

A tubular europium–organic framework exhibiting selective sensing of Fe³⁺ and Al³⁺ over mixed metal ions†

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A luminescent europium–organic framework with tubular channels based on the H₄BTMIPA ligand (H₄BTMIPA = 5,5′-methylenebis(2,4,6-trimethylisophthalic acid)) was assembled and characterized. The [H₂N(CH₃)₂]⁺ ions as counterions are located in the channels. The cation exchange between [H₂N(CH₃)₂]⁺ and metal ions resulted in complex **1 that can selectively sense Fe³⁺ and Al³⁺ ions through fluorescence quenching and enhancement, respectively.**

Iron and aluminium are two important metals in industry.¹ However, their cationic forms, Fe³⁺ and Al³⁺, have different influences on the human body and other biological tissues. Fe³⁺ ions play an essential part in a variety of vital cell functions such as hemoglobin formation, muscle and brain function, and electron transfer processes in DNA and RNA synthesis.² But excess amounts of Fe³⁺ in a living cell may cause damage to nucleic acids and proteins through catalyzing the production of reactive oxygen species (ROS).³ Conversely, aluminum is not a trace element necessary for the human body, and its concentration level in the human body has a direct impact on human health.⁴ Due to the frequent use of aluminum foil and vessels, the risk of absorption of Al³⁺ ions by the human body is increasing. The iron binding protein can carry Al³⁺ ions to enter the brain to damage the central nervous system.⁵ Al³⁺ and Fe³⁺ have been implicated as some of the causative factors in Alzheimer's disease. Hence, selective detection or sensing of Fe³⁺ and Al³⁺ over other metal ions seems to be very important for human health.

Although various analytical techniques such as spectrophotometry, voltammetry and atomic absorption spectroscopy have been developed for determination of iron,⁶ some other metal ions were shown to interfere, which makes the pretreatment

more complicated. Recently, fluorescent sensors have been considered as some of the promising and compelling devices for sensing metal ions or other small molecules.^{7–9} Of particular interest are luminescent lanthanide–organic frameworks due to their potential applications in fluorescence probes and luminescence bioassays.^{10,11} In the past decade, studies on luminescent Ln–MOFs for sensing metal ions or organic molecules have been developed significantly, and some excellent studies have reported selective sensing of metal ions such as Cu²⁺, Fe³⁺, *etc.* In particular, Chen and coworkers pioneered the luminescent Ln–MOF with Lewis basic pyridyl sites or open metal sites to sense Cu²⁺ ions or small molecules through partial fluorescence quenching.¹² Very recently, a luminescent europium–organic framework with chelating terpyridine sites for sensing Fe³⁺ was also documented.¹³ Unfortunately, selective sensing of Fe³⁺ and Al³⁺ without the interference of other mixed metal ions through fluorescence quenching and enhancement, respectively, in a luminescent Ln–MOF has never been explored. In this communication, we report a tubular europium–organic framework, [H₂N(CH₃)₂][Eu(H₂O)₂(BTMIPA)]·2H₂O (**1**) (H₄BTMIPA = 5,5′-methylenebis(2,4,6-trimethylisophthalic acid)), that can selectively sense Fe³⁺ and Al³⁺ through a cation-exchange approach. Although excellent work on a highly selective fluorescent probe for detection of Fe³⁺ through a cation-exchange approach was reported by Sun and coworkers recently,¹⁴ the advantage of **1** is that it can sense Fe³⁺ and Al³⁺ through fluorescence quenching and enhancement, respectively. Especially, the selectivity to Fe³⁺ and Al³⁺ is not interfered by Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Zn²⁺, Cd²⁺, Co²⁺, Pb²⁺.

The structure of **1** was determined by single-crystal X-ray diffraction study. As shown in Fig. 1, the electrically anionic framework is constructed using single Eu³⁺ as a building block bridged by deprotonated BTMIPA ligands. The counterions of [H₂N(CH₃)₂]⁺ are located in the channels to balance the charge. In the anionic framework, each BTMIPA ligand links four Eu³⁺ ions, each carboxylate group of the BTMIPA ligand coordinates one Eu³⁺ ion using its four carboxylate groups, three of which adopt chelating mode and the fourth one adopts a monodentate coordination mode. The central Eu³⁺ ion is coordinated by seven oxygen atoms of BTMIPA ligands and two coordinated water molecules. Thus, the central Eu³⁺ ions were connected by BTMIPA ligands through their three chelating carboxylate

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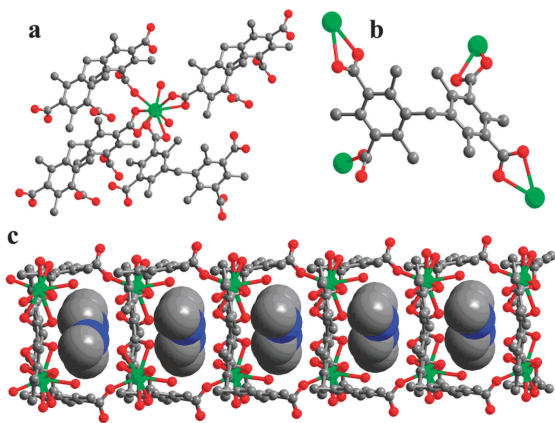


Fig. 1 The coordination environment of Eu^{3+} ions in **1** (a), the linking mode of the BTMIPA ligand (b), and the 2D tubular framework of **1** with the counterions of $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ in a space-filling mode (c). (Oxygen atoms are in red, carbon atoms are in gray, europium atoms are in light green and nitrogen atoms are in deep blue.)

groups to generate a 1D stitching needle-like ladder (Fig. S1†), which was further connected to the monodentate-coordinated carboxylate groups to give rise to a 2D tubular framework with the dimensions of $5.0 \times 8.0 \text{ \AA}$, in which $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ resides (Fig. 1c).

The luminescence spectra of **1** are shown in Fig. S3.† Complex **1** exhibits luminescence at $\lambda_{\text{max}} = 593, 617, 653, 696 \text{ nm}$, upon excitation at 395 nm . The emissions of **1** show the characteristic transitions of Eu^{3+} ions and can probably be assigned to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1, {}^5\text{D}_0 \rightarrow {}^7\text{F}_2, {}^5\text{D}_0 \rightarrow {}^7\text{F}_3, {}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transitions, respectively.

As mentioned above, $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ is located in the channels of the anionic framework, providing us a chance to study the ion-exchange behavior and its effect on luminescence properties. The results of energy-dispersive X-ray spectroscopy (EDS) analyses, inductively coupled plasma-atomic emission spectrometry (ICP-AES) and powder X-ray diffraction (PXRD) clearly demonstrate the ion-exchange behaviour (Fig. S14–S16†). To examine the potential of **1** for the sensing of metal ions through cation exchange, the as-synthesized samples were ground and suspended in DMF solution containing different metal ions ($\text{Na}^+, \text{Li}^+, \text{K}^+, \text{Cu}^+, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cr}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Al}^{3+}, \text{Fe}^{3+}$). The luminescent properties are recorded and shown in Fig. 2. Interestingly, most metal ions have varying degrees of quenching effects on the luminescence intensity. For example, the luminescence intensity at 617 nm is about half of the original one when Cu^+ and Cu^{2+} ions are involved, and Fe^{3+} ions can almost quench the luminescence of **1**. However, when Al^{3+} ions are present, the luminescence intensity is enhanced compared to the original one. As shown in the inset of Fig. 2, under the irradiation of UV light of 365 nm , the samples after being immersed in DMF solutions containing different metal ions showed red color, except for Fe^{3+} ions that showed dark color. These results indicate that complex **1** can selectively sense Fe^{3+} ions through fluorescence quenching and Al^{3+} ions through fluorescence enhancement, which was quite rare in the previous reports on luminescent MOFs.

To further prove that the fluorescence quenching and enhancement are caused by a cation exchange process, detailed studies on the luminescence properties of **1** when Fe^{3+} and Al^{3+} ions are present, were carried out. The ground sample of **1** was suspended in DMF solutions containing Fe^{3+} and Al^{3+} ions and time-dependent luminescence measurements were carried out (Fig. S4a and b†).

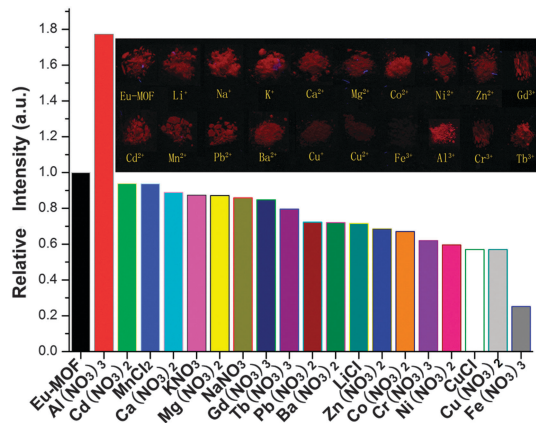


Fig. 2 Photoluminescence intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition (617 nm) of **1** treated with different metal ions (10^{-3} M) in DMF solution for 72 hours. Inset: the colors of the treated samples with different metal ions under the irradiation of UV light of 365 nm .

With increasing time, the PL intensity decreases for the Fe^{3+} -loaded sample, but increases for the Al^{3+} -loaded sample, which indicate that after the $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cations in the channels were replaced by Fe^{3+} and Al^{3+} , they have a significant effect on the fluorescence emissions. Concentration-dependent luminescence measurements were also carried out (Fig. S4c and d†). However, the PL intensities for Fe^{3+} - and Al^{3+} -loaded samples are quite different upon the increase of the concentration. For the Fe^{3+} -loaded sample, the PL intensity decreases gradually and there is a sharp decrease at a concentration of 0.001 mol L^{-1} . When the concentration reaches 0.01 mol L^{-1} , the luminescence quenches completely. However, for the Al^{3+} -loaded sample, the PL intensity increases gradually and reaches a maximum at a concentration of 0.001 mol L^{-1} , and after that, the intensity decreases gradually. So we chose the suitable concentration to be 0.01 mol L^{-1} for Fe^{3+} ions and 0.001 mol L^{-1} for Al^{3+} ions for subsequent experiments. At the same time we discovered that the framework of **1** dissolved gradually when the concentration was greater than 0.001 mol L^{-1} for Al^{3+} and Fe^{3+} (Fig. S10†). On the basis of these results, we report a mechanism: firstly, Fe^{3+} and Al^{3+} were exchanged with the $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cations in the channels at the low concentration, which led to the partial fluorescence quenching and enhancement gradually. The mechanism for enhancement and quenching of the emission intensity has been provided in ESL.† Secondly, with the concentration increasing to 0.001 mol L^{-1} where the exchange between $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ and $\text{Fe}^{3+}/\text{Al}^{3+}$ is complete, the framework of **1** collapsed which may have been caused by the exchange between $\text{Fe}^{3+}/\text{Al}^{3+}$ and Eu^{3+} (Fig. S9†),¹³ resulting in the decrease in the PL intensity of the Al^{3+} -loaded sample. When the concentration of $\text{Al}^{3+}/\text{Fe}^{3+}$ reaches 0.01 mol L^{-1} , the framework of **1** collapses completely (Fig. S10†). However, for other metal ions, **1** would not collapse, which can be proved by determining the luminescence properties of the filtrate. For example, there are no characteristic emissions of Eu^{3+} ions for Ca^{2+} - and Cd^{2+} -loaded samples (Fig. S11†). In order to further confirm this two processes are isolated. The solid-state luminescence spectra of the solid sample after immersion were also investigated which eliminated the possible influence of collapse of **1** or formation of new complexes (Fig. S17†). We obtained similar luminescence spectra and the fluorescence intensity for Al^{3+} -loaded samples was stronger than the liquid fluorescence which proved that the fluorescence quenching occurred partly and enhancement gradually caused

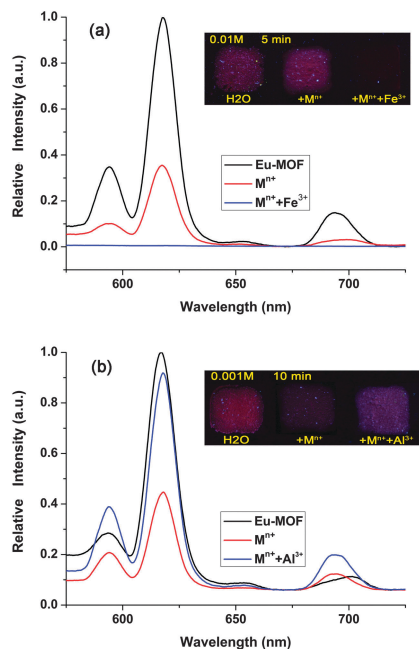


Fig. 3 Comparison of the photoluminescence intensity of **1** exchanged with M^{3+} ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+}) in the absence and presence of 0.01 M Fe^{3+} (a) and 0.001 M Al^{3+} (b). Inset: optical images of the test plates under the irradiation of UV light of 365 nm.

by the exchange between $[H_2N(CH_3)_2]^+$ and Fe^{3+}/Al^{3+} . In addition, the fluorescence lifetime of the Eu-MOFs was studied (Fig. S18†).

To make the detection simple and portable, we prepared a test plate for sensing metal ions. Hence, the detection of Fe^{3+} and Al^{3+} in aqueous solution was carried out. In order to check the high selectivity to Fe^{3+} and Al^{3+} ions over other metal ions, the test plates were immersed in an aqueous solution containing mixed metal ions (the mixed ions can be Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+}) for several minutes, and then exposed to air for drying. Under the irradiation of UV light of 365 nm, to the naked eye, the test plate showed a pink color, which was slightly different from the original one. The emission spectrum of the mixed-ion-loaded sample decreases significantly, compared to the original one, as shown in Fig. 3a. However, when the test plate was immersed in an aqueous solution containing mixed metal ions including Fe^{3+} ions, the test plate showed a dark color; the color difference was easily distinguishable by the naked eye. The measurement of the emission spectrum shows that the luminescence is quenched completely, indicating that the selectivity for Fe^{3+} ions is not interfered by the existence of other metal ions. The detection of Al^{3+} ions over other metal ions was also carried out following the same procedure as for Fe^{3+} ions. Although one cannot easily distinguish the color difference of the test plates for Al^{3+} ions by the naked eye, the emission spectrum shows that the intensity decreases significantly when Al^{3+} ions are absent, but remains almost unchanged when Al^{3+} ions are present, as shown in Fig. 3b. In the past decade, although many excellent studies concerning luminescent MOFs for selectively sensing metal ions were reported, in which several Ln-MOFs can sense Fe^{3+} ions with high selectivity, complex **1** represents, to the best of our knowledge, the first example that can selectively sense Fe^{3+} and Al^{3+} ions through fluorescence quenching and enhancement, respectively, without the interference of the other mixed metal ions present.

In conclusion, a luminescent europium-organic framework (**1**) with tubular channels based on a semirigid carboxylate ligand was synthesized and characterized. The $[H_2N(CH_3)_2]^+$ ions as counterions are located in the channels and can be exchanged with other metal ions. The cation exchange resulted in complex **1** that can selectively sense Fe^{3+} and Al^{3+} ions through fluorescence quenching and enhancement, respectively. The significant property of **1** is that the selectivity to Fe^{3+} and Al^{3+} ions is not subject to interference by other mixed metal ions, which makes **1** possess potential applications in fluorescence probes. The present results may provide a facile route to design and synthesize functional MOFs with applications in fluorescent sensors.

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