

# A Luminescent Cd-MOF Used as a Chemosensor for High-Efficiency Sensing of Fe<sup>3+</sup>, Cr(IV), Trinitrophenol, and Colchicine

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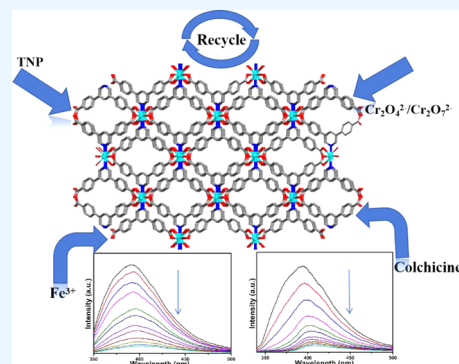


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**ABSTRACT:** A Cd-MOF was constructed based on 3,5-bis(4-carboxyphenyl)pyridine under solvothermal conditions. Its structure and phase purity were verified by single-crystal X-ray diffraction. Thereafter, some studies on the morphology, structure, and luminescent properties of the compound were carried out. The compound exhibited a highly sensitive response to Fe<sup>3+</sup>, Cr(IV), trinitrophenol (TNP), and colchicine based on the fluorescence-quenching mechanism. The possible mechanism of luminescence quenching was discussed in detail.



## 1. INTRODUCTION

Environmental pollution has grown in importance as a global concern for public health and the ecosystem over the past few decades due to social development,<sup>1</sup> and many types of pollutants such as nitroaromatic compounds, heavy metal ions, toxic anions, and colchicine are associated with health risks. Chemical synthesis and production of explosive materials are two common uses of nitroaromatic compounds (NACs), such as nitrobenzene (NB), 2,4,6-trinitrotoluene (TNT), and trinitrophenol (TNP), and they pose a substantial risk to human health and social security since they can contaminate air, groundwater, and soil.<sup>2</sup> TNP is the most dangerous among these explosives because of its tremendous explosive strength and numerous uses in dye, leather, explosive manufacturing, textile, and pharmaceutical industries.<sup>3</sup>

Fe<sup>3+</sup> is a fundamental element that is widely distributed in ecological systems and the environment and plays a significant role in the processes of hemoglobin formation, oxygen metabolism, and electron transfer. Both an excess and shortage of iron can lead to various health problems, including reduced immunity, iron deficiency anemia, multiple organ failure, and even cancers of the esophagus and bladder.<sup>4</sup>

Inorganic pollutants, especially toxic anions, also pose a serious environmental hazard due to their excessive emissions from industrial facilities such as electroplating, metallurgy, etc.<sup>5</sup> Hexavalent chromium ions, particularly Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup> anions, are extensively utilized in numerous industrial processes, including pigment printing, leather tanning, electroplating, and other associated domains. On the other hand, it has also been shown that they are two of the most dangerous pollutants in the environment. Since they can build up in living

things and seriously harm human health by causing maladies such as cancers, deformities, and gene mutations, they are not easily broken down by nature. Hence, the detection of Cr(IV) is of great significance.<sup>6</sup>

Colchicine has also been observed to suppress many inflammatory processes (Scheme S1); it is a naturally occurring toxic compound derived initially from *Colchicum* spp. In humans, even minute amounts of colchicine can induce nausea, vomiting, diarrhea, and bone marrow suppression. It is also a traditional medication used to treat cirrhosis, spontaneous inflammation, and gout.<sup>7</sup> Therefore, the detection of colchicine is of interest.

Recently, various analytical methods have been developed and applied to identify and quantify these contaminations, and these methods primarily include spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS), gas chromatography/mass spectrometry, atomic absorption spectrophotometry (AAS), and electrochemical analysis.<sup>8</sup> However, these techniques are usually costly and time-consuming and require complex instruments and advanced operational skills. Therefore, there is a great need to find more effective techniques with a simple operation, fast response time, and high sensitivity. Optical sensing is well recognized as an effective, economical, and prompt detection approach, making

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it a viable tool for contaminant detection.<sup>9</sup> Luminescent metal–organic frameworks (LMOFs) are a novel family of optical materials that have experienced rapid development because of their unique photophysical characteristics, easily tailored structures, and permanent porosity, all of which fascinating properties endow them with potential applications for detecting explosives, biomolecules, gases, heavy metal ions, and solvents.<sup>10</sup> Nevertheless, there are very few research studies on multifunctional LMOFs for the simultaneous detection of TNP, colchicine, and metal ions. In particular, detecting trace levels of Fe<sup>3+</sup>, Cr<sup>3+</sup>, TNP, or colchicine in the presence of other interfering analogs is extremely challenging to accomplish selectively and sensitively.

Based on the above discussions, we herein employ 3,5-bis(4-carboxyphenyl) pyridine (H<sub>2</sub>L) as an organic linker with Cd<sup>2+</sup> to fabricate a new LMOF-CdL, denoted as compound **1**. The structure of compound **1** can be viewed as a three-dimensional network featuring one-dimensional triangular channels, which can be utilized as a multifunctional material for sensing Fe<sup>3+</sup>, Cr(IV), TNP, and colchicine in methanol with high sensitivity and selectivity through effective quenching reactions.

## 2. EXPERIMENTAL SECTION

**2.1. Physical Measurements.** FT-IR spectra were acquired using a Nicolet Impact 410 FTIR spectrometer employing KBr pellets within the 4000–400 cm<sup>-1</sup> spectral range. Both the excitation and emission pass widths were 2.0 nm. A 15 mL stainless steel autoclave lined with Teflon was used to perform a solvothermal reaction. C, H and N elemental studies were carried out using a PerkinElmer 2400 element analyzer. An X-ray powder diffraction (model Rigaku D/max 2550) instrument was used to acquire data for powder X-ray diffraction measurements. TGA was performed by utilizing a TGA Q500 V20.10 Build 36 instrument. The analysis was conducted from room temperature to 800 °C employing a heating rate of 10 °C/min under a flowing N<sub>2</sub> atmosphere. UV–vis spectra were collected at ambient temperature by using a TU-1900 spectrometer. Luminescent spectra were acquired by utilizing the FLS920 spectrofluorimeter employing excitation and emission pass widths of 2.0 nm.

**2.2. Synthesis of Compound 1.** Cadmium(II) nitrate tetrahydrate (15.4 mg), 3,5-bis(4-carboxyphenyl) pyridine (4.8 mg), 4,4'-bipyridine (15.6 mg), and three drops of concentrated HNO<sub>3</sub> were ultrasonically dissolved in DMA (5 mL), CH<sub>3</sub>CH<sub>2</sub>OH (2 mL), and H<sub>2</sub>O (1 mL) in a 20 mL vial at 75 °C for 72 h. Columnar yellow crystals were then collected and washed with DMA, followed by drying at 60 °C. Yield: 58% (based on 3,5-bis(4-carboxyphenyl) pyridine); IR (KBr 4000–400 cm<sup>-1</sup>): 3418 (w), 1639 (w), 1509 (s), 1598 (s), 1397 (s), 1280 (m), 1263 (w), 1011 (m), 912 (w), 855 (m), 817 (m), 779 (s), 707 (s), 669 (m), 593 (w), 526 (w), 503 (w), 486 (m). Elemental analysis (%): Calcd for C<sub>25</sub>H<sub>28</sub>N<sub>2</sub>O<sub>7</sub>Cd: C 51.6, H 4.82, N 4.82; found: C 51.4, H 4.84, N 4.86.

**2.3. Crystal Structure Determination.** The Rigaku RAXIS-RAPID, equipped with a narrow-focus, 5.4 kW sealed-tube X-ray source using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), facilitated data collection and structural analysis. The data were collected at a temperature of 20  $\pm$  2 °C. The PROCESS-AUTO processing program was used to process the data. The direct methods of the SHELXL crystallographic software package were employed to solve the structure, and full-matrix least-squares approaches were applied

to refine them on F2. Anisotropic thermal parameters were used to refine all of the compound's non-hydrogen atoms. Every hydrogen atom in the organic molecule was incorporated into the structure factor calculation geometrically. The additional crystallographic data for this study is CCDC-2205947. The atomic coordinates detailing this structure were submitted to the Cambridge Crystallographic Data Center. Since it is challenging to identify the precise solvent molecules in the structure, we further determined the molecular formula of the as-synthesized compound **1** using Platon/Squeeze, TGA, IR, and elemental analysis. The coordinates are available from the Cambridge Crystallographic Data Center (CCDC) at <https://www.ccdc.cam.ac.uk/>

**2.4. Fluorescence Sensing Experiments.** For the purpose of the fluorescence sensing tests, a mixed solution containing 3 mg of compound **1**'s milled samples and 3 mL of CH<sub>3</sub>OH was prepared. The mixture was then sonicated for 30 min.

## 3. RESULTS AND DISCUSSION

**3.1. Crystal Structure of Compound 1.** Compound **1** is classified as a member of the monoclinic space group *I2/a* based on crystallographic study (Table 1). In compound **1**, the

**Table 1. Crystallographic Data and Structure Refinement Summary for Compound 1**

|   |   |
|---|---|
| compound  | <b>1</b>  |
| molecular formula   | C <sub>25</sub> H <sub>28</sub> CdN <sub>2</sub> O <sub>7</sub> |
| formula weight  | 580.8   |
| crystal system  | monoclinic  |
| space group   | <i>I2/a</i>   |
| <i>a</i> , Å  | 8.0481(3)   |
| <i>b</i> , Å  | 16.0917(5)  |
| <i>c</i> , Å  | 14.9654(5)  |
| $\alpha$ , deg  | 90  |
| $\beta$ , deg   | 96.636(3)   |
| $\gamma$ , deg  | 90  |
| <i>V</i> , Å <sup>3</sup>   | 1925.15   |
| <i>Z</i>  | 4   |
| <i>D</i> <sub>calc</sub> , g/cm <sup>3</sup>  | 1.620   |
| <i>F</i> (000)  | 848.0   |
| GoF   | 1.073   |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup><i>a,b</i></sup>  | <i>R</i> <sub>1</sub> = 0.0308, <i>wR</i> <sub>2</sub> = 0.0863 |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)   | <i>R</i> <sub>1</sub> = 0.0321, <i>wR</i> <sub>2</sub> = 0.0876 |
| <sup><i>a</i></sup> <i>R</i> <sub>1</sub> = $\ F_o\  -  F_c  / \sum  F_o $ . <sup><i>b</i></sup> <i>wR</i> <sub>2</sub> = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} \cdot w = 1 / [\sigma^2(F_o^2) + (ap)^2 + (bp)^2]$ , <i>p</i> = $[\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$ . <i>a</i> = 0.0539, <i>b</i> = 2.3313. |   |

asymmetric unit has one Cd<sup>2+</sup> ion and 0.5 L<sup>2-</sup> ligand (Figure S1). Six carboxylate O atoms from four different L<sup>2-</sup> ligands and one N atom from one L<sup>2-</sup> ligand coordinate the Cd<sup>2+</sup> center (Figure 1a). The L<sup>2-</sup> ligand is pentacoordinated to three Cd centers, and each carboxyl group of the L<sup>2-</sup> ligand adopts a double coordination pattern of  $\mu_2$ - $\eta^2$ : $\eta^1$  (Figure 1b). The Cd–O distances vary from 2.226 (2) to 2.628 (3) Å, while the O–Cd–O angles are in the range from 53.56 to 174.25°. Additionally, the O–Cd–N angles are observed within the range of 74.82–104.65°. Both the Cd center and L<sup>2-</sup> can be considered as five-coordinated nodes, resulting in the framework forming a uninodal (5,5)-connected bnn topology denoted by the point symbol of (4<sup>6</sup>·6<sup>4</sup>) as illustrated in Figure 2.

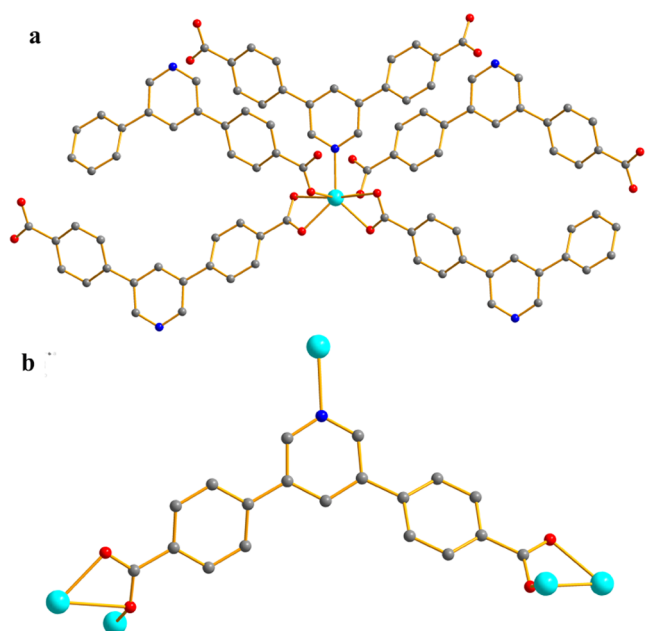


Figure 1. Coordination mode of (a) Cd center and (b)  $L^{2-}$ .

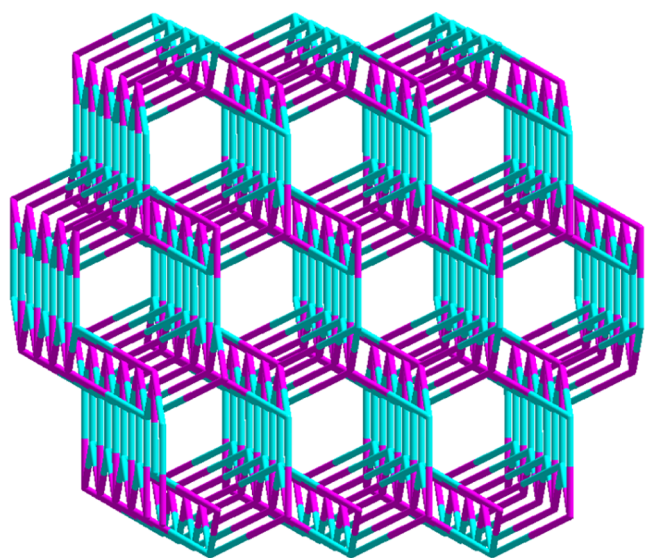


Figure 2. Topology of compound 1.

The one-dimensional Cd-ion chains are formed by a carboxyl group bridging all of the metal ions in the structure as presented in Figure 3a. The one-dimensional Cd-ion chains then interconnect along the  $b$ -axis through ligands, resulting in the formation of a two-dimensional layer. This layer is then extended by Cd–N bonding, contributing to the generation of a three-dimensional framework (Figure 3b,c). Furthermore, one-dimensional ultramicroporous channels with a diameter of  $\sim 3$  Å exist along the  $a$ -axis, regardless of the van der Waals radius. Platon calculations reveal that the total solvent accessible volume of the 3D framework is  $620.1 \text{ \AA}^3$ , accounting for 48.7% of the total cell volume.

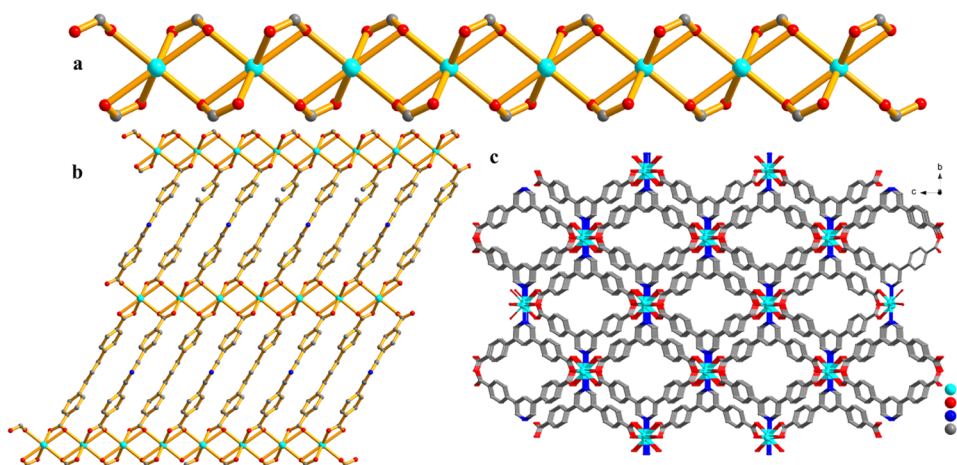
**3.2. Fluorescence Properties of Compound 1.** The solid-state fluorescence characteristics of compound 1 and  $H_2L$  were studied at room temperature. As depicted in Figure 4,  $H_2L$  ( $\lambda_{\text{ex}} = 330 \text{ nm}$ ) obtained the maximum emission peak at  $378 \text{ nm}$ , potentially arising from  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transitions.

Conversely, compound 1 exhibited the maximum emission peak at  $414 \text{ nm}$  ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ), which was attributed to the challenging oxidation or reduction of the Cd(II) ion because of its  $d^{10}$  electronic configuration. These emissions are neither MLCT nor LMCT. Thus, the emissions can be assigned to intraligand and interligand luminescence emissions. Due mostly to the ligand–metal coordination effect, compound 1's emissions were seen to be red-shifted when compared to free  $H_2L$ .<sup>11</sup>

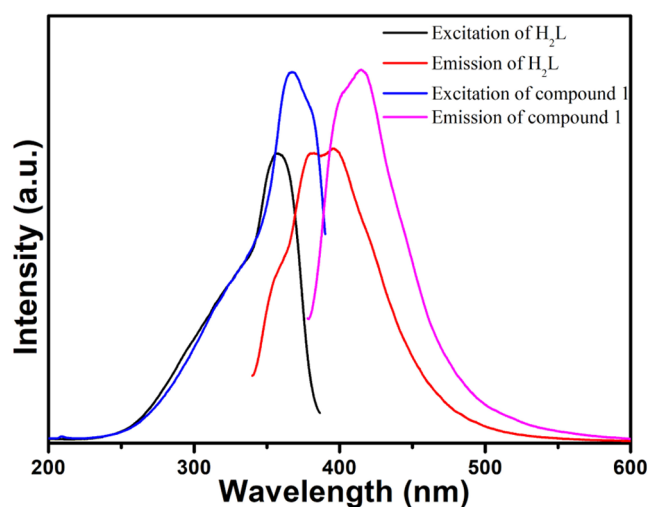
**3.2.1. Fluorescence Detection of Compound 1 in Various Solvents.** The fluorescence properties of compound 1 were further tested by suspending the milled samples (3 mg in 3 mL) in various solvents like methanol, NMP (*N*-methyl-2-pyrrolidone), DMF, ethanol, DMA, DMSO, acetonitrile ( $\text{CH}_3\text{CN}$ ),  $\text{CH}_2\text{Cl}_2$ , acetone, 1,4-dioxane, and  $\text{H}_2\text{O}$ , treated with ultrasonication at room temperature for 30 min. Compound 1 displayed the greatest fluorescence emission in  $\text{CH}_3\text{OH}$ , as demonstrated by Figure 5, which also confirms that compound 1's fluorescence intensity was significantly dependent on the solvents. Hence, in fluorescence measurements,  $\text{CH}_3\text{OH}$  was selected as the dispersion solvent.

**3.2.2. Fluorescence Detection of Compound 1 in Different Cations.** The determination potential of compound 1 was evaluated by sonicating 3 mg of milled samples in 3 mL of  $\text{M}(\text{NO}_3)_x$  methanol solution (0.01 M) ( $\text{M} = \text{K}^+, \text{Na}^+, \text{Cd}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Pb}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}, \text{Ag}^+$ ) for 30 min to produce homogeneous suspensions. The photoluminescence response for the obtained emulsion containing different metal ions was recorded (Figure 6). The metal-ion identities play a major role in determining the fluorescence intensities. Most of the metal ions, such as  $\text{K}^+$  and  $\text{Cd}^{2+}$ , have little effect on the fluorescence intensity of compound 1. It is noteworthy that compound 1 exhibits a clear drop in emission intensity when  $\text{Fe}^{3+}$  is present. Additionally,  $\text{Fe}^{3+}$  demonstrates a 100% quenching, indicating that  $\text{Fe}^{3+}$  has the greatest quenching impact on compound 1. To assess the stability of compound 1 in a methanol solution, the collapse of framework-related fluorescence quenching after sensing different metal ions is excluded according to PXRD measurement (Figure S10).

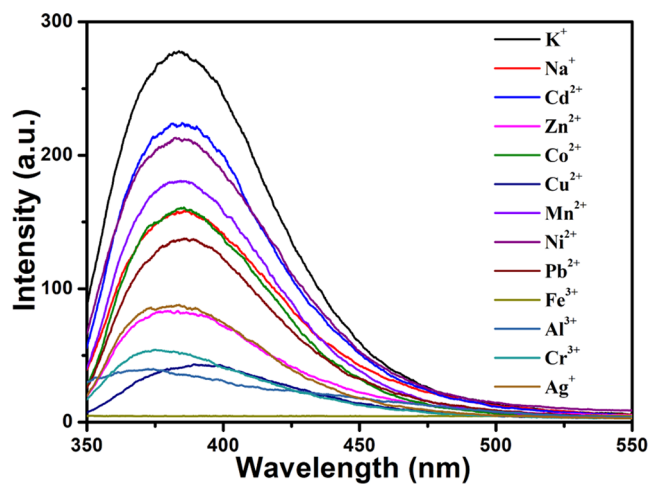
**3.2.3. Fluorescence Detection of Compound 1 in Different Concentrations of  $\text{Fe}^{3+}$  Solution.** To further evaluate the sensing selectivity toward  $\text{Fe}^{3+}$ ,  $1 \times 10^{-3} \text{ M}$   $\text{Fe}^{3+}$  was prepared to test the emission response (3 mg compound 1 in 3 mL methanol), and the fluorescence intensity decreased continuously with gradually increasing concentrations of  $\text{Fe}^{3+}$  solution (Figure 7). The analysis of the quenching effect involved applying the linear Stern–Volmer (S–V) equation:  $I_0/I = 1 + K_{\text{sv}} [M]$ , where  $K_{\text{sv}}$  signifies the quenching constant,  $[M]$  represents the concentration of metal ions,  $I_0$  denotes the initial fluorescence intensity, and  $I$  stands for the intensities observed after the addition of  $\text{Fe}^{3+}$ . The SV plot pertaining to  $\text{Fe}^{3+}$  demonstrated an almost linear correlation, boasting a strong correlation coefficient of 0.999. The calculated slope, denoting  $K_{\text{sv}}$ , amounted to  $1.1 \times 10^4 \text{ M}^{-1}$  (as depicted in Figure S3). Compound 1's luminescence intensity was nearly entirely quenched in the presence of  $\text{Fe}^{3+}$  methanol solution for a given metal ion (Figure S11). To evaluate a material's efficacy as a fluorescence sensor, it is critical to determine its limit of detection (LOD). Compound 1 has the potential to be a very sensitive fluorescent probe for  $\text{Fe}^{3+}$ , as evidenced by the limit of detection of 0.028 mM for  $\text{Fe}^{3+}$ , calculated from the equation,  $\text{LOD} = 3\sigma/k$ .



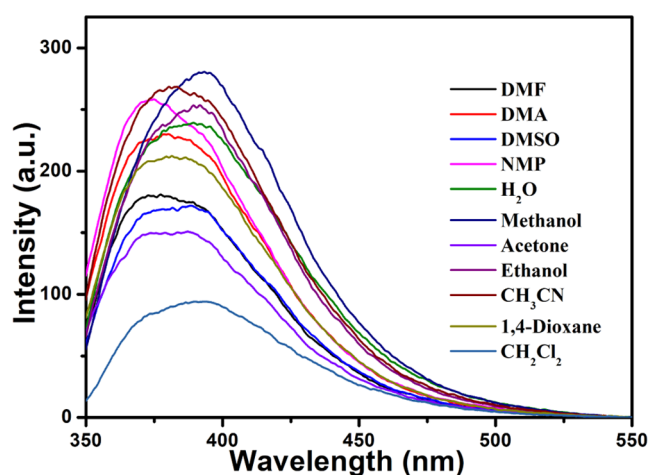
**Figure 3.** (a) Rod shape of the one-dimensional Cd-ion chain; (b) two-dimensional layer of compound 1 without Cd–N coordination; and (c) three-dimensional structure of compound 1.



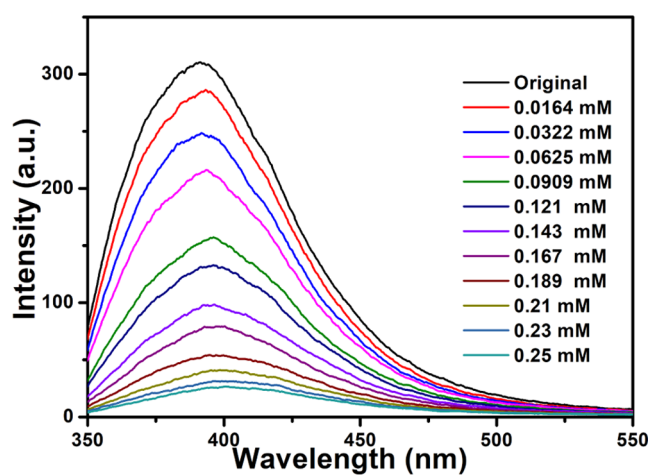
**Figure 4.** Solid-state fluorescence of compound 1 and H<sub>2</sub>L.



**Figure 6.** Fluorescence spectra of compound 1 toward different metal ions.



**Figure 5.** Fluorescence spectra of compound 1 in different solvents.



**Figure 7.** Fluorescence spectra of compound 1 with addition of Fe<sup>3+</sup> (1 × 10<sup>-3</sup> M).

**3.2.4. Fluorescence Detection of Compound 1 in Different Anions.** Experiments on anion sensing were conducted similarly to those on cation sensing. The milled sample of 3 mg compound 1 was dispersed in the individual methanol solutions of 0.01 M KX (3 mL, X<sup>-</sup> = Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>,

C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, Cl<sup>-</sup>, F<sup>-</sup>) and then subjected to 30 min of ultrasonication, after which a stable suspension was obtained for testing and investigating the fluorescence formed (Figure 8). Their fluorescence intensities

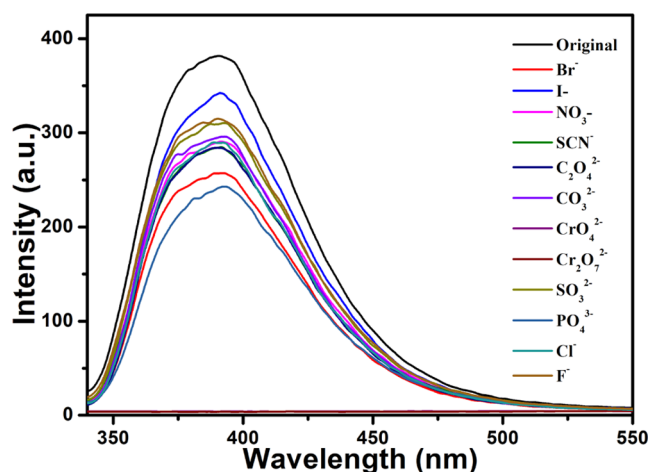


Figure 8. Fluorescence spectra of compound 1 with addition of anions ( $1 \times 10^{-2}$  M).

were prominently dependent on anions. Compound 1 was primarily affected by the  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  anions, which sharply quenched the compound's fluorescence and significantly reduced it. On the contrary, the other anions showed a slight effect under the same conditions. The findings suggest that among other common anions, compound 1 could serve as a capable fluorescence sensor with excellent selectivity for Cr(VI). Competitive experiments on compound 1's anti-interference sensing ability provide evidence for this point. These experiments showed that compound 1's intensity was acutely quenched in the presence of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  anions, but no discernible changes were seen when competitive anions were added to the corresponding solutions (Figures S12 and S13). Hence, compound 1's outstanding anti-interference sensing capability and high selectivity as a chemical sensor for  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  anions in methanol are amply supported by the aforementioned results.

**3.2.5. Fluorescence Detection of Compound 1 in Different Concentrations of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  Solutions.** Fluorescence titration studies were conducted to examine the sensitivity during quenching. This was achieved by adding varying amounts of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  anions. As the concentration of  $\text{Cr}_2\text{O}_7^{2-}$  or  $\text{CrO}_4^{2-}$  anions increased, compound 1's emission intensity in methanol progressively reduced, as depicted in Figures 9 and 10, further supporting the existence of the luminescence quenching effects. According to the Stern–Volmer equation analysis, the quenching constants ( $K_{sv}$  values) for compound 1 were determined to be  $1.14 \times 10^4 \text{ M}^{-1}$  for  $\text{Cr}_2\text{O}_7^{2-}$  and  $8.6 \times 10^3 \text{ M}^{-1}$  for  $\text{CrO}_4^{2-}$ , yielding  $R^2$  values of 0.993 ( $\text{Cr}_2\text{O}_7^{2-}$ ) and 0.998 ( $\text{CrO}_4^{2-}$ ) (refer to Figures S6 and S7). Furthermore, the detection limits of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  were about 16.7 and 22.1  $\mu\text{M}$ , respectively, as determined by the  $K_{sv}$  values and standard deviation of the repeated fluorescence measurements of the blank solution. When compared to other MOF-based fluorescent probes, compound 1 is a superior material for Cr(VI) anion detection in methanol.<sup>12</sup>

**3.2.6. Fluorescence Detection of Compound 1 in Various NACs.** The investigation of compound 1's fluorescence properties aimed to discern its capability to detect NACs within a methanol solution. In this study, NACs such as 2,4-NT, 2-NT, TNP, TNT, p-NT, and NT were employed. Figure 11 shows compound 1's fluorescence intensity at different

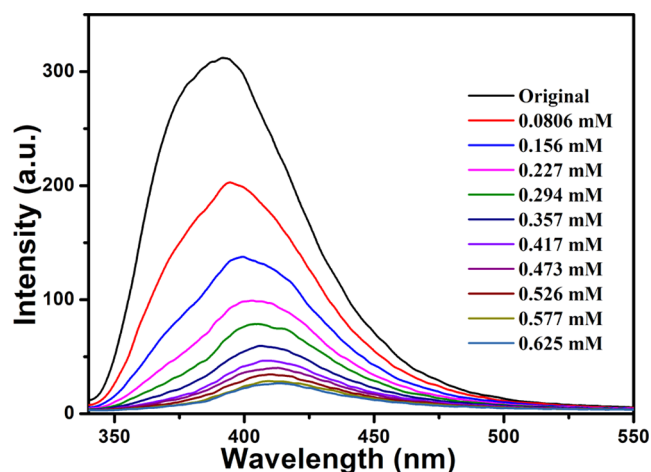


Figure 9. Fluorescence spectra of compound 1 upon adding various concentrations of  $\text{Cr}_2\text{O}_7^{2-}$  ( $2.5 \times 10^{-3}$  M).

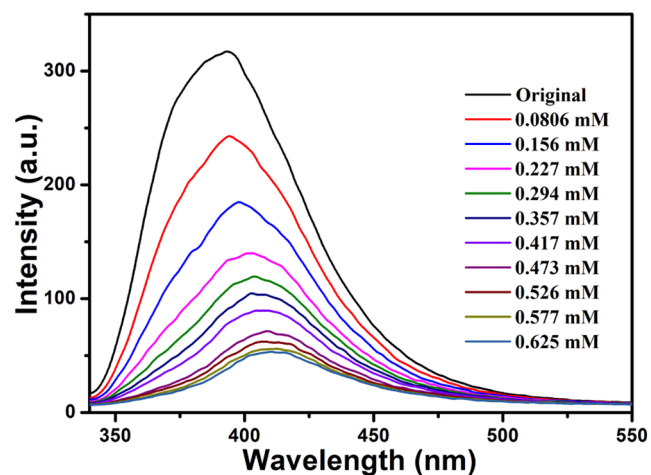


Figure 10. Fluorescence spectra of compound 1 with addition of  $\text{CrO}_4^{2-}$  ( $2.5 \times 10^{-3}$  M).

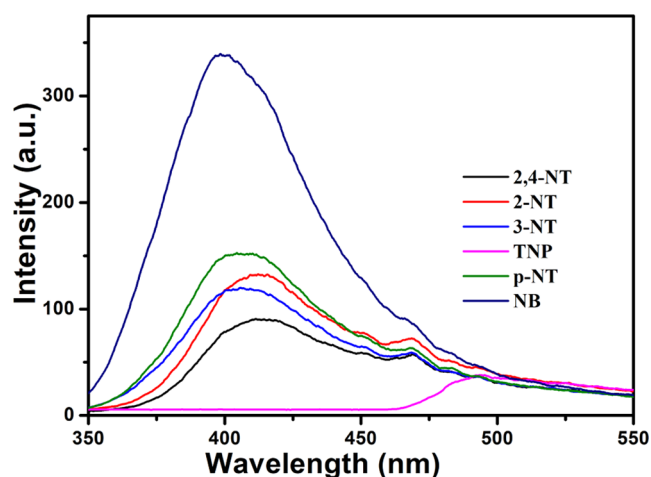


Figure 11. Fluorescence spectra of compound 1 after adding various concentrations of NACs ( $1 \times 10^{-3}$  M).

NACs ( $1 \times 10^{-3}$  M). The fluorescence intensity of compound 1 was continuously quenched at 385 nm, and its quenching efficiency reached 100% in a TNP methanol solution. Additionally, a highly noticeable amount of fluorescence

quenching was detected in this solution. Compound **1** showed minimal variation in fluorescence intensity when compared to that of the other five NACs.

**3.2.7. Fluorescence Detection of Compound 1 in Different Concentrations of TNP.** A fluorescence-quenching titration investigation was carried out to examine compound **1**'s sensitivity for TNP detection. TNP methanol solution ( $1 \times 10^{-4}$  M) was gradually added to compound **1**'s suspension, resulting in a notable reduction in luminescence intensity (Figure 12). Based on the titration data, the SV curve was

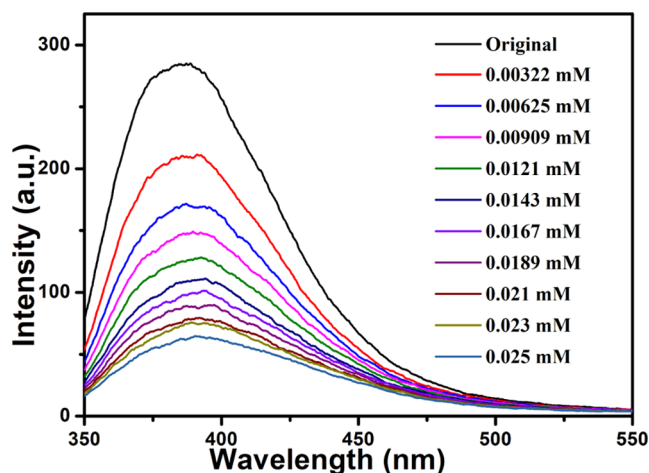


Figure 12. Fluorescence spectra of compound **1** upon addition of TNP ( $1 \times 10^{-4}$  M).

plotted using the equation  $I_0/I = 1 + K_{sv} [M]$ , and a linear relationship was obtained; meanwhile, the  $K_{sv}$  of TNP was calculated as  $7220 \text{ M}^{-1}$  ( $R^2 = 0.9946$ ) (Figure S4), with a detection limit of  $26.3 \mu\text{M}$ , calculated using  $3\sigma/k$ .

**3.2.8. Fluorescence Detection of Compound 1 in Different Concentrations of Colchicine.** The fluorescence response of compound **1** in a methanol solution of colchicine ( $1 \times 10^{-2}$  M) was also examined (Figure S9), and the fluorescence intensity exhibited a substantial decrease, signifying the remarkable sensitivity of compound **1** toward colchicine. Following that, a colchicine fluorescence titration investigation was carried out, in which incremental amounts of colchicine methanol solution ( $5 \times 10^{-4}$  M) were added to the suspension of compound **1**, and there was a discernible decline in the luminescence intensity of compound **1**, as shown in Figure 13. Based on the titration data, an SV plot was acquired. The results showed that  $K_{sv}$  was equal to  $4.26 \times 10^4 \text{ M}^{-1}$  ( $R^2 = 0.994$ ) (Figure S5), and the detection limit of colchicine was  $4.46 \mu\text{M}$ . These results reveal that compound **1** has a good sensitivity for the detection of colchicine in methanol.

**3.3. PXRD of Compound 1.** Furthermore, the recycling performance must be simple and quick. Luminescence and PXRD were used to examine the recycled samples of compound **1**, which was acquired by repeatedly washing it in methanol. Following five cycles, the luminescence intensity of compound **1** in solutions containing  $\text{Fe}^{3+}$ ,  $\text{Cr}(\text{IV})$ , TNP, and colchicine was found to be nearly constant from its initial state (Figure S14), and the framework structure remained intact (Figure S15). Therefore, compound **1** is an excellent sensor for  $\text{Fe}^{3+}$ ,  $\text{Cr}(\text{IV})$ , TNP, and colchicine in terms of stability and recyclability.

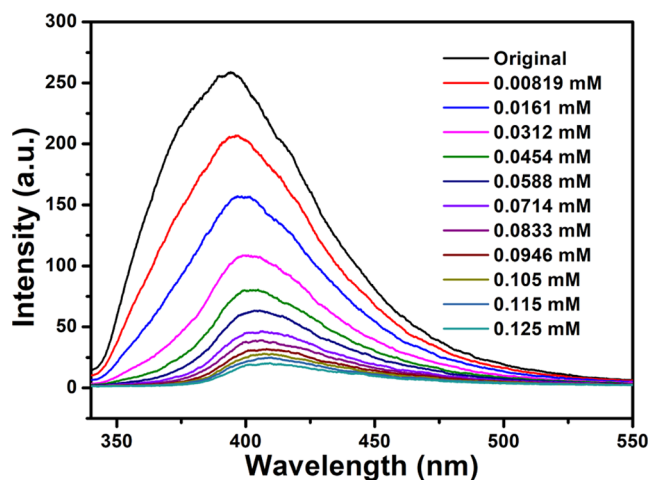


Figure 13. Fluorescence spectra of compound **1** after adding different concentrations of colchicine ( $5 \times 10^{-4}$  M).

**3.4. Fluorescence-Quenching Mechanism.** Meanwhile, UV-vis absorption spectra of  $\text{Fe}^{3+}$ ,  $\text{Cr}(\text{IV})$ , TNP, and colchicine depict overlaps with the luminescence excitation peak of compound **1** (Figure S8). This phenomenon indicates that the excited light's energy is absorbed by  $\text{Fe}^{3+}$ ,  $\text{Cr}(\text{IV})$ , TNP, and colchicine, impeding the transfer of energy from  $\text{L}^{2-}$  to  $\text{Cd}^{2+}$  and consequently inducing the quenching effect on compound **1**, which suggested a possible energy transfer between  $\text{Fe}^{3+}$ ,  $\text{Cr}_2\text{O}_7^{2-}/\text{CrO}_4^{2-}$ , TNP, colchicine, and compound **1**.<sup>13</sup>

## 4. CONCLUSIONS

A novel luminescent Cd-MOF was synthesized via a solvothermal method and thoroughly characterized. Luminescence sensing investigations suggest its potential as an excellent probe for highly sensitive detection of  $\text{Fe}^{3+}$ ,  $\text{Cr}(\text{IV})$ , TNP, and colchicine. This flexible detection capability is greatly anticipated to offer valuable insights into the development of new multifunctional MOFs for chemical sensing.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c07110>.

Supporting Crystallography Data (ZIP)

Table S1: selected bond distances (Å) and angles (deg) for compound **1**; Scheme S1: structure of colchicine; Figure S1: asymmetric unit of compound **1**; Figure S2: PXRD of compound **1**; Figures S3–S7: SV plots for luminescence intensity of compound **1**; Figure S8: UV absorption; Figure S9: fluorescence spectra of compound **1** in colchicine solution ( $1 \times 10^{-2}$  M); Figure S10: PXRD of compound **1** and after sensing of the metal ions; Figures S11–S13: anti-interference performance of  $\text{Fe}^{3+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$ ; Figure S14: five cycle tests of compound **1** toward sensing  $\text{Fe}^{3+}$ ,  $\text{Cr}_2\text{O}_7^{2-}/\text{CrO}_4^{2-}$ , TNP, and colchicine in methanol; Figure S15: PXRD patterns of the recycled compound **1** after sensing  $\text{Fe}^{3+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$ , TNP, and colchicine; Figure S16: PXRD patterns of compound **1** and the luminescence intensity at three different temperatures; Figure S17: fluorescence intensity of compound **1** in  $\text{K}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Mg}^{2+}$  methanol solutions; Figure

S18: TGA of compound **1**; and Figure S19: IR of compound **1**. (PDF)

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### Author Contributions

The experiments were conceived and designed by X.Z.; X.Z., Y.N., and D.W. carried out the experimental work; data were analyzed by L.L., S.Z., Y.F. and J.L.; supervision for this work was carried out by X.T. All authors contributed to the revision of the manuscript.

### Notes

The authors declare no competing financial interest.

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