

# 间苯二甲酸和二咪唑基苯构建锌化合物的合成,晶体结构和荧光性质

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**摘要:** 由水热法合成了锌化合物 $[\text{Zn}_2(\text{dib})(1,3\text{-BDC})_2(\text{H}_2\text{O})]$  (**1**), 1,3- $\text{H}_2\text{BDC}$ =间苯二甲酸,  $\text{dib}$ =1,4-二咪唑基苯, 并进行了元素分析、IR、TG 及 X-射线衍射法表征。晶体结构表明: 配合物 **1** 属于单斜晶系,  $P2_1/n$  空间群。配合物 **1** 是由羧酸配体间苯二甲酸阴离子连接成一维双链, 然后由 1,4-二咪唑基苯连接成层状, 此二维结构被氢键拓展成三维超分子结构。

**关键词:** 水热合成; 锌配合物; 晶体结构; 荧光性能

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## Synthesis, Crystal Structure and Photoluminescent Property of Zn(II) Complex Constructed from 1,3-Benzenedicarboxylate and 1,4-Di(1-imidazolyl)benzene

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**Abstract:** A new 2D Zn(II) metal-organic framework,  $[\text{Zn}_2(\text{dib})(1,3\text{-BDC})_2(\text{H}_2\text{O})]$  (**1**), has been synthesized by the hydrothermal reaction of 1,3-benzenedicarboxylate with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in the presence of 1,4-di(1-imidazolyl)benzene ( $\text{dib}$ =1,4-di(1-imidazolyl)benzene, 1,3- $\text{H}_2\text{BDC}$ =1,3-benzenedicarboxylate). The crystal is of monoclinic system, space group  $P2_1/n$ , with  $a=0.803\ 67(12)$  nm,  $b=1.332\ 7(2)$  nm,  $c=2.372\ 5(4)$  nm,  $\beta=97.394(3)^\circ$ ,  $V=2.519\ 9(7)$  nm<sup>3</sup>,  $Z=4$ ,  $F(000)=1\ 392$ ,  $R=0.052\ 0$  and  $wR=0.099\ 4$  ( $I>2\sigma(I)$ ). The two central zinc(II) ions in the complex locate in a different coordination geometry, one is a distorted tetrahedral and the other is a distorted square-pyramidal coordination geometry, respectively. The dib ligand acts as a bridging ligand, which links the 1D double-chain into 2D layer structure. The net is linked into three-dimensional supramolecular network by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. CCDC: 895702.

**Key words:** hydrothermal synthesis; zinc(II) complex; crystal structure; luminescence property

## 0 Introduction

In recent years, metal-organic frameworks (MOFs) with carboxylate-containing ligands have been extensively studied because the carboxylate groups can have varied coordination modes resulting in the

formation of different structures<sup>[1-3]</sup>. Generally, the multidentate organic ligands containing coordination sites challenge to control the final products because many factors, such as the coordination geometry of the central metal ions, connection modes of organic ligands as well as the synthetic method, show great

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influence on the desirable structures. Among them, the multifunctional auxiliary ligands and metal ions have an important role in the construction of MOFs with distinctive structures<sup>[7-9]</sup>.

On the other hand, mixed ligands with N-donor groups acting as ancillary connectors are another group of effective building units to construct novel coordination polymers, because they have strong coordination affinity and can satisfy the geometric need of metal centers<sup>[10-12]</sup>. In this case, in order to further investigate the influence of organic ligands on the coordination architectures and related properties, we report on the synthesis, crystal structure and properties of a new coordination polymer  $[\text{Zn}_2(1,3\text{-BDC})_2(\text{dib})(\text{H}_2\text{O})]_n$  (**1**) with 1,3-benzenedicarboxylate (1,3-H<sub>2</sub>BDC),  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  as well as rigid N-donor bridging ligands (dib).

## 1 Experimental

### 1.1 Materials and instruments

All chemicals and solvents were of reagent grade and used as received without further purification. The dib ligand was synthesized according to the reported method<sup>[13]</sup>. Elemental analysis was carried out on a Perkin-Elmer 2400 (II) elemental analyzer. Infrared (IR) spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer by using KBr discs. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer

with a xenon arc lamp as the light source. In the measurement of emission and excitation spectra the pass width is 5 nm, all the measurements were carried out under the same experimental conditions.

### 1.2 Synthesis of the complex

A mixture containing dib (11.0 mg, 0.05 mmol),  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (28.8 mg, 0.1 mmol), 1,3-H<sub>2</sub>BDC (16.8 mg, 0.1 mmol) and NaOH (8.0 mg, 0.2 mmol) in 10 mL H<sub>2</sub>O was sealed in a 16 mL Teflon lined stainless steel container and heated at  $150\text{ }^\circ\text{C}$  for 3 d. After the mixture was slowly cooled to room temperature, colorless block crystals of **1** were obtained by filtration and washed with water and ethanol several times with a yield of ca. 52% based on dib ligand. Anal. Calcd for  $\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_9\text{Zn}_2$  (%): C, 48.89; H, 2.91; N, 8.15; found (%): C, 48.87; H, 2.94; N, 8.12. IR main absorption parameters (KBr pellet,  $\text{cm}^{-1}$ ) are as below: 3 430.5(s), 1 616.6(s), 1 580.3(s), 1 427.2(m), 1 396.4 (s), 1 346.2 (m), 1 255.6 (s), 1 168.8 (s), 1 143.7(m), 1 087.4(s), 1 028.0(m), 852.5(s), 746.9(m), 727.1(m), 646.5(w), 473.0(w).

### 1.3 X-ray crystallography

A single crystal with dimensions of  $0.28\text{ mm} \times 0.24\text{ mm} \times 0.22\text{ mm}$  was selected and determined by a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatic Mo  $K\alpha$  radiation ( $\lambda = 0.071\ 073\text{ nm}$ ) by using an  $\omega$ - $2\theta$  scan mode at  $291(2)\text{ K}$ . Out of the total 13 325 reflections collected in the range of  $2.32^\circ \leq \theta \leq 26.71^\circ$ , 4 927 were independent with  $R_{\text{int}} = 0.047\ 0$ , of which 3 596 were considered to be observed ( $I > 2\sigma(I)$ ). The structure of **1** was solved by direct methods and refined on  $F^2$  by full-matrix

Table 1 Crystallographic data of the title complex

Empirical	$\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_9$	Absorption coefficient $\mu$ (Mo $K\alpha$ ) / $\text{cm}^{-1}$	19.72
Formula weight	687.22	$F(000)$	1 392
Crystal system	Monoclinic	Crystal size / mm	$0.28 \times 0.24 \times 0.22$
Space group	$P2_1/n$	$\theta$ range for data collection / ( $^\circ$ )	0.996 to 26.00
$a$ / nm	0.803 67(12)	Reflections collected	13 325
$b$ / nm	1.332 7(2)	Reflections collected / unique	4 927 ( $R_{\text{int}} = 0.047\ 0$ )
$c$ / nm	2.372 5(4)	Goodness-of-fit on $F^2$	1.039
Volume / $\text{nm}^3$	2.519 9(7)	Final $R$ indices ( $I > 2\sigma(I)$ )	$R = 0.072\ 1$ , $wR = 0.102\ 3$
$\beta$ / ( $^\circ$ )	97.394(3)	$R$ indices (all data)	$R = 0.052\ 0$ , $wR = 0.099\ 4$
$Z$	4	Largest diff. peak and hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	396 and $-731$

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

Zn(1)-O(2)	0.203 3(3)	Zn(1)-O(6)	0.195 2(3)	Zn(1)-N(2B)	0.200 7(3)
Zn(1)-O(4A)	0.191 7(3)	Zn(2)-O(1)	0.221 1(3)	Zn(2)-O(2)	0.220 7(3)
Zn(2)-O(8A)	0.194 7(3)	Zn(2)-N(4)	0.199 0(3)	Zn(2)-O(1W)	0.199 5(3)
O(4A)-Zn(1)-O(6)	108.45(12)	O(4A)-Zn(1)-N(2B)	95.97(13)	O(6)-Zn(1)-N(2B)	131.38(14)
O(4A)-Zn(1)-O(2)	123.15(13)	O(6)-Zn(1)-O(2)	99.19(12)	N(2B)-Zn(1)-O(2)	101.46(14)
O(8A)-Zn(2)-N(4)	97.37(14)	O(8A)-Zn(2)-O(1W)	105.45(13)	N(4)-Zn(2)-O(1W)	120.41(14)
O(8A)-Zn(2)-O(2)	94.26(13)	N(4)-Zn(2)-O(2)	138.83(14)	O(1W)-Zn(2)-O(2)	93.82(12)
O(8A)-Zn(2)-O(1)	150.66(14)	N(4)-Zn(2)-O(1)	95.43(13)	O(1W)-Zn(2)-O(1)	90.40(13)
O(2)-Zn(2)-O(1)	59.56(11)				

Symmetry code: A:  $5/2-x, -1/2+y, 3/2-z$ ; B:  $1-x, -y, 1-z$ .

least-squares method<sup>[14]</sup>. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated geometrically. The crystallographic data and the selected bond lengths and bond angles are given in Table 1 and Table 2.

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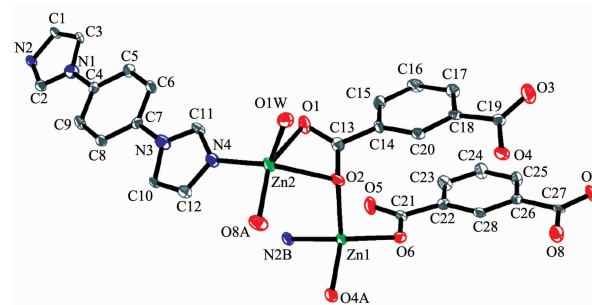
## 2 Results and discussion

### 2.1 Structure description

The structure of the title complex, **1D** and **2D** nets of the complex and crystalline packing are revealed in Fig.1~Fig.3, respectively.

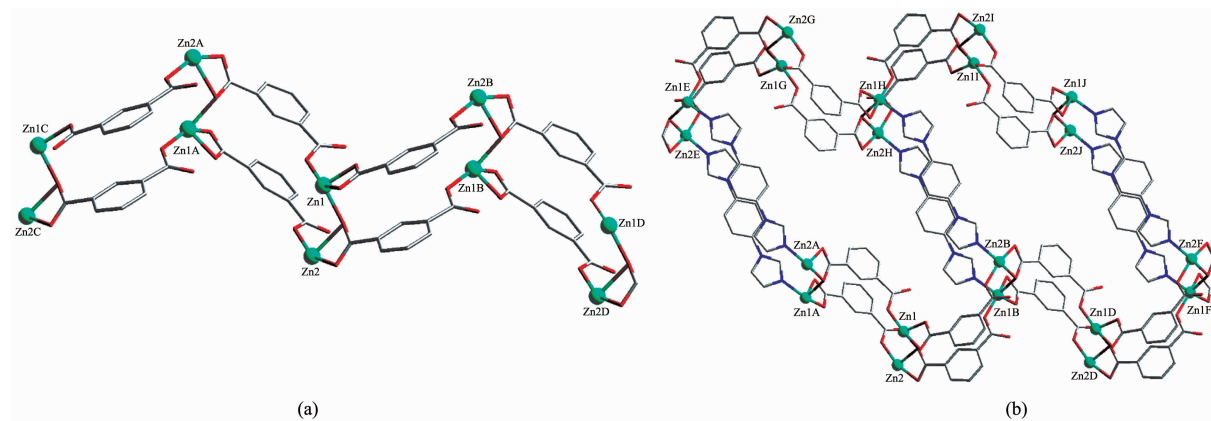
Single crystal X-ray diffraction analysis reveals that complex **1** is a unique two-dimensional supramolecular framework in which the asymmetric unit contains two Zn atoms, one dib ligand, two 1,3-BDC<sup>2-</sup> ligands and one coordinated water molecule. Fig.1 shows the coordination environment of two

independent Zn(II) atoms with the atom numbering scheme. It can be clearly seen that Zn1 atom is in a distorted tetrahedral coordination environment with three O atoms from three different 1,3-BDC<sup>2-</sup> ligands with Zn1-O4A, Zn1-O6, Zn1-O2 bond distances of 0.191 7(3), 0.195 2(3), and 0.203 3(3) nm, respectively,



Hydrogen atoms were omitted for clarity; Symmetry code: A:  $5/2-x, -1/2+y, 3/2-z$ ; B:  $1-x, -y, 1-z$

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



Symmetry code: A:  $5/2-x, -1/2+y, 3/2-z$ ; B:  $1-x, -y, 1-z$ ; C:  $x, -1+y, z$ ; D:  $x, 1+y, z$ ; E:  $3/2+x, -1/2-y, 1/2+z$ ; F:  $5/2-x, 3/2+y, 3/2-z$ ; G:  $4-x, -y, 2-z$ ; H:  $3/2+x, 1/2-y, 1/2+z$ ; I:  $4-x, 1-y, 2-z$ ; J:  $3/2+x, 3/2-y, 1/2+z$

Fig.2 (a) A view of the double 1D chain of **1**; (b) Undulated (6,3) 2D double-layer framework

and one N atom from dib ligand with Zn1-N2B bond distance of 0.200 7 (3) nm (Table 2). However, the other central Zn2 atom shows a distorted square-pyramidal geometry by coordinating to three O atoms from two 1,3-BDC<sup>2-</sup> ligands, one terminal water molecule and one N atom from the dib ligand. Three O atoms (O1, O2, O8A) and one N atom (N4) constitute the base of the square-pyramid with Zn-O bond lengths varying from 1.947(3) to 0.221 1(3) nm, whereas one O atom (O1w) occupies the apical position with a Zn2-O1w distance of 0.199 5(3) nm (Table 2). It is noticeable that the completely deprotonated 1,3-BDC<sup>2-</sup> ligands adopt  $\mu_2\text{-}\eta^1\text{:}\eta^1$  and  $\mu_3\text{-}\eta^1\text{:}\eta^2$  two types of coordination modes to connect Zn(II) atoms. Firstly, each 1,3-BDC<sup>2-</sup> ligand links Zn(II) atoms using its two carboxylate groups to form a one-dimensional (1D) double chain which can be seen clearly from Fig.2. Then, the 1D chain is pillared through dib ligands, resulting in a novel two-dimensional (2D) double-layer framework (Fig.2). It is interesting that the bridging O2 atoms display the connection of the double-layer network. Finally, the 2D layers are further linked together through O-H $\cdots$ O hydrogen bonds (O1W $\cdots$ O7A=0.281 2(4) nm, A: 5/2-x, -1/2+y, 3/2-z; O1W $\cdots$ O6K=0.2812(4) nm, K: -1+x, y, z; and the D-H-A angles are 132° and 153°) to generate a three-dimensional (3D) packing structure.

## 2.2 Infrared spectroscopy and TG of the complex

The absorption peaks  $\nu_{\text{C=O}}(\text{COOH})$  (1 695.0 cm<sup>-1</sup>) and  $\nu_{\text{C=O}}(\text{COOH})$  (1 012.0 cm<sup>-1</sup>) of the ligand 1,3-H<sub>2</sub>BDC disappeared in the title complex, while  $\nu_{\text{as}}(\text{COO})$  (1 580.3 cm<sup>-1</sup>) and  $\nu_{\text{s}}(\text{COO})$  (1 396.4 cm<sup>-1</sup>) were found, which indicated that the oxygen atoms of carboxyl group were coordinated with the central ions. And  $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}} = 183.9$  cm<sup>-1</sup>, further showing that the oxygen atoms of carboxyl group were coordinated with the centric ions in the form of bidentate bridge<sup>[15]</sup>, which was identical with the analytical results of crystal structure. The infrared spectrum of the complex also exhibits the strong and broad band of H<sub>2</sub>O at ca. 3 430.5 cm<sup>-1</sup><sup>[16]</sup>. TGA were carried out for the synthesized complex, and a weight loss of 2.70%

was observed in the temperature range of 80~130 °C (Calcd. 2.62%) due to the loss of solvated water molecules and the anhydrous compositions begin to decompose at 305 °C.

## 2.3 Fluorescence property of the title complex

Inorganic-organic hybrid coordination complexes, especially with  $d^{10}$  metal centers, have been investigated for fluorescence properties owing to their potential applications as luminescent materials<sup>[17]</sup>. Thus the luminescent spectra of complex **1**, dib as well as free 1,3-H<sub>2</sub>BDC ligand were investigated in the solid state at room temperature. As shown in Fig. 4, complex **1** exhibits an intense broad photoluminescence with maximum emission at 478 nm upon excitation at 410 nm, which is close to the emission at 474 nm of the dib ligand under the same conditions, rather than the free 1,3-H<sub>2</sub>BDC ligand (448 nm). Therefore, the emission observed in **1** is attributed to the  $\pi\text{-}\pi^*$  intraligand photoluminescence due to its resemblance to that of dib ligand. And the enhancement and slight red-shift of **1** compared to that of the dib ligand probably result from the fact that the coordination of Zn(II) ions increases the ligand conformational rigidity and thus reduces the loss of energy by thermal vibrational decay<sup>[18]</sup>.

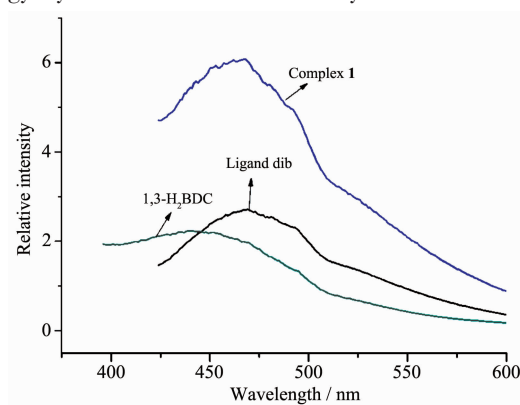


Fig.3 Solid emission spectra of the title complex and ligands

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