

## 具有二维网格结构的 5-(4-硝基苯基)四唑-锌(II)配合物

肖 杰 赵玉媛 王文祥 赵 红\*

(东南大学化学化工学院有序物质科学研究中心, 南京 211189)

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### A Novel 2D Zn-coordination Polymer Based on a 5-(4-nitrophenyl)-1H-tetrazole Ligand

XIAO Jie ZHAO Yu-Yuan WANG Wen-Xiang ZHAO Hong\*

(Ordered Matter Science Research Center, School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189)

**Abstract:** A zinc(II) complex  $[(5-(4\text{-nitrophenyl})\text{tetrazolato})_2\text{Zn}]_n$  was obtained by the hydrothermal treatment of  $\text{ZnBr}_2$  and  $\text{NaN}_3$  with 4-nitrobenzonitril in water at 120 °C in Pyrex tube. The crystal belongs to orthorhombic system with space group  $Pbcn$ , and  $a=1.040\,7(5)$  nm,  $b=1.382\,1(7)$  nm,  $c=2.435\,1(13)$  nm,  $V=3.503(3)$  nm<sup>3</sup>,  $Z=8$ . This complex is a good blue fluorescent material in solid state at room temperature. CCDC: 684226.

**Key words:** zinc complex; hydrothermal synthesis; crystal structure; fluorescence

Tetrazole compounds have been studied for more than one hundred years and applied in various areas. Several yeas ago Sharpless and his co-workers reported an environmentally friendly process for the preparation of 5-substituted 1H-tetrazoles in water with zinc salt as catalysts<sup>[1-6]</sup>. To reveal the exact role of the zinc salt in this reaction, a series of hydrothermal reactions aimed at trapping and characterizing the solid intermediates were investigated<sup>[7-9]</sup>. This study allowed us to obtain a myriad of interesting metal-organic coordination polymers that not only partially showed the role of the metal species in the synthesis of tetrazole compounds but also provided a class of complexes displaying interesting chemical and physical properties such as second harmonic generations (SHG), fluorescence, ferroelectric and dielectric behaviors<sup>[10]</sup>. In this context

and as part of an ongoing program in our laboratory to explore the medicinal and physical properties of tetrazole coordination compounds<sup>[11-17]</sup>, we would like to report the synthesis, crystal structure and fluorescence of a Zn coordination polymer with 5-(4-nitrophenyl)-1H-tetrazole ligand,  $[(5-(4\text{-nitrophenyl})\text{tetrazolato})_2\text{Zn}]_n$  (1).

## 1 Experimental

### 1.1 Materials and instruments

4-Nitrobenzonitril was synthesized according to an analogous method reported earlier<sup>[18]</sup>. All other reagents were commercially available. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained with KBr pellets in the 4 000~400 cm<sup>-1</sup> region, using a Shimadzu IRprestige-21 spectrophotometer.

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\*通讯联系人。E-mail: zhaohong@seu.edu.cn

第一作者: 肖 杰, 男, 23 岁, 硕士生; 研究方向: 金属配合物的铁电、介电和压电性质。

The crystal structures were determined by Rigacu SCX mini diffractionmeter. Electronic spectrum was recorded on Shimadzu RF-5301pc spectrophotometer.

## 1.2 Synthesis of [(5-(4-nitrophenyl)tetrazolato-*to*)<sub>2</sub>Zn]<sub>n</sub>

ZnBr<sub>2</sub> (1 mmol), NaN<sub>3</sub> (2 mmol) and 4-nitrobenzonitril (2 mmol) were placed in a thick Pyrex tube (ca. 20 cm in length). After addition of 2.0 mL of water, the tube was frozen with liquid N<sub>2</sub>, evacuated under vacuum, and sealed with a torch. The tube was heated at 120 °C for 2 days to give colorless prism crystals (pure phase) in 52% yield based on ZnBr<sub>2</sub>. Anal. Calc. for C<sub>14</sub>H<sub>8</sub>N<sub>10</sub>O<sub>4</sub>Zn (%): C, 37.73, H, 1.81, N, 31.43; Found (%): C, 37.01, H, 1.75, N, 32.01. IR (cm<sup>-1</sup>): 3 093.8(w), 3 036.9(w), 1 601.9(m), 1 520.9(s), 1 464.0(m), 1 446.6(m), 1 425.4(m), 1 347.0(s), 1 333.8(m), 1 284.6(w), 1 211.0(w), 1 111.02(w), 1 069.6(m), 852.5(m), 745.5(m), 731.0(m), 696.3(m), 510.1(w).

## 1.3 Crystal structure determination

A colorless crystal of the title compound with dimensions of 0.25 mm × 0.18 mm × 0.18 mm was selected for the X-ray diffraction experiment. Diffraction data were collected with a Rigacu SCX mini diffractionmeter using Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm). The structure was solved by direct methods with SHELXS-97 and refined by full matrix least squares on  $F^2$  with SHELXL-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with riding model and fixed isotropic thermal parameters. Detailed data collection, crystallographic data and refinement parameters of the compound **1** are summarized in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 684226.

Table 1 Crystallographic data for compound **1**

Empirical formula	C <sub>14</sub> H <sub>8</sub> N <sub>10</sub> O <sub>4</sub> Zn	Absorption coefficient / mm <sup>-1</sup>	1.451
Formula weight	445.67	$\theta$ range / (°)	2.57~28.28
Temperature / K	293(2)	Index ranges	-13 ≤ <i>h</i> ≤ 13, -18 ≤ <i>k</i> ≤ 18, -32 ≤ <i>l</i> ≤ 32
Crystal system	Orthorhombic	Reflections collected	34 154
Space group	<i>Pbca</i>	Independent reflections ( <i>R</i> <sub>int</sub> )	4 323 (0.037 3)
<i>a</i> / nm	1.040 7(5)	Obs. reflections	3 699
<i>b</i> / nm	1.382 1(7)	Data / restraints / parameter	4 323 / 0 / 263
<i>c</i> / nm	2.435 1(13)	Goodness-of-fit on $F^2$	1.159
Volume	3.503(3)	Final <i>R</i> indices [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.043 9, <i>wR</i> <sub>2</sub> =0.109 9
<i>Z</i>	8	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.052 8, <i>wR</i> <sub>2</sub> =0.115 1
<i>D</i> <sub>calc</sub> / (Mg·m <sup>-3</sup> )	1.69	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	466 and -423
<i>F</i> (000)	1 792		

Table 2 Selected bond lengths (nm) and angles (°) for compound [(5-(4-nitrophenyl)tetrazolato)<sub>2</sub>Zn]<sub>n</sub> (**1**)

Zn(1)-N(1)#1	0.197 9(2)	Zn(1)-N(1)	0.197 9(2)	Zn(1)-N(7)#1	0.199 6(2)
Zn(1)-N(7)	0.199 6(2)	Zn(2)-N(4)#2	0.196 3(2)	Zn(2)-N(4)#3	0.196 3(2)
Zn(2)-N(8)	0.202 1(2)	Zn(2)-N(8)#1	0.202 1(2)	C(1)-N(1)	0.132 8(3)
C(1)-N(4)	0.133 2(3)	C(1)-C(2)	0.147 9(3)	C(5)-N(5)	0.148 6(4)
C(8)-N(6)	0.134 0(3)	N(1)-N(2)	0.136 5(3)	N(2)-N(3)	0.128 3(3)
N(3)-N(4)	0.136 6(3)	N(6)-N(7)	0.132 3(3)	N(7)-N(8)	0.132 8(3)
N(8)-N(9)	0.132 8(3)				
N(1)#1-Zn(1)-N(1)	109.75(12)	N(1)#1-Zn(1)-N(7)#1	111.51(8)	N(1)-Zn(1)-N(7)#1	109.57(8)
N(1)#1-Zn(1)-N(7)	109.57(8)	N(1)-Zn(1)-N(7)	111.51(8)	N(7)#1-Zn(1)-N(7)	104.87(12)
N(4)#2-Zn(2)-N(4)#3	125.43(12)	N(4)#2-Zn(2)-N(8)	108.88(8)	N(4)#3-Zn(2)-N(8)	103.58(8)
N(4)#2-Zn(2)-N(8)#1	103.58(8)	N(4)#3-Zn(2)-N(8)#1	108.88(8)	N(8)-Zn(2)-N(8)#1	104.95(12)

Continued Table 2

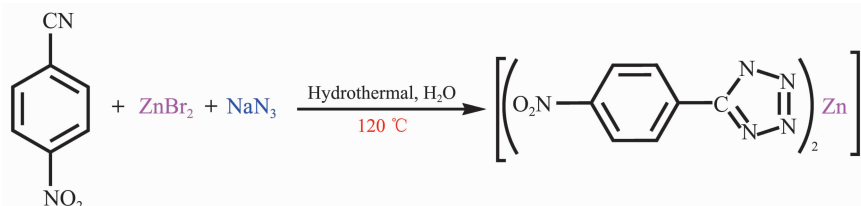
N(1)-C(1)-N(4)	108.8(2)	N(1)-C(1)-C(2)	125.4(2)	N(4)-C(1)-C(2)	125.8(2)
N(6)-C(8)-N(9)	112.2(2)	N(6)-C(8)-C(9)	123.1(2)	N(9)-C(8)-C(9)	124.7(2)
C(1)-N(1)-N(2)	106.98(18)	C(1)-N(1)-Zn(1)	136.61(16)	N(2)-N(1)-Zn(1)	116.33(14)
N(3)-N(2)-N(1)	108.65(19)	N(2)-N(3)-N(4)	108.93(18)	C(1)-N(4)-N(3)	106.64(19)
C(1)-N(4)-Zn(2)#4	138.88(16)	N(3)-N(4)-Zn(2)#4	114.40(14)	N(7)-N(6)-C(8)	104.06(18)
N(6)-N(7)-N(8)	110.17(18)	N(6)-N(7)-Zn(1)	120.79(15)	N(8)-N(7)-Zn(1)	128.42(14)
N(7)-N(8)-N(9)	109.48(17)	N(7)-N(8)-Zn(2)	126.62(14)	N(9)-N(8)-Zn(2)	123.61(15)
N(8)-N(9)-C(8)	104.11(18)				

Symmetry transformations used to generate equivalent atoms: #1:  $-x+1, y, -z+1/2$ ; #2:  $-x+1/2, y-1/2, z$ ; #3:  $x+1/2, y-1/2, -z+1/2$ ;

#4:  $x-1/2, y+1/2, -z+1/2$ .

## 2 Results and discussions

The hydrothermal reaction of  $\text{ZnBr}_2$ ,  $\text{NaN}_3$  and 4-nitrobenzonitrile in the molar ratios of 1:2:2 at 120 °C afforded a novel zinc 2D coordination polymer  $[(5-(4\text{-nitrophenyl})\text{tetrazolato})_2\text{Zn}]_n$  (**1**) (Scheme 1). The IR



The crystal structure of **1** reveals that the complex is a 2D coordination polymer that contains four ligands and two zinc center. Fig.1 gives structure of **1**, in that the coordination environment of two zinc center is very similar. The local coordination geometry around the Zn center can be best described as a slightly distorted tetrahedron with four nitrogen atoms from four ligands. In the structure of **1**, two ligands afford the adjacent N atoms to chelated two zinc center and form the six numbers ring, in which the distance between two Zn

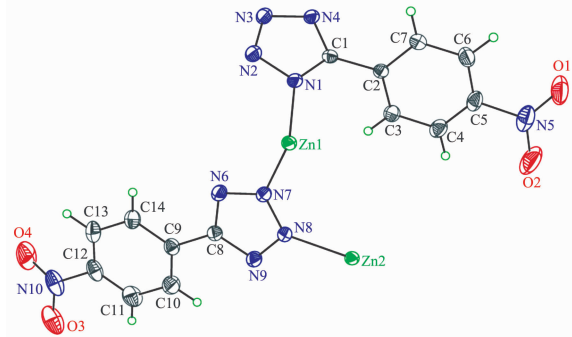
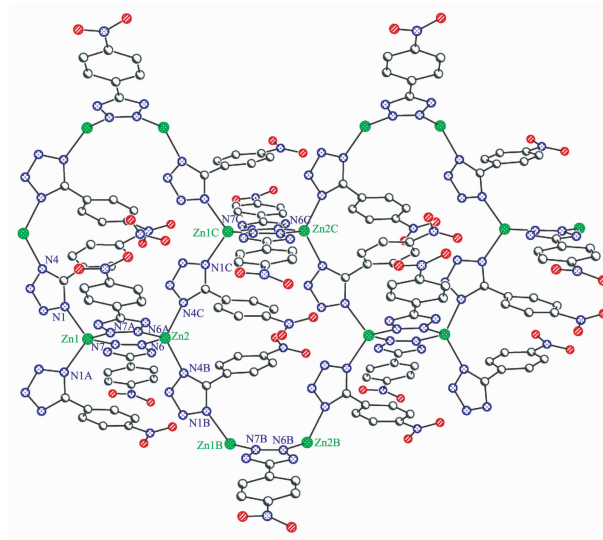


Fig.1 Asymmetric unit of  $[(5-(4\text{-nitrophenyl})\text{tetrazolato})_2\text{Zn}]_n$  (**1**), displacement ellipsoids are drawn at the 30% probability level

spectrum of **1** shows the absence of a cyano peak in the  $2100\text{ cm}^{-1}$ , which supports the proposed reaction between the nitrile and the azide. The formation of a tetrazole group is supported by the emergence of peaks at *ca.*  $1440\text{ cm}^{-1}$ .

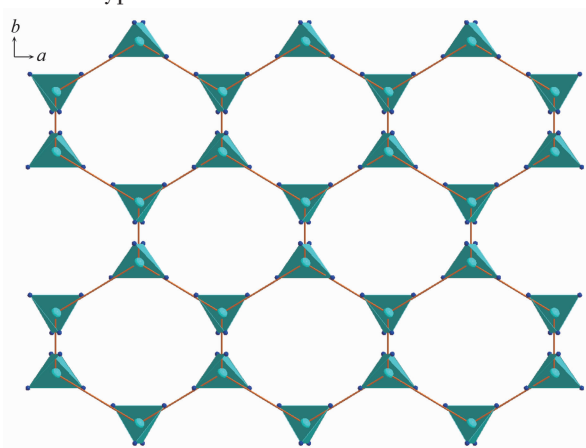
atoms is  $0.3775(2)\text{ nm}$ . Another two ligands connect four zinc centers as bridges (the distance between two Zn atoms is  $0.6075(2)\text{ nm}$ ), resulting in the formation of a 2D framework, as shown in Fig.2 and Fig.3. The



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

Fig.2 2D net structure of the title complex, hydrogen atoms are omitted for clarity

packing view (Fig.4) shows that the two adjacent layers are in a staggered arrangement and adopt an ABAB... type.



Only the Zn centers and the coordinated N atoms are shown

Fig.3 A 2D framework representation of **1** highlighting Zn tetrahedron

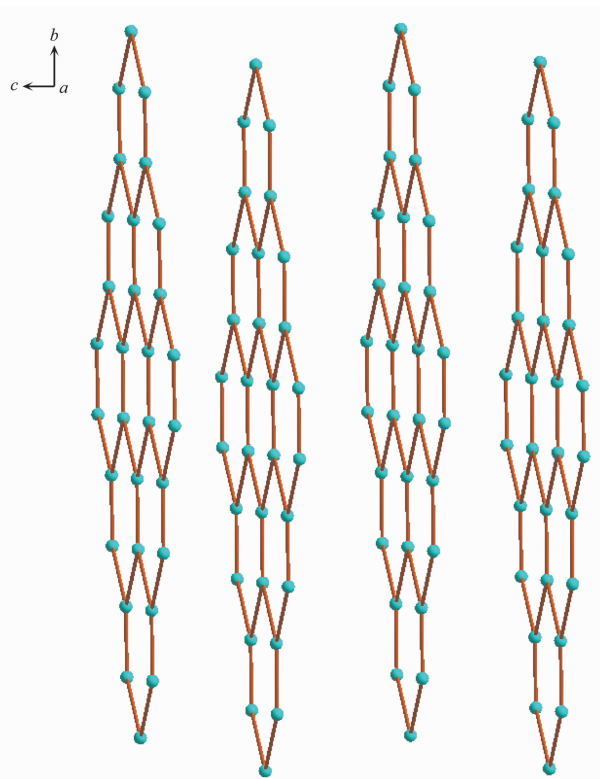


Fig.4 Packing view of **1** along the *a*-axis

The solid state fluorescent emission spectrum of complex **1** at room temperature shows that maximum emission peak occurs in *ca.* 470 nm ( $\lambda_{\text{ex}}=234$  nm) (Fig. 5), suggesting **1** maybe good blue-light emitted materials. The photoluminescent mechanism may be considered ligand to ligand transition, which is in fairly

good agreement these Zn-coordination polymers<sup>[19,20]</sup>.

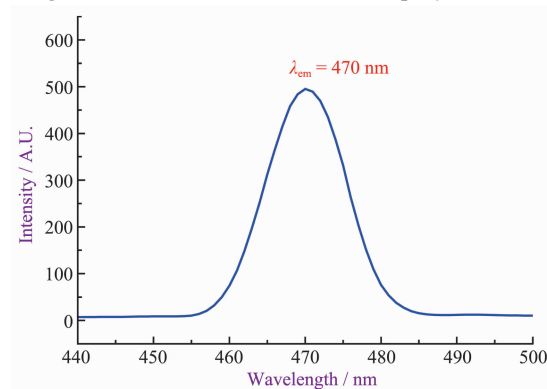


Fig.5 Fluorescence spectra of **1** in the solid state at room temperature ( $\lambda_{\text{ex}}=234$  nm)

In conclusion, apart from demonstrating the value of hydrothermal approaches in the generation of novel coordination polymers, the work described here will enlighten how to synthesize and explore the functional tetrazole coordination polymers.

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