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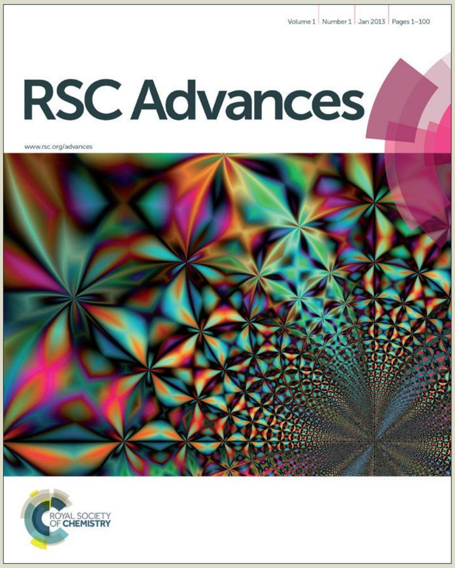

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Luminescent Lanthanide-Organic Polyrotaxane Framework as a Turn-Off Sensor for nitrobenzene and Fe^{3+}

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Three isomorphous lanthanide-organic polyrotaxane frameworks [Ln(mtpc)$_{1.5}$(DMA)(H_2O)]·$2H_2O$ [Ln = Tb (1); Dy (2); Er (3)] were assembled and characterized. In 1, the mtpc ligand transfer absorbed energy to Tb^{3+} center to emit characteristic fluorescent. 1 can act as fluorescent probe for selectivity detecting nitrobenzene and iron(III) ions through the luminescence quenching. Importantly, the detection limit of nitrobenzene lows to 15-150 ppm scale.

On account of the environmental pollution and homeland security, nitroaromatic explosives and heavy metal ions have drawn extensive attentions.[1] Nitrobenzene (NB) is a vital component of nitroaromatic explosives and an infamous environmental contaminant,[2] which can give rise to grisly health problems. The rapid and precise detection of NB is crucial to environmental protection and homeland security. Iron is a necessary element for the human body. Deficient iron will result in tissue damage or increase cardiovascular diseases.[3] Excess iron is also an important pollutant owing to its high toxicity. Therefore, selective detection of Fe^{3+} with a lower detection limit is also of prime importance.

Lanthanide-organic frameworks (LnOFs) have become a content-rich research field over the past decade due to their unique optical properties and extensive applications in many areas,[4] such as luminescent devices,[5] luminescence bioassays[6] and fluorescent probes[7]. Among the multifarious potential applications, the fluorescent probes of chemicals are the most promising one because of their operability, rapidity, high sensitivity and high selectivity. Qian *et al.* reported a nanoscale luminescent metal-organic framework which could sense nitroaromatics resulting from the antenna effect.[8] Recently, a luminescent europium-organic framework was reported by Sun and coworkers,[9] displaying selectively sensing Fe^{3+} and Al^{3+} ions through a cation-exchange approach.

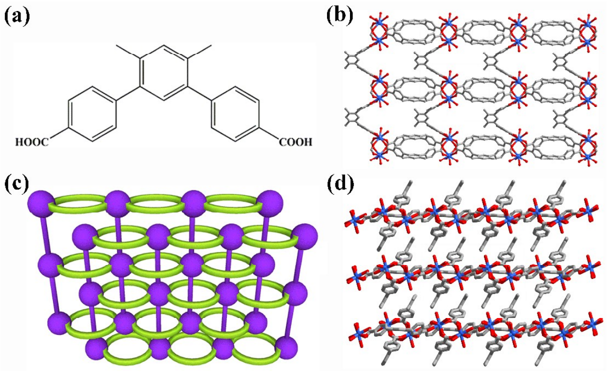

Fig. 1 (a) H_2mtpc ligand. (b) A two-dimensional polymeric layer structure of **1.** (c) Schematic representation of the 2D polyrotaxane layer. (d) View of the stacking framework via the b-axis.

Although some intriguing polyrotaxane LnOFs have been well documented in the literature,[10] their potential applications still remain unexplored. Herein, we report a series of isomorphous lanthanide-organic frameworks [Ln(mtpc)$_{1.5}$(DMA)(H_2O)]·$2H_2O$ [Ln = Tb (**1**); Dy (**2**); Er (**3**)] (H_2mtpc=2',4'-dimethyl,1,1':3',1"-terphenyl,4,4"-dicarboxylic acid), which exhibit polyrotaxane structural features combining interpenetration and interdigitation. Remarkably, the H_2mtpc, a V-shape rigid ligand (Fig. 1a), was used for constructing LnOFs for the first time. Furthermore, **1** displays high stability and excellent fluorescent property, which can serve as luminescent probe of nitrobenzene and Fe^{3+}.

Three lanthanide-organic polyrotaxane frameworks are isomorphous (Table S1, ESI†) as proved by Single-crystal X-ray diffraction and powder X-ray diffraction. Thus, only the crystal structure of **1** is described here in detail. Single-crystal X-ray crystallography reveals that **1** feartures an interesting 3D interdigitated architecture. Its asymmetric unit consists of one Tb(III) center, a half of mtpc ligand, one aqua ligand, one coordinated DMA and two lattice water molecules (Fig. S3, ESI†). Each Tb(III) center is eight-coordinated and surrounded by six carboxylate oxygen atoms from five individual mtpc ligands, one oxygen atom

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†Electronic Supplementary Information (ESI) available: Experimental details, syntheses of **1**, **2** and **3**, PXRD, TG, IR, fluorescence spectra. For ESI and crystallographic data in CIF. See DOI: 10.1039/x0xx00000x

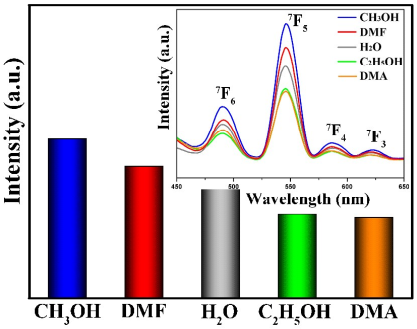


Fig. 2 Luminescence emission spectra of **1** (1 mg) at room temperature in different solvents (4 mL), respectively (λ_{ex}= 314 nm).

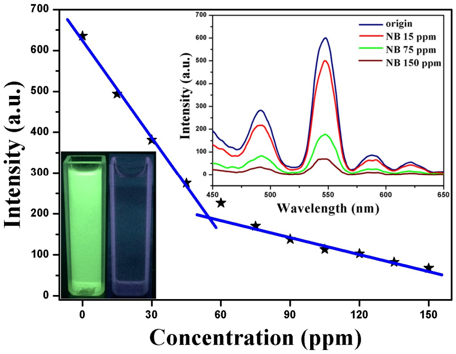


Fig. 4 Luminescence emission spectra of **1** in methanol at room temperature in the presence of 15-150 ppm of NB with respect to **1** (excited and monitored at 314 nm and 545 nm). Inset: photograph showing the change of the original luminescence of methanol suspension of **1** (left) and the decreased fluorescence upon the addition of NB in the methanol suspension of **1** (right).

from an aqua ligand and the one oxygen atom is from a DMA molecule. As illustrated in Fig. S4, ESI†, two adjacent Tb(III) centres are interconnected by four V-shape mtpc ligands via the *syn-syn* mode of bridging carboxylate groups to form a 1D chain structure, which contains paddlewheel [Tb$_2$(COO)$_4$] secondary building units and [Tb$_4$(mtpc)$_2$] loops.[11] Furthermore, the adjacent chains linked by V-shape mtpc ligands forming a 2D thick layer structure (Fig. 1b). The [Tb$_4$(mtpc)$_2$] loop can be seen as a wheel and the mtpc linkers among the adjacent 2D thick layers can be seen as axles based on polyrotaxane theme.[12] The mtpc ligands act as both the axle-like segments and two half-loops of each [Tb$_4$(mtpc)$_2$] loop.[13] Two adjacent layers interpenetrate and knit together to form 2D polyrotaxane sheets as shown in Fig. 1c and Fig. S5 ESI †. Furthermore, the adjacent knitted layers assemble *via* $\pi-\pi$ stacking interactions between phen ligands to generate a 3D interdigitated framework (Fig. 1d). Meanwhile, the $\pi-\pi$ stacking interactions enhance the stability of the framework.[14]

The solid-state luminescence spectra of **1** were investigated at room temperature. **1** exhibits four characteristic peaks at 490, 545, 587 and 622 nm upon excitation at 314 nm, which are attributed to $^5D_4 \rightarrow {}^7F_J$ (J=3, 4, 5, 6) transitions of the Tb^{3+}, respectively.[15] Among these transitions, $^5D_4 \rightarrow {}^7F_5$ (545 nm) is the strongest one. Fine grinding sample of **1** was immersed in methanol, DMF, H$_2$O, ethanol, DMA solvents, respectively, for luminescence studies. As shown in Fig. 2, the luminescence intensity is the strongest in methanol suspension, so the followed fluorescent detection experiments were carried out in the methanol suspension of **1**. The chemical stability of **1** was tested by soaking **1** in methanol, DMF, H$_2$O, ethanol, DMA solvents for 24h. The immobile PXRD patterns indicated that the crystallinity of 1 was well retained after solvent treatment (Fig. S7, ESI†).

The capacity of selective sensing aromatic compounds of **1** was further studied. Some aromatic compounds with the same concentration (150 ppm), such as benzene (BZ), toluene (TO), phenol (PhOH), o-xylene (OX), chlorobenzene (Cl-BZ), bromobenzene (Br-BZ), iodobenzene (I-BZ), nitrobenzene (NB), o-nitrophenol (NP), m-nitrobenzoic acid (NBA), m-dinitrobenzene (DNB), 2,4-dinitrophenol (DNP) and 2,4,6-trinitrotoluene (TNT) were added to the methanol suspension of **1** (Fig. 3). The result indicates that only NB causes an obvious quenching on the luminescence intensity of methanol suspension of **1**, all other NB derivatives, NP, NBA, DNB, DNP, TNT showed little effect on the luminescence intensity, while other aromatic compounds, BZ, TO, PhOH, OX, Cl-BZ, Br-BZ and I-BZ have negligible effects on the luminescence intensity. These results show that **1** has a selective luminescence response to NB through obvious luminescence quenching, providing a possibility of **1** being a wonderful luminescence sensor for NB.

Further studies on the exploring the detection limit of NB were carried out. As shown in Fig. 4, the luminescence quenching degree

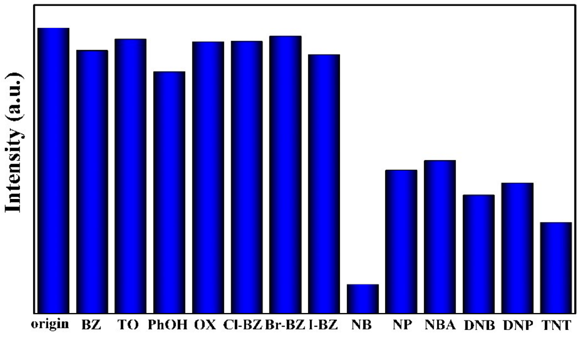
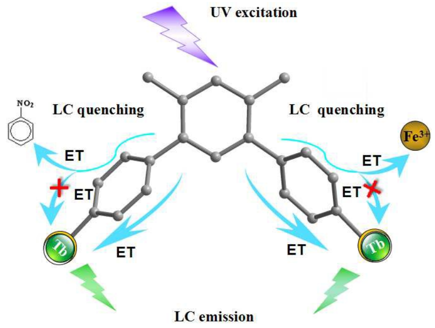


Fig. 3 The $^5D_4$ - $^7F_5$ transition intensities of the methanol suspension of **1** with 150 ppm of different aromatic compounds (λ_{ex}= 314 nm).



Scheme. The mechanism of luminescence quenching.

decreased gradually with the reducing of the NB concentration. When the concentration of NB was 150 ppm, the quenching efficiency reached 87.9%, indicating a nearly complete quenching, which showed a higher quenching efficiency than that reported at the 150 ppm by Qian *et al.,*[8] and the order of quenching efficiencies for the selected NB derivatives at the same concentration with 150 ppm was NB (87.9%) > TNT (66.7%) > DNB (56.7%) ≈ DNP (52.4%) > NP (47.6%) ≈ NBA (44.1%) (Fig. 3 and Fig. S8, ESI †). The detectable luminescence responses of NB were still observed at 15 ppm with the quenching efficiency of 16.6%, and this phenomenon give evidence to that **1** possess excellently high sensitivity toward NB.

The mechanism of quenching might be attributed to energy photo-screening (Scheme).[8] In **1**, the ligand mtpc adsorbs photo energy and transfers the energy to Tb^{3+} by vibronic coupling between mtpc and Tb^{3+}, which results in the luminescence properties of **1**. The luminescence quenching of **1** in methanol suspension after adding NB is due to a competition of absorption of the excitation wavelength energy and the π–π electronic interaction between the NB and the mtpc.[8,16] NB screens the energy which pristinely will be adsorbed by mtpc, thus reducing the possibility of energy transfer (ET) from mtpc to Tb^{3+} and quenching the luminescence of Tb^{3+} soon afterwards. Additionally, the reason for the high efficiency in luminescence quenching of NB compared to other NB derivatives is presumably due to the stereo-hindrance effect. The unique polyrotaxane structure of **1** with the small pores, which have controlled larger NB derivative molecules to enter into the channel of **1**, leading to that the polyrotaxane structure of **1** is quite different from other porosity metal organic frameworks for the sensing of chemical species.[16a] This may explain the unprecedented selectivity for NB than other NB derivatives.

We also investigated the potential function of **1** for the sensing of metal ions. The studies were performed by adding $M(NO_3)_n$ (M^{n+}= Ba^{2+}, Na^{+}, Cd^{2+}, Al^{3+}, Pb^{2+}, Fe^{3+} Cr^{3+}, Zn^{2+}, Mg^{2+} and K^{+}) to the methanol suspension of **1** at room temperature, respectively. As shown in Fig. 5, Fe^{3+} quenches the luminescence of **1** completely, while Al^{3+}, Pb^{2+} and Cr^{3+} weaken the emission intensity of **1** in a small degree, and others had negligible effect on the photoluminescence of **1**. In addition, the luminescence intensity of **1** shrinks gradually upon addition of 0.1-2.0 equiv of Fe^{3+} (Fig. 6) until the emission was completely quenched when 2.0 equiv of Fe^{3+} was introduced. The decrease of emission intensity after adding Fe^{3+} may be assigned to an energy-absorbing rivalry between Fe^{3+} and Tb^{3+} (Scheme). Meanwhile, in accordance with the previous reports,[17] the selectivity to Fe^{3+} is not influenced by some other metal ions (Fig. S9 and S10, ESI †) as demonstrated by introduction of Ba^{2+}, Na^{+}, Cd^{2+}, Al^{3+}, Pb^{2+}, Cr^{2+}, Zn^{2+}, Mg^{2+} and K^{+} into the system. Therefore, the results indicate that **1** can selectively sense Fe^{3+} among other metalions.

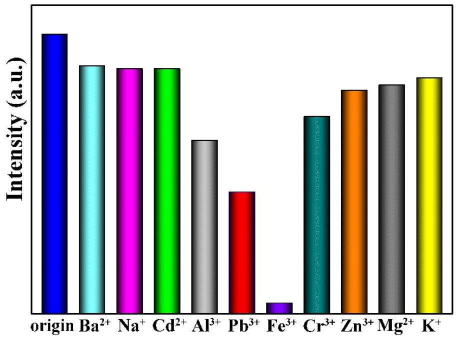


Fig. 5 Room-temperature luminescent intensity of **1** at 545 nm in methanol suspension of **1** upon addition of various metal ions (λ_{ex}= 314 nm).

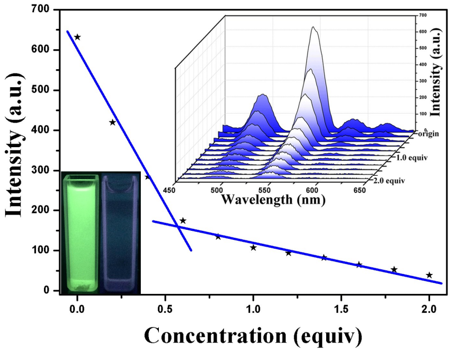


Fig. 6 Emission spectra of the complex **1** in methanol at room temperature in the presence of different equiv of Fe^{3+} ions with respect to 1, respectively (λ_{ex}= 314 nm). Inset: photograph showing the change of the original fluorescence of methanol suspension of **1** (left) and the decreased luminescence upon the addition of Fe^{3+} ions in the methanol suspension of **1** (right)

In summary, three isomorphous polyrotaxane lanthanide-organic frameworks based on V-shape rigid ligands have been successfully constructed. The high-stability Tb(III) compound in methanol suspension can not only selectively sense nitrobenzene at the ppm scale, even in the presence of other NB derivatives, but selectively sense Fe^{3+} without interference by Ba^{2+}, Na^{+}, Cd^{2+}, Al^{3+}, *etc.* Furthermore, the optical observation of quenching makes **1** a promising material to trace NB and Fe^{3+}. Our work demonstrated that lanthanide-organic frameworks could be excellent candidates for luminescent molecular probes, switches and sensors under realistic conditions in the near future.

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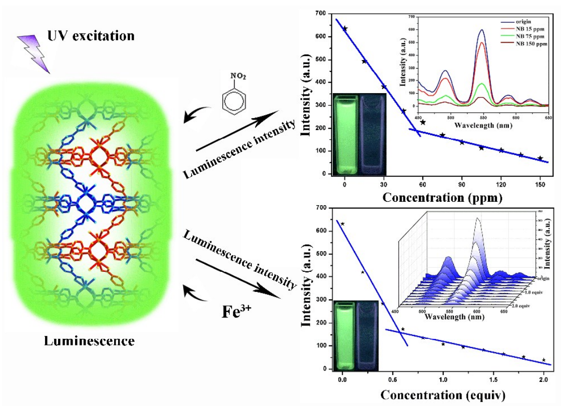

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