基于一维锌(II)配位聚合物的水中2,4,6-三硝基苯酚 和氟啶胺的选择性检测

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摘要:以1,1':4',1":4'',1"'-四联苯-2,4,2"',4"'-四羧酸(H₄L)和4,4'-联吡啶(4,4'-bpy)为配体,采用水热法合成了一维锌配位聚 合物[Zn₂(H₂L)₂(4,4'-bpy)₂(H₂O)]₄(1),并通过单晶X射线衍射分析、元素分析、红外光谱分析和热重分析等方法对其结构进行了 表征。单晶结构分析表明1属于三斜晶系,空间群为Pī。配合物1含有2种配位构型不同的锌离子,分别处于扭曲的三角双锥 {ZnNO₄}和八面体{ZnNO₅}几何构型中。配合物中2个H₂L²配体之间通过锌离子相互连接,构成了无限的一维zigzag平面结构。 荧光传感实验表明配合物1的荧光能够被2,4,6-三硝基苯酚和氟啶胺猝灭,且具有较高的灵敏度和选择性,抗干扰性也非常好。

关键词:配位聚合物;Zn(II);1,1':4',1":4",1"'四联苯-2,4,2"',4"'四羧酸;2,4,6-三硝基苯酚;氟啶胺;荧光传感性质 中图分类号:O614.24⁺¹ 文献标识码:A 文章编号:1001-4861(2023)02-0375-10 DOI:10.11862/CJIC.2023.002

Selective detection of 2,4,6-trinitrophenol and fluazinam in water based on a 1D Zn(II) coordination polymer

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Abstract: A 1D coordination polymer $[Zn_2(H_2L)_2(4,4'-bpy)_2(H_2O)]_n$ (1) $(H_4L=1,1':4',1'':4'',1'''-quterphenyl-2,4,2''',4'''-$ tetracarboxylic acid, 4,4'-bpy=4,4'-bipyridine) was synthesized by hydrothermal method, and its structure was characterized by single-crystal X-ray diffraction analysis, elemental analysis, infrared spectroscopy, thermogravimetric analysis, *etc.* The crystallographic analysis shows that complex 1 belongs to the triclinic crystal system with the space group of $P\overline{1}$. Complex 1 consists of two zinc ions with different coordination geometries, which lie in a distorted trigonal bipyramidal {ZnNO₄} and octahedral {ZnNO₅} geometrical configuration, respectively. The two H_2L^{2-} ligands in complex 1 are linked to each other by zinc ions, forming an infinite 1D zigzag planar structure. The fluorescence sensing experiments indicated that the fluorescence of complex 1 could be quenched by 2,4,6-trinitrophenol and fluazinam with high sensitivity and selectivity. Moreover, the anti-interference of detection was also quite excellent. CCDC: 2107201.

Keywords: coordination polymer; Zn(II); 1,1':4',1":4",1"'-quterphenyl-2,4,2"',4"'-tetracarboxylic acid; 2,4,6-trinitrophenol; fluazinam; fluorescence sensing properties

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0 Introduction

In the past several decades, with the rapid development of society, more and more organic compounds, such as nitroaromatic compounds (NACs) and pesticides have been widely used in the chemical and agricultural industry and thus resulting in serious environmental pollution^[1-2]. NACs such as 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT) are hazardous and explosive, which extensively used to synthesize dyes, aniline, pesticides and fabricate explosive devices^[3]. Among NACs, TNP has received extensive attention due to its strong explosiveness and hazardous properties^[4]. Furthermore, TNP often appears in the leather, dyes, fireworks, and glass industries^[5-8]. However, it also will inevitably cause environmental pollution to the soil and aquatic system^[9]. Accordingly, the selective detection of TNP is indispensable for environmental governance and ensuring military security. On the other hand, pesticides have been extensively used to kill pests in the agricultural field^[10]. However, excessive use of pesticides is becoming an increasingly serious environmental problem, which gives rise to polluting soil and underground water^[11]. For example, fluazinam (FLU) is a pyridinamine fungicide with relatively low toxicity and controls effectively phytophthora blight^[12]. Nevertheless, excessive use in agriculture still leads to a huge threat to the environment and food safety, although FLU is regarded as a low-toxic pesticide^[13]. Furthermore, it is reported that FLU could remain a long time in the soil and leaf surfaces, thus reducing the quality of soil and destroying the balance of the microbial population^[14-15]. What's worse, the ingestion of FLU in the body can give rise to dermatitis and asthma^[16-17]. Accordingly, the simple, convenient, effective, and reliable detection of FLU is more and more meaningful and imperative in agriculture and food safety.

Coordination polymers (CPs), consisting of metal ions and organic ligands or clusters, have made significant progress in various areas such as luminescence sensing^[18-21], catalysis^[22-25], magnetism^[26-27], gas adsorption and separation^[28-29], and biological imaging^[30-31]. Luminescent CPs have attracted extensive attention among the aforementioned applications. A large number of CPs with luminescent sensing properties were synthesized and used for the detection of nitroaromatic explosives, pesticides, antibiotics, small organic compounds, anion and metal ions, *etc*^[32-40].

Based on the above considerations, therefore, in this work, we herein report on the synthesis, crystal structure, and selective fluorescence sensing behaviors of NACs and pesticides of a new Zn (II) - CP, namely $[Zn_2(H_2L)_2(4,4'-bpy)_2(H_2O)]_n$ (1) $(H_4L=1,1':4',1'':4'',1'''$ quterphenyl-2,4,2''',4'''-tetracarboxylic acid, 4,4'-bpy= 4,4'-bipyridine). More importantly, the as-synthesized complex 1 exhibited a dual functional fluorescent response to detect TNP and FLU with high sensitivity and selectivity as well as excellent anti-interference properties.

1 Experimental

1.1 Materials and general methods

All solvents and reagents were purchased directly from pharmaceutical companies and used directly without further purification. The element analysis of C, H, and N was conducted with a Perkin Elmer PE-2400 element analyzer. The infrared spectrum was recorded using a Nicolet 170SXFT-4000 infrared spectroscopy (500 - 4 000 cm⁻¹). Thermogravimetric analysis (TGA) was performed with a STA449F3 thermogravimetric analyzer in flowing nitrogen at a heating rate of 10 $^{\circ}$ C \cdot min⁻¹. The powder X-ray diffraction (PXRD) measurement was carried out by a Shimadzu XRD-7000 diffractometer operating at 40 kV and 40 mA with Cu Kα radiation (λ =0.154 18 nm) at a scanning rate of 2 (°) · min⁻¹ from 5° to 50° . Fluorescence sensing experiments were tested on a Hitachi F-7000 fluorescence spectrophotometer.

1.2 Synthesis of complex 1

A mixture of H_4L (24.1 mg, 0.05 mmol), $Zn(NO_3)_2$. 4 H_2O (29.7 mg, 0.10 mmol), DMF (0.5 mL), and H_2O (2 mL) was stirred for 30 min at ambient temperature and then heated at 95 °C for 3 d. Colorless crystals of **1** were obtained. Yield: 42% (based on Zn). Anal. Calcd. 第2期

for $C_{76}H_{50}N_4O_{17}Zn_2(\%)$: C 64.19; H 3.54; N 3.94; Found (%): C 64.18; H 3.56; N 3.95. IR (KBr, cm⁻¹): 3 030 (w), 2 500 (s), 1 700 (s), 1 610 (w), 1 380 (s), 1 280 (w), 1 120 (m), 1 000 (w), 810 (w), 711 (s), 633 (s).

1.3 Single-crystal X-ray crystallography

The X-ray diffraction data were collected by the Bruker Smart APEX II CCD diffractometer equipped with graphite monochromatic Mo $K\alpha$ radiation (λ = 0.071 073 nm) at 293(2) K. The diffraction intensity data were corrected using the SADABS program by

semi-empirical absorption. The structure was solved by the direct method in the SHELXS-2014 program and all non - hydrogen atoms and anisotropy parameters were refined using the full-matrix least-squares on F^2 method by the SHELXL - 2014 program. The coordinates of all hydrogen atoms were obtained through theoretical hydrogenation. The relevant crystallographic data of complex **1** are presented in Table 1. Selected bond lengths and bond angles of **1** are listed in Table 2. CCDC: 2107201.

Empirical formula	$\rm C_{76}H_{50}N_4O_{17}Zn_2$	μ / mm ⁻¹	0.876	
Formula weight	1 421.94	F(000)	1 460	
Crystal system	Triclinic	θ range / (°)	1.091-24.999	
Space group	$P\overline{1}$	Limiting indices	$-11 \leq h \leq 12, -18 \leq k \leq 14, -22 \leq l \leq 22$	
<i>a /</i> nm	1.066 71(19)	R _{int}	0.029 0	
<i>b</i> / nm	1.533 0(3)	Reflection collected	15 457	
<i>c</i> / nm	1.920 1(4)	Unique reflection	10 598	
α / (°)	83.706(3)	Number of parameters	904	
eta / (°)	77.367(3)	Completeness to θ / %	99.3	
γ / (°)	82.280(3)	Goodness of fit on F^2	1.005	
V / nm^3	3.025 6(10)	Final R indices $[I>2\sigma(I)]^*$	$R_1 = 0.051 \ 2, \ wR_2 = 0.107 \ 3$	
Ζ	2	R indices (all data)*	R_1 =0.097 0, wR_2 =0.120 4	
$D_{\rm c} /({\rm g} \cdot {\rm cm}^{-3})$	1.561	Largest diff. peak and hole / $({\rm e} {}^{\bullet} nm^{-3})$	595 and -429	

 Table 1
 Crystal data and structure refinement for complex 1

 $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|; wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum (F_0^2)^2]^{1/2}$

Table 2 Selected bond lengths (nm) and bond angles (°) for complex 1

	Zn1-01	0.199 0(3)	Zn1—N1	0.205 0(3)	Zn2—010	0.248 6(3)
	Zn1—O2A	0.194 5(2)	Zn2—05	0.271 4(3)	Zn2—017	0.203 4(3)
	Zn1-013A	0.203 6(3)	Zn2—06	0.196 0(3)	Zn2—N3	0.204 5(3)
	Zn1-014A	0.230 0(2)	Zn2—09	0.196 4(3)		
0	1—Zn1—N1	94.16(12)	01—Zn1—013A	103.00(11)	09—Zn2—010	57.30(10)
0	2A—Zn1—N1	99.38(11)	06—Zn2—N3	106.01(12)	09—Zn2—017	102.33(12)
0	2A—Zn1—014A	99.13(10)	06—Zn2—05	52.81(11)	017—Zn2—N3	91.55(12)
0	13A—Zn1—O14A	59.61(10)	05—Zn2—010	86.13(10)		

Symmetry code: A: -x, -y, 1-z.

1.4 Fluorescence sensing experiments

1.4.1 Fluorescence sensing experiments toward NACs The as-synthesized crystal powder sample (30 mg) was dispersed in an aqueous solution (100 mL), ultrasonicated for 1 h, and let stand for 3 d. The obtained supernatant containing 10 mmol·L⁻¹ of TNP, nitrobenzene (NB), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 4-nitrophenylhydrazine (4-NPH), 4-nitrobenzoic acid (4-NBA), 2, 4-dinitrophenylhydrazine (DNP), and 2nitroaniline (2-NA) was used to conduct fluorescence sensing experiments and the fluorescent intensity was measured at room temperature.

1.4.2 Fluorescence sensing experiments toward pesticides The prepared crystal powder sample (30 mg) was immersed in a 100 mL aqueous solution, treated with ultrasound for 1 h, and the suspension was placed for 3 d. The obtained supernatant containing 10 mmol·L⁻¹ of zhongshengmycin (MYC), imazalil (IMA), emamectin benzoate (EMB), pyraclostrobin (PST), 24-epibrassinolide (24-EPI), triadimefon (TDI), prochloraz (PRO), and FLU was used to carry out fluorescence sensing experiments and the fluorescent intensity was recorded at room temperature.

2 Results and discussion

2.1 Description of crystal structure

Single-crystal X-ray diffraction analysis of complex 1 reveals that it crystallizes in the triclinic system with the space group of $P\overline{1}$. The composition of complex 1 contains two independent Zn(II) ions, two H₂L²⁻ ions, two 4, 4' - bpy molecules, and one coordinated water molecule. As described in Fig. 1, the Zn1 center is penta-coordinated and possesses a distorted trigonal



All hydrogen atoms are omitted for clarity; 50% ellipsoid probability; Symmetry code: A: -x, -y, 1-z

Fig.1 Coordination environment of Zn(II) in complex 1

bipyramidal {ZnNO₄} environment, which is occupied by four carboxylate oxygen atoms (O1, O2A, O13A, and O14A) from two different H_2L^{2-} ions and one nitrogen atom (N1) from 4,4'-bpy moiety. The six-coordinated Zn2 center is surrounded by four carboxylate oxygen atoms (O5, O6, O9, and O10) from two individual H_2L^{2-} ions and one oxygen atom (O17) from the water molecule as well as one nitrogen atom (N3) from 4,4'-bpy moiety, forming the distorted octahedral {ZnNO₅} environment. The bond lengths of Zn—O range from 0.194 5(2) to 0.248 6(3) nm and the Zn—N bond lengths range from 0.204 5(3) to 0.205 0(3) nm, respectively (Table 2).

As depicted in Fig. 2, the H₄L ligand is partially deprotonated and consists of two carboxyl groups. The H₂L²⁻ ion adopts a μ_3 -(κ^1 - κ^1)-(κ^1 - κ^0) coordination mode in **1**, in which four carboxylate groups show uncoordinated, monodentate or chelating bidentate modes. The carboxylate groups from H₂L²⁻ ions are alternately connected to Zn(II) ions, forming a similar 1D infinite zig-zag chain (Fig.3).



All hydrogen atoms are omitted for clarity; 50% ellipsoid probability

Fig.2 Coordination mode of H_2L^{2-} in complex 1

2.2 TGA for complex 1

The TGA curve of complex 1 was measured to



4,4'-bpy molecules and all hydrogen atoms are omitted for clarity

Fig.3 One-dimensional zigzag chain of complex 1

evaluate the thermal stability of complex **1**. As can be seen in Fig.4, the structure of complex **1** was gradually disintegrated into two steps with the increase in temperature. The initial weight loss of 1.27% before 179 °C was assigned to the removal of one coordinated water molecule (Calcd. 1.26%). The framework began to decompose and collapse when the temperature was elevated to 279 °C. Finally, the remaining weight of 33.25% may be attributed to the final residue of ZnO (Calcd. 34.20%).



Fig.4 TGA curve of complex 1

2.3 PXRD analysis of complex 1

To evaluate the phase purity of as - synthesized complex **1**, the PXRD measurement was conducted. The experimental and simulated data are presented in Fig.5. As depicted in Fig.5, the main characteristic diffraction peak positions of complex **1** were consistent with the theoretically fitted peak ones of the single crystal data, confirming the high purity of complex **1**.



Fig.5 PXRD patterns of complex 1

2.4 Fluorescent sensing

2.4.1 Solid-state fluorescence of complex 1 and H_4L

The fluorescent properties of complex 1 and the free ligand H₄L were investigated in the solid state at room temperature (Fig. 6). It can be seen in Fig. 6 that H₄L exhibited one emission band at 485 nm with excitation at 350 nm, while complex 1 performed slight fluorescence enhancement and the strong emission band was observed at 435 nm under the same excitation. It is well known that Zn(II) is very difficult to oxidize or reduce due to its d^{10} - filled configuration^[41]. Accordingly, the emission of complex 1 is attributed to a mixture character of intraligand and ligand-to-ligand charge transition (LLCT)^[42]. The blue shift of ca. 50 nm may derive from coordination interactions between Zn(II) and the ligand.



Fig.6 Emission spectra of complex 1 and H_4L in solid state at room temperature

2.4.2 Fluorescence detection performance of complex1 for various NACs in an aqueous solution

Complex 1 has a potential application as a fluorescence probe because of strong fluorescence emission and good stability and dispersion of complex 1 in an aqueous system. Accordingly, the fluorescence sensing experiments of complex 1 for various NACs were investigated in detail. A variety of NACs (DNP, 4-NPH, NB, 4-NP, 2-NP, 4-NBA, 2-NA, and TNP) were selected to evaluate the sensing ability of complex 1. As shown in Fig.7, compared with other NACs, complex 1 exhibited obvious fluorescent quenching behaviors in the presence of TNP, indicating the possible selective fluorescent sensing toward TNP. 无



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Fig.7 Relative fluorescence intensity of complex 1 towards various NACs

To further understand the fluorescence sensing of complex **1** for TNP, the fluorescent titration experiments with the addition of TNP were investigated (Fig.8). The fluorescence intensity of complex **1** gradually decreased as the concentration of TNP increased and the intensity was almost completely quenched with the concentration of TNP up to 291 μ mol·L⁻¹ (Fig.8a). The fluorescence quenching effect was calculated according to the Stern-Volmer equation: $I_0/I=K_{sv}c_{TNP}+1$, where I_0 is the initial fluorescence intensity, I is the fluorescence intensity in the presence of TNP, c_{TNP} is the concentration of TNP, and K_{sv} is the quenching constant. As depicted in the inset of Fig.8b, the TNP concentration had an almost linear relationship with I_0/I (R^2 =0.982 1) at low concentrations (0 - 50 μ mol·L⁻¹). The calculated K_{sv} was 3.11×10^4 L·mol⁻¹ and the LOD (limit of detection) of TNP was 0.617 μ mol·L⁻¹ according to the calculation of $3\sigma/K_{sv}$ (σ is the standard error).

The anti-interference experiments of complex **1** were also conducted in the existence of other NACs. As described in Fig. 9, the fluorescence intensity of com-



Inset: linear response of complex 1 to TNP in a low concentration range of 0-50 µmol·L⁻¹

Fig.8 (a) Fluorescence titration curves of complex **1** after the continuous addition of TNP; (b) Stern-Volmer equation fitting for fluorescence response of complex **1** to TNP



Fig.9 Comparison of fluorescent intensity of complex 1 in the presence of other interfering NACs

plex **1** was only slightly reduced when other NACs were added. Nevertheless, the fluorescence intensity was immediately quenched after adding TNP. Consequently, complex **1** performed high selection and recognition ability for TNP even in the presence of other interfering NACs.

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2.4.3 Fluorescence detection performance of complex

1 for various pesticides in an aqueous solution

Currently, the environmental problems concerned with the use of high-concentration pesticides are becoming very serious because the pesticide compounds are often detected in ground and surface waters. Thus, the fluorescence sensing experiments of complex **1** for different pesticides were explored. On this basis, all kinds of pesticides (MYC, IMA, EMB, PST, 24-EPI, TDI, PRO, and FLU) were selected to evaluate the sensing ability of complex **1**. Notably, complex **1** displayed an obvious fluorescent quenching effect with FLU compared with other pesticides (Fig. 10), revealing a highly selective fluorescent sensing toward FLU in an aqueous solution.

To further illustrate the fluorescence sensing of complex **1** for FLU, the FLU titration experiments with the addition of FLU were carried out (Fig.11). As illustrated in Fig.11a, as the concentration of FLU increased, the fluorescence intensity of complex **1** gradually decreased and the intensity was almost completely quenched when the concentration of FLU was up to $654 \ \mu \text{mol} \cdot \text{L}^{-1}$. Moreover, the fluorescence quenching



Fig.10 Relative fluorescence intensity of complex **1** for various pesticides

effect is expressed through the Stern-Volmer equation: $I_0/I=K_{sv}c_{FLU}+1$, where I_0 denotes the initial fluorescence intensity, *I* denotes the fluorescence intensity after the addition of FLU, c_{FLU} denotes the concentration of FLU. At low concentrations (0-60 µmol·L⁻¹), the FLU concentration had a close linear relationship with I_0/I ($R^2=$ 0.989 1). The calculated K_{sv} was 3.69×10^4 L·mol⁻¹. According to the calculation of $3\sigma/K_{sv}$, the LOD of FLU was 0.575 µmol·L⁻¹ (Fig.11b).

In addition, the anti-interference experiments displayed that the fluorescence quenching effect did not be affected in the presence of other pesticides, further confirming its high selectivity for FLU (Fig. 12). This shows that complex **1** could be a fluorescence sensor for high selection and recognition ability toward FLU in the presence of other interfering pesticides.



Inset: linear response of complex 1 to FLU in a low concentration range of 0-60 µmol·L⁻¹

Fig.11 (a) Fluorescence titration curve of complex 1 after adding FLU with different concentrations;(b) Stern-Volmer equation fitting for fluorescence response of complex 1 to FLU



Fig.12 Comparison of fluorescent intensity of complex **1** in the presence of other interfering pesticides

2.4.4 Luminescence quenching mechanism

To illustrate the fluorescence quenching mecha-

nism of complex **1** toward TNP and FLU, the UV-Vis absorption spectra of various NACs and pesticides along with the emission and excitation spectra of complex **1** were recorded. As portrayed in Fig. 13a, compared to other NACs, an obvious overlap between the UV-Vis absorption band of TNP and the emission spectrum of complex **1** was observed. Therefore, the fluorescence quenching of complex **1** by TNP may be mainly due to the resonance energy transfer^[43]. Similarly, as depicted in Fig. 13b, an obvious overlap between the UV - Vis absorption band of FLU and the excitation spectrum of complex **1** was observed in comparison with other pesticides. Therefore, the fluorescence quenching of complex **1** by FLU may be mostly caused by competitive absorption^[43].



Fig.13 (a) UV-Vis absorption spectra of various NACs and emission spectrum of complex **1**;(b) UV-Vis absorption spectra of different pesticides and excitation spectrum of complex **1**

3 Conclusions

In summary, we have synthesized a novel type of Zn(II)-CP, $[Zn_2(H_2L)_2(4,4'-bpy)_2(H_2O)]_n$ (1), based on an aromatic tetracarboxylic acid ligand $(H_4L=1,1':4',1'':4'',1''')$ -quterphenyl-2,4,2''',4'''-tetracarboxylic acid, 4,4'-bpy=4,4'-bipyridine) under hydrothermal conditions. The crystallographic analysis of complex 1 exhibits that it possesses a 1D zigzag chain framework. H_2L^{2-1} ions and 4,4'-bpy molecules in complex 1 are alternately connected to Zn(II) ions, forming a 1D infinite zigzag chain planar configuration. The fluorescence detection experiments displayed that complex 1 could highly sensitive and selective detection for the nitro-explosive 2,4,6-trinitrophenol (TNP) and the pesticide fluazinam

(FLU) in aqueous solution with excellent anti-interference ability, and the detection limits are low as 0.617 μ mol·L⁻¹ for TNP and 0.575 μ mol·L⁻¹ for FLU. This study provides further insights into the design of luminescent Zn(II)-CPs, which could be used as a potential probe material for the detection of TNP and FLU.

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