were obtained on a Perkin-Elmer Lambda 20 spectrometer. Photoluminescence analyses and luminescence decay curves were performed on an Edinburgh FLS920 fluorescence spectrometer at room temperature in the range of 300–800 nm.

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Scheme 1. The molecular structure of H₃pimda.

2.2. Syntheses of complexes

2.2.1. Cd(H₂pimda)₂(H₂O)₂(H₂O)₄ (**1**) and [Zn(H₂pimda)₂(H₂O)₂].3.5 H₂O (**2**)

A mixture of H₃pimda (198 mg, 0.1 mmol), 3,3',4,4'-biphenyltetracarboxylic acid (33.0 mg, 0.1 mmol) and Cd(NO₃)₂·4H₂O (61.6 mg, 0.2 mmol) were dissolved in H₂O (5 mL), and stirred for half an hour, then heated in a sealed vial at 75 °C for 3 days. Colorless block crystals of **1** were obtained. Yield: 23.67 mg (77%). The products were washed with distilled water and dried in air. *Anal. Calc.* for **1**: C, 31.25; H, 4.89; N, 9.12. Found: C, 31.65; H, 4.83; N, 9.45%. IR (KBr pellet, cm⁻¹): 3433 (s), 2968 (m), 1712 (s), 1534 (vs), 1472 (m), 1391 (s), 1267 (m), 1052 (w), 776 (m). ¹H NMR (400 MHz, DMSO): δ = 13.73 (s, 1H, N-H), 4.35 (t, *J* = 5.0 Hz, 2H, -CH₂CH₂CH₃), 3.44 (m, *J* = 5.2 Hz, 2H, -CH₂CH₂CH₃), 1.06 (t, *J* = 7.0 Hz, 3H, -CH₂CH₂CH₃) ppm. ESI-MS: *m/z* = 615.0 [M]⁻, 614.0 [M-H]⁻, 569.9 [M-COOH]⁻.

A procedure similar to **1** was followed to prepare **2** except Cd(NO₃)₂·4H₂O (61.6 mg, 0.2 mmol) was replaced by Zn(AcO)₂ (43.9 mg, 0.2 mmol). Colorless block crystals of **2** were obtained. Yield: 19.97 mg (72%). The products were washed by distilled water and dried in air. *Anal. Calc.* for **2**: C, 34.61; H, 5.23; N, 10.09. Found: C, 34.25; H, 5.09; N, 9.92%. IR (KBr pellet, cm⁻¹): 3425 (s), 3169 (s), 2967 (m), 1713 (s), 1538 (vs), 1462 (m), 1400 (s), 1277 (m), 774 (w). ¹H NMR (400 MHz, DMSO): δ = 13.70 (s, 1H, N-H), 2.54 (br s, 2H, -CH₂CH₂CH₃), 1.46 (br s, 2H, -CH₂CH₂CH₃), 0.71 (t, *J* = 4.0 Hz,

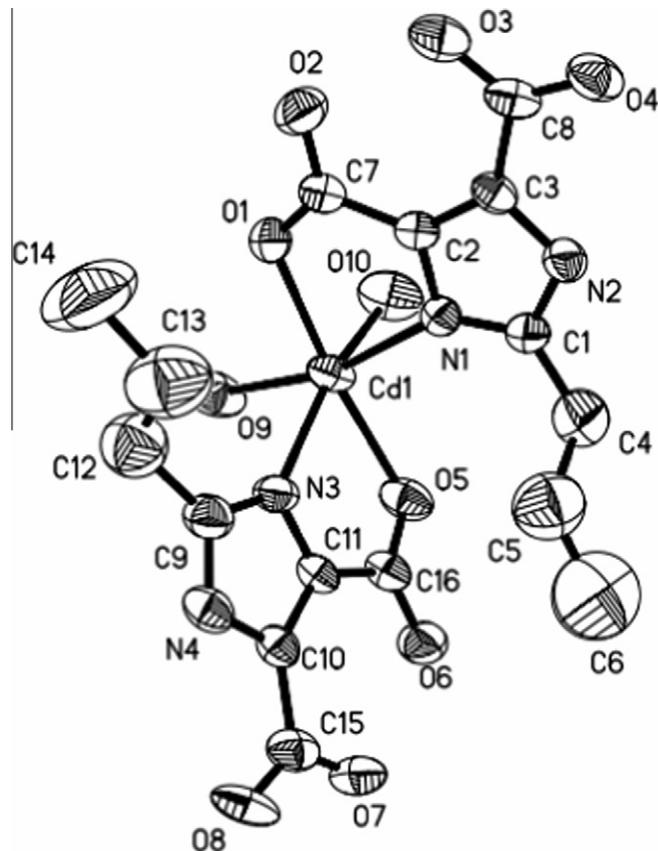


Fig. 1. The molecular structure of complex **1**.

3H, -CH₂CH₂CH₃) ppm. ESI-MS: *m/z* 910.8 [2M-H-11H₂O]⁻, 733.9 [2M-11H₂O-2CO₂-2COOH]⁻, 457.0 [M-5.5H₂O]⁻, 413.0 [M-CO₂]⁻. (It is a Zn monomer consisting of two crystallographically independent molecules in the asymmetric unit.)

Table 1

Crystal data and structure refinement parameters of complexes **1–3**.

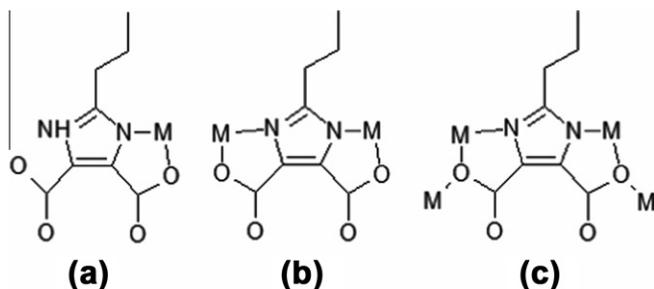
Complex	1	2	3
Formula	C ₁₆ H ₃₀ N ₄ O ₁₄ Cd	C ₁₆ H ₂₉ N ₄ O _{13.5} Zn	C ₂₂ H ₃₀ N ₆ O ₁₀ Cd ₂
Formula weight	614.85	554.77	763.34
<i>T</i> (K)	293		
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.6281(7)	10.6363(8)	9.5135(19)
<i>b</i> (Å)	10.7064(6)	14.3275(12)	20.601(4)
<i>c</i> (Å)	11.3800(8)	16.0498(13)	16.168(5)
α (°)	83.705(5)	85.909(10)	90
β (°)	81.723(6)	83.585(10)	112.72(2)
γ (°)	87.348(5)	85.733(10)	90
<i>V</i> (Å ³)	1273.09(14)	2418.9(3)	2922.8(12)
<i>Z</i>	2	2	4
<i>D</i> _{calc} (g cm ⁻³)	1.604	1.523	1.516
<i>F</i> (000)	628	1148	1520
θ Range for data collection (°)	3.27–29.21	1.86–25.04	3.05–27.48
Limiting indices	-14 ≤ <i>h</i> ≤ 14 -14 ≤ <i>k</i> ≤ 12 -15 ≤ <i>l</i> ≤ 11	-12 ≤ <i>h</i> ≤ 12 -13 ≤ <i>k</i> ≤ 17 -19 ≤ <i>l</i> ≤ 18	-12 ≤ <i>h</i> ≤ 12 -26 ≤ <i>k</i> ≤ 25 -20 ≤ <i>l</i> ≤ 20
Absorption correction	semi-empirical		
Data/restraints/parameters	5741/30/316	8377/0/622	6675/228/338
Goodness-of-fit (GOF) on <i>F</i> ²	0.736	1.028	1.661
<i>R</i> indices (all data)			
<i>R</i> ₁ ^a	0.1272	0.0707	0.0812
<i>wR</i> ₂ ^b	0.0979	0.1578	0.2095

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

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

Table 2a
Selected bond distance (Å) and angles (°) in complexes 1–2.

Complex 1		Complex 2			
Cd1–N1	2.309(4)	Zn1–O11	2.168(3)	Zn2–O1	2.154(3)
Cd1–N3	2.288(4)	Zn1–O15	2.189(3)	Zn2–O5	2.163(3)
Cd1–O1	2.361(3)	Zn1–O19	2.081(3)	Zn2–O9	2.118(3)
Cd1–O5	2.347(3)	Zn1–O20	2.098(3)	Zn2–O10	2.049(3)
Cd1–O9	2.286(4)	Zn1–N5	2.101(3)	Zn2–N1	2.135(3)
Cd1–O10	2.237(4)	Zn1–N7	2.150(3)	Zn2–N3	2.148(3)
O10–Cd1–N3	162.67(14)	O19–Zn1–O20	89.59(13)	O10–Zn2–O9	87.81(13)
O9–Cd1–N3	86.14(15)	O19–Zn1–N5	168.24(13)	O10–Zn2–N1	166.86(13)
O9–Cd1–N1	165.76(14)	O20–Zn1–N5	87.71(13)	O9–Zn2–N1	85.71(13)
N3–Cd1–N1	99.76(15)	O19–Zn1–N7	87.45(12)	O10–Zn2–N3	92.13(13)
O9–Cd1–O5	95.99(14)	O20–Zn1–N7	169.62(13)	O9–Zn2–N3	169.53(13)
N3–Cd1–O5	72.35(14)	N5–Zn1–N7	97.13(13)	N1–Zn2–N3	96.31(13)
O10–Cd1–O1	91.15(14)	O19–Zn1–O11	90.51(11)	O10–Zn2–O1	91.07(12)
O9–Cd1–O1	94.07(13)	O20–Zn1–O11	93.63(12)	O9–Zn2–O1	93.92(12)
N1–Cd1–O1	71.90(12)	N5–Zn1–O11	78.25(12)	N1–Zn2–O1	78.00(12)
O5–Cd1–O1	169.56(13)	N7–Zn1–O11	96.34(12)	N3–Zn2–O1	96.55(12)
		O19–Zn1–O15	92.17(11)	O10–Zn2–O5	90.05(12)
		O20–Zn1–O15	92.75(12)	O9–Zn2–O5	91.36(12)
		N5–Zn1–O15	99.39(12)	N1–Zn2–O5	101.50(12)
		N7–Zn1–O15	77.44(12)	N3–Zn2–O5	78.16(12)
		O11–Zn1–O15	173.09(11)	O1–Zn2–O5	174.64(11)



Scheme 2. (a) The coordination fashions of H₃pimda observed in complex 1 and 2; (b) the coordination fashions of H₃pimda observed in complex 3 on *ab* plane; (c) the coordination fashions of H₃pimda observed in complex 3 on *bc* plane.

2.2.2. [Cd₂(Hpimda)₂(DMF)₂]_n (**3**)

Complex **3** was synthesized by heating a mixture of Cd(NO₃)₂·4H₂O (61.6 mg, 0.2 mmol), H₃pimda (198 mg, 0.1 mmol), benzidine (18.4 mg, 0.1 mmol), terephthalic acid (16.6 mg, 0.1 mmol) in mixed solutions of DMF (3 mL) and H₂O (3 mL) at 75 °C for 48 h. Colorless block crystals of **3** were obtained. Yield: 56.64 mg (74%). The products were washed by distilled water and dried in air. *Anal. Calc.* for **3**: C, 34.61; N, 11.01; H, 3.93. *Found*: C, 34.92; N, 11.35; H, 3.99%. IR (KBr pellet, cm⁻¹): 3435 (s), 2965 (m), 1658 (vs), 1571 (vs), 1474 (vs), 1383 (vs), 1269 (s), 1125 (s), 921 (m), 787 (w), 677 (w). ¹H NMR (400 MHz, DMSO): δ = 13.71 (s, 1H, N–H), 4.35 (t, *J* = 5.0 Hz, 2H, –CH₂CH₂CH₃), 3.45 (m, *J* = 5.6 Hz, 2H, –CH₂CH₂CH₃), 1.05 (t, *J* = 7.0 Hz, 3H, –CH₂CH₂CH₃) ppm. ESI-MS: *m/z* = 572.9 [M–2DMF–COOH]⁻.

2.3. X-ray crystallography

Suitable single crystals of three complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected on a Siemens SMART 1000 CCD diffractometer equipped with graphite-monochromated MoK α radiation (λ = 0.71073 Å), operating at 293 ± 2 K. The structures were solved by direct method and refined by full-matrix least squares based on *F*² using the SHELXTL 5.1 software package [17]. The zinc and cadmium atoms were first located, carbon and nitrogen atoms were found in difference Fourier maps. The hydrogen atoms residing in the carbon atoms were located geometrically. All non-hydrogen atoms were refined anisotropically. Crystallographic data is given in Table 1.

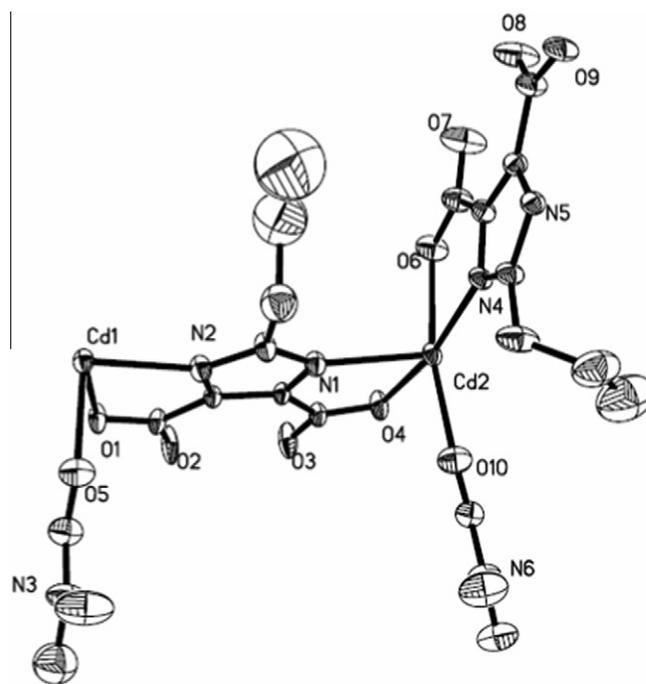


Fig. 2. The asymmetric unit of complex 3.

3. Results and discussion

3.1. Synthesis and characterization

By hydrothermal (for **1** and **2**) and solvothermal (for **3**) methods, we have obtained three complexes which are suitable for single crystal X-ray diffraction analyses. All complexes were characterized using elemental analysis, ¹H NMR, ESI-MS, IR spectroscopy and UV–Vis. Complexes **1**–**3** were subject to single crystal X-ray diffraction studies.

Complex **3** was synthesized based on that of complexes **1** and **2**. As different anionic environment causes different coordination modes of the ligand, we change the anionic environment of H₃

Table 2b
Selected bond distance (Å) and angles (°) in complexes **3**.

Complex 3					
Cd1–N5#1	2.227(3)	Cd1–O5	2.265(4)	Cd–N2	2.283(4)
Cd1–O1#2	2.292(3)	Cd1–O9#1	2.354(4)	Cd1–O1	2.511(3)
Cd2–N4	2.237(3)	Cd2–N1	2.268(4)	Cd2–O10	2.270(4)
Cd2–O4#3	2.294(3)	Cd2–O6	2.344(4)	Cd2–O4	2.534(3)
N5#1–Cd1–O5	101.45(14)	N5#1–Cd1–N2	110.85(14)	O5–Cd1–N2	96.09(16)
N5#1–Cd1–O1#2	111.74(13)	O5–Cd1–O1#2	89.41(14)	N2–Cd1–O1#2	134.93(12)
N5#1–Cd1–O9#1	74.20(12)	O5–Cd1–O9#1	173.83(14)	N2–Cd1–O9#1	89.61(15)
O1#2–Cd1–O9#1	88.22(13)	N5#1–Cd1–O1	167.02(13)	N5#1–Cd1–O1	167.02(13)
O5–Cd1–O1	91.33(13)	N2–Cd1–O1	69.53(12)	O1#2–Cd1–O1	65.64(12)
O9#1–Cd1–O1	92.88(12)	N4–Cd2–N1	111.54(13)	N4–Cd2–O10	99.60(13)
N1–Cd2–O10	93.60(15)	N4–Cd2–O4#3	113.24(13)	N1–Cd2–O4#3	134.21(12)
O10–Cd2–O4#3	88.11(14)	N4–Cd2–O6	74.24(12)	N1–Cd2–O6	97.07(15)
O10–Cd2–O6	169.07(15)	O4#3–Cd2–O6	86.18(14)	N4–Cd2–O4	164.71(13)
N1–Cd2–O4	68.97(11)	O10–Cd2–O4	95.59(13)	O4#3–Cd2–O4	65.33(12)
O6–Cd2–O4	90.48(12)				

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1/2, z - 1/2$; #2 $-x - 1, -y + 1, -z - 1$; #3 $-x - 1, -y + 1, -z$; #4 $x, -y + 1/2, z + 1/2$.

pimda using benzidine and terephthalic acid during the synthesis process of complex **3**, and we also change the solvent by mixed solutions of DMF and water, which can coordinate to the metal center, accordingly, result in different structures ranging from 0D molecule (for **1** and **2**) to infinite 2D network (for **3**).

Complexes **1–3** were prepared in good yields (>70%), all complexes are stable in the solid state and in the common solutions such as DMSO, CH₃CN, CH₂Cl₂ and DMF in the air conditions. All complexes were characterized by UV–Vis, IR spectroscopy and elemental analyses.

In the IR spectra of the complexes, the signals in complex **1** at 1534 and 1391 cm⁻¹ (1538 and 1400 cm⁻¹ for **2**) correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups of H₃pimda, respectively. The IR spectra of complexes **1** and **2** are similar, which indicates these two complexes may be isostructural, this was further confirmed by the single crystal X-ray diffraction analyses. The asymmetric stretching vibrations of the carboxylate groups in complex **3** were observed at ca. 1571 cm⁻¹ as a broad band, and the band of symmetric stretching vibrations was observed at ca. 1383 cm⁻¹, while that of the carboxylate groups of free H₃pimda ligand is at ca. 1700 cm⁻¹, which indicate the carboxylate groups of H₃pimda coordinate to the metal center [9,18] (Figs. 1–3 in Supplementary material).

3.2. Description of structures

The crystal structures of complexes **1** and **2** are similar. Single crystal X-ray diffraction analysis reveal that both complexes exhibit approximate octahedral geometry and crystallize in the triclinic space group $P\bar{1}$. The molecular structure of **1** consists of one Cd(II) cation, two H₂pimda⁻ anion ligands, two coordinated water molecules, and four solvate water molecules (Fig. 1). While the asymmetric unit of complex **2** consists of two independent complex molecules, each complex molecule contains one Zn(II) cations, two H₂pimda⁻ anion ligands, two coordinated water molecules, as well as three and half solvate water molecules. Complexes **1** and **2** are similar, so we take complex **1** as example to depict the structures of **1** and **2** in detail. Crystallographic data for the three complexes is summarized in Table 1 and selected bond lengths and angles are listed in Table 2a.

The coordination mode of H₂pimda⁻ dianion ligand in complex **1** is shown in Scheme 2(a). In complex **1**, the central Cd(II) ion is six-coordinated, forming a slightly distorted octahedron with CdO₄N₂ coordination mode; the two deprotonated carboxylate groups from the H₂pimda⁻ ligand provide two donor oxygen atoms, the two imidazolyl rings provide two nitrogen atoms, and two coordinated water molecules provide two oxygen atoms,

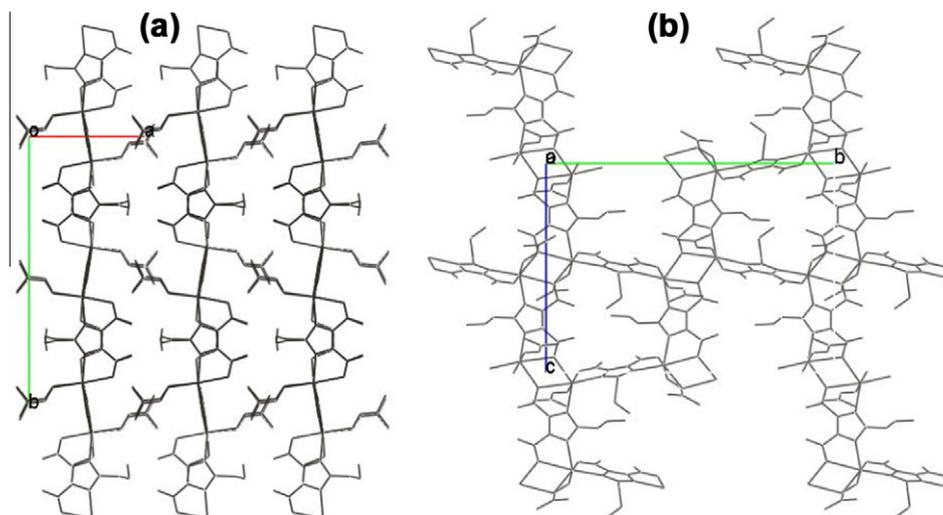


Fig. 3. (a) The packing structure of **3** on *ab* plane. (b) The packing structure of **3** on *bc* plane.

respectively, to bond to the central ion. Each deprotonated H_2pimda^- anion adopts a bidentate coordination mode providing two sites to bond to the central Cd(II) ion. Two imidazole rings nitrogen atoms chelate to the Cd(II) ion with Cd–N bond lengths of 2.288(4) and 2.309(4) Å, respectively, and the N–Cd–N bond angle is 99.8(2)°. All Cd–N and Cd–O bond lengths as well as the bond angles around Cd(II) ion are in the range expected for such coordination complexes (Table 2a).

Single crystal X-ray diffraction analysis revealed that the architecture of **3** is a two-dimensional network with monoclinic space group $P2_1/c$. The asymmetric unit of complex **3** consists of two cadmium ions, two Hpimda^{2-} dianion ligands and two DMF molecules, which is shown in Fig. 2. The central Cd(II) ion is

six-coordinated by two carboxyl oxygen atoms and two imidazole rings nitrogen atoms from two single Hpimda^{2-} ligands, one carboxyl oxygen atom from a single Hpimda^{2-} ligand and one oxygen atom from DMF molecule; forming a slightly distorted CdO_4N_2 octahedron. Bond lengths of Cd–O vary from 2.265(4) to 2.534(3) Å and the Cd–N distances range from 2.227(3) to 2.283(4) Å, respectively (Table 2b).

The Hpimda^{2-} dianion ligand has two different coordination modes in complex **3** on ab plane and bc plane because of the coordination of the DMF molecule (Fig. 3(a) and (b)), which are shown in Scheme 2(b) and (c). Hpimda^{2-} dianion ligand connect four Cd(II) ion centers in bis-(bridging) bidentate and monodentate modes; both carboxylate groups adopt the bidentate coordination modes,

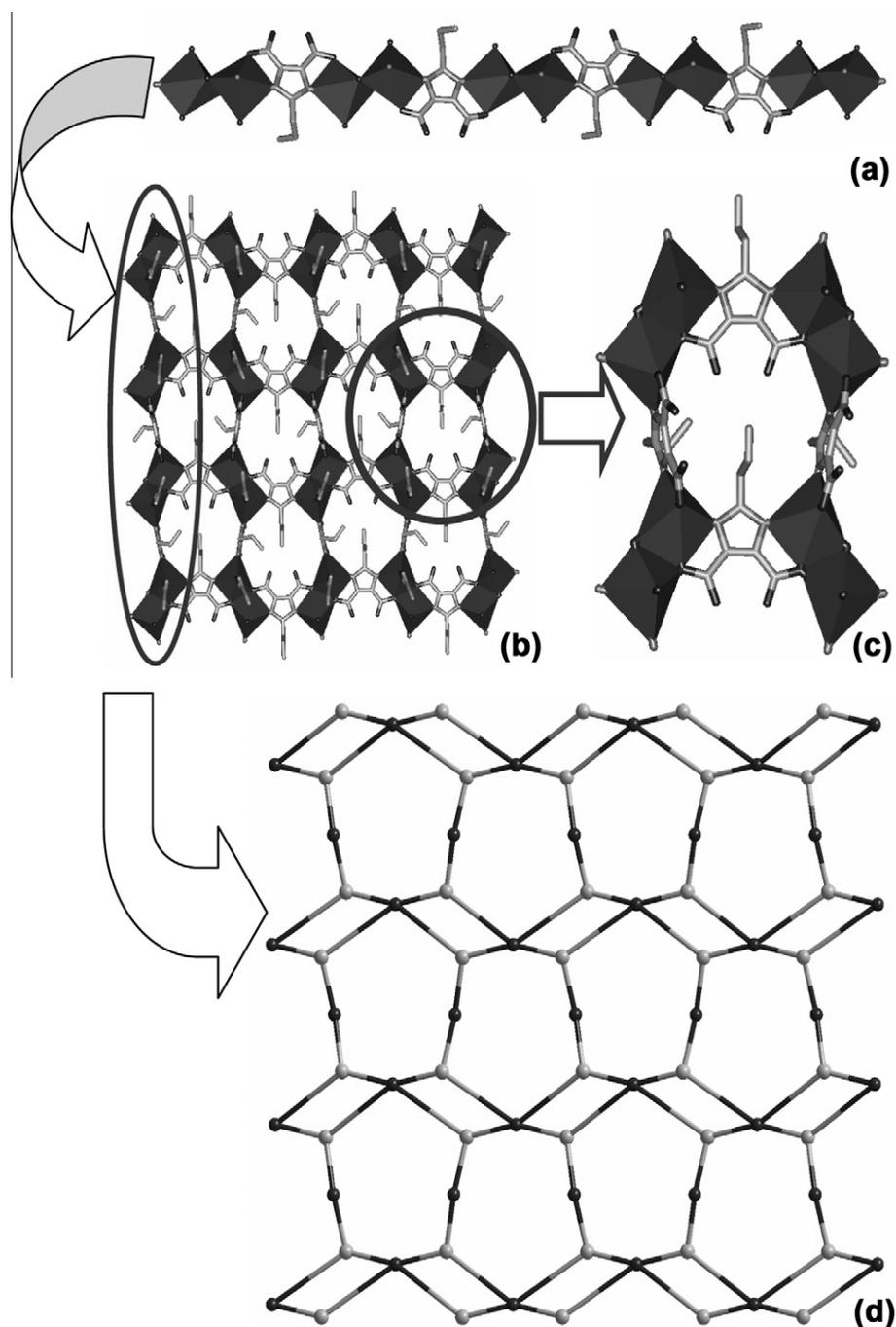


Fig. 4. (a) A polyhedral view of the zigzag chain constructed from Cd^{2+} ions and Hpimda^{2-} ligands. (b) A polyhedral view of the 2D layer in **3** along the a -axis. (c) The structure of an individual $\text{Cd}_8(\text{pimda})_4$ ring in **3**. (d) The fold ladder structure of **3**. Color codes: black balls represent Hpimda^{2-} ligands; gray balls represent Cd(II) cations.

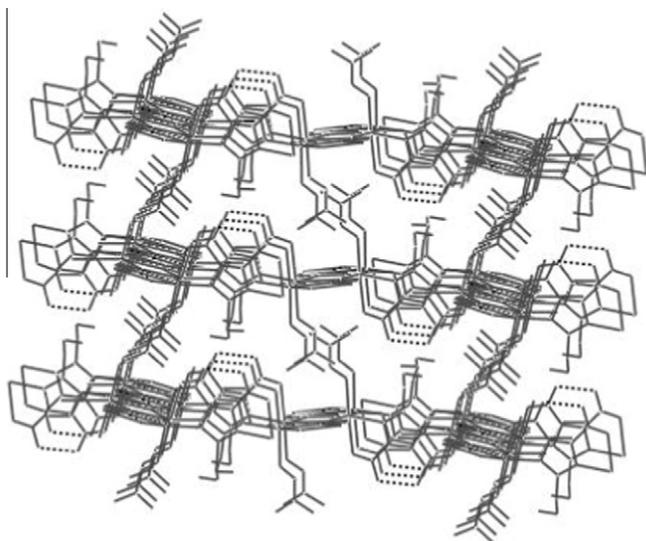


Fig. 5. The intramolecular hydrogen bonds diagram of complex 3.

and one oxygen atom of 4-carboxylate group of Hpimda^{2-} dianion ligand links two adjacent Cd(II) ions to form a dimer. The nitrogen atoms from Hpimda^{2-} dianion ligand bond the metal center and transfer these dimers by connecting to the central Cd(II) atoms to form a zigzag chain as described in Fig. 4(a). The propyl groups of Hpimda^{2-} dianion ligands are in trans arrangement mode in the complex, which can reduce the steric hindrance. Hpimda^{2-} dianion ligand in bc plane acts as a tetradentate ligand in **3** and connect two Cd(II) ion centers in bis-(bridging) bidentate mode Fig. 3(b); an oxygen atom of 4-carboxylate group of Hpimda^{2-} ligand and a nitrogen atom of the imidazole ring link to the same Cd(II) ion; an oxygen atom of 5-carboxylate group of Hpimda^{2-} ligand and a nitrogen atom of imidazole ring simultaneously link to another Cd(II) ion. Then, these chains are further connected into a novel 2D grid by the Hpimda^{2-} dianion ligand (Fig. 4(b)). Two adjacent Cd(II) ions forms a dimer through the carboxylate group of Hpimda^{2-} dianion ligand, then four adjacent dimers arrange in an individual $\text{Cd}_8(\text{pimda})_4$ ring as a secondary building unit (Fig. 4(c)). If consider the Hpimda^{2-} dianion ligand as a nod, each Cd(II) ion simultaneously links to three Hpimda^{2-} dianion ligands. Hpimda^{2-} dianion ligand has two connection modes, link to four and two Cd(II) ions, respectively, further form a distorted quadrilateral and octagon with (4.8.8) topological structure (Fig. 4(d)). If consider these dimers as nodes, these $\text{Cd}_8(\text{pimda})_4$ rings are further connected into a fold ladder. Additionally, because of the partial deprotonation of the carboxyl group, there are two

intramolecular hydrogen bonds in the asymmetric unit, namely $\text{O3-H3}\cdots\text{O2}$ (1.656 Å, 177.45°) and $\text{O7-H7}\cdots\text{O8}$ (1.633 Å, 177.62°), which make the complex more stable (Fig. 5). To further understand this 2D structure, the familiar dimeric Cd(II) units can be considered as a node, and the Hpimda^{2-} dianion ligand is a linker.

3.3. Luminescent properties

Table 3 presents the absorption and emission data for complexes **1–3** and H_3pimda in DMSO solution and in the solid state at room temperature. Three complexes show two main absorption bands, which are similar to H_3pimda in the UV region. The electronic absorption spectra of complexes show low energy absorption bands at ca. 334–365 nm (340 nm for ligand H_3pimda), and higher energy absorption bands at ca. 284–301 nm (291 nm for ligand H_3pimda), which can be attributed to ligand-centered $\pi \rightarrow \pi^*$ transitions [19].

The luminescent properties of these three metal complexes and H_3pimda have been investigated in the solutions of DMSO (Fig. 4 in Supplementary material). The emission bands of H_3pimda are observed at 417, 439^{sh} and 466 nm under excitation at maximum excitation wavelength of 312 nm in solution of DMSO. Complex **1** has blue fluorescent emissions in DMSO solution (concentration: $[\text{M}] \approx 10^{-4}$) at room temperature, with emission bands at 420, 439^{sh} and 466 nm (415, 439^{sh} and 465 nm for complex **2**; 415, 438^{sh}, 464 nm for **3**). For the multiple emission bands of complexes **1–3**, the main peaks locate at their expected positions compared with the free ligand. The resemblance of the emission spectra of complexes **1–3** and the free H_3pimda ligand in DMSO solution supports that the luminescence emissions of these complexes are due to ligand-centered $\pi^* \rightarrow \pi$ transitions. The quantum yields of complexes **1–3** and H_3pimda in DMSO solution were determined, with the value of H_3pimda is 0.022, while that of complexes **1–3** are 0.33, 0.34 and 0.11, respectively. The quantum yields of these complexes are greatly improved compared with free ligand. That because the chelation of H_3pimda to the metal center, which increases the rigidity of the ligand H_3pimda , and reduces the loss of energy by thermal vibration decay, enhances the ligand-centered $\pi^* \rightarrow \pi$ fluorescent emission [20]. Furthermore, the quantum yield of the complex **2** is higher than that of complexes **1** and **3**, which can be attributed to the heavy atom effect caused by the coordination of the ligand to the heavy Cd(II) center [21].

Complexes **1–3** have blue-green fluorescent emissions in the solid state at room temperature. Fig. 6 shows the excitation and emission spectra of complexes **1–3** as well as the free ligand in the solid state measured at room temperature. The emission bands of complex **1** are located at 404 and 460^{sh} nm (408, 467^{sh} and

Table 3
Photoluminescent data for **1–3** and H_3pimda .^a

Compound	Absorption (nm) $\epsilon/\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$	Excitation (λ , nm)	Emission (λ_{max} , nm)	Lifetime (μs)	Quantum yields (ϕ) ^b	Conditions
1	292 (22850), 360 (5491)	345	420, 439 ^{sh} , 466 404, 460	$\tau_1 = 1.07$ (51.73%) $\tau_2 = 7.97$ (48.27%)	0.33	DMSO, 298 K solid, 298 K
2	301 (16014), 365 (4397)	320	415, 439 ^{sh} , 465 408, 467 ^{sh} , 507	$\tau_1 = 1.43$ (43.36%) $\tau_2 = 9.85$ (56.64%)	0.34	DMSO, 298 K solid, 298 K
3	284 (16180), 334 (7640)	338	415, 438 ^{sh} , 464 480	$\tau_1 = 1.51$ (37.10%) $\tau_2 = 9.10$ (62.90%)	0.11	DMSO, 298 K solid, 298 K
H_3pimda	291 (16528), 340 (7998)	300	417, 439 ^{sh} , 466 415, 436 ^{sh} , 476		0.02	DMSO, 298 K solid, 298 K

^a Concentration: $[\text{M}] = 1 \times 10^{-4}$ M.

^b Determined using quinine sulfate in 0.1 M sulfuric acid as a standard.

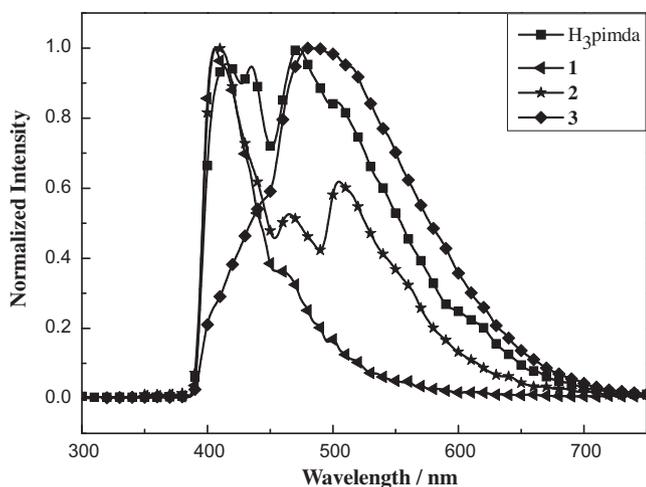


Fig. 6. The emission spectra of **1–3** and H₃pimda in the solid state measured at room temperature.

507 nm for complex **2**, 480 nm for **3**), which is similar to that of free ligand. The fluorescent emissions of complexes **1–3** can be assigned to the intra-ligand $\pi^* \rightarrow \pi$ transitions. In addition to the steady-state emission, we also performed time-resolved measurements of complexes **1–3**. The luminescence decay curves of complexes **1–3** are measured by the time-correlated single photon counting (TCSPC) technique at room temperature. The decay curves are well fitted into a double-exponential function: $I_0 = I + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, I_0 and I are the luminescent intensities when time $t = t$ and $t = 0$, respectively, whereas τ_1 and τ_2 are defined as the luminescent lifetimes (Fig. 5 in Supplementary material). The fluorescence decay processes of complexes **1–3** all consist of two components, corresponding lifetimes are $\tau_1 = 1.07 \mu\text{s}$, $\tau_2 = 7.97 \mu\text{s}$ for **1**; $\tau_1 = 1.43 \mu\text{s}$, $\tau_2 = 9.85 \mu\text{s}$ for **2**; $\tau_1 = 1.51 \mu\text{s}$, $\tau_2 = 9.10 \mu\text{s}$ for **3**, respectively (Table 3).

4. Conclusions

In conclusion, three new metal–organic complexes based on rigid H₃pimda ligand have been successfully synthesised under hydrothermal or solvothermal conditions, respectively. The structures of the complexes can affect their fluorescence emission features. We found that the luminescent properties of **1** and **2** are similar because of the similarity of the coordination environment around the metal center. Meanwhile, we use organic acid and amine to change the coordination environment of the ligand, which result in the NH site cannot coordinate to the metal center.

Owing to this, the structures of the complexes change from discrete molecule (for **1** and **2**) to 2D (structure for **3**). In complex **3**, the coordination behaviors of H₃pimda ligands on *ab* plane and *bc* plane are different because of the coordination of DMF. Their luminescent properties show that they all have potential applications in optoelectronic devices.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 20971031, 21071035 and 21171044), the China Postdoctoral Science Foundation Funded Project (No. 65204), and key the Natural Science Foundation of the Heilongjiang Province, China (No. ZD201009).

Appendix A. Supplementary data

CCDC 818014, 818016 and 818015 contain the supplementary crystallographic data for complexes **1–3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.11.015.

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