

# 一维 Z 型链状配合物 $[\text{Cd}(\text{BDC})(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})]_n$ 的水热合成、晶体结构和荧光性质研究

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**摘要:** 水热合成了 1 个新配合物 $[\text{Cd}(\text{BDC})(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})]_n$ (BDC=对二甲酸; $\text{H}_2\text{C}_2\text{EIm}$ =2,2'-乙基双苯丙咪唑)。通过元素分析、红外光谱、热重以及 X-射线单晶衍射对其进行了表征。该晶体属三斜晶系, $P\bar{1}$  空间群。 $\text{Cd}(\text{II})$ 原子通过 BDC 和  $\text{H}_2\text{C}_2\text{EIm}$  2 种配体连接成一维 Z 型带状结构,带与带之间通过  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{O}$  连接成三维超分子结构。室温下配合物具有较强的荧光发射光谱。

**关键词:** 镉配合物; 晶体结构; 对二甲酸; 双苯并咪唑; 荧光

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## Hydrothermal Synthesis, Crystal Structure and Photoluminescence of a One-Dimensional Zigzag Chain Cadmium(II) Complex: $[\text{Cd}(\text{BDC})(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})]_n$

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**Abstract:** A one-dimensional cadmium(II) complex  $[\text{Cd}(\text{BDC})(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})]_n$  with 1,4-benzenedicarboxylic acid (BDC) and 2,2'-(ethanediyl)bis (1H-benzimidazole) ( $\text{H}_2\text{C}_2\text{EIm}$ ) has been synthesized by means of hydrothermal method and characterized by elemental analysis, thermal analysis, IR spectroscopy and X-ray single-crystal diffraction. The crystal is triclinic, space group  $P\bar{1}$  with  $a=10.307(5)$  nm,  $b=10.907(5)$  nm,  $c=11.934(5)$  nm,  $\alpha=63.021(5)^\circ$ ,  $\beta=73.308(5)^\circ$ ,  $\gamma=79.423(5)^\circ$ ,  $V=1.143(9)$  nm<sup>3</sup>,  $D_c=1.618$  g·cm<sup>-3</sup>,  $Z=2$ ,  $F(000)=560$ ,  $\text{Goof}=1.027$ ,  $R_1=0.0233$ ,  $wR_2=0.0617$ . The complex shows a one-dimensional (1D) zigzag chain structure and further extends into a 3D supramolecular structure through  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding interactions. Luminescent studies show that the complex exhibits intense blue fluorescent emission. CCDC: 802048.

**Key words:** cadmium(II) complex; crystal structure; 1,4-benzenedicarboxylic acid; bis(1H-benzimidazole); luminescence

## 0 Introduction

Recently, owing to the variety of intriguing architectures and topologies and the potential applications in magnetism, electric conductivity, molecular adsorption, heterogeneous catalysis, and

fluorescent materials<sup>[1-2]</sup>, the construction of metal-organic framework (MOF) structures has been received increasing attention<sup>[3-5]</sup>. However, the rational design and synthesis of MOFs with unique structure and function is still a challenge. Various factors such as the nature of metal ions, medium, pH value of solution,

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temperature, and number of coordination donors provided by organic ligands<sup>[6]</sup> are frequently influenced the resultant structural framework. The 1,4-benzenedicarboxylic acid (BDC), an organic ligands with carboxylate groups, are especially interesting because of their various coordination modes to metal ions<sup>[7]</sup> and their abilities to act as H-bond acceptors and donors to assemble various supramolecular structures<sup>[8]</sup>. Comparatively, bis (2-benzimidazoles) and some substituted bis (2-benzimidazolyl)alkanes containing *N*-donors are also particularly attractive as excellent building blocks with charge and multi-connecting ability. Very recently, a series of cadmium or zinc coordination polymers attract extensive interest for their non-linear optical and fluorescence properties<sup>[9-10]</sup>. While compared with aforementioned cases, we report syntheses, crystal structure and luminescent properties of a coordination polymer  $[\text{Cd}(\text{BDC})(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})]_n$  based on the mixed ligands of aromatic carboxylates, 1,4-benzenedicarboxylic acid (BDC), and *N*-donor Ligands, 2,2'-(ethanediyl)bis(1H-benzimidazole)( $\text{H}_2\text{C}_2\text{EIm}$ ).

## 1 Experimental

### 1.1 Materials and general methods

All chemicals for syntheses and analyses were commercially purchased and used without further purification. The  $\text{H}_2\text{C}_2\text{EIm}$  ligand was prepared according to the reported method<sup>[11]</sup>. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. FTIR spectra were recorded in the range of 400~4 000  $\text{cm}^{-1}$  on a Nicolet AVATAR-360 spectrophotometer with KBr pellets. The emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer. All the measurements were carried out under the same experimental conditions. TG analyses were performed on a Perkin-Elmer TGA instrument in flowing  $\text{N}_2$  with a heating rate of 10  $^\circ\text{C} \cdot \text{min}^{-1}$ .

### 1.2 Synthesis of $[\text{Cd}(\text{BDC})(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})]_n$ (1)

The title complex was prepared by the mixture of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.154 g, 0.5 mmol),  $\text{H}_2\text{C}_2\text{EIm}$  (0.106 g, 0.5 mmol), BDC (0.166 g 1 mmol), 0.6 mmol of NaOH dissolved in 8 mL distilled water and  $\text{H}_2\text{O}$  (16

mL). This mixture was heated in sealed Teflon-lined autoclave for three days at 150  $^\circ\text{C}$ . After the reaction mixture was slowly cooled down to room temperature, colorless prism like crystals were produced with a yield of 75%. Anal. Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_5\text{Cd}(\%)$ : C, 51.90; H, 3.26; N, 10.09. Found (%): C, 51.31; H, 3.19; N, 9.71. IR spectrum ( $\text{cm}^{-1}$ ): 3 420, 3 111, 2 881, 1 558, 1 506, 1 455, 1 271, 1 209, 1 081, 1 002, 952, 854, 745 and 551.

### 1.3 X-ray crystallography

A colorless block single crystal of **1** with 0.28 mm×0.23 mm×0.18 mm was carefully selected under a polarizing microscope and were mounted on a glass fiber and used for X-ray diffraction analyses. Single crystal structure determination by X-ray diffraction measurements were performed using a Bruker Smart Apex II CCD diffractometer with graphite monochromated  $\text{Mo K}\alpha$  ( $\lambda=0.071\,073\text{ nm}$ ) radiation. Absorption corrections were applied using the multi-scan technique<sup>[12]</sup>. The structures were solved by the Direct Method and refined by full-matrix least-square techniques on  $F^2$  using SHELXTL-97<sup>[13]</sup>. All of the non-hydrogen atoms were refined anisotropically<sup>[14]</sup>. The H atoms attached to C atoms were positioned geometrically, with  $U_{\text{iso}}$  values derived from  $U_{\text{eq}}$  values of the corresponding C atom.

CCDC: 802048.

## 2 Results and discussion

### 2.1 Description of crystal structure

Crystallographic and structural refinement data for the complex are given in Table 1. Selected bond distances and angles are shown in Table 2.

The single crystal X-ray analysis shows that the asymmetrical unit of title complex contains one Cd(II) ion, one  $\text{H}_2\text{C}_2\text{EIm}$  ligand, one TPA molecules and one coordinated water molecule. As shown in Fig.1, the Cd site shows a distorted-octahedral geometry, being chelated by four O atoms from one BDC ligand and one O atom from one coordinated water. The remaining two coordination sites are chelated by two N atoms from one  $\text{H}_2\text{C}_2\text{EIm}$  ligand. The Cd-O bond lengths are in the range of 0.225 4(2)~0.261 7(2) nm and the Cd-N bond length is 0.221 7 (2)~0.235 4 (2) nm. The Cd(II) atoms are bridged by BDC ligands with an intramolecular Cd

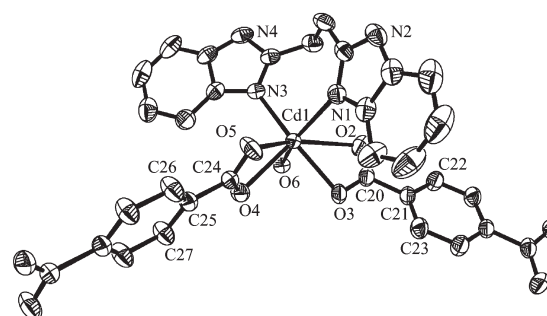
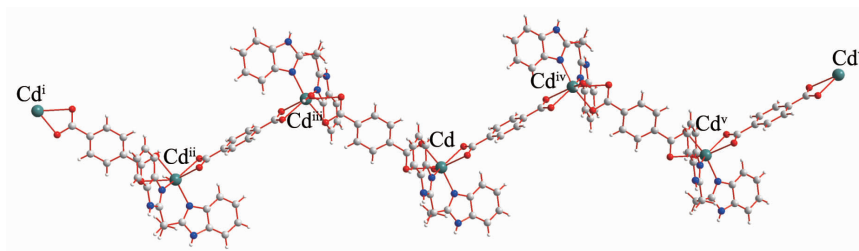
**Table 1** Crystal data and structure refinement for title complex

Formula	C <sub>24</sub> H <sub>20</sub> N <sub>4</sub> O <sub>5</sub> Cd	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.618
Formula weight	556.84	Absorption coefficient / mm	0.999
Temperature / K	293(2)	$F(000)$	560
Crystal system	Triclinic	$\theta$ range / (°)	1.97 to 25.50
Space group	$P\bar{1}$	Limiting indices	$-12 \leq h \leq 6, -13 \leq k \leq 13, -13 \leq l \leq 14$
$a$ / nm	1.030 7(5)	Reflections collected	6 048
$b$ / nm	1.090 7(5)	Independent reflections ( $R_{int}$ )	4 194 (0.012 4)
$c$ / nm	1.193 4(5)	Completeness to $\theta=25.00\%$ / (°)	98.7
$\alpha$ / (°)	63.021(5)	Data / restraints / parameters	4 194 / 0 / 323
$\beta$ / (°)	73.308(5)	Goodness-of-fit on $F^2$	1.027
$\gamma$ / (°)	79.423(5)	$R_1, wR_2$ ( $I > 2\sigma(I)$ )	$R_1=0.023\ 3, wR_2=0.061\ 7$
$V$ / nm <sup>3</sup>	1.143 0(9)	Largest difference peak and hole / (e·nm <sup>-3</sup> )	254, -464
$Z$	2		

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

Cd(1)-N(3)	0.221 7(2)	Cd(1)-O(4)	0.238 57(19)	Cd(1)-O(6)	0.263 6(2)
Cd(1)-O(3)	0.225 4(2)	Cd(1)-O(5)	0.247 5(2)		
Cd(1)-N(1)	0.235 4(2)	Cd(1)-O(2)	0.261 7(2)		
N(3)-Cd(1)-O(3)	160.23(7)	O(3)-Cd(1)-O(5)	103.42(8)	O(3)-Cd(1)-O(6)	83.02(6)
N(3)-Cd(1)-N(1)	93.29(8)	N(1)-Cd(1)-O(5)	81.90(7)	N(1)-Cd(1)-O(6)	143.57(6)
O(3)-Cd(1)-N(1)	94.39(8)	O(4)-Cd(1)-O(5)	53.59(6)	O(4)-Cd(1)-O(6)	82.24(6)
N(3)-Cd(1)-O(4)	101.18(8)	N(3)-Cd(1)-O(2)	110.95(7)	O(5)-Cd(1)-O(6)	134.16(6)
O(3)-Cd(1)-O(4)	86.39(7)	O(4)-Cd(1)-O(2)	132.46(7)	O(2)-Cd(1)-O(6)	70.41(7)
N(1)-Cd(1)-O(4)	134.03(7)	O(5)-Cd(1)-O(2)	147.87(7)	O(3)-Cd(1)-O(2)	53.08(7)
N(3)-Cd(1)-O(5)	95.68(8)	N(3)-Cd(1)-O(6)	80.00(7)	N(1)-Cd(1)-O(2)	79.04(8)

...Cd distance of 1.132 8 nm. Each BDC dianion acts as a  $\mu_2$ -bridge linking two Cd atoms into a zigzag chain with chelating coordination mode (Fig.2). Owing to the abundant nitrogen atoms in the H<sub>2</sub>C<sub>2</sub>EIm ligand, hydrogen-bonding interactions are formed. The complex are linked in to a three-dimensional supramolecular framework by the intermolecular hydrogen bonds N-H ... O, O-H ... O and  $\pi$ - $\pi$  stacking interactions ( $d = 3.473$ ). Hydrogen-bonding details for title complex are given in Table 3.

**Fig.1** Coordination environment of Cd(II) atom in complex with 50% thermal ellipsoids

Symmetry code: <sup>i</sup> 1-x, 4-y, -1-z; <sup>ii</sup> x, 2+y, -1+z; <sup>iii</sup> 1-x, 2-y, -z; <sup>iv</sup> 1-x, -y, 1-z; <sup>v</sup> x, -2+y, 1+z; <sup>vi</sup> 1-x, -2-y, 2-z

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

Table 3 Distance and angles of hydrogen-bonding for complex

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
N4-H-O6 <sup>ii</sup>	0.071	0.213	0.284 3	173
N2-H-O5 <sup>i</sup>	0.083	0.198	0.277 3	160
O(6)-H(111)-O(4) <sup>iii</sup>	0.077	0.215	0.284 4	151
O(6)-H(222)-O(3) <sup>iii</sup>	0.077	0.198	0.272 9	164

Symmetry code: <sup>i</sup> -*x*, -*y*+1, -*z*+1; <sup>ii</sup> -*x*, -*y*+1, -*z*. <sup>iii</sup> 1-*x*, 1-*y*, -*z*.

## 2.2 IR spectra

The IR spectral data show features attributable to the carboxylate stretching vibrations of the complex (Fig.3). The broad bands centered at 3 420 cm<sup>-1</sup> due to the stretching vibrations of N-H bond and the peak on 3 111 cm<sup>-1</sup> are ascribed to presence of water ligands<sup>[15-16]</sup>. The strong peaks occurring at 1 558 and 1 506 cm<sup>-1</sup> demonstrating the antisymmetric and symmetric stretching vibrations of carboxylate with the vicinal values emphasize that the carboxyl groups are coordinated in chelating fashion, which is consistent with the results of the single-crystal X-ray analysis<sup>[17]</sup>. The bands for the H<sub>2</sub>C<sub>2</sub>EIm ligand at 1 271 and 1 455 cm<sup>-1</sup> shows the C-N stretching vibration of arylamine group and the C=N stretching vibration of imidazole group<sup>[18]</sup>, respectively.

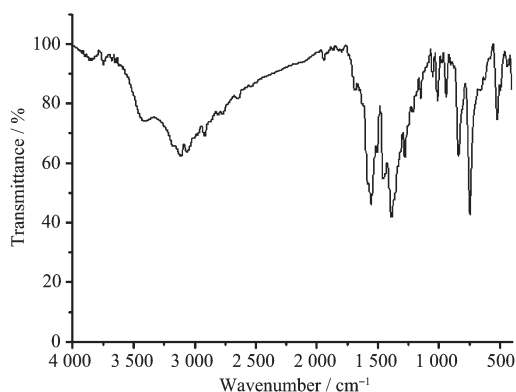


Fig.3 IR spectra of the title complex

## 2.3 Thermogravimetric analyses

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of the complex (Fig. 4). The samples were heated up in N<sub>2</sub> at 101 kPa pressure with a heating rate of 10 °C · min<sup>-1</sup>. The 4.1% weight loss below 150 °C for the two samples is attributed to a release of the physisorbed water<sup>[19]</sup>. A weight loss of 2.0% occurred in the temperature range of 231 ~331 °C is attributed to the release of one

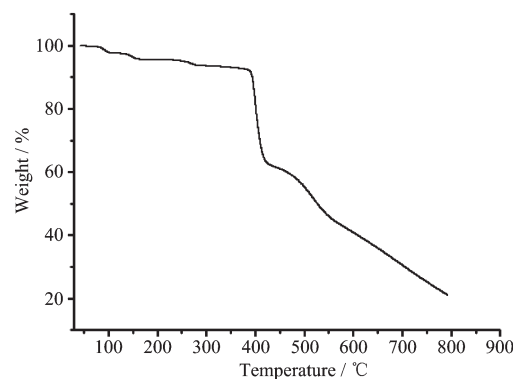
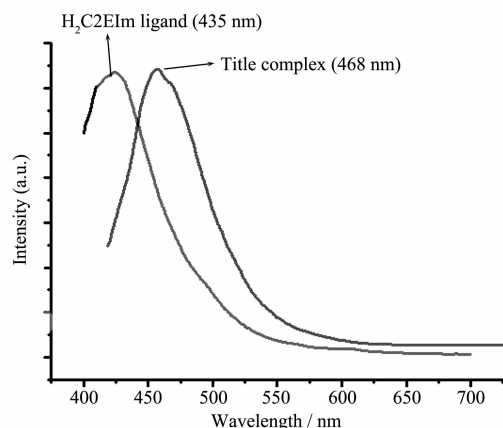


Fig.4 TGA curve for the complex

coordinated water molecule per formula. Then a sharp weight-loss step is observed between 340 and 750 °C attributed to the decomposition of organic ligands.

## 2.4 Luminescent properties

Luminescent complexes are of great current interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display<sup>[20-21]</sup>. As it is depicted in Fig.5, the complex in solid state at room temperature exhibits strong blue photoluminescence with an emission maximum at 468 nm, upon excitation at 332 nm. In addition, it can be seen that the free H<sub>2</sub>C<sub>2</sub>EIm ligand shows a sharp peak

Fig.5 Normalized fluorescence emission spectrum of the complex and the H<sub>2</sub>C<sub>2</sub>EIm ligand in the solid state at room temperature

with a maximum emission at 435 nm (under 291 nm excitation). The fluorescence emission of the complexes might be attributed to ligand-to-metal charge transfer (LMCT)<sup>[22-23]</sup>. This observation indicates that the complex may be a good candidate for potential photoactive materials.

### 3 Conclusion

In summary, a novel one-dimensional (1D) cadmium(II) coordination polymer with the features an uncommon zigzag chain structure based on ligand (H<sub>2</sub>C<sub>2</sub>EIm) and a chelate ligand (BDC) has been synthesized in hydrothermal reaction condition. The successful syntheses of the complex indicate that it is promising to build up unusual architectures via transition metals and imidazole-carboxylate ligands. Moreover, the complex displays blue fluorescent property indicating that the polymer may has potential applications in optical materials.

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