A Multifunctional Tb-MOF Detector for $\text{H}_2\text{O}_2$, $\text{Fe}^{3+}$, $\text{Cr}_2\text{O}_7^{2−}$, and TPA Explosive Featuring Coexistence of Binuclear and Tetranuclear Clusters

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ABSTRACT: A novel three-dimensional microporous terbium-(III) metal–organic framework (Tb-MOF) named as $[\text{Tb}_{10}(\text{DBA})_9(\text{OH})_4(\text{H}_3\text{O})_3(\text{H}_2\text{O})_4]$ (1), was successfully obtained by a solvothermal method based on terbium nitrate and 5-di(2′,4′-dicarboxylyphenyl) benzoic acid (H$_5$DBA). The Tb-MOF has been characterized by single crystal X-ray diffraction, elemental analysis, thermogravimetry, and fluorescence properties, and the purity was further confirmed by powder X-ray diffraction (PXRD) analysis. Structural analysis shows that there are two kinds of metal cluster species: binuclear and tetranuclear, which are linked by H$_5$DBA ligands in two $μ_2$- high coordination fashions into a three-dimensional microporous framework. Fluorescence studies show that the Tb-MOF can detect H$_2$O$_2$, Fe$^{3+}$, and Cr$_2$O$_7^{2−}$ with high sensitivity and selectivity and can also be used for electrochemical detection of exposed 2,4,6-trinitrophenylamine (TPA) in water. The highly selective and sensitive detection ability of the Tb-MOF might make it a potential multifunctional sensor in the future.

1. INTRODUCTION

Metal–organic frameworks (MOFs) have drawn increasing attention due to their tunable pore sizes, diverse structures, and abundant functional designs. Compared with transition metals, lanthanide metal organic frameworks (Ln-MOFs), especially Eu/Tb-MOFs, have been studied widely due to their outstanding luminescence features, including high-purity color, large Stokes shift, high quantum yields, long decay lifetime, and undisturbed emissive energy. Recently, many Eu/Tb-MOFs were applied as an ideal material for identifying small molecules, metal ions, inorganic anions, organic anions, solvents, gases, and explosives. With the rapid growth of the modern industry, more and more harmful chemical pollutants were released into the environment, including heavy metal ions, volatile organic and toxic gases, etc., which have a serious adverse effect on people’s health and life in the past decades. For example, hydrogen peroxide (H$_2$O$_2$) is an essential participant in the energy, food, electrochemistry, enzyme catalysis, and environmental detection as one of the reactive oxygen species (ROS) and is an effective biomarker of several cellular processes, including protein folding, growth, signaling, differentiation, and migration in the cells. Although H$_2$O$_2$ is nontoxic, it produces many free radicals such as a superoxide anion (O$_2^{−}$) and hydroxyl radical (OH) when decomposing, which might induce the initiation of cancer, autoimmunity, neurodegenerative disorders, etc. Aberrant accumulation of H$_2$O$_2$ resulted in oxidative stress, and the level of H$_2$O$_2$ was also connected to aging and some serious diseases, including diabetes, cardiovascular disorder, cancer, and Alzheimer. Therefore, it is urgent and necessary to develop a rapid and sensitive H$_2$O$_2$ detection strategy for the early capture and treatment.

Fe$^{3+}$ ions are one of the indispensable elements in the human body due to their crucial role in a variety of biochemical processes such as oxygen storage and transport in blood, and they can cause many diseases including anemia, skin ailments, insomnia, kidney damage, dysfunction of organs, and even cancers when they are deficient. However, excessive Fe$^{3+}$ also causes a series of serious problems to metabolism and homeostasis of human beings, including vomiting, loss of appetite, and diarrhea. Therefore, it is of high importance to develop a rapid, simple, and low-cost approach for sensitive detection of Fe$^{3+}$ ions for the surveillance of human health.

As we all know, Cr$_2$O$_7^{2−}$ is a widely used strong oxidant, widely employed in chromium electroplating, pigment production, leather tanning, metallurgy, etc. However, Cr$_2$O$_7^{2−}$ has been listed as the most harmful anionic contaminant by the U.S. Environmental Protection Agency because it can be absorbed...
and accumulated by organisms and can do great harm to human health and the environment such as gastrointestinal problems, carcinoma, kidney damage, gene mutation, cardiovascular failure, skin irritation, respiratory infection, and ecological risks, etc.26,28,29 Hence, it is important to design and prepare useful sensor materials to detect Cr$_2$O$_7^{2-}$ precisely for the environmental conservation and health of human beings.26

Furthermore, 2,4,6-trinitrophenylamine (TPA) is one of the nitroaromatic compounds (NACs), which can be used in the preparation of large-versus explosives and fur dyes. Since the 1970s, scientists have increasingly paid attention to the environmental effects of nitroaromatic explosives. However, the focus of these studies was mostly on 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TP), 2,4,6-trinitrophenylmethylnitramine (tetryl), various nitrodiphenylamines, and nitronaphthalenes.30−34 According to the documentation, the special explosive 2,4,6-trinitrophenylamine was never taken into consideration in risk assessment studies of military contaminated sites.

Chromatography and its coupled techniques are the most widely used methods in determining environmental contaminants.35,36 However, chromatography-based techniques often require expensive equipment, complex pretreatment, and long test time. Thus, it is very urgent and necessary to establish simple, easy, effective, and new sensing technologies for environmental pollutants such as H$_2$O$_2$, Fe$^{3+}$ ions, Cr$_2$O$_7^{2-}$ inorganic anions, and 2,4,6-trinitrophenylamine.

In this paper, a novel 3D microporous Tb-MOF has been constructed based on a flexible multidentate penta-carboxylate ligand of 3,5-bis(p-carboxyphenyl) benzoic acid (H$_5$L) under the solvothermal condition. Crystal structure and luminescence properties of the Tb-MOF have been investigated. It features two kinds of metal cluster species: binuclear and tetranuclear, which are linked by H$_5$DBA ligands in two μ$_7$ coordination fashions into a 3D microporous framework. It was found that the Tb-MOF has excellent luminescence sensing properties for H$_2$O$_2$, Fe$^{3+}$, and Cr$_2$O$_7^{2-}$ and excellent electrochemical activity.

Figure 1. (a) Coordination environment of Tb1−Tb4 (symmetry codes: a: 4/3-y,2/3+x-y,-1/3+z; b: 1-x+y,1-x,-z; c: 1/3+x,1/3+y,-4/3+z; d: 4/3-y,2/3+x-y,2/3+z; e: 1-x+y,1-x,-1+z; f: 1-x+y,1-x,1+z). (b) Six-angle group based on one tetranuclear cluster, six DBA ligands, and binuclear units. (c) 3D microporous framework. (d) Topology of 3D.
for sensing recognition of trinitroaniline by a Tb-MOF-doped carbon paste electrode (Tb-MOF/CPE).

2. RESULTS AND DISCUSSION

2.1. Crystal Structure Description. Single-crystal X-ray analysis shows that the Tb-MOF is a three-dimensional microporous structure featuring the coexistence of binuclear (Tb1 and Tb4) and tetranuclear (Tb2, Tb2, Tb2, and Tb3) species as the inorganic building unit. There are four crystallographic independent Tb3+ ions and two DBA5− ligands, two hydroxyl groups, and three coordination water molecules in the asymmetric units of the complex (Figure 1a). Tb1 ions are located at the center of the nine-coordinated single-capped anti-square-prism configuration with the carboxyl oxygen atoms of the surrounding five DBA5− ligands, of which O6b is the capped atom, and O1d, O5b, O22e, and O18c and O3a, O4a, O7a, and O8a atoms occupy four vertices of two planes (Figure S2a). Among these nine carboxyl oxygen atoms, six oxygen atoms (O3a, O4a, O5b, O6b, O7a, and O8a) are chelated and the other three oxygen atoms (O1d, O18c, and O22e) are bidentate bridged coordination with Tb1 ions. The Tb2 ion is located at the center of a twisted nine-coordination tri-capped triangular prism, of which O9, O13b, and O29 and O10, O1a, and O14 constitute two bottoms of the prism, and O12, O11, and O15 are the capped atoms (Figure S2b). In oxygen atoms coordinated to the Tb2 ion, O14 and O15 are chelated, O9 and O10 are bridged carboxyl oxygen atoms, O12, O13a, and O13b are μ3-hydroxyl oxygen atoms, and O11 and O29 are the coordination water molecules. Similar to Tb2 ions, the Tb3 ion also lies in a distorted nine-coordinated triangular prismatic environment (Figure S2c). Among them, three hydroxyl oxygen atoms O13a, O13b, and O13c and three coordination water molecules O30a, O30b, and O30c constitute the two bottoms of the triangular prism, and three μ3-carboxyl O15 atoms are three cap atoms. Also, the Tb4 ion is located at the center of an eight-coordination distorted anti-square-prism geometry (Figure S2d), of which four bridged carboxyl oxygen atoms (O19c, O23e, O6b, and O2d) and four chelated carboxyl oxygen atoms (O16f, O17f, O20f, and O21f) constitute two bottoms. The scope of the Tb−O bond lengths is 2.291−2.892 Å, and the range of the O−Tb−O bond angle is 33−149.06°, which conforms to the reported ranges of Tb−Tb bond length and O−Tb−O bond angle.20,22 Interestingly, there are two kinds of inorganic building units in the Tb(III) 3D framework: binuclear and tetranuclear cubic metallic clusters. A binuclear metal unit consists of Tb1 and Tb4 ions (the distance of Tb⋯Tb is 4.0478 Å), surrounded with six DBA5− ligands. Meanwhile, the distorted tetranuclear metal cube cluster comprises three Tb2 ions and one Tb3 ion, together with four μ3-hydroxyl oxygen atoms (the distance of the Tb⋯Tb range: 3.6964−3.8670 Å). The DBA5− ligand adopts two high coordination fashions: (a) $\kappa_1\kappa_2\kappa_1\kappa_1\kappa_1\kappa_1\mu_7$ and (b) $\kappa_1\kappa_2\kappa_1\kappa_1\kappa_1\kappa_1\mu_7$ to link seven Tb ions (Scheme 1). One tetranuclear cubic cluster is surrounded by six DBA5− ligands in six directions forming a six-angle group with the angles of binuclear units as shown in Figure 1b; such six-angle groups extend in six directions into a three-dimensional microporous framework (Figure 1c), the topology of 3D as shown in Figure 1d.

2.2. PXRD and TG Analyses. The phase purity of complex I has been confirmed by powder X-ray diffraction (PXRD) (Figure 2). The peaks on the PXRD of as-synthesized complex I are coincident with those on their respective simulated patterns.

Figure 2. PXRD patterns of the Tb-MOF (simulated, determination, and after sensing performances of H2O2, Fe3+, and Cr2O73−).

Thermal gravimetric analysis (TGA) of the Tb-MOF was performed by a Netzsch TG-209 thermogravimetric analyzer in an air atmosphere at a heating rate of 10 °C min−1 from 30 to 900 °C. As shown in Figure 3, it was decomposed at the beginning of the TG experiment, which means that the complex is unstable and the whole skeleton collapses when heated.

2.3. Luminescence Properties. 2.3.1. Solid-State Photoluminescence Spectra. The solid-state fluorescence spectra of the Tb-MOF and H2L have been measured at room temperature under the excitation of 351 nm (slits, 5 nm/10 nm) (Figure 4). The ligand displays a broad band emission range from 350 to 400 nm, which centered at about 389 nm, which could be assigned to the intraligand π* → π transitions.23 The Tb-MOF exhibits four well-resolved characteristic emissions, which are
indicates that the inherent nm excitation is negligible relative to the Tb-MOF, which acetone (CP), aldehyde (AH) (40%), and H2O2 (30%), or including methanol (MT), ethanol (EA), water (H2O), ethylene (CYH), (EAC), isopropanol (IPA), formaldehyde (HCHO), hexamethylene (CYH), N,N-dimethyloxamide (DMF), acetic acid (HAc), trichloromethane (CHCl3), normal hexane (NH), acetone (CP), aldehyde (AH) (40%), or H2O2 (30%), or Tb-MOF powder (3 mg) was dispersed in H2O solution containing different concentrations of H2O2 (0.1–300 μM). Then, the sample was treated with ultrasonication for 30 min and then aged for 2 days to form a stable emulsion before the fluorescence experiments (Figure 5a). Interestingly, the fluorescence intensity depends largely on the solvent molecules. It is worth noting that the complex has a strong fluorescence intensity in H2O2 showing the potential capability of the Tb-MOF as an ideal fluorescent probe for the detection of pollutants in water. However, the emission in H2O2 is the weakest, and the quenching effect is the most remarkable, indicating that this Tb-MOF can be used highly selectively as a sensor to detect H2O2 molecules in water, and the stability of the Tb-MOF after sensor performances of H2O2 was checked by PXRD (Figure 2). Then, the luminescence intensity of the Tb-MOF gradually decreases with increasing concentration of H2O2. It was found that there is a good double exponential relationship between the concentration of H2O2 at 0.1–300 μM and the fluorescence intensity, with a nonlinear equation of y = 1961.11 × exp(−x/0.27) + 3340.74 × exp(−x/0.02) + 43.51 (R2 = 0.9916) (Figure 5b inset). The quenching mechanism may be due to the presence of unstable O–O bonds in H2O2, which makes its bi-electron electrophilic. Moreover, H2O2 is also an excellent nucleophile with the existence of the ortho-effect of adjacent nonbonding orbitals on its oxygen atoms.24 So, when the complex is immersed in H2O2 aqueous solution, the electrophilicity and nucleophilicity of H2O2 lead to weak hydrogen bonds and other forces between H2O2 and the organic ligand, which weaken the partial energy transfer from the organic ligand H5L to Tb.10–15,20

2.3.3. Metal Cation Sensing. Tb-MOF powder (3 mg) was immersed in M(NO3)3 (M = Na+, Al3+, Ag+, Cd2+, Ga3+, Mg2+, K+, Sr2+, Zn2+, Pb2+, Bi3+, Hg2+, Ni2+, Co2+, Cu2+ or Fe3+ (10−2 M)). Also, 3 mg of Tb-MOF powder was dispersed in H2O solutions containing different concentrations of Fe3+. Before photoluminescence measurements, the suspensions were ultrasound for 30 min and stood at room temperature for 2 days. Interestingly, the Tb-MOF exhibited significantly different luminescence properties in different metal ion solutions (Figure 6a). It is noted that when Tb-MOF samples are immersed in an aqueous solution containing Fe3+ ions, the luminescence of the Tb-MOF is obviously quenched. It shows that the Tb-MOF can be used as a highly select fluorescent sensor for Fe3+; furthermore, the Tb-MOF is very sensitive to Fe3+, and the lowest detectable concentration can reach 10−9 M; the stability of the Tb-MOF after sensor performances of Fe3+ ions was checked by PXRD (Figure 2). The luminescence intensity of the system decreases gradually when the concentration of Fe3+ ions increases. It was found that there is a good nonlinear relationship.
the UV (Figure S3). Among them, the absorption spectrum of Fe$^{3+}$ has ligand; in other words, photo-excited electrons are hardly the addition of other ions almost does not affect its fluorescence quenching effect on Tb-MOF aqueous solution. This may be because Fe$^{3+}$ can completely shift the LUMO from Tb$^{3+}$ to the ligand; in other words, photo-excited electrons are hardly injected to the Tb center.12

2.3.4. Inorganic Anion Sensing. Tb-MOF powder (3 mg) was immersed in H$_2$O solution containing 13 potassium salts K$\lambda$X (X = SCN$^-$, Cl$^-$, IO$_3^-$, CH$_3$COO$^-$ (Ac$^-$), I$^-$, SO$_4^{2-}$, Br$^-$, NO$_2^-$, SO$_3^{2-}$, C$_6$O$_4^{2-}$, PO$_4^{3-}$, and Cr$_2$O$_7^{2-}$ (10$^{-2}$ M)) or 3 mg of Tb-MOF powder was dispersed in H$_2$O solutions containing different concentrations of Cr$_2$O$_7^{2-}$. Before photoluminescence measurements, the suspensions were ultrasound for 30 min and stood at room temperature for 2 days. Luminescence emissions are recorded in Figure 8a. Noteworthy is that most of the inorganic anion ions possess varying degrees of luminescence quenching effects. Especially, Cr$_2$O$_7^{2-}$ ions could almost completely quench the luminescence of the Tb-MOF, which shows that the Tb-MOF has high selectivity for sensing Cr$_2$O$_7^{2-}$ ions, and the stability of the Tb-MOF after sensor performances of Cr$_2$O$_7^{2-}$ ions was checked by PXRD (Figure 2). The luminescence intensity of the Tb-MOF decreased gradually with the increase in Cr$_2$O$_7^{2-}$ ion concentration. It was found that there is a good nonlinear relationship between the luminescence intensity and Cr$_2$O$_7^{2-}$ ion concentration. This quenching effect on Tb-MOF aqueous solution was studied by recording the UV–visible absorption spectrum of the metal ion system (Figure S3). Among them, the absorption spectrum of Fe$^{3+}$ has an observable peak in the range of 260–398 nm, and there is no other metal ion absorption in this wavelength range. Under light conditions, the competitive absorption of Fe$^{3+}$ and the Tb-MOF at 325 nm results in fluorescence quenching of the system.23

To further understand the interference of other metal cations on the Tb-MOF system, adding nitrates of the 16 metals to the Fe$^{3+}$ solution (10$^{-2}$ M) containing 3 mg of Tb-MOF powder so that the nitrate concentration is 10$^{-2}$ M too, the results are shown in Figure 7. It can be seen that as long as Fe$^{3+}$ is 10$^{-2}$ M, NO$_2^-$, SO$_3^{2-}$, C$_6$O$_4^{2-}$, PO$_4^{3-}$, and Cr$_2$O$_7^{2-}$ (10$^{-2}$ M) or 3 mg of Tb-MOF powder was dispersed in H$_2$O solutions containing different concentrations of Cr$_2$O$_7^{2-}$.

The quenching coefficient $K_{qv}$ for Fe$^{3+}$ mixed with the Tb-MOF in H$_2$O (0.01 M) is 9580 M$^{-1}$.

In order to understand the fluorescence quenching mechanism of Fe$^{3+}$ to the Tb-MOF, the quenching mechanism of different metal ion aqueous solutions was studied by recording the UV–visible absorption spectrum of the metal ion system (Figure S3). Among them, the absorption spectrum of Fe$^{3+}$ has an observable peak in the range of 260–398 nm, and there is no other metal ion absorption in this wavelength range. Under light conditions, the competitive absorption of Fe$^{3+}$ and the Tb-MOF at 325 nm results in fluorescence quenching of the system.23

The quenching coefficient $K_{qv}$ for Fe$^{3+}$ mixed with the Tb-MOF in H$_2$O (0.01 M) is 9580 M$^{-1}$.16–18 The quenching coefficient $K_{qv}$ for Fe$^{3+}$ mixed with the Tb-MOF in H$_2$O (0.01 M) is 9580 M$^{-1}$.

The quenching coefficient $K_{qv}$ for Cr$_2$O$_7^{2-}$ mixed with the Tb-MOF in H$_2$O (0.01 M) is 6543 M$^{-1}$.16–18 The quenching coefficient $K_{qv}$ for Cr$_2$O$_7^{2-}$ mixed with the Tb-MOF in H$_2$O (0.01 M) is 6543 M$^{-1}$.

In order to know the luminescence quenching mechanism of the Tb-MOF toward Cr, different inorganic anion ionic aqueous solution were researched by UV–vis absorption spectroscopy (Figure S4), which shows that the strong absorption bands of only Cr$_2$O$_7^{2-}$ aqueous solution were found to be between 230–312 nm and 312–500 nm, whereas other anionic aqueous solutions did not overlap with these absorption bands. The luminescence quenching of the Tb-MOF is due to the competition of Cr$_2$O$_7^{2-}$ aqueous solution and carboxylic acid ligands for the absorption of energy at an excitation wavelength (325 nm).

2.3.5. Electrochemical Sensing Experiment (Carbon Paste Electrode). Due to the excellent electrochemical sensing properties of MOF materials, many researchers tried to use

**Figure 6.** (a) Luminescence spectra and histogram of the Tb-MOF introduced into different metal ions ($\lambda_{ex}$ = 351 nm). (b) Luminescence spectra of the Tb-MOF in different concentrations of Fe$^{3+}$ ions.

**Figure 7.** Interference of metal ions with Tb-MOF fluorescence sensing Fe$^{3+}$. 

between the luminescence intensity and Fe$^{3+}$ concentration in the range of 10$^{-9}$–0.01 M, with a nonlinear equation of $y = 3841.80 \times \exp(-x/4.86 \times 10^{-4}) + 2575.51 \times \exp(-x/4.71 \times 10^{-7}) + 27.20$ ($R^2 = 0.9614$) (Figure 6b inset). This quenching effect can be expressed by the Stern–Volmer quenching coefficient in the equation $I_0/I = 1 + K_{sv}[M]$ (where $I_0$ and $I$ are the luminescence intensity of the Tb-MOF and the suspension of the Tb-MOF mixed with metal ions, respectively, [M] is the molar concentration of metal ions, and $K_{sv}$ is the quenching coefficient of metal ions).16–18 The quenching coefficient $K_{sv}$ for Cr$_2$O$_7^{2-}$ ions, respectively, [M] is the molar concentration of Cr$_2$O$_7^{2-}$ ions, and $K_{sv}$ is the quenching coefficient of Cr$_2$O$_7^{2-}$ ions).16–18 The traditional methods for the determination of Cr$_2$O$_7^{2-}$ such as atomic spectroscopy and ICP generally have the disadvantages of expensive equipment, complicated sample processing, and low selectivity. However, the method has the characteristics of high sensitivity, a low detection limit, and simple operation and effects.

In order to know the luminescence quenching mechanism of the Tb-MOF toward Cr, different inorganic anion ionic aqueous solution were researched by UV–vis absorption spectroscopy (Figure S4), which shows that the strong absorption bands of only Cr$_2$O$_7^{2-}$ aqueous solution were found to be between 230–312 nm and 312–500 nm, whereas other anionic aqueous solutions did not overlap with these absorption bands. The luminescence quenching of the Tb-MOF is due to the competition of Cr$_2$O$_7^{2-}$ aqueous solution and carboxylic acid ligands for the absorption of energy at an excitation wavelength (325 nm).
A good linear relationship is obtained with the equation of concentration of TPA, the current response increases gradually. The reduction peak of TPA at ~0.8 V compared with the Tb-MOF bare electrode. At the TPA concentration of 0.1 mM, the current change of the electrode increases by 10 μA, indicating that this material has good electrochemical activity. On the other hand, as shown in the inset of Figure 9, with the increase in the concentration of TPA, the current response increases gradually. A good linear relationship is obtained with the equation of y = -2.733x + 6.142 (R² = 0.9987). These results indicate that the Tb-MOF has a very broad application prospect in the field of electrochemical sensing. With the slope of this fitting line and the measurement error of the current intensity with blank samples, the detection limit for TNA was calculated to be 1.24 μM (3σ/k). In addition, the carbon paste electrode has the advantages of simple fabrication and easy updating of the electrode surface, which can be further studied to establish a highly selective electrochemical sensor for the detection of TPA compounds.

3. CONCLUSIONS
A three-dimensional porous multifunctional Tb-MOF fluorescent probe has been successfully constructed for sensing small molecules, metal ions, and inorganic anions. The structural feature exhibits two kinds of inorganic building units: binuclear and tetranuclear cubic clusters and high coordination organic building units of flexible μ-DBA ligands. Fluorescence analysis shows that the Tb-MOF could act as a fluorescent probe for highly sensitive induced aqueous solutions of Fe³⁺ (10⁻⁹ M), Cr₂O₇²⁻ (10⁻⁹ M), and H₂O₂ molecules (10⁻⁷ M) as well. In addition, the electrochemical performance of the Tb-MOF/CPE detection of 2,4,6-trinitrophenylamine (TPA) (1.24 μM) shows that the Tb-MOF also had good electrochemical activity (10 μA/0.1 mM) to detect TPA. In a word, the Tb-MOF is a multifunctional fluorescent detection probe for Fe³⁺ ions, Cr₂O₇²⁻, and H₂O₂ molecules and the electrochemical sensing of TPA, which makes it potentially useful for analyzing these pollutants in wastewater.

4. EXPERIMENTAL SECTION
4.1. Materials and Methods. All reagents are commercially purchased without further purification. Single-crystal data of the Tb-MOF were collected on a SHIMADZU XRD-7000 X-ray diffractometer on a Bruker D8 Venture system with Mo Kα radiation (λ = 0.71073 Å) at 150 K. Fluorescence spectra have been recorded by a fluorescence spectrophotometer (Hitachi F-7000). Infrared spectra have been recorded by an FT-IR spectrometer (Nicolet Avatar 3600) from KBr pellets in the range of 4000–400 cm⁻¹. Elemental analyses (C, H, and N) were performed using a Vario EL elemental analyzer. Electrochemical properties were performed by a CHI660D electrochemical workstation (Shanghai Chenhuan Instrument Co., Ltd.). Thermal gravimetric analysis (TGA) was performed by a Netzsch TG-209.

4.2. Synthesis of the Tb-MOF. A mixture of 3,5-di(2’,4’-dicarboxyphenyl) benzoic acid (H₄L) (0.075 mmol), Tb(NO₃)₃·6H₂O (0.05 mmol), and DMF (1 mL), water (4 mL), and NaOH (0.1 mol/L, SD) was placed in a Teflon-lined stainless steel autoclave and heated at 160 °C for 72 h then dropped until 30 °C with the rate of 4 °C/h⁻¹. After being filtered and washed with H₂O, some colorless bulk crystals (Tb-MOF) were obtained and dried in air (83% yield based on the Tb element). Anal. Calcd for C₁₃₈H₇₆O₇₃Tb₁₀ (%): C, 36.88; H, 1.69. Found (%): C, 36.90; H, 1.68. IR (KBr, cm⁻¹) (Figure S1): 3405 (m), 1621 (s), 1605 (s), 1557 (s), 1493 (m), 1441 (s), 1330 (m), 1230 (m), 1180 (m), 1125 (m), 1048 (m), 1014 (m), 870 (m), 821 (m), 743 (m), 695 (m), 618 (m), 467 (m).
X-ray Crystallography. X-ray crystallographic treatment of the Tb-MOF in the same literature,13 crystallographic data and structure refinements, and the selected bond lengths and bond angles for the Tb-MOF are summarized in Tables S1 and S2.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.0c04526.

Crystallographic information for C_{414}H_{204}O_{232}Tb_{30} (CIF)

Infrared spectroscopy of complex 1; coordination mode of Tb1, coordination mode of Tb2, coordination mode of Tb3, and coordination mode of Tb4; UV–visible absorption spectrometry of the inorganic anion system; crystallographic data for complex 1; selected bond lengths (Å) and angles (°) for complex 1 (PDF)

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Notes

The authors declare no competing financial interest.

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