

## 由吡嗪二甲酸及双咪唑基配体构筑的 锌配位聚合物的合成、晶体结构及荧光性质

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**摘要:** 通过水热法合成了一个新的金属-有机配位聚合物 $[\text{Zn}(\text{pzdc})(\text{bix})_{0.5}(\text{H}_2\text{O})]_n$  (**1**) ( $\text{H}_2\text{pzdc}$ =吡嗪-2,3-二甲酸,  $\text{bix}$ =1,4-双(咪唑基-1-甲基)-苯)。并对其进行了元素分析、红外光谱、紫外光谱和 X-射线单晶衍射测定。该配合物属于三斜晶系,  $P\bar{1}$  空间群。晶体学数据:  $a=0.737\ 27(8)$ ,  $b=1.004\ 45(12)$ ,  $c=1.079\ 10(13)$  nm,  $\alpha=113.771(2)$ ,  $\beta=102.005(2)$ ,  $\gamma=93.586(2)^\circ$ ,  $V=0.705\ 71(14)$  nm<sup>3</sup>,  $\text{C}_{13}\text{H}_{11}\text{N}_4\text{O}_5\text{Zn}$ ,  $M_r=368.63$ ,  $D_c=1.735\ \text{g}\cdot\text{cm}^{-3}$ ,  $\mu(\text{Mo } K\alpha)=1.773\ \text{mm}^{-1}$ ,  $F(000)=374$ ,  $Z=2$ , 最终  $R=0.027\ 6$ ,  $wR=0.067\ 7$  用于 2 460 个可观测点。在晶体结构中, 锌离子通过吡嗪-2,3-二甲酸和 1,4-双(咪唑基-1-甲基)-苯配体桥联成二维层状结构。而且该配合物通过氢键和  $\pi$ - $\pi$  堆积作用扩展成三维超分子网状结构。此外还研究了它的荧光性质。

**关键词:** 锌配合物; 晶体结构; 荧光

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## Synthesis, Crystal Structure and Fluorescent Property of Zinc Coordination Polymer Assembled by Pyrazine-2,3-dicarboxylic Acid and Bis(imidazol) Ligands

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**Abstract:** A new metal-organic coordination polymer  $[\text{Zn}(\text{pzdc})(\text{bix})_{0.5}(\text{H}_2\text{O})]_n$  (**1**) ( $\text{H}_2\text{pzdc}$ =pyrazine-2,3-dicarboxylic acid,  $\text{bix}$ =1,4-bis(imidazol-1-ylmethyl)-benzene) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, UV spectrum and single-crystal X-ray diffraction. The complex crystallizes in triclinic, space group  $P\bar{1}$  with  $a=0.737\ 27(8)$ ,  $b=1.004\ 45(12)$ ,  $c=1.079\ 10(13)$  nm,  $\alpha=113.771(2)$ ,  $\beta=102.005(2)$ ,  $\gamma=93.586(2)^\circ$ ,  $V=0.705\ 71(14)$  nm<sup>3</sup>,  $\text{C}_{13}\text{H}_{11}\text{N}_4\text{O}_5\text{Zn}$ ,  $M_r=368.63$ ,  $D_c=1.735\ \text{g}\cdot\text{cm}^{-3}$ ,  $\mu(\text{Mo } K\alpha)=1.773\ \text{mm}^{-1}$ ,  $F(000)=374$ ,  $Z=2$ , the final  $R=0.027\ 6$  and  $wR=0.067\ 7$  for 2 460 observed reflections ( $I>2\sigma(I)$ ). In the crystal structure, **1** shows a two-dimensional layer structure bridged by pzdc and bix ligands. Furthermore, it exhibits a 3D supramolecular network through hydrogen bonding and  $\pi$ - $\pi$  stacking interactions. Moreover, its luminescent property has been investigated in the solid state. CCDC: 878878.

**Key words:** Zn(II) complex; crystal structure; fluorescence

## 0 Introduction

Recently, the effective combination of coordination bond and hydrogen bond has been applied in the engineering study of inorganic-organic

hybrid material and the construction of metal-organic coordination supramolecular complexes. The suitable organic ligand makes the complex not only possess novel structure but also produce unique optical,

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electric and magnetic properties. Pyrazine-2,3-dicarboxylic acid ( $\text{H}_2\text{pzdc}$ ) has been proved to be well suited for the construction of multidimensional frameworks due to the presence of two adjacent carboxylate groups (O donor atoms) as substituents on the N-heterocyclic pyrazine ring (N donor atoms). A series of one-, two- and three-dimensional metal-organic coordination supramolecular complexes have been synthesized and characterized<sup>[1-8]</sup>. On the other hand, the employment of mixed ligands during the self-assembly process has gradually become an effective approach, which is expected to obtain frameworks with more diverse structural motifs compared to using only one type of ligands. Therefore, the auxiliary ligands such as imidazole-containing ligands, are introduced into the reaction systems so as to tune up the metal coordinated sites<sup>[9-11]</sup>. Taking all the above discussion into account, we utilized the pyrazine-2,3-dicarboxylic acid ( $\text{H}_2\text{pzdc}$ ) and polycyclic aromatic bidentate bridging ligands, bix, to generate coordination polymers. In this communication, we report the hydrothermal synthesis and structural characterization of  $[\text{Zn}(\text{pzdc})(\text{bix})_{0.5}(\text{H}_2\text{O})]_n$  (**1**). It shows a two-dimensional layer structure bridged by pzdc and bix ligands. Moreover, their luminescent properties have been investigated in the solid state.

## 1 Experimental

### 1.1 General procedures

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectrum was recorded in the range of 4 000~400  $\text{cm}^{-1}$  on an Alpha Centaur

FT/IR Spectrophotometer using a KBr pellet. The fluorescent studies were carried out on a computer-controlled JY Fluoro-Max-3 spectrometer at room temperature.

### 1.2 Synthesis

The title complex was prepared from a mixture of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.2 mmol, 0.044 g),  $\text{H}_2\text{pzdc}$  (0.4 mmol, 0.068 g), bix (0.2 mmol, 0.048 g) and  $\text{H}_2\text{O}$  (18 mL) in a 30 mL Teflon-lined autoclave under autogenous pressure at 150 °C for 7 d. After cooling to room temperature, pale yellow block crystals were collected by filtration and washed with distilled water in 37% yield (based on Zn). Anal. Calcd. (%) for  $\text{C}_{13}\text{H}_{11}\text{N}_4\text{O}_5\text{Zn}$ : C, 42.35; H, 3.00; N, 15.20. Found(%): C, 41.89; H, 2.31; N, 14.96. IR (KBr,  $\text{cm}^{-1}$ ): 3 253m, 3 093w, 2 362w, 1 660m, 1 626m, 1 571w, 1 532m, 1 451 w, 1 430w, 1 388s, 1 365s, 1 282w, 1 244m, 1 197 w, 1 173 w, 1 125m, 1 112w, 1 090m, 1 063w, 1 028w, 952w, 890 w, 859w, 840w, 771m, 752m, 720m, 659w, 627w, 612 w, 545w, 467w.

### 1.3 Structure determination

A single crystal of the title complex with dimensions of 0.389 mm×0.285 mm×0.244 mm was mounted on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatic Mo  $K\alpha$  ( $\lambda = 0.071\ 073\ \text{nm}$ ) radiation using an  $\varphi$ - $\omega$  scan mode at 292(2) K. In the range of  $4.26^\circ < 2\theta < 52.06^\circ$ , a total of 3 905 reflections were collected and 2 734 were independent with  $R_{\text{int}} = 0.010\ 9$ , of which 2 460 were observed with  $I > 2\sigma(I)$ . The correction for Lp factors was applied. The structure was solved by direct methods with SHELXS-97 program<sup>[12]</sup> and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-97<sup>[13]</sup>. All non-hydrogen atoms were refined anisotro-

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

Zn(1)-O(1)	0.204 91(15)	Zn(1)-O(5)	0.200 39(17)	Zn(1)-N(3)	0.211 83(18)
Zn(1)-O(3A)	0.205 40(16)	Zn(1)-N(1)	0.202 68(19)		
O(5)-Zn(1)-N(1)	100.95(8)	N(1)-Zn(1)-O(3A)	92.54(7)	N(1)-Zn(1)-N(3)	117.39(7)
O(5)-Zn(1)-O(1)	87.35(7)	O(1)-Zn(1)-O(3A)	164.29(7)	O(1)-Zn(1)-N(3)	78.06(6)
N(1)-Zn(1)-O(1)	103.15(7)	O(5)-Zn(1)-N(3)	141.08(8)	O(3A)-Zn(1)-N(3)	94.16(7)
O(5)-Zn(1)-O(3A)	90.46(7)				

Symmetry transformations used to generate the equivalent atoms: A:  $x+1, y, z$ .

pically and hydrogen atoms isotropically. All H atoms were placed in calculated positions and refined as riding with  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ . The final  $R=0.027\ 6$  and  $wR=0.067\ 7$  ( $w=1/[\sigma^2(F_o^2)+(0.034\ 5P)^2+0.264\ 3P]$ , where  $P=(F_o^2+2F_c^2)/3$ ).  $S=1.084$ ,  $(\Delta\rho)_{\text{max}}=341\ \text{e}\cdot\text{nm}^{-3}$ ,  $(\Delta\rho)_{\text{min}}=-389\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta/\sigma)_{\text{max}}=0.001$ . The selected important bond parameters are given in Table 1.

CCDC: 878878.

## 2 Results and discussion

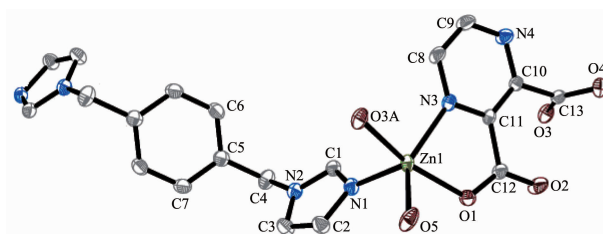
### 2.1 IR spectrum

The  $\text{COO}^-$  is coordinated with its asymmetric and symmetric stretching appearing at  $1\ 660\ \text{cm}^{-1}$  ( $\nu(\text{OCO})_{\text{asym}}$ ) and  $1\ 365\ \text{cm}^{-1}$  ( $\nu(\text{OCO})_{\text{sym}}$ )<sup>[14]</sup>, respectively. The  $\Delta\nu(\nu(\text{OCO})_{\text{asym}}-\nu(\text{OCO})_{\text{sym}})$  is  $295\ \text{cm}^{-1}$  ( $>200$ ), showing the presence of monodentate linkage of carboxylates in the dianions. Thus the carboxylates coordinate to the metal as monodentate ligands via the carboxylate groups<sup>[15]</sup>. The absence of the characteristic bands at about  $1\ 700\ \text{cm}^{-1}$  in compound **1** attributed to the protonated carboxylic group indicates that the complete deprotonation of cbba ligand upon reaction with Zn ions<sup>[16]</sup>. In addition, X-ray diffraction analysis further indicates the existence of monodentate coordination manners of the carboxylate groups and prence deprotonation of pzdc ligands.

### 2.2 Description of the structure

Complex **1** crystallizes in  $P\bar{1}$  space group. The molecular structure of **1** is shown in Fig.1. There are one Zn(II) ion, one pzdc ligand, half bix ligand and one coordinated water molecule in the asymmetric unit. Each Zn(II) ion is five-coordinated by two carboxylate oxygen atom from two different pzdc ligands, one nitrogen atom from bix ligand, one nitrogen atom from pzdc ligand and one coordinated water molecule to form distorted square-pyramidal coordination architecture. Its equatorial plane is occupied by two carboxylate oxygen atoms, O1, O3A, one nitrogen atom, N3, and one coordinated water molecule, O5, while the apical position is occupied by one nitrogen atom, N1. The Zn-O bond lengths are in the range of  $0.200\ 39(17)\sim 0.205\ 40(16)\ \text{nm}$ , the Zn-N bond lengths are  $0.202\ 68(19)\sim 0.211\ 83(18)\ \text{nm}$ . The

N(O)-Zn-O(N) angles range from  $78.06(6)^\circ$  to  $164.29(7)^\circ$ . The bix ligand adopts trans-conformation with a dihedral angle between the two imidazole rings of  $0^\circ$ . The pzdc anions adopt  $\mu_3$  coordination mode and linked Zn(II) ions to form a one-dimensional chain. The distance of neighboring Zn(II) ions is about  $0.737\ 3\ \text{nm}$  as illustrated in Fig.2. The neighboring chains are bridged by bix ligands to afford a 2D sheet with (4,4) topology (Fig.2). The Zn $\cdots$ Zn distances separated by bix ligands are  $1.429\ 7\ \text{nm}$ . The resulting layers are packed in a parallel fashion and stacked along the  $c$  axis.



Symmetric code: A:  $x+1, y, z$

Fig.1 ORTEP drawing of **1** showing the labling of atoms with thermal ellipsoids at 30% probability

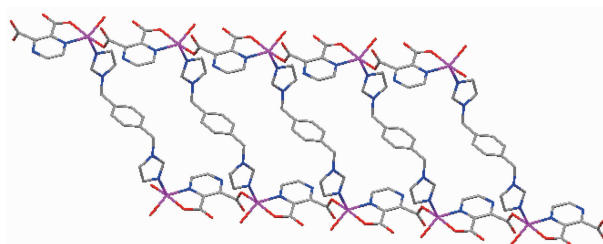
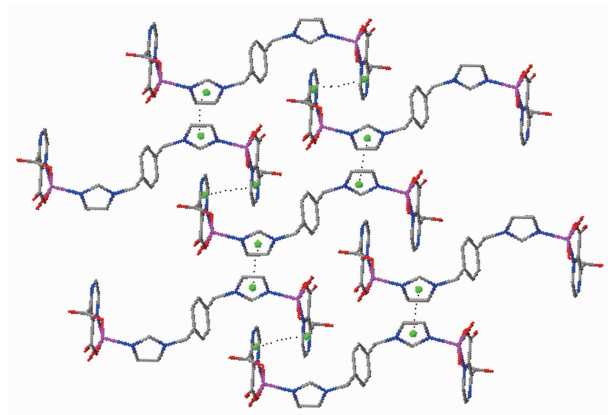


Fig.2 View of the two-dimensional layer constructed from  $[\text{Zn}_4(\text{pzdc})_2(\text{bix})_2]$  units

Hydrogen bonding interactions are usually important in the synthesis of supramolecular architecture<sup>[17]</sup>. There are persistent O—H $\cdots$ O hydrogen bonding interactions between carboxylate oxygen atom and coordinated water molecule (O5 $\cdots$ O4<sup>A</sup> ( $0.266\ 7\ \text{nm}$ ,  $151.32^\circ$ , <sup>A</sup>  $-x+1, -y, -z+1$ ); O5 $\cdots$ O2<sup>B</sup> ( $0.262\ 8\ \text{nm}$ ,  $155.32^\circ$ , <sup>B</sup>  $x+1, y, z$ )) in complex **1**. Moreover, there are  $\pi$ - $\pi$  interactions in complex **1** (Fig.3) between bix ligands from adjacent chains and pzdc ligands from adjacent chains too. The centroid-to-centroid distances between adjacent aromatic rings are  $0.378\ 5\ \text{nm}$  for N1C1N2C3C2 and N1'C1'N2'C3'C2' ( $2-x, 1-y, 2-z$ ) and  $0.369\ 2\ \text{nm}$  for N3C8C9N4C10C11 and N3'C8'C9'N4'C10'C11' ( $1-x, 1-y, 1-z$ ) aromatic rings. The

perpendicular distances are 0.368 6 nm for N1C1N2 C3C2 and N1' C1' N2' C3' C2' ( $2-x, 1-y, 2-z$ ) and 0.352 6 nm for N3C8C9N4C10C11 and N3' C8' C9' N4' C10' C11' ( $1-x, 1-y, 1-z$ ) aromatic rings. Therefore, through hydrogen bonds and  $\pi$ - $\pi$  interactions, the two-dimensional layers are further extended into a three-dimensional supramolecular framework.



The dotted lines show the  $\pi$ - $\pi$  interactions

Fig.3 A view of  $\pi$ - $\pi$  stacking interactions in complex **1**

### 2.3 Photoluminescent properties

The emission spectrum of complex **1** in the solid state at room temperature is shown in Fig.4. It can be observed that complex **1** exhibits green photoluminescence with an emission maximum at *ca.* 531 nm upon excitation at 325 nm. In order to understand the nature of these emission bands, we first analyzed the photoluminescence properties of free pyrazine-2,3-dicarboxylic acid, and confirmed that it does not emit any luminescence in the range of 400~800 nm. And then we investigated the emission spectrum of bix itself and the result indicated that it does not emit any luminescence in the range 400~800 nm, which has

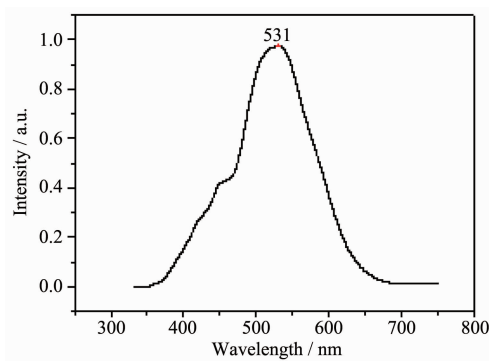


Fig.4 Solid-state emission spectrum of **1** at room temperature

also been confirmed previously<sup>[18]</sup>. Thus, according to the previous literature<sup>[19]</sup>, the emission band could be assigned to the emission of ligand-to-metal charge transfer (LMCT). For possesses strong fluorescent intensity, it appears to be good candidates for novel hybrid inorganic-organic photoactive materials.

### 2.4 UV spectrum

The UV spectra for the title compound, H<sub>2</sub>pzdc and bix ligands have been investigated in the solid state (Fig.5). For bix ligand, there is no absorption band, while both the title compound and H<sub>2</sub>pzdc have one absorption band at about 274 nm, which should be assigned to the  $n \rightarrow \pi^*$ <sup>[20]</sup> transition of H<sub>2</sub>pzdc. However, after H<sub>2</sub>pzdc coordinating to the Zn<sup>2+</sup> ion, the absorption intensity slightly decreases. It is clearly that the absorption band in H<sub>2</sub>pzdc remains in the same position with that in the title compound, showing that they are not affected basically by the metal coordination.

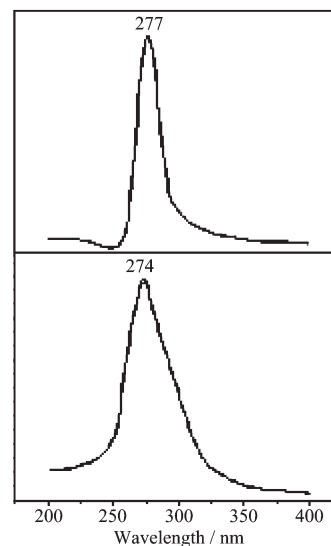


Fig.5 UV spectrum of H<sub>2</sub>pzdc ligand and the title compound

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