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A luminescent terbium metal-organic framework for selective sensing of nitroaromatic compounds in high sensitivity



Wei Sun, Jinzeng Wang, Houting Liu, Siyuan Chang, Xiaoting Qin, Zhiliang Liu*

College of Chemistry and Chemical Engineering, Key Lab of Nanoscience and Nanotechnology, Inner Mongolia University, Hohhot 010021, Inner Mongolia, China

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ABSTRACT

A novel luminescent terbium metal-organic framework $[\text{Tb}(\text{HL})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**1**) has been successfully prepared by the facile hydrothermal reaction of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and the π -conjugated ligand H_4L ($\text{H}_4\text{L} = 1,1'$ -biphenyl-2,3,3',5'-tetracarboxylic acid). Single crystal structure analysis reveals that **1** exhibits a 2D layered structure. The solid sample of **1** emits high bright green light which can be readily observed by the naked eye when excited at 288 nm at ambient temperature. Interestingly, the luminescence of fine grinding **1** particles dispersed in ethanol can be selectively and sensitively quenched by nitroaromatic compounds, which indicates that **1** is a potential luminescent sensory material for nitro explosives.

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1. Introduction

In recent years, designing functional metal-organic framework (MOF) materials has attracted considerable attention, because of their interesting structural topologies [1] and the extensive applications they embodied in catalysis [2], drug delivery [3], selective sensing [4], and so on. Among the various applications, selective molecule sensing properties seems interesting and fascinating. So far, a large number of MOFs have been reported for their sensing properties, especially the luminescent MOFs. The sensing function of luminescent MOFs was applied to recognize metal cations [5], anions [6], and small organic molecules [7].

Considering the fact that nitroaromatic compounds are both environment pollutional small molecules in the black list of priority pollutants [8] and explosive threatening to public security [7], their rapid and trace detection is crucial to environmental protection and homeland security. Compared to other reported explosive detection technologies, such as gas chromatography coupled with mass spectrometry, some reported new detection methods based on luminescence quenching of MOFs are inexpensive, simpler and sensitive [9]. Due to the presence of electron withdrawing nitro-group, nitroaromatic compounds can serve as strong oxidants and interact with some electron donor conjugated polymers containing delocalized π electrons. So designing a luminescent MOF with the electron-rich ligand and proper metal ion is critical for its use as detecting nitroaromatics.

So far, most of reported luminescent MOFs for nitroaromatic compounds sensing are constructed by Zn/Cd ions and π -conjugated ligands [10,11], and the luminescence bands of which are non-characteristic or weak. However, to date, the luminescence MOFs for nitroaromatic compounds sensing based on enhanced characteristic luminescence of rare earth ions have been rarely reported [12]. Herein, we report a new 2D layered Tb(III)-MOF (**1**) which exhibits high selectivity and sensitivity towards nitroaromatic compounds. We select H_4L as a π -conjugated ligand (Scheme S1 in ESI) and Tb(III) ion as the metal connector due to its high affinity to carboxylates and nondetrimental nature to fluorescence. Moreover, because of the lanthanide-centered emission can be sensitized by electron conjugated systems with efficient energy-transfer (so called “antenna effect”), the solid sample of **1** emits high bright green light which can be readily observed by the naked eye when excited at 288 nm at ambient temperature. The luminescence of **1** can be selectively and sensitively quenched by nitroaromatic compounds, indicating its possibility of being a luminescent sensory material for nitro explosives.

2. Experimental

A mixture of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2718 g, 0.6 mmol), H_4L (0.099 g, 0.3 mmol), NaOH (4 drops, 1 mol/L) and water (12 ml) was sealed in a 25 ml Teflon-lined stainless vessel and heated at 120 °C for 72 h. After being cooled to room temperature, the white rod-like crystals were obtained. Yield of 40% based on Tb (NO_3)₃·6H₂O. (CCDC reference number 988819). IR (KBr pellet, ν/cm^{-1}): 437(m), 658(w), 692(m), 765(s), 1254(m), 1382(s), 1448

* Corresponding author. Tel.: +86 471 4995414; fax: +86 471 4992147.
E-mail address: cezliu@imu.edu.cn (Z. Liu).

(s), 1549(s), 1609(w), 1656(w). Elemental Anal.(%) Calcd for: C, 33.35, H, 2.97; Found: C, 33.36, H: 2.96.

3. Results and discussion

[Tb(HL)(H₂O)₄]·H₂O crystallizes in monoclinic space group *P*2₁/*n*. Each asymmetric unit consists of one terbium ion, one HL³⁻ anion ligand, four coordinated water molecules and an isolated solvent water molecule. The nine-coordinated terbium ion exhibits a distorted tricapped trigonal prism geometry completed by five carboxyl oxygen atoms of the HL³⁻ ligand and four oxygen atoms of the coordinated water molecule (Fig. 1(a)). Tb–O distances range from 2.361(5) Å to 2.565(5) Å, the O–Tb–O' angles are in the range of 51.47(2)–151.21(2)° (see Table S2 for selected bond lengths and angles). Each HL³⁻ ligand connects three Tb(III) ions acting in bidentate-chelating and monodentate coordination modes. All the metal centers are further connected via the carboxylic oxygen atoms of HL³⁻ ligands to construct an undulated 2D layered framework (Fig. 1(b)).

The thermal gravimetric analysis curve of **1** displays an initial weight loss of 13.16% (calculated: 15.61%) in the range of 100–250 °C probably attributed to loss of five water molecules (coordinated and lattice) (see Fig. S1). The major mass loss occurs in the temperature range of 250–800 °C with the loss of 37.25% corresponding to the decomposition of the compound.

The solid-state luminescence spectra of **1** was investigated upon excitation at 288 nm under ambient temperature, which exhibits four characteristic peaks of Tb (III) (⁵D₄→⁷F₆: 492 nm, ⁵D₄→⁷F₅: 546 nm, ⁵D₄→⁷F₄: 580 nm, and ⁵D₄→⁷F₃: 623 nm) (Fig. S2). It is well-known that the luminescence of terbium cation has a low molar absorptivity and that the f–f transitions are spin and parity-forbidden. However, it has been shown that the lanthanide-centered emission can be sensitized by electron conjugated systems with efficient energy-transfer, which is known as the “antenna effect”. The most prominent line in **1** is presented at 546 nm which can be readily observed as bright green light by the naked eye. The strong visible emission provides the possibility of **1** acting as a luminescence sensor.

To explore the potential luminescence sensing properties of **1**, the fine grinding sample **1** was dispersed in common organic small molecule solvents such as MeOH, EtOH, MeCN, DMF, isopropanol (IPA), benzene (BZ), toluene (TO), chlorobenzene (Cl-BZ) and nitrobenzene (NB) (see Fig. 2(a)). As depicted in Fig. 2(a) and (c), the

significant quenching of fluorescence intensity was observed upon addition of aromatic ring containing molecules such as TO, Cl-BZ and NB and the most important one is NB. Such observations demonstrate the possibility of **1** for selective sensing of nitroaromatics. Fig. 2(b) shows that the PXRD patterns of obtained samples are consistent with the corresponding simulated pattern which indicates the good phase purity of **1**. The PXRD pattern of **1** and NB-immersed **1** suggests that the basic framework remains in the process of sensing NB.

Three reasons may account for the quenching effect of **1** towards NB. (1) There exists a competition of absorption of the excitation wavelength energy between carboxylate ligand and NB (see Fig. S3). Thus the energy delivered by the carboxylate ligand to Tb³⁺ ion could be decreased significantly, quenching the luminescence of Tb³⁺ in response [8]. (2) There are π–π interactions between NB molecules and frameworks, during which the NB with electron-withdrawing groups serves as electron acceptor and frameworks in **1** can be regarded as electron donor. So the photoinduced electron transfers from the benzene rings of the ligands to the NB and the fluorescence quenching behavior was observed [12]. (3) All the MOF particles could be dispersed well in the analyte solution when being measured. The surface of the crystals absorbs most part of the excitation energy. Thus the excitation radiation cannot reach the inner crystals completely and significant electron transfer takes place from the framework to NB on the surface of the MOF particles [13]. In this case, the quenching effect occurs on the surface of the crystals.

The significant quenching of luminescent intensity shows that **1** is likely to be a good luminescence sensor for NB. So the further investigation was done for examining the relationship of luminescence quenching degree with the concentration of NB (Fig. 3(a)). **1** was dispersed in ethanol as the standard suspension, and then the NB concentration in ethanol was gradually increased to monitor the emissive response. It turns out that the luminescence intensity gradually decreased with increasing content of NB. The luminescence spectra with emission intensity of **1** was completely quenched when the concentration of NB reached 769 ppm (5 mM), indicating the extremely high sensitivity towards NB. Meanwhile, the **1** particles could be regenerated and reused for several cycles through centrifuging and washing the solid sample several times (Fig. S4).

In order to explore whether the substituent groups of NB influence the sensor ability of **1**, some mononitro-aromatic compounds have also been examined with a concentration of 1 mM in

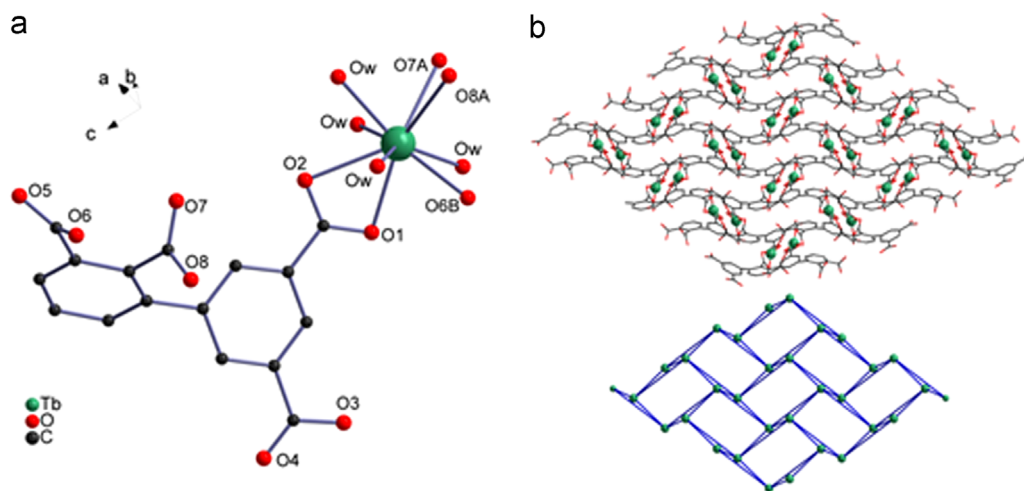


Fig. 1. (a) Coordination environment of Tb³⁺ in **1** (symmetry codes, A: $-x+3/2, y+1/2,$ and $-z+3/2$; B: $x-1/2, -y+3/2,$ and $z-1/2$). Hydrogen atoms and one solvent water molecule are omitted. (b) The undulated 2D layered structure with the coordinated water molecules omitted (along the *c* axial) and its corresponding simplified uninodal 5-connected net of (3³.4³.5⁴) topology.

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