

以对苯二甲酸及咪唑并[4,5-f][1,10]邻菲咯啉为配体的镉(II)、锌(II)配合物的构筑及晶体结构

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摘要: 在水热条件下, 以对苯二甲酸(H_2bdc)和咪唑并[4,5-f][1,10]邻菲咯啉(Imphen)为配体构筑了两种配合物 $[Cd(bdc)(Imphen)(H_2O)]_n \cdot nH_2O$ (**1**)和 $[Zn(bdc)(Imphen)(H_2O)]_n \cdot nH_2O$ (**2**), 并利用元素分析和 X-射线单晶衍射对其结构进行了表征。结构分析表明: bdc^{2-} 在 2 个配合物中展示了不同的配位模式, 配合物 **1** 和 **2** 都具有一维链状结构, 并且都通过分子间氢键和 $\pi-\pi$ 相互作用形成三维网状结构。此外, 对配合物的热稳定性和发光性质也进行了研究。

关键词: 镉(II)配合物; 锌(II)配合物; 对苯二甲酸; 咪唑并[4,5-f][1,10]邻菲咯啉; 晶体结构

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Hydrothermal Syntheses and Crystal Structures of Cd(II) and Zn(II) Complexes Constructed with 1,4-Benzenedicarboxylic Acid and Imidazo[4,5-f][1,10]phenanthroline Ligands

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Abstract: Two novel metal-organic frameworks (MOFs), $[Cd(bdc)(Imphen)(H_2O)]_n \cdot nH_2O$ (**1**) and $[Zn(bdc)(Imphen)(H_2O)]_n \cdot nH_2O$ (**2**) based on 1,4-benzenedicarboxylic acid (H_2bdc) and imidazo[4,5-f][1,10]phenanthroline (Imphen) ligands, have been constructed under hydrothermal conditions. The complexes are characterized by elemental analyse, single crystal X-ray diffraction. Structural analyses show that the complexes **1** and **2** all present one dimensional chain and bdc^{2-} ligands display different coordination modes. Furthermore, the adjacent chains are further connected by the hydrogen-bonding and $\pi-\pi$ stacking interactions generating three-dimensional supramolecular structures. In addition, thermal stability and luminescent properties of two complexes were also investigated. CCDC: 947287, **1**; 947288, **2**.

Key words: cadmium(II) complex; zinc(II) complex; 1,4-benzenedicarboxylic acid; imidazo[4,5-f][1,10]phenanthroline; crystal structure

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Metal-organic frameworks (MOFs), an emerging class of functional solid state materials, have provoked significant interest owing to their enormous variety of intriguing structural topologies as well as great potential applications as microporous, magnetic, nonlinear optical and fluorescent materials^[1-4]. Although the design and synthesis of such materials are highly influenced by many factors, such as the coordination trend of metal centers, the nature of ligands used, metal-ligand ratio and reaction conditions etc.^[5-8], the judicious selection for multifunctional organic ligands is still an effective approach to construct MOFs with unique structures and properties^[9-17]. Our group has explored a series of 1,10-phenanthrolines derivatives ligands, e.g. Pyphen, TTBT and dppz as rigid ligands for the construction of MOFs. In this contribution, we selected imidazo [4,5-f][1,10]phenanthroline (Imphen) as the neutral chelating ligand and 1,4-benzenedicarboxylic acid (H_2bdc) as directional bridging ligand which possesses different coordination modes^[18]. Two complexes $[Cd(bdc)(Imphen)(H_2O)]_n \cdot nH_2O$ (**1**) and $[Zn(bdc)(Imphen)(H_2O)]_n \cdot nH_2O$ (**2**) have been synthesized under hydrothermal conditions. The thermal behaviors and luminescent properties of **1** and **2** have been investigated in detail.

1 Experimental

1.1 Chemicals and general methods

The ligands Imphen was synthesized according to literature method^[19]. All other analytical grade chemicals and solvent were purchased commercially and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240C element analyzer. 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

Complex 1: A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.154 g, 0.5 mmol), H_2bdc (0.083 g, 0.5 mmol), Imphen (0.110 g, 0.5 mmol) and water (15 mL) was sealed in

a 23 mL Teflon-lined stainless autoclave, and heated at $145\text{ }^{\circ}\text{C}$ for 3 d. 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% yield based on $Cd(NO_3)_2 \cdot 4H_2O$. Anal. calcd. for **1** $C_{21}H_{16}N_4O_6Cd$ (%): C, 47.34; H, 3.03; N, 10.52. Found(%): C, 47.45; H, 3.27; N, 10.48.

Complex 2: An identical procedure with **1** was followed to prepare **2** except $Cd(NO_3)_2 \cdot 4H_2O$ was replaced by $Zn(NO_3)_2 \cdot 6H_2O$. Yellow crystals of complex **2** suitable for X-ray single-crystal diffraction analysis were picked out from the solid mixture in 51% yield based on $Zn(NO_3)_2 \cdot 6H_2O$. Anal. Calcd. for **2** $C_{21}H_{16}N_4O_6Zn$ (%): C, 51.92; H, 3.32; N, 11.53. Found(%): C, 51.99; H, 3.40; N, 11.47.

1.3 Structure determination

Crystallographic data of two complexes were collected at room temperature on a Bruker SMART APEX CCD diffractometer equipped with equipped with a graphite-monochromatized Mo $K\alpha$ ($\lambda=0.071\text{ }073\text{ nm}$) 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^[20] and refined by full-matrix least-squares techniques on F^2 with SHELXL 97^[21]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The crystallographic data of the complexes are summarized in Table 1, and selected bond lengths and angles of **1** and **2** are listed in Table 2.

CCDC: 947287, **1**; 947288, **2**.

2 Results and discussion

2.1 Description of the crystal structure

2.1.1 Crystal structure of $[Cd(bdc)(Imphen)(H_2O)]_n \cdot nH_2O$ (**1**)

There are one Cd^{2+} cation, one bdc^{2-} ligand, one Imphen ligand, one coordinated water molecule and one free water molecule in the asymmetric unit. The Cd center is six-coordinate via two nitrogen atoms ($Cd-N1=0.230\text{ }5(2)\text{ nm}$ and $Cd-N2=0.231\text{ }99(19)\text{ nm}$) derived from a Imphen ligand and three oxygen atoms ($Cd-O1=0.237\text{ }2(2)\text{ nm}$, $Cd-O2=0.237\text{ }39(17)\text{ nm}$, and $Cd-O3=0.219\text{ }50(17)\text{ nm}$) from two different bdc^{2-}

Table 1 Crystallographic data for **1** and **2**

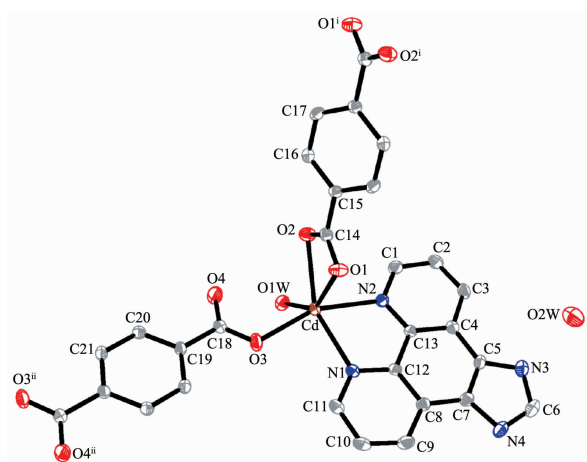
Complex	1	2
Formula	C ₂₁ H ₁₆ N ₄ O ₆ Cd	C ₂₁ H ₁₆ N ₄ O ₆ Zn
Formula mass	532.78	485.77
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Crystal size / mm	0.436×0.327×0.186	0.483×0.279×0.193
<i>a</i> / nm	1.066 03(3)	1.041 6(2)
<i>b</i> / nm	1.441 73(4)	1.428 3(3)
<i>c</i> / nm	1.309 40(3)	1.296 0(3)
β / (°)	98.922(3)	98.18(3)
<i>V</i> / nm ³	1.988 10(9)	1.908 5(7)
<i>Z</i>	4	4
μ / mm ⁻¹	1.148	1.338
Goodness-of-fit on <i>F</i> ²	1.077	1.079
Reflns collected / unique	7 488 / 3 496	18 458 / 4 368
<i>D_c</i> / (g·cm ⁻³)	1.780	1.691
θ range / (°)	2.70 to 25.01	3.06 to 27.48
<i>R</i> (<i>I</i> >2 σ (<i>I</i>))	<i>R</i> ₁ =0.024 3, <i>wR</i> ₂ =0.065 3	<i>R</i> ₁ =0.028 2, <i>wR</i> ₂ =0.071 0
<i>R</i> (all data)	<i>R</i> ₁ =0.031 0, <i>wR</i> ₂ =0.066 8	<i>R</i> ₁ =0.036 4, <i>wR</i> ₂ =0.073 5

Table 2 Selected bond lengths (nm) and bond angles (°)

Complex 1					
N1-Cd	0.230 5 (2)	N2-Cd	0.231 99(19)	O1-Cd	0.237 2(2)
O2-Cd	0.237 39(17)	O1W-Cd	0.228 2(2)	O3-Cd	0.219 50(17)
N1-Cd-N2	71.93(7)	N2-Cd-O2	91.07(7)	N2-Cd-O1W	97.75(8)
O2-Cd-O3	109.59(7)	O1-Cd-O2	55.07(6)	O1W-Cd-O3	86.16(8)
Complex 2					
N1-Zn	0.210 38(16)	N4-Zn	0.217 53(15)	O1-Zn	0.207 46(15)
O3-Zn	0.203 69(13)	O1W-Zn	0.207 33(15)		
N1-Zn-N4	77.28(6)	N4-Zn-O1	88.36(6)	O1-Zn-O3	98.95(6)
O1-Zn-O1W	139.34(6)	N4-Zn-O1W	93.50(6)	O3-Zn-O1W	87.79(6)

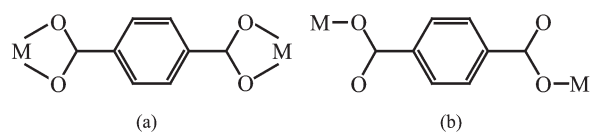
ligands, and one oxygen atom (Cd-O1W=0.228 2(2) nm) from a coordinated water molecule in a slightly distorted octahedral coordination geometry (Fig.1). Adjacent Cd atoms are bridged alternatively by one bidentate chelating bdc²⁻ ligand (Cd-Cd 1.118 7 nm) and one monodentate bdc²⁻ ligand (Cd-Cd 1.156 8 nm) to form a single-chain structure (Fig.2, Scheme 1a and 1b), and the Imphen ligands are attached on both sides of the 1D chain. Notably, the adjacent chains are linked through aromatic π - π interactions between Imphen ligands (six-member-ring: C4-C5-C7-C8-C12-C13 and six-member-ring: C4ⁱ-C5ⁱ-C7ⁱ-C8ⁱ-C12ⁱ-C13ⁱ,

centroid-to-centroid distance *ca.* 0.346 6 nm, ⁱ 1-*x*, 1-*y*, 1-*z*, centroid coordinates -0.150 02, 0.525 04, 0.036 62 and 0.150 02, 0.474 96, -0.036 62, dihedral angle between two planes: 0.000°), and between bdc²⁻ ligands and Imphen ligands (six-member-ring: C19-C20-C21-C19ⁱⁱ-C20ⁱⁱ-C21ⁱⁱ and six-member-ring: C4-C5-C7-C8-C12-C13, centroid-to-centroid distance *ca.* 0.368 7 nm, ⁱⁱ 2-*x*, 1-*y*, 1-*z*, centroid coordinates -0.000 00, 1.000 00, 1/2 and -0.349 98, 1.025 04, 0.463 38, dihedral angle between two planes: 8.716°) (Fig.3). In addition, the O-H...O and N-H...O hydrogen bonds (Table 3) involving the water



Symmetry codes: ⁱ 1-x, -y, 1-z; ⁱⁱ 2-x, 1-y, 1-z

Fig.1 Crystal structure of complex 1

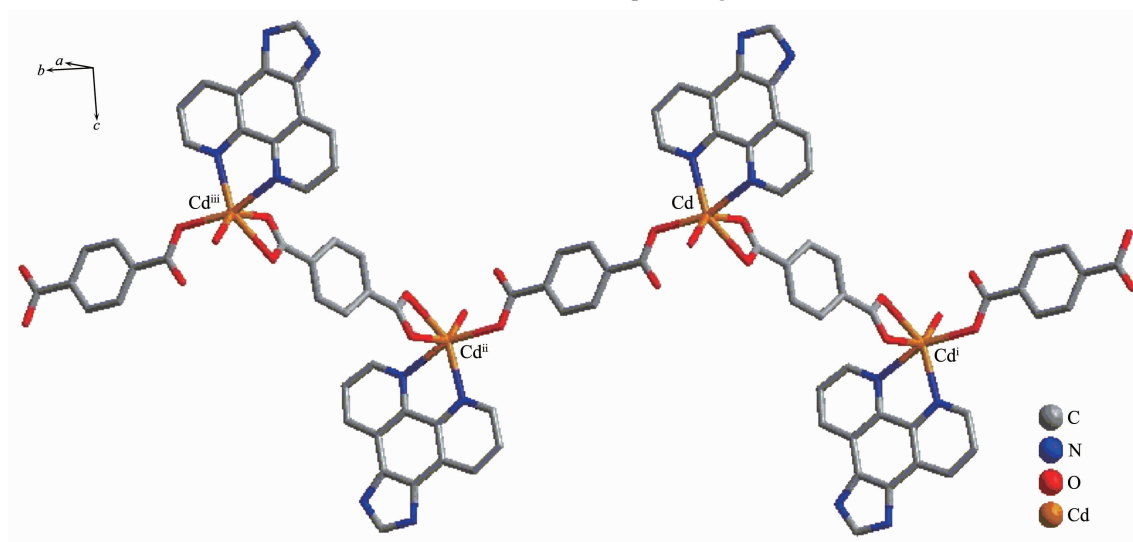


Scheme 1 Coordination modes of H₂bdc ligand in complexes **1** and **2**

molecules, the carboxylic groups of bdc²⁻ anions and Imphen ligands further extend the 1D chains into an interesting 3D supramolecular structure.

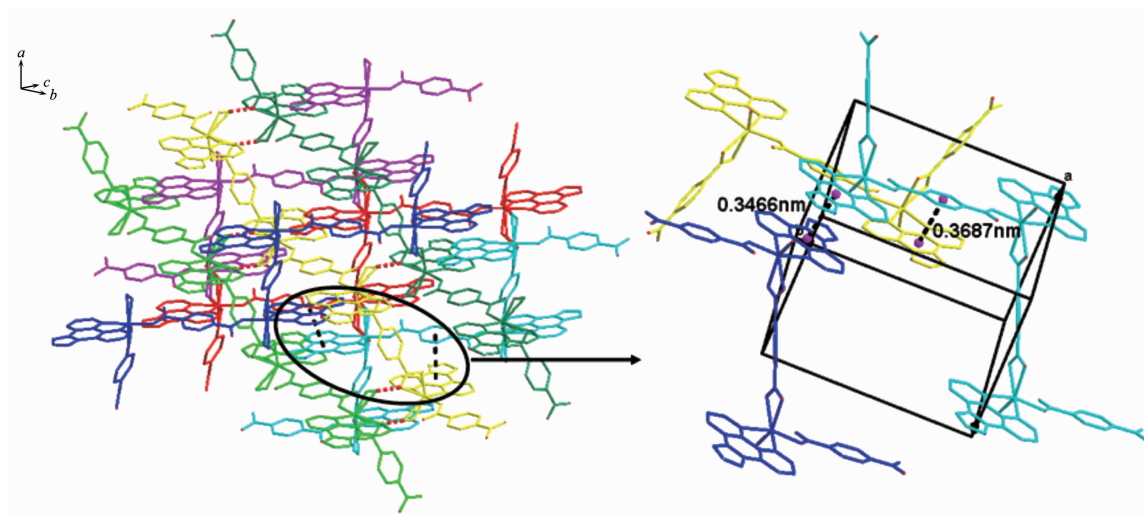
2.1.2 Crystal structure of [Zn(bdc)(Imphen)(H₂O)]_n · nH₂O (**2**)

X-ray analysis revealed that the asymmetric unit of **2** contains one Zn atom, one bdc²⁻ ligand, one Imphen ligand, one coordinated water molecule and



Symmetry codes: ⁱ 1-x, -y, 1-z; ⁱⁱ 2-x, 1-y, 1-z; ⁱⁱⁱ 1+x, 1+y, z

Fig.2 One-dimensional chain structure of **1**



Red dashed line: hydrogen bonds; Black dashed line: aromatic π - π interactions

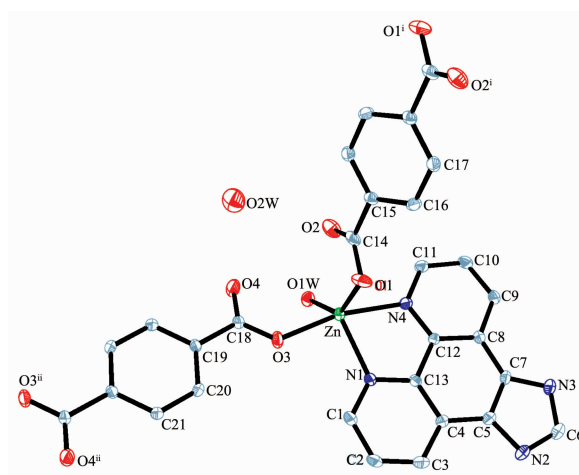
Fig.3 3D supramolecular network of **1**

Table 3 Hydrogen bond lengths and bond angles

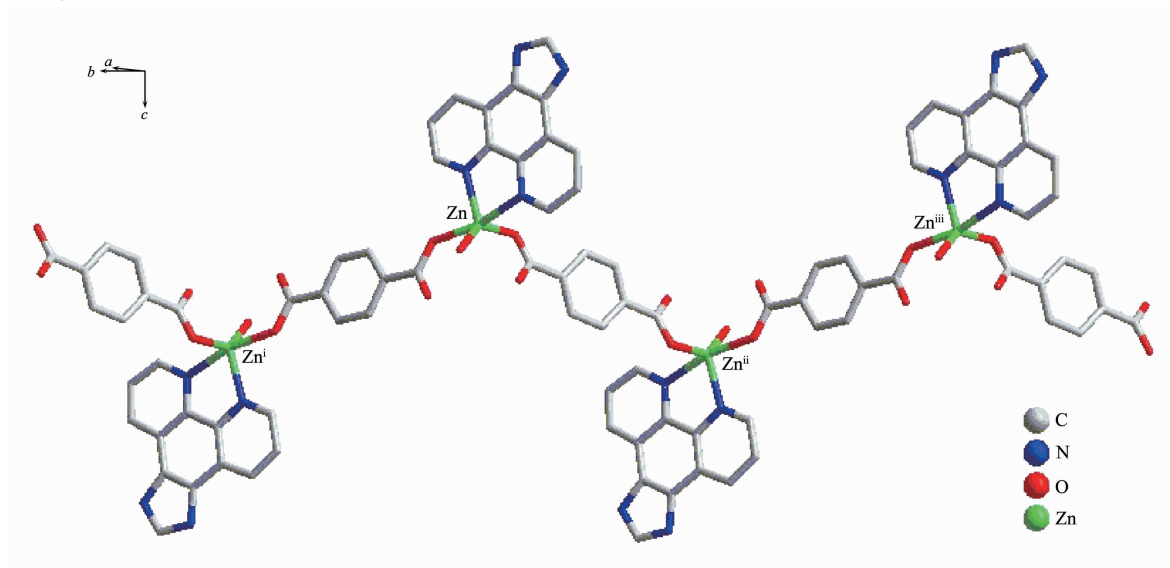
D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
Complex 1				
O1W-H1WB...O4	0.073(3)	0.204(3)	0.274 6(3)	164(4)
N3-H4...O2W	0.083(2)	0.206(2)	0.283 3(4)	155(2)
O1W-H1WA...O2 ⁱ	0.084(3)	0.188(3)	0.272 3(3)	178(3)
O2W-H2WA...O4 ⁱⁱ	0.068(5)	0.249(5)	0.314 7(5)	163(6)
Complex 2				
O1W-H1WA...O4	0.086(3)	0.185(3)	0.268 4(2)	164(2)
O2W-H2WA...O4	0.080(9)	0.247(9)	0.326 6(4)	171(7)
O1W-H1WB...O2 ⁱ	0.084(3)	0.190(3)	0.274 1(2)	176(3)
O2W-H2WB...N2 ⁱⁱ	0.087(5)	0.235(5)	0.321 4(3)	174(4)
N3-H4...O2W ⁱⁱⁱ	0.085(2)	0.204(2)	0.282 7(3)	154(2)

Symmetry codes: **1:** ⁱ -*x*+2, -*y*, -*z*+1; ⁱⁱ -*x*+3/2, *y*-1/2, -*z*+1/2; **2:** ⁱ -*x*+2, -*y*+1, -*z*+3; ⁱⁱ *x*, *y*, *z*+1; ⁱⁱⁱ -*x*+3/2, *y*-1/2, -*z*+5/2.

one free water molecule. As is shown in Fig.4, each Zn atom is five coordinated with two nitrogen atoms of one Imphen ligand (Zn-N1 0.210 38(16) nm and Zn-N4 0.217 53 (15) nm), two oxygen atoms from two bdc²⁻ ligands (Zn-O1=0.207 46 (15) nm and Zn-O3 0.203 69(13) nm) and one oxygen atom from water molecule (Zn-O1W 0.207 33 (15) nm). The Zn atoms are linked together by monodentate bdc²⁻ ligands to form a one-dimensional single chain structure (Fig.5, Scheme 1b). One-dimensional chains were connected together by two types of π - π interactions: one is between Imphen ligands (six-member-ring: C4-C5-C7-C8-C12-C13 and six-member-ring: C4ⁱ-C5ⁱ-C7ⁱ-C8ⁱ-C12ⁱ-C13ⁱ, centroid-to-centroid distance *ca.* 0.346 8

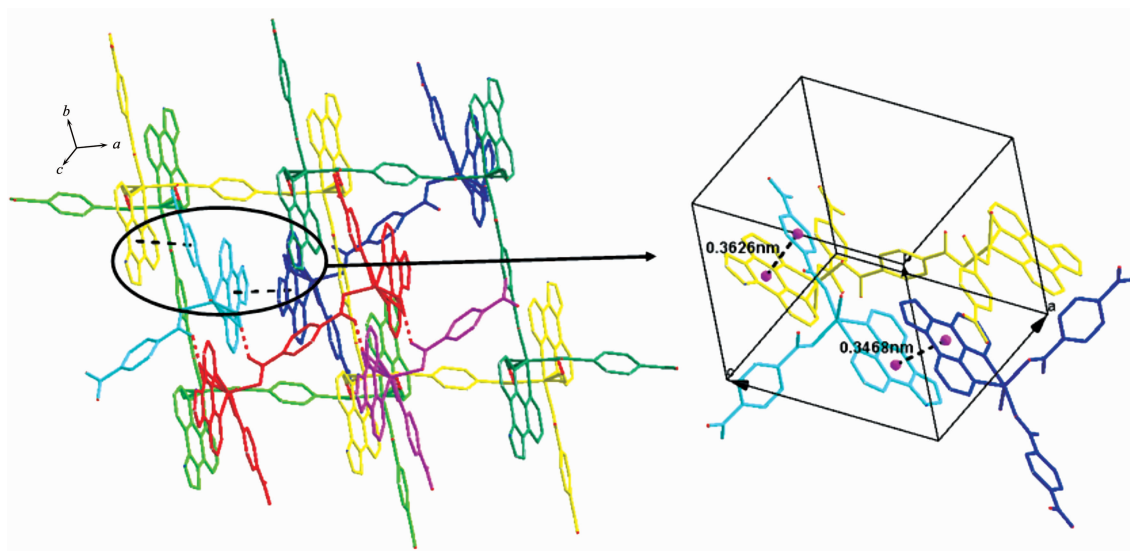


Symmetry codes: ⁱ 1-*x*, 1-*y*, 3-*z*; ⁱⁱ 2-*x*, 2-*y*, 3-*z*

Fig.4 Crystal structure of complex **2**

Symmetry codes: ⁱ 2-*x*, 2-*y*, 3-*z*; ⁱⁱ 1-*x*, 1-*y*, 3-*z*; ⁱⁱⁱ -1+*x*, -1+*y*, *z*

Fig.5 One-dimensional chain structure of complex **2**

Fig.6 3D supramolecular network of **2**

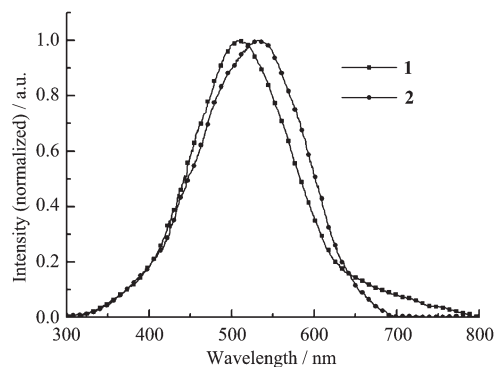
nm, $i -x, 1-y, -z$, centroid coordinates $-0.150\ 02, 0.525\ 04, 0.036\ 62$ and $0.150\ 02, 0.474\ 96, -0.036\ 62$, dihedral angle between two planes: 0.000°), and another is between bdc^{2-} and Imphen ligand (six-member-ring: C19-C20-C21-C19 ii -C20 ii -C21 ii and six-member-ring: C4-C5-C7-C8-C12-C13, centroid-to-centroid distance *ca.* $0.362\ 6\text{ nm}$, $^{ii} -1+x, y, -1+z$, centroid coordinates $-0.000\ 00, 1.000\ 00, 1/2$ and $-0.349\ 98, 1.025\ 04, 0.463\ 38$, dihedral angle between two planes: 8.530°), as shown in Fig.6. Furthermore, the O-H \cdots O, O-H \cdots N and N-H \cdots O hydrogen-bond interactions between the coordinated water molecules, free water molecules or -NH- groups and carboxylate O atoms or N atoms of Imphen ligands lead to the construction of a stable 3D network (Table 3).

2.2 TGA

Although the coordination models of two complexes are slightly different, TGA curves of **1** and **2** are similar. So **1** represents **2** for detailed TGA. Three distinct weight losses were observed for **1**. The first weight loss of 3.40% is in the range $80\sim 110^\circ\text{C}$, assigned to the release of the free water molecules (Calcd. 3.38%). The second weight loss of 3.45% is in the range $120\sim 220^\circ\text{C}$, assigned to the loss of the coordinated water molecules (Calcd. 3.38%). The third sharp weight loss of 71.80% is ascribable to the decomposition of organic ligands bdc^{2-} and Imphen (Calcd. 72.14%). The final product may be CdO.

2.3 Photoluminescence properties

It is well known that the d^{10} metal coordination polymers have interesting photoluminescent properties. The solid-state luminescence spectra of **1** and **2** at room temperature are determined (Fig.7). Complex **1** and **2** exhibit strong luminescence peaks at 506 and 531 nm upon excitation at 365 nm, respectively. In order to understand the nature of these emission bands, the luminescent properties of free ligands H_2bdc and Imphen were analyzed, showing they exhibit the strongest emission peaks at about $390^{[22]}$ and $460\text{ nm}^{[23]}$ from 300 to 720 nm, respectively. Compared with the luminescent spectra of free ligand, the emission spectra of two complexes are obviously similar to that of Imphen, which might be ascribable to chelating coordination of the planar Imphen ligand in both complexes. The photoluminescent emissions of **1** and **2** also mainly originate from the intraligand

Fig.7 Photoluminescent spectra of complex **1** and **2**

fluorescent emissions of Imphen^[24].

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