Research Article

Three-dimensional terbium(III) metal–organic framework constructed by thiophene-2,5-dicarboxylate: synthesis, crystal structure and fluorescent properties

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Abstract

A novel Tb(III) metal–organic framework was synthesized by a multi-layer diffusion method at room temperature. Adjacent Tb(III) ions were connected together by bridging carboxylic groups to construct one-dimensional chains and the metal–organic framework based on these parallel 1D chains was formed through thiophene-2,5-dicarboxylate bridges. UV–Vis and fluorescent emission spectra as well as theoretical calculation showed that organic ligands acted as sensitizers to Tb(III) fluorescence. With the excitation of 325 nm, the emission peaks of this compound were found at 488, 545, 587, and 621 nm which were attributed to $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$ transitions, respectively. The quantum yield for solid sample was 36.98% and this compound can emit strong green light in the solid state.

Graphic abstract One new Tb(III) metal-organic framework was synthesized by a multi-layer diffusion method at room temperature using thiophene-2,5-dicarboxylate as the bridging ligand and investigated by single-crystal structure, UV-Vis absorption, and fluorescent emission.

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Keywords Tb(III) · Metal–organic framework · Thiophene-2,5-dicarboxylate · Fluorescence

1 Introduction

Metal–organic frameworks (MOFs) have attracted great interests due to the fluorescent properties [1–5], as well as the significant applications, such as magnetism [6–8], gas adsorption and separation [9–11], sensors or detectors [12–17], proton conduction [18], etc. Lanthanide coordination polymers including lanthanide–organic frameworks, one of the important MOFs, are generally synthesized by hydrothermal methods which require high pressure and high temperature that has impeded scalable synthesis of lanthanide MOFs and their industrial utilization [19–21]. Other reported synthetic methods such as solvothermal, microwave-assisted solvothermal, and sonochemical synthesis are also energy consumable [22–24]. Diffusion method, which is seen as low-yield and time-consuming method, has ever been used to synthesize MOFs. However, it is an energy-free method and has seldom been used to synthesize lanthanide MOFs. In our previous work [25], we came up with a three-layer diffusion method with pyridine and some of its basic derivatives acting both as weak bases to deprotonate carboxylic acids (bridging ligands) and as terminal ligands to synthesize coordination polymers with different magnetic properties at room temperature (Scheme 1a). In this work, we applied the same method and successfully synthesized a fluorescent lanthanide metal–organic framework with an angular dicarboxylic acid (H_2L : thiophene-2,5-dicarboxylic acid) as a bridging ligand under normal pressure at room temperature (Scheme 1b–d).

Among applications of lanthanide MOFs, fluorescence has been widely studied and highlighted because sharp emissive peaks from lanthanide ions are unique and its emission covers a wide range of spectrum from visible to NIR and far NIR. Furthermore, organic ligands as linkers in lanthanide MOFs can act as sensitizers to the emission of lanthanide ions which possess very small molar extinction coefficients (ϵ) due to the forbidden nature of f–f transitions in lanthanide atomic shells [22]. However, synthesizing strong emissive lanthanide MOFs with good quantum yield is not easy to be done. In this paper, we synthesized a high yield Tb(III)-MOF showing a strong fluorescent emission and experimentally investigated its fluorescence properties arising from Tb(III) ions sensitized by organic ligands in solid state as well as studied with theoretical calculations (Scheme 1d). Its single crystal structure was described and thermal stability by thermogravimetric analysis (TGA) under air atmosphere was also described.

2 Experimental

2.1 Materials and physical measurements

All reagents and solvents were commercially available without further purification. Fourier transform infrared spectra were recorded on an FTS-40 infrared spectrometer as KBr pellets. Thermogravimetric analyses were performed under air atmosphere at a heating rate of 10 °C/min on a Netzsch STA409 PC instrument, in the temperature range of 30–820 °C. UV–Vis spectra were measured by TU-1901 spectrometer. Fluorescent properties were determined by Thermo Scientific Nicolet iS10 spectrometer (for measurement of excitation and emission spectra) and Edinburgh Analytical Instrument FLS980 (for measurement of life time and absolute quantum yield). The morphology of MOFs was investigated by scanning electron microscopy (JSM7001F, NEC).

2.2 X-ray diffraction studies

X-ray diffraction data for single crystals were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite crystal and incident beam monochromator using

Scheme 1. Synthesis route of fluorescent Tb(III) MOF

Table 1 Crystallographic data and structure refinement summary for compound **1**

Compd	1
Empirical formula	C ₃₀ H ₂₄ N ₂ O ₁₄ S ₃ Tb ₂
Formula weight	1050.53
Crystal size(mm)	0.30 × 0.29 × 0.26
Crystal system	triclinic
Space group	P-1
<i>a</i> (Å)	11.250(4)
<i>b</i> (Å)	12.061(4)
<i>c</i> (Å)	13.480(5)
α (°)	93.245(4)
β (°)	91.197(5)
γ (°)	96.875(4)
<i>Z</i>	2
ρ_{calcd} (g·cm ⁻³)	1.925
μ (mm ⁻¹)	0.670
<i>F</i> (000)	1016
2 θ scan range	4.42–52.00
<i>R</i> (int)	0.0312
Total reflections	6914
Unique reflections	5852
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0474, 0.1347
Goodness of fit	1.080
Max/min electron density (e Å ⁻³)	2.315/–2.333

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

Table 2 Selected Bond Lengths (Å) and Angles (°) around Tb atoms for compound **1**

Tb(1)–O(1)	2.446 (5)	Tb(1)–O(5)	2.470 (5)
Tb(1)–O(2)	2.472 (5)	Tb(1)–O(12)	2.482 (5)
Tb(1)–O(3)	2.491 (4)	Tb(1)–O(7)	2.541 (5)
Tb(1)–O(6)	2.609 (5)	Tb(1)–N(1)	2.733 (6)
Tb(2)–O(10)	2.416 (5)	Tb(2)–O(11)	2.442 (5)
Tb(2)–O(13)	2.453 (5)	Tb(2)–O(8)	2.460 (5)
Tb(2)–O(9)	2.463 (5)	Tb(2)–O(4)	2.472 (5)
Tb(2)–O(14)	2.578 (5)	Tb(2)–N(2)	2.756 (6)
O(1)–Tb(1)–O(5)	71.08 (16)	O(5)–Tb(1)–O(12)	146.94 (16)
O(5)–Tb(1)–O(2)	70.50 (17)	O(1)–Tb(1)–O(7)	75.31 (18)
O(3)–Tb(1)–O(6)	67.11 (16)	O(2)–Tb(1)–O(12)	140.42 (16)
O(1)–Tb(1)–N(1)	143.80 (20)	O(2)–Tb(1)–N(1)	69.66 (19)
O(10)–Tb(2)–O(14)	68.68 (16)	O(8)–Tb(2)–O(14)	73.65 (18)
O(10)–Tb(2)–O(8)	74.94 (19)	O(13)–Tb(2)–O(8)	85.19 (18)
O(10)–Tb(2)–O(11)	119.95 (18)	O(9)–Tb(2)–O(14)	133.66 (19)
O(10)–Tb(2)–N(2)	143.60 (20)	O(4)–Tb(2)–N(2)	69.27 (19)

Mo K α radiation ($\lambda = 0.71073$ Å). Crystal data, data collection parameters, and analysis statistics for compound **1** are listed in Table 1. Selected bond lengths and angles are given in Table 2. The frames were integrated in the Siemens SAINTPLUS software package [26], and the data were

corrected for absorption using the SADABS program [27]. The structures were solved by the direct method (SHELXS 97) and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms and oxygen atoms were inserted at the calculated positions and allowed to ride on their respective parent atoms. Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as CCDC 1835084.

3 Results and discussion

3.1 General characterization

In the Fourier transform infrared spectrum (FT-IR) of compound **1** (Fig. S1), the absence of the bands around 1666 cm⁻¹, 1274 cm⁻¹, and 934 cm⁻¹ (the characteristic bands of $\nu_{\text{C=O}}$, $\nu_{\text{O-H}}$, and $\delta_{\text{O-H}}$ of carboxylic acid groups in free ligands, respectively) indicates the complete coordination and deprotonating of the carboxylic group of the ligand **H₂L**. On the other hand, the frequency separations ($\Delta\nu$) between the asymmetric (ν_{as}) and symmetric (ν_{s}) stretching modes of the carboxylic units also provide an indication of its bridging coordination mode. For compound **1**, ν_{as} (COO⁻) = 1553 cm⁻¹, ν_{s} (COO⁻) = 1384 cm⁻¹, $\Delta\nu$ is 169 cm⁻¹ which lies in the range of 160–170 cm⁻¹ (bridging mode for COO⁻ group) [28, 29]. $\Delta\nu$ for free ligand **H₂L** is 251 cm⁻¹ (Fig. S2). The broad band at ca. 3396 cm⁻¹ is ascribed to the OH vibration for the coordinating methanol molecule.

3.2 Preparation of compound **1**, [Tb₂L₃(Py)₂(CH₃OH)₂]_n

A solution of Tb(NO₃)₃·6H₂O (0.0453 g, 0.1 mmol) in 10 mL methanol was carefully layered on a solution of **H₂L** (0.017 g, 0.1 mmol) in a mixed solvent of 10 mL H₂O and 1.5 mL pyridine with 1 mL H₂O as a buffer in the middle of two layers in a vial and then sealed. About 2 weeks later, colorless block crystals were found on the wall of vial. Products were carefully picked and washed with methanol three times, and then dried at room temperature. Yield: 63.7% (based on Tb). Anal. Calcd% (found%) for C₃₀H₂₄N₂O₁₄S₃Tb₂: C, 34.30 (34.19); H, 2.30 (2.28); N, 2.67 (2.71). IR ν_{KBr} (cm⁻¹): 3397 br, 1553 s, 1473 w, 1441 w, 1384 s, 1215 w, 1128 w, 1033 w, 825 w, 773 m, 703 w, 684 w, 546 w, 473 w.

The experimental powder X-ray diffraction (PXRD) pattern of compound **1** agrees mainly with the simulated one from the single-crystal X-ray diffraction data (Fig. S3), indicating that it is in pure phase. The minor difference

between small peaks should be due to little amorphous component in the crystallized product or the loss of coordinated methanol and pyridine molecules when preparing powder sample for PXRD experiment.

Photos taken by scanning electron microscopy (SEM) showed that MOFs were formed with shapes of prism and other kinds of blocks (Fig. 1). It can be seen from the last three photos that MOF was formed layer by layer with the thickness of about 2 μm . From the last photo we can see some small amorphous solid covering the layers of MOF with clear edges.

3.3 Description of crystal structure

Compound **1** crystallizes in the space group $P-1$. In this structure, there are two independent Tb(III) metal centers, Tb(1) and Tb(2). However, both Tb(III) metal centers are all coordinated by one pyridine N atom, one O atom from one methanol molecule, and six carboxylic O atoms from six different organic ligands, defining a distorted square antiprism (D_{4d}) geometry (Fig. 2). The bond angles around the Tb(1) and Tb(2) metal centers range from $67.11(16)^\circ$ to $146.94(16)^\circ$. The Tb–N bond distances relating to two metal centers range from $2.733(6)$ Å to $2.756(6)$ Å, the Tb–O_{methanol} bond distances range from $2.578(5)$ Å to $2.609(5)$ Å, and the Tb–O_{carboxylate} bond distances range from $2.416(5)$ Å to $2.578(5)$ Å which are in

Fig. 2 Ball-stick diagram showing the coordination arrangement around the Tb center (hydrogen atoms omitted for clarity. Symmetric codes: #1 1-x, 1-y, -z; #2 -1+x, y, z; #3 1+x, y, -1+z)

accordance with those in previously reported Tb(III) coordination polymers [30–32].

Angular organic ligands **L** act as the only bridges that a three-dimensional Terbium-organic framework is constructed. Four Tb(III) ions are linked by one **L** anion as a bridging bidentate ligand through two carboxylic groups in *syn-syn* and *syn-anti* configurations in one ligand (Fig. S4). First, two adjacent Tb(III) ions are linked together by four carboxylic groups in the *syn-syn* mode and another two neighboring Tb(III) ions are linked together by two

Fig. 1 SEM images of MOFs

Fig. 3 Ball-stick diagram showing the two-dimensional layer (hydrogen atoms omitted for clarity)

Fig. 4 Ball-stick diagram showing the metal–organic frameworks along *a* axis (hydrogen atoms omitted for clarity)

carboxylic groups in the *syn-anti* mode. In this way, one-dimensional metal clusters are constructed. Then, those parallel one-dimensional metal clusters are linked together by parallel organic ligands along one direction to form two-dimensional planes (Fig. 3). Finally, two-dimensional layers are also linked together by organic ligands along the perpendicular direction of layers to form the three-dimensional metal–organic frameworks. Along with *a* axis, there are channels with the dimension of ca. $0.5 \times 0.5 \text{ nm}^2$ among the organic ligands and coordinated methanol molecules (Fig. 4). Furthermore, along the direction that is parallel to one-dimensional metal clusters

there are possible large-scale channels (ca. $1.6 \times 1.6 \text{ nm}^2$) occupied by coordinating pyridine molecules which can be removed by heating as illustrated in TGA curve in the next part (Fig. 5). Unfortunately, nitrogen gas adsorption and desorption experiments at 77 K showed that solid sample after removing methanol and pyridine at 300 °C did not possess large pores and surface area maybe due to the framework collapse without methanol or pyridine support (Fig. S5).

3.4 Thermal analysis

Thermogravimetric analysis (TGA) was performed on a powder sample of compound **1** under air circumstances. The thermogravimetric curve of this compound has four steps of obvious weight loss (Fig. 6). The first weight loss of 5.62% from 30 to 200 °C corresponds to the loss of two coordinating methanol molecules (calcd 6.10%). The second step weight loss of 13.88% from 200 to 350 °C corresponds to the loss of two coordinating pyridine molecules (calcd 15.06%). The third step from 350 to 600 °C is attributed to decomposition and part loss of the **L** organic ligands and the last loss from 600 to 800 °C is the loss of all component of **L** with residue of Tb_2O_3 . The remaining weight at 35.20% is likely that of inorganic residue of Tb_2O_3 (calcd 34.83%).

3.5 Photophysical properties

UV–Vis adsorption properties were performed to low concentration suspension of compound **1** in DMF (10^{-4} mol/L) and dilute solution of ligand H_2L in DMF (10^{-4} mol/L) at room temperature (Fig. 7). The adsorption peak of compound **1** was significantly higher than that of the organic ligand H_2L of the same concentration based on the deprotonated organic ligand L^{2-} . For compound **1**, the coordination of Tb(III) to ligand did not change the π – π^* gap but shared the energy absorbed by π system in organic ligand and then the whole coordination compound can absorb more energy than organic ligand. Meanwhile, we investigated the fluorescent emission using low concentration suspension of compound **1** in DMF with the concentration of 10^{-4} mol/L . It emitted weak light with the lifetime of 2.36 ns and small absolute quantum yield of 10.42% (Fig. S6).

Solid-state fluorescent spectrum determinations were also performed on powder sample of compound **1** at room temperature. As shown in Fig. 8, upon the optimized excitation of 325 nm in the excitation spectrum (Fig. S7), the emission peaks were found at 490 nm, 545 nm, 586 nm, and 622 nm, which attribute to $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions, respectively. As indicated in the fluorescent emission graph, the transition of

Fig. 5 Ball-stick diagram showing the metal–organic frameworks along the one-dimensional metal cluster's direction (hydrogen atoms omitted for clarity)

Fig. 6 TGA curve of compound **1**

$^5D_4 \rightarrow ^7F_5$ shows the strongest emission due to its easiest sensing by organic ligands because the Tb(III) metal ion is located on the non-centrosymmetric ligand-field position [33]. The lifetime for the solid sample was 2.98 ns which is a little longer than that for solution (Fig. S8). However, the absolute quantum yield of solid sample was significantly increased to 36.98% (Fig. S9) that made the powder sample emit very strong green light seen by naked eyes (Fig. 9).

In order to investigate the fluorescent emission of Tb(III) metal ion sensitized by organic ligand thiophene-2,5-dicarboxylate, theoretical calculation by DFT/TD-DFT method using B3LYP/6-31G(d) basis sets was performed to

Fig. 7 UV-Vis absorption spectra of compound **1** and H_2L in DMF (10^{-4} mol/L) at room temperature (red line: compound **1**; black line: H_2L)

assess the molecular orbitals and triplet state of ligand in MOF. As shown in Fig. 10, the electron density of HOMO is mainly located the π -systems of the thiophene ring while more electron density of LUMO is located at two carboxylic groups. This can explain why this ligand can be used to sensitize the emission of Tb(III) ion because of more LUMO occupation on carboxylic groups which directly coordinate to Tb(III) ions and facilitate the energy transfer from organic ligand to Tb(III) ions. Furthermore, the calculated lowest triplet state energy (T_1) is $22,099\text{ cm}^{-1}$ which

Fig. 8 Emission spectra of compound **1** upon the excitation of 325 nm in the solid state at room temperature

is 1599 cm^{-1} (between 1000 and 2000 cm^{-1}) higher than the $^5\text{D}_4$ emitting level ($20,500\text{ cm}^{-1}$) of Tb(III) ion and sufficiently make the energy transfer process more efficient [34, 31].

4 Conclusion

In summary, we successfully synthesized a lanthanide metal–organic framework by an angular dicarboxylic acid bridging ligand at room temperature and characterized its fluorescent property. The fluorescent emissions are significant due to the antenna effect of organic ligands that this lanthanide metal–organic compound can be used as lighting materials such as OLEDs.

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Compliance with ethical standards

Conflict of interest There is no conflict of interest.

Appendix A. Supplementary material

Figure S1–S9. Crystallographic data (excluding structure factors) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication (CCDC no.: 1835084). Copies of the data can be obtained free of charge on application to

Fig. 9 Photos taken under white light (left) and UV light (365 nm) (right)

Fig. 10 Calculated HOMO and LUMO of H_2L

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