

基于 2-(4-吡啶基)-1*H*-咪唑-4,5-二羧酸配体的 镉(II)配合物的晶体结构及发光性质

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摘要: 在水热条件下, 以 2-(4-吡啶基)-1*H*-咪唑-4,5-二羧酸(H₃PIDC)和 1,10-菲咯啉衍生物为混合配体合成了 2 个镉(II)配合物 $[\text{Cd}_3(\text{HPIDC})_3(\text{DPPZ})_3 \cdot 7\text{H}_2\text{O}]_n$ (**1**)和 $[\text{Cd}(\text{HPIDC})(\text{Imphen})(\text{H}_2\text{O})]_2$ (**2**)(DPPZ=二吡啶并[3,2-*a*:2',3'-*c*]吩嗪; Imphen=咪唑并[4,5-*f*][1,10]菲咯啉), 利用元素分析、红外光谱以及单晶 X-射线衍射表征其结构。分析表明配合物 **1** 和 **2** 分别为一维链状与零维结构。此外, 2 个配合物展示了优良的热稳定性及光致发光特性。

关键词: 镉(II)配合物; 2-(4-吡啶基)-1*H*-咪唑-4,5-二羧酸; 1,10-菲咯啉衍生物; 晶体结构; 发光

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Cd(II) Complexes Based on 2-(Pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylic Acid Ligand: Crystal Structures and Luminescent Properties

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Abstract: Two cadmium(II) complexes based on 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylic acid (H₃PIDC) and 1,10-phenanthroline's derivatives mixed ligands, namely, $[\text{Cd}_3(\text{HPIDC})_3(\text{DPPZ})_3 \cdot 7\text{H}_2\text{O}]_n$ (**1**) and $[\text{Cd}(\text{HPIDC})(\text{Imphen})(\text{H}_2\text{O})]_2$ (**2**) (DPPZ=dipyrido[3,2-*a*:2',3'-*c*]phenazine, Imphen=imidazo[4,5-*f*][1,10]phenanthroline), have been synthesized under hydrothermal conditions and characterized by elemental analysis, infrared spectrum and single-crystal X-ray diffraction. Complexes **1** and **2** are one-dimensional chain and zero-dimensional structures, respectively. Two complexes exhibit excellent thermal stabilities and photoluminescent properties. CCDC: 1040581, **1**; 1040582, **2**.

Key words: cadmium(II) complex; 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylic acid; 1,10-phenanthroline's derivative; crystal structure; luminescence

The design and synthesis of metal-organic frameworks (MOFs) are of great interest not only for their potential applications in luminescence^[1], absorption^[2],

catalysis^[3] and magnetism^[4], but also for their intriguing variety of architectures and fascinating new topologies^[5]. So far, a large number of mixed-ligand MOFs

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with versatile dimensional structures have been rationally designed and physically characterized^[6]. The choice of organic ligands is extremely important because they can control and adjust the structures of MOFs. Much attention has been paid to employing the multifunctional *N,O*-donor ligands, which usually possess two or more coordination sites and can be assembled around metal ions in various arrangements. These ligands include pyrazine dicarboxylic acids^[7], pyridine dicarboxylic acids^[8], some carboxyl derivatives of 1,10-phenanthroline^[9-10] and imidazole-4,5-dicarboxylic acids ligands. It is well known that imidazole-4,5-dicarboxylic acids are excellent candidates for preparing novel MOFs, because of their versatile coordination modes and potential hydrogen-bonding donors and acceptors. There are some reports of MOFs bearing 2-propyl-imidazole-4,5-dicarboxylic acid^[11], 2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid^[12], 2-(3-methoxyphenyl)-1*H*-imidazole-4,5-dicarboxylic acid^[13], 2-(pyridine-2-yl)-1*H*-imidazole-4,5-dicarboxylic acid^[14], 2-(pyridine-3-yl)-1*H*-imidazole-4,5-dicarboxylic acid^[15], 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylic acid (H_3PIDC)^[16]. Nevertheless, to date, there are no reports concerning MOFs based on imidazole-4,5-dicarboxylic acids and 1,10-phenanthroline's derivatives mixed ligands. In this context, we report the syntheses and characterization of two novel cadmium (II) MOFs, $\{[Cd_3(HPIDC)_3(DPPZ)_3] \cdot 7H_2O\}_n$ (**1**) and $[Cd(HPIDC)(Imphen)(H_2O)]_2$ (**2**) (DPPZ=dipyrido [3,2-*a*:2',3'-*c*] phenazine, Imphen=imidazo[4,5-*f*] [1,10]phenanthroline). Furthermore, the thermal stabilities and luminescence properties of these two complexes have also been investigated.

1 Experimental

1.1 Chemicals and general methods

All chemicals were used as supplied from commercial sources without further purification. Elemental analyses of carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240C element analyzer. Fourier transform infrared (FT-IR) spectra was recorded on a Nicolet Nexus 470 FT-IR (America thermo-electricity Company) with 2 cm^{-1} resolution in

the range of $4\ 000\sim400\text{ cm}^{-1}$, using KBr pellets. Thermogravimetric analysis (TGA) was performed on a TA Instruments with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under air atmosphere. The photoluminescent behaviors of the complexes were studied using a Perkin-Elmer LS55 spectrometer.

1.2 Syntheses of complexes

1.2.1 Synthesis of complex **1**

$CdSO_4 \cdot 8H_2O$ (0.025 7 g, 0.1 mmol), H_3PIDC (0.042 2 g, 0.2 mmol) and DPPZ (0.056 4 g, 0.2 mmol) were dissolved in distilled water (15 mL), and NaOH aqueous solution was added until the pH value of the system was adjusted to about 4. The resulting solution was sealed in a 23 mL Teflon-lined stainless autoclave and heated at $150\text{ }^\circ\text{C}$ for 3 d under autogenous pressure. After cooling to room temperature, a mixture of yellow block crystals and powder were obtained. The crystals of **1** are picked out from the solid mixture in 43.4% yield based on $CdSO_4 \cdot 8H_2O$. Anal. Calcd. for **1** $C_{84}H_{59}N_{21}O_{19}Cd_3(\%)$: C, 50.35; H, 2.97; N, 14.68. Found(%): C, 50.73; H, 3.09; N, 14.48. IR spectrum (KBr, cm^{-1}): 3 431(s), 1 690(m), 1 640(s), 1 562(s), 1 415(s), 1 134(m), 1 021(m), 963(w), 927(w), 809(m), 644(s), 528(m).

1.2.2 Synthesis of complex **2**

An identical procedure with **1** was followed to prepare **2** except DPPZ was replaced by Imphen. Yellow crystals of complex **2** suitable for X-ray single-crystal diffraction analysis were picked out from the solid mixture in 54.8% yield based on $CdSO_4 \cdot 8H_2O$. Anal. Calcd. for **2** $C_{46}H_{30}N_{14}O_{10}Cd_2(\%)$: C, 47.48; H, 2.60; N, 16.85. Found(%): C, 47.40; H, 2.71; N, 16.80. IR spectrum (KBr, cm^{-1}): 3 424(s), 1 686(m), 1 577(s), 1 439(s), 1 361(s), 1 251(m), 1 044(m), 924(w), 804(m), 732(m), 649(m), 537(w).

1.3 Structure determination

Crystallographic data of two complexes were collected at room temperature on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ ($\lambda=0.071\ 073\text{ nm}$) radiation by using an ω - 2θ scan method at $292(2)\text{ K}$. All the structures were solved by direct methods with SHELXS-97 program^[17] and refined by full-matrix least-squares techniques on F^2 with SHELXL 97^[18]. All of

the non-hydrogen atoms were easily found from the different Fourier map and refined anisotropically, whereas the hydrogen atoms of the complexes were placed by geometrical considerations and were added to the structure factor calculation. In complex **1**, the hydrogen atoms attached to water molecules could not be positioned reliably. The detailed crystallographic data and structure refinement parameters for two complexes are summarized in Table 1, and selected bond lengths and angles of **1** and **2** are listed in

Table 2.

CCDC: 1040581, **1**; 1040582, **2**.

2 Results and discussion

2.1 Description of the crystal structures

2.1.1 Structure description of **1**

As shown in Fig.1, the asymmetric unit of **1** contains one point five crystallographically independent Cd²⁺ cations (Cd1 and Cd2), one point five HPIDC²⁻ ligands, one point five DPPZ ligands and three point

Table 1 Crystal data and structure refinements for complexes **1 and **2****

Complex	1	2
Formula	C ₈₄ H ₅₉ N ₂₁ O ₁₉ Cd ₃	C ₄₆ H ₃₀ N ₁₄ O ₁₀ Cd ₂
Formula weight	2 003.72	1 163.64
Crystal system	Orthorhombic	Triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> $\bar{1}$
Crystal size / mm	0.403×0.306×0.176	0.373×0.225×0.104
<i>a</i> / nm	1.939 3(3)	0.971 19(19)
<i>b</i> / nm	1.392 8(2)	0.996 2(2)
<i>c</i> / nm	1.457 1(2)	1.287 3(3)
α / (°)	90.00	73.587(3)
β / (°)	90.00	76.304(3)
γ / (°)	90.00	61.486(2)
<i>V</i> / nm ³	3.935 7(10)	1.042 2(4)
<i>Z</i>	2	1
Goodness-of-fit on <i>F</i> ²	0.966	0.998
Reflns collected / unique	21 872 / 7 789	5 633 / 3 999
θ range / (°)	1.40 to 26.12	1.66 to 26.15
<i>R</i> (<i>I</i> >2 σ (<i>I</i>))	<i>R</i> ₁ =0.052 9, <i>wR</i> ₂ =0.078 0	<i>R</i> ₁ =0.037 2, <i>wR</i> ₂ =0.081 2
<i>R</i> (all data)	<i>R</i> ₁ =0.123 6, <i>wR</i> ₂ =0.096 9	<i>R</i> ₁ =0.042 3, <i>wR</i> ₂ =0.083 8

Table 2 Selected bond lengths (nm) and bond angles (°) for complexes **1 and **2****

Complex 1					
Cd2-N1	0.235 0(9)	Cd2-N6	0.224 3(9)	Cd2-O4	0.250 1(11)
Cd1-N5	0.226 2(9)	Cd1-N8	0.234 1(9)	Cd1-O1	0.237 6(8)
N1-Cd2-N2	71.1(3)	O5-Cd2-O4	118.0(4)	N6-Cd2-O5	93.7(3)
N5-Cd1-N8	97.1(4)	N5-Cd1-O1	72.5(3)	O1-Cd1-O1 ⁱ	120.8(4)
Complex 2					
Cd1-O1W	0.225 7(3)	Cd1-N1	0.234 4(3)	Cd1-O3	0.233 0(3)
Cd1-N5	0.232 0(3)	Cd1-N2	0.233 1(4)	Cd1-O3 ⁱ	0.229 3(3)
O1W-Cd1-N5	91.09(11)	O1W-Cd1-O3	96.70(11)	N5-Cd1-O3	72.34(10)
O1W-Cd1-N2	167.22(11)	N5-Cd1-N2	93.52(11)	N2-Cd1-N1	71.15(11)

Symmetry codes: ⁱ -*x*+1, -*y*+1, -*z*+1

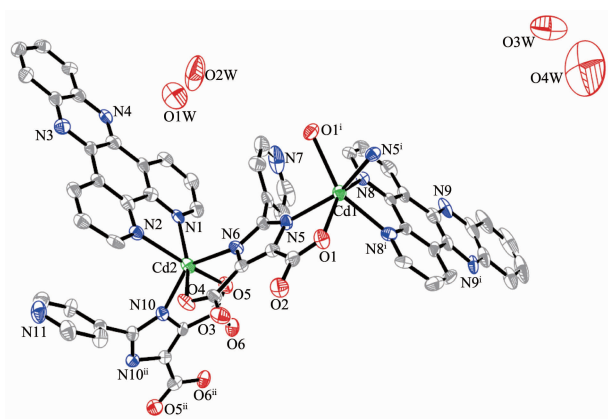


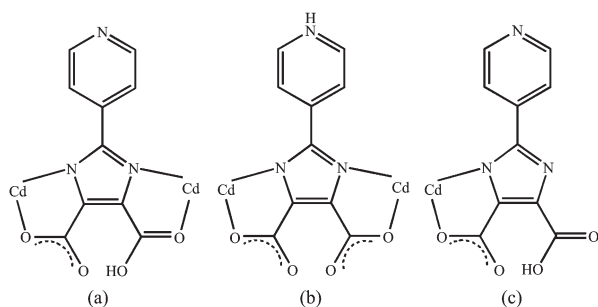
Fig.1 Coordination environments of Cd^{2+} atoms in complex **1** with displacement ellipsoids at 30% probability level

ⁱ $-x+1, -y+1, -z+1$; ⁱⁱ $-x+2, -y+1, z$

Fig.1 Coordination environments of Cd^{2+} atoms in complex **1** with displacement ellipsoids at 30% probability level

five lattice water molecules. Cd2 lies in general positions, while Cd1 is located at an inversion center. Cd2 and Cd1 are all six coordinated O_2N_4 and reside in the distorted octahedral coordination environment: two oxygen atoms (O4, O5 or O1, O1ⁱ, Symmetry code: ⁱ $-x+1, -y+1, -z+1$) from two different HPIDC²⁻ ligands, and four nitrogen atoms (N1, N2, N6, N10 or N8, N8ⁱ, N5, N5ⁱ, Symmetry code: ⁱ $-x+1, -y+1, -z+1$) from one DPPZ ligand and two different HPIDC²⁻ ligands. The Cd-O and Cd-N bond lengths are in the range of 0.237 6(8)~0.250 1(11) nm and 0.224 3(9)~0.238 6(9) nm, respectively. All Cd-O and Cd-N bond lengths are in agreement with those reported in other Cd^{2+} coordination compounds^[19].

The neighboring two Cd^{2+} units are linked by one HPIDC²⁻ ligand in bis-chelating mode (Scheme 1(a) and 1(b)) to form an infinite 1D chain along the *a* axis with all the DPPZ ligands attached to three sides, as



Scheme 1 Coordination patterns of H_3PIDC ligand in complexes **1** and **2**

shown in Fig.2. The $\text{Cd2} \cdots \text{Cd1}$ and $\text{Cd2} \cdots \text{Cd2}^{\text{ii}}$ distances bridged by the one HPIDC²⁻ ligand are 0.674 1 and 0.671 2 nm, respectively. The neighboring 1D chains interact through π - π stackings between the DPPZ ligands (centroid-to-centroid distance *ca.* 0.343 2 nm, Fig.3) to yield a two-dimensional layer structure.

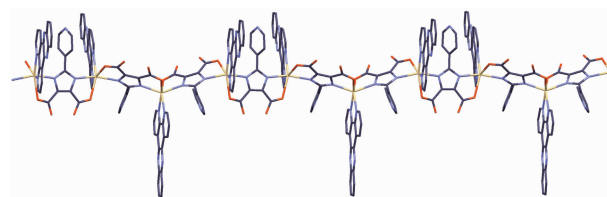


Fig.2 One-dimensional chain structure of complex **1** along *a* axis

Fig.2 One-dimensional chain structure of complex **1** along *a* axis

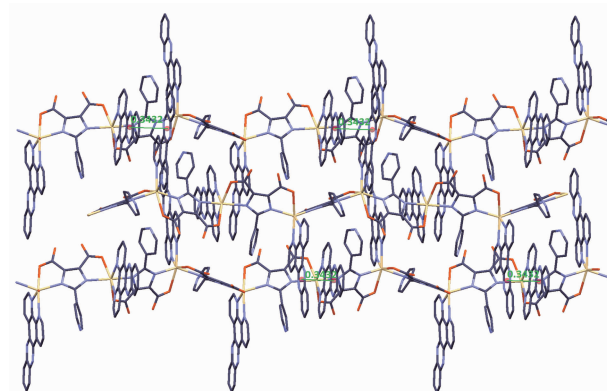


Fig.3 Two-dimensional layer structure of **1**

Fig.3 Two-dimensional layer structure of **1**

Although the HPIDC²⁻ ligand in complex **1** has only one bis-chelating coordination mode, two carboxylic groups in a H_3PIDC ligand exist in partially (Scheme 1(a)) and fully (Scheme 1(b)) deprotonated forms. It is remarkable that there are the partially protonated pyridine of HPIDC²⁻ ligands in complex **1** and it is not surprising to find protonated pyridine^[20].

2.1.2 Structure description of **2**

As shown in Fig.4(a), the crystal structure of **2** consists of a discrete dinuclear $[\text{Cd}(\text{HPIDC})(\text{Imphen})(\text{H}_2\text{O})_2]$. The $[\text{Cd}(\text{HPIDC})(\text{Imphen})(\text{H}_2\text{O})_2]$ dimer comprises two HPIDC²⁻ ligands, two Imphen ligands, two water molecules and two Cd(II) atoms. Each Cd(II) atom in **2** is coordinated by three nitrogen atoms (N1 and N2 atoms from a chelating Imphen, and N5 from a HPIDC²⁻ ligand), two oxygen atoms (O3 and O3ⁱ

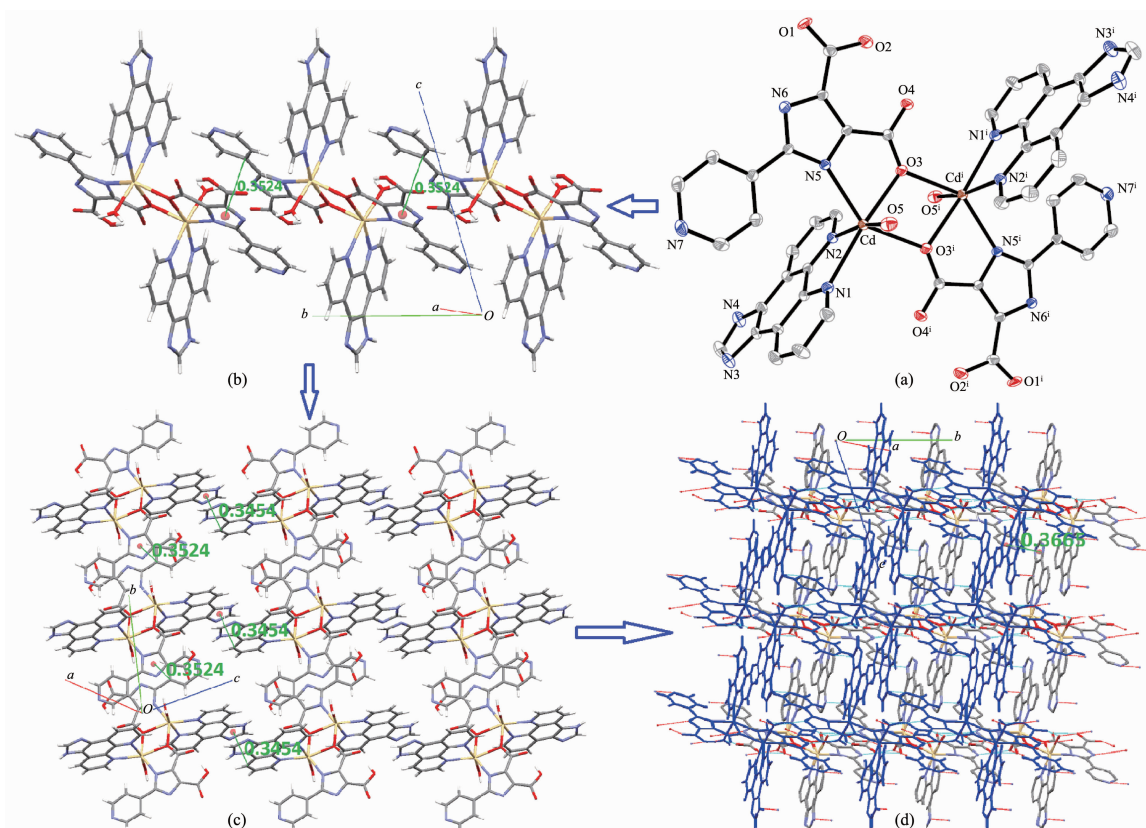


Fig.4 (a) Coordination environment of Cd^{2+} in complex **2** with displacement ellipsoids at 30% probability level (All the hydrogen atoms are omitted for clarity; Symmetry code: $^i -x+1, -y+1, -z+1$); (b) One-dimensional chain structure of **2**; (c) Two-dimensional layer structure of **2**; (d) Three-dimensional supramolecular network of **2** via hydrogen bonds and π - π interactions

atoms from two different HPIDC^{2-} ligands) and one water molecule in a slightly distorted octahedral geometry. Coordination mode of H_3PIDC ligand in complex **2** is shown in Scheme 1(c).

The distances of the Cd-O bond (0.225 7(3)~0.233 0(3) nm) and Cd-N bond (0.232 0(3) and 0.234 4(3) nm) are near to those of reported^[19]. The adjacent Cd(II) atoms are bridged by two HPIDC^{2-} ligands to form a dimer with Cd...Cd distance of 0.373 9 nm. The neighboring discrete dimers are assembled via π - π stacking interactions between two HPIDC^{2-} ligands (atom-to-centroid distance: 0.352 4 nm) into a 1D

chain motif (Fig.4(b)), and then the adjacent chain further interact to form a 2D layer structure through π - π interactions between Imphen ligands (atom-to-centroid distance: 0.345 4 nm, Fig.4(c)). Simultaneously, these 2D layers ulteriorly stacked to furnish a 3D supramolecular network (Fig.4(d)) via π - π interactions between Imphen ligands (centroid-to-centroid distance *ca.* 0.366 5 nm). In addition, the N-H...N, O-H...N, O-H...O hydrogen bonds (Table 3) involving Imphen ligands, HPIDC^{2-} ligands and the water molecules play a vital role in further extend and consolidate the 0D dimers arrays into an interesting 3D supramolecular

Table 3 Hydrogen bond lengths (nm) and bond angles ($^\circ$) of complex **2**

D-H...A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle \text{DHA}$
N3-H4...N7 ⁱⁱ	0.078(6)	0.220(6)	0.295 9(5)	165(6)
O1W-H1WA...N6 ⁱⁱⁱ	0.084 2(10)	0.199(3)	0.278 5(4)	158(6)
O1W-H1WA...O1 ⁱⁱⁱ	0.084 2(10)	0.265(7)	0.314 4(4)	119(6)
O1W-H1WB...O1 ^{iv}	0.084 2(10)	0.202(6)	0.267 9(4)	135(7)

Symmetry code: ⁱⁱ $-x+2, -y, -z$; ⁱⁱⁱ $-x+1, -y, -z+1$; ^{iv} $x+1, y, z$

structure.

2.2 TGA

Thermogravimetric experiment of complexes **1** and **2** was performed to explore their thermal stabilities. As shown in Fig.5, two distinct weight losses were observed for these two complexes. The first obvious weight loss of 6.01% and 3.20% for **1** and **2** are in the range of 97~140 °C and 140~220 °C, assigned to the release of the water molecules (Calcd. 6.29% and 3.09%, respectively). The second sharp weight loss of 77.29% and 75.99% are ascribable to the decomposition of organic ligands HPIDC²⁻ and DPPZ/Imphen (Calcd. 76.83%: HPIDC²⁻ 34.61% and DPPZ 42.22% for **1**; Calcd. 77.58%: HPIDC²⁻ 39.73% and Imphen 37.85% for **2**) occurring from 313 to 670 °C and 285 to 653 °C, which means the degradation of the frameworks. The final products may be CdO for complexes **1** and **2**.

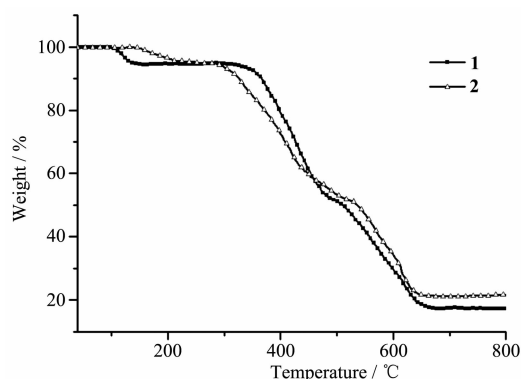


Fig.5 TG curves of complexes **1** and **2**

2.3 Photoluminescence properties

The photoluminescent emission properties of **1** and **2** were investigated in the solid state at room temperature. The free ligands H₃PIDC, DPPZ and Imphen exhibit the strongest emission peaks at about 470 nm^[19], 444 nm^[21] and 460 nm^[22] from 300 to 720 nm, respectively. Compared to the free ligands, the strongest emission peaks for **1** and **2** are at 582 and 545 nm (Fig.6, excitation at 365 nm), respectively. According to the documents, the Cd(II) ions is difficult to oxidize or reduce because of the *d*¹⁰ configuration. As a result, the emissions of the two complexes are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT). Compared with

the luminescent spectra of free ligands, the emission spectra of two complexes are red-shifted and obviously similar to that of H₃PIDC, DPPZ or Imphen. So, the photoluminescence of **1** and **2** might originate from the intraligand $\pi \rightarrow \pi^*$ transitions mainly through the H₃PIDC and/or DPPZ/Imphen ligands, namely ligand-to-ligand charge transfer (LLCT)^[19,23]. The reason of spectra red-shift are considered to mainly arise from the increased rigidity of the organic ligands when coordinating to Cd(II) ions.

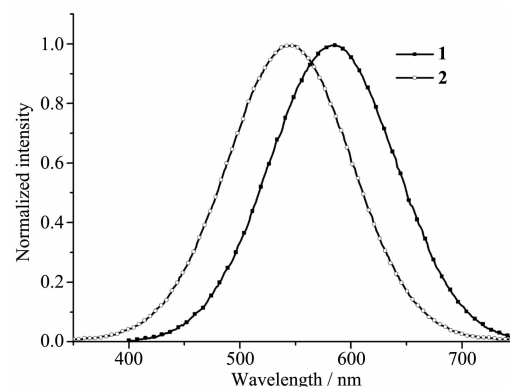


Fig.6 PL spectra of complexes **1** and **2**

3 Conclusions

Two Cd²⁺ complexes formulated as {[Cd₃(HPIDC)₃(DPPZ)₃·7H₂O]_n (**1**) and [Cd(HPIDC)(Imphen)(H₂O)]₂ (**2**) have been hydrothermally synthesized and structurally characterized. The complex **1** exhibits 1D chain structure, and further extends to 2D layer through π - π stacking between the DPPZ ligands. The complex **2** shows a discrete dimer, and these dimers stacks to furnish a 3D supramolecular layer structure via π - π interactions between two ligands. The thermogravimetric analyses data indicate that the framework structures of complexes **1** and **2** are thermally stable up to 285 °C. The complexes **1** and **2** exhibit strong fluorescent emissions in the visible region at room temperature.

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