

一种用于检测罗红霉素和 $B_4O_7^{2-}$ 的高稳定性Cd(II)配位聚合物

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摘要: 在溶剂热条件下, 成功合成了一种稳定的配位聚合物 $[Cd_2(L)(bpb)(H_2O)_4] \cdot 0.5H_4L$ (**1**) ($H_4L=1,1'$ -乙烷基联苯-3,3',5,5'-四羧酸, $bpb=1,4$ -二(4-吡啶基)苯)。 **1** 在不同的有机溶剂和水中表现出优异的稳定性。 **1** 可通过荧光猝灭检测水中的罗红霉素(ROX)和 $B_4O_7^{2-}$, 检测限分别为0.21和1.59 $\mu\text{mol} \cdot \text{L}^{-1}$ 。 **1** 可成功用于延河水中ROX和 $B_4O_7^{2-}$ 的测定。此外, 分析讨论了其传感机理。

关键词: 罗红霉素; $B_4O_7^{2-}$; 荧光传感器; 配位聚合物

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A Highly Stable Cd(II) Coordination Polymer for Detection of Roxithromycin and $B_4O_7^{2-}$

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Abstract: A stable coordination polymer, $[Cd_2(L)(bpb)(H_2O)_4] \cdot 0.5H_4L$ (**1**) ($H_4L=1,1'$ -ethylbiphenyl-3,3',5,5'-tetracarboxylic acid, $bpb=1,4$ -di(pyridin-4-yl) benzene), were successfully constructed under solvothermal conditions. **1** exhibited excellent stability in different organic solvents and water. **1** could detect roxithromycin (ROX) and $B_4O_7^{2-}$ in water by fluorescence quenching, and the detection limits were 0.21 and 1.59 $\mu\text{mol} \cdot \text{L}^{-1}$, respectively. **1** could be successfully used for the determination of ROX and $B_4O_7^{2-}$ in Yanhe River water. Moreover, the possible sensing mechanisms are also discussed in detail. CCDC: 2162322.

Keywords: roxithromycin; $B_4O_7^{2-}$; fluorescence sensor; coordination polymer

0 Introduction

Roxithromycin (ROX) is a semi-synthetic antibiotic containing 14-membered macrolides, which can be used to treat inflammatory diseases caused by a variety of pathogen infections, and its antibacterial effect in the body is stronger than that of erythromycin^[1]. ROX has the advantages of rapid absorption, elimination of

long half-life, and a good therapeutic effect on fungi, such as Streptococcus and Corynebacterium. However, the abuse or irregular use of macrolide antibiotics may cause gastrointestinal discomfort, allergic reactions, liver and kidney damage, and other diseases^[2]. Therefore, it is very urgent and important to find an efficient detection method for ROX. Boron is an essential element in the human body and is indispensable in many

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parts of the body, especially bones. Boron is generally present in the human body in the form of boric acid. However, boron is a limited element, and the content in the body should not be too much. Studies have shown that abnormal boric acid content can cause adverse reactions such as anorexia, vomiting, and diarrhea^[3]. Even ingesting small amounts of boron can cause poisoning due to slow excretion. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is also a form of boron and is a very important chemical raw material that is widely used in industry and consumer products. Because it exists in food and some consumer products, long-term consumption or use of such products will lead to the accumulation of borax in the body, which is harmful to various organs of the human body^[4]. Therefore, the detection of borate content is very important.

Coordination polymers (CPs) are organic-inorganic hybrid materials composed of inorganic metal centers and organic ligands^[5-6]. Due to the diversity of metal and organic ligands, or the introduction of two or more metal and organic ligands at the same time, the structure of CPs is more diverse^[7-9]. CPs have attracted the attention of more and more researchers due to their structural diversity, high porosity, tunable functions, and large specific surface area^[10-15]. CPs are widely used in gas storage, bioimaging, adsorption, drug delivery, and sensing due to their excellent chemical properties^[16-18]. In particular, fluorescent materials based on CPs are more favored by researchers due to their high selectivity, low detection limit, high sensitivity, good recovery performance, and short response time^[19-20]. For instance, Zhang et al. synthesized a Zn(II)-based CP with high selectivity and sensitivity for Ni^{2+} and PO_4^{3-} ^[21]. A complex that can detect oridazole antibiotics and nitrophenol with low detection limits was reported by Li et al^[22].

In this work, we constructed a Cd(II) CP, $[\text{Cd}_2(\text{L})(\text{bpb})(\text{H}_2\text{O})_4] \cdot 0.5\text{H}_4\text{L}$ (**1**) ($\text{H}_4\text{L}=1,1'$ -ethylbiphenyl-3,3',5,5'-tetracarboxylic acid, $\text{bpb}=1,4$ -di(pyridin-4-yl)benzene). **1** exhibited excellent stability in different organic solvents and water and high selectivity and sensitivity to ROX and $\text{B}_4\text{O}_7^{2-}$. Furthermore, **1** was a reusable material with good recyclability. The possible

mechanism of fluorescence quenching is also discussed in detail in the article. Finally, the detection of ROX and $\text{B}_4\text{O}_7^{2-}$ in Yanhe River water indicated the actual availability of complex **1**. To our knowledge, this is the first complex that can detect ROX. This is of great significance for the new fluorescent probe in future research.

1 Experimental

1.1 Materials and instrumentation

The chemicals used were all commercially available and could be used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8ADVANCE diffractometer operating at 40 kV and 40 mA using Cu $K\alpha$ radiation ($\lambda = 0.154\ 18\ \text{nm}$) at a scanning rate of $8\ (^{\circ}) \cdot \text{min}^{-1}$ from 5° to 50° . Fluorescence experiments were carried out on a Hitachi F-7100 Fluorescence Spectrophotometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449F5 thermal analyzer.

1.2 Synthesis of **1**

A solid mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 mmol, 0.030 8 g), H_4L (0.05 mmol, 0.017 9 g), and bpb (0.05 mmol, 0.011 6 g) was dissolved in the mixed solvent of DMF (3 mL), H_2O (3 mL), and HNO_3 (0.1 mL, $6\ \text{mol} \cdot \text{L}^{-1}$). The mixed solution was placed in a 10 mL inner glass bottle and reacted at $95\ ^{\circ}\text{C}$ for three days. Finally, colorless crystals were obtained. Yield: 57% (based on Cd). Anal. Calcd. for $\text{C}_{43}\text{H}_{37}\text{Cd}_2\text{N}_2\text{O}_{16}$ (%): C, 48.60; H, 3.52; N, 2.64. Found(%): C, 48.32; H, 3.62; N, 2.87.

1.3 Crystal structure determination

Single crystal data of **1** were collected on a Bruker SMART APEX-II diffractometer (Mo $K\alpha$ radiation and $\lambda = 0.071\ 073\ \text{nm}$). The crystal structures were solved using direct methods and then refined by the full-matrix least-squares techniques on F^2 using SHELXL^[23-24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were obtained by geometric calculation. All calculations were performed using the SHELXTL program. Partial data for crystals are given in Table S1 and S2 (Supporting information).

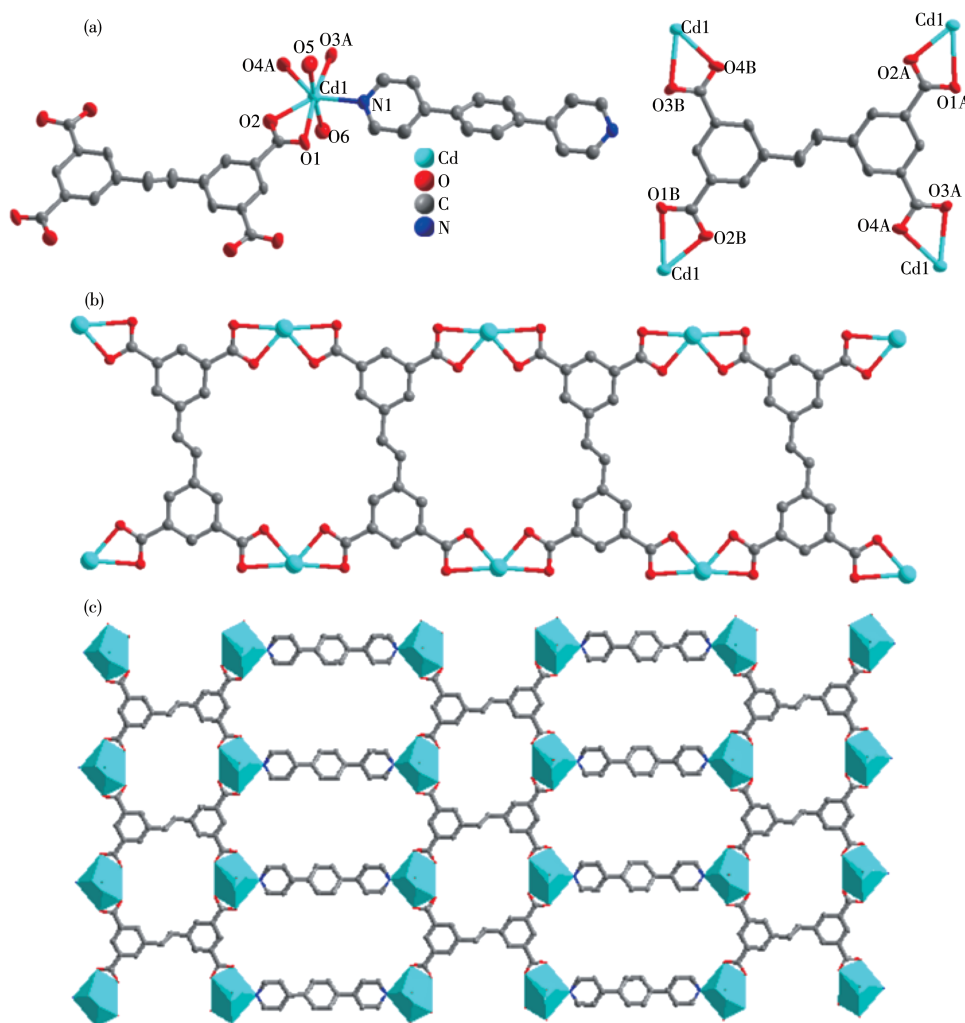
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2 Results and discussion

2.1 Crystal structure

Complex **1** crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit of **1** includes two Cd^{2+} ions, one and a half L^{4-} anions, one bpb molecule, four coordinated H_2O molecules, and a half free H_4L molecule. Every Cd^{2+} ion is seven-coordinated by four O atoms (O1, O2, O3A, O4A) from two L^{4-} anions, two oxygen

atoms (O5, O6) from two coordinated water molecules, and one N atom (N1) from one bpb molecule (Fig. 1a). In complex **1**, the H_4L ligand is completely deprotonated and the coordination mode is $\mu_4 - \eta^2: \eta^2: \eta^2: \eta^2$ (Fig. 1a). Adjacent Cd(II) ions are connected by O atoms in L^{4-} to form a 1D chain structure (Fig. 1b). Then 1D chains are linked by bpb ligands to form 2D framework (Fig. 1c).



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

Fig.1 (a) Ellipsoid diagram of molecular structure with 50% ellipsoid probability; (b) 1D chain structure; (c) 2D framework

2.2 Purity and stability of **1**

TGA was performed to explore the stability of **1**. The weight loss of **1** was 8.52% below 100 °C (Fig.S1), which can be regarded as the loss of coordinated water molecules (Calcd. 6.78%) and release of lattice H_2O . The second weight loss in 350-450 °C should be due to the loss of free carboxylic acid ligands in the pores. In

the 450-800 °C range, the skeleton collapsed and disintegrated. The residual (36.79%) after 800 °C is attributed to CdO (Calcd. 36.25%). The PXRD pattern of **1** was almost identical to the simulated, implying the pure phase of **1** (Fig.S2). The skeleton was unchanged when **1** was immersed in acidic and basic aqueous solutions (pH=2.0 and 12.6) for 24 h, indicating that **1** had

good acid and alkali resistance (Fig.S3). **1** could keep the original skeleton in an organic solvent for seven days and could be stable in boiling water for 30 days, which further showed the chemical stability of **1** (Fig. S4). Finally, the persistent luminescence ability of **1** in deionized water was tested. As shown in Fig.S5, after seven consecutive days, the fluorescence still maintained its original relative intensity, indicating its durability and application potential.

2.3 Photoluminescence property of **1**

The photoluminescence of H_4L and **1** in the solid state was investigated (Fig. S6). H_4L had an emission peak at 400 nm ($\lambda_{ex}=310$ nm), corresponding to a stronger emission peak at 444 nm ($\lambda_{ex}=362$ nm). The emission peak of **1** was stronger than that of the ligand, which may be due to coordination interactions^[25]. The

emission spectrum of **1** has a partial redshift, which may be caused by the charge transfer between H_4L and Cd^{2+} ^[26].

2.4 Antibiotics sensing

Complex **1** is a very promising sensing material due to its excellent water stability and luminescence properties. Therefore, the luminescence sensing of **1** for different antibiotics was investigated, including penicillin sodium (PEN), tetracycline (TET), ROX, metronidazole (MDZ), azithromycin (AZM), chloramphenicol (CAP), gentamicin sulfate (GEN), ornidazole (ODZ), lincomycin hydrochloride (LIN), cefixime (CEF). As shown in Fig.2a, the fluorescence of **1** was almost completely quenched when ROX was added. The other antibiotics mixed into the suspension of **1** had a small effect on the luminescence intensity of **1**. Next, the

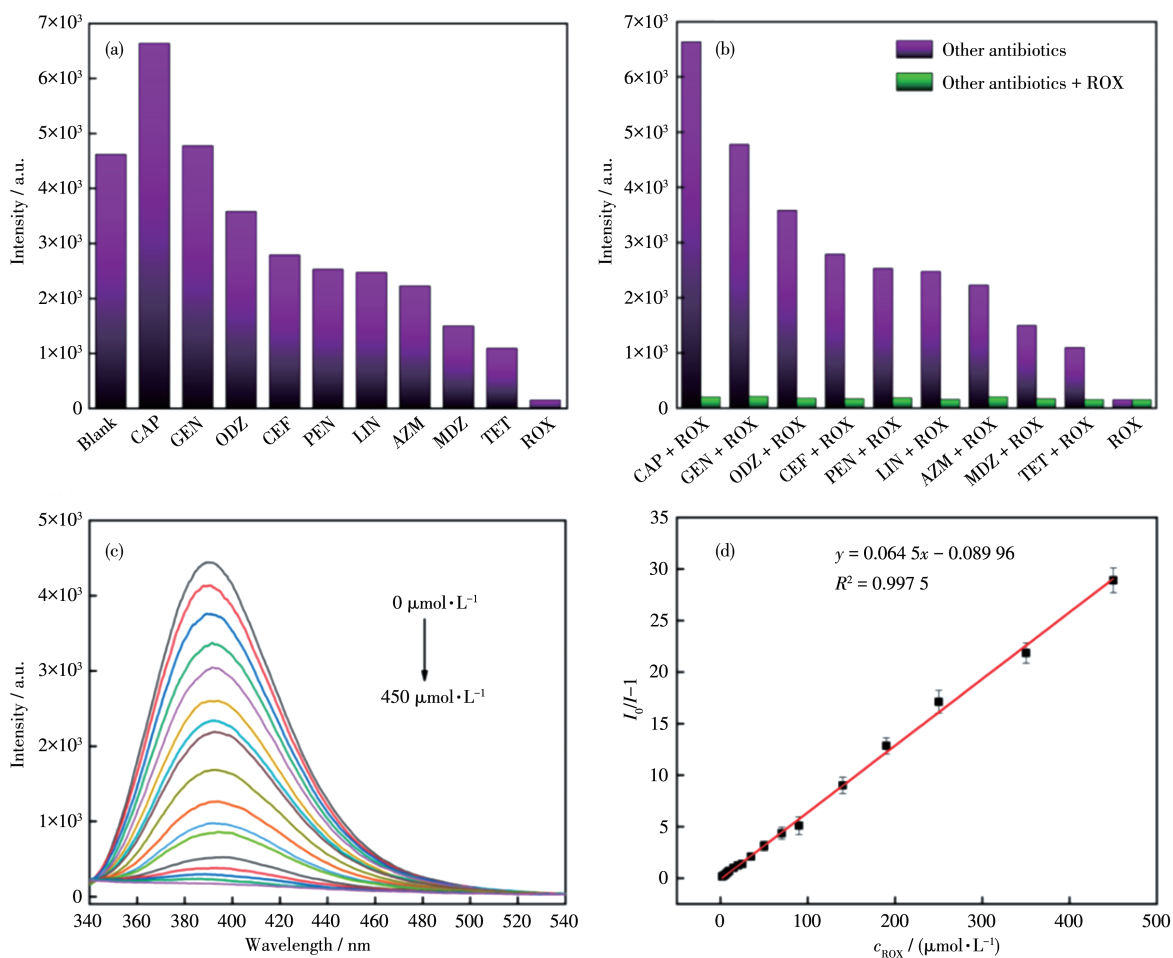


Fig.2 (a) Fluorescence intensities of different antibiotics added to the suspension of **1**; (b) Luminescence intensity of **1** in the presence of different antibiotics with the addition of ROX; (c) Emission spectra of **1** dispersed in the ROX solutions with different concentrations; (d) Plot of $I_0/I-1$ vs c_{ROX} for **1** in a concentration range of 0–450 $\mu\text{mol} \cdot \text{L}^{-1}$

effect of adding ROX on the fluorescence intensity in the presence of other antibiotics was tested. It can be seen from Fig.2b that in the presence of other antibiotics, the addition of ROX could still greatly quench the fluorescence of **1**, showing that it was an excellent ROX sensor. Then, concentration gradient experiments were carried out to study the quenching situation in detail (Fig.2c). When the concentration of ROX was $450\ \mu\text{mol}\cdot\text{L}^{-1}$, the fluorescence was almost quenched by 97.0%. And the plot of $I_0/I-1$ vs c_{ROX} exhibited a linear relationship over the entire concentration range (Fig.2d). This phenomenon was rarely seen in previously reported articles. The detection limit (LOD) was $0.21\ \mu\text{mol}\cdot\text{L}^{-1}$ according to $\text{LOD}=3\sigma/k^{[27-29]}$, where σ is the standard deviation of blank measurement; k is the slope. Then, we investigated the change in fluores-

cence intensity over time with the addition of ROX. When a $450\ \mu\text{mol}\cdot\text{L}^{-1}$ ROX solution was added, the fluorescence intensity was almost completely quenched, and the fluorescence hardly changed after 20 s (Fig.S7a). Finally, the cycling experiment was carried out, and it was found that the fluorescence could still recover to the original intensity after four cycles, indicating that **1** was a very potential ROX sensor (Fig. S7b). As far as we know, this should be the first complex that can detect ROX. This is of great significance for the new fluorescent probe in future research.

2.5 Inorganic anions sensing

The luminescence sensing of **1** for different inorganic anions was investigated, including Cl^- , S^{2-} , ClO_4^- , IO_3^- , I^- , NO_3^- , ClO_3^- , MoO_4^{2-} , CH_3COO^- , $\text{Cr}_2\text{O}_4^{2-}$, Br^- , MnO_4^- , SO_4^{2-} , $\text{B}_4\text{O}_7^{2-}$. As shown in Fig.3a, the fluores-

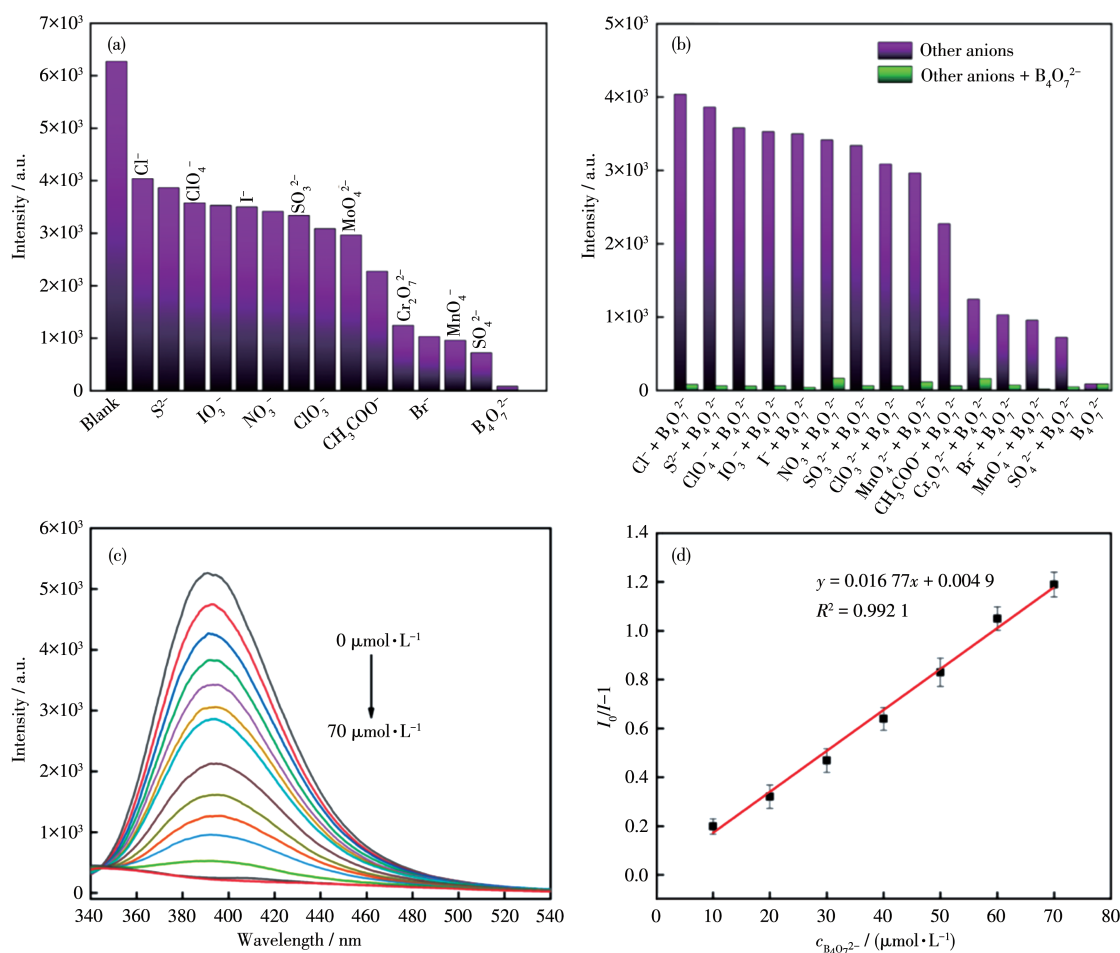


Fig.3 (a) Fluorescence intensities of different inorganic anions added to the suspension of **1**; (b) Luminescence intensity of **1** with the addition of $\text{B}_4\text{O}_7^{2-}$ in the presence of different inorganic anions; (c) Emission spectra of **1** upon the gradual addition of $\text{B}_4\text{O}_7^{2-}$; (d) Plot of $I_0/I-1$ vs $c_{\text{B}_4\text{O}_7^{2-}}$ for **1** in a concentration range of 0-70 $\mu\text{mol}\cdot\text{L}^{-1}$

cence of **1** was almost completely quenched when $\text{B}_4\text{O}_7^{2-}$ was added, while the other inorganic anions mixed into the suspension of **1** had a small effect on the luminescence intensity. Next, the effect of adding $\text{B}_4\text{O}_7^{2-}$ on the fluorescence intensity in the presence of other inorganic anions was tested. It can be seen from Fig. 3b that in the presence of other inorganic anions, the addition of $\text{B}_4\text{O}_7^{2-}$ could still greatly quench the fluorescence intensity of **1**, showing that it was an excellent $\text{B}_4\text{O}_7^{2-}$ sensor. Then, concentration gradient experiments were carried out in order to study the quenching situation detailedly (Fig. 3c). When the concentration of $\text{B}_4\text{O}_7^{2-}$ was $70 \mu\text{mol}\cdot\text{L}^{-1}$, the fluorescence was almost quenched by 97.2%. And the plot of $I_0/I-1$ vs $c_{\text{B}_4\text{O}_7^{2-}}$ exhibited a linear relationship in the low concentration range (Fig. 3d). The LOD was $1.59 \mu\text{mol}\cdot\text{L}^{-1}$. Then, we investigated the change in fluorescence intensity over time with the addition of $\text{B}_4\text{O}_7^{2-}$. It was found that when $70 \mu\text{mol}\cdot\text{L}^{-1}$ was added, the fluorescence intensity was almost completely quenched, and the fluorescence hardly changed after 20 s (Fig. S8a). Finally, the cycling experiment was carried out, and it was found that the fluorescence could still recover to the original intensity after four cycles, indicating that **1** was a very potential $\text{B}_4\text{O}_7^{2-}$ sensor (Fig. S8b).

2.6 Possible sensing mechanism

To explore the possible mechanism of fluorescence quenching, the following experiments were carried out. First, the samples after fluorescence sensing were tested by XRD, and it was found that the peak positions were almost consistent with the peak positions of the crystal simulation (Fig. S2), indicating that the crystal structure was intact. Therefore, the collapse of the crystal framework was not the cause of fluorescence quenching. The emission spectrum of **1** had little overlap with the UV-Vis spectrum of ROX and $\text{B}_4\text{O}_7^{2-}$, implying that the reason for fluorescence quenching should not be caused by energy transfer (Fig. S9)^[30]. Then, it is found that the LUMO level (-0.69 eV) of ROX was higher than **1**, indicating that the electron of **1** cannot be transferred to ROX basically (Fig. S9)^[30-32]. Finally, the emission of **1** was almost invisible after the addition of ROX, indicating that the internal filtering

effect plays an important role in the detection of ROX and $\text{B}_4\text{O}_7^{2-}$ by complex **1**. This explains the process of ROX and $\text{B}_4\text{O}_7^{2-}$ quenching the fluorescence of complex **1**^[30].

2.7 Detection of ROX and $\text{B}_4\text{O}_7^{2-}$ in Yanhe River water

We tested ROX and borate in Yanhe River water to demonstrate the practical usability of the method. As shown in Table 1 and 2, the estimated recoveries of ROX and $\text{B}_4\text{O}_7^{2-}$ at different concentrations were obtained, ranging from 98.7% to 102% and 103% to 108%. The relative standard deviation (RSD) values were 1.8%-2.3% and 1.4%-2.1% respectively, meaning the reliability and practicality of **1** to detect ROX and $\text{B}_4\text{O}_7^{2-}$ in real samples.

Table 1 Recovery test of ROX spiked in Yanhe River water samples

Spiked / ($\mu\text{mol}\cdot\text{L}^{-1}$)	Detected / ($\mu\text{mol}\cdot\text{L}^{-1}$)	RSD* / %	Recovery / %
0	Not detected	—	—
20	20.4	1.8	102
30	29.6	1.7	98.7
50	51.3	2.3	101

* $n=3$.

Table 2 Recovery test of $\text{B}_4\text{O}_7^{2-}$ spiked in Yanhe River water samples

Spiked / ($\mu\text{mol}\cdot\text{L}^{-1}$)	Detected / ($\mu\text{mol}\cdot\text{L}^{-1}$)	RSD* / %	Recovery / %
0	Not detected	—	—
5	5.4	1.4	108
20	20.9	2.1	104
30	30.8	1.9	103

* $n=3$.

3 Conclusions

In summary, a cadmium coordination polymer was synthesized with high selectivity and sensitivity for the detection of ROX and $\text{B}_4\text{O}_7^{2-}$. The sensing mechanism is discussed in detail. Finally, it can also detect ROX and $\text{B}_4\text{O}_7^{2-}$ in real Yanhe River water samples through standard recovery experiments. This experiment provides a promising fluorescent sensor for the detection of ROX and $\text{B}_4\text{O}_7^{2-}$. To our knowledge, this sample is

the first complex that can detect ROX.

Conflicts of interest: The authors declare no competing financial interest.

Supporting information is available at <http://www.wjhxxb.cn>

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