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Polyiodine-Modified 1,3,5-Benzenetricarboxylic Acid Framework Zn(II)/Cd(II) Complexes as Highly Selective Fluorescence Sensors for Thiamine Hydrochloride, NACs, and Fe³⁺/Zn²⁺

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ABSTRACT: Four new complexes, $[Zn(TIBTC)(DMA)]$. $[NH_2(CH_3)_2]$ (1), $[Cd(TIBTC)(H_2O)] \cdot [NH_2(CH_3)_2] \cdot DMA$ (2), $[Cd_2(TIBTC)(2,2'-bipy)_2(HCOO)]$ (3), and $[Cd_2(DIBTC)(2,2'-bipy)_2(HCOO)]$ (4) $(H_3TIBTC = 2,4,6$ -triiodo-1,3,5-benzenetri- carboxylic acid, $H_3DIBTC = 2,4$ -diiodo-1,3,5-benzenetricarboxylic acid, $2,2'$ -bipy = $2,2'$ -bipyridine, and DMA = dimethylacetamide), were successfully synthesized and characterized by elemental anal- ysis, powder X-ray diffraction, infrared spectroscopy, ultraviolet-	Re ³ Compart 2a ² Color		

1. INTRODUCTION

Thiamine, vitamin B₁, is one of the important trace elements and is essential for maintaining the normal life activities of humans and animals. The lack of vitamin B1 can cause diseases such as beriberi and neuritis. Humans cannot synthesize thiamine, so thiamine can be obtained only in vitro; the main component of the vitamin B₁ drug on the market is thiamine hydrochloride (TCL).¹⁻⁹ Therefore, establishing a sensitive method for detecting thiamine hydrochloride is an urgent need. In addition, nitroaromatic complexes (NACs) are important chemical materials for the production of pesticides, explosives, and other substances.^{10–19} For example, 2,4,6-trinitrophenol and p-nitrophenol easily cause environmental pollution and have an explosion risk. Therefore, the detection of NACs is essential for environmental governance and ensuring military security. Furthermore, zinc and iron are two kinds of trace elements that are indispensable to the human body; they have physiological functions such as promoting the growth and development of the human body and enhancing its immunity. However, the excessive intake of these two ions may cause serious harm to the body; excessive consumption of zinc can cause vomiting, headache, diarrhea, convulsions, etc.,²⁰⁻²⁸ and iron poisoning can occur when an excess of iron is ingested.^{29–36} Moreover, the large-scale utilization of these two ions in industrial production also causes serious environmental pollution problems. Therefore, selective detection of zinc and iron ions is essential for biology and environmental fields. Scientists have developed various methods for detecting these substances, including atomic

and 2 are three-dimensional supramolecular network structures, while complex 4 has a two-dimensional network structure. We preliminarily studied the fluorescence properties of the complexes and found that complexes 1-3 can detect thiamine hydrochloride, NACs, and Fe^{3+}/Zn^{2+} with high sensitivity and selectivity.



Scheme 1. Synthesis of 2,4,6-Triiodo-1,3,5-trimethylbenzene

Scheme 2. Synthesis of 2,4,6-Triiodo-1,3,5 benzenetricarboxylic Acid



absorption spectroscopy, voltammetry, spectrophotometry, and chemiluminescence.^{37,38} Among them, the chemiluminescence

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visible spectroscopy, and thermogravimetric analysis. Complexes 1

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Scheme 3. Synthesis of 2,4-Diiodo-1,3,5-benzenetricarboxylic Acid



Scheme 4. Synthetic Routes of Complexes 1-4





Figure 1. (a) Coordination environment of the Zn(II) ion in complex 1. (b) Coordination mode of $TIBTC^{3-}$. (c) 1D chain structure of 1. (d) 2D planar structure of 1. (e) 3D supramolecular network of 1.

method is widely used because of its convenience and speed, as well as high sensitivity and selectivity.

Metal organic frameworks (MOFs) are easy to synthesize, have an adjustable structure and a large surface area, and aid in the formation of fluorescent sensors. To date, although many MOF materials have been designed as single-function chemical sensing compounds, multifunctional sensing research of thiamine hydrochloride, NACs, and metal ions (Fe^{3+}/Zn^{2+}) is

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Figure 2. (a) Coordination environment of the Cd(II) atom in complex 2. (b) Coordination mode of the $TIBTC^{3-}$. (c) 1D chain structure. (d) 2D planar structure. (e) 3D structure. (f) 3D stacked pattern of complex 2 containing solvent molecules.

still in its infancy. Therefore, the study of using MOF material simultaneously detecting these three types of substances is a challenge. For luminescent MOFs, the types of organic ligands affect the fluorescence properties of MOFs. Generally, organic ligands are classified into two major classes: poly(carboxylic acid)s and nitrogen heterocycles. Among them, the most widely reported organic ligands of poly(carboxylic acid)s can be classified into two types: aliphatic carboxylic acids and aromatic carboxylic acids.³⁹ Aromatic carboxylic acid ligands have more advantages and are loved by a majority of chemists. They exhibit the following characteristics. On one hand, they have a rigid ring skeleton ligand, which provides powerful conditions for the formation of multidimensional structures; in these structures, there are often holes, so that these assembled complexes have a novel topology. On the other hand, the conjugated system of the aromatic ring can facilitate the transfer of electrons, making the complex have special properties such as magnetism, electricity, photocatalysis, etc. 40-43

For the reasons given above, we chose 2,4,6-triiodo-1,3,5benzenetricarboxylic acid (H_3 TIBTC) and 2,4-diiodo-1,3,5benzenetricarboxylic acid (H_3 DIBTC) as the ligands because they have the characteristics of aromatic carboxylic acids described above. In addition, (1) the conjugated system on the benzene ring with symmetrically arranged carboxyl groups promotes the transfer of electrons, so that the constructed complexes have some special fluorescence properties. (2) Introduction of a halogen atom into the aromatic ring to form a halogen bond may increase the size and change electron cloud density of the organic skeleton.⁴⁴ On the basis of our research idea described above, we have reported several lanthanide metal MOFs, including (i) $[Ln(TIBTC)(DMF)_3]_n$ $(Ln = Eu, Gd, Sm, or Nd)^{45}$ and (ii) $[Pr(TIBTC)(DMF)_3]_n^{45}$ $(H_3TIBTC = 2,4,6$ -triiodo-1,3,5-benzenetricarboxylic acid). In this work, as a part of our continued research, we developed four new transition metal coordination complexes, [Zn(TIBTC)(DMA)]. $[NH_2(CH_3)_2]$ (1), $[Cd (TIBTC)(H_2O)] \cdot [NH_2(CH_3)_2] \cdot DMA$ (2), $[Cd_2(TIBTC)(2,2'-bipy)_2(HCOO)]$ (3), and $[Cd_2(DIBTC)(2,2'-bipy)_2(HCOO)]$ (4) under solvothermal conditions, and preliminarily explored their fluorescence properties to detect thiamine hydrochloride, NACs, and Fe^{3+}/Zn^{2+} .

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. More detailed information about the materials and methods is provided in the Supporting Information.

2.2. Preparation of the Ligand and Complexes. 2.2.1. 2,4,6-Triiodo-1,3,5-benzenetricarboxylic Acid (H₃TIBTC). The synthesis



Figure 3. (a) Coordination environment of the Cd(II) ion in complex 4. (b) Coordination mode of the DIBTC³⁻. (c) Building block. (d) 1D chain structure. (e) 2D planar structure.

method of ref 46 has been improved, and the specific method is as follows.

2.2.1.1. 2,4,6-Triiodo-1,3,5-trimethylbenzene (**M**-1). To a threeneck flask were added 1,3,5-trimethylbenzene (**M**) (12.0 g), iodine (38.8 g), HIO₄·2H₂O (14.0 g), CH₃COOH (100 mL), and H₂O (20 mL). After the mixture had been stirred, 3 mL of concentrated H₂SO₄ was added dropwise. The mixture was heated to reflux at 90 °C for 10 h, filtered with a vacuum line, repeatedly washed with distilled water, purified with solvent acetone, and suction filtered to yield 2,4,6-triiodo-1,3,5-trimethylbenzene (**M**-1) (Scheme 1). The IR spectra and ¹H NMR spectra of **M**-1 are shown in Figures S1 and S3. Yield: 76%. IR data (KBr, cm⁻¹): 1525, 1372, 1322, 1240, 940, 871, 595. ¹H NMR (400 MHz, CDCl₃): δ 3.00 (d, 1H). Mp: 205.5–207.1 °C.

2.2.1.2. H_3T/BTC . Triiodotrimethylbenzene (5.0 g), H_2O (25 mL), and pyridine (70 mL) were added to a flask, and the mixture was stirred until the solid was completely dissolved to obtain a milky white liquid. Then, the temperature was increased to 90 °C, and solid KMnO₄ (10.0 g) was added at 1 h intervals a total of six times. After the mixture had been heated for 10–12 h, it was filtered while hot, the solid was washed with a hot 5% KOH solution, and the pyridine solvent was removed with a rotary evaporator. Then, 75 mL of distilled water was added to remove insoluble species, and the filtrate was adjusted to pH = 1 with

concentrated HCL. Finally, it was extracted with ethyl acetate (125 mL), washed with water (20 mL), and then evaporated to give 2,4,6-triiodo-1,3,5-benzenetricarboxylic acid (Scheme 2). Yield: 86%. Anal. Calcd for $C_9H_3I_3O_6$ (587.81): C, 18.39; H, 0.51; I, 64.77. Found: C, 18.32; H, 0.76; I, 64.98. IR data (KBr, cm⁻¹): 3162, 1692, 1405, 1512, 1307, 1201. Mp: >280 °C.

2.2.2. 2,4-Diiodo-1,3,5-benzenetricarboxylic Acid (H_3DIBTC). 2,4-Diiodo-1,3,5-benzenetricarboxylic acid was synthesized by a reaction similar to that for 2,4,6-triiodo-1,3,5-benzenetricarboxylic acid, except with addition of 1,3,5-trimethylbenzene (12.0 g), iodine (31.0 g), HIO₄·2H₂O (14.0 g), CH₃COOH (100 mL), and H₂O (20 mL) to the three-neck flask in the first step. The synthetic route is shown in Scheme 3. The IR spectra and ¹H NMR spectra of 2,4-diiodo-1,3,5-trimethylbenzene (M-2) are shown in Figures S2 and S4. M-2. Yield: 76%. IR data (KBr, cm⁻¹): 2995, 1516, 1376, 946, 864, 670, 608. ¹H NMR (400 MHz, CDCl₃): δ 7.01 (s, 1H), 2.94 (s, 2H), 2.44 (s, 6H). Mp: 120.2–123.5 °C. H₃DIBTC. Yield: 78%. Anal. Calcd for C₉H₄I₂O₆ (461.89): C, 23.40; H, 0.87; I, 54.95. Found: C, 23.32; H, 0.74; I, 55.08. IR data (KBr, cm⁻¹): 3108, 1683, 1403, 1523, 1244, 1137. Mp: >280 °C.

2.2.3. [Zn(TIBTC)(DMA)]· $[NH_2(CH_3)_2]$ (1). $Zn(CH_3COO)_2$ · $2H_2O$ (0.0550 g, 0.25 mmol) was dissolved in a mixed solvent of C_3H_3OH



Figure 4. PXRD spectra of complexes 1-4 before and after detection.

(1 mL), and H₃TIBTC (0.0280 g, 0.05 mmol) was dissolved in a DMA solution (1.5 mL). Then, the two solutions were mixed, and 4 mol/L HNO₃ was used to adjust the pH of the solution to 3; then the solution was stirred for 1 h until it turned into a yellow clear liquid at room temperature and was transferred to a high-pressure glass bottle. After being heated at 100 °C for 24 h, it was taken out and cooled for 2 h to obtain colorless diamond-shaped bulk crystals. Yield: 42% (based on Zn). Anal. Calcd for C₁₅H₁₇I₃N₂O₇Zn (783.38): C, 22.98; H, 2.17; N, 3.57. Found: C, 22.99; H, 2.16; N, 3.55. IR data (KBr, cm⁻¹): 3424, 1595, 1389, 1520, 1304, 1198.

2.2.4. $[Cd(TIBTC)(H_2O)] \cdot [NH_2(CH_3)_2] \cdot DMA$ (2). $Cd(NO_3)_2 \cdot 4H_2O$ (0.0308 g, 0.10 mmol), H₃TIBTC (0.0280 g, 0.05 mmol), water (2 mL), and DMA (1.5 mL) were mixed in a beaker (25 mL) and stirred for 1 h. The mixed solution was placed in a high-pressure glass bottle, adjusted to pH = 3 with HNO₃, heated at 100 °C for 1 day, and cooled slowly at room temperature. After the product had been washed with water, it was further dried under vacuum conditions to yield colorless crystals. Yield: 46% (based on Cd). Anal. Calcd for C₁₅H₁₉I₃N₂O₈Cd (848.42): C, 21.22; H, 2.24; N, 3.77. Found: C, 21.24; H, 2.21; N, 3.76. IR data (KBr, cm⁻¹): 3490, 1584, 1380, 1519, 1304, 1191.

2.2.5. $[Cd_2(TIBTC)(2,2'-bipy)_2(HCOO)]$ (3). The procedure for obtaining crystals of complex 3 is similar to that for 2. The only difference is the addition of a second ligand, 2,2'-bipy (0.0170 g, 0.10 mmol), and using C₂H₅OH instead of H₂O. Yield: 52% (based on Cd). Anal. Calcd for C₃₁H₁₇I₃N₄O₈Cd₂ (1180.09): C, 31.52; H, 1.44; N, 5.42. Found: C, 31.53; H, 1.42; N, 5.41. IR data (KBr, cm⁻¹): 3440, 1576, 1373, 1512, 1308, 1137.

2.2.6. $[Cd_2(DIBTC)(2,2'-bipy)_2(HCOO)]$ (4). The method for obtaining the crystals of complex 4 is almost the same as the method for 3, except that H₃DIBTC (0.0230 g, 0.05 mmol) is used instead of H₃TIBTC in the starting reactant. Yield: 50% (based on Cd). Anal. Calcd for C₃₁H₁₈I₂N₄O₈Cd₂ (1054.09): C, 35.29; H, 1.71; N,

6.07. Found: C, 35.32; H, 1.65; N, 6.05. IR data (KBr, cm⁻¹): 3418, 1587, 1373, 1512, 1287, 1158.

2.3. Luminescence Experiments. A powder sample of the complex (5 mg) was dispersed into C_2H_5OH (5 mL) and sonicated for 30 min to form a MOF suspension. Then, 2 mL of the suspension was placed in a cuvette; various test solutions were gradually added to form different concentrations of the suspension, and the fluorescence intensity at room temperature was measured and compared.

2.4. X-ray Crystallographic Determination. Specific X-ray crystallographic methods are described in the Supporting Information. Tables S1–S3 give the crystallographic details of complexes 1, 2, and 4, respectively, and the selected bond lengths and angles. The CCDC numbers of 1, 2, and 4 are 1951693, 1951692, and 1951592, respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis. Complexes 1–4 are all synthesized by using a solvothermal reaction in a high-pressure glass bottle (Scheme 4). For complexes 1 and 2, we first tried to opt for the best reaction solvents. It is found that the solvents that favored the growth of crystals of the complex were a mixed solvent of C_2H_5OH , CH_3OH , and DMA for complex 1 and a mixed solvent of H_2O and DMA for complex 2. Next, we used different reaction temperatures (80, 100, and 120 °C) and found that tiny crystals were obtained at 100 °C. Then, we adjusted the molar ratio of the main reaction reagents (metal salt and ligand) and found that at a metal:ligand ratio of 5:1 (complex 1) or 2:1 (complex 2), we obtained ideal crystals of complex 1 or 2, respectively, for single-crystal testing while adjusting the pH value of 3 and 4.

To extend crystalline state complexes with various structures for comparison of structure and function, we introduced the



Figure 5. Fluorescence spectra upon detection of TCL by complexes 1-4.

second ligand, 2,2'-bipy, into the reaction system and obtained the corresponding complexes 3 and 4 containing mixed ligands. Through a large number of experiments, we found that when the mixed solvent consists of C_2H_5OH and DMA at 100 °C and pH = 3-4, we can obtain the perfect crystal of complex 4, but the crystals of complex 3 that can be analyzed by X-ray single-crystal diffraction have never been obtained in spite of our efforts; however, we characterized complex 3 by element analysis, IR, and XRD. We are sure that the structure of complex 3 was consistent with that of complex 4.

3.2. Structural Descriptions. 3.2.1. [Zn(TIBTC)(DMA)]- $[NH_2(CH_3)_2]$ (1). Complex 1 belongs to the orthorhombic system and $Pca2_1$ space group. The molecular structure of 1 includes a central metal Zn(II), a ligand TIBTC³⁻, a coordinated DMA molecule, and a free dimethylamine cation that come from the decomposition of DMA. Figure 1a shows the coordination environment around the central metal Zn(II). The central metal Zn(II) is coordinated with four carboxylic acid oxygen atoms (O1, O2, O4, and O6) to form a tetrahedral structure, where O2, O4, and O6 are from three TIBTC³⁻ ions and O1 is from solvent DMA molecular coordination. The coordination mode of the ligand TIBTC³⁻ moiety is μ_3 - η_0 ¹ η_0 ¹ η_0 ¹ (Figure 1b). The Zn–O bond length is 1.948(9)–1.994(16) Å, which is close to the Zn–O bond length [1.954(3)–1.973(3) Å] in the literature.⁴⁷ The Zn- Ω zn distance is ~8.7 Å.

The two carboxyl groups (COO^{-}) in the ligand connect adjacent Zn atoms along the *a*-axis to form a one-dimensional (1D) chain structure (Figure 1c). The 1D chain structure was extended along the *c*-axis by another carbonyl group (COO^{-}) of the ligand to produce a two-dimensional (2D) network

structure, which is furthermore connected by a hydrogen bond [N2–H14A···O7, N2–H14B···O3^{#8} (#8: -x + 1, -y + 1, $z - \frac{1}{2}$)] from the free protonated dimethylamine cation to yield a three-dimensional (3D) supramolecular network (Figure 1d,e).

3.2.2. $[Cd(TIBTC)(H_2O)] \cdot [NH_2(CH_3)_2] \cdot DMA$ (2). One can see from the structural analysis that complex 2 is a monoclinic system in the $P2_1/c$ space group. The molecular structure of the complex comprises a central metal Cd(II), a ligand TIBTC³⁻, a coordinating water molecule, a free dimethylamine cation that is from the decomposition of DMA, and a free DMA solvent molecule. The Cd(II) coordinates with the carboxyl oxygen atoms (O2–O6) from three TIBTC³⁻ ions and the oxygen atom (O1) of a solvent water molecule to form an octahedral configuration (Figure 2a). The TIBTC³⁻ is connected in a $\mu_3 \eta_0^2 \eta_0^2 \eta_0^{-1}$ manner, and the carboxyl oxygen atom in the structure adopts a monodentate or bidentate coordination mode (Figure 2b). The Cd–O bond length is 2.226(3)–2.584(4) Å, which is consistent with the Cd–O bond length [2.272(6)–2.508(7) Å] in the literature.⁴⁸ The Cd…Cd distance is ~10 Å.

Adjacent Cd atoms are connected by the COO⁻ of the TIBTC³⁻ along the *a*-axis to constitute a 1D chain structure (Figure 2c), which further extends along the *b*-axis to produce a 2D layered structure (Figure 2d); the 2D layer in the structure is stacked along the *c*-axis direction, and adjacent layers are hydrogen-bonded $[O1-H1A\cdotsO3^{\#6} (\#6 -x + 2, -y, -z), O1-H1B\cdotsO7^{\#7} (\#7 -x + 2, y - 1/2, -z + 1/2)]$ to form a 3D porous structure having a one-dimensional pore. The pores extend infinitely along the *a*-axis direction (Figure 2e). The complex is an anionic backbone structure with a free protonated



Figure 6. (a, c, and e) Fluorescence intensity after the addition of other amino acids to the suspension of complexes 1-3 containing TCL. (b, d, f) After the addition of other amino acids, comparison of the intensity of the strongest fluorescence emission peak of the suspension of complexes 1-3 containing TCL.

dimethylamine cation and DMA solvent molecules filled in one dimension of the pores as shown in Figure 2f.

3.2.3. $[Cd_2(DIBTC)(2,2'-bipy)_2(HCOO)]$ (4). This complex crystallizes in the monoclinic $P2_1/c$ space group, which has two Cd(II) centers, one DIBTC³⁻, two coordinated 2,2'-bipy ligands, and one coordinated HCOO⁻ in its molecular structure (HCOOH is from the decomposition of DMA). In the structure of complex 4, the central Cd(II) has two coordination modes. (1) Cd(II) is six-coordinated with four oxygen atoms (O1, O5, O3, and O2) from three DIBTC³⁻ ions and two nitrogen atoms (N1 and N2) of one 2,2'-bipy ligand to form an octahedral geometry (Figure 3a). (2) Cd(II) is five-coordinated with O3, O6, N3, N4, and O8 to form a distorted tetrahedral geometry (O3 and O6 are from two DIBTC³⁻ ions, N3 and N4 are from one 2,2'-bipy ligand, and O8 is from coordinated HCOO⁻). The connection mode of the ligand is μ_5 - η_0 ² η_0 ^{1} η_0 ¹ η_0 ¹ η_0 ¹ (Figure 3b). Two oxygen atoms on one carboxylic acid adopt}

bidentate chelate coordination; two oxygen atoms on one carboxylic acid group adopt bidentate coordination, and oxygen atoms on another carboxylic acid group are in a monatomic bridge coordination mode. The Cd–O bond distances (from the DIBTC^{3–} ligand) are in the range of 2.220(4)-2.393(2) Å, and Cd–N bond lengths are 2.305(17)-2.309(5) Å. The Cd1… Cd2 distance in the building block is 3.6516 Å.

In complex 4, the structural unit $[Cd_2O_7N_4]$ (Figure 3c) is linked in the *c*-axis direction by a carboxyl group in the DIBTC³⁻ ligand to form the 1D chain structure (Figure 3d), which is joined in the *b*-axis direction by another ligand DIBTC³⁻ to extend into the 2D planar structure (Figure 3e).

3.3. IR Spectra. Figure S5 and Table S4 give the infrared spectral data of ligands and complexes. The infrared peaks of complexes 1–4 are roughly similar. For the complexes, the peaks at 1576–1595 and 1373–1389 cm⁻¹ correspond to the asymmetric and symmetry stretching vibrations of COO⁻. A red

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Figure 7. Changes in the fluorescence intensity after the addition of four NACs to the C_2H_5OH solution of complex 1: (a) 2,4,6-trinitrophenol, (b) *p*-nitrophenol, (c) 4-nitrotoluene, and (d) nitrobenzene. (e) Line graph of the fluorescence response of different NACs to complex 1.

shift occurred in relation to ν_{asCOO^-} and ν_{sCOO^-} of the ligand, indicating that the metal coordinated with the ligand. In particular, for complexes 3 and 4, the peaks from 612 to 1019 cm⁻¹ prove that 2,2'-bipy participates in coordination.

3.4. UV–Vis **Spectra.** The UV spectra were recorded for solid samples at room temperature (Figure S6 and Table S5). The absorption peaks at 217 and 283 nm of 1, 220 and 283 nm of 2, 216 and 281 nm of 3, and 219 and 280 nm of 4 are the π – π * and n– π * electronic transitions of the ligand, respectively. The peaks at 336 nm (1), 338 nm (2), 332 nm (3), and 330 nm (4) are from the charge transfer transition from the ligand to the central metal ion.

3.5. PXRD. The simulated peaks were compared with experimentally measured diffraction peaks in the PXRD pattern (Figure 4), and the positions of the peaks were matched, indicating that complexes 1–4 were pure phases.

3.6. Thermal Analysis. In the protective environment of N_2 , thermogravimetry of the complex was performed at 30–800 °C (Figure S7).

For complex 1, the weight loss in the range of 30-169 °C was 2.02% (theoretical value of 2.12%), corresponding to the loss of coordination H₂O molecules; the weight loss at 169–305 °C was 5.28% (theoretical value of 5.38%), which should be the loss

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Figure 8. Changes in the fluorescence intensity after the addition of four NACs to the C_2H_5OH solution of complex 2: (a) 2,4,6-trinitrophenol, (b) *p*-nitrophenol, (c) 4-nitrotoluene, and (d) nitrobenzene. (e) Line graph of the fluorescence response of different NACs to complex 2.

of free dimethylamine cations; and the weight loss at 305-800 °C was 80.70% (theoretical value of 80.90%), which should be the collapse of the ligand framework. The residue was the residue of zinc oxide and organic framework carbon.

For complex 2, below 234 °C, the weight loss was 5.85% (theoretical value of 5.87%), which indicated the loss of free dimethylamine cations. The weight loss at 234-330 °C was 11.05% (theoretical value of 11.10%), which indicated the loss of coordination DMA molecules. The final weight loss at 330-800 °C was 63.50% (theoretical value of 63.95%), which corresponded to the collapse of the ligand framework, and the cadmium oxide was the final residue.

For complex 3, the first weight loss that occurred during the 371-414 °C interval was 26.65%, which was consistent with the theoretical weight loss value (26.45%) of losing two 2,2'-bipy molecules; the weight loss during the heating process from 414 to 429 °C was ~3.83%, which coincided with the theoretical weight loss value (3.81%) of the HCOO⁻. In the third stage, the weight loss during heating from 429 to 795 °C was ~53.12%, which was the destruction of the ligand skeleton (theoretical value of 53.95%). The final residue was the residue of cadmium oxide.

For complex 4, the first weight loss of 29.67% in the 336-418 °C interval was the loss of two 2,2'-bipy ligands (theoretical value of

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Figure 9. Changes in the fluorescence intensity after the addition of four NACs to the C_2H_5OH solution of complex 3: (a) 2,4,6-trinitrophenol, (b) *p*-nitrophenol, (c) 4-nitrotoluene, and (d) nitrobenzene. (e) Line graph of the fluorescence response of different NACs to complex 3.

29.67%); in the range of 418–433 °C, the weight loss was 4.32%, which was ascribed to the loss of HCOO⁻ (theoretical value of 4.27%); and the final residue correponded to the collapse of the skeleton of the ligand in the range of 433–800 °C with a weight loss of 40.92% (theoretical value of 41.59%). The final residue corresponded to cadmium oxide.

3.7. Solid State Photoluminescence Property and Solvent Selection. For the emission spectrum, upon excitation at 270 nm, the H₃TIBTC ligand has an emission peak at 352 nm, which is derived from the π - π * transition of the ligand (Figure S8), while complexes 1-4 showed emission peaks at 357, 359, 363, and 358 nm, respectively. The complexes showed red shifts of 2, 7, 11, and 6 nm, respectively, compared to the emission peak of H₃TIBTC. This may be due to the coordination between the metal and the ligand that changed the density distribution of the electron cloud in the molecular

structure and then decreased the nonradiative transition energy of the excited state in the ligand molecule, which changed the luminescence band.⁴⁹ The solid fluorescence lifetimes of the complexes are 0.217 \pm 0.003 (complex 1), 0.145 \pm 0.001 (complex 2), 0.167 \pm 0.002 (complex 3), and 0.186 \pm 0.001 (complex 4).

We first explored the photoluminescence properties of complexes in several solvents. Five milligrams of the complex powder was added to 5 mL of various solvents and sonicated for 30 min to achieve a uniform dispersion of the MOF. It was found that the complex had the best fluorescence effect in C_2H_5OH (Figure S9), and because C_2H_5OH was less toxic and environmentally friendly, C_2H_5OH was chosen as the solvent for the next fluorescence experiment.

3.8. Fluorescence Detection Applications. *3.8.1. Detection of Thiamine Hydrochloride (TCL).* We first investigated the

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Figure 10. Changes in the fluorescence intensity after the addition of four NACs to the C_2H_5OH solution of complex 4: (a) 2,4,6-trinitrophenol, (b) *p*-nitrophenol, (c) 4-nitrotoluene, and (d) nitrobenzene. (e) Line graph of the fluorescence response of different NACs to complex 4.

ability of complexes 1-4 to sense thiamine hydrochloride (TCL). The specific experimental procedure was as follows. The C₂H₅OH solution of the solid powder of the complexes was sonicated for 30 min (1 mg/mL); 2 mL of the suspension described above was added to the cuvette, and then an aqueous solution of thiamin hydrochloride (TCL) (1 mM) was gradually added and the fluorescence intensity tested as shown in Figure 5.

We observed that as the concentration of TCL increased, the fluorescence intensity of complexes 1-3 was significantly quenched; however, the effect on the fluorescence intensity of complex 4 was very weak, so complex 4 was not suitable for detection of TCL. The Stern–Volmer equation is $I_0/I = 1 + K_{sv}[Q]$, where I_0 is the initial fluorescence intensity of the complex 1-3 suspension, I is the fluorescence intensity of the complex suspension after the addition of TCL, K_{sv} represents the Table 1. Comparison of Photoluminescence Properties of2,4,6-Trinitrophenol Detected by Complexes 1–4

sample	$K_{\rm sv} \left({{ m M}^{ - 1}} ight)$	LOD (μ M)
complex 1	1.22×10^{5}	0.77
complex 2	1.66×10^{5}	0.81
complex 3	8.85×10^{5}	0.80
complex 4	4.35×10^{6}	0.01

quenching constant (M⁻¹), and [Q] is the molar concentration of the detected TCL. The $K_{\rm sv}$ values of complexes 1–3 with respect to TCL were calculated to be 1.48×10^5 , 8.69×10^4 , and 1.35×10^4 M⁻¹, respectively (Figure S10). The detection limit is calculated by the formula $D = 3\sigma/K_{\rm sv}$ (where D is the detection limit and σ represents the standard deviation of the initial

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Figure 11. Fluorescence intensity response of different metal ions to complexes 1-4.



Figure 12. Fluorescence spectra of complexes 1-4 with a concentration gradient of Fe³⁺ or Zn²⁺.

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Figure 13. In the presence of Fe^{3+} and other metal ions, the fluorescence spectra of (a) complex 1 and (c) complex 2. Comparison of the strongest emission intensity with and without the addition of Fe^{3+} to the suspension of complexes containing other metal ions: (b) complex 1 and (d) complex 2.

luminous intensity of 20 groups of blank MOF suspensions). The calculated detection limits are 0.97 μ M (for complex 1), 1.54 μ M (for complex 2), and 5.52 μ M (for complex 3), which are much lower than that of $[In_2(OH)_2(H_2TTHA)(H_2O)_2]_n^{.50}$ We found that complexes 1-3 are promising as fluorescent sensors for detecting thiamine hydrochloride. By comparison, the fluorescence quenching performance decreased in the following order: 1 > 2 > 3. The possible reason for the quenching of the fluorescence intensity of complexes 1-3 with respect to thiamine hydrochloride (TCL) is that a weak interaction including hydrogen bond and electrostatic interaction between the TCL and ligand moiety of the complexes reduces the nonradiative transition between the ligand and the central metal, furthermore weakening the fluorescence intensity. The fluorescence quenching performance decreases in the following order: 1 > 2 > 3. This may be due to the difference in the strength of the weak interaction formed by TCL and complexes as well as the structural change of complexes 1-3.

Biological small molecules mainly include vitamins, water, amino acids, nucleotides, monosaccharides, and lipids. In the process of biofluorescence detection, the presence of several other small biological molecules may affect the experimental results. A good fluorescent probe should have high selectivity, and other substances should not interfere with the test results. Therefore, we initially tested several amino acids (Gly, DL-Ala, Arg, Lys, Leu, Ser, Asp, and Val) in interference experiments for detecting TCL. First, 200 μ L (10 mM) portions of different aqueous solutions of amino acids were added to the C₂H₅OH suspension of the complexes, and then 200 μ L (10 mM) of a TCL solution was added. After the fluorescence test had been conducted, it was found that other competing amino acids did not interfere with the results of TCL detection of complexes 1–3 (Figure 6).

3.8.2. Detection of NACs. We further investigated the fluorescent properties of complexes 1-4 in the presence of NACs by gradually adding four NACs (2,4,6-trinitrophenol, p-nitrophenol, nitrotoluene, and nitrobenzene) at 0.1 mM to the C₂H₅OH solution containing complexes 1-4 (1 mg/mL). Figures 7-10 show that increasing the concentration of NACs decreases the fluorescence intensity of complexes 1-4; in particular, the solution containing 2,4,6-trinitrophenol has the largest decrease in fluorescence intensity. By comparison, it can be found that the quenching efficiency decreases in the following order: 2,4,6trinitrophenol > *p*-nitrophenol > 4-nitrotoluene > nitrobenzene. This is consistent with the order of polarity of the four NACs: 2,4,6-trinitrophenol > *p*-nitrophenol > 4-nitrotoluene > nitrobenzene; therefore, the fluorescence intensity of complexes 1-4 is quenched by NACs, which is related to the polarity of NACs, and the greater the polarity of the NACs, the better the fluorescence quenching effect on the complexes.

According to the equations $I_0/I = 1 + K_{sv}[Q]$ and $D = 3\sigma/K_{sv}$, the K_{sv} and the detection limit of 2,4,6-trinitrophenol detected by complexes 1–4 were calculated (Figure S11 and Table 1); from Table 1, we can see that complexes 1–4 all have the higher



Figure 14. In the presence of Zn^{2+} and other metal ions, the fluorescence spectra of (a) complex **3** and (c) complex **4**. Comparison of the strongest emission intensity with and without the addition of Zn^{2+} to the suspension of complexes containing other metal ions: (b) complex **3** and (d) complex **4**.

 $K_{\rm sv}$ values and lower detection limits for detecting 2,4,6-trinitrophenol, and among them, complex 4 has the best detection effect.

3.8.3. Detection of the Metal Ion. The fluorescence intensities of complex suspensions containing different metal ions were determined, and we could see that their fluorescence intensity is affected by the type of metal ion. For single-ligand complexes 1 and 2, adding Fe^{3+} can significantly weaken their fluorescence intensity, while for mixed ligands complexes 3 and 4, adding Zn^{2+} can significantly enhance their fluorescence intensity (Figure 11).

To further investigate the sensitivity of complexes 1 and 2 to Fe^{3+} ions and complexes 3 and 4 to Zn^{2+} ions, we gradually added an aqueous Fe^{3+} solution (1 mM) to the MOF suspension of complexes 1 and 2 and added an aqueous Zn^{2+} solution (1 mM) to the MOF suspension of complexes 3 and 4. As shown in Figure 12, as the concentration of the Fe^{3+} or Zn^{2+} solution in the system gradually increased, the fluorescence intensities of complexes 1 and 2 gradually decreased while the fluorescence intensities of complexes 3 and 4 gradually increased. According to the equation $I_0/I = 1 + K_{sv}[Q]$ [where I_0 is the initial fluorescence intensity of the complex suspension, I is the fluorescence intensity of the complex suspension after the addition of Fe³⁺, K_{sv} represents the quenching constant (M⁻¹), and [Q] is the molar concentration of the detected Fe³⁺], the K_{sv} for **1** is $9.71 \times 10^4 \text{ M}^{-1}$ and the K_{sv} for **2** is $2.43 \times 10^4 \text{ M}^{-1}$. According to the same equation, ⁵¹ the K_{sy} for 3 is 1.79×10^4 M⁻¹ and the K_{sy} for 4 is $6.60 \times 10^3 \text{ M}^{-1}$ (Figure S12). According to the equation

 $D = 3\sigma/K_{sv}$, the detection limits were calculated to be 3.45 μ M (complex 1), 5.51 μ M (complex 2), 4.16 μ M (complex 3), and 9.67 μ M (complex 4). The results show that the detection of Fe³⁺ for complexes 1 and 2 and the detection of Zn²⁺ for complexes 3 and 4 have good selectivity and high sensitivity. Complexes 1 and 2 with a single ligand have a fluorescence quenching effect on Fe³⁺ ions, while complexes 3 and 4 with mixed ligands have a fluorescence enhancement effect on Zn²⁺, which may be attributed to the structures in the complexes, which is different from the cause of the difference in fluorescence performance.

To test whether the effect of the complexes in detecting Zn^{2+} or Fe^{3+} ions is affected by other metal ions, we initially conducted the following experiments. After different metal ion aqueous solutions (1 mM, 160 mL) had been added to a 2 mL C_2H_5OH suspension of the complex, additional Fe^{3+} or Zn^{2+} solution (1 mM, 160 mL) was added and the fluorescence intensity was measured. Figures 13 and 14 show that the complexes can still detect Fe^{3+} or Zn^{2+} normally under the complex conditions in the presence of other metal ions.

3.8.4. Cycle Test Experiment. As a fluorescence sensor, recycling is also very important. Therefore, we collected the complex powder after the fluorescence sensing test, washed it with C_2H_5OH , and performed five cycles of experimental determination on it. The experimental results show that the fluorescence quenching/enhancing of the complex is basically unchanged even if five cycles are used as described above, showing that the fluorescence detection has good recoverability (Figure S13).

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Figure 15. Comparison of the UV-vis spectra of the MOF suspension after the addition of the test substance with the original MOF suspension.



Figure 16. Changes in lifetimes before and after detection of Zn^{2+} by (a) complex 3 and (b) complex 4.

3.8.5. Fluorescence Response Mechanism. To further explore the mechanism of fluorescence sensing, we measured the PXRD spectra of complexes after the addition of three analytes (Figure 4). It was found that the PXRD spectra of the complexes after immersion in the three test solutions for 24 h remained unchanged, eliminating the possibility of fluorescence quenching caused by collapse of the skeleton. ^{52,53}

The UV–vis absorption spectra after the addition of the guest species to the MOF suspension were recorded and compared with the UV–vis absorption spectra of the MOF suspension (Figure 15); we found that in addition to the detection of Zn^{2+} , the detection solution of complexes that detected TCL, 2,4,6-trinitrophenol, and Fe³⁺ showed strong absorption in the range

Table 2. Fluorescence Lifetimes of Complexes 3 and 4 before and after the Addition of ${\rm Zn}^{2+}$

	lifetime	lifetime (nm)	
	suspension	Zn ³⁺ @complex	
3	0.617 ± 0.002	1.008 ± 0.003	
4	0.586 ± 0.001	0.672 ± 0.002	

of 200–410 nm, and the overlap in the UV–vis absorption region indicates that the detector absorbs the excited state photons of the complexes and reduces the extent of transfer of energy from the ligand to the central metal ion, which causes fluorescence quenching when the complex detects TCL, 2,4,6-trinitrophenol, and Fe³⁺.⁵⁴

The lifetimes of the suspensions of 3 and 4 were determined	Qing-Lin Guan – College of Chemistry and Chemical
before and after the addition of the test substance Zn^{2+} . After the	Engineering, Liaoning Normal University, Dalian 116029, P. R.
addition of the test substance Zn ²⁺ , the luminescence lifetimes of	China
the complexes increased (Figure 16 and Table 2), implying that	Xiao-Dong Yang – College of Chemistry and Chemical
the interaction between the detection substance and the com-	Engineering, Liaoning Normal University, Dalian 116029, P. R.
plexes led to the more efficient transfer of energy to the metal	China
center, thereby increasing the luminescence intensity.	Li-Xian Sun – Guangxi Key Laboratory of Information Materials,
	Guilin University of Electronic Technology, Guilin 541004, P. R.
4. CONCLUSIONS	China
We synthesized four new complexes, $[Zn(TIBTC)(DMA)]$.	Yong-Heng Xing – College of Chemistry and Chemical
$[NH_{2}(CH_{3})_{2}]$ (1), $[Cd(TIBTC)(H_{2}O)] \cdot [NH_{2}(CH_{3})_{2}] \cdot DMA$	Engineering, Liaoning Normal University, Dalian 116029, P. R.
$(2), [Cd_2(TIBTC)(2,2'-bipy)_2(HCOO)] (3), and$	<i>China;</i> © orcid.org/0000-0002-7550-2262
$[Cd_2(DIBTC)(2,2'-bipy)_2(HCOO)]$ (4). Fluorescence experi-	Complete contact information is available at:
ments show that complexes $1-3$ can quickly and sensitively	https://pubs.acs.org/10.1021/acs.inorgchem.0c00391
detect TCL, NACs, and metal ions (Fe^{3+} and Zn^{2+}). Other amino	
acids do not interfere with the result of detecting TCL. Interestingly,	Notes
complexes 1 and 2 with a single ligand showed a fluorescence	The authors declare no competing financial interest.
quenching effect on Fe^{3+} ions, whereas complexes 3 and 4 with	1 0

the mixed ligands showed a fluorescence enhancement effect on Zn^{2+} ions. The results show that complexes 1-3 may be candidates

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for multifunctional fluorescent sensors for thiamine hydrochloride,

NACs, and Fe^{3+} and Zn^{2+} that have high sensitivity and selectivity.

This work provides a new idea for extending the application of

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Crystallographic data, bond lengths and angles, and hydro-

gen bond data for complexes 1, 2, and 4 (Tables S1-S3,

respectively); IR and ¹H NMR spectra of ligand

intermediates M-1 and M-2 (Figures S1–S4, respectively);

IR spectra, UV-vis spectra, and thermal analysis of

H₃TIBTC, H₃DIBTC, and complexes 1-4 (Figures S5-

S7, respectively) and the corresponding data assignments

(Tables S4 and S5); solid state emission spectra of

complexes 1-4 and fluorescence intensities in different

solvents (Figures S8 and S9, respectively); SV-fitted graphs

of fluorescence detection for complexes (Figures S10-

S12); quenching/enhancing efficiency of fluorescence for

complexes after five cycles of experiments (Figure S13)

CCDC 1951592 and 1951692-1951693 contain the supple-

mentary crystallographic data for this paper. These data can be

obtained free of charge via www.ccdc.cam.ac.uk/data request/

cif, or by emailing data request@ccdc.cam.ac.uk, or by

contacting The Cambridge Crystallographic Data Centre, 12

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MOF materials as multiresponse sensors.

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Inorganic Chemistry

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