Highly Selective and Sensitive Detection of PO$_4^{3-}$ Ions in Aqueous Solution by a Luminescent Terbium Metal–Organic Framework

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Supporting Information

ABSTRACT: A luminescent terbium metal–organic framework [Tb–(HPIA$^{-}$)(PIA$^{2-}$)(H$_2$O)$_3$] (Tb-MOF), synthesized by a lanthanide metal ion (Tb$^{3+}$) and nitric heterocyclic carboxylic acid ligands H$_2$PIA (H$_2$PIA = 5-(1H-pyrazol-3-yl)isophthalic-acid), was structurally characterized as a three-dimensional skeleton structure in which layered coordination frameworks are connected by hydrogen bonds. Based on the antenna effect, Tb-MOF can emit bright green fluorescence under 254 nm excitation, and the fluorescence emission presents excellent durability in aqueous solutions among a wide pH range. Moreover, the structure of Tb-MOF also possesses outstanding thermal stabilities. In some ways, PO$_4^{3-}$ and its derivatives are thought to be a kind of pollutant ion causing series environmental and health problems. The as-synthesized Tb-MOF exhibits prominent selectivity and remarkable sensitivity for detecting PO$_4^{3-}$ as an easy-to-use fluorescent probe with low detection limit, fast response, and wide detection range. Therefore, Tb-MOF has significant applications in the fields of human health and environmental monitoring.

INTRODUCTION

Metal–organic frameworks (MOFs), as one of the research hotspots over the past few years, are a sort of self-assembly supermolecular crystalline porous materials. MOF is usually centered on metal ions or clusters to combine a periodic framework with organic ligands. For multiple articles reported, due to its well-developed porosity, high surface area, and tunable uniform pore size, MOF shows great potential application prospect, such as drug loading, gas adsorption, storage and separation, heterogeneous catalysis, chemical sensing, heterogeneous catalysis, and bioimaging. Recently, the influence of certain anions on environmental pollution has become more and more serious, therefore such pollutant ions have received extensive attention in many aspects. For instance, acid rain is made from excessive emission of NO$_3^-$ and SO$_4^{2-}$, which result from burning fossil fuels and automobile exhausts in the air. Not only are halogen ions extremely irritating and highly toxic to human bodies, but they are also very corrosive to many substances. About PO$_4^{3-}$, as a derivative of phosphorus, plays a vital role in the process of living things such as gene regulation, genetic material, signal transmission, and energy storage. From another perspective, PO$_4^{3-}$ is a common pollutant anion of industrial production in aquatic ecosystems, which leads to overgrowth of algae and eutrophication of water. Besides, excessive phosphate and its derivatives can also affect the absorption of calcium ions in the human bodies and cause irreversible harm to people’s life. As a pollutant anion, PO$_4^{3-}$ possesses less binding reactive sites and lower reactivity, so detection of PO$_4^{3-}$ emerges a major challenge in the field of chemosensors.

Conventionally, contaminant anion detection methods are expensive, complicated, time-consuming, and difficult to operate. As one branch of MOF, lanthanide-based MOF (Ln-MOF) has unique luminescence properties with high luminescence purity, long fluorescence-emission lifetime, and high luminescence quantum efficiency, which make them widely used in research and preparation of fluorescent sensors. Meanwhile, nitrogen-containing carboxylic acid ligands have plurality of coordination sites, and high charge density of the lanthanide ions making it possesses unique Lewis basic sites. In summary, Ln-MOF assembled by lanthanide ions coordinated has critical influence on detection properties because of possessing varied topologies and suitable pore size, which make it possibly get high selectivity and sensitivity of detecting phosphate radicals. Yet compared to ordinary instrument detection methods, fluorescence-based chemosensors have attracted widespread attention because of their fascinating properties.

In this work, a lanthanide fluorescent MOF characterized as a novel three-dimensional skeleton structure was fabricated by mixing lanthanide salts of Tb(Cl$_3$)$_3$.6H$_2$O and nitric heterocyclic carboxylic acid ligands of H$_2$PIA (H$_2$PIA = 5-(1H-pyrazol-3-yl)isophthalic-acid) (Figure S1 of Supporting Information).
RESULTS AND DISCUSSION

Crystal Structure. The single-crystal X-ray diffraction analysis indicated that Tb-MOF crystallizes in $P\bar{1}$ space group belonging to the triclinic system. As shown in Figure 1a, there are one Tb(III) metal center, one HPIA$^-$ ligand, one PIA$^{2-}$ ligand, and two coordinated water molecules in an asymmetric unit. Tb$^{3+}$ adopts octahedral-coordinated bi-augmented trigonal prism geometric configuration analyzed by the Shape software, in which coordinated atoms originate from six carboxylate oxygen atoms, four different ligands, and two coordinated water molecules. The Tb−O bond lengths and O−Tb−O bond angles are in the range of 2.322(2)−2.493(2) Å and 52.71(7)−145.42(7)$^\circ$, respectively, which correspond with other reported Tb-MOF.38,39 The Tb$^{3+}$ ions are linked by ligand HPIA$^-$ and PIA$^{2-}$ to construct a 2D layered structure (Figure 1b). Furthermore, the 2D sheet structures are joined through the O−H···O hydrogen bond to fabricate a 3D framework with a channel of 8.8 × 3.5 Å$^2$ (Figure 1c,d). Intriguingly, the ligand H$_2$PIA adopts two different coordination modes. In ligand HPIA$^-$, one protonated carboxylate group is free while another is deprotonated using $\mu_1$−$\eta^1$−$\eta^1$-chelating coordination mode. In ligand PIA$^{2-}$, two deprotonated carboxylate groups have the same coordination fashion as the $\mu_2$−$\eta^1$−$\eta^1$-bridging coordination mode. In both ligand HPIA$^-$ and PIA$^{2-}$, the pyrrole group is free and not involved in coordination configuration, which can be the active sites to bind specific chemicals (Figure 2a,b). The crystallographic data and structure refinement, main bond length, bond angle, and hydrogen data for Tb-MOF are listed in Tables S1−S3 of the Supporting Information.

Figure 1. (a) Asymmetric unit of Tb-MOF. (b) View of the 2D layered structural unit formed by Tb(III) ions and ligand. (c) View of the 3D skeleton structure through the connection of hydrogen bond between the 2D layered structure. (d) 1D pore structure.

General Characterization of Tb-MOF. It is shown in Figure S2 of the Supporting Information that the tested powder X-ray diffraction (PXRD) pattern of the Tb-MOF corresponds to main diffraction peaks of the simulated pattern which is obtained by Mercury software, displaying that Tb-MOF has good phase purity. Otherwise, the FT-IR spectrum was performed and exhibited that the as-synthesized Tb-MOF has broad and scattered bands at 3300−2540 cm$^{-1}$ as it is shown in Figure S3 of the Supporting Information, which can be attributed to stretching vibration of −OH. The band at 1696 cm$^{-1}$ of Tb-MOF shifts to 1616 cm$^{-1}$, indicating that the carboxyl group of the ligand has been successfully deprotonated and coordinated with the Tb$^{3+}$ ions. As shown in Figures S4 and S5 of the Supporting Information, the PXRD analysis indicated that the Tb-MOF maintains structural integrity not only in aqueous solution for 3 days but also in distilled water at the different pH values of 2, 5, 7, 8, and 10. To further explore the thermal stability of Tb-MOF, the thermogravimetric analysis (TGA) was carried out in range 30−1200 °C (Figure S6, Supporting Information). When the temperature rises from 30 to 120 °C, the TGA curve of Tb-MOF does not show an obvious weightless platform, demonstrating that the structure of Tb-MOF has not begun to breakdown. However, the weight loss of the Tb-MOF is about 2.9% from 120 to 182 °C, which is consistent with one coordinated water molecule contained in the asymmetric unit of Tb-MOF (calculated as 2.8%). When the temperature is between 244 and 315 °C, the weight loss is also about 2.9%, which can be attributed to the removal of another coordinated water molecule (calculated as 2.8%). Finally, the structure is collapsed gradually after 493 °C.

Photoluminescence Properties. The solid-state fluorescence property of Tb-MOF has been investigated under room temperature (Figure 3). The spectrum of the ligand shows a broad emission peak at 393 nm with the excitation wavelength at 331 nm, which can be responding to the $\pi-\pi^*$ transition of H$_2$PIA ligands. At the excitation of 319 nm, the solid-state fluorescence spectrum of Tb-MOF has four characteristic emission peaks of Tb$^{3+}$ at 493, 546, 589, and 624 nm, corresponding to the $f-f$ transition of $^5D_{4-}^7F_{5/2}$, $^5D_{4-}^7F_{7/2}$, $^5D_{4-}^7F_{5}$, and $^5D_{4-}^7F_{3/2}$, respectively. Moreover, as shown in the inset photography of Figure 3b, the Tb-MOF can emit strong green fluorescence color under the portable ultraviolet lamp (excitation wavelength of 254 nm). Studies have shown that the energy absorbed by the ligands has been transferred to the central Tb$^{3+}$ ion, which means the center metal ion is sensitized by the ligand, basing on the antenna effect.32,40−42

![Figure 2](image-url)
Furthermore, the Tb-MOF shows splendid chemical stability not only in the framework structure but also in relative fluorescence intensity. There is no obvious change in the fluorescence intensity spectra of Tb-MOF by soaking in deionized water for 7 days (Figure 4a). Besides, when the ground solid samples were treated by acid–base aqueous solutions (Figure 4b), there is no significant difference in the luminescence intensity spectra of Tb-MOF.
solutions with pH from 1 to 14, the fluorescence intensity was measured and shown substantially stable with pH in the range of 3–10 at room temperature (Figure 4b).

**Detecting PO₄³⁻ in Aqueous Solutions.** For testing the effect on the fluorescence signal of the anions detected by Tb-MOF, the ground Tb-MOF is dispersed in aqueous solutions containing different anionic sodium salts (NaX, X⁻ = F⁻, Cl⁻, Br⁻, I⁻, Cr₂O₇⁻, N₃⁻, SCN⁻, PO₄³⁻, CO₃²⁻, SO₄²⁻, AC⁻, NO₃⁻, NO₂⁻) (with concentration of 0.01 M). The suspensions were treated by ultrasonication for 10 min. For its bright visible green fluorescent color, it was observed that Tb-MOF in the solution containing PO₄³⁻ showed significant fluorescence quenching phenomenon and can be easily captured by naked eyes under a portable UV lamp (the excitation wavelength is 254 nm) (bottom graph in Figure 5a). Besides, there is no obvious fluorescence change while suspension contains other anions. In order to confirm this phenomenon, fluorescence spectra of Tb-MOF in different solutions were measured (Figure 5a). By comparing the relative fluorescence intensity of Tb-MOF at 546 nm, only the solution containing PO₄³⁻ has distinct fluorescence quenching. To further explore the identification properties of Tb-MOF about PO₄³⁻, more experimental methods were adopted. The ground solid sample was uniformly dispersed into the aqueous solution with gradually increasing the concentration of PO₄³⁻. As shown in Figure 5c, when the concentration of PO₄³⁻ reached 3.27 × 10⁻⁴ M, the fluorescence intensity at 546 nm is almost quenched entirely. Then, the luminescent intensities at 3D₂⁰⁻F₂ transitions (546 nm) were monitored which reveals orderly gradual decline, and the detection limit is down to 4.5 ppm. Moreover, the quenching curve of phosphate recognition analyzed by the Stern–Volmer nearly shows a quadratic linear at the whole concentration range with a linear fit correlation coefficient of 0.9958 (Figure 5d). The comparisons of the Tb-MOF probe and other sensing methods for PO₄³⁻ are listed in Table S4 of the Supporting Information.

Actual sewage treatment usually contains many other anions that may interfere with sensing of MOF-based sensors. Therefore, the anti-interference sensing experiment was carried out. The ground Tb-MOF (2 mg) was dispersed in 3 mL deionized water and ultrasonicated, and the luminescent intensity of the suspension has no obvious change after adding other anions. Because the equal PO₄³⁻ was added, the fluorescence intensity at 546 nm quenched instantly. As shown in Figure 5b, it has been found that the fluorescence intensity of the MOF-based sensors was still quenched effectively while mixed with other anionic solutions after being treated by PO₄³⁻.

Undoubtedly, fast response is also important for practical applications of fluorescence chemosensors. Hence, by mixing the ground Tb-MOF suspension solution (1 mg, 2 mL) with phosphate ions (0.01 M, 1 mL), we collected the time-response profile of Tb-MOF toward PO₄³⁻, as shown in Figure S7 of the Supporting Information, in a short period of ~60 s contact with PO₄³⁻, the emission intensity of the Tb-MOF suspension remains only ~40%, which reveals that PO₄³⁻ has a relatively rapid weakening effect on the luminescence of Tb-MOF.

**Mechanism of the Luminescent Quenching Effect.** Mechanism of sensing analytes by fluorescence quenching of MOF materials has been reported in several literatures in recent years. Above all, it is likely that the following four statements: (a) the interaction of ions with organic ligands in MOF, (b) the collapse of the MOF structure, (c) a weak interaction of anions with metal ions in MOF, and (d) the coverage between the UV absorption peak of the analyte and the excitation or emission spectra of the MOF. As shown in Figure S8 of the Supporting Information, for exploring the mechanism of the chemical sensing by Tb-MOF to PO₄³⁻, first, the PXRD patterns of Tb-MOF treated with PO₄³⁻ were obtained. Obviously, there is no significant change, which means that the structure is not destroyed. Thus, the fluorescence quenching caused by the collapse of the MOF structure does not make sense. Then, the UV–vis absorption peak of PO₄³⁻ shows no distinct overlap with the excitation and emission spectra of Tb-MOF (Figure S9). As shown in Figure S10, the luminescent lifetime has a certain degree of attenuation after being treated by PO₄³⁻, hence the recognition mechanism is a dynamic quenching process. After this, a further exploration of X-ray photoelectron spectroscopy (XPS) was carried out (Figure 6). After being treated with PO₄³⁻, a newly observed peak can be assigned to 2p orbital of P element at around 135 eV (Figure S11 of Supporting Information). Other than this, by analyzing the XPS spectra of the 3d orbital of Tb, it can be seen that it is negatively shifted from 1244.1 to 1243.2 eV. It is proved that PO₄³⁻ has a weak interaction with Tb³⁺ after entering the pore channel, which affects the energy transfer from the ligand to the central ion. Moreover, according to the Figure S12, it is obviously that the binding energy of N 1s and O 1s has little change, suggesting the N and O atoms from the ligand do not interact with PO₄³⁻ ions. Above all, the fluorescence quenching mechanism maybe attributing to the weak coordination between Tb³⁺ and PO₄³⁻ ions.
CONCLUSIONS
In conclusion, a novel luminescent Tb-MOF was obtained as colorless block crystals by means of the hydrothermal method to assemble Tb²⁺ and nitric heterocyclic carboxylic acid. The colorless crystals can emit characteristic green fluorescence color under the irradiation of ultraviolet light. We found that the as-synthesized Tb-MOF can specifically recognize phosphate ions from a series of common inorganic anions. More importantly, with regard to phosphate ions sensing in aqueous solution, Tb-MOF displays high sensitivity and selectivity, visible for the naked eyes, fast response, and low detection limit (4.5 ppm). In addition, Tb-MOF exhibits good structural and fluorescent stability against water with a relatively wide range of pH value (3–10). Given all the previous performance, it is believed that our work may provide a simple and highly efficient method to monitor the content of phosphate ions in aqueous solution.

EXPERIMENTAL SECTION

Materials and Methods. All reactants of H₂PIA ligands, TbCl₃·6H₂O, and other reagents were purchased from commercial sources and were used without further purifications. The FT-IR spectra were analyzed with PerkinElmer Spectra (4000–400 cm⁻¹) using KBr pellets. Elemental analyses for C, H, and N were characterized on a PerkinElmer 2400 elemental analyzer. The PXRD patterns were carried out for crystalline phases on an Empyrean Panalytical apparatus equipped with Cu Kα radiation. Fluorescence excitation and emission spectra were monitored by a Hitachi F-7000 spectro-photometer at room temperature (the slit width for the excitation and the emission were kept at 5.0 and 2.5 nm, respectively). TGA curves were measured with a NETZSCH STA409pc apparatus under a nitrogen flow. The FT-IR spectra were analyzed with PerkinElmer Spectra (4000–400 cm⁻¹) using KBr pellets. Elemental analyses for C, H, and N were characterized on a PerkinElmer 2400 elemental analyzer. The PXRD patterns were carried out for crystalline phases on an Empyrean Panalytical apparatus equipped with Cu Kα radiation. Fluorescence excitation and emission spectra were monitored by a Hitachi F-7000 spectro-photometer at room temperature (the slit width for the excitation and the emission were kept at 5.0 and 2.5 nm, respectively). TGA curves were measured with a NETZSCH STA409pc apparatus under a nitrogen flow.

Synthesis of Tb-MOF. By mixing TbCl₃·6H₂O (0.05 mmol), H₂PIA (0.12 mmol) and then ultrasonic dispersed in H₂O (7 mL) evenly with pH adjusted by adding 20 μL HCl (1 M) solution. Transfer the suspension to a 25 mL Teflon-lined stainless steel vessel. The sealed autoclave was heated to 140 °C for 3 days and cooled to room temperature at 2 °C per hour. The samples were washed with deionized water two or three times to remove the impurities, and then a series of colorless block crystals were gained. Yield: 12.8% based on TbCl₃·6H₂O. C₂₂H₁₅N₄O₁₀Tb (654.30): calcd C, 40.38; H, 4.02; N, 8.56. Found C, 39.23; H, 2.54; N, 7.70. IR: 3412.15(s), 1699.62(m), 1624.18(s), 1557.85(s), 1390.11(s), 1236.86(s), 1091.23(s), 930.35(m), 777.09(s), 681.79(m), 609.35(m), 507.19(m).

pH Stability Experiments. An amount of ground Tb-MOF (1 mg) has been ultrasonicated and dispersed in 3 mL aqueous solution (adjust pH with NaOH or HCl) of pH at 1, 2, 3, ... 13, 14, and then immersed in these acid–base aqueous solutions and sonicated for 10 min. The suspension samples were used to do fluorescence monitoring. After 24 h storage in beakers, the ground solid samples were washed with deionized water two or three times and desiccated for PXRD testing.

Sensing Experiments. Two milligrams of ground Tb-MOF were uniformly dispersed in 3 mL of varied anionic aqueous solutions (NaX, X⁻ = F, Cl⁻, Br⁻, I⁻, Cr₂O⁷²⁻, N₃⁻, SCN⁻, PO₄³⁻, CO₃²⁻, SO₄²⁻, AC⁻, NO₃⁻, NO₂⁻) (with concentration of 0.01 M) by sonicating for 10 min, the samples of several suspensions were used for sensing experiments with fluorescent measurements. The concentration-depending sensing experiment was as followed. Ground Tb-MOF (1 mg) was uniformly dispersed into the aqueous solution 1 mL by sonicating for 10 min. Meanwhile, a PO₄³⁻ aqueous solution of 10⁻³ M was added dropwise to the suspension for evaluating the sensitivity toward PO₄³⁻. Then, the luminescent intensities at λD₄₋₅F₅ transitions (546 nm) were monitored. Furthermore, to study whether selectively identifying PO₄³⁻ of Tb-MOF can be affected by other anionic species, different anions were added with 0.01 M concentration of 3 mL (NaX, X⁻ = F⁻, Cl⁻, Br⁻, I⁻, Cr₂O₇²⁻, N₃⁻, SCN⁻, PO₄³⁻, CO₃²⁻, SO₄²⁻, AC⁻, NO₃⁻, NO₂⁻) in 3 mg of ground solid samples, then added 2 mL of PO₄³⁻ aqueous solution (0.01 M) and sonicated for 10 min to get the suspensions, and the fluorescence test was conducted immediately.

Crystallography. The single-crystal X-ray diffraction data for relevant Tb-MOF crystal were collected on a Bruker APEX-II CCD X-ray single-crystal diffractometer equipped with a graphite-monochromatic Mo Kα radiation at 273.15 K. The SADABS program was used for absorption corrections. The crystal structure was solved by the direct method through SHELXTL-97 and OLEX-2 program, and the crystal data were refined against F² values by the full-matrix least-squares technique method. The position of hydrogen atoms was determined in theory using the riding model. The detailed crystallographic data and structural refinement information are listed in Table S1. Selected bond lengths and bond angles are given in Table S2. Crystallographic data for the Tb-MOF fabricated in this paper have been deposited free of charge with the Cambridge Crystallographic Data Centre as supplementary publication as the CCDC number 1852839.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01911.

PXRD patterns, representation of crystal structure, FTIR spectra, TGA curves, UV–vis spectra and other fluorescence data (PDF)

Crystallographic data for Tb-MOF (CIF)

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Notes
The authors declare no competing financial interest.

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