



# A microscale multi-functional metal-organic framework as a fluorescence chemosensor for Fe(III), Al(III) and 2-hydroxy-1-naphthaldehyde

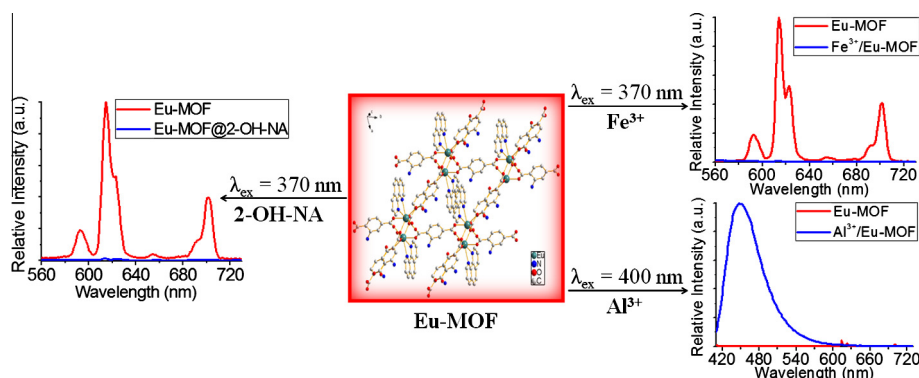


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## GRAPHICAL ABSTRACT

The Eu-MOFs could recognize  $\text{Fe}^{3+}$  and 2-hydroxy-1-naphthaldehyde (2-OH-NA) by quenching the emission of  $\text{Eu}^{3+}$  when excited by 370 nm, and detect  $\text{Al}^{3+}$  due to the enhancement of the ligand-based emission when excited by 400 nm.



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## ABSTRACT

A microscale metal-organic framework  $[\text{Eu}(\text{atpt})_{1.5}(\text{phen})(\text{H}_2\text{O})]_n$  ( $\text{H}_2\text{atpt}$  = 2-aminoterephthalic acid, phen = 1,10-phenanthroline) (Eu-MOF) was synthesized and characterized by elemental analysis, luminescence spectrum, powder X-ray diffraction, dynamic light scattering and scanning electron microscope. The fluorescence response of Eu-MOF to metal ions and aldehydes showed that Eu-MOF is highly selective to Fe(III), Al(III) and 2-hydroxy-1-naphthaldehyde (2-OH-NA). Eu-MOF could be utilized as a multi-functional fluorescence chemosensor for Fe(III), Al(III) and 2-hydroxy-1-naphthaldehyde (2-OH-NA). The detection limit of Fe(III), Al(III) and 2-OH-NA was 45, 10 and 36  $\mu\text{M}$ , respectively. The corresponding sensing mechanisms were explored.

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## 1. Introduction

Metal-organic frameworks (MOFs) have attracted great attention due to their unique structures and interesting properties. They have been widely applied for gas storage/separation, catalysis,

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magnetism and drug delivery [1–5]. In recent years, there are some reports about MOF-based sensors [6–9], in which the lanthanide MOFs (Ln-MOFs) are popular because of their superior luminescent properties: photostability, sharp emission bands and long luminescence lifetimes. For instance, europium- and terbium-organic frameworks emit red and green light, respectively. Their lifetimes are in the range of milliseconds.

In fact, some Ln-MOFs have been successively developed for the sensing of metal ions [10–13], anions [14,15], small organic molecules [16], explosives [17,18], humidity [19] and pH value [20], and a few of the recognition mechanisms for metal ions and organic compounds have been illustrated. For instance, the sensing of Ln-MOFs to metal ions may be attributed to the following factors: (1) collapse of the crystal structure [21,22]; (2) cation exchange between the central metal ion of Ln-MOFs and targeted metal ions [23,24]; (3) the interaction between the metal ions and the organic ligands [25,26]. The sensing mechanism of Ln-MOFs for compounds might be attributed to the interaction between the analytes and Ln-MOFs on the surface/in the channels [27,28] or a competition of absorption of the light source energy [29,30].

The development of multifunctional MOF materials [31–33] is one of the most significant achievements in materials chemistry. The Ln-MOFs may be more suitable to be implemented as multifunctional sensors in comparison to other compounds because the diversified bridge ligands of Ln-MOFs usually have uncombined functional groups or uncoordinated sites. They are beneficial to form d-f complexes and transition metal complexes when sensing metal ions or to be modified at the surface when sensing organic molecules, resulting in fluorescence change of Ln-MOFs. And the Ln-MOFs could response to the analytes by not only the characteristic emission of lanthanide ions but also the luminescent properties of their ligands. In order to improve the selectivity and sensitivity, scaling down the size of MOFs [34,35] is often used as a method to increase the surface areas, so that the guest-host interaction is facilitated. It is important to select appropriate ligands which should own a binding site and a powerful luminophore in order to achieve a multi-functional sensor.

In the crystal of  $[\text{Eu}(\text{atpt})_{1.5}(\text{phen})(\text{H}_2\text{O})]_n$  (Eu-MOF) [36], the  $\text{Eu}^{3+}$  ion is coordinated by mixed ligands, of which atpt acts the role of bridge and light harvest antenna and phen helps to strengthen the antenna effects. When the collapse of the crystal structure occurs or the central metal ion is exchanged by other metal ions, the change of the emission intensity of  $\text{Eu}^{3+}$  will be enlarged due to the existence of phen. This will provide a method to improve the sensitivity. Meanwhile, the amino group of the bridge ligand atpt is free in Eu-MOF, which will provide the possibility to react with aldehydes. Therefore, we report that Eu-MOF could be used as a multi-functional chemosensor. Eu-MOF not only recognizes  $\text{Fe}^{3+}$  and 2-hydroxy-1-naphthaldehyde conformed by the quenching of  $\text{Eu}^{3+}$  emission, but also detects  $\text{Al}^{3+}$  by the enhancement of the ligand-based emission.

## 2. Experimental section

### 2.1. Material and instrumentation

$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  was prepared by dissolving  $\text{Eu}_2\text{O}_3$  in concentrated hydrochloric acid and then evaporating the solvents to dryness. The other reagents we used were of analytical grade and obtained from commercial sources without further purification. Ethanol solutions of metal ions were prepared from LiCl, NaCl, KCl,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{Al}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ . Fluorescence spectra and lifetimes were recorded on an Edinburgh FS5

spectrophotometer with a quartz cuvette (path length = 1 cm). The UV–Vis absorption spectra were carried out with a SHIMADZU UV-2600 spectrophotometer. The C, H, N microanalyses were performed with a Vario EL elemental analyzer. The powder X-ray diffraction (PXRD) were carried out on a PANalytical X'Pert PRO MPD diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), with a step size of  $0.017^\circ$  in  $2\theta$ . The Scanning electron microscope (SEM) image was conducted by S-4800. The dynamic light scattering (DLS) was recorded by a Brookhaven Zeta Plus Zeta Potential Analyzer. ESI-MS spectrum was measured with a Thermo LTQ XL mass spectrometer. The inductively coupled plasma (ICP) analysis was performed with a JY ULTIMA spectrometer.

### 2.2. Synthesis of Eu-MOF

Microparticles of Eu-MOF were synthesized from a conventional heating method [37].  $\text{H}_2\text{atpt}$  (0.3 mmol) and  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.2 mmol) were separately dissolved in 18 mL and 6 mL of the 0.1 mol/L NaAc/HAc buffer (pH 5.7), and phen (0.2 mmol) was solved in 2 mL EtOH. The solution of  $\text{H}_2\text{atpt}$  and the solution of phen were mixed well and heated up to  $100^\circ\text{C}$ , then the solution of  $\text{EuCl}_3$  was added. The mixture of  $\text{EuCl}_3$ ,  $\text{H}_2\text{atpt}$  and phen with a molar ratio of 1:1.5:1 was allowed to react for 4 h at  $100^\circ\text{C}$ . After cooling, the mixture was centrifuged with 15,000 r/min for 5 min. The obtained precipitate was washed with deionized water twice and EtOH once. Finally, the product was dried. Yield: 51.81% based on Eu. Elemental analysis (%) calcd for  $\text{C}_{24}\text{H}_{17.5}\text{EuN}_{3.5}\text{O}_7$ : C, 46.58; H, 2.85; N, 7.92. Found: C, 46.44; H, 2.93; N, 7.89.

### 2.3. Luminescent sensing experiment

The dispersed solution of Eu-MOF with a concentration of 1 mM (based-on  $\text{Eu}^{3+}$  ion) was prepared in ethanol, and ethanol solutions of 10 mM metal ions and 10 mM aldehydes were stocked. The selectivity of Eu-MOF to analytes was measured with the concentration of 0.1 mM Eu-MOF and 1.0 mM analytes. The titration experiments were carried out by taking 0.1 mM Eu-MOF with the increasing concentration of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and 2-hydroxy-naphthaldehyde, respectively.

## 3. Results and discussion

### 3.1. Properties of Eu-MOF

$[\text{Eu}(\text{atpt})_{1.5}(\text{phen})(\text{H}_2\text{O})]_n$  crystals have been prepared by hydrothermal method [36].

In this work, the Eu-MOF particles were synthesized by a conventional method. As seen in Fig. 1a, the SEM image showed that most of the particles are hexagonal and the size of the heterogeneous particles was about  $1 \mu\text{m}$ . The dynamic light scattering analysis revealed the particle size mainly falls in the range of  $1.185\text{--}1.220 \mu\text{m}$  (Fig. 1a). To confirm the phase purity, X-ray diffraction analysis was carried out. As shown in Fig. 2, the peak positions and the relative intensity of simulated and experimental patterns are in good agreement with each other, which indicates the prepared microparticles are isostructural to the reported Eu-MOF [36].

Ethanol was used as the detection medium in order to disperse the particles homogeneously. Before studying the selectivity of Eu-MOF to metal ions and compounds, we first examined its luminescent property in ethanol solution (Fig. S1). The excitation spectrum of Eu-MOF exhibited a broad band centered at 370 nm when monitored by 614 nm of  $\text{Eu}^{3+}$  emission. When excited by 370 nm, the characteristic emission bands of Eu-MOF at 594, 614, 656 and 701 nm, which are attributed to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $j = 1\text{--}4$ ) transitions

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