

由 Cd 和二(1-亚甲基咪唑)取代苯配体组装的三个配位聚合物: 合成, 结构及荧光性质

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摘要: 在水热条件下合成了 3 个配合物, $[\text{Cd}_{0.5}(\text{o-bix})\text{NO}_3]_n$ (**1**), $[\text{Cd}(\text{m-bix})_2(\text{H}_2\text{O})_2 \cdot 2\text{NO}_3]_n$ (**2**) 和 $[\text{Cd}(2,3\text{-pidc})(\text{p-bix})]_n$ (**3**) (bix=二(1-亚甲基咪唑)取代苯, 2,3-pidc=2,3-二羧基吡嗪)。配合物 **1** 具有一维链状结构, 配合物 **2** 具有双重相互平行穿插的结构, 配合物 **3** 则是二维平面结构。同时, 对配合物 **1~3** 进行了热稳定性和荧光性质的研究。配合物 **1** 的结构在 215 °C 以下是稳定的。配合物 **2** 从 82 到 150 °C 失去参与配位的水分子。配合物 **3** 在 273 °C 以下结构保持稳定。在室温下, 360 nm 处的荧光激发导致配合物 **1**、**2**、**3** 分别在 450、460、460 nm 处有荧光发射。

关键词: 配合物; 晶体结构; 荧光

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Three Coordination Polymer Complexes Assembled from Cadmium(II) and *ortho*-, *meta*-, and *para*-bisubstituted Bix Ligands: Syntheses, Structures, and Fluorescence Studies

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Abstract: Three complexes, $[\text{Cd}_{0.5}(\text{o-bix})\text{NO}_3]_n$ (**1**), $[\text{Cd}(\text{m-bix})_2(\text{H}_2\text{O})_2 \cdot 2\text{NO}_3]_n$ (**2**) and $[\text{Cd}(2,3\text{-pidc})(\text{p-bix})]_n$ (**3**) (bix=bis(imidazol-1-ylmethyl)-benzene, 2,3-pidc=2,3-pyrazinedicarboxylic acid), have been synthesized under hydrothermal conditions. Complex **1** shows a one-dimensional (1D) chain structure, complex **2** features a 2-fold parallel interpenetrated framework, and complex **3** represents a two-dimensional (2D) layer structure. The thermal stabilities and fluorescent properties of complexes **1~3** are investigated. CCDC: 680905, **1**; 680906, **2**; 680904, **3**.

Key words: coordination complex; crystal structure; fluorescent property

0 Introduction

In the design and assembly of metal-organic frameworks (MOFs), nitrogen-containing flexible ligands have received remarkable attention, and played an important role in preparing fascinating complexes with

novel architectures and functional properties^[1~6]. For example, neutral bis (imidazole) ligands are able to coordinate to various metal centers in diversified modes to generate new types of MOFs. It has already proven a certain ability to form interpenetrating networks and uncommon species, including polycatenated arrays,

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polyrotaxane-like species, interlocked motifs of different dimensionality^[7~11]. In the previous studies, it has been reported that the neutral bis (imidazole) ligands gave an infinite 1D chain with cobalt sulfate or zinc acetate^[10,12], an infinite 2D polyrotaxane network by reactions with silver(I) nitrate^[7], a 3D framework by reaction with cobalt sulfate^[8], a 3D (2D+1D) architecture by reaction with Mn(II) nitrate^[11].

Herein we employed three different neutral bis (imidazole) ligands, *o*-bix, *m*-bix and *p*-bix (Chart 1), investigated their coordination chemistry and abilities in constructing intriguing MOFs. In addition, 2,3-pidc ligand, which possess the capability to bridge metal atoms in various coordination modes using the carboxylate oxygen atoms and nitrogen atoms of the pyrazine ring, were incorporated as an auxiliary ligand in our syntheses of MOFs. As Cd²⁺ was used as metal center, three complexes, [Cd_{0.5}(*o*-bix)NO₃]_n (**1**), [Cd(*m*-bix)₂(H₂O)₂·2NO₃]_n (**2**) and [Cd(2,3-pidc)(*p*-bix)]_n (**3**), have been obtained.

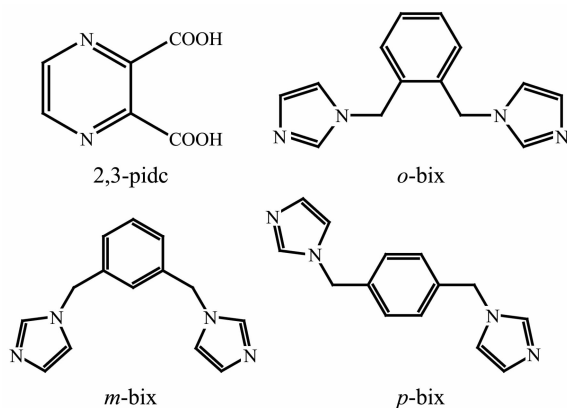


Chart 1 Ligands used in the construction of complexes **1~3**

1 Experimental

1.1 Materials and methods

All the starting materials were obtained from commercial sources and were used without further purification. The bix ligands were synthesized as reported previously^[7]. Elemental analyses were performed on a PE 240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer using KBr disk methods. The fluorescent spectra were recorded on a SHIMADZU VF-320 spectrometer with polycrystalline samples.

1.2 Syntheses of complexes **1~3**

The three complexes were synthesized under very similar experimental conditions. For complex [Cd_{0.5}(*o*-bix)NO₃]_n (**1**), a mixture of Cd(NO₃)₂·4H₂O (0.031 g, 0.1 mmol), 2,3-pidc (0.017 g, 0.1 mmol), *o*-bix (0.024 g, 0.1 mmol), Et₃N (0.2 mmol) and water (8 mL) was sealed in a 25 mL teflonlined stainless autoclave, which was heated to 120 °C and held for 3 days. After slowly cooling down to room temperature, colorless needlelike crystals of complex **1** were collected as a monophasic material, judged by powder XRD measurements. For complexes [Cd(*m*-bix)₂(H₂O)₂·2NO₃]_n (**2**) and [Cd(2,3-pidc)(*p*-bix)]_n (**3**), *m*-bix (0.024 g, 0.1 mmol) and *p*-bix (0.024 g, 0.1 mmol) were used respectively as reactants instead of *o*-bix. Monophasic colorless needlelike crystals of complexes **2** and **3** were obtained as well.

Complex **1**: Yield: 47% based on Cd. Anal. Calcd for C₂₈H₂₈CdN₁₀O₆ (%): C 47.17; H 3.96; N 19.64. Found (%): C 47.25; H 4.02; N 19.72. IR (KBr, cm⁻¹): 3 411s, 3 135w, 2 344w, 1 626s, 1 587s, 1 561w, 1 463w, 1 387m, 1 356m, 1 238w, 1 116m, 1 083m, 930w, 838w, 736m, 657w, 538w, 439w.

Complex **2**: Yield: 62% based on Cd. Anal. Calcd for C₂₈H₃₂CdN₁₀O₈ (%): C 44.90; H 4.31; N 18.70. Found (%): C 44.95; H 4.41; N 18.90. IR (KBr, cm⁻¹): 3 447s, 3 125w, 2 364w, 1 617s, 1 568w, 1 519m, 1 447m, 1 384s, 1 233w, 1 115m, 1 086m, 936w, 839w, 749m, 658m, 442w.

Complex **3**: Yield: 45% based on Cd. Anal. Calcd for C₂₀H₁₆CdN₆O₄ (%): C 46.48; H 3.12; N 16.26. Found (%): C 46.57; H 3.19; N 16.29. IR (KBr, cm⁻¹): 3 444s, 3 112w, 1 627s, 1 516m, 1 386w, 1 360m, 1 341m, 1 238w, 1 199w, 1 159w, 1 114m, 1 092m, 932w, 848w, 821w, 762w, 713w, 658m, 428w.

1.3 Crystal structure analysis

Intensity data for the three complexes were collected at 293(2) K on a Siemens SMART-CCD diffractometer with graphite-monochromatized Mo K α radiation ($\lambda=0.071\,073\,\text{nm}$). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively. The structures were solved by direct method using SHELXS-97^[13] and were refined by full matrix least-squares method

using SHELXL-97^[14]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms except for those of water molecules were generated geometrically and refined using a riding model. Crystallographic data and other pertinent information for **1**~**3** are summarized in Table 1. Selected

bond lengths and bond angles are listed in Table 2. More details on the crystallographic studies as well as atom displacement parameters are given in Supporting Information.

CCDC: 680905, **1**; 680906, **2**; 680904, **3**.

Table 1 Crystal data and structure refinement information for complexes **1**~**3**

	1	2	3
Empirical formula	C ₂₈ H ₂₈ CdN ₁₀ O ₆	C ₂₈ H ₃₂ CdN ₁₀ O ₈	C ₂₀ H ₁₆ CdN ₆ O ₄
Formula weight	713.00	749.04	516.79
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
<i>a</i> / nm	0.884 9(3)	1.783 8(4)	0.769 60(18)
<i>b</i> / nm	0.892 1(2)	0.821 8(2)	1.013 2(3)
<i>c</i> / nm	1.008 5(3)	2.330 2(6)	1.242 7(3)
α / (°)	70.741(4)		90.561(4)
β / (°)	85.558(4)	109.531(5)	105.405(4)
γ / (°)	76.584(4)		92.928(5)
<i>V</i> / nm ³	0.731 1(4)	3.219 2(14)	0.932 7(4)
<i>Z</i>	1	4	2
μ / mm ⁻¹	0.808	0.743	1.215
Reflections collected	3 920	16 674	4 695
Unique reflections	2 793	6 316	3 234
Obs reflections [<i>I</i> >2 σ (<i>I</i>)]	2 336	4 886	2 952
<i>R</i> _{int}	0.028 7	0.035 8	0.035 1
<i>R</i> ₁ [<i>I</i> >2 σ (<i>I</i>)]	0.056 6	0.049 1	0.038 2
<i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.122 8	0.090 6	0.077 3
Goodness-of-fit	1.028	1.075	1.037

Table 2 Selected bond lengths (nm) and bond angles (°) for **1**~**3**

Complex 1					
Cd(1)-N(1)	0.227 0(4)	Cd(1)-N(1A)	0.227 0(4)	Cd(1)-N(4B)	0.233 2(4)
Cd(1)-N(4C)	0.233 2(4)	Cd(1)-O(1)	0.243 1(4)	Cd(1)-O(1A)	0.243 1(4)
N(1)-Cd(1)-N(1A)	180.0(3)	N(1)-Cd(1)-N(4B)	90.00(16)	N(1A)-Cd(1)-N(4B)	90.00(16)
N(1)-Cd(1)-N(4C)	90.00(16)	N(1A)-Cd(1)-N(4C)	90.00(16)	N(4B)-Cd(1)-N(4C)	180.00(9)
N(1)-Cd(1)-O(1)	80.71(15)	N(1A)-Cd(1)-O(1)	99.29(15)	N(4B)-Cd(1)-O(1)	97.42(15)
N(4C)-Cd(1)-O(1)	82.58(15)	N(1)-Cd(1)-O(1A)	99.29(15)	N(1A)-Cd(1)-O(1A)	80.71(15)
N(4B)-Cd(1)-O(1A)	82.58(15)	N(4C)-Cd(1)-O(1A)	97.42(15)	O(1)-Cd(1)-O(1A)	180.0
Complex 2					
Cd(1)-N(8A)	0.227 2(3)	Cd(1)-N(1)	0.228 7(3)	Cd(1)-N(4B)	0.231 3(3)
Cd(1)-N(5)	0.232 3(3)	Cd(1)-O(7)	0.236 7(3)	Cd(1)-O(8)	0.241 2(3)
N(8A)-Cd(1)-N(1)	172.37(12)	N(8A)-Cd(1)-N(4B)	91.78(12)	N(1)-Cd(1)-N(4B)	89.18(11)
N(8A)-Cd(1)-N(5)	92.18(12)	N(1)-Cd(1)-N(5)	88.01(11)	N(4B)-Cd(1)-N(5)	170.67(12)
N(8A)-Cd(1)-O(7)	91.21(11)	N(1)-Cd(1)-O(7)	96.42(11)	N(4B)-Cd(1)-O(7)	84.39(10)

Continued Table 2

N(5)-Cd(1)-O(7)	87.08(11)	N(8A)-Cd(1)-O(8)	88.29(11)	N(1)-Cd(1)-O(8)	84.09(11)
N(4B)-Cd(1)-O(8)	93.71(10)	N(5)-Cd(1)-O(8)	94.85(11)	O(7)-Cd(1)-O(8)	178.02(9)
Complex 3					
Cd(1)-N(3)	0.228 2(3)	Cd(1)-N(1)	0.230 2(4)	Cd(1)-O(1A)	0.230 6(3)
Cd(1)-N(5B)	0.234 5(3)	Cd(1)-O(3B)	0.236 9(3)	Cd(1)-O(1)	0.239 5(3)
N(3)-Cd(1)-N(1)	86.66(12)	N(3)-Cd(1)-O(1A)	93.18(11)	N(1)-Cd(1)-O(1A)	104.82(11)
N(3)-Cd(1)-N(5B)	163.83(12)	N(1)-Cd(1)-N(5B)	96.20(12)	O(1A)-Cd(1)-N(5B)	101.40(11)
N(3)-Cd(1)-O(3B)	92.97(11)	N(1)-Cd(1)-O(3B)	83.32(11)	O(1A)-Cd(1)-O(3B)	170.06(9)
N(5B)-Cd(1)-O(3B)	71.65(11)	N(3)-Cd(1)-O(1)	89.03(11)	N(1)-Cd(1)-O(1)	175.67(11)
O(1A)-Cd(1)-O(1)	75.79(11)	N(5B)-Cd(1)-O(1)	87.84(10)	O(3B)-Cd(1)-O(1)	96.53(9)

Symmetry codes: (1) A: $-x+2, -y, -z$; B: $-x+2, -y, -z+1$; C: $x, y, z-1$; D: $x, y, z+1$; (2) A: $x, -y+1/2, z-1/2$; B: $x, -y+5/2, z-1/2$; C: $x, -y+5/2, z+1/2$; D: $x, -y+1/2, z+1/2$; (3) A: $-x+2, -y+2, -z+1$; B: $-x+1, -y+2, -z+1$.

2 Results and discussion

2.1 Crystal structure of $[\text{Cd}_{0.5}(\text{o-bix})\text{NO}_3]_n$ (1)

Complex **1** crystallizes in the $P\bar{1}$ space group and has a 1D structure. As shown in Fig.1a, there are a half Cd^{2+} ion, one *o*-bix ligand, and one nitrate anion in the asymmetric unit. Cd ion is surrounded by an octahedral coordination sphere that is defined by two oxygen atoms (O1, O1A) from different nitrate groups occupying the axial positions while the equatorial positions furnished by four independent *o*-bix nitrogen donors (N1, N1A,

N4B and N4C). (Symmetry codes: A: $-x+2, -y, -z$; B: $-x+2, -y, -z+1$; C: $x, y, z-1$).

In complex **1**, the Cd-N bond lengths vary from 0.227 0(4) and 0.233 2(4) nm, and the Cd-O bond lengths for the coordinating nitrate groups are 0.243 1(4) nm. Complex **1** consists of ribbons of 24-membered cycles, each ring involving two cadmium atoms and two *o*-bix ligands (Fig.1b), and the distance of $\text{Cd} \cdots \text{Cd}$ is 1.008 5 nm. The structure is similar to previously reported complex $[\text{Co}(\text{bix})_2(\text{H}_2\text{O})_2](\text{SO}_4) \cdot 7\text{H}_2\text{O}$ ^[8].

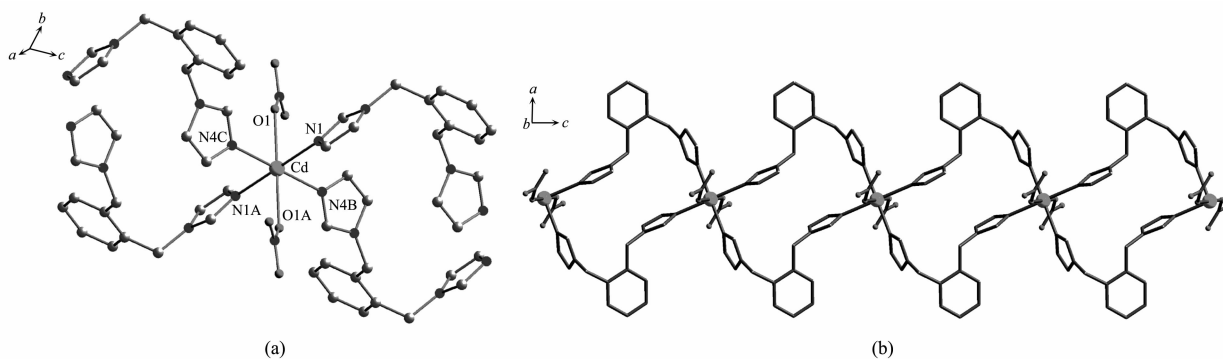


Fig.1 (a) Perspective view of the coordination environments of the Cd^{2+} ion, (b) the ribbon of rings, with hydrogen atoms omitted for clarity in complex **1**

2.2 Crystal structure of $[\text{Cd}(m\text{-bix})_2(\text{H}_2\text{O})_2 \cdot 2\text{NO}_3]_n$ (2)

Complex **2** crystallizes in the $P2_1/c$ space group and adopts a 2D structure. As shown in Fig.2a, the asymmetric unit of **2** contains one Cd^{2+} ion, two *m*-bix ligands, two coordinating water molecules and two nitrate anions. The Cd ion lies in an octahedral

geometry with N1, N5, N4B and N8A (from independent *m*-bix) on the equatorial plane, O7 and O8 (from coordinated waters) in the axial position. (Symmetry codes: A: $x, -y+1/2, z-1/2$; B: $x, -y+5/2, z-1/2$).

In complex **2**, the Cd-N bond lengths vary from 0.227 2(3) and 0.232 3(3) nm, which is very close to those in complex **1**; and the Cd-O bond lengths for the

coordinating water molecules range from 0.236 7(3) to 0.241 2(3) nm. Each Cd^{2+} ion binds to four *m*-bix, and each *m*-bix connects two Cd^{2+} ion, thus yielding a 2D (4,4) infinite sheet in the *bc* plane (Fig.2b). All the *m*-bix ligands assume *cis*-conformation ($\text{N}\cdots\text{N}$ distance 1.053 nm or 1.001 nm). This produce large grid (1.405 nm \times 1.447 nm). Furthermore, each (4,4) grid is interpenetrated by another sheet, with inter-plane distances of 0.482 nm (Fig.2c). Upon inter-penetration, the PLATON calculation shows that the unit cell contains no residual solvent-accessible void.

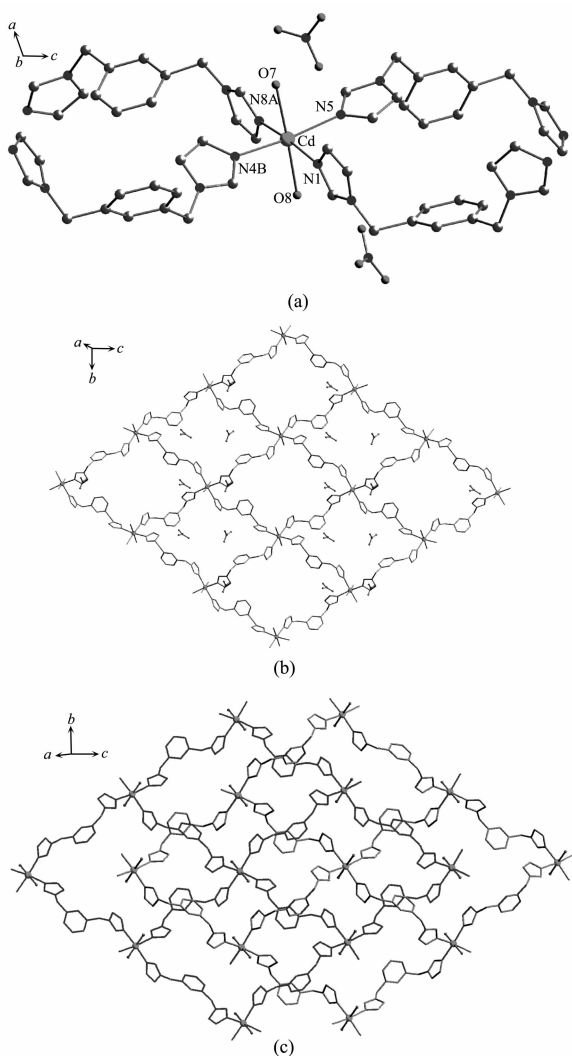


Fig.2 (a) Perspective view of the coordination environments of the Cd^{2+} ion, (b) 2D (4,4) infinite sheet in the *bc* plane, with hydrogen atoms omitted for clarity, (c) the 2-fold parallel interpenetrated framework in complex **2**, with nitrate anions omitted

2.3 Crystal structure of $[\text{Cd}(2,3\text{-pidc})(p\text{-bix})]_n$ (**3**)

A single-crystal X-ray diffraction study reveals

that complex **3** crystallizes in the $P\bar{1}$ space group and adopts a 2D structure. Different from complex **1** and **2**, complex **3** contains a 2,3-pidc ligand, as the result of self-assembly. As shown in Fig.3a, the asymmetric unit of **3** is composed of one Cd^{2+} ion, one 2,3-pidc ligands, and two half *p*-bix ligands. Cd^{2+} ion is in a distorted octahedral geometry with O1, O1A, O3B (from the carboxylate groups), N1, N3 (from different bix) and N5B (from 2,3-pidc). (Symmetry codes: A: $-x+2, -y+2, -z+1$; B: $-x+1, -y+2, -z+1$).

In complex **3**, the Cd-N bond lengths vary from 0.228 2(3) and 0.234 5(3) nm, which are similar to those of **1** and **2**. In each pidc ligand, N5 and O3 atoms coordinate to Cd ion in a monodentate fashion, while O1 atom binds to two Cd ions in a bidentate mode. A pair of symmetry-related Cd ions are bridged by two μ_2 -O1 atoms from two separate carboxylate moieties into a binuclear cadmium unit with the $\text{Cd}\cdots\text{Cd}$ separation of 0.371 0 nm. The binuclear cadmium units are bridged by the pidc ligands to form the 1D chain along *a* axis (Fig.3b).

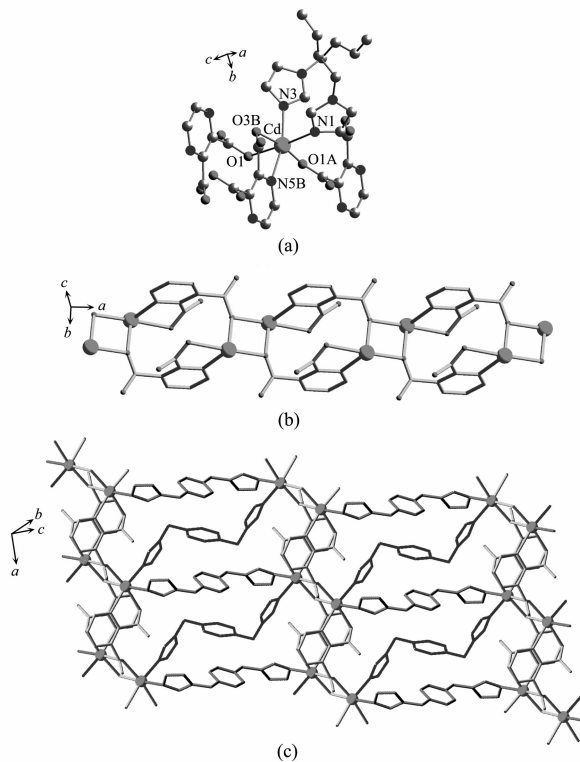


Fig.3 (a) Perspective view of the coordination environments of the Cd^{2+} ion, (b) the 1D chain along *a* axis, (c) the 2D structure with hydrogen atoms omitted for clarity in complex **3**

As illustrated in Fig.3c, all *p*-bix in complex **3** adopt *trans*-conformation. For the bix ligand containing N1 (shown in red), the imidazole ring and phenyl group are twisted by *ca.* 59.8°; for the bix containing N5 (shown in blue), the two planes are inclined by *ca.* 73.8°. Thus each Cd center connects to other two Cd centers of adjacent chain via two different bix ligands, with Cd...Cd separations of 0.129 57 nm and 1.409 8 nm, respectively. Additionally, π - π interactions are observed between the phenyls rings of the adjacent chains (The centroid contact of adjacent phenyls rings is 0.384 8 nm, and the dihedral angle is 13.1°). A 2D layer structure is formed in the *ac* plane.

2.4 XRD patterns and thermal analyses

The purity of complexes **1~3** were confirmed by X-ray power diffraction analyses, in which the experimental spectra of **1~3** are almost consistent with their simulated ones.

Results of thermogravimetric analysis (TGA) for complexes **1~3** measured under a N₂ atmosphere are shown in Fig.4. For complex **1**, no weight loss was found below 215 °C. And above this temperature, the structure collapsed due to the liberation of organic ligands. For complex **2**, the weight loss (3.97%) from 82 to 150 °C (calcd 4.80%) of **1** corresponds to that of two coordinating water molecules per formula, followed by a plateau region ranging from 150 to 268 °C. And the consecutive decompositions suggest the total destruction of the framework. Complex **3** is stable up to 273 °C, whereafter the framework structures begin to collapse.

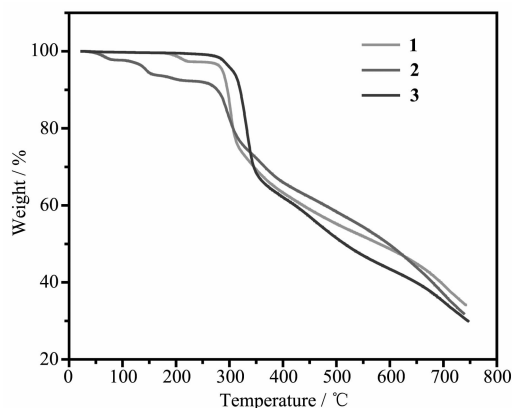


Fig.4 TGA curves for **1**, **2** and **3**

2.5 Luminescent properties

The emission spectra of complexes **1~3** and free

bix ligands in their solid states are investigated at room temperature under the same conditions. As depicted in Fig.5a, complex **1** and free *o*-bix ligand exhibit weak fluorescent emission bands at *ca.* 450 nm upon excitation at *ca.* 360 nm. Excitation at 360 nm leads to moderate fluorescent emission band at 460 nm for complex **2** and free *m*-bix ligand (Fig.5b). Excitation at 360 nm leads to moderate fluorescent emission band at 460 nm for complex **3** and free *p*-bix ligand (Fig.5c). Because similar emissions are observed in free ligands respectively, emissions of complexes **1~3** can probably be assigned to the intra-ligand (π - π^*) fluorescent emission. The enhancement of the emissions for complex **2** compared with free *m*-bix ligand may be ascribed to the increase in the ligand conformational rigidity due to their coordinating to the Cd²⁺ ion that resulting in

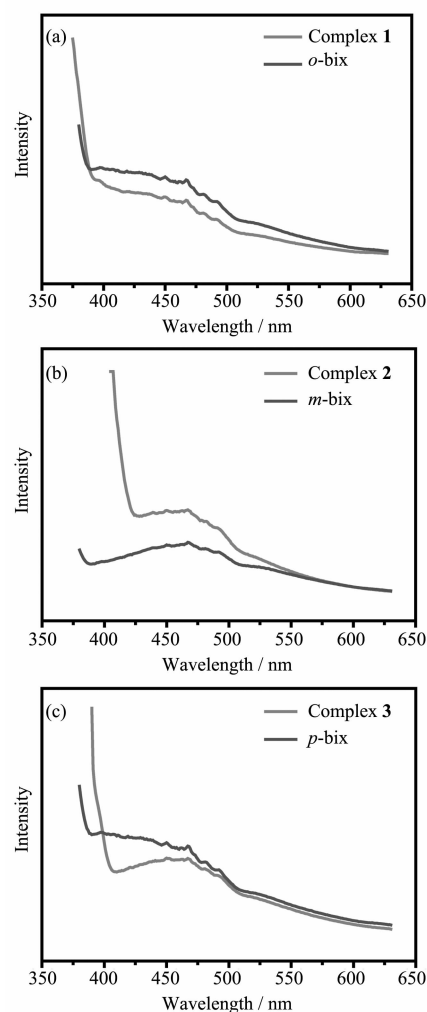


Fig.5 Emission spectra of complexes **1~3** and free ligands at room temperature

a decrease in the non-radiative decay of intra-ligand excited states^[15]. The emissions of complexes **1** and **3** are weak, may be because they are less rigid.

In summary, we have successfully prepared and characterized three complexes based on the flexible bis(imidazole) ligands. Complex **1** shows a one-dimensional (1D) chain structure, complex **2** features a 2-fold parallel inter-penetrated framework, and complex **3** represents a two dimensional (2D) layer structure. Moreover, complexes **1~3** display fluorescent emissions at room temperature when excited at 360 nm.

Supplementary material: The data can be obtained free of charge via E-mail: luchsh@nju.edu.cn.

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