

含苯并咪唑基配体 Zn(II)、Cd(II)配位聚合物的合成、结构以及荧光性质研究

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摘要: 以 3,5-二(苯并咪唑基)吡啶(L)、间苯二甲酸(*m*-H₂BDC)、4-羧基肉桂酸(H₂CCA)、ZnSO₄·7H₂O 和 Cd(NO₃)₂·4H₂O 为原料, 使用溶剂热方法合成了两个配位聚合物[Zn(L)(*m*-BDC)] (**1**)和[Cd(L)(CCA)]·2H₂O (**2**), 利用红外、元素分析、热重分析和 X-射线粉末衍射对其进行了表征, 利用 X-射线单晶衍射对结构进行了测定, 并研究了配合物的荧光性质。在配合物 **1** 中, L 与金属离子连接形成了一维(1D)链结构, 而间苯二甲酸根离子与金属离子构成了一个 M₂(*m*-BDC)₂(M=金属离子)的单元。一维链之间通过 M₂(*m*-BDC)₂ 单元连接形成二维网状(2D)结构。在配合物 **2** 中, 和配合物 **1** 类似, L 与金属离子连接形成一维链, 但与 **1** 不同的是羧酸配体与金属离子配位也构成了一维链结构, 两种一维链通过配位作用连接构成二维结构。

关键词: 配位聚合物; 荧光; 晶体结构

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Synthesis, Crystal Structure and Fluorescence Property of Zn(II), Cd(II) Coordination Polymers with Benzoimidazol-Containing Ligand

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Abstract: Two new coordination polymers [Zn(L)(*m*-BDC)] (**1**) and [Cd(L)(CCA)]·2H₂O (**2**) were synthesized by solvothermal method using 3,5-di(1*H*-benzoimidazol-1-yl)pyridine (L), isophthalic acid (*m*-H₂BDC), 4-(2-carboxyvinyl)benzoic acid (H₂CCA). And the complexes were characterized by FT-IR, elemental analysis, thermogravimetric analysis (TGA) and power X-ray diffraction (PXRD), meanwhile the crystal structures and fluorescence properties of the complexes have been studied. In complex **1**, the ligand L connects the metal atoms to give a 1D chain structure, and the *m*-BDC²⁻ coordinates with metal atom to form a M₂(*m*-BDC)₂ unit (M=metal). Moreover, the adjacent 1D chains are linked by the M₂(*m*-BDC)₂ to produce a 2D network structure. In complex **2**, the ligand joins the metal atoms to generate a 1D chain like that in **1**. However, the carboxylate ligand coordinates with metal atoms to form a 1D chain, and two kinds of the 1D chains crosslink each other to produce a 2D structure. CCDC: 958416, **1**; CCDC: 958417, **2**.

Key words: coordination polymers; fluorescence property; crystal structure

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In recent years, the construction of novel metal-organic frameworks (MOFs) using pre-designed organic ligands continues to attract interest of chemists for their fascinating structures, interesting properties and potential applications in nonlinear optics, ferroelectrics, magnetism, luminescence and so on^[1-2]. In the previous reports, a series of coordination frameworks have been obtained by combination of transition metal centers with specific coordination requirement and ligands with definite conformations^[3-4]. However, not all of the resulting structures can be exactly predicted owing to the influence of the coordination sphere of metal centers, the structure of ligands, reaction solvent and so on^[5-7]. In our previous studies, we designed and synthesized a tridentate ligand 3,5-di(1*H*-imidazol-1-yl)pyridine to probe the formation of supramolecular structures. As a result, this ligand can coordinate with various transition metal ions to generate one-dimensional (1D) chain, two-dimensional (2D) network and three-dimensional (3D) frameworks^[8]. From another point of view, metal ions with d^{10} configuration, for example Zn^{2+} and Cd^{2+} , usually have potential application in optical areas, such as fluorescence probe and nonlinear optical materials^[9-12]. In order to further investigate the influence of this bridging ligand in constructing coordination frameworks and to produce coordination polymers having optical properties, especially with those having d^{10} configuration, in this work, a new ligand 3,5-di(1*H*-benzoimidazol-1-yl)pyridine (**L**) is synthesized, which reacts with auxiliary carboxylic acid ligands and zinc sulfate and cadmium sulfate to give two different complexes $[\text{Zn}(\text{L})(m\text{-BDC})]$ (**1**), $[\text{Cd}(\text{L})(\text{CCA})] \cdot 2\text{H}_2\text{O}$ (**2**). And the fluorescence properties of the complexes were studied.

1 Experimental

1.1 Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Elemental analysis for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer at the analysis center of Nanjing University. Thermogravimetric analyses

(TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$. FT-IR spectra were obtained in the range of $400 \sim 4\,000\text{ cm}^{-1}$ on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.154\,18\text{ nm}$) radiation at room temperature. The luminescent spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source.

1.2 Preparation of $[\text{Zn}(\text{L})(m\text{-BDC})]$ (**1**)

Complex **1** was prepared by solvothermal method. **L** (15.5 mg, 0.05 mmol), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (43.1 mg, 0.15 mmol) and *m*- H_2BDC (8.3 mg, 0.05 mmol) were mixed in 8 mL of DMF/ H_2O (1:3, *V/V*) and sealed in a 16 mL Teflon lined stainless steel container, then heated at $120\text{ }^\circ\text{C}$ for 3 d. After being cooled to room temperature, block crystals of **1** were collected by carefully picking out under microscope to give a yield of 30%. Anal. Calcd. for $\text{C}_{27}\text{H}_{17}\text{N}_5\text{O}_4\text{Zn}(\%)$: C 59.96, H 3.17, N 12.95. Found(%): 59.99, H 3.18, N 12.97. IR (KBr pellet, cm^{-1}): 33 408(m), 3 066(m), 1 613(s), 1 450(m), 1 369(s), 1 156(m), 756(m), 705(w).

1.3 Preparation of $[\text{Cd}(\text{L})(\text{CCA})] \cdot 2\text{H}_2\text{O}$ (**2**)

Complex **2** was obtained by similar procedure used for preparation of **1**. **L** (15.5 mg, 0.05 mmol), $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$ (46.2 mg, 0.15 mmol) and H_2CCA (9.6 mg, 0.05 mmol) were mixed in 8 mL of DMF/ H_2O (1:3, *V/V*) and sealed in a 16 mL Teflon lined stainless steel container, then heated at $120\text{ }^\circ\text{C}$ for 3 d. After being cooled to room temperature, block crystals of **2** were collected with a yield of 30%. Anal. Calcd. for $\text{C}_{29}\text{H}_{21}\text{N}_5\text{O}_6\text{Cd}(\%)$: 53.76, H 3.27, N 10.81. Found(%): 53.75, H 3.26, N 10.83. IR (KBr pellet, cm^{-1}): 3 401(s), 3 086(w), 1 590(m), 1 504(m), 1 391(s), 1 238(m), 979(w), 744(m).

1.4 Crystal structure determination

Crystallographic data collections for **1** and **2** were carried out on a Bruker Smart Apex II CCD area detector diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.071\,073\text{ nm}$) at $20(2)\text{ }^\circ\text{C}$ using

ω -scan technique. The diffraction data were integrated using the SAINT program^[13], which was also used for the intensity corrections for the Lorentz and polarization effects. Semiempirical absorption corrections were applied using SADABS program. The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using

the SHELXL-97 crystallographic software package^[14]. The hydrogen atoms except those of water molecules were generated geometrically and refined isotropically using the riding model. The details of the crystal parameters, data collection, and refinements for the complexes are listed in Table 1, and selected bond lengths and angles are summarized in Table 2.

CCDC: 958416, **1**; CCDC: 958417, **2**.

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

Complex	1	2
Empirical formula	C ₂₇ H ₁₇ N ₃ O ₄ Zn	C ₂₉ H ₂₁ N ₃ O ₆ Cd
Formula weight	540.83	647.91
Crystal system	Orthorhombic	Triclinic
Space group	<i>Ccca</i>	<i>P</i> $\bar{1}$
<i>a</i> / nm	1.415 5(4)	1.080 1(2)
<i>b</i> / nm	1.596 5(4)	1.210 5(2)
<i>c</i> / nm	1.960 6(5)	1.215 6(3)
α / (°)		60.293(3)
β / (°)		83.089(5)
γ / (°)		78.436(3)
<i>T</i> / K	293(2)	293(2)
<i>V</i> / nm ³	4.431(2)	1.351 3(5)
<i>Z</i>	8	2
<i>D_c</i> / (g·cm ⁻³)	1.622	1.592
μ / mm ⁻¹	1.157	0.861
<i>F</i> (000)	2 208	652
<i>R_{int}</i>	0.050 4	0.023 1
Reflections collected	8 065	14 423
Unique reflections	1 963	4 726
Goodness-of-fit	1.059	1.071
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.041 4, 0.109 1	0.036 0, 0.087 1
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.066 0, 0.121 9	0.039 0, 0.089 1

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2)/3$.

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

Compound 1					
Zn(1)-O(1)	0.192 1(3)	Zn(1)-N(1)	0.203 2(3)		
O(1)-Zn(1)-O(1A)	95.00(18)	N(1A)-Zn(1)-N(1)	97.31(17)	O(1)-Zn(1)-N(1)	120.46(13)
O(1A)-Zn(1)-N(1)	112.68(12)				
Compound 2					
Cd(1)-O(1)	0.239 3(3)	Cd(1)-O(2)	0.228 2(3)	Cd(1)-O(4)	0.226 6(3)
Cd(1)-N(2)	0.2269(3)	Cd(1)-O(3)	0.245 9(3)	Cd(1)-N(5A)	0.227 4(3)
O(4)-Cd(1)-N(2)	105.49(12)	O(4)-Cd(1)-N(5A)	90.20(12)	O(4)-Cd(1)-O(2)	106.78(11)

Continued Table 2

N(2)-Cd(1)-O(2)	140.17(10)	O(4)-Cd(1)-O(1)	160.21(12)	N(2)-Cd(1)-O(1)	88.20(11)
O(2)-Cd(1)-O(1)	55.40(10)	O(4)-Cd(1)-O(3)	55.00(13)	N(5A)-Cd(1)-O(3)	145.20(12)
O(2)-Cd(1)-O(3)	84.55(11)	C(20)-Cd(1)-C(26)	117.62(14)	N(2)-Cd(1)-N(5A)	94.24(11)
N(5A)-Cd(1)-O(2)	108.30(10)	N(5A)-Cd(1)-O(1)	103.22(11)	N(2)-Cd(1)-O(3)	95.43(11)
O(1)-Cd(1)-O(3)	110.43(13)				

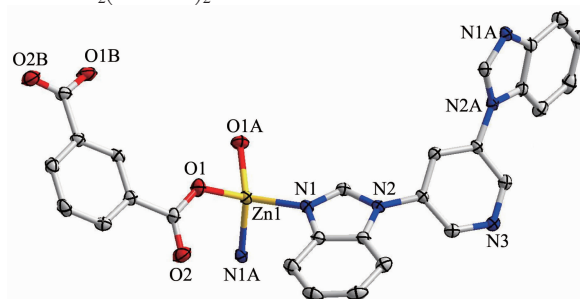
Symmetry operators: A: $1-x, 1/2-y, z$ for **1**; A: $1+x, y, z$ for **2**.

2 Results and discussion

2.1 Crystal structure description of [Zn(L)(*m*-BDC)] (**1**)

The result of X-ray diffraction analysis reveals that complex **1** crystallizes in orthorhombic with space group of *Ccca* and the asymmetric unit consists of one Zn (II) atom located at special position with half occupancy, half ligand L and half *m*-BDC²⁻. As depicted in Fig.1, Zn1 atom is coordinated by two oxygen (O1, O1A) from two different *m*-BDC²⁻ and two nitrogen atoms (N1, N1A) from two distinct L ligands. The bond lengths around Zn are 0.192 1(3) and 0.203 2(3) nm, the bond angles around Zn are from 95.00(18)° to 120.46(13)° (Table 2). In complex **1**, each L joins two zinc atoms, and each Zn atom connects two L to form a 1D chain (Fig.2). And two *m*-BDC²⁻ ligands coordinate with two metal atoms to generate a Zn₂(*m*-BDC)₂ unit (Fig.3). Furthermore, the adjacent 1D

chains are linked together by the Zn₂(*m*-BDC)₂ units to give a 2D network (Fig.4). Similarly, a previously reported complex [Zn(tib)(*m*-BDC)]·H₂O (**3**) also with 2D network structure was obtained by using 1,3,5-tris(1-imidazolyl)benzene (tib) and *m*-BDC²⁻ ligands, in which the *m*-BDC²⁻ ancillary ligands connect the Zn(II)-tib chains to produce the 2D network^[15], however, there are no Zn₂(*m*-BDC)₂ units in **3**.



Hydrogen atoms are omitted for clarity; Symmetry code: A $1-x, 1/2-y, z$; B $1-x, y, 1/2-z$

Fig.1 Coordination environment of Zn(II) in **1** with the ellipsoids drawn at the 30% probability level

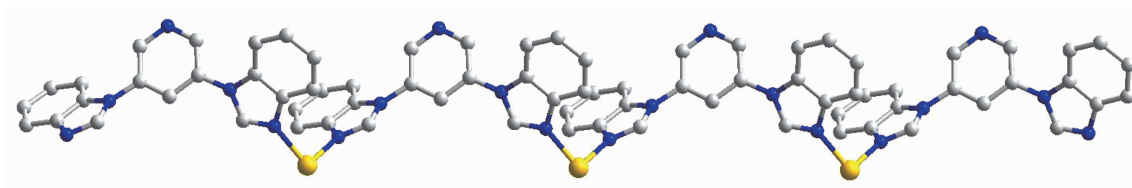


Fig.2 1D chain formed by Zn(II) and L ligands

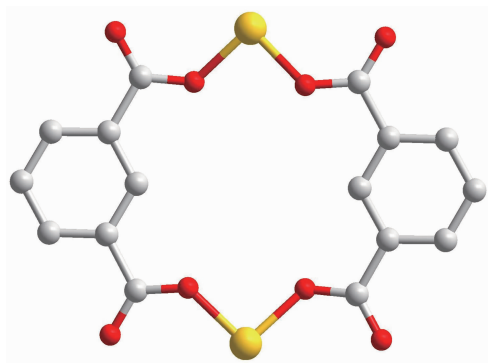


Fig.3 Structural unit formed by Zn(II) and *m*-BDC²⁻ ligands

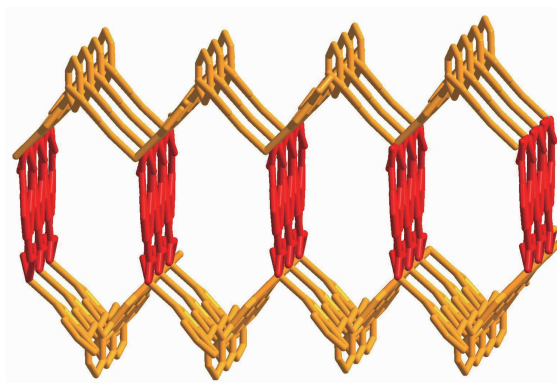


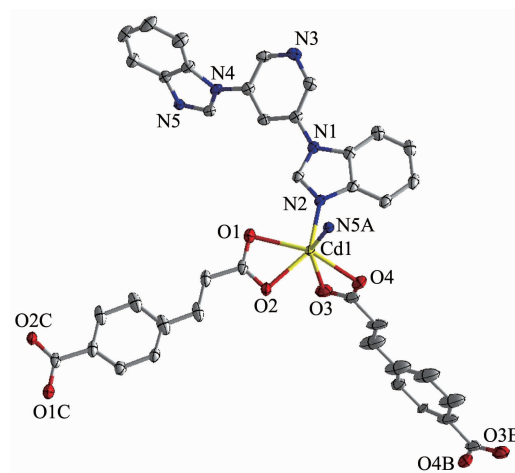
Fig.4 2D network of **1**

2.2 Crystal structure description of [Cd(L)(CCA)]·2H₂O (**2**)

When the ancillary ligand and metal salt were changed to H₂CCA and CdSO₄·4H₂O, a new coordination polymer **2** with different structure was isolated. Single crystal X-ray diffraction analysis revealed that **2** crystallized in triclinic $P\bar{1}$ space group. In the asymmetric unit of **2**, there are one Cd(II) atom, one L, one CCA²⁻ and two free water molecules. As depicted in Fig.5, each Cd1 atom adopts six-coordinated octahedral geometry formed by two nitrogen atoms (N2, N5A) from two distinct L ligands, four oxygen ones (O1, O2, O3, O4) from two different CCA²⁻. Similar with complex **1**, the L ligands and metal atoms constitute a 1D chain (Fig.6). However, the CCA²⁻ ligands and metal atoms also form a 1D chain (Fig.7). Two kinds of 1D chains crosslink each other to produce a 2D structure of **2** (Fig.8). Furthermore, the adjacent 2D network are connected by the hydrogen bond O—H···O between free water and ligands to give a 3D structure (Fig.9). The hydrogen bond data are showed in Table 3.

It is noteworthy that both **1** and **2** have 2D network structures and there are Zn-L and Cd-L 1D chains in **1** and **2**, respectively. However, there is

remarkable difference between them, namely the 1D chains in **1** are connected by Zn₂(*m*-BDC)₂ units while the 1D chains in **2** are joined together by CCA²⁻ ligands. Such difference may be caused by the different structure of *m*-BDC²⁻ and CCA²⁻ since the meta-positioned two carboxylate groups in *m*-BDC²⁻ can form Zn₂(*m*-BDC)₂ unit, while the two ones at para-positions in CCA²⁻ could not form the Cd₂(CCA)₂ unit.



Hydrogen atoms and free water molecules are omitted for clarity;

Symmetry code: A: 1+x, y, z; B: 1-x, -y, 3-z; C: -x, 2-y, 2-z

Fig.5 Coordination environment of Cd(II) in **2** with the ellipsoids drawn at the 30% probability level

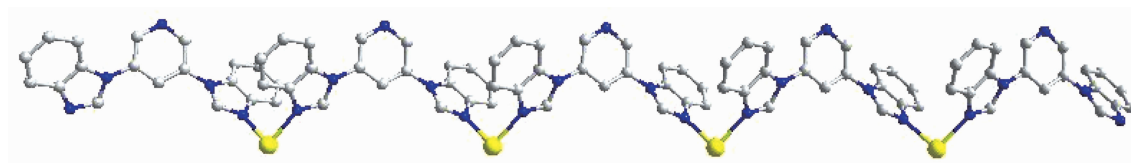


Fig.6 1D chain formed by Cd(II) and L ligands

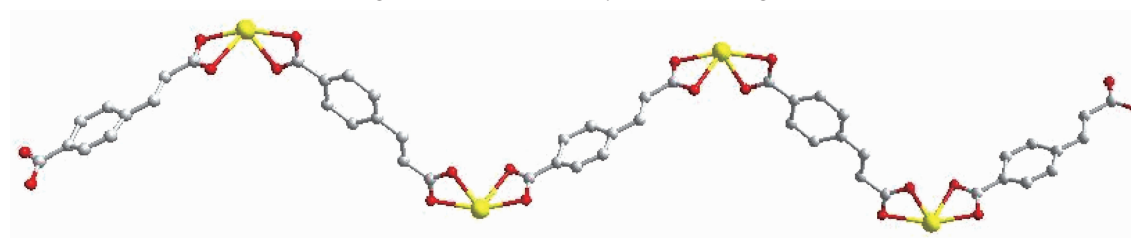
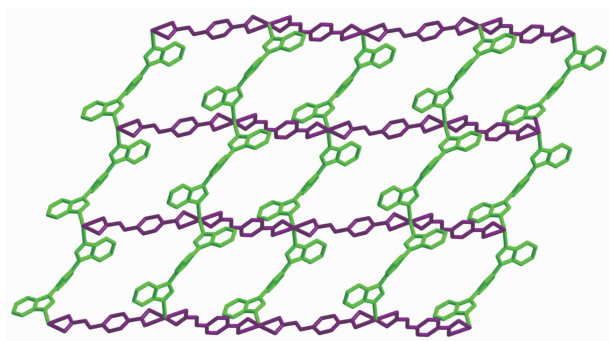


Fig.7 1D chain formed by Cd(II) and CCA²⁻ ligands

Table 3 Hydrogen bonding distances and angles for complex **2**

D—H···A	<i>d</i> (D—H) / nm	<i>d</i> (H···A) / nm	<i>d</i> (D···A) / nm	∠DHA / (°)
O1W—H1Wa···O3A	0.104	0.217	0.279 3	116
O1WB—H1Wa···O1B	0.103	0.177	0.268 3	145
O2W—H2Wa···O1W	0.087	0.206	0.250 9	146

Symmetry codes: A: 1-x, 1-y, 2-z; B: 1+x, y, z.

Fig.8 2D network of **2**

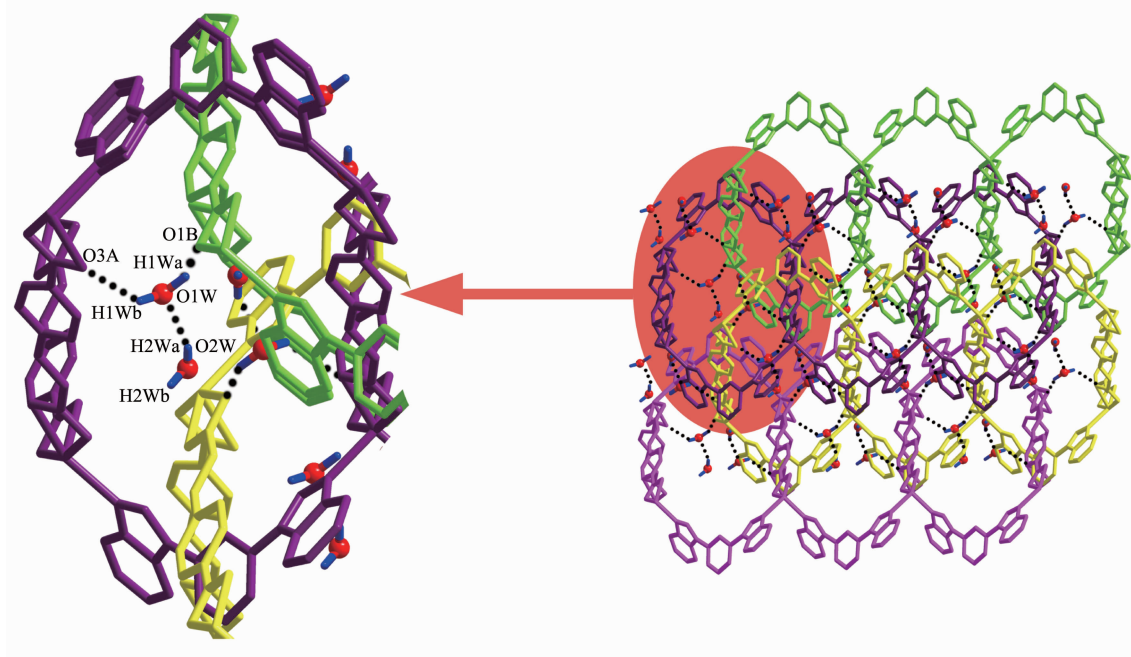
2.3 Thermal stability and powder X-ray diffraction (PXRD)

The pure phases of complexes **1** and **2** were confirmed by PXRD measurements, and the results

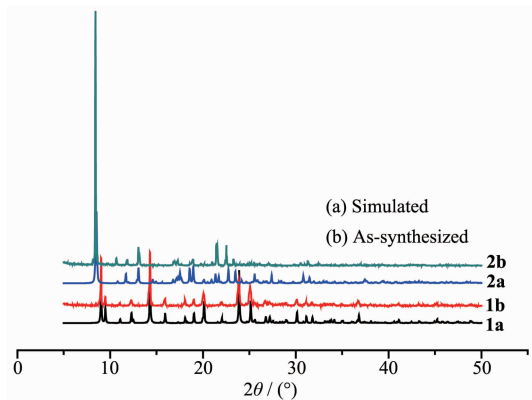
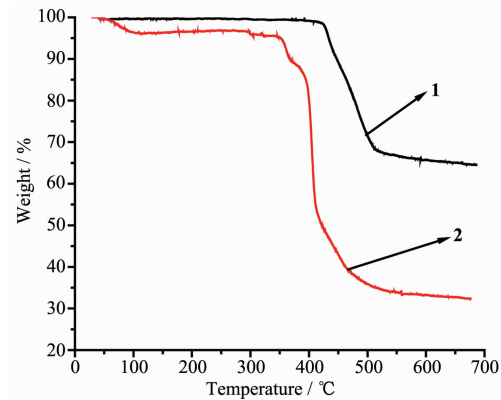
are shown in Fig.10. Each PXRD pattern of the as-synthesized sample is consistent with the simulated one. The thermal stability of **1** and **2** was examined by thermogravimetric analysis (TGA), and the results are shown in Fig.11. Complex **1** can be stabilized to 420 °C. Complex **2** undergoes a weight loss of 5.54%, which can be assigned to the loss of free water molecules (Calcd. 5.56%) confirming the presence of water molecules in **2**, and the residue remains stable up to approximately 370 °C.

2.4 Photoluminescence properties

The solid-state photoluminescent properties of complexes **1** and **2**, together with the free L, *m*-H₂BDC and H₂CCA ligands, have been investigated at



Symmetry code: A: 1-x, 1-y, 2-z; B: 1+x, y, z

Fig.9 3D structure of **2** with the hydrogen bonds indicated by the dash linesFig.10 PXRD curves of the complexes **1**, **2**Fig.11 TGA curves of **1** and **2**

room temperature under the same conditions. The emission spectra of the complexes and ligands are depicted in Fig.12. It can be seen that the emission bands of complexes and ligands were observed at 417 nm ($\lambda_{\text{ex}}=366$ nm) for **1**, 440 nm ($\lambda_{\text{ex}}=370$ nm) for **2**, 455 nm ($\lambda_{\text{ex}}=372$ nm) for L, 386 nm ($\lambda_{\text{ex}}=338$ nm) for *m*-H₂BDC and 425 nm ($\lambda_{\text{ex}}=367$ nm) for H₂CCA, respectively. Thus the observed emissions of the complexes can be tentatively assigned to the ligands fluorescence of L and/or *m*-BDC²⁻ (for **1**) and L and/or CCA²⁻ (for **2**) due to their similarity. And the blue- or red-shifted emissions of **1** and **2** are caused by the coordination of the ligands to the metal centers and the deprotonation of the *m*-H₂BDC to *m*-BDC²⁻ and H₂CCA to CCA²⁻ [16-17]. The difference between the fluorescence of the two complexes **1** and **2** may be due to the different emissions of *m*-H₂BDC at 386 nm and H₂CCA at 425 nm.

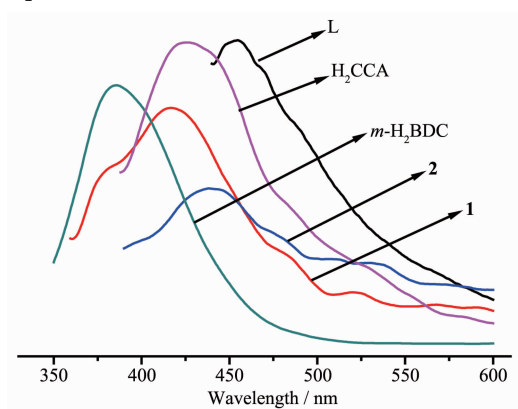


Fig.12 Emission spectra of L, H₂CCA, *m*-H₂BDC, **1** and **2** in the solid state at room temperature

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