

基于原位反应合成的一个锌的配位聚合物

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A Photoluminescent Zinc(II) Metal-organic Framework Constructed from a *in-situ* Synthesized Tetrazole Ligand

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Abstract: A coordination polymer of $\text{Zn}(\text{IBT})_2$ (**2**) (HIBT=5-(4-((1H-imidazol-1-yl)methyl)phenyl)-2H-tetrazole) has been prepared by hydrothermal method and characterized by IR spectroscopy, elemental analysis and single-crystal X-ray diffraction structure analysis. Compound **2** has one-dimensional (1D) hinged chain structure and displays strong photoluminescent emission at room temperature. CCDC: 654610.

Key words: zinc(II) coordination polymer; *in-situ* synthesis; tetrazole ligand; photoluminescent property

Inorganic-organic hybrid coordination complexes have attracted considerable attention in recent years because of their intriguing molecular topologies and crystal packing motifs, alongside their potential applications such as gas storage, separation, catalysis, magnetism, optics, as well as electrical conductivity^[1,2]. Among them, there have been tremendous research interests focused on the exploration of *in situ* tetrazole organic ligand synthesis through 2+3 cycloaddition reactions between organic cyano compounds and NaN_3 in the presence of Zn^{2+} ion as Lewis acid catalyst. Actually tetrazole organic ligand synthesis is prepared through the decomposition of Zn-complex (intermediate) under acidic conditions. As a result, there is much

research concentrated on the crystallographic characterization of such intermediates containing metal ion (most of them are metal-coordination polymers) and exploration of their applications in nonlinear optical, fluorescent (or phosphorescent), ferroelectric, and chiral properties^[3,4]. More recently, Sharpless et al. reported the preparation of a variety of 5-substituted 1H-tetrazoles in water, it allows us to explore the coordination chemistry of tetrazoles more extensively than in the past^[5,6]. We are interested in the construction of novel supramolecular motifs through *in situ* ligand reactions. Herein we report on the synthesis, structure and photoluminescent property of a 1D hinged chain coordination compound of $\text{Zn}(\text{IBT})_2$ (**2**).

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1 Experimental

1.1 Materials and general methods

All reagents for syntheses and analyses were purchased from commercial sources and used as received without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C elemental analyzer. ^1H NMR spectra were obtained with Bruker Avance spectrometer operating in the quadrature mode at 500 MHz. The IR spectrum as a KBr disk was recorded on a Nicolet Avatar 360 FTIR spectrometer. The emission/excitation spectra were recorded on a Hitachi F-4500 fluorescence spectro-photometer.

1.2 Syntheses of compounds

The compound **1** was prepared as follows^[7] (Scheme 1): imidazole (0.68 g, 10 mmol) and sodium hydroxide (0.8 g, 20 mmol) were dissolved in dimethylsulfoxide (DMSO) (25 mL) and the solution was stirred for 2 h at room temperature, then 4-(bromomethyl)benzonitrile (1.95 g, 10 mmol) was added. After stirring for another 24 h at room temperature, an equivalent volume of water was added to the mixture. The aqueous solution was extracted with chloroform (4×25 mL) and the chloroform solution was dried over anhydrous sodium sulfate and filtered. Solvent was removed on a rotary evaporator and excess diethyl ether was added to the residue. After standing overnight at $-15\text{ }^\circ\text{C}$, the white powder was filtered, washed with diethyl ether and dried in a vacuum desiccator. Yield: 1.5 g (83%). Anal. Calc. for $\text{C}_{11}\text{H}_9\text{N}_3$ (%): C, 72.11; H, 4.95; N, 22.94. Anal. Found(%): C, 72.04; H, 5.00; N, 22.90. ^1H NMR (500 MHz, CDCl_3 , δ ppm): 5.31 (s, 2H, $-\text{CH}_2-$), 6.73 (m, 1H, $^4\text{H}_{\text{im}}$), 7.05 (m, 1H, $^5\text{H}_{\text{im}}$), 7.25 (m,

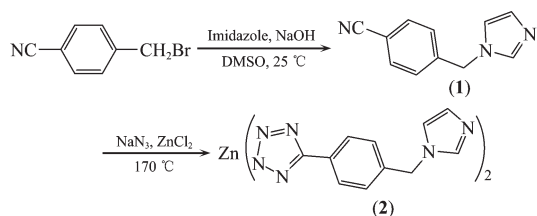
2H, benzene ring), 7.34 (m, 2H, benzene ring), 7.70 (m, 1H, $^2\text{H}_{\text{im}}$). IR spectrum: 3 056, 2 962, 2 198 and 1 521 cm^{-1} .

The single crystals of **2** were prepared by hydrothermal reaction. A mixture of ZnCl_2 (0.068 g, 0.5 mmol), **1** (0.092 g, 0.5 mmol), NaN_3 (0.033 g, 0.5 mmol) and H_2O (5 mL) was added in a Teflon-lined stainless steel vessel. The vessel was sealed and heated for 3 d at $170\text{ }^\circ\text{C}$. After the mixture was slowly cooled to room temperature, colorless block crystals of **2** were obtained. Yield: 62%. IR spectrum: 3 421, 3 053, 2 962, 1 774, 1 662, 1 644, 1 609, 1 583, 1 518, 1 453, 1 419, 1 373, 1 349, 1 334, 1 207, 1 142, 1 120, 1 066, 1 017, 937, 818, 699, 652, and 550 cm^{-1} .

1.3 X-ray crystal structure analysis

A colorless platelet single crystal of **2** with $0.26\text{ mm}\times0.22\text{ mm}\times0.08\text{ mm}$ was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal X-ray diffraction data collection was performed on a Bruker Smart Apex II CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source (Mo $K\alpha$ radiation, $\lambda=0.071\text{ 073 nm}$) operating at 50 kV and 30 mA. A total of 5 088 reflections were collected in the range of $1.73^\circ\leq\theta\leq25.00^\circ$ ($-30\leq h\leq22$, $-6\leq k\leq7$, $-18\leq l\leq18$), of which 1 933 are unique ($R_{\text{int}}=0.062\text{ 5}$) and 1 215 with $I>2\sigma(I)$ were used in the structure solution and the refinement of the complex **2**. Data processing was accomplished with the SAINT program^[8]. Empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELX-97 software^[9,10]. All of the non-hydrogen atoms were refined anisotropically^[10]. The hydrogen atoms were added according to the theoretical model. The crystallographic data and refinement results for complex **2** are shown in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 654610.



Scheme 1 *In situ* synthesis of **2**

Table 1 Crystal data and structure refinement for compound **2**

Formula	$\text{C}_{22}\text{H}_{18}\text{N}_{12}\text{Zn}$	Absorption coefficient / mm	1.154
Formula weight	515.85	$F(000)$	1 056

Continued Table 1

Temperature	293(2)	θ range / ($^{\circ}$)	1.73~25.00
Crystal system	Monoclinic	Limiting indices	$-30 \leq h \leq 22, -6 \leq k \leq 7, -18 \leq l \leq 18$
Space group	$C2/c$	Reflections collected	5 088
a / nm	2.547 0(14)	Independent reflections (R_{int})	1 933 (0.062 5)
b / nm	0.592 1(3)	Reflections observed [$I > 2\sigma(I)$]	1 215
c / nm	1.579 0(9)	Data / restraints / parameters	1 933 / 0 / 159
β / ($^{\circ}$)	112.248(7)	Goodness-of-fit on F^2	0.985
V / nm ³	2.204(2)	R_1, wR_2 [$I > 2\sigma(I)$]	0.053 1, 0.117 4
Z	4	Largest difference peak and hole / ($e \cdot \text{nm}^{-3}$)	251, -458
D_c / ($\text{g} \cdot \text{cm}^{-3}$)	1.555		

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$)

Zn1-N1	0.195 7(4)	Zn1-N5 ⁱⁱ	0.197 8(4)
N1-Zn1-N1 ⁱ	123.6(2)	N5 ⁱⁱ -Zn1-N5 ⁱⁱⁱ	111.7(2)
N1-Zn1-N5 ⁱⁱ	107.35(15)	N1 ⁱ -Zn1-N5 ⁱⁱⁱ	103.45(15)

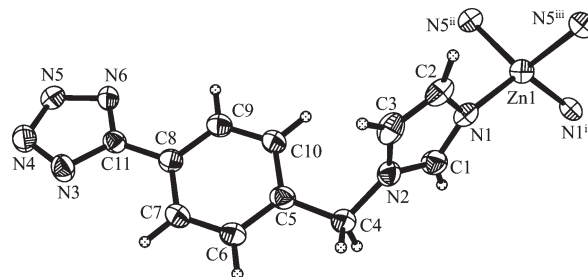
Symmetry code: ⁱ $-x, y, -1/2-z$; ⁱⁱ $1/2-x, 1/2-y, -z$; ⁱⁱⁱ $-1/2+x, 1/2-y, z-1/2$.

2 Results and discussion

The *in situ* reactions between compound **1** and ZnCl_2 offer a colorless crystalline coordination compound, $\text{Zn}(\text{IBT})_2$ (**2**), in which its IR spectra further confirm the absence of a peak at about $2\,200\text{ cm}^{-1}$, suggesting that the cyano group has turned in to the tetrazole group with several typical tetrazolyl group peaks at about $1\,453$, and $1\,349\text{ cm}^{-1}$. The $\text{C}=\text{N}$ stretching vibration of imidazolyl group in the infrared spectrum at $1\,519\text{ cm}^{-1}$.

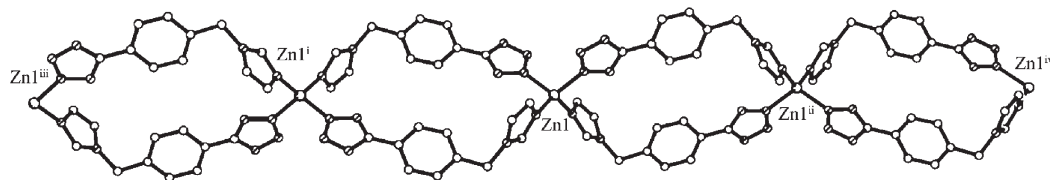
Compound **2** crystallizes in the monoclinic $C2/c$ space group, and the coordination environment around the zinc(II) center is shown in Fig.1. The zinc(II) atom is four coordinated by four N atoms from four different IBT ligands with N-Zn-N bond angles in the range of $103.45(15)^{\circ} \sim 123.6(2)^{\circ}$ and Zn-N bond distances of $0.195\,7(4)\text{ nm}$ and $0.197\,8(4)\text{ nm}$. Therefore, the local coordination geometry of the zinc(II) center is a distorted

tetrahedron. On the other hand, two IBT ligands link two metal atoms using their arms to generate an infinite 1D hinged chain containing 24-membered M_2L_2 macrocyclic rings (Fig.2), and the $\text{Zn} \cdots \text{Zn}$ distance within the M_2L_2 ring is 1.218 nm . It can be seen that the ligand IBT in complex **2** has an “L-shape” with the dihedral angles of 14.31° between the phenyl and each tetrazolyl group and 76.57° between the phenyl and each imidazolyl group, respectively. Similar 1D chain structure has been observed in the previously reported Pb(II) and Mn(II) compounds with the dimb ligand^[11,12]. There are $\text{C}-\text{H} \cdots \text{N}$ hydrogen bonds between the N atoms of tetrazole ring and the imidazole ring C-H with $\text{C} \cdots \text{N}$ distances of $0.324\,3(7)\text{ nm}$. Such hydrogen bonds link the 1D chains into the 2D network structure (Fig.3).



Symmetry code: ⁱ $-x, y, -1/2-z$; ⁱⁱ $1/2-x, 1/2-y, -z$; ⁱⁱⁱ $-1/2+x, 1/2-y, z-1/2$

Fig.1 ORTEP drawing of **2** showing the labeling of atoms with thermal ellipsoids at 30% probability



Symmetry code: ⁱ $1/2-x, 1/2-y, -z$; ⁱⁱ $-1/2-x, 1/2-y, -1/2-z$; ⁱⁱⁱ $1+x, 1/2-y, 1+z$; ^{iv} $1-x, y, 1-z$

Fig.2 1D polymeric chain representation for compound **2**

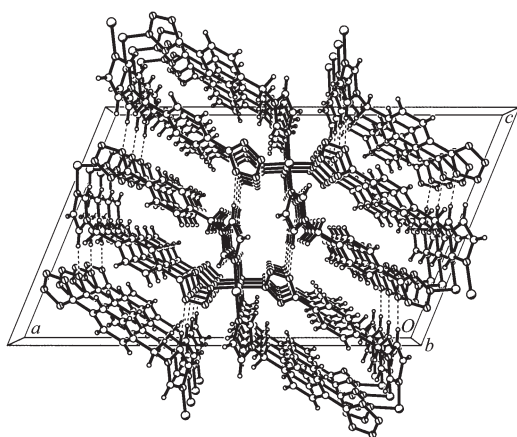


Fig.3 A packing diagram for **2** along *b*-axis (dotted lines represent hydrogen bonding)

We investigated the photoluminescent property of **2** and the emission spectrum is shown in Fig.4. In the solid state, strong photoluminescence emission bands at 402 nm ($\lambda_{\text{exc}}=280$ nm) is observed for compound **2**. The emission may be ascribed to the cooperative effects of intraligand emission and ligand to-metal charge transfer (LMCT)^[13].

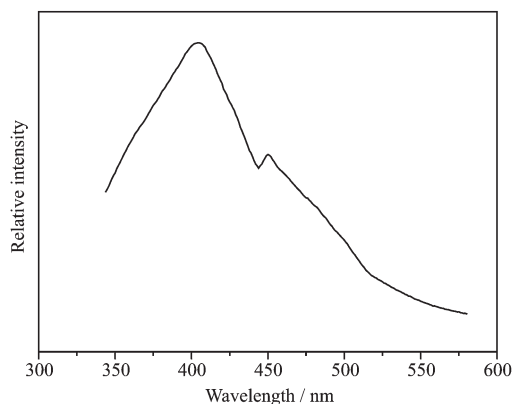


Fig.4 Photoluminescent spectrum of **2** in the solid state at room temperature

3 Conclusion

In this paper, we have prepared a novel one-dimensional (1D) hinged chain zinc coordination polymer by hydrothermal method, which displays strong photoluminescent emission at room temperature.

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