Novel “Turn-On” Fluorescent Probe for Highly Selectively Sensing Fluoride in Aqueous Solution Based on Tb$^{3+}$-Functionalized Metal–Organic Frameworks

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ABSTRACT: A Zr-based metal–organic framework (Zr-MOF) which has free carbonyl groups is synthesized successfully through mix-ligand strategy. Subsequently, Tb$^{3+}$ is encapsulated into a Zr-MOF by postcoordinated modification. The Tb$^{3+}$@Zr-MOF exhibits the characteristic emission of Tb$^{3+}$ because of efficient sensitization through antenna effects. The Tb$^{3+}$@Zr-MOF is further developed as a novel “turn-on” fluorescent probe to detect fluoride ions in aqueous solution. The results show that Tb$^{3+}$@Zr-MOF exhibits excellent selectivity, high stability, low detection limits, and good anti-interference for sensing fluoride ions. In addition, the possible sensing mechanism that the induced luminescence properties may be attributed to Lewis acid–base interactions is discussed.

INTRODUCTION

Fluoride is one kind of essential trace elements of human body; however, intake of excessive fluoride will cause serious health problems including dental and skeletal fluorosis.1–3 Fluoride ion (F$^-$) is considered as one of the most serious pollutants in water because of its high toxicity.4–6 To make matters worse, it is accessible in many fields of human activities, including toothpaste, drinking water, and dietary supplements.7–9 World Health Organization (WHO) sets that the maximum limit of fluoride ions in drinking water is 1.5 ppm10,11 because of their critical threats to human health. As a result, it is extremely vital to monitor the concentrations of fluoride ions in aqueous solution with high selectivity and sensitivity.

Up to now, a number of analytical methods have been utilized for detecting fluoride, including ion-selective electrode,12,13 liquid chromatography,14 inductively coupled plasma mass spectrometry,15 and so on.7,16 However, these methods have limitations, such as requiring practical skills, well-equipped instrumentation, and time-consuming, which impedes the further application in monitoring the F$^-$. Thus, developing a simple, rapid, and selective sensing technology for determining F$^-$ is very significant. Among the approaches, a fluorescent sensor is an active area of investigation because of its convenient utilization, low cost, high selectivity, and naked-eye sensing ability.

Metal–organic frameworks (MOFs) that also called porous coordination polymers are novel porous crystalline materials.20–23 MOFs have gained more and more attentions in the fields of gas capture/separation,30–34 heterogeneous catalysis,35–38 drug delivery,39–42 and chemical sensing43–51 because of their good crystallization, high surface areas, and tunable chemical properties. Among the multitudinous reported MOFs,47,52–54 lanthanide-based MOFs (Ln-MOFs) are most promising candidates for sensing applications because of their prominent luminescence properties arising from the Laporte forbidden 4f–4f transitions of the lanthanide ions.55 Design and preparation of ideal Ln-MOFs, however, still remain great challenge that is ascribed to the variable nature of coordination sphere and high coordination numbers.56 Fortunately, postsynthesis modification (PSM)56,57 provides possibility for constructing Ln-MOFs succinctly. The major strategies of PSM to fabricate Ln-MOFs include ion-exchange,58 coordinate PSM,59 and covalent PSM.60 To date, Ln-MOFs that were prepared by PSM have been successfully utilized for sensing cations,61 anions,62 gases,63 organic molecules,64 biomarkers65, and monitoring the food spoilage.66 Nevertheless, Ln-MOFs employed in detecting F$^-$ were reported rarely.67–69 In a consequence, developing a reliable fluorescent probe based on Ln-MOFs needs further efforts.

In this work, we report a novel turn-on fluorescent probe for sensing fluoride ions based on Tb$^{3+}$-functionalized MOFs. Herein, the Zr-based MOF (Zr-MOF) is fabricated by mixed ligands. The Zr-MOF is isostructural to UiO-66 and has uncoordinated carbonyl groups.70 Postcoordinated encapsulation generates the Tb$^{3+}$-loaded luminescent Tb$^{3+}$@Zr-MOF. The as-prepared Tb$^{3+}$@Zr-MOF has a similar crystalline framework but different luminescence properties compared to the parent Zr-MOF. The Tb$^{3+}$@Zr-MOF is then applied in...
sensing anions in aqueous solution. The results exhibit that it could detect $\text{F}^-$ with high selectivity, good stability, excellent anti-interference, and low limit of detection (LOD), which indicates its great potential in chemical sensing. The possible mechanism is discussed for that Lewis acid–base interactions cause the enhancement of luminescence intensity.

## RESULTS AND DISCUSSION

### Characterization of Zr-MOF and Tb$^{3+}$@Zr-MOF

The Zr-MOF is fabricated under hydrothermal conditions from a mixture of ZrCl$_4$, terephthalic acid (TPA), and isophthalic acid (IPA) according to previous reports$^{70}$ with some modifications. Powder X-ray diffraction (PXRD) analysis (Figure S1) of the resultant Zr-MOF confirms that it is isostructural to UiO-66 which is constructed from a cluster of six Zr atoms $[\text{Zr}_6\text{O}_4(\text{OH})_4]$ interconnected by TPA ligands to build up a three-dimensional framework with tetrahedral and octahedral cages (Figure S2). It is worth noting that only one carboxylate arm of the IPA coordinates with Zr$^{4+}$, whereas the other is nonbonded because of the asymmetrical structure of IPA compared with TPA. The synthetic method is done in one step, indicating facile synthesis of acidic MOFs from mixed linkers. The existence of free $-\text{COOH}$ groups within the Zr-MOF is demonstrated by infrared spectroscopy. As shown in Figure S3, the new band $\sim$1700 cm$^{-1}$ disappearing in the Fourier transform infrared spectra (FTIR) spectrum of UiO-66 is ascribed to the stretching vibration of $\text{C}=\text{O}$ of free carboxylate groups. What is more, explicit evidences are located at $\sim$2900 cm$^{-1}$ which is originated from the stretching vibration of $\text{O}^{-}\text{H}$ in the free $-\text{COOH}$ groups.$^{71}$ The parent Zr-MOF still remains highly stable that had been proved in the literature even though the imperfect bonds within MOFs due to the high coordination numbers (12) of Zr$^{4+}$. As a result, the Zr-MOF is suitable for constructing Ln-MOFs through PSM because of its robust skeleton and uncoordinated $-\text{COOH}$. Postcoordinated encapsulation could introduce Tb$^{3+}$ into the Zr-MOF successfully. PXRD patterns (Figure 1a) indicate that the framework of Zr-MOF still remains integral after PSM. The stretching vibration of C=O of free carboxylate groups is weakened after coordinating with Tb$^{3+}$ (Figure S3). The N$_2$ adsorption–desorption isotherms of Zr-MOF and Tb$^{3+}$@Zr-MOF are shown in Figure 1b. Both of the materials exhibit porosity toward N$_2$. The Brunauer–Emmett–Teller (BET) surface area of Zr-MOF derived from the isotherms is calculated as 662 m$^2$ g$^{-1}$. After encapsulating Tb$^{3+}$, the value of BET surface area is 483 m$^2$ g$^{-1}$ that is lower than that of the parent Zr-MOF. It might be attributed to the steric hindrance of coordinated Tb$^{3+}$ ions, which also confirms the successful introduction of Tb$^{3+}$ into channels of Zr-MOF. Furthermore, the X-ray photoelectron spectroscopy (XPS) analysis (Figure S4) also verifies the successful encapsulation of Tb$^{3+}$. The XPS of Tb$^{3+}$@Zr-MOF exhibits the characteristic Tb 4d peaks that the Zr-MOF does not possess. In addition, the binding energy of O 1s is increased from 529.1 to 529.4 eV which implies the successful coordination between $-\text{COOH}$ and Tb$^{3+}$.

### Photoluminescence Properties and Sensing Anions

The luminescence spectra of Zr-MOF and Tb$^{3+}$@Zr-MOF in the solid state are recorded at ambient temperature and represented in Figures S8 and 2, respectively. When the Zr-MOF is excited at 302 nm, it exhibits a strong and broad band.
around 398 nm, which originates from the ligand-to-metal charge transfer. After postsynthetic modification, the excitation spectrum of Tb\(^{3+}\)@Zr-MOF is similar to that of the parent Zr-MOF. However, the original emission of ligands is extremely suppressed. With the excitation wavelength at 302 nm, the Tb\(^{3+}\)@Zr-MOF exhibits strong and sharp emissions of Tb\(^{3+}\) which also proves the successful synthesis of Tb\(^{3+}\)@Zr-MOF. The emission peaks located at 488, 544, 584, and 620 nm are assigned to \( ^{5}D_{4} \rightarrow ^{7}F_{j} \) (\( j = 6, 5, 4, \) and 3) translations of Tb\(^{3+}\), respectively. No residual ligand centered broad emission of Zr-MOF locates at the near-UV region, indicating that ligands can high efficiently sensitize the luminescence of Tb\(^{3+}\) through antenna effect. The Tb\(^{3+}\)@Zr-MOF exhibits bright green color and could be easily distinguished visually under UV-light irradiation because of its dominant peak presented at 544 nm originating from \( ^{3}D_{4} \rightarrow ^{7}F_{5} \). Excellent photoluminescence (PL) properties endow Tb\(^{3+}\)@Zr-MOF with high potential as a fluorescent probe.

The luminescence spectrum (Figure S9) of Tb\(^{3+}\)@Zr-MOF is also obtained when it was suspended in aqueous solution. Compared with the solid-state PL spectrum of Tb\(^{3+}\)@Zr-MOF, the ligand-centered emission is recovered and the luminescence intensity of Tb\(^{3+}\) is decreased, which may be attributed to stretching vibration of O−H that can quench the emission of Tb\(^{3+}\). The photoluminescence stability of Tb\(^{3+}\)@Zr-MOF when it is immersed in water also plays an important role in luminescence sensors. As a result, it is supposed to be researched whether the emission intensity of Tb\(^{3+}\) changes intensely with time going by. The results (Figure S10) exhibit that there is no obvious change of the emission spectra of Tb\(^{3+}\)@Zr-MOF when it is suspended in water after 1 week, which means that Tb\(^{3+}\)@Zr-MOF has good luminescence stability in aqueous solutions.

Because of the imperfect bonds within the Zr-MOF, the coordination numbers of Zr\(^{4+}\) may be less than 12, which results in bare metal sites, according to previous reports.\(^{70,72}\) Subsequently, the Tb\(^{3+}\)@Zr-MOF was utilized for sensing anions that can interact with host MOFs through Lewis acid–base interactions. The Tb\(^{3+}\)@Zr-MOF (3 mg) is ground and immersed in aqueous solution containing various anions. The mixture is sonicated to form homogeneous suspension and recorded the luminescence spectra immediately. As shown in Figure 3, the obtained luminescence spectra reveal that various anions have different impacts on the emission of Tb\(^{3+}\). When Br\(^{-}\), NO\(_{3}\)\(^{-}\), CO\(_{3}\)\(^{2-}\), HCO\(_{3}\)\(^{-}\), SiO\(_{3}\)\(^{2-}\), SO\(_{4}\)\(^{2-}\), and PO\(_{4}\)\(^{3-}\) are introduced into the system, luminescence intensity of Tb\(^{3+}\) decreases slightly. I\(^{-}\), S\(^{2-}\), and NO\(_{2}\)\(^{-}\) could quench the emission of Tb\(^{3+}\) thoroughly. Compared with unobviously increasing the luminescence intensity with the influence of Cl\(^{-}\), F\(^{-}\) could extremely enhance the emission of Tb\(^{3+}\). It is worth mentioning that the above phenomenon that various anions affect the luminescence intensity can be distinguished by naked eyes under UV-light irradiation. As shown in the inset of Figure 3, these dark colors of suspensions sever as foils to that of F\(^{-}\), which displays bright green color. The corresponding CIE coordinates of Tb\(^{3+}\)@Zr-MOF immersed in different anions are marked in the diagram (Figure S11). The point of F\(^{-}\) is far from the other anions.

Because of the complicated environment of aqueous solution, the influence of the other anions on the sensing fluorides ions should also be evaluated, which implies the possibility of practical applications. As can be seen in Figure 4, when F\(^{-}\) is added to the other anion solution, the luminescence intensity of Tb\(^{3+}\) is increased apparently compared to that in the absence of F\(^{-}\). This indicates that sensing of fluoride ions by the Tb\(^{3+}\)@Zr-MOF has good anti-interference that is vital for fluorescent probes. On the other hand, we have also estimated the PL stability of sensing F\(^{-}\) through the Tb\(^{3+}\)@Zr-MOF in water of different pHs, which plays a significant role in practice utilization due to different water samples. As shown in Figures S5 and S12, the \( ^{3}D_{4} \rightarrow ^{7}F_{5} \)
respectively. We have also estimated the LOD according to the IUPAC criteria using the following equation.

\[ \sigma = \frac{3S_b}{S} \]

where \( S_b \) is the standard deviation for replicating detection of blank \( \text{H}_2\text{O} \) solution (\( N = 15 \)). \( S \) is the slope of the linear relationship of eq 1. The LOD is calculated as 0.35 ppm that is lower than the maximum limit (1.5 ppm) of fluoride ions in drinking water stipulated by WHO, although the Tb\(^{3+}\)@Zr-MOF did not have apparent advantages compared with the other sensors (Table S2).

According to previous reports, the enhanced effect on luminescence MOFs may be attributed to (1) interactions between guest specials and MOFs and (2) collapse of the crystal structure. To confirm the anticipation that the induced PL enhancement by \( F^- \) may be ascribed to Lewis acid–base interactions between \( F^- \) and bared metal sites, many experiments are performed. First, PXRD (Figure S13) is employed to study the crystal structure of Tb\(^{3+}\)@Zr-MOF. After being soaked in water with or without \( F^- \), the sharp diffraction peaks in the original Tb\(^{3+}\)@Zr-MOF do not change apparently. This implies that the introduction of \( F^- \) cannot destroy the structure of parent MOFs. Subsequently, the Tb\(^{3+}\)@Zr-MOF that is immersed in \( F^- \) solution for hours and washed with distilled water richly to remove the \( F^- \) by physical absorption is used for XPS tests. Compared with the original Tb\(^{3+}\)@Zr-MOF, it shows characteristic peaks of \( F^- \) in the XPS spectrum (Figure S14). What is more, the binding energy of Zr\(^{4+}\) within the Tb\(^{3+}\)@Zr-MOF has a slight shift (ca. 0.3 eV) after the encapsulation of \( F^- \), which indicates that \( F^- \) coordinates with bared Zr\(^{4+}\) sites due to the imperfect bonds within MOFs and strong nucleophilic ability of \( F^- \). Comparing the luminescence spectra of Tb\(^{3+}\)@Zr-MOF in the absence and presence of \( F^- \), they both exhibit two emission bands that originate from ligands and Tb\(^{3+}\), respectively. However, the intensity ratio (see Figure S15) of Tb\(^{3+}\) and ligands (\( I_{598}/I_{398} \)) is different. The value of \( I_{598}/I_{398} \) is 1.5 when the Tb\(^{3+}\)@Zr-MOF was suspended in water. Introducing \( F^- \) into the system, the value increases to 29. As a result, the enhancement effect of Tb\(^{3+}\)@Zr-MOF induced by \( F^- \) may be attributed to the Lewis acid–base interaction between \( F^- \) and Zr\(^{4+}\) that restores the energy transfer from ligands to Tb\(^{3+}\), which is hindered in water.

**CONCLUSIONS**

In conclusions, we fabricate a novel turn-on fluorescent probe based on the Tb\(^{3+}\) postcoordination functionalized Zr-MOF that is synthesized through mixed ligands and possess free carbonyl groups because of the asymmetrical structure of IPA. The luminescence spectrum confirms that ligands can highly efficiently sensitize the emission of Tb\(^{3+}\) through antenna effect. Bared Zr metal sites that are ascribed to imperfect bonds within MOF make us to explore the sensing performance of Tb\(^{3+}\)@Zr-MOF for anions. Interestingly, the Tb\(^{3+}\)@Zr-MOF exhibits distinguishable luminescence response to fluoride ions among the other common anions. This may be attributed to Lewis acid–base interactions between \( F^- \) and bare Zr\(^{4+}\) sites within MOFs, which has been proved by the XPS spectrum. The sensor detecting \( F^- \) in aqueous solution exhibits preeminent performance, including high selectivity, excellent stability, good anti-interference, and low LOD. It is conceivable that the Tb\(^{3+}\)@Zr-MOF has high potential to monitor the concentration of \( F^- \) in practice water samples.
**EXPERIMENTAL SECTION**

**Materials and Reagents.** TbCl₃·6H₂O was prepared by dissolving the corresponding lanthanide oxide compounds in excess concentrated hydrochloric acid (37%), followed by evaporation and crystallization. TPA, IPA, and ZrCl₄ were purchased from Adamas and used without further purification. All of the other starting materials and reagents were AR and were used as purchased. All aqueous solutions of F⁻, Cl⁻, Br⁻, I⁻, S²⁻, NO₃⁻, NO₂⁻, CO₃²⁻, HCO₃⁻, SiO₃²⁻, SO₄²⁻, and PO₄³⁻ were prepared from sodium or potassium salts.

**Instrumentation.** The powder X-ray diffraction (PXRD) was performed on a Bruker D8 ADVANCE diffractometer for structure analysis using Cu Kα radiation (40 mA and 40 kV), with a scan range of 2θ from 5° to 50°. SEM was monitored with a Hitachi S-4800 field emission scanning electron microscope. FTIR were collected with the KBr pellets from 4000 to 400 cm⁻¹ using a Nicolet IS10 infrared spectrum radiometer. With the Mg Kα anode, X-ray photoelectron spectra were analyzed under ultrahigh vacuum (<10⁻⁶ Pa) at a pass energy of 93.90 eV using a PerkinElmer PHI 5000C ESCA system. All binding energies of elements were calculated with contaminant carbon (C 1s = 284.6 eV). Under nitrogen protection, TGA was measured with a Netzsch STA 449C system at a heating rate of 5 K min⁻¹. Nitrogen adsorption–desorption isotherms were collected at liquid nitrogen temperature with a Tristar 3020 analyzer. The excitation and emission spectra of the materials were recorded on Edinburgh System at a heating rate of 5 K min⁻¹. Nitrogen adsorption–desorption isotherms were collected at liquid nitrogen temperature with a Tristar 3020 analyzer. The excitation and emission spectra of the materials were recorded on Edinburgh Instruments FLS920 at ambient temperature.

**Preparation of Zr-MOF and UiO-66.** Zr-MOF was synthesized according to previous reports with a little modification. Briefly, 1.165 g of ZrCl₄·0.665 g of IPA and 0.166 g of IPA were dissolved in 30 mL of N,N-dimethylformamide (DMF). Then, 1.042 g of HCl was added to the solution. The mixture was stirred at ambient temperature for 30 min. The mixed precursor was transferred to a 50 mL Teflon lined autoclave and heated at 180 °C for 24 h in a preheated oven. The resultant white product was filtrated and washed plenty with DMF and acetone orderly. The powder was dried at 100 °C for 24 h in vacuum.

UiO-66 was prepared similarly to Zr-MOF. The only different was that the mixed ligands were replaced by 0.831 g of TPA.

**Preparation of Tb³⁺@Zr-MOF.** The Tb³⁺@Zr-MOF was synthesized through the postcoordinated modification. The Zr-MOF (200 mg) was immersed in 25 mL of ethanol solution of TbCl₃·6H₂O (0.004 M) for 12 h at ambient temperature with sustained stirring. Subsequently, the solid product was separated from the mixture by centrifugation and washed sustainently stirring. Subsequently, the solid product was separated from the mixture by centrifugation and washed plenty with ethanol at least three times to remove the Tb³⁺ by physical adsorption into the channel of MOFs. The resulting powder was dried at 80 °C.

**Luminescence Sensing Experiment.** For experiments of sensing anions, 3 mg of Tb³⁺@Zr-MOF was immersed in aqueous solution (3 mL, 1 mM) of various anions, including F⁻, Cl⁻, Br⁻, I⁻, S²⁻, NO₃⁻, NO₂⁻, CO₃²⁻, HCO₃⁻, SiO₃²⁻, SO₄²⁻, and PO₄³⁻. These suspensions were sonicated for 3 min to get homogeneous mixture and then recorded the luminescence spectra immediately.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02134.

PXRD patterns; representation of the crystal structure; ATR–FTIR spectra; XPS spectra; SEM images; EDX spectrum and mapping images; TGA; luminescence decay curves; excitation and emission spectra; CIE diagrams; histogram of the luminescence intensity in pH; PXRD patterns; XPS spectra; and solvents sensing data (PDF)

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Notes

The authors declare no competing financial interest.

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