



A multifunctional chemical sensor based on a three-dimensional lanthanide metal-organic framework



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ABSTRACT

A 3D lanthanide MOF with formula $[\text{Sm}_2(\text{abtc})_{1.5}(\text{H}_2\text{O})_3(\text{DMA})] \cdot \text{H}_2\text{O} \cdot \text{DMA}$ (**1**) has been successfully synthesized via solvothermal method. Luminescence studies reveal that **1** exhibits dual functional detection benzyl alcohol and benzaldehyde among different aromatic molecules. In addition, **1** displays a turn-on luminescence sensing with respect to ethanol among different alcohol molecules, which suggests that **1** is also a promising luminescent probe for high selective sensing of ethanol.

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1. Introduction

In recent times, metal-organic frameworks (MOFs) as one of the emerging porous solid materials have attracted considerable attention for the numerous potential applications such as biomedicine [1], catalysis [2,3], storage and separation of gases [4] because of their large surface areas, tunable pore sizes, rich functionalities and high thermal stability [5,6]. Compared to MOFs based on transition metal ions, the design and fabricate of MOFs bearing lanthanide ions have attracted more great interest owing to their exceptional magnetic and optical properties arising from 4f electrons and unusual coordination natures typical of lanthanide ions [7–9]. The synthesis of lanthanide MOFs with unique structures and accompanying excellent properties, elaborate selection of organic ligands plays an important roles to a great extent. By now, many aromatic multicarboxylate ligands [10–12] have been successfully used to construct lanthanide coordination polymers. Our group have focused on use 3, 3', 5, 5'-azobenzene-tetracarboxylic acid (H_4abtc) to construct lanthanide coordination polymers, recently [13,14]. For example, in the previous work, we reported a 1D anionic lanthanide coordination polymer based on H_4abtc as an adsorbent to selectively capture anionic dyes [15].

Benzyl alcohol and benzaldehyde are important chemical raw

material. In addition, benzyl alcohol is often used as the solvent for spectinomycin hydrochloride injection and an excipient in diclofenac injections [16–18]. Benzaldehyde can be used as a fragrance and flavoring additive in soap, cosmetics and food [19]. It is important to keep the concentration dose does not exceed the normal range since it can produce undesirable effects on public's health and seriously pollute the environment. In addition, alcohol are widely used in the clinical analysis and food industry. Especially, it is crucial to monitor ethanol during fermentation processes in biotechnological production of beverages to ensure food quality and safety [20]. Thus, it is necessary to have a cost-effective, simple, and convenient method for the detection of benzaldehyde, benzyl alcohol and ethanol. Amongst the generally employed analytical tools, which include chromatography, colorimetric detection and electrochemical, MOF based luminescence detection is most attractive owing to its simple preparation, rapid detection and high sensitivity [21–25]. To the best of our knowledge, although various luminescence MOFs have been extensively exploited for detecting, the selective detection of benzaldehyde [26] and benzyl alcohol have rarely been reported, to date.

In this paper, we report a new metal-organic framework composed of lanthanide metal ions and H_4abtc : $[\text{Sm}_2(\text{abtc})_{1.5}(\text{H}_2\text{O})_3(\text{DMA})] \cdot \text{H}_2\text{O} \cdot \text{DMA}$. Luminescent studies reveal that **1** can displays a significant luminescence enhancing for benzyl alcohol and quenching effect for benzaldehyde among the different aromatic molecules, thus, **1** can be used as a good candidate material to detect benzaldehyde in benzyl alcohol based injections, with

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potential applications in medicine. Moreover, **1** displays a turn-on luminescence sensing with respect to ethanol among different alcohol molecules. Our finding open directions for possible applications of MOFs in practical medicine and food safety management.

2. Experimental section

2.1. Materials and physical measurements

H₄abtc [27] was synthesized according to the reported literature. Other reagents and solvents were commercially purchased and used without further purification. X-ray powder diffraction (XRPD) intensities were collected on a Rigaku D/max-III A diffractometer with Cu K α radiation ($\lambda = 1.54056$ Å). Infrared spectra (KBr pellets) were recorded in the range of 400–4000 cm⁻¹ on a Perkin-Elmer spectrometer. Thermogravimetric analysis (TGA) were carried out using a NETZSCH TG 209 instrument under nitrogen stream with a temperature ramp of 10 °C min⁻¹ in the temperature range of 25–800 °C. The photoluminescence emission spectra were measured on an Edinburgh Instruments FLS920P fluorescence spectrometer.

2.2. Preparation of coordination polymer

Sm(NO₃)₃·6H₂O (0.2 mmol), H₄abtc (0.1 mmol), dimethylacetamide (DMA) (8 ml), H₂O (4 ml), and HNO₃ (0.8 ml) were placed in a 25 ml Teflon-lined stainless steel autoclave and heated at 130 °C for 48 h, then cooled down to room temperature. Orange block crystals of the product were obtained by filtration, washed with water, and air-dried. The obtained yield based on the H₄abtc were 36%. Anal. Calcd for C₃₂H₃₅N₅O₁₈Sm₂: C, 35.64; H, 3.27; N, 6.49. Found C, 35.74; H, 3.21; N, 6.57.

2.3. X-ray crystallography

Single crystal X-ray diffraction analyses were carried out on a Bruker SMART 1000 CCD diffractometer with Mo K α monochromated radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares fitting on F² using the SHELXL crystallographic software package [28]. Crystallographic and refinement details are summarized in Table 1. Selected bond lengths and bond angles are listed in Table S1 in the Supporting information†. Crystallographic information files corresponding to **1** have been deposited to Cambridge Crystallographic Data Centre (CCDC number 1046360).

Table 1
Crystal data and structure refinement for **1**.

1	
Empirical formula	C ₃₂ H ₃₅ N ₅ O ₁₈ Sm ₂
Formula weight	1078.37
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
a (Å)	11.038(2)
b (Å)	11.249(2)
c (Å)	16.132(3)
α (deg)	75.24(3)
β (deg)	82.80(3)
γ (deg)	75.26(3)
V (Å ³)	1869.3(7)
Z	2
R (int)	0.0294
Goodness-of-fit on F ²	1.032
R ₁ , wR ₂ [I > 2 σ (I)]	0.0463, 0.1489
R ₁ , wR ₂ (all data)	0.0523, 0.1557

3. Results and discussion

3.1. Description and discussion of the crystal structure

Single-crystal X-ray diffraction study reveals that **1** crystallizes in the triclinic crystal system with *P* $\bar{1}$ space group (Table 1). The asymmetric unit of **1** contains two crystallographically unique Sm³⁺ ions, one and a half of abtc⁴⁻ ligand, three coordinated water molecules, one coordinated DMA molecule, one free DMA molecule, as well as one lattice water molecule. In compound **1**, abtc⁴⁻ anions adopt two different coordination modes, one abtc⁴⁻ anion in μ_7 - η^9 coordination fashion and the remaining one in μ_6 - η^6 coordination fashion, as shown in Fig. 1b. Notably, there exists two types of Sm(III) ion environments (Fig. 1a). Sm1 is eight-coordinated and surrounded by seven oxygen atoms from six ligands and one oxygen from coordinated DMA molecule, whereas Sm2 is eight-coordinated with five oxygen atoms from four different ligands and three terminally coordinated water molecules. The Sm1-O and Sm2-O bond lengths are in the range of 2.328(5)–2.784(5) Å and 2.279(5)–2.503(5) Å, which fall into the Sm(III)-based compounds range values reported previously [29–31]. The adjacent two eight-coordinated Sm³⁺ centers (Sm1 and Sm2) in **1** are bridged together by two μ_2 - η^1 : η^1 carboxylate groups and one μ_2 - η^1 : η^2 carboxylate group from three different abtc⁴⁻ ligands to give a dinuclear subunit (SBU) with a Sm ··· Sm distance of 4.4441 (15) Å. The dinuclear subunit are bridged by abtc⁴⁻ ligands to form a layer (Fig. 1c), and the resulting layers are further interconnected to generate the final 3D coordination framework (Fig. 1d).

3.2. IR, PXRD and thermal analysis

The IR spectra of compound **1** was measured in the range of 400–4000 cm⁻¹, as shown in Fig. S1. In complex **1**, the absorbance at 3415 cm⁻¹ is attributed to O-H stretching vibration. The strong absorption at 1618 cm⁻¹ in complex is assigned to ν_{as} (C=O) stretching vibration of the carboxylic group. Bands in the region around 1700 cm⁻¹ are not observed, indicating that H₄abtc are all completely deprotonated in the polymer. As shown in Fig. S2, the PXRD patterns of the obtained crystalline samples closely match those simulated from the single crystal diffraction data, demonstrating a high phase purity of the samples. The thermal behavior of **1** has been measured to study the thermal stability of **1** from room temperature to 800 °C in a flowing nitrogen atmosphere. For **1**, a weight loss of 9.07% was observed in the temperature range of 25–300 °C, which corresponded to the loss of one free water molecule and one free DMA molecule. Then, there is a sharp weight loss, which is ascribed to the decomposition of the framework (Fig. S3).

3.3. Photoluminescent properties

The photoluminescence spectra of **1** and free ligand in the solid state at room temperature are given in Fig. S4. **1** shows a broadband emission centered at 612 nm under the excitation at 400 nm. Such broadband emission is assigned to the intraligand $\pi \leftarrow \pi^*$ transition of abtc⁴⁻, because the emission was observed at 622 nm ($\lambda_{ex} = 310$ nm) for the free H₄abtc ligand.

In order to examine the potential of **1** towards sensing of target aromatic molecules, we soaked finely ground samples of **1** (3 mg) in 4 ml different solvents (benzyl alcohol, benzene, 1, 2-dichlorobenzene, methylbenzene, ethylbenzene, benzaldehyde), treated by ultrasonication for 30 min, and then aged to form stable emulsions prior to luminescence measurements. As shown in Fig. 2 and 3a, the peak shifts and intensity changes in the emission spectra of the emulsions are clearly illustrated for the different solvent molecules. The emission intensities are largely dependent

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