

研究简报

## 一维链状锌配位聚合物[Zn(Pyphen)(PZDC)(H<sub>2</sub>O)] 的水热合成、结构与荧光性质

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## Hydrothermal Synthesis, Structure and Photoluminescence of a 1D Chain Zinc(II) Coordination Polymer: [Zn(Pyphen)(PZDC)(H<sub>2</sub>O)]

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**Abstract:** The title coordination polymer, [Zn(Pyphen)(PZDC)(H<sub>2</sub>O)] (**1**) (Pyphen=pyrazino [2,3-f][1,10]phenanthroline and H<sub>2</sub>PZDC=pyrazine-2,3-dicarboxylic acid) has been obtained by using hydrothermal synthesis and characterized by elemental analysis, IR, TG, fluorescence spectrum and X-ray diffraction single-crystal structure analysis. The crystal is of triclinic, space group  $P\bar{1}$  with  $a=0.681\ 8(14)$  nm,  $b=0.743\ 9(15)$  nm,  $c=1.759\ 8(35)$  nm,  $\alpha=94.329(30)^\circ$ ,  $\beta=95.514(30)^\circ$ ,  $\gamma=97.043(3)^\circ$ ,  $V=0.878\ 2(3)$  nm<sup>3</sup>,  $Z=2$ ,  $M_r=481.73$ ,  $D_c=1.822\ \text{g}\cdot\text{cm}^{-3}$ ,  $\mu=1.452\ \text{mm}^{-1}$ ,  $F(000)=448$ ,  $R_{\text{int}}=0.033\ 9$ ,  $R=0.042\ 5$ ,  $wR=0.090\ 7$ . In complex **1**, PZDC ligands link the Zn(II) ions to form 1D chain structures, and further extended into a 3D supramolecular framework through  $\pi$ - $\pi$  interactions and hydrogen bonding interactions. In addition, complex **1** exhibits strong photoluminescence at room temperature. CCDC: 649569.

**Key words:** zinc coordination polymer; pyrazino[2,3-f][1,10]phenanthroline; pyrazine-2,3-dicarboxylic acid; photoluminescence

The design and synthesis of new coordination polymers have received much attention recently owing to their interesting crystal structures and potential application in magnetism, electrical conductivity, luminescence, biology and catalysis etc<sup>[1-9]</sup>. In this res-

pect, the critical issue is the rational choice and assembly of metal ions and organic bridging ligands<sup>[10]</sup>. In recent years, as a part of our efforts toward the assembly of transition  $d^{10}$  metal ions with nitrogen-containing heteroaryldicarboxylate ligand, such as

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pyrazine-2,3-dicarboxylic acid ( $\text{H}_2\text{PZDC}$ ), which possesses the capability to bridge and chelate metal atoms in various coordination modes using the carboxylate oxygen atoms and nitrogen atoms of the pyrazine ring<sup>[11]</sup>. Pyrazino[2,3-*f*][1,10]phenanthroline (Pyphen) as an important phen derivative is gradually studied due to its excellent coordinating ability, extensive face-to-face  $\pi$ -stacking interactions which lead to eminent luminescent properties of its complexes<sup>[12-14]</sup>. Thus, it will be valuable to construct extended frameworks based on  $\text{H}_2\text{PZDC}$  and Pyphen ligands. Consequently, we choose the mixed ligands and zinc (II) ion to design and synthesize a new coordination polymer:  $[\text{Zn}(\text{Pyphen})(\text{PZDC})(\text{H}_2\text{O})]$  (**1**), which has an unusual 3D structure constructed from 1D hybrid chains linked by hydrogen bonds and  $\pi$ - $\pi$  stacking interactions.

## 1 Experimental

### 1.1 Materials and instruments

The ligand Pyphen was prepared according to our literature procedure<sup>[15]</sup>. Other reagents and solvents for the synthesis and analysis were commercially available and used as received. Elemental analysis was performed on a Perkin-Elmer 240C element analyzer. IR spectra were recorded on a Perkin-Elmer 2400LS II spectrometer using KBr discs. Thermogravimetric analysis (TG) was conducted on a NETZSCH STA 449C analyzer. The visible luminescent property of compound **1** was measured on a Perkin-Elmer LS55 spectrometer.

### 1.2 Synthesis of the title compound

The title compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot$

$6\text{H}_2\text{O}$  (0.149 g, 0.5 mmol),  $\text{H}_2\text{PZDC}$  (0.084 g, 0.5 mmol), Pyphen (0.116 g, 0.5 mmol) and  $\text{H}_2\text{O}$  (15 mL) was sealed in a 20 mL Teflon-lined autoclave and heated to 170 °C for 72 h. After cooling to room temperature, yellow block crystals of **1** were obtained by filtration. The crystals were washed with distilled water for several times and finally dried in air. Yields based on Zn: 79%. Elemental analysis (%) for **1**: C 49.82; H 2.49; N 17.44. Found (%): C 49.85; H 2.52; N 17.42. Main IR bands ( $\text{cm}^{-1}$ ): 3 415s, 1 646s, 1 618s, 1 447w, 1 405w, 1 378m, 1 345m, 1 123m, 821m.

### 1.3 Crystal structure determination

A yellow crystal with dimensions of 0.33 mm  $\times$  0.28 mm  $\times$  0.24 mm was selected for the measurement. The diffraction data were collected at 292 K on a Rigaku R-Axis RAPID diffractometer equipped with a graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm). A total of 8 279 reflections were collected in the range of  $3.03^\circ \leq \theta \leq 27.47^\circ$ , of which 3 902 ( $R_{\text{int}}=0.033\ 9$ ) were independent and 3 157 with  $I>2\sigma(I)$  were used in the structure determination and refinement. The structure was solved by direct methods with SHELXS-97 program<sup>[16]</sup> and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-97<sup>[17]</sup>. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The final  $R=0.042\ 5$  and  $wR=0.090\ 7$  ( $w=1/[\sigma^2(F_o^2)(0.036\ 6P)^2+1.605\ 8P]$ , where  $P=(F_o^2+2F_c^2)/3$ ).  $S=1.074$ ,  $(\Delta\rho)_{\text{max}}=1\ 101\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta\rho)_{\text{min}}=-449\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta/\sigma)_{\text{max}}=0.001$ . Crystal data and structure refinement parameters are listed in Table 1.

CCDC: 649569.

Table 1 Crystal data and structure refinement parameters for the title complex

Empirical formula	$\text{C}_{20}\text{H}_{12}\text{N}_6\text{O}_5\text{Zn}$	Absorption coefficient / $\text{mm}^{-1}$	1.452
Formula weight	481.73	$F(000)$	448
Temperature / K	292(2)	Crystal size / mm	0.33 $\times$ 0.28 $\times$ 0.24
Crystal system	Triclinic	$\theta / (^\circ)$	3.03 to 27.47
Space group	$P\bar{1}$	Limiting indices	$-8 \leq h \leq 8, -9 \leq k \leq 9, -22 \leq l \leq 22$
$a / \text{nm}$	0.681 82(14)	Reflections collected / unique	8 279 / 3 902 ( $R_{\text{int}}=0.033\ 9$ )
$b / \text{nm}$	0.743 85(15)	Refinement method	Full-matrix least-squares on $F^2$
$c / \text{nm}$	1.759 7(35)	Data / restraints / parameters	3 902 / 0 / 297
$V / \text{nm}^3$	0.878 2(3)	Goodness of fit on $F^2$	1.074
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.822	Final $R$ indices [ $I>2\sigma(I)$ ]	$R_1=0.042\ 5, wR_2=0.090\ 7$
$Z$	2	Largest diff. peak and hole / ( $\text{e}\cdot\text{nm}^{-3}$ )	1 101, -449

## 2 Results and discussion

### 2.1 Crystal structure of the title complex

The selected bond distances and angles are listed in Table 2. The 1D chain structure of **1** was revealed by X-ray single-crystal determination, in which the Zn(II) center is coordinated by two Pyphen nitrogen atoms (Zn-N1=0.216 6(3) and Zn-N2=0.212 4(3) nm), one PZDC nitrogen atom (Zn-N5=0.214 7(3) nm), and three oxygen atoms from two different PZDC ligands (Zn-O1=0.218 8(2) and Zn-O4A=0.204 9(2) nm) and one water molecule (Zn-O1W=0.213 3(3) nm) in a slightly distorted octahedral coordination environment with the plane constructed by N1, N2, N5 and O1W and the axial positions occupied by O1 and O4A, as shown in Fig.1. In complex **1**, PZDC ligands through their carboxylate oxygen atoms and pyrazine nitrogen atoms link the Zn(II) ions to form 1D chain structures, and PyPhen

ligands locate on one side of the chain (Fig.2). Although PZDC has two carboxylate groups, it acts actually as  $\mu_2$  bridge ligand. It is different with the related structures reported by Wang et al.<sup>[18]</sup>, in which two carboxylate groups of each ligand acted as not less than  $\mu_3$  models. In this structure, there exist two types of hydrogen bonds that involved in the coordinated water molecule O1W and symmetric carboxylate oxygen atom O3 at ( $x+1, y+1, z$ ) and symmetric PZDC nitrogen atom N6 at ( $-x+1, -y, -z+1$ ). Interestingly, there are two  $\pi$ - $\pi$  stacking interactions in the supramolecular structure: one is the Pyphen-Pyphen interaction (the nearest center length is *ca.* 0.409 9 nm) in neighboring 1D chains, and the other is the pyrazine-pyrazine interaction (the nearest center length is *ca.* 0.351 1 nm) between adjacent 1D chains in above different direction (see Fig.2). Therefore, a 3D supramolecular framework is formed via hydrogen bonds and  $\pi$ - $\pi$  stacking interactions.

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

Zn-N(1)	0.216 6(3)	Zn-N(2)	0.212 4(3)	Zn-N(5)	0.214 7(3)
Zn-O(1)	0.218 8(2)	Zn-O(1W)	0.213 3(3)	Zn#1-O(4)	0.204 9(2)
Zn-O(4)#2	0.204 9(2)				
O(4)#2-Zn-N(2)	91.30(10)	O(4)#2-Zn-O(1W)	90.64(11)	N(2)-Zn-O(1W)	95.51(11)
O(4)#2-Zn-N(5)	97.01(10)	N(2)-Zn-N(5)	171.02(10)	O(1W)-Zn-N(5)	87.82(11)
O(4)#2-Zn-N(1)	99.31(10)	N(2)-Zn-N(1)	77.40(11)	O(1W)-Zn-N(1)	167.83(11)
N(5)-Zn-N(1)	97.82(10)	O(4)#2-Zn-O(1)	173.30(10)	N(2)-Zn-O(1)	95.32(10)
O(1W)-Zn-O(1)	89.74(11)	N(5)-Zn-O(1)	76.32(9)	N(1)-Zn-O(1)	81.20(11)

Symmetry transformations used to generate equivalent atoms: #1:  $x, y-1, z$ ; #2:  $x, y+1, z$ .

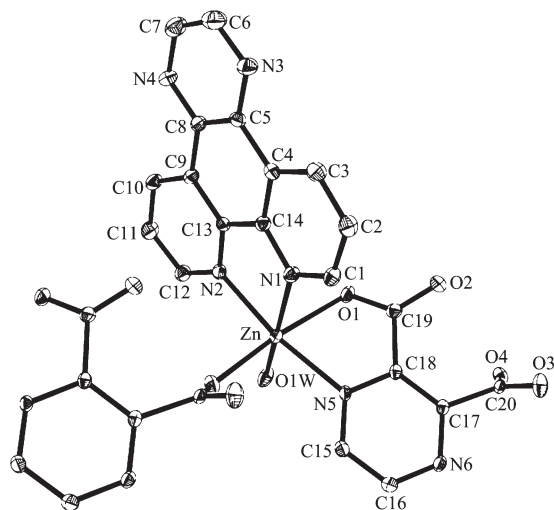
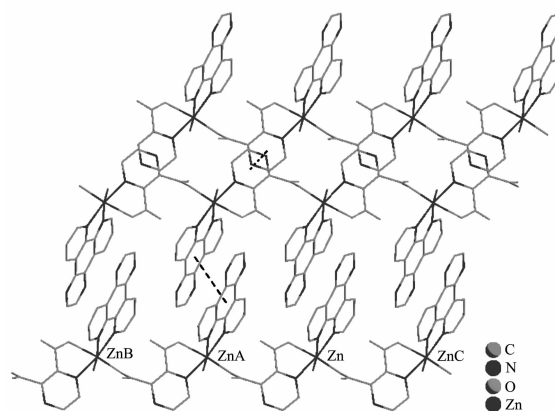


Fig.1 Coordination environment of Zn(II) atom in **1**



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

Fig.2 Extended 1D chains in the complex **1** viewed from *a* axis

## 2.2 Thermal analysis

Complex **1** is stable at ambient conditions, and thermogravimetric experiment was performed to explore its thermal stability. For **1**, the first gradual weight loss is 3.76% in the temperature range of 110 to 245 °C, corresponding to the loss of coordinated water molecules (calcd. 3.74%). The second step (34.41%) from 260 to 365 °C is attributed to the decomposition of the PZDC ligand (calcd. 34.46%); The last step (48.10%) from 400 to 520 °C assigned to the removal of the Pyphen ligand (calcd. 48.16%). The final residual weight of 13.73% (calcd. 13.64%) corresponds to ZnO (see Fig.3).

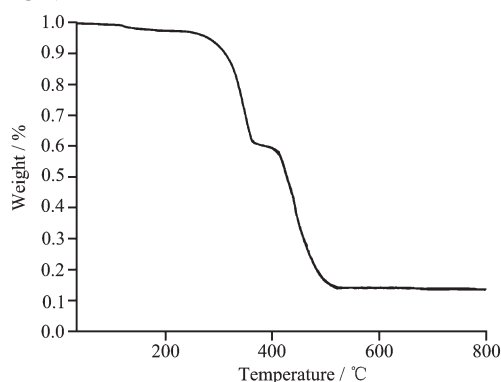


Fig.3 TG curve for compound **1**

## 2.3 Fluorescent property

The solid-state photoluminescent spectrum of complex **1** at room temperature is depicted in Fig.4. It can be observed that complex **1** exhibits intense orange photoluminescence with an emission maximum at ca. 576 nm upon excitation at 365 nm. In order to understand the nature of this emission band, the photoluminescence properties of free H<sub>2</sub>PZDC and

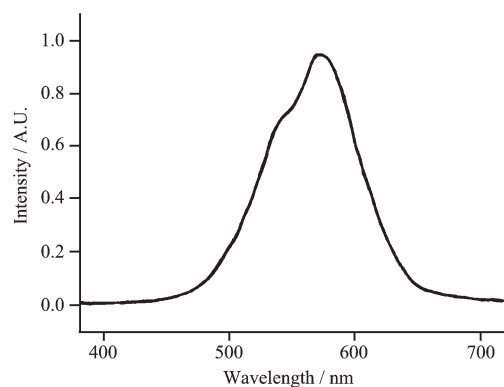


Fig.4 Photoluminescent spectrum of the compound **1** at room temperature

PyPhen were analyzed, showing they don't emit any luminescence from 400 to 800 nm. Thus, according to the previous literature<sup>[14]</sup>, the fluorescent emission of complex **1** can be probably assigned to ligand-to-metal charge transfer (LMCT). This observation indicates that complex **1** may be an excellent candidate for potential photoactive material.

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