



A multifunctional metal-organic framework showing excellent fluorescence sensing and sensitization



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ABSTRACT

Luminescent metal-organic frameworks (LMOFs) have been widely used as sensors and sensitizers for some chemical species due to their functional sites and porosity. In this work, a new metal-organic frameworks, $[\text{Cd}_2(\text{H}_2\text{L})_2(\text{H}_2\text{O})_5] \cdot 5\text{H}_2\text{O} \cdot 2\text{DMF}$ (**1**), has been successfully synthesized using 2,5-bis-(3,5-dicarboxyphenyl)thiopheneamide (H_4L) under solvothermal condition. Single crystal X-ray diffraction analysis reveals that **1** has a basic tetranuclear unit, in which H_4L is incompletely deprotonated. Furthermore, the basic tetranuclear units are connected into 3D supramolecular network by hydrogen bonds and π - π stacking interactions. As expected, the participation of the fluorescent ligand H_4L endows **1** with a strong fluorescence emission. Thus, we systematically explored the fluorescence sensing responses of **1** to small organic molecules and metal ions. Notably, complex **1** can act as a potential multifunctional fluorescence material for sensing of *p*-nitroaniline and Fe^{3+} ion with high stability, selectivity and sensitivity. In addition, complex **1** also protects Eu^{3+} cations from solvent quenching and sensitizes encapsulated Eu^{3+} hydrates emitting in the UV–vis region. This work highlights the practical application of luminescent MOFs as sensors and sensitizers.

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1. Introduction

Metal-organic frameworks (MOFs), a relatively new class of porous and crystalline materials, has become a frontier research field not only because of their intriguing architectures and topologies but also for their potential applications in gas storage and separation [1,2], catalysis [3,4], drug delivery [5–7], sensors [8–10], and so on. Recently, a wide range of functional luminescent MOF-based sensing materials have been developed for detecting nitroaromatic explosives [11–14], metal ions [15–19], anions [20,21] and even biomacromolecules [22]. It is because that the MOF-based luminescent sensors have certain advantages over conventional fluorescence sensing materials, such as high surface areas and chemistry stability, tunability of pore size and functionality, and ease of synthesis. The specific structures and functional porosity of MOFs can help to enhance the host–guest interactions between MOF frameworks and target analytes. In turn, the effec-

tive interactions between the MOF skeletons and the analytes may increase the sensitivity of sensing and the rate of response. Besides, MOFs as fluorescence chemosensors have the advantageous of ease of manipulation, cost-effective approaches, visualization and reusability [23–29].

On the other hand, nitroaromatic compounds (NACs), which are widely used in the agrochemical industry, are not only well-known explosives but also notorious environmental pollutants. The increase in terrorism related explosive attacks and pollution to the environment in recent years has aroused people's concerns on the effect of NACs on the security and the environment [30–33]. Additionally, Fe^{3+} ions, as one of the most important elements for humans and other living organisms, play a crucial role in biological and environmental systems. The deficiency and excess of Fe^{3+} ions can induce a number of physiological disorders [34–38]. Therefore, the design and synthesis of MOF-based chemical sensors for rapid and efficient detection of nitroaromatic compounds and metal ions is not only an exigent requirement in the field of public security, but also critical for environmental protection.

Generally, the functional luminescent MOFs materials can be obtained by incorporation of aromatic polycarboxylates ligands

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and d^{10} configuration metal ions together with manipulating proper reaction conditions. The π -electron rich aromatic rings endow the MOFs with good fluorescence properties, which can efficiently promote the fluorescence sensing performances. Thus, the use of π -electron rich aromatic polycarboxylates as organic linker is a promising method for constructing luminescent MOFs for sensing applications. In the previous work, we reported several luminescent MOF-based sensors, which exhibit significant sensing performance in detecting organic molecules and metal ions [39–41]. As the continuous our work, we selected a semi-rigid thiophene-2,5-dicarboxylicamide-based derivatives (H_4L), which has four carboxylate groups as coordination sites and two amide groups as functional sites, as the organic linker to construct a Cd-based MOF fluorescence material, $[Cd_2((H_2L)_2(H_2O)_5)] \cdot 5H_2O \cdot 2DMF$ (**1**). The functional organic ligand endows the luminescent MOF with functionalized pore surface, which may effectively enhance the host–guest interactions between the MOF framework and the analytes. So, we systematically explored the sensing performance of **1** in detail. As expected, the as-synthesized **1** exhibits a good potential as a luminescent sensor material for multi-responsive *p*-nitroaniline and Fe^{3+} ions. In addition, **1** also serves as both a host and an antenna for trapping and sensitizing encapsulated Eu^{3+} hydrates emitting in the UV–vis region.

2. Experimental section

2.1. General procedures

All the reagents were obtained from commercial sources and used as received. 2,5-bis-(3,5-dicarboxyphenyl)thiopheneamide (H_4L) was prepared according to the literature [42]. Infrared spectra were recorded on a FTIR-650 system using KBr pellets in the range 4000–400 cm^{-1} . Elemental analyses (C, H and N) were measured on a Perkin-Elmer auto-analyzer. Thermogravimetric (TG) analysis was carried out on a Netzsch STA 409 PG/PC analyzer at a heating rate of 5 $^{\circ}C\ min^{-1}$ from ambient temperature to 800 $^{\circ}C$. Powder X-ray diffraction (PXRD) data was recorded on a D/MAX-2500 automated diffractometer. The photoluminescence spectra of the complex studied in the solid state and the sample in isopropanol solution were measured on an F-380 spectrophotometer.

2.2. Synthesis of $[Cd_2((H_2L)_2(H_2O)_5)] \cdot 5H_2O \cdot 2DMF$ (**1**)

A mixture of H_4L (17.4 mg, 0.035 mmol), $CdCl_2 \cdot 5/2H_2O$ (22.8 mg, 0.1 mmol), DMF (3 mL) and H_2O (2 mL) were sealed in a 25 mL stainless vessel and heated at 85 $^{\circ}C$ for 3 days under autogenous pressure, and then cooled to room temperature. Colorless block crystals of **1** were obtained by filtration. Yield: 76.7% based on Cd. Elemental analysis (%) calcd for $C_{50}H_{58}Cd_2N_6O_{32}S_2$: C, 38.86; H, 3.76; N, 5.44. Found: C, 38.90; H, 3.66; N, 5.72. IR (KBr pellet cm^{-1}): 3381 br, 1650 m, 1554 m, 1415 s, 1382 m, 1328 s, 1284 s, 1241 w, 1159 w, 1078 s, 952 m, 860 m, 781 m, 732 m, 665 m, 593 m, 547 m.

2.3. Fluorescence titrations in dispersed medium

To examine the potential of **1** for sensing nitroaromatic compounds and metal ions, 3 mg of **1** was immersed in isopropanol of 3 mL, respectively, which was treated by ultrasonication for 1.5 h. All titrations were carried out by gradually adding the analytes in an incremental fashion. The corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated several times to get concordant values. For all measurements, the suspension of **1** was excited at $\lambda_{ex} = 340$ nm and the corresponding emission wavelengths were monitored from 350 to 670 nm. The fluorescence efficiency was calculated by using the formula $[(I_0 - I)/I_0] \times 100\%$ (I_0 is the initial fluorescence intensity). Fluorescence quenching titration was further evaluated using the Stern-Volmer equation $I_0/I = 1 + K_{sv}[M]$, where the values I_0 and I are the fluorescence intensity of the MOFs suspension without and with addition of analytes, respectively, K_{sv} is the quenching constant, $[M]$ is the analytes concentration.

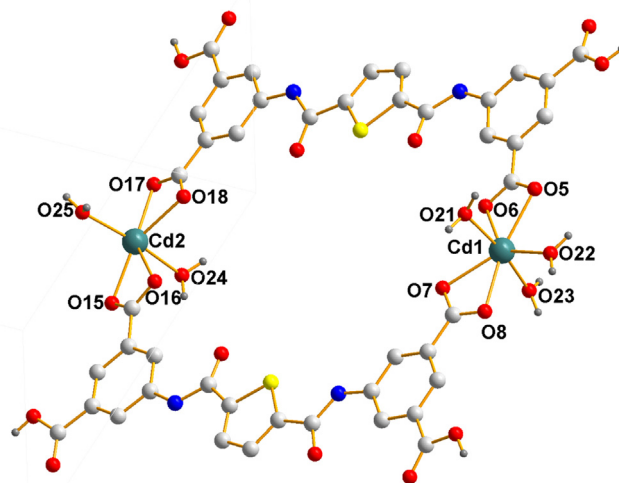


Fig. 1. The coordination environments of Cd (II) ions in **1**.

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2.4. X-ray crystallography

Single crystal X-ray diffraction measurement for **1** was carried out on computer-controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromatized Mo-K α with a radiation wavelength of 0.71073 \AA using the ω -scan technique. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXS 97 and SHELXL 97 programs [43,44]. Semiempirical absorption corrections were applied using the SADABS program [45]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent or constrained refinement. The crystallographic data for **1** are listed in Table S1, and selected bond lengths (\AA) and angles ($^{\circ}$) are listed in Table S2.

3. Results and discussion

3.1. Structure description of **1**

Single crystal X-ray diffraction determination shows that complex **1** crystallizes in the triclinic crystal system with $P\bar{1}$ space group. The asymmetric unit of **1** consists of two crystallography independent Cd (II) ions, two H_2L^{2-} ligands and five coordinated water molecules. The coordination environments of Cd (II) ions are shown in Fig. 1. The Cd1 ion is seven-coordinated by seven oxygen atoms: four oxygen atoms from two carboxylate groups of two different H_2L^{2-} ligands, the remaining three oxygen atoms from three coordinated water molecules. The Cd1–O distances are in the range of 2.263(4)–2.412(4) \AA . So, the coordination geometry configuration of Cd1 displays a distorted pentagonal bipyramid. Different from Cd1 ion, the Cd2 ion is six-coordinated by six oxygen atoms: four oxygen atoms from two carboxylate groups of two different H_2L^{2-} ligands, the remaining two oxygen atoms from two coordinated water molecules. The Cd2–O distances are in the range of 2.276(4)–2.474(4) \AA . Thus, the coordination geometry configuration of Cd2 displays a distorted octahedron.

In complex **1**, H_4L ligand is incompletely deprotonated: two carboxylate groups are deprotonated, which connect two Cd(II)

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