

苯并咪唑-5,6-二羧酸 Mn(II)和 Cd(II)混配配合物的合成、结构及性质

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摘要: 在水热条件下, 合成了 2 个配位聚合物 $\{[\text{Mn}(\text{Hbidc})(2,2'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**) 和 $\{[\text{Cd}(\text{Hbidc})(\text{phen})][\text{Cd}(\text{phen})_2\text{Cl}_2]\}_n$ (**2**) (H_3bidc =苯并咪唑-5,6-二羧酸, $2,2'\text{-bpy}$ =2,2'-联吡啶, phen=菲咯啉), 并通过 X 射线单晶衍射、红外、元素分析、X 射线粉末衍射和热重对配合物结构进行了表征。配合物 **1** 是一维无限 zig-zag 链结构, 可以通过 O-H...O 和 N-H...O 氢键的相互作用形成三维超分子结构。配合物 **2** 也是一维无限链结构。此外, 测试了配合物 **1** 和 **2** 的固体紫外吸收光谱和研究了配合物 **2** 的固体荧光性能。

关键词: 苯并咪唑-5,6-二羧酸; N-供体辅助配体; 晶体结构; 荧光性能

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Manganese(II) and Cadmium(II) Mixed-Ligand Complexes Constructed from Benzimidazole-5,6-dicarboxylic Acid: Syntheses, Crystal Structures and Properties

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Abstract: Two coordination polymer, $\{[\text{Mn}(\text{Hbidc})(2,2'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**) and $\{[\text{Cd}(\text{Hbidc})(\text{phen})][\text{Cd}(\text{phen})_2\text{Cl}_2]\}_n$ (**2**) (H_3bidc =benzimidazole-5,6-dicarboxylic acid, $2,2'\text{-bpy}$ =2,2'-bipyridine and phen=1,10-phenanthroline) have been synthesized under hydrothermal method. They were characterized by single-crystal X-ray diffraction, IR spectroscopy, elemental analysis, powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA). Complex **1** exhibits one-dimensional infinite zig-zag chain, which is extended into a three dimensional supramolecular network via O-H...O and N-H...O hydrogen bonding interactions. Complex **2** also possesses one dimensional chain structure. In addition, the UV-Vis absorption spectra of **1** and **2** were measured at room temperature and the solid fluorescent property of **2** was studied at room temperature. CCDC: 1040339, **1**; 1472092, **2**.

Keywords: benzimidazole-5,6-dicarboxylic acid; N-donor ancillary ligand; crystal structures; luminescent properties

There is great current interest in the synthesis of novel coordination polymers, not only due to their fascinating variety of architectures and topologies, but

also due to their potential applications in functional materials, such as gas adsorption^[1], separation^[2], catalysis^[3], magnetism^[4] and photoluminescent properties^[5-6].

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Until now, a number of novel coordination polymers with outstanding properties have been obtained^[7-9].

It is well-known that rational selection of a ligand with suitable shape, functionality, flexibility, and symmetry makes a pivotal role in constructing and tailoring metal-organic architectures with desirable properties^[10-11]. Recently, metal complexes for heterocyclic carboxylic acid benzimidazole-5,6-dicarboxylic acid (H₃bdc) have attracted particular attention, owing to providing various coordination modes and multidimensional structures^[12]. It can act as a multidentate ligand with both N- and O-donor atoms, and easily coordinate with metal ions to form multidimensional complexes; the benzimidazole ring might contribute much to form $\pi \cdots \pi$ stacking interactions, and the N-H group on the imidazole ring can act as proton-donor to form hydrogen bonds, which also play important roles in the formation of coordination complexes.

At the same time, N-donor ligands are frequently used as auxiliary ligands to design and synthesis of novel structural motifs. N-donor ligands, such as 2,2'-bipyridine^[13], 4,4'-bipyridine^[14] and 1,10-phenanthroline^[15], which were usually selected to construct interesting supramolecular architectures as the auxiliary co-ligands, can provide some insight in the construction of novel structures.

Considering all these above-mentioned, we think that the simultaneous use of the N-donor auxiliary ligand and benzimidazole-5,6-dicarboxylic acid may generate diverse supramolecular structures and potential applications. However, only a few examples of the metal complexes containing the mixed ligands of benzimidazole-5,6-dicarboxylic acid and 1,10-phenanthroline have been reported in coordination chemistry until now^[16]. In this paper, two coordination polymers from metal ions, benzimidazole-5,6-dicarboxylic acid, and N-donor auxiliary ligand, namely $\{[\text{Mn}(\text{Hbdc})(2,2'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**), and $\{[\text{Cd}(\text{Hbdc})(\text{phen})][\text{Cd}(\text{phen})_2\text{Cl}_2]\}_n$ (**2**) are reported. In addition, the UV-Vis absorption spectra of **1** and **2** were measured at room temperature and the fluorescent property of **2** was studied in the solid at room temperature in detail.

1 Experimental

1.1 Materials and general methods

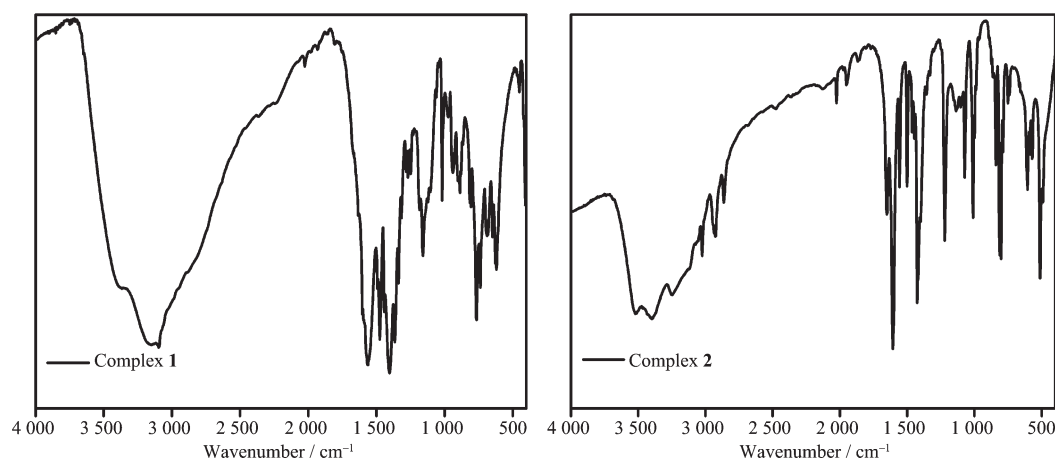
All chemicals were commercially available and used as received without further purification. Elemental analyses (C, H, N) were carried out on an Elementar Vario EL III analyzer. The infrared spectra were recorded from KBr pellets in the 4 000~400 cm⁻¹ range on a FTIR-650 spectrometer. The powder XRD data were collected on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda=0.1548$ nm) generated at 40 kV and 40 mA in a 2θ range of 5°~50°. Thermogravimetry analyses (TGA) were performed with a PTC-10ATG-DTA instrument in flowing N₂ at a heating rate of 10 °C·min⁻¹ from 25~800 °C. The UV-Vis absorption spectra were obtained using a Hitachi UV-3010 UV-Vis spectrophotometer. The luminescence spectra were detected on a Hitachi F-4500 fluorescence spectrophotometer.

1.2 Synthesis of complex $\{[\text{Mn}(\text{Hbdc})(2,2'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**)

A mixture of MnSO₄·H₂O (0.2 mmol), H₃bdc (0.2 mmol), 2,2'-bpy (0.2 mmol), H₂O (8 mL), and an aqueous solution of NaOH (2.0 mol·L⁻¹, 0.25 mL) was sealed in a 25 mL Teflon-lined reactor and heated at 170 °C for 3 days. After slow cooling to room temperature, yellow bulk crystals of the complexes were obtained. Yield: 65% based on MnSO₄·H₂O. Anal. Calcd. for C₁₉H₁₉MnN₄O_{7.50} (%): C, 47.71, H, 4.00, N, 11.71. Found(%): C, 47.32, H, 4.06, N, 11.65. IR data (KBr pellets, cm⁻¹, Fig.1): 3 150 (vs), 1 600 (s), 1 561(vs), 1 490(s), 1 473(s), 1 440(s), 1 402(vs), 1 361(s), 1 336 (m), 1 313(m), 1 280(w), 1 267(w), 1 245(w), 1 182(w), 1 157(w), 1058(vw), 1016(w), 937(w), 885(w), 811(w), 761(s), 736(m), 666(m), 647(w), 616(m), 449(vw), 406 (ww).

1.3 Synthesis of complex $\{[\text{Cd}(\text{Hbdc})(\text{phen})][\text{Cd}(\text{phen})_2\text{Cl}_2]\}_n$ (**2**)

A solution of H₃bdc (0.5 mmol) in 6 mL H₂O was added dropwise with stirring at room temperature to a solution of Cd(NO₃)₂·4H₂O (1.0 mmol) and phen (0.5 mmol) in the mixture of 10 mL water and 5 mL ethanol. Then an aqueous solution of hydrochloric acid was added dropwise with stirring to adjust the

Fig.1 FT-IR spectra of **1** and **2**

pH value of the solution being 4. The resulting mixture was sealed in a 25 mL Teflon-lined stainless reactor, kept under autogenous pressure at 160 °C for 3 days, and then slowly cooled to room temperature at a rate of 10 °C·h⁻¹. The colorless block crystals for X-ray diffraction were isolated directly, washed with ethanol and dried in air. Yield: 62% based on Cd(NO₃)₂·4H₂O. Anal. Calcd. for C₅₇H₃₆Cd₂Cl₂N₁₀O₄(%): C, 56.08, H, 2.97, N, 11.47. Found (%): C, 56.02, H, 2.65, N, 11.55. IR data (KBr pellets, cm⁻¹, Fig.1): 3 432(vs), 1 621(s), 1 554(vs), 1 515(vs), 1 467(s), 1 421(s), 1 392(s), 1 357(m), 1 338(m), 1 220(w), 1 182(w), 1 139(w), 1 009(vw), 944(w), 862(w), 844(w), 781(s), 727(m), 636(m), 418(ww).

1.4 Structure determination

Single-crystal X-ray analysis of the complexes **1**

and **2** were carried out on a Bruker SMART APEX CCD diffract meter using graphite-monochromatized Mo K α radiation ($\lambda=0.071\ 073\ \text{nm}$) at room temperature using the ω -scan technique^[17]. Crystal size of complexes **1** and **2** are 0.20 mm×0.20 mm×0.16 mm and 0.24 mm×0.20 mm×0.18 mm, respectively. The structure was solved by direct methods with SHELXS-97^[18] and refined with the full-matrix least-squares technique using the SHELXL-97 program^[19]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. The crystallographic data are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC: 1040339, **1**; 1472092, **2**.

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

Empirical formula	C ₁₉ H ₁₉ MnN ₄ O _{7.50}	C ₅₇ H ₃₆ Cd ₂ Cl ₂ N ₁₀ O ₄
Empirical weight	478.32	1 220.66
Temperature / K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / nm	0.960 22(19)	2.273 3(2)
<i>b</i> / nm	1.174 9(2)	1.519 88(11)
<i>c</i> / nm	1.934 9(4)	1.481 6(2)
β / (°)	103.99(19)	96.060(12)
<i>V</i> / nm ³	2.118 22(7)	5.090 5(11)
<i>Z</i>	4	4
<i>D_c</i> / (g·cm ⁻³)	1.500	1.593
Absorption coefficient	0.675	1.000
<i>F</i> (000)	984	2 440

Continued Table 1

θ range / ($^{\circ}$)	3.18~24.99	3.41~25.0
Limiting indices	$-8 \leq h \leq 11, -13 \leq k \leq 12, -23 \leq l \leq 13$	$-20 \leq h \leq 27, -15 \leq k \leq 18, -17 \leq l \leq 15$
Reflection collected	8 075	22 627
Independent reflection (R_{int})	3 714	8 938
Data, restraint, parameter	3 714, 0, 306	8 938, 0, 676
Goodness-of-fit on F^2	1.052	1.062
$R_1, wR_2 [I > 2\sigma(I)]$	0.029 8, 0.068 7	0.108 4, 0.269 4
R_1, wR_2 (all data)	0.034 6, 0.071 7	0.126 7, 0.286 2

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) for complexes **1** and **2**

1					
Mn(1)-O(6)	0.213 3(13)	Mn(1)-O(4)	0.214 8(12)	Mn(1)-N(3)	0.213 6(15)
Mn(1)-N(2)	0.224 8(17)	Mn(1)-N(1)	0.225 1(16)	Mn(1)-O(5)	0.225 3(12)
O(6)-Mn(1)-O(4)	176.94(5)	O(6)-Mn(1)-N(3)	90.76(6)	O(4)-Mn(1)-N(3)	90.14(5)
O(6)-Mn(1)-N(2)	92.10(6)	O(4)-Mn(1)-N(2)	87.22(5)	N(3)-Mn(1)-N(2)	175.00(6)
O(6)-Mn(1)-N(1)	88.86(6)	O(4)-Mn(1)-N(1)	93.79(5)	N(3)-Mn(1)-N(1)	102.90(6)
N(2)-Mn(1)-N(1)	73.06(6)	O(6)-Mn(1)-O(5)	87.22(5)	O(4)-Mn(1)-O(5)	89.87(4)
N(3)-Mn(1)-O(5)	88.60(5)	N(2)-Mn(1)-O(5)	95.63(6)	N(1)-Mn(1)-O(5)	167.90(6)
2					
Cd(1)-N(1)	0.239 1(10)	Cd(1)-N(2)	0.239 2(11)	Cd(1)-O(1)	0.225 6(9)
Cd(1)-O(4)#1	0.226 8(10)	Cd(1)-N(4)	0.245 6(9)	Cd(1)-N(3)	0.235 4(10)
Cd(2)-Cl(2)	0.252 2(4)	Cd(2)-Cl(1)	0.251 0(3)	Cd(2)-N(8)	0.240 4(10)
Cd(2)-N(10)	0.240 6(10)	Cd(2)-N(9)	0.244 4(10)	Cd(2)-N(7)	0.246 6(12)
N(1)-Cd(1)-N(2)	69.3(3)	N(1)-Cd(1)-N(4)	85.2(3)	N(2)-Cd(1)-N(4)	84.9(3)
O(1)-Cd(1)-N(1)	96.1(4)	O(1)-Cd(1)-N(2)	99.9(3)	O(1)-Cd(1)-O(4)#1	85.1(4)
O(1)-Cd(1)-N(4)	175.3(3)	O(1)-Cd(1)-N(3)	109.3(4)	O(4)#1-Cd(1)-N(1)	87.8(4)
O(4)#1-Cd(1)-N(2)	156.9(4)	O(4)#1-Cd(1)-N(4)	90.4(3)	O(4)#1-Cd(1)-N(3)	95.6(4)
N(3)-Cd(1)-N(1)	154.6(3)	N(3)-Cd(1)-N(2)	103.8(3)	N(3)-Cd(1)-N(4)	69.6(3)
Cl(1)-Cd(2)-Cl(2)	106.15(13)	N(8)-Cd(2)-Cl(2)	90.5(3)	N(8)-Cd(2)-Cl(1)	104.1(3)
N(8)-Cd(2)-N(10)	153.7(4)	N(8)-Cd(2)-N(9)	89.2(3)	N(8)-Cd(2)-N(7)	68.5(4)
N(10)-Cd(2)-Cl(2)	101.7(3)	N(10)-Cd(2)-Cl(1)	94.9(2)	N(10)-Cd(2)-Cl(9)	68.1(3)
N(10)-Cd(2)-N(7)	95.6(4)	N(9)-Cd(2)-Cl(2)	89.1(3)	N(9)-Cd(2)-Cl(1)	159.5(3)
N(9)-Cd(2)-N(7)	85.0(3)	N(7)-Cd(2)-Cl(2)	158.2(3)	N(7)-Cd(2)-Cl(1)	85.3(3)

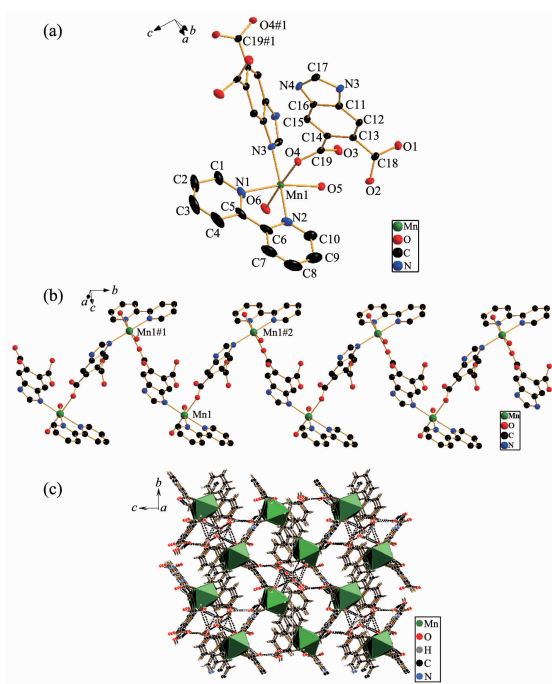
Symmetry codes: #1: $x, 3/2-y, 1/2+z$ for **2**.

2 Results and discussion

2.1 Structure description of **1**

Single-crystal X-ray diffraction study reveals that complex **1** belongs to $P2_1/n$ space group. The asymmetric unit of complex **1** consists of one Mn(II) ion, two Hbdc²⁻ ligands, one 2,2'-bpy ligand, two coordinated water molecules. As shown in Fig.2a, each Mn(II) ion

is six-coordinated in a distorted octahedron arrangement by two atoms (N3, O4) from two Hbdc²⁻ ligands, two nitrogen atoms (N1, N2) from one 2,2'-bpy ligand, and two oxygen atoms (O5, O6) from two coordinated water molecules. The Mn-O bond lengths are in the range of 0.213 3(13)~0.225 3(12) nm, while the Mn-N bond lengths are slightly longer, 0.213 6(15)~0.225 1(16) nm. The bond angles vary from 88.60(5) $^{\circ}$



80% probability ellipsoids; Solvent molecules and all hydrogen atoms were omitted for clarity; Symmetry codes #1: $-x+5/2, y+1/2, -z+3/2$; #2: $-x+5/2, y-1/2, -z+3/2$

Fig.2 (a) Molecular structure of **1** with numbering scheme; (b) View of an infinite chain of complex **1**; (c) Hydrogen-bonding interactions linking layers into a 3D supramolecular network of complex **1**

to $176.94(5)^\circ$, all of which are similar to those found in other six coordinated Mn(II) compounds with O- and N-donating complexes^[20]. The two oxygen atoms (O4, O6) occupy the axial positions, and the other nitrogen atoms (N1, N2, N3) and oxygen atom (O5) comprise the equatorial plane.

In this manner, a zig-zag chain is formed by direct connection of Mn(II) atoms bridged by Hbidc²⁻ ligands along the *b*-axis, with the Mn...Mn separation being 1.037(5) nm (Fig.2b). Adjacent 1D chains connect to form a 2D layer network through intermolecular O1W-H1WB...O6 and O6-H6B...O1 hydrogen bonds (Table 3). Furthermore, the 2D layer network is extended into a 3D supramolecular network by O2W-H2WA...O1, O2W-H2WB...O3, O5-H5B...O3 and O6-H6A...O3W hydrogen bonds (Fig.2c). Therefore, the O-H...O and N-H...O hydrogen bonds play an important role in stabilizing the crystal structure.

2.2 Structure description of **2**

Single-crystal X-ray diffraction analysis reveals that complex **2** crystallizes in the $P2_1/c$ space group. The asymmetric unit contains two Cd(II) ions, one Hbidc²⁻ ligand, four phen ligands, and two chloride

Table 3 Hydrogen-bonding geometry for **1**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O1W-H1WA...O2W	0.095 0	0.229 0	0.265 0(6)	101.00
O1W-H1WA...O1	0.095 0	0.185 0	0.279 5(4)	171.00
O1W-H1WB...O2W	0.092 0	0.195 0	0.265 0(6)	132.00
O1W-H1WB...O6	0.092 0	0.092 0	0.287 8(4)	136.00
O2W-H2WA...O1W	0.076 0	0.209 0	0.265 0(6)	131.00
O2W-H2WA...O1	0.076 0	0.225 0	0.285 3(5)	137.00
O2W-H2WB...O3	0.080 0	0.205 0	0.280 1(4)	156.00
O2W-H3WA...O3	0.101 0	0.186 0	0.280 1(4)	154.00
O5-H5A...O2	0.088 0	0.180 0	0.266 0(18)	166.00
O5-H5B...O3	0.081 0	0.187 0	0.263 9(18)	159.00
O6-H6A...O2W	0.078 0	1.840 0	0.260 9(4)	171.00
O6-H6A...O3W	0.078 0	0.198 0	0.269 9(4)	153.00
O6-H6B...O1	0.086 0	0.176 0	0.259 7(19)	162.00
N4-H25...O5	0.086 0	0.20	0.284 0(19)	164.00
C2-H2...O1W	0.093 0	0.229 0	0.292 5(5)	125.00
C3-H3...O2	0.093 0	0.246 0	0.332 6(3)	154.00
C8-H8...O1	0.093 0	0.243 0	0.335 5(3)	170.00
C9-H9...O3W	0.093 0	0.229 0	0.317 3(5)	158.00
C17-H17...O2	0.093 0	0.247 0	0.328 8(2)	147.00

ions. The Cd1 ion adopts a slightly distorted octahedral geometry via coordinating to one N atom (N4) of phen and one O atom (O1) of Hbdc²⁻ in the axial position, two N atoms (N1 and N2) of one phen ligand, one N atom (N3) of phen and one O atom (O4) of Hbdc²⁻ in the equatorial plane. The Cd2 center also adopts a distorted octahedral geometry, which is provided by one Cl ion (Cl1) and one phen N atom (N9) in the axial position, as well as three N atoms

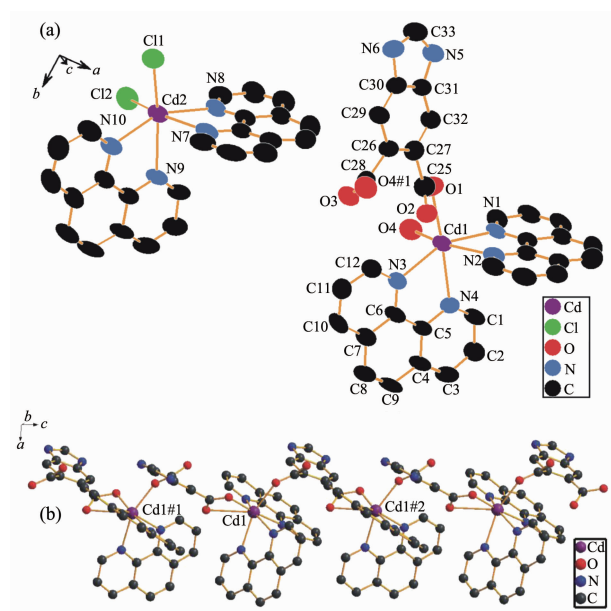
from two phen ligands (N7, N8, N10), one Cl ion (Cl2) in the equatorial plane (Fig.3a). The Cd-N, Cd-O bond lengths and O-Cd-O, O-Cd-N, N-Cd-N angles, all of which are within the range of those observed for analogous Cd complexes^[21]; e.g., 0.225 6(9)~0.252 2(4) nm, and 68.1(3)°~175.3(3)°. In the complex **2**, Hbdc²⁻ chelates in a monodentate manner, whereas the phen ligand displays a chelating bidentate coordination modes to link two Cd(II) ions. The Hbdc²⁻ ligands link the Cd1 ions to form a one-dimensional chain with a Cd...Cd distance of 0.740 8(16) nm along the *c* axis (Fig.3b).

2.3 PXRD patterns

To confirm the mass identities and phase purity of **1** and **2**, powder X-ray diffraction (PXRD) experiments were carried out for complexes **1** and **2**. The PXRD experimental and computer-simulated patterns of the corresponding complexes are shown in Fig.4. The PXRD patterns of as-synthesized complexes **1** and **2** are coincident with the simulated ones from the single-crystal data, indicative of its high purity and homogeneity.

2.4 Thermogravimetric analysis

To investigate their thermal stabilities, thermogravimetric analyses (TGA) of complexes **1** and **2** were carried out at a heating rate of 10 °C · min⁻¹. TGA traces for complexes **1** and **2** are depicted in Fig.5. For complex **1**, the first weight loss of 8.17% in the range of 102~135 °C corresponds to the loss of the release of the free water molecules and one



80% probability ellipsoids; Solvent molecules and all hydrogen atoms were omitted for clarity; Symmetry codes: #1: $x, 3/2-y, 1/2+z$; #2: $x, 3/2-y, -1/2+z$

Fig.3 (a) Molecular structure of **2** with numbering scheme; (b) View of an infinite chain of complex **2**

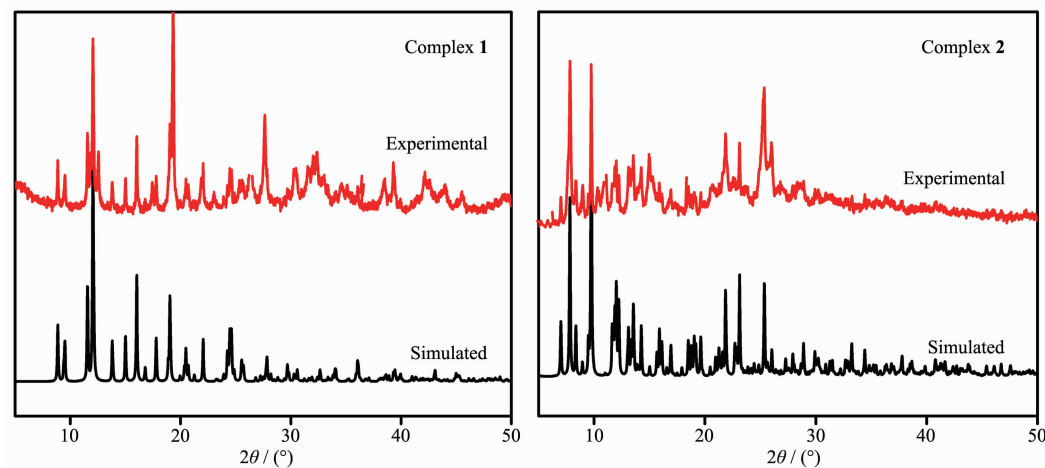
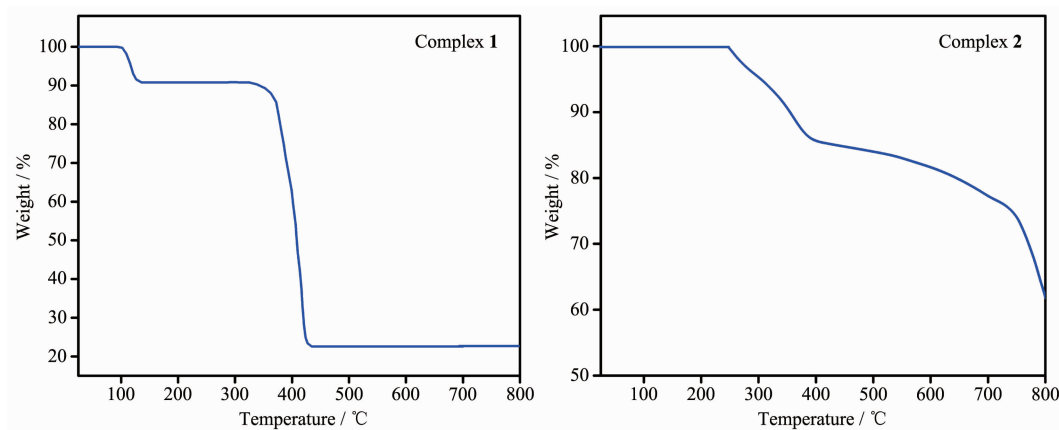


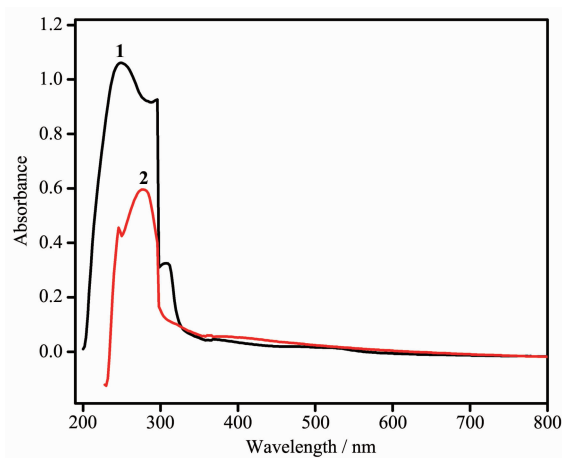
Fig.4 PXRD patterns of **1** and **2**

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

coordinated water molecule (Calcd. 9.4%). The TGA curve displays that it was stable up to about 351 °C. The other weight loss in a temperature range of 352~434 °C were attributed to the remaining coordinated water molecule and the decomposition of all organic ligands. For complex **2**, a weight loss of 14.5% between 243 and 400 °C is in accordance with the release of two chloride ions and two phen water molecules in complex **2** (Calcd. 17.6%). Further heating above 401 °C causes the network to collapse accompanied by the decomposition of the organic ligands, but this degradation does not end upon 800 °C. It suggests that complex **2** is rather stable on heating, which shows higher thermal stability.

2.5 Semiconductor properties and optical band gaps

Several coordination architectures have been certified to be promising semiconductors, so the UV-Vis absorption spectra of **1** and **2** were measured in the solid state at room temperature. The UV-Vis absorption spectra of **1** and **2** show a broad absorption bands in the UV regions at 200~300 nm as shown in Fig.6, which can be principally ascribed to the π - π^* or n - π^* transitions of ligands^[22]. Meanwhile, the band gap energy of **1** and **2** can be calculated according to the formula: $E_g = 1240/\lambda_g$ (eV), where E_g is the band gap energy (eV) and λ_g is the absorption edge wavelength (nm). The E_g values are 4.12 eV for **1** and 4.04 eV for **2**, as shown in Fig.7, which indicates that **1** and **2** may be beneficial to catalysis and that **1** and **2** have potential semiconductor properties.

Fig.6 UV-Vis spectra of **1** and **2** in the solid state at room temperature

2.6 Luminescent properties

Luminescence properties of Zn(II) complexes have attracted considerable attention because of their potential applications as valuable luminescent materials. The solid-state luminescence properties of complex **2** as well as the benzimidazole-5,6-dicarboxylic acid ligand and 1,10-phenanthroline auxiliary ligand were investigated at room temperature. According to the reported literature^[16], upon excitation at 365 nm for benzimidazole-5,6-dicarboxylic acid and 378 nm for 1,10-phenanthroline, the pure ligands display fluorescence spectra with emission maxima bands at 430 nm for benzimidazole-5,6-dicarboxylic acid and 438 nm for 1,10-phenanthroline. The emission spectrum of complex **2** is depicted in Fig.8. Complex **2** exhibits an intense blue luminescent property with emission maxima at 416 nm under excitation at 370 nm, which

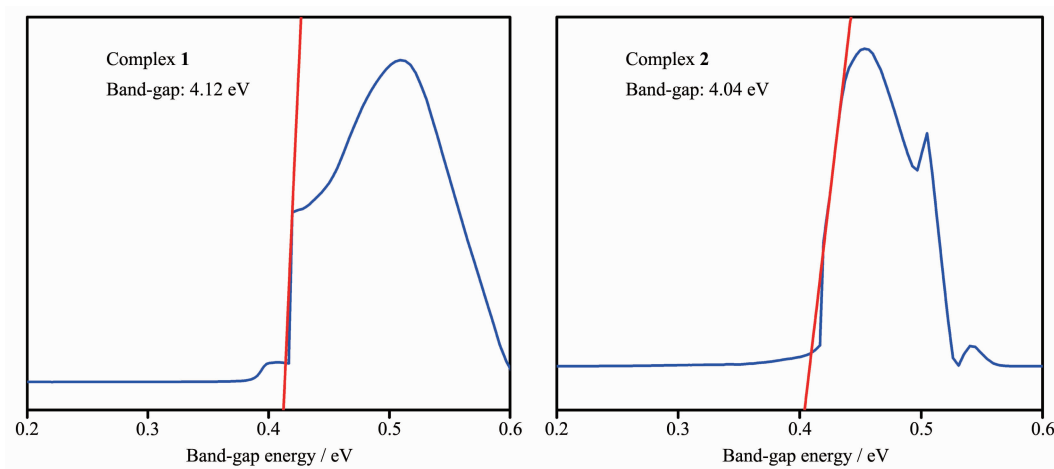


Fig.7 Diffuse reflectance spectra of K-M functions versus band-gap energy of complexes **1** and **2** at room temperature

indicates that this emission band of **2** is neither ligand-to-metal charge transfer (LMCT) nor metal-to-ligand charge transfer (MLCT) because Zn(II) ion is difficult to reduce or oxidize, but rather could be attributed to intraligand transition. The luminescent emission band in the blue area demonstrates that complex **2** may be potential emitting material.

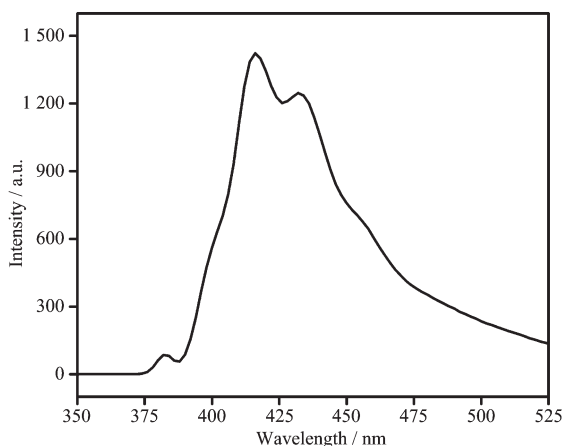


Fig.8 Emission spectrum of **2** in the solid state at room temperature

3 Conclusions

In summary, two new coordination polymers with benzimidazole-5,6-dicarboxylic acid, 2,2'-bipyridine or 1,10-phenanthroline ligands have been synthesized and structurally characterized by single-crystal X-ray diffraction, IR spectroscopy, elemental analysis, powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA). Complexes **1** and **2** consist of different 1D chain structures. The one-dimensional zig-zag

chain is formed by the Hbide^{2-} ligands and the Mn(II) ions, which are extended into a 3D supramolecular framework via $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding interactions for complex **1**. In addition, the UV-Vis absorption spectra indicate that complexes **1** and **2** show a broad absorption band in the UV regions of 200~300 nm and **1** and **2** have the E_g values of 4.12 eV for **1** and 4.04 eV for **2**, which demonstrates that **1** and **2** have potential semiconductor properties. The emission spectrum of complex **2** exhibits an intense blue fluorescent emission with emission maxima at 416 nm under excitation at 370 nm, indicating that complex **2** may be potential emitting material.

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