



# Construction of three lanthanide metal-organic frameworks: Synthesis, structure, magnetic properties and highly selective sensing of metal ions



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## ABSTRACT

Three lanthanide metal-organic frameworks (Ln-MOFs),  $[\text{Ln}(\text{TZI})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$  ( $\text{Ln}=\text{Gd}$  (**1**) and  $\text{Tb}$  (**2**) and  $\text{Dy}$  (**3**),  $\text{H}_3\text{TZI}=5-(1\text{H-tetrazol-5-yl})\text{isophthalic acid}$ ), have been synthesized under hydrothermal conditions. Single crystal X-ray diffraction reveals that **1–3** are isostructural and display a 1D double chain based on dinuclear motifs with  $(\mu\text{-COO})_2$  double bridges. Magnetic studies indicate anti-ferromagnetic interactions in **1**, ferromagnetic interactions in **2** and **3**. Furthermore, compound **3** displays a slow relaxation behavior. Compound **2** exhibits intense characteristic green emission of  $\text{Tb}(\text{III})$  ions in the solid state, which can be observed by the naked eye under UV light. Interestingly, **2** can selectively sense  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$  ions through luminescence enhancement and quenching, respectively. The luminescence quenching mechanisms have been investigated in detail. The study on luminescence Ln-MOFs as a probe for sensing  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$  ions is exceedingly rare example.

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## 1. Introduction

The research of metal-organic frameworks (MOFs) have attracted great attention over the past two decades, due to their intriguing structural and topological diversities, as well as their fascinating physical properties [1–9]. In particular, lanthanide-based MOFs are studied widely as an important system of functional MOFs because of their optical, electronic, magnetic and luminescence properties and so on. Among them, magnetic studies on molecule-based systems derived from significant magnetic anisotropy of lanthanide ions such as  $\text{Tb}(\text{III})$ ,  $\text{Dy}(\text{III})$ ,  $\text{Ho}(\text{III})$ , and  $\text{Er}(\text{III})$ , which can increase the D value for the material resulting in high-barrier single-molecule magnets (SMMs), have been of interest in high-density information storage, quantum computing, and molecular spintronics [10–19]. The microporous lanthanide MOFs have evoked increasing interest due to their potential applications in luminescence and gas adsorption [20,21]. Beside lanthanide-based MOFs displaying typical sharp emissions, long luminescent lifetime, high optical purity and high luminescence quantum efficiency, are gaining much attention, which are used as chemosensors for small molecules and metal ions [22–35].  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  are two important metal ions in industry, environmental science and life science and they can influence the human health

and environment [36–38].  $\text{Fe}^{3+}$  is favorable to the formation of haemoglobin and muscle and improve brain functions.  $\text{Pb}^{2+}$  is one of the most hazardous in the environment and the excess amounts of  $\text{Pb}^{2+}$  in the body may cause diseases such as growth retardation, soreness of the extremities, digestive, reproductive, and developmental disorders. Thus, a highly effective and rapid method to select sensing trace amounts of  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  ions over mixed metal ions is very important for human health. In this context, luminescent MOFs are among the most extensively investigated detection technologies for their short response time, high sensibility and simplicity. Luminescent MOFs as sensors mainly depend on the change of luminescence intensity (enhanced or quenched). Many luminescent Ln-MOFs are used as sensor for  $\text{Fe}^{3+}$  ions based on cation-exchange, or interactions between  $\text{Fe}^{3+}$  ions and Lewis-base groups (pyridyl nitrogen,  $-\text{NH}_2$  or  $-\text{OH}$ ) of the organic ligands. Therefore, the selection of organic ligands also is important to control the structures and functions of MOFs. The 5-(1H-tetrazol-5-yl)isophthalic acid ( $\text{H}_3\text{TZI}$ ) ligand that contains both tetrazolate and carboxylate groups, is expected to be versatile modes for the formation of structural diversity coordination polymers. Carboxylate can serve as various bridging modes ( $\mu\text{-O}$ , *syn-syn*, *anti-anti*, and *syn-anti*) to connect two or more lanthanide ions into Ln-MOFs with fascinating architectures and magnetic properties. And carboxylate can form strong H-bonds, which can reinforce the coordination networks or form high-dimensional supramolecular structures. The  $\text{H}_3\text{TZI}$  ligand also is  $\pi$ -conjugated rigid organic ligand, which can provide luminescence and rigid backbones. Here

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we report the structure, magnetic and luminescent properties of three 1D double chains lanthanide metal-organic framework based on  $(\mu\text{-COO})_2$  double bridges,  $[\text{Ln}(\text{TZI})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$  (Ln=Gd (**1**) and Tb (**2**) and Dy (**3**),  $\text{H}_3\text{TZI}=5\text{-}(1\text{H-tetrazol-5-yl})\text{isophthalic acid}$ ). They show different magnetic properties: **1** displays anti-ferromagnetic behavior, **2** and **3** are ferromagnetic behaviors, moreover **3** displays relaxation dynamics at the low temperature. Such behavior, which stems from the molecule itself, can form SMMs [39,40] and single-chain magnets (SCMs) [41]. The luminescence studies revealed that the Tb(III)-based emission peaks of **2** can be highly selectively quenched and enhanced by  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  ions in ethanol suspension. Compound **2** provides a platform for luminescent sensing research. It is very exciting that **2**, as  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  -probes, were not influenced by the presence of other common metal ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ), which suggests the potential use of the Ln-MOFs for metal ions sensing.

## 2. Experimental

### 2.1. Physical measurements

Elemental analysis was carried out on an Elementar Vario El III elemental analyzer. Infrared spectra were recorded in the range  $4000\text{--}500\text{ cm}^{-1}$  on a NEXUS 670 FT-IR spectrometer using the KBr pellets. The phase purity of the samples was confirmed by powder X-ray diffraction collected on a Bruker D8-ADVANCE diffractometer equipped with Cu K $\alpha$  at a scan speed of  $1^\circ\text{ min}^{-1}$ . TG analyses were carried out on a Mettler Toledo TGA/SDTA851 instrument under a flowing air atmosphere at a heating rate of  $283\text{ K min}^{-1}$ . Temperature-dependent and field-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-5 magnetometer. Diamagnetic corrections were made with Pascal's constants. Photoluminescent spectra were recorded using a Jasco FP-8300. Luminescent life measurements were performed on an FLUOROLOG-3-TAL luminescence spectrometer. Inductively coupled plasma spectroscopy (ICP) was performed on a Optima 7300 DV. UV-vis spectroscopic studies were measured on Pgeneral TU-1901.

### 2.2. Materials and synthesis

All the solvents and reagents including 5-(1H-tetrazol-5-yl)isophthalic acid (H3TZI) were of reagent grade quality, and they were purchased from commercial sources and used as received.

Syntheses of  $[\text{Ln}(\text{TZI})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$  (**1–3**). A mixture of  $\text{H}_3\text{TZI}$  (0.01 mmol, 0.0117 g),  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, Ln=Gd, Tb, Dy) in  $\text{CH}_3\text{CN}$  (6 mL) and  $\text{H}_2\text{O}$  (6 mL) was stirred for 20 min at room temperature, then sealed in a Teflon-lined stainless steel vessel (25 mL), heated at 413 K for 2 days under autogenous pressure, and then cooled to room temperature. The colorless block crystals of **1–3** were obtained.

**Gd(TZI)(H<sub>2</sub>O)<sub>4</sub> · 3H<sub>2</sub>O (1)** Yield, 59% based on Gd. Elemental analysis (%) calcd for  $\text{GdC}_9\text{H}_{17}\text{N}_4\text{O}_{11}$ : C, 21.01; N, 10.89; H, 3.33%. Found: C, 21.06; N, 10.85; H, 3.36%. IR (KBr,  $\text{cm}^{-1}$ ): 3067 m, 1632 s, 1588 m, 1532 s, 1497 m, 1447 s, 1391 s, 1109 m, 789 w, 747 w, 710 w.

**[Tb(TZI)(H<sub>2</sub>O)<sub>4</sub> · 3H<sub>2</sub>O (2)** Yield, 55% based on Tb. Elemental analysis (%) calcd for  $\text{TbC}_9\text{H}_{17}\text{N}_4\text{O}_{11}$ : C, 20.94; N, 10.85; H, 3.32%. Found: C, 20.96; N, 10.84; H, 3.35%. IR (KBr,  $\text{cm}^{-1}$ ): 3069 m, 1632 s, 1594 m, 1537 s, 1490 m, 1453 s, 1391 s, 1109 m, 789 w, 752 w, 710 w.

**[Dy(TZI)(H<sub>2</sub>O)<sub>4</sub> · 3H<sub>2</sub>O (3)** Yield, 61% based on Dy. Elemental analysis (%) calcd for  $\text{DyC}_9\text{H}_{17}\text{N}_4\text{O}_{11}$ : C, 20.80; N, 10.78; H, 3.30%. Found: C, 20.78; N, 10.80; H, 3.32%. IR (KBr,  $\text{cm}^{-1}$ ): 3071 m, 1632 s, 1588 m, 1538 s, 1494 m, 1447 s, 1397 s, 1109 m, 787 w, 752 w, 704 w.

### 2.3. Crystallographic analysis

Diffraction data for **1–3** were collected at 293 K on a Bruker Apex II CCD area detector equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda=0.71073\text{ \AA}$ ). Empirical absorption corrections were applied using the SADABS program [42]. The structures were solved by the direct method and refined by the full-matrix least-squares method on  $F^2$ , with all non-hydrogen atoms refined with anisotropic thermal parameters [43]. All the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. The water hydrogen atoms were located from the difference maps. But, a hydrogen atom of uncoordinated water (O9) in **1–3** was not located. A summary of the crystallographic data, data collection, and refinement parameters are provided in Table 1. Selected bond lengths and angles for **1–3** are listed in Tables S1–S3 (ESI†).

## 3. Results and discussion

### 3.1. Description of the structure of compound 1

#### 3.1.1. The structural features

X-ray crystallographic analyses revealed that compounds **1**, **2** and **3** are isomorphous, crystallizing in the Triclinic space group  $P\bar{1}$ . Here only the structure of **3** is described in details. The asymmetric unit consists of one Dy(III) ion, one TZI ligand, four coordinated water molecules and three lattice water molecules. Each Dy(III) ion coordinates with eight oxygen atoms: four (O1, O2A, O3B, O4B) from three different TZI ligands and the other four from four water molecules (O5, O6, O7, O8). The Dy–O bond distances fall in range of 0.2225–0.2528 nm, which are comparable to those reported for other Dy–O compounds [44,45]. Two equivalent Dy(III) ions (Dy1 and Dy1A) are doubly bridged by two equivalent carboxylate groups in the *syn-syn* bridging mode to give a dinuclear motif with the Dy ··· Dy distance of 0.52806(6) nm (Fig. 1a). The TZI ligands bind Dy(III) ions in the  $\mu_4$ -tetradentate coordination mode via the chelating and *syn-syn* carboxylate groups and thus interlink the dinuclear motifs to generate a 1D double chain along the *b* direction (Fig. 1a). The carboxylate groups, water molecules and tetrazolate groups, which lie in the specific position, provide rich store of hydrogen bonding sites for interchain interactions. The

**Table 1**  
Crystal data and structure refinement for compounds **1**, **2** and **3**.

Compounds	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{GdC}_9\text{H}_{17}\text{N}_4\text{O}_{11}$	$\text{TbC}_9\text{H}_{17}\text{N}_4\text{O}_{11}$	$\text{DyC}_9\text{H}_{17}\text{N}_4\text{O}_{11}$
Formula weight	514.52	516.20	519.77
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> /Å	7.4963(10)	7.4990(10)	7.4832(10)
<i>b</i> /Å	10.9105(13)	10.9055(13)	10.9344(13)
<i>c</i> /Å	11.4669(15)	11.4538(15)	11.4824(15)
$\alpha$ /deg	111.743(4)	111.761(4)	111.817(4)
$\beta$ /deg	99.371(4)	99.506(4)	99.390(4)
$\gamma$ /deg	100.616(4)	100.499(4)	100.699(4)
<i>V</i> /Å <sup>3</sup>	828.34(18)	827.14(18)	828.86(18)
<i>Z</i>	2	2	2
<i>D<sub>c</sub></i> (g m <sup>−3</sup> )	2.063	2.073	2.083
$\mu$ (mm <sup>−1</sup> )	4.068	4.340	4.573
<i>F</i> (000)	502	504	506
Reflections collected	8809	8760	13312
Unique reflections	2902	2875	2902
GOF on $F^2$	1.193	1.226	1.145
<i>R</i> <sub>int</sub>	0.0183	0.0224	0.0191
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0197	0.0176	0.0130
<i>wR</i> <sub>2</sub> (all data)	0.0542	0.0487	0.0324

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