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Research paper

# High-efficiency fluorescent probe constructed by triazine polycarboxylic acid for detecting nitro compounds



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### ABSTRACT

Keywords: Lanthanide organic frameworks Triazine polycarboxylic acid (H<sub>6</sub>TTHA) Crystal structure Fluorescence sensing Nitroaromatic compounds By means of hydrothermal synthesis, a series of isomorphic lanthanide rare earth complexes  $[Ln_2(TTHA) (H_2O)_4]$ -7H<sub>2</sub>O (Ln = Sm(1), Eu(2), Gd(3), Tb(4) and Dy(5)) were constructed by triazine polycarboxylic acid ligand (H<sub>6</sub>TTHA). They were characterized by elemental analysis, IR, TG, PXRD, UV–vis, etc. In particular, the structure of complex 1 was analyzed as a representative, and the results showed that it was a porous 3D structure. Fluorescence sensing tests showed that complexes 2 and 4 can be used as novel fluorescent probes for the efficient detection of nitroaromatic compounds.

#### 1. Introduction

Nitroaromatic compounds (NACs) act as a kind of all important chemical raw materials are widely used in the fields of rocket fuels, fireworks, dyes, medicines, pesticides and so on [1–5]. However, NACs is also considered one of the most dangerous explosives due to their high explosiveness, low security coefficient as well as the enormous energy will be released during process of the explosion [6–10], and has been used in war on a large scale by terrorists in wars, which not only poses a serious threat to the lives and safety of people all over the world, but also causes environmental pollution that is difficult to eliminate [11–13]. Therefore, finding a fast, efficient and easy-to-operate method to detect NACs has become a common concern worldwide and urgently need to be solved [14–17]. Fortunately, among many detection methods [18–20], fluorescent probes constructed by metalorganic framework materials (MOFs) have stood out owing to their high efficiency, sensitivity, recyclability and other advantages [21–24].

Lanthanide-based metal-organic framework materials are widely used in the field of fluorescence sensing because of their flexible structure, high surface area, permanent porosity, and high color purity. As a new type of chemical sensor, MOFs have attracted great attention in recent years [25–28]. It well known that the structure of complexes determines their properties. The structure of MOFs is crucial to its luminescence performance, particularly, ligands play an important part of the structure of complexes. Therefore, the significance of choosing a suitable ligand is self-evident. Among them, due to the particularity of the structure of triazine polycarboxylic acid ligands, they have always been research hotspots [29–31]. The main reasons are as follows: (i) their structure contains multiple carboxyl functional groups, which provides conditions for the coordination between metal ions and carboxyl oxygen; (ii) rare earth metal ions generally have more coordination numbers when forming complexes, which further provides possibility for building complexes with multiple configurations; (iii) triazine ligands rifely have larger pores and have higher application prospects in gas adsorption and luminescence and other aspects; (iv) Triazine ligands have a number of unique properties, such as the presence of aromatic C—N bonds (triazine units) and the absence of weak bonds (except for aromatic rings) [32–35]. This special structure makes them highly chemically stable, and the presence of a large amount of nitrogen atoms in the structure leads to its abundant nitrogen content, which brings tremendous value to its practical application [36–38].

MOFs constructed by 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H<sub>6</sub>TTHA), a typical triazine polycarboxylic acid ligand with three iminodiacetic acid groups, have been reported many times. For example, Professor Wu group reported a series of lanthanide coordination polymers [Ln<sub>2</sub>(TTHA)(H<sub>2</sub>O)<sub>4</sub>]·9H<sub>2</sub>O (Ln = Eu, Tb, Gd, Dy) and  $[Yb_2(TTHA)(H_2O)_2]$ as well as{Na<sub>2</sub>[Co<sub>3</sub>(H<sub>2</sub>TTHA)<sub>2</sub>(H<sub>2</sub>O)<sub>12</sub>]  $(H_2O)_2$  ·4 $(H_2O)$ , {Na[Cu<sub>4</sub>(H<sub>2</sub>TTHA)(HTTHA)(H<sub>2</sub>O)<sub>8</sub>](H<sub>2</sub>O)<sub>3</sub> ·5(H<sub>2</sub>O),  $[Cd_3(TTHA)(H_2O)_4]$  and  $[Ca_5(HTTHA)_2(H_2O)_8]$  [39,40]; Complexes  $([Na_4(H_3TTHA)Cl(H_2O)],$  $[Mg_2(H_2TTHA)(H_2O)],$ [Cu<sub>2</sub>(H<sub>2</sub>TTHA)  $(H_2O)_6]$ ,  $[Cu_2(H_2TTHA)(H_2O)_4] \cdot 4H_2O$ ,  $[Zn_5Na_2(TTHA)_2(H_2O)_8]$  and [Zn<sub>2</sub>(H<sub>2</sub>TTHA)(H<sub>2</sub>O)<sub>7</sub>]·2H<sub>2</sub>O) constructed by H<sub>6</sub>TTHA were also reported by Arunachalam Ramanan's group [41]. Prof. H. Xia research team prepared a novel inorganic-organic hybrid compound [Cu2(TTHA)

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 $(bpy)_2(H_2O)]_2\cdot 6H_2O$  (bpy = 2,2'-bipyridine) through coordination interaction of Cu<sup>2+</sup> and H<sub>6</sub>TTHA [42]. Our research group also reported two complexes  $[Cd_4(\mu_3-O)(TTHA)(H_2O)_2]\cdot 3H_2O$  and  $[Zn_5Na_2(TTHA)_2(H_2O)_{10}]$ , and introduced their photoelectric properties and potential nitro derivatives sensing [43]. Based on the above research background, a lot of follow-up research works were also carried out by our research group, a sequence of isomorphic Ln-H<sub>6</sub>TTHA MOFs ([Ln<sub>2</sub>(TTHA)(H<sub>2</sub>O)<sub>4</sub>]·7H<sub>2</sub>O (Ln = Sm(1), Eu(2), Gd(3), Tb(4) and Dy(5))) were synthesized by the hydrothermal methods. Base on luminescence properties of Eu<sup>3+</sup>, Tb<sup>3+</sup>, complexes 2 and 4 were used firstly as fluorescent probes for fluorescent sensing of NACs.

#### 2. Experimental section

#### 2.1. Materials and methods

All the chemicals purchased were of reagent grade or better and were used without further purification. Ligand H<sub>6</sub>TTHA was successfully synthesized by referencing to the methods described in the literature (see Supporting information). IR spectra were performed on a Bruker AXS TENSOR-27 FT-IR spectrometer to compress KBr pellets in the range of 400-4000 cm<sup>-1</sup>. The elemental analyses of C, H, and N were analyzed by a Perkin-Elmer 240C automatic analyzer. Thermogravimetric analyses (TG) were performed under the condition of N2 atmosphere at a heating rate of 10 °C min<sup>-1</sup> using a Perkin Elmer Diamond TG/DTA. The photoluminescent spectra of the complexes were measured on a HORIBA Fluoromax-4-TCSPC spectrofluorometer equipped with Spectra LED Pulsed with LED source at room temperature (200-1000 nm) with 3.2-in Integrating Sphere that can be installed in seconds replacing standard cuvette holder. UV-vis spectra were recorded with JASCO V-570 spectrophotometer with  $\Phi$  = 60 mm Integrating Sphere that can be installed in standard cuvette holder (200-2500 nm, in the form of solid sample) and Lambda 35 UV-vis Spectrometer (200-800 nm). PXRD patterns were obtained with a Bruker Advance-D8 equipped with Cu-Ka radiation, in the range of  $5^{\circ} < 2\theta < 60^{\circ}$ , with a step size of 0.02° (20) and a count time of 2 s per step.

#### 2.2. Preparation

#### 2.2.1. Preparation of the $H_6TTHA$

Ligand  $H_6TTHA$  was synthesized on the basis of the method in related literature [44,45], see the Supplementary materials for specific synthesis methods. The synthetic route is as follows (Scheme 1):

#### 2.2.2. Preparation of the complexes

0.0432 g of Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.1 mmol) and 0.0237 g of H<sub>6</sub>TTHA (0.05 mmol) were dissolved in 3 mL of deionized water respectively. After stirring at room temperature for 5 min, the obtained clarified solution was mixed and stirred again for 0.5 h to make the solution fully mixing, the pH of the mixture was adjusted to 4. Then, the mixture solution was put into Teflon-lined stainless steel autoclave and heated at 160 °C for 3 days, then cooled to room temperature, transparent block crystals were obtained. The synthesis method of complexes **2–5** is similar to that of complex **1**, except that the rare earth nitrates used are different. Detailed elemental analysis and infrared data are as follows:

 $[Sm_2(TTHA)(H_2O)_4]$ ·7H<sub>2</sub>O (1) Yield: 90% (based on Sm



**Scheme 1.** The synthetic route of the ligand H<sub>6</sub>TTHA.

 $(NO_3)_3$  ;6H2O). Elemental Analysis (%) Calcd for  $C_{15}H_{34}N_6O_{23}Sm_2$ : C, 19.73; H, 2.96; N, 9.20. Found: C, 19.85; H, 2.85; N, 9.32. IR data (KBr, cm $^{-1}$ ): 3452, 2931, 2848, 1619, 1551, 1496, 1434, 1386.

 $[Gd_2(TTHA)(H_2O)_4]$ ·7H<sub>2</sub>O (3) Yield: 87% (based on Gd (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O). Elemental Analysis (%) Calcd for C<sub>15</sub>H<sub>34</sub>N<sub>6</sub>O<sub>23</sub>Gd<sub>2</sub>: C, 18.85; H, 3.47; N, 8.56. Found: C, 18.50; H, 3.50; N, 8.65. IR data (KBr, cm<sup>-1</sup>): 3431, 2931, 2841, 1606, 1558, 1496, 1441, 1393.

#### 2.3. X-ray crystal structure determination

Complex 1 was selected for testing single crystals of suitable dimensions for complex 1 was mounted on glass fibers for the X-ray structure determinations. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A semiempirical absorption correction was applied by the program SADABS [46]. The program suite SHELXTL-97 was used for space-group determination (XPREP), direct method structure solution (XS), and least-squares refinement (XL) [47,48]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms of coordination water molecules and lattice water molecules were found in the difference Fourier map. Crystal data and structure refinement parameters are given in Table S1.

#### 3. Results and discussion

#### 3.1. Synthesis

Complexes 1-5 as crystal or precipitates were obtained at the hydrothermal condition by heating to 160 °C for 72 h, pH was adjusted to 4, and molar ratio of metal salt to ligand H<sub>6</sub>TTHA of 2:1. First, in the synthesis process, the products of the complexes 1-5 were first obtained at 100 °C, but there were many impurities in the crystals, and it was difficult to eliminated impurities by washing so that we cannot obtain pure crystals for X-ray diffraction. Furthermore, through the constant exploration and improvement of the experimental environment, it was found finally that crystals were obtained at both 80 °C and 120 °C, but it is worth noting that when the reaction temperature was 160 °C, the crystal of complex 1 obtained were the most transparent, and the yield was higher with almost no impurities. Second, when the initial pH of the reaction system was alkaline, only precipitation can be obtained. Under neutral conditions, the crystallites began to appear. When we adjusted the reaction system to an excessively acidic state, only clear solution can be obtained. After many adjustments, we finally found that when the pH of the system was 4, the crystals of the complex obtained were the most perfect. Last, for the mol ratio of H<sub>6</sub>TTHA and rare earth metal nitrates, considering that the rare earth metals generally adopt a high coordination mode, we first selected a high ratio of metal to ligand for experiments. However, as a ligand with six carboxyl groups simultaneously, H<sub>6</sub>TTHA itself can also be coordinated with a plurality of metals. After a number of experimental trials, we finally found optimal molar amount of the metal and ligand is 2:1.



**Fig. 1.** (a) Coordination mode of metal ion in complex 1; (b) Building block of complex 1; (c) Connection fashions of  $H_6$ TTHA ligand; (d) One-dimensional structure; (e) Two-dimensional structure; (f)  $Sm_1O_9$  single-capped square anti-prism geometry configuration; (g)  $Sm_2O_9$  single-capped square anti-prism geometry configuration; (h) Three-dimensional structure.



Fig. 2. Sold-state luminescent spectrum of the complex 2: (a) excitation spectrum; (b) emission spectrum.

#### 3.2. IR spectra

Due to center metal atom of the complexes 1–5 has similar coordination modes, indicate they are isomorphic rare earth complexes, so the infrared spectra are similar to each other. Under this premise, we take the infrared spectrum of complex 1 as an example for analysis. By infrared spectroscopy analysis, the broader absorption band appeared at 3452 cm<sup>-1</sup> shown the presence of water molecules in the structure of complex 1. The peak position at 1619 cm<sup>-1</sup> and 1386 cm<sup>-1</sup> can be assigned to the asymmetric stretching vibration of the C=O bond ( $\nu as_{COO}^{-}$ ) and the C=O symmetric stretching vibration ( $\nu s_{COO}^{-}$ ) respectively. Red shift occurred compared to main position of the carboxyl peak at 1722 and 1397 cm<sup>-1</sup> of the ligand H<sub>6</sub>TTHA, indicating that the metal atom combinated with the ligand to form the complex. Detailed infrared spectral data of complexes **1–5** are shown in Table S3. The infrared spectra of all complexes are shown in Fig. S1.

#### 3.3. Solid UV-vis absorption spectra

The UV-vis absorption spectra as well as attribution of the complexes 1–5 and the ligand  $H_6$ TTHA were recorded (See Fig. S2 and Table S4). Base on the luminescent characteristics of Eu<sup>3+</sup> and Tb<sup>3+</sup>,







Fig. 4. CIE chromaticity diagram of complex 2 (a) and complex 4 (b).

(a)



Fig. 5. Time resolved emission intensity of complex 2 (a) and complex 4 (b).

complexes **2** and **4** were selected for detailed UV–vis analysis. The two absorption bands appeared at 217 nm and 250 nm of ligand H<sub>6</sub>TTHA were attributed to its  $\pi$ - $\pi^*$  and n- $\pi^*$  transition. Similarly, complex **2** also presented two bands at 218 nm and 251 nm, which be assigned to ligand-to-ligand transition (LLCT). Because of the f-f transition of Eu<sup>3+</sup> is a spin-forbidden transition, lead to its UV absorption is too weak to cannot be observed, the peak positions and shapes of complex **2** and H<sub>6</sub>TTHA are almost identical. For complex **4**, the absorption band

occurred at 264 nm also be ascribed to the ligand-to-ligand transition (LLCT).

(b)

#### 3.4. PXRD analyses

Fig. S3 shows the X-ray powder diffraction spectrum of complexes 1–5, where (a) is the diffraction of theoretical data obtained by performing simulation calculation of the crystallographic data of the



Fig. 6. Luminescent spectra of complex 4 (1 mg/3 mL) in different solvents.

complex 1, and (b) is the powder diffraction pattern measured by experiments. By comparing a series of data, we found that the positions of peaks in the five sets of data were one-to-one corresponding, indicating that complexes 1–5 were pure phases, which provided a possibility for us to further study the functions and properties of complexes. However, through the careful comparison of the two groups of peaks, the simulated and measured spectra still show different peak intensity, which may be related to the low degree of crystallinity.

#### 3.5. Structure descriptions

Complexes 1-5 have similar coordination environments, and all five complexes are all belong to the Monoclinic crystal system,  $C_2/c$  space group. Here we take complex 1 as an example to analyze its structure. In complex 1, there are two metal Sm atoms (Sm1 and Sm2), one completely deprotonated TTHA<sup>6-</sup> ligand, four coordinated waters in asymmetric unit structure. Fig. 1a shows the coordination mode of the center metal Sm. Both Sm atoms adopt the same nine-coordination mode to form a single-capped square anti-prism geometry (Fig. 1f and g). Sm1 is coordinated with seven carboxyl oxygen atoms (O3, O4, O5, O6, O7, O8 and O11) from the H<sub>6</sub>TTHA, and two oxygen atoms from the coordinated water (O1, O2). Among it, O1, O2 adopt monodentate coordination mode, O3, O4 in a bidentate chelation mode, O5, O6, O11 in a chelated monodentate mode, O7, O8 in bidentate mode respectively coordinated with the central metal Sm1. Sm2 is also connected by nine oxygen atoms, among O6, O9, O10, O11, O12, O13 and O14 from the H<sub>6</sub>TTHA, O15 and O16 from the coordinated water. Among, O15, O16 adopt monodentate coordination mode, O13, O14 adopt bidentate chelation mode, O11, O12 and O6 in a chelated monodentate mode, O9, O10 in bidentate mode respectively coordinated with the central metal Sm2. Two Sm atoms are connected by O6 and O11, forming a Sm<sub>2</sub>O<sub>4</sub>(COO)<sub>6</sub> building block (Fig. 1d). The deprotonated ligand TTHA is connected in the manner of  $\mu_{6-\eta}^2 \eta^2 \eta^1 \eta^1 \eta^2 \eta^2 \eta^1 \eta^1 \eta^1$  to link six Sm atoms (Fig. 1c). Neighboring the building block were connected by oxygen in two carboxyl groups from two arm from in the triazine ring ligand to form one-dimensional chain (Fig. 1d), which extends to form two-dimensional structure (Fig. 1e). In the building block, wherein each ligand H<sub>6</sub>TTHA connects three building blocks, each building block connects the four ligands, finally, forms a three-dimensional structure by cross-linking (Fig. 1h). There are pores in the three-dimensional structure, and the channel length and width are 16.1162 Å and 10.8367 Å, respectively. The crystallographic parameters of coordination complexes 1–5 are listed in Table S1, and some of the bond lengths are listed in Table S2.

#### 3.6. Thermal properties

In order to confirm the thermal stability of the complexes, thermogravimetric analysis was carried out under a  $N_2$  atmosphere at a temperature increase rate of 10 °C min<sup>-1</sup>, and the temperature range was 30–1000 °C. Since the five complexes are isomorphic, TG curves are also similar, so complex 1 was selected as the representative for discussion and analysis. The specific thermogravimetric loss is shown in the Fig. S4. TG curve of complex 1 can be divided into two stages of weight loss. The first weight loss occurred between 35 and 370 °C, which we attributed to the loss of seven free water molecules and four coordinated water molecules (measured value: 21.0%: calculated value: 20.49%). The second weight loss, is about 42.0% (calculated value: 48.4%), during the temperature rise of 370–1000 °C should be due to the collapes of ligand skeleton as deprotonated TTHA<sup>6-</sup> ligand. At this point, the skeleton starts to collapse, eventually leaving the metal oxide (measured value: 31.5%: calculated value: 36.10%).

#### 3.7. Solid-state photoluminescent spectra

Based on the unique fluorescence properties of Eu<sup>3+</sup> and Tb<sup>3+</sup>, solid samples of complexes 2 and 4 were selected for fluorescence determination at room temperature (See Figs. 2 and 3). For complex 2, under the monitoring of 613 nm, the excitation spectra include a wide band at 360–385 nm attributed to  $\pi$ - $\pi$ \* electron transition of organic ligand. At the same time, the narrow peaks at 390-460 nm, are belong to the energy level transition of Eu<sup>3+</sup> ion and the interaction with ligand. These results suggest that the excitation spectra of the complex 2 contain not only from the organic ligands  $\pi$ - $\pi$ \* transitions, but also from the strong energy level transitions of Eu<sup>3+</sup> ions. In the emission spectrum of complex 2 ( $\lambda_{ex}$  = 394 nm), the characteristic peaks appearing at 590, 613, 638, and 696 nm are attributed to  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1-4), which are the characteristic emission peaks of Eu<sup>3+</sup>, respectively. At 578 nm, owing to the symmetry-forbidden transition of  $Eu^{3\,+},$  the emission peak of  $^5D_0 \rightarrow \,^7F_0$  is particularly weak. The extra strong peak at 613 nm belongs to the  ${}^{5}D_{0}-{}^{7}F_{2}$  transition, which is an electric dipole transition. Its emission intensity varies significantly with the change of the coordination environment of  $Eu^{3+}$ , while the  ${}^{5}D_{0}-{}^{7}F_{1}$ transition at 590 nm is a magnetic dipole transition. Without being limited by symmetry, its emission intensity is hardly affected by the Eu<sup>3+</sup> coordination environment, and the ratio of the relative intensity of the  ${}^{5}D_{0}-{}^{7}F_{2}$  transition to the  ${}^{5}D_{0}-{}^{7}F_{1}$  transition can indicate the symmetry of the central ion lattice. From the emission spectrum of the complex 2. It can be seen that the transition intensity of  ${}^{5}D_{0}-{}^{7}F_{2}$  is much stronger than the  ${}^{5}D_{0}-{}^{7}F_{1}$ , indicating that the central ion Eu<sup>3+</sup> is in a lower symmetrical environment, which is in line with the crystal structure of the complex. For complex 4, at the emission wavelength of 542 nm, a wide peak band of appeared in complex 4 within the range of 330–380 nm, which should be ascribed to the  $\pi$ - $\pi$  \* transition of ligand H<sub>6</sub>TTHA, and the peak at 490 nm could be attributed to the strong energy level transition of  $\text{Tb}^{3+}$  ion. It can be known that in the complex 4, part of the energy is derived from the electronic transition of the  $Tb^{3+}$  ion itself, and some is derived from the "antenna effect" of the ligand H<sub>6</sub>TTHA. At the exciting wavelength of 370 nm, the characteristic emission peaks at 543, 581, 619, 704 nm are respectively emitted for  ${}^{5}D_{4}-{}^{7}F_{J}(J = 6-4)$  of  $Tb^{3+}$ . Both CIE chromaticity diagrams of complex 2 and 4 are present to Fig. 4.

#### 3.8. Fluorescence lifetime

For luminescent materials, excited state lifetime is a key index to evaluate their performance, therefore, we measured the excited state lifetime of solid complexes 2 and 4, respectively (See Fig. 5). The luminescence lifetimes of complexes 2 and 4 present a multi-exponential decay process, in which the fluorescence lifetime of complex 2 consists of three stages, by fitting a three-exponential decay curve the average



Fig. 7. Quenching behavior of 4 (1 mg/3 mL) in EtOH: (a) nitrobenzene (NB); (b) 4-nitrotoluene (PNT); (c) 2,4,6-Trinitrophenol (TNP); (d) nitrosonaphthol (NNa); (e) 4-(4-nitrophenylazo)resorcinol (AV).

Wavelength(nm)

Table 1						
Quenching	constants (	(Ksv) and	D of the	complex	4 (1	mg/3

Quenching constants (Ksv) and D of the complex 4 (1 mg/3 mL).					
quenching agent	Ksv	LOD (M)			
Nitrobenzene (NB) 4-Nitrotoluene (PNT) 2,4,6-Trinitrophenol (TNP) Nitrosonaphthol (NNa) 4-(4-Nitrophenylazo) resorcinol (AV)	$\begin{array}{c} 1.362 \times 10^{4} \\ 1.093 \times 10^{4} \\ 7.25 \times 10^{3} \\ 2.548 \times 10^{4} \\ 3.037 \times 10^{4} \end{array}$	0.489 0.609 0.919 0.261 0.219			

fluorescence lifetime value calculated by formula with  $\tau_{ave} = \Sigma B_i \tau_i$  is 843 µs and the lifetime of complex 4 consists of two stages, and average fluorescence lifetime value is 129.4 ms, corresponding related

parameters are listed Table S5, which are similar to the excited state lifetime of some Eu<sup>3+</sup> and Tb<sup>3+</sup> organic framework materials. Such as a MOF [EuL<sub>1.5</sub>(H<sub>2</sub>O)<sub>2</sub>]·1.75H<sub>2</sub>O (H<sub>2</sub>L = 5-methyl-1-(4-carboxylphenyl)-1H-1,2,3-triazole-4-carboxylic acid) reported by prof. Xing group, the excited state lifetime of this complex is 299  $\mu$ s [49]; and the excited state lifetime of complexes Eu(L)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O) (HL: 4-(Dipyridin-2-yl) aminobenzoic acid) and Tb(PBI)<sub>3</sub>(DPEPO) (HPBI: 3-phenyl-4-benzoyl-5-isoxazolone, DPEPO: bis(2-(diphenylphosphino)phenyl)) are 428  $\mu$ s and 168  $\mu$ s, respectively [50,51].



Fig. 8. Quenching behavior of the complex 2 and 4 for 4-(4-nitrophenylazo)resorcinol (AV) in repetitive experiments: (a) complex 2; (b) complex 4.

#### 3.9. Fluorescence sensing detected for nitro compounds

#### 3.9.1. Fluorescence sensing of complex 4 for nitro compounds

At an excitation wavelength of 370 nm, the potential sensing properties of complex 4 on nitro compounds were investigated and tested in nine different solvents (EtOH, Toluene, methanol (MeOH), tetrahydrofuran (THF), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), deionized water (H<sub>2</sub>O), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) and nitrobenzene (NB). As shown as Fig. 6, in different solvents, although there is some changes for the fluorescence intensity of the complex, it is obvious that the characteristic peak position of  $Eu^{3+}$  does not shift, which indicates that in the different systems, the first excited state level change of the complex is not occurred, and it can draw a conclusion that the polarity of the solvents does not affect the first excited state level of the complex. However, in different solvents, the fluorescent intensity luminescence intensity of complex 4 varies to some extent, which is due to the different degree of electron transfer transition between solvents and complex dispersed in different polarities, so that the transfer rate of excited electrons in different solvents is different. Among the above solvents, the fluorescence intensity of complex 4 in ethanol is the highest, so ethanol is taken as the solvent for post-detecting work. Meanwhile, nitrobenzene (NB) has obvious fluorescence quenching behavior, which further proves that it is wise for us to choose nitro compounds to study fluorescence sensing performance.

Next, we investigated the fluorescence sensing of complex 4 aim at five kinds of nitro compounds: nitrobenzene (NB); 4-nitrotoluene (PNT); 2,4,6-trinitrophenol (TNP); nitrosonaphthol (NNa) and 4-(4-nitrobenzoazo) resorcinol (AV). The specific experimental process is as follows: 1 mg of complex 4 was dissolved in 3 mL of ethanol, sonicated to make a suspension, and then above five nitro compounds were continuously added to the suspension respectively to record changes in fluorescence intensity. After the addition of five nitro compounds to the system, the decrease of fluorescence intensity can be clearly seen, and the quenching behavior are recorded in Fig. 7.

In order to understand the quenching effect more accurately, the quenching efficiency of five quenching agents was calculated by Stern-Volmer equation:  $I_0/I = K_{SV}$  [Q] + 1 (Where  $I_0$  represents the initial emission peak intensity, I shown the emission peak intensity after quenching agent is added, and [Q] exhibits the molar concentration of quenching agent, Ksv is the quenching constant [ $M^{-1}$ ]). Fig. S5 shows the S-V plots of complex 4 after the addition of five quenchers. The Ksv values and corresponding detection limits (LOD) (Calculated by formula:  $3\sigma/Ksv$  ( $\sigma$  is the standard deviation of the fluorescence intensity of the blank solution) of the five quenching agents are listed in Table 1.



Similarly, we also carried out corresponding fluorescence sensor

detection of complex **2**. The fluorescence intensity changes of complex **2** after addition of nitro compound were recorded in Fig. S6. The S-V plots are shown in Fig. S7. The Ksv values and corresponding detection limits of the five quenching agents are listed in Table S6.

# 3.9.3. Study on the cyclability and stability of sensor based on complexes 2 and 4 $\,$

For fluorescent probes, good stability and recyclability are important indicators to judge whether they can be used in practical production and life. Therefore, we investigated the difference in fluorescence intensity of complexes **2** and **4** by using five groups of parallel experiments with 4-(4-nitrophenylazo) resorcinol (AV) as an example (See Fig. 8). The test results show that the quenching efficiency of the two complexes for the 4-(4-nitrophenylazo) resorcinol (AV) solution is only slightly reduced and can be considered to be almost constant. It can be seen that complexes **2** and **4** can be applied as a potential fluorescent probe with repeatability.

#### 3.9.4. Fluorescence respond mechanism

Nitroaromatic compounds (NACs) are powerful oxidants due to the presence of electron-withdrawing groups. When these compounds are exposed to electron-rich complexes, their unoccupied lower  $\pi^*$  orbitals are capable of absorbing electrons from the excited state of the complexes, resulting in fluorescence attenuation. Generally, the conduction band (CB) of an electron-rich MOF has an energy higher than the lowest unoccupied orbital energy of a nitro compound. When the excited electrons of the CB of MOFs are transferred to the LUMO, the nitro compound will cause fluorescence quenching, and the fluorescence quenching performance will be improved with the decrease of LUMO orbital energy. That is to say, the photoinduced electron transfer mechanism (PET) leads to fluorescence quenching. In addition, by comparing the fluorescence lifetime value of complex 4 before and after the addition of NACs, it was found that the lifetime value of complex 4 decreased after the addition of NACs, furthermore, indicating that the photoinduced electron transfer mechanism (PET) leads to fluorescence quenching.

#### 4. Conclusion

In this work, a series of new MOFs materials with 3D structure were obtained through the interaction between rare earth nitrate and triazine polycarboxylic acid ligand  $H_6$ TTHA, and they were characterized by IR, X-ray, PXRD, TG, UV–vis, etc.

Among them, complex 1 as perfect crystal was discussed in detail, complexes 2 and 4 were used for the detection of aromatic nitro compounds due to their superior fluorescence properties. Their high quenching ability and high sensitivity make them promising as potential fluorescent probes for practical work.

#### CRediT authorship contribution statement

Nan Zhang: Conceptualization, Methodology, Writing - original draft, Data curation, Software. Bing Li: Conceptualization, Methodology, Writing - original draft, Data curation, Software. Xuemeng Wang: Data curation, Writing - review & editing, Software, Investigation. Dongqi Liu: Data curation, Writing - review & editing, Software, Investigation. Xue Han: Data curation, Writing - review & editing, Software, Investigation. Fengying Bai: Supervision. Yongheng Xing: Validation.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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#### References

- J.Y. Shen, J.F. Zhang, Y. Zuo, L.J. Wang, X.Y. Sun, J.S. Li, W.Q. Han, R. He, Biodegradation of 2, 4, 6-trinitrophenol by Rhodococcus sp. isolated from a picric acid-contaminated soil, J. Hazard. Mater. 163 (2009) 1199–1206.
- [2] V. Bhalla, A. Gupta, M. Kumar, D.S. Rao, S.K. Prasad, Self-assembled pentacenequinone derivative for trace detection of picric acid, ACS Appl. Mater. Interfaces 5 (3) (2013) 672–679.
- [3] V. Bhalla, S. Kaur, V. Vij, M. Kumar, Mercury-modulated supramolecular assembly of a hexaphenylbenzene derivative for selective detection of picric acid, Inorg. Chem. 52 (9) (2013) 4860–4865.
- [4] G. He, H.N. Peng, T.H. Liu, M.N. Yang, Y. Zhang, Y. Fang, A novel picric acid film sensor via combination of the surface enrichment effect of chitosan films and the aggregation-induced emission effect of siloles, J. Mater. Chem. 19 (39) (2009) 7347–7353.
- [5] Y. Salinas, R. Martínez-Máñez, M.D. Marcos, F. Sancenón, A.M. Castero, M. Parra, S. Gil, Optical chemosensors and reagents to detect explosives, Chem. Soc. Rev. 41 (2012) 1261–1296.
- [6] M.E. Germain, M.J. Knapp, Discrimination of nitroaromatics and explosives mimics by a fluorescent Zn (Salicylaldimine) sensor array, J. Am. Chem. Soc. 130 (16) (2008) 5422–5423.
- [7] S.A. Boyd, G.Y. Sheng, B.J. Teppen, C.T. Johnston, Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays, Environ. Sci. Technol. 35 (2001) 4227–4234.
- [8] Y. Peng, A.J. Zhang, M. Dong, Y.W. Wang, A colorimetric and fluorescent chemosensor for the detection of an explosive-2, 4, 6-trinitrophenol (TNP), Chem. Commun. 47 (15) (2011) 4505–4507.
- [9] H. Muthurajan, R. Sivabalan, M.B. Talawar, S.N. Asthana, Computer simulation for prediction of performance and thermodynamic parameters of high energy materials, J. Hazard. Mater. 112 (1–2) (2004) 17–33.
- [10] H.Q. Li, Z.Y. Ding, Y. Pan, C.H. Liu, Y.Y. Zhu, Fluorescence tuning of Zn (ii)-based metallo-supramolecular coordination polymers and their application for picric acid detection, Inorg. Chem. Front. 3 (11) (2016) 1363–1375.
- [11] Y.J. Hu, S.Z. Tan, G.L. Shen, R.Q. Yu, A selective optical sensor for picric acid assay based on photopolymerization of 3-(N-methacryloyl) amino-9-ethylcarbazole, Anal. Chim. Acta 570 (2) (2006) 170–175.
- [12] B. Roy, A.K. Bar, B. Gole, P.S. Mukherjee, Fluorescent tris-imidazolium sensors for picric acid explosive, J. Org. Chem. 78 (3) (2013) 1306–1310.
- [13] P. Ju, E. Zhang, L. Jiang, Z. Zhang, X.Y. Hou, Y.Q. Zhang, H. Yang, J.J. Wang, A novel microporous Tb-MOF fluorescent sensor for highly selective and sensitive detection of picric acid, RSC Adv. 8 (39) (2018) 21671–21678.
- [14] B. Joarder, A.V. Desai, P. Samanta, S. Mukherjee, S.K. Ghosh, Selective and sensitive aqueous-phase detection of 2, 4, 6-trinitrophenol (TNP) by an amine-functionalized metal-organic framework, Chem. Eur. J. 21 (3) (2015) 965–969.

- [15] W.L. Che, G.F. Li, X.M. Liu, K.Z. Shao, D.X. Zhu, Z.M. Su, M.R. Bryce, Selective sensing of 2, 4, 6-trinitrophenol (TNP) in aqueous media with "aggregation-induced emission enhancement" (AIEE)-active iridium (iii) complexes, Chem. Commun. 54 (2018) 1730–1733.
- [16] Y.J. Deng, N.J. Chen, Q.Y. Li, X.J. Wu, X.L. Huang, Z.H. Lin, Y.G. Zhao, Highly fluorescent metal–organic frameworks based on a benzene-cored tetraphenylethene derivative with the ability to detect 2, 4, 6-trinitrophenol in water, Cryst. Growth Des. 17 (6) (2017) 3170–3177.
- [17] K.M. Wang, L. Du, Y.L. Ma, Q.H. Zhao, Selective sensing of 2, 4, 6-trinitrophenol and detection of the ultralow temperature based on a dual-functional MOF as a luminescent sensor, Inorg. Chem. Commun. 68 (2016) 45–49.
- [18] J.S. Caygill, F. Davis, S.P.J. Higson, Current trends in explosive detection techniques, Talanta 88 (2012) 14–29.
- [19] Y.C. He, H.M. Zhang, Y.Y. Liu, Q.Y. Zhai, Q.T. Shen, S.Y. Song, J.F. Ma, Luminescent anionic metal–organic framework with potential nitrobenzene sensing, Cryst. Growth Des. 14 (2014) 3174–3178.
- [20] D. Tian, Y. Li, R.Y. Chen, Z. Chang, G.Y. Wang, X.H. Bu, A luminescent metalorganic framework demonstrating ideal detection ability for nitroaromatic explosives, J. Mater. Chem. A 2 (2014) 1465–1470.
- [21] L. You, D.J. Zha, E.V. Anslyn, Recent advances in supramolecular analytical chemistry using optical sensing, Chem. Rev. 115 (15) (2015) 7840–7892.
- [22] J.Q. Liu, G.P. Li, W.C. Liu, Q.L. Li, B.H. Li, R.W. Gable, L. Hou, S.R. Batten, Two unusual nanocage-based In-MOFs with triazole sites: highly fluorescent sensing for Fe<sup>3+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, and selective CO<sub>2</sub> capture, Chem. Plus. Chem. 81 (2016) 1299–1304.
- [23] Z.C. Hu, B.J. Deibert, J. Li, Luminescent metal-organic frameworks for chemical sensing and explosive detection, Chem. Soc. Rev. 43 (2014) 5815–5840.
- [24] R. Ni, R.B. Tong, C.C. Guo, G.L. Shen, R.Q. Yu, An anthracene/porphyrin dimer fluor-escence energy transfer sensing system for picric acid, Talanta 63 (2) (2004) 251–257.
- [25] Y.C. He, H.M. Zhang, Y.Y. Liu, Q.Y. Zhai, Q.T. Shen, S.Y. Song, J.F. Ma, Luminescent anionic metal-organic framework with potential nitrobenzene sensing, Cryst. Growth Des. 14 (7) (2014) 3174–3178.
- [26] T. Komatsu, J.M. Taylor, H. Kitagawa, Design of a conducting metal-organic framework: orbital-level matching in MIL-140A derivatives, Inorg. Chem. 55 (2) (2016) 546–548.
- [27] S. Roy, A. Dey, P.P. Ray, J. Ortega-Castro, A. Frontera, Application of a novel 2D cadmium (II)-MOF in the formation of a photo-switch with a substantial on-off ratio, Chem. Commun. 51 (65) (2015) 12974–12976.
- [28] M.E. Mahmoud, Z. Moussa, T. Prakasam, L. Liang, G.A. Mohamad, P. Digambara, H. Mohamas, Lanthanides based metal organic frameworks for luminescence sensing of toxic metal ions, J. Solid State Chem. (281) (2020,) 121031.
- [29] X. Jiang, G. Yan, Y.H. Liao, C.X. Huang, H. Xia, Synthesis, structure and topological analysis of a novel 3D Cu coordination polymer from a flexible ligand of 1, 3, 5triazine-2, 4, 6-triamine hexaacetic acid and coligand ethylenediamine, Inorg. Chem. Commun. 14 (12) (2011) 1924–1927.
- [30] J. Song, X. Gao, Z.N. Wang, C.R. Li, Q. Xu, F.Y. Bai, Z.F. Shi, Y.H. Xing, Multifunctional uranyl hybrid materials: structural diversities as a function of pH, luminescence with potential nitrobenzene sensing, and photoelectric behavior as ptype semiconductors, Inorg. Chem. 54 (18) (2015) 9046–9059.
- [31] H. Zhang, J.G. Ma, D.M. Chen, J.M. Zhou, S.W. Zhang, W. Shi, P. Cheng, Microporous heterometal–organic framework as a sensor for BTEX with high selectivity, J. Mater. Chem. A 2 (48) (2014) 20450–20453.
- [32] X.S. Wang, S.Q. Ma, D.F. Sun, S. Parkin, H.C. Zhou, A mesoporous metal-organic framework with permanent porosity, J. Am. Chem. Soc. 128 (51) (2006) 16474–16475.
- [33] K.A. Kolmakov, An efficient, "Green" approach to aryl amination of cyanuric chloride using acetic acid as solvent, J. Heterocycl. Chem. 45 (2) (2008) 533–539.
- [34] H.F. Zhu, J. Fan, T.A. Okamura, Z.H. Zhang, G.X. Liu, K.B. Yu, W.Y. Sun, N. Ueyama, Metal-organic architectures of silver(I), cadmium(II), and copper(II) with a flexible tricarboxylate ligand, Inorg. Chem. 45 (10) (2006) 3941–3948.
- [35] M.Y. Liu, L.P. Guo, S.B. Jin, B. Tan, Covalent triazine frameworks: synthesis and applications, J. Mater. Chem. A 7 (10) (2019) 5153–5172.
- [36] S. Hug, M.E. Tauchert, S. Li, U.E. Pachmayr, B.V. Lotsch, A functional triazine framework based on N-heterocyclic building blocks, J. Mater. Chem. 22 (28) (2012) 13956–13964.
- [37] P.J. Hall, M. Mirzaeian, S.I. Fletcher, F.B. Sillars, A.J.R. Rennie, G.O. Shitta-Bey, G. Wilson, A. Cruden, R. Carter, Energy storage in electrochemical capacitors: designing functional materials to improve performance, Energy Environ. Sci. 3 (9) (2010) 1238–1251.
- [38] D. Hulicova-Jurcakova, M. Kodama, S. Shiraishi, H. Hatori, Z.H. Zhu, G.Q. Lu, Nitrogen-enriched nonporous carbon electrodes with extraordinary supercapacitance, Adv. Funct. Mater. 19 (11) (2009) 1800–1809.
- [39] Q.L. Zhu, T.L. Sheng, R.B. Fu, S.M. Hu, J.S. Chen, S.C. Xiang, C.J. Shen, X.T. Wu, Novel structures and luminescence properties of lanthanide coordination polymers with a novel flexible polycarboxylate ligand, Cryst. Growth Des. 9 (12) (2009) 5128–5134.
- [40] Q.L. Zhu, T.L. Sheng, R.B. Fu, S.M. Hu, C.J. Shen, X. Ma, X.T. Wu, Syntheses, structural aspects, luminescence and magnetism of four coordination polymers based on a new flexible polycarboxylate, CrystEngComm 13 (6) (2011) 2096–2105.
- [41] P.K. Goswami, M. Singh, R. Thaimattam, A. Ramanan, Extending the supramolecular synthon concept in flexible polyaminocarboxylate based coordination polymers, CrystEngComm 15 (45) (2013) 9787–9797.
- [42] X. Jiang, H. Xia, Y.F. Zhu, C.X. Huang, Y.H. Liao, Synthesis and magnetic properties of a tetranuclear copper (II) coordination compound constructed of a multi-carboxylate ligand and 2, 2'-bipyridine, Z. Anorg. Allg. Chem. 637 (14–15) (2011)

#### N. Zhang, et al.

2273-2277.

- [43] S. Li, J. Song, J.C. Ni, Z.N. Wang, X. Gao, Z. Shi, F.Y. Bai, Y.H. Xing, Photoelectric properties and potential nitro derivatives sensing by a highly luminescent of Zn(II) and Cd(II) metal–organic frameworks assembled by the flexible hexapodal ligand, 1, 3, 5-triazine-2, 4, 6-triamine hexaacetic acid, RSC Adv. 6 (42) (2016) 36000–36010.
- [44] X. Jiang, B. Tao, H. Xia, G.Y. Liao, Supramolecular architectures based on various macrocyclic metallic tectons with 1,3,5-triazine-2,4,6-triamine hexaacetic acid ligand, CrystEngComm 14 (9) (2012) 3271–3282.
- [45] X.H. Synthesis, Structure and Properties of Complexes Based on Iminoacetic Acid Modified Triazine Polycarboxylic Acid Ligands, (2019).
- [46] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr A: Found Crystallogr 64 (1) (2008) 112122.
- [47] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction for Area

Detector Data, University of Gottingen, Gottingen, Germany, 1996.

- [48] G.M. Sheldrick, SHELXS 97, Program for Crystal Structure Refinement, University of Gottingen, Gottingen, Germany, 1997.
- [49] Y. Wang, S.H. Xing, F.Y. Bai, Y.H. Xing, L.X. Sun, Stable lanthanide–organic framework materials constructed by a triazolyl carboxylate ligand: multifunction detection and white luminescence tuning, Inorg. Chem. 57 (20) (2018) 12850–12859.
- [50] A.R. Ramya, D. Sharma, S. Natarajan, M.L.P. Reddy, Highly luminescent and thermally stable lanthanide coordination polymers designed from 4-(dipyridin-2-yl) aminobenzoate: efficient energy transfer from Tb<sup>3+</sup> to Eu<sup>3+</sup> in a mixed lanthanide coordination compound, Inorg. Chem. 51 (16) (2012) 8818–8826.
- [51] S. Biju, M.L.P. Reddy, A.H. Cowley, V. Vasudevan, Molecular ladders of lanthanide-3-phenyl-4-benzoyl-5-isoxazolonate and bis (2-(diphenylphosphino) phenyl) ether oxide complexes: the role of the ancillary ligand in the sensitization of Eu<sup>3+</sup> and Tb<sup>3+</sup> luminescence, Cryst. Growth Des. 9 (8) (2009) 3562–3569.