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# The construction of Tb<sup>3+</sup> doped Sr–BDC metal–organic framework materials and their high-sensitivity fluorescent detection of Fe<sup>3+</sup>

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This study presents the synthesis of a strontium-based metal–organic framework (Sr–BDC) through a solvothermal method, employing strontium chloride and terephthalic acid as primary precursors. The as-prepared Sr–BDC was subsequently functionalized with terbium ions (Tb<sup>3+</sup>) to yield a Tb<sup>3+</sup>@Sr–BDC composite. Extensive structural characterization, including X-ray diffraction (XRD), thermogravimetric analysis (TG), and the scanning electron microscope (SEM), confirmed that the Tb<sup>3+</sup> incorporation preserved the integrity of the Sr–MOF framework without inducing structural degradation. Photoluminescence analysis demonstrated that Tb<sup>3+</sup>@Sr–BDC exhibits distinct Tb<sup>3+</sup> emission peaks at 545 nm upon excitation at 294 nm, showcasing exceptional selectivity and sensitivity toward Fe<sup>3+</sup> ions. Stern–Volmer quenching analysis revealed a remarkably low detection limit of  $7.3 \times 10^{-6}$  mol L<sup>-1</sup> for Fe<sup>3+</sup>, with a linear response range spanning from  $5 \times 10^{-6}$  to  $1 \times 10^{-4}$  mol L<sup>-1</sup>. The potential mechanisms responsible for Fe<sup>3+</sup>-induced fluorescence quenching in Tb<sup>3+</sup>@Sr–BDC was also analysed in the study. These results underscore the potential of Tb<sup>3+</sup>@Sr–BDC as a highly efficient fluorescent probe for applications in environmental monitoring and biomedical sensing.

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## 1 Introduction

With the rapid advancements in analytical chemistry and materials science, there is an increasing demand for fluorescent sensing materials with high sensitivity and selectivity.<sup>1,2</sup> This is particularly critical in environmental monitoring and biomedical applications,<sup>3,4</sup> where the detection of metal ions such as iron (Fe<sup>3+</sup>) is of paramount importance.<sup>5,6</sup> Iron ions not only play a vital role in biological systems but are also frequently detected in industrial wastewater and environmental pollutants. Rare-earth metal–organic frameworks (Ln–MOFs) have emerged as a research hotspot in the field of fluorescent sensing<sup>7,8</sup> due to their unique porous structures and tunable chemical functionalities, offering broad application prospects for the detection of cations, anions, small organic molecules, and biomolecules.<sup>9–15</sup>

Metal–organic frameworks (MOFs) possess tunable porosity and abundant active sites, and have demonstrated great potential in electronics,<sup>16</sup> photocatalysis,<sup>17,18</sup> and other fields. Post-synthetic modification (PSM) strategies<sup>19–25</sup> further extend their application in highly sensitive detection. Embedding photoactive Ln<sup>3+</sup> ions into MOF lattices offers significant advantages:

the intrinsic porosity of the MOF is preserved, while characteristic lanthanide emission—long fluorescence lifetimes, narrow emission bands, and large Stokes shifts—is introduced. Compared with conventional luminescent probes, this approach markedly improves the signal-to-noise ratio and thus detection sensitivity, especially in biological systems with endogenous organic fluorescence. However, the high and variable

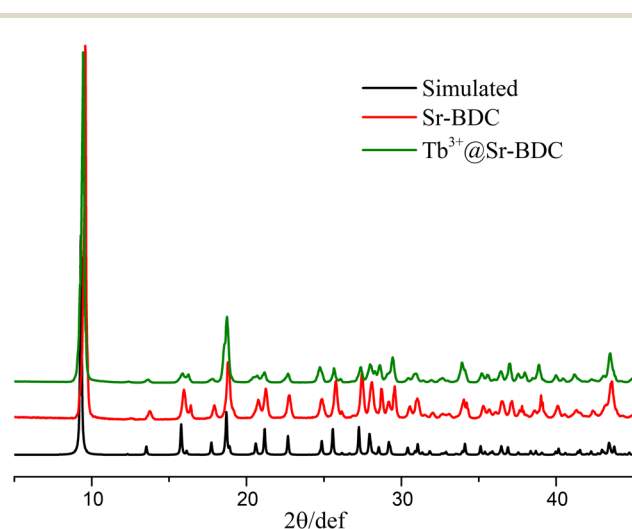


Fig. 1 X-ray powder diffraction (XRD) patterns of Sr–BDC and Tb<sup>3+</sup>@Sr–BDC.

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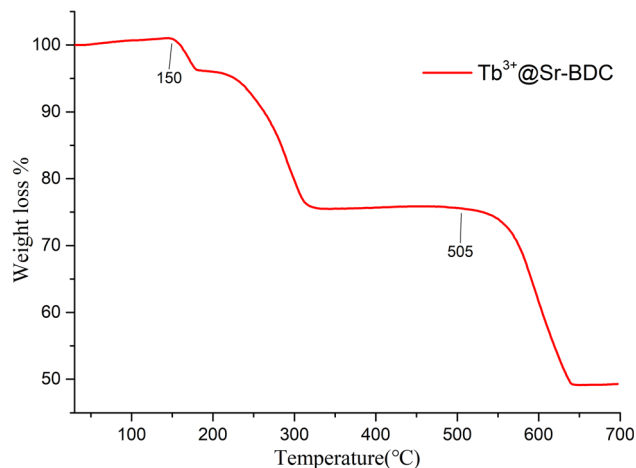


Fig. 2 Thermogravimetric analysis (TGA) curve of  $\text{Tb}^{3+}$ @Sr-BDC.

coordination numbers of rare-earth ions<sup>26</sup> render the direct synthesis of targeted Ln-MOFs challenging. Terbium(III), with its unique electronic configuration and excellent luminescence properties, has been widely used to construct high-performance fluorescent probes. In this work, we employed a post-synthetic modification strategy to embed  $\text{Tb}^{3+}$  into the Sr-BDC framework, yielding a novel fluorescent probe for the efficient detection of  $\text{Fe}^{3+}$ .

Among rare-earth ions, terbium ( $\text{Tb}^{3+}$ ) is widely utilized for constructing high-performance fluorescent probes due to its unique electronic configuration and luminescent properties. In

this study, we employed a post-synthetic modification strategy to incorporate  $\text{Tb}^{3+}$  into the Sr-BDC framework, successfully developing a novel fluorescent probe for the highly efficient detection of  $\text{Fe}^{3+}$ .

## 2 Materials and methods

### 2.1. Reagents and instruments

Strontium chloride hexahydrate ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ), terephthalic acid ( $\text{H}_2\text{BDC}$ ), *N,N*-dimethylacetamide (DMA), terbium(III) nitrate hexahydrate ( $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), copper(II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), chromium(III) nitrate nonahydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), iron(III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), potassium nitrate ( $\text{KNO}_3$ ), sodium chloride ( $\text{NaCl}$ ), cobalt(II) nitrate ( $\text{Co}(\text{NO}_3)_2$ ), cadmium(II) nitrate ( $\text{Cd}(\text{NO}_3)_2$ ), silver nitrate ( $\text{AgNO}_3$ ), zinc(II) nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), lead(II) nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), and absolute ethanol were purchased as analytical-grade reagents and further purified prior to use. All the reagents above were purchased from Macklin.

Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449F3 instrument under a nitrogen atmosphere, with a temperature range of 30–700 °C and a heating rate of 10 °C  $\text{min}^{-1}$ . X-ray diffraction (XRD) patterns were collected at room temperature using a Rigaku Miniflex 600 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Fluorescence spectra were recorded at room temperature using a Horiba-HR320 fluorescence spectrophotometer.

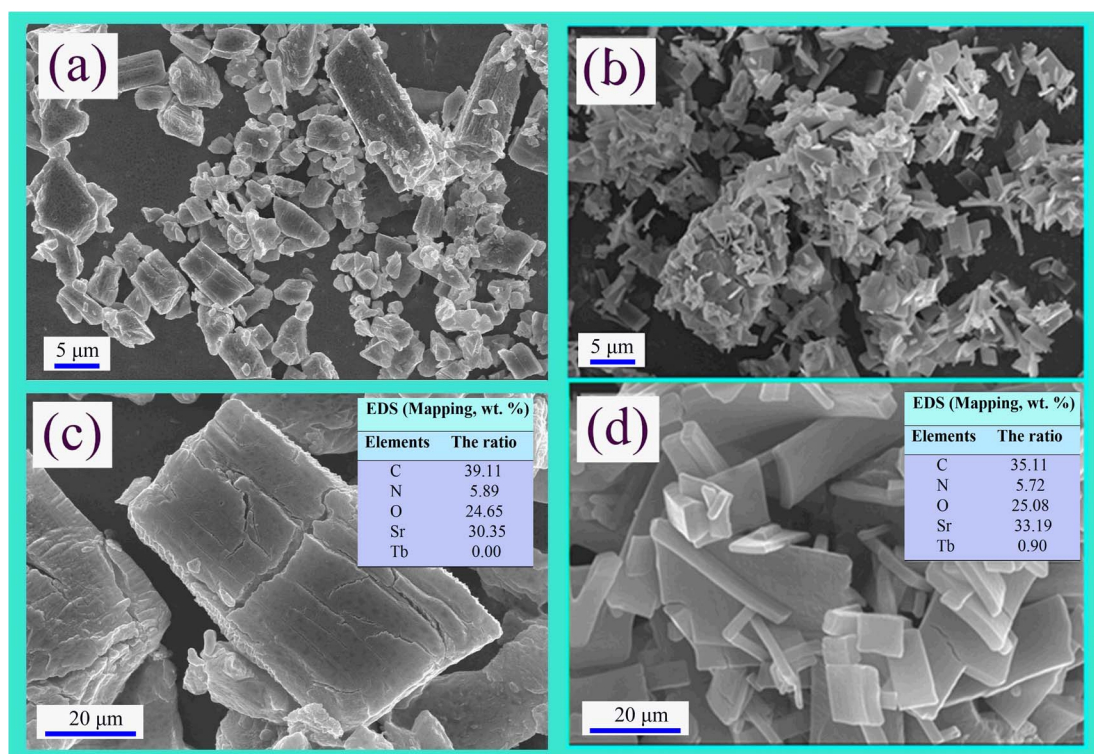


Fig. 3 The SEM images and EDS of the Sr-BDC and  $\text{Tb}^{3+}$ @Sr-BDC (SEM images: (a) Sr-BDC; (c)  $\text{Tb}^{3+}$ @Sr-BDC. EDS (mapping): (b) Sr-BDC; (d)  $\text{Tb}^{3+}$ @Sr-BDC).



The microstructural characterization of the specimens was performed using a Hitachi SU-5000 field-emission scanning electron microscope (FE-SEM, Hitachi High-Tech, Japan) operated at an acceleration voltage of 5–10 kV under high-vacuum conditions. Elemental distribution analysis was conducted *via* energy-dispersive spectroscopy (EDS) utilizing a Bruker Quantax system (Bruker, Germany).

## 2.2. Synthesis of Sr-BDC and Tb<sup>3+</sup>@Sr-BDC

The synthesis methods and technique were similar with that provided in the previous studies.<sup>27</sup> A mixture of strontium chloride hexahydrate (SrCl<sub>2</sub>·6H<sub>2</sub>O, 0.1 mmol, 26.6 mg) and terephthalic acid (H<sub>2</sub>BDC, 0.1 mmol, 16.6 mg) was dissolved in 3 mL of *N,N*-dimethylacetamide (DMA). The solution was transferred into a stainless steel autoclave lined with a polytetrafluoroethylene (PTFE) inner tube and heated at 80 °C for 72 h. After the reaction, the autoclave was allowed to cool naturally to room temperature. The resulting colorless block crystals were collected by filtration, washed thoroughly, and dried in air. The final product was weighed for further use.

To prepare Tb<sup>3+</sup>@Sr-BDC, the as-synthesized Sr-BDC powder (100 mg) was immersed in 50 mL of an ethanolic solution of terbium(III) nitrate hexahydrate (Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), with a Tb(NO<sub>3</sub>)<sub>3</sub> concentration of 10<sup>-2</sup> mol L<sup>-1</sup>, for 24 h. The powder was then separated by centrifugation, washed three times with ethanol, and dried in air for 24 h.

## 3 Results and discussion

### 3.1. The property and structure of the samples

The X-ray powder diffraction (XRD) patterns of Sr-BDC and Tb<sup>3+</sup>@Sr-BDC were recorded at room temperature (Fig. 1). The experimental diffraction peaks of Sr-BDC align well with the simulated pattern (CCDC: 1551141), confirming the synthesis of the Sr-BDC framework. Notably, the diffraction peak positions remain unchanged after Tb<sup>3+</sup> doping, suggesting that Tb<sup>3+</sup> ions partially substitute Sr<sup>2+</sup> sites within the original framework

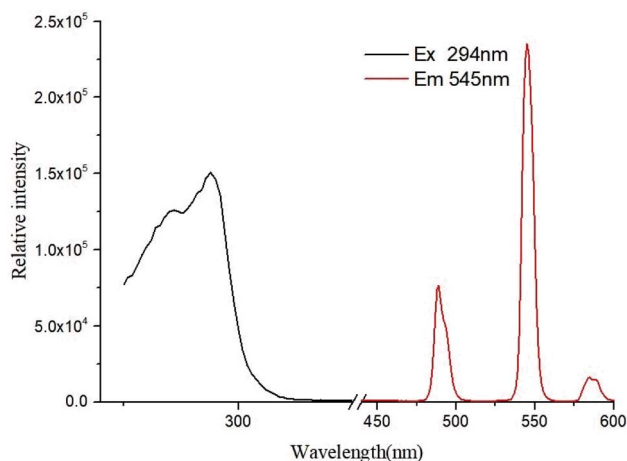


Fig. 4 Excitation (black line) and emission (red line) spectra of Tb<sup>3+</sup>@Sr-BDC.

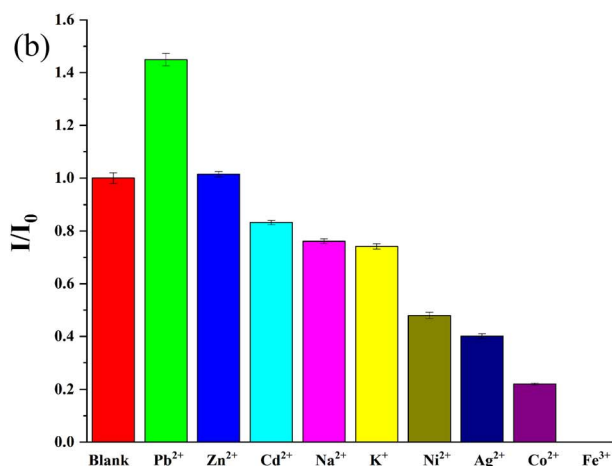
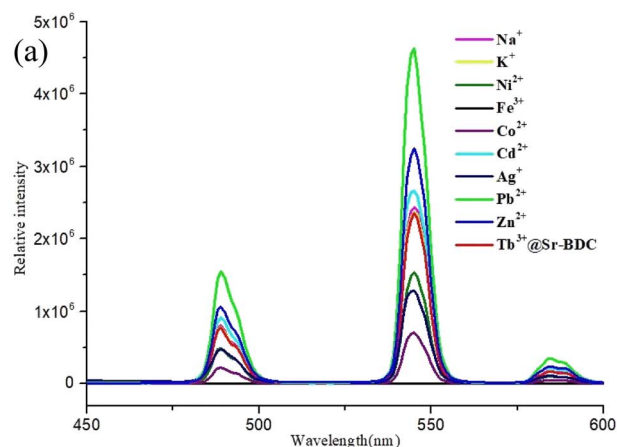


Fig. 5 (a) Emission spectra of Tb<sup>3+</sup>@Sr-BDC in the presence of various metal ions ( $\lambda_{\text{ex}} = 294$  nm) and (b) intensity of the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition at 545 nm for Tb<sup>3+</sup>@Sr-BDC in the presence of blank ( $I_0$ ) and the different metal ions solution ( $I$ ).

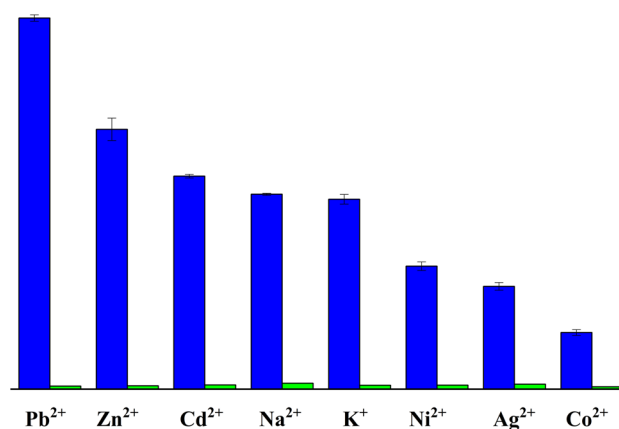


Fig. 6 Intensity of the  $^5\text{D}_4 \rightarrow ^7\text{F}_J$  transitions for Tb<sup>3+</sup>@Sr-BDC upon addition of different metal ions ( $1 \times 10^{-3}$  M, blue bars) and subsequent introduction of Fe<sup>3+</sup> ( $1 \times 10^{-3}$  M, green bars) ( $\lambda_{\text{ex}} = 294$  nm).

while preserving its structural integrity. This observation indicates that Tb<sup>3+</sup>@Sr-BDC retains the same crystallographic structure as the parent Sr-BDC.



Thermogravimetric analysis (TGA) of  $\text{Tb}^{3+}@Sr\text{-BDC}$  was conducted in the temperature range of 30–700 °C (Fig. 2). The initial weight loss (150–320 °C) corresponds to the removal of free and coordinated DMA solvent molecules. The Sr-BDC complex (chemical formula:  $\text{C}_{12}\text{H}_{15}\text{NO}_6\text{Sr}$ ) exhibited an experimental weight loss of 24.54% within the temperature range of 150–320 °C, demonstrating close agreement with the theoretical mass percentage (24.41%) calculated for the coordinated dimethylacetamide molecule ( $\text{C}_4\text{H}_9\text{NO}$ ) in its crystal structure. At approximately 505 °C, a structural collapse of the Sr-BDC framework occurs.

Microstructural characterization revealed that  $\text{Tb}^{3+}@Sr\text{-BDC}$  crystals (Fig. 3c and d) exhibited well-faceted short-rod or plate-like morphologies, in contrast to the irregular granular particles observed in undoped Sr-BDC (Fig. 3a and b). Energy-dispersive X-ray spectroscopy (EDS) confirmed the presence of trace Tb (0.90 wt%, Fig. 3d) in  $\text{Tb}^{3+}@Sr\text{-BDC}$ , while no detectable terbium signal was observed in Sr-BDC. These results demonstrate successful  $\text{Tb}^{3+}$  incorporation into the crystal lattice, which significantly modified the crystallization kinetics and consequently altered the morphological evolution of the crystals.

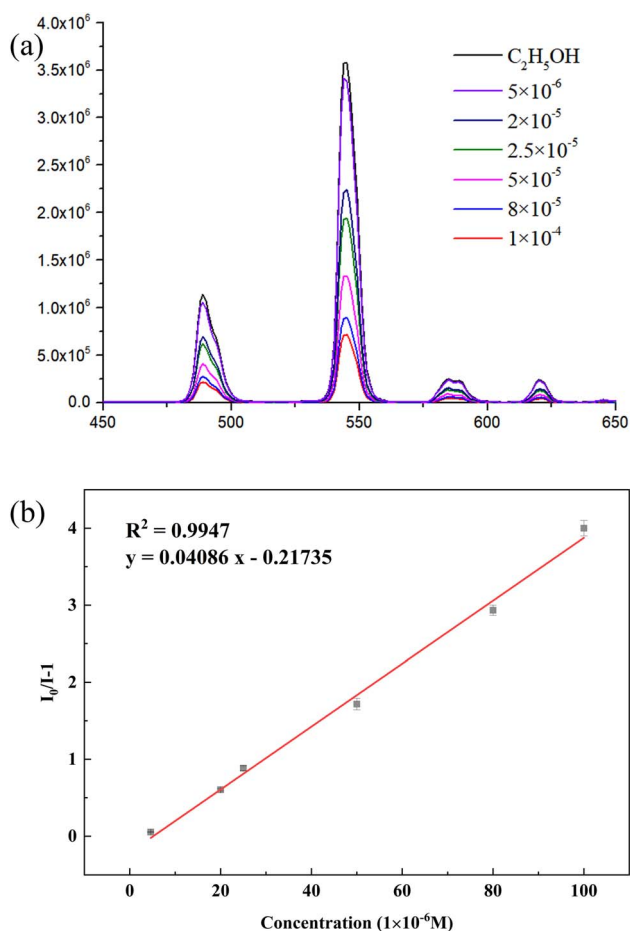


Fig. 7 (a) Emission spectra of  $\text{Tb}^{3+}@Sr\text{-BDC}$  in ethanol solutions with varying  $\text{Fe}^{3+}$  concentrations ( $\lambda_{\text{ex}} = 294$  nm) and (b) linear relationship between the luminescence intensity of  $\text{Tb}^{3+}$  and  $\text{Fe}^{3+}$  concentration in the range of  $1 \times 10^{-4}$  to  $5 \times 10^{-6}$  mol  $\text{L}^{-1}$ .

### 3.2. Luminescence properties of $\text{Tb}^{3+}@Sr\text{-BDC}$

As illustrated in Fig. 4, the  $\text{Tb}^{3+}@Sr\text{-BDC}$  material exhibits characteristic emission peaks of  $\text{Tb}^{3+}$  ions at 489 nm, 545 nm, and 583 nm under 294 nm excitation. These peaks are attributed to the electronic transitions of  $^5\text{D}_4 \rightarrow ^7\text{F}_J$  ( $J = 6, 5, 4$ ) within  $\text{Tb}^{3+}$  ions. Notably, the intense green emission at 545 nm suggests that this material can serve as an efficient luminescent sensor.

To evaluate the fluorescence sensing capability of  $\text{Tb}^{3+}@Sr\text{-BDC}$ , its luminescent properties were investigated in the presence of various metal cations. The  $\text{Tb}^{3+}@Sr\text{-BDC}$  powder was finely ground and dispersed in ethanol to form a 5 mg  $\text{mL}^{-1}$  suspension. Subsequently, 200  $\mu\text{L}$  of the suspension was uniformly mixed with 3.8 mL of ethanol solutions containing 0.001 mol  $\text{L}^{-1}$  of  $\text{M}(\text{NO}_3)_x$  ( $\text{M} = \text{Pb}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Na}^+, \text{K}^+, \text{Ni}^{2+}, \text{Ag}^+, \text{Co}^{2+},$  and  $\text{Fe}^{3+}$ ). The luminescence spectra were recorded and are presented in Fig. 5. The results reveal that the luminescence intensity of  $\text{Tb}^{3+}$  ions is significantly influenced by the presence of different metal ions. The ratio ( $I/I_0$ ) of the fluorescence intensity at 545 nm for the sample after metal ion introduction ( $I$ ) to the  $\text{Tb}^{3+}@Sr\text{-BDC}$  sample ( $I_0$ ) was shown in Fig. 5b. The results suggest that  $\text{Fe}^{3+}$  induces pronounced luminescence quenching of  $\text{Tb}^{3+}@Sr\text{-BDC}$ , indicating its selective response to  $\text{Fe}^{3+}$ .

To further investigate the selectivity of  $\text{Tb}^{3+}@Sr\text{-BDC}$  for  $\text{Fe}^{3+}$ , the material was dispersed in ethanol solutions containing  $\text{Fe}^{3+}$  alongside other metal ions ( $\text{Pb}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Na}^+, \text{K}^+, \text{Ni}^{2+}$ ,

Table 1 Comparison of  $\text{Fe}^{3+}$  ion detection based on different MOF materials

MOF	LOD/(mol $\text{L}^{-1}$ )	Ref.
[Tb(BTB)(DMF)]	$10 \times 10^{-6}$	1
[ $\text{Zn}_2(\text{tpt})(\text{tda})_2$ ] $\cdot\text{H}_2\text{O}$	$4.72 \times 10^{-6}$	29
$\text{Eu}^{3+}@UiO-66$	$12.5 \times 10^{-6}$	30
Zn-MOF-74	$1.04 \times 10^{-6}$	31
Tb(3+@Zn-MOF	$7.5 \times 10^{-6}$	32
$\text{Tb}^{3+}@Sr\text{-BDC}$	$7.3 \times 10^{-6}$	This work

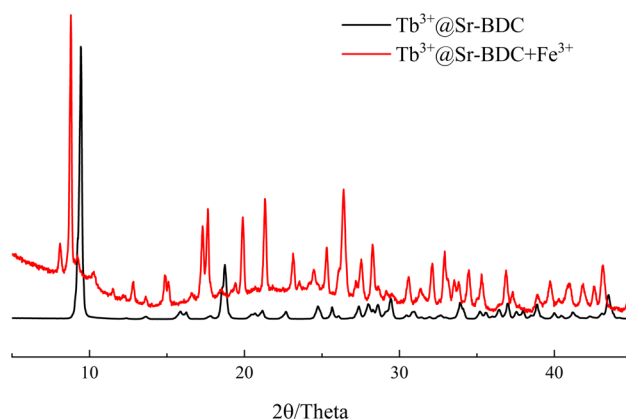


Fig. 8 XRD patterns of  $\text{Tb}^{3+}@Sr\text{-BDC}$  before and after treatment with iron ions.



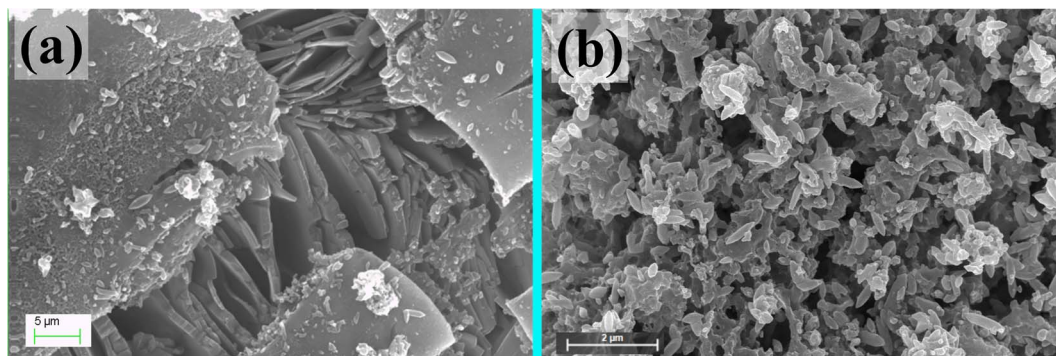


Fig. 9 SEM images of  $\text{Tb}^{3+}@\text{Sr-BDC}$  after treatment with  $\text{Fe}^{3+}$  at the microscopic scale.

$\text{Ag}^+$ , and  $\text{Co}^{2+}$ ). Under 294 nm excitation, the luminescence intensity of  $\text{Tb}^{3+}@\text{Sr-BDC}$  in the presence of individual metal ions (blue bars in Fig. 6) differs significantly from that in mixed-ion solutions containing  $\text{Fe}^{3+}$  (green bars in Fig. 6). When  $\text{Tb}^{3+}@\text{Sr-BDC}$  is immersed in ethanol solutions containing a mixture of  $1 \times 10^{-3} \text{ mol L}^{-1}$  of other metal ions and  $1 \times 10^{-3} \text{ mol L}^{-1}$  of  $\text{Fe}^{3+}$ , complete luminescence quenching is observed, demonstrating the material's selective detection capability for  $\text{Fe}^{3+}$  in complex environments.

To quantify the  $\text{Fe}^{3+}$  detection performance, a concentration gradient of  $\text{Fe}^{3+}$  solutions was prepared ( $1 \times 10^{-4} \text{ mol L}^{-1}$ ,  $2 \times 10^{-5} \text{ mol L}^{-1}$ ,  $2.5 \times 10^{-5} \text{ mol L}^{-1}$ ,  $5 \times 10^{-5} \text{ mol L}^{-1}$ ,  $8 \times 10^{-5} \text{ mol L}^{-1}$ , and  $5 \times 10^{-6} \text{ mol L}^{-1}$ ). A 0.2 mL aliquot of the 5 mg per mL  $\text{Tb}^{3+}@\text{Sr-BDC}$ -DMA suspension was mixed with 3.8 mL of each  $\text{Fe}^{3+}$  solution, and the luminescence intensity was measured using a fluorescence spectrophotometer (Fig. 7). The results demonstrate a well-defined linear relationship between  $\text{Fe}^{3+}$  concentration and the luminescence intensity of  $\text{Tb}@\text{Sr-BDC}$ , with the emission intensity decreasing progressively as  $\text{Fe}^{3+}$  concentration increases from  $5 \times 10^{-6}$  to  $1 \times 10^{-4} \text{ mol L}^{-1}$ . Stern-Volmer analysis of the  $\text{Tb}@\text{Sr-BDC} + \text{Fe}^{3+}$  system reveals a strong quenching effect, exhibiting a linear correlation coefficient ( $R$ ) of 0.9947. The limit of detection ( $\text{LOD} = 3\delta/S$ ,  $\delta$  represents the blank solution was measured ten times, and  $S$  stands for the slope of the calibration curve) was about  $7.3 \times 10^{-6} \text{ mol L}^{-1}$ .<sup>28</sup> Compared with the reported literature (Table 1), the  $\text{Tb}^{3+}@\text{Sr-BDC}$  sensor exhibits a markedly lower detection limit. These findings confirm that  $\text{Tb}@\text{Sr-BDC}$  not only enables qualitative identification but also facilitates quantitative detection of  $\text{Fe}^{3+}$  ions.

### 3.3. Quenching mechanism

The luminescence quenching mechanisms of cations can be attributed to four primary factors:<sup>33,34</sup> (1) interactions between

target metal ions and MOFs; (2) exchange between lanthanide ions in MOFs and central metal ions; (3) collapse of the crystalline structure; (4) energy competition between linkers and cations. To elucidate the potential sensing mechanism of  $\text{Fe}^{3+}$ -induced quenching in  $\text{Tb}^{3+}@\text{Sr-BDC}$ , comprehensive characterization was performed using XRD, SEM, and EDS before and after  $\text{Fe}^{3+}$  treatment. XRD patterns (Fig. 8) revealed distinct differences between  $\text{Fe}^{3+}$ -treated and untreated  $\text{Tb}^{3+}@\text{Sr-BDC}$ , indicating framework modification. SEM showed significant morphological alterations in the powdered samples (Fig. 3 and 9). EDS data (Table 2) confirmed the replacement of  $\text{Tb}^{3+}$  by  $\text{Fe}^{3+}$  in the framework. The quenching effect is likely caused by displacement of luminescent  $\text{Tb}^{3+}$  ions by  $\text{Fe}^{3+}$  and the concurrent framework collapse. This aligns with known cation-MOF interaction paradigms, where heavy metal ions disrupt lanthanide-centered emission through structural and electronic perturbations.

## 4 Conclusions

A strontium-based metal-organic framework (Sr-MOF) was synthesized *via* a solvothermal reaction using terephthalic acid ( $\text{H}_2\text{BDC}$ ) and strontium chloride ( $\text{SrCl}_2$ ) as precursors. The as-prepared Sr-BDC was further functionalized with terbium ions ( $\text{Tb}^{3+}$ ) to yield  $\text{Tb}^{3+}@\text{Sr-BDC}$ , which exhibited excellent luminescent properties. Fluorescence sensing studies revealed that  $\text{Tb}^{3+}@\text{Sr-BDC}$  demonstrates high sensitivity and selectivity toward  $\text{Fe}^{3+}$  ions, with a distinct linear correlation ( $R^2 > 0.99$ ) between fluorescence intensity and  $\text{Fe}^{3+}$  concentration. The detection limit was determined to be approximately  $7.3 \times 10^{-6} \text{ mol L}^{-1}$ . These findings highlight the potential of rare-earth-functionalized Sr-BDC materials as efficient fluorescent probes for the detection and quantification of  $\text{Fe}^{3+}$  in environmental and biomedical applications.

## Author contributions

Drafting and the manuscript, H. Y.; investigation, H. Y. and Y. Y.; analysis and interpretation of the data, C. X. and Y. W.; formal analysis, B. Q.; writing-review and editing, C. Z. and S. L.; conception and planning of the work, C. L.

Table 2 Elemental composition analysis (wt%) of  $\text{Tb}^{3+}@\text{Sr-BDC}$  before and after  $\text{Fe}^{3+}$  coordination (EDS)

Elements	$\text{Sr}^{2+}$	$\text{Tb}^{3+}$	$\text{Fe}^{3+}$
$\text{Tb}^{3+}@\text{Sr-BDC}$	33.19	0.90	0
$\text{Tb}^{3+}@\text{Sr-BDC} + \text{Fe}^{3+}$	32.47	0	3.47



## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data presented in this study are available on request.

## Acknowledgements

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