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## ARTICLE

# Visible Detection of Explosive Nitroaromatics Facilitated by Large Stokes Shift of Luminescence using Europium and Terbium Doped Yttrium based MOFs

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To use the large stokes shift and low self quenching of luminescence, we have successfully constructed two luminescent yttrium based MOFs doped with europium and terbium,  $[Y_{0.9}Eu_{0.1}(OBA)(Ox)_{0.5}(H_2O)_2]$ , **Y-MOF:Eu** and  $[Y_{0.9}Tb_{0.1}(OBA)(Ox)_{0.5}(H_2O)_2]$ , **Tb-MOF:Tb** through isomorphous substitution technique using a two dimensional metal-organic framework (MOF)  $[Y_{1.0}(OBA)(Ox)_{0.5}(H_2O)_2]$ , [OBA = 4,4'- Oxybis(benzoic acid), Ox = Oxalate], **Y-MOF**, as structural basis. The structure and size of **Y-MOF**, **Y-MOF:Eu** and **Y-MOF:Tb** were systematically characterized by PXRD, TGA, SEM and EDX analysis. **Y-MOF:Eu** and **Y-MOF:Tb** shows high intense visible red and green emission, respectively, on the exposure of UV light. These emissions of **Y-MOF:Eu** and **Y-MOF:Tb** were used for the visible detection of nitro explosives such as 2,4,6-trinitrophenol (TNP), 1,3-dinitro benzene (DNB), 2,4-dinitro toluene (DNT), nitro benzene (NB), 4-nitro toluene (NT) in acetonitrile through luminescence quenching. **Y-MOF:Eu** and **Y-MOF:Tb** shows superior sensitivity towards TNP and NT compared to other nitroaromatic explosives. The large stokes shift of **Y-MOF:Eu** and **Y-MOF:Tb** allows the naked eye detection of these nitroaromatics. The observed  $K_{SV}$  (quenching constant obtained from Stern-Volmer plots) values are in the range  $3.2 \times 10^4 - 0.4 \times 10^4 \text{ M}^{-1}$  for **Y-MOF:Eu** and  $3.19 \times 10^4 - 0.47 \times 10^4 \text{ M}^{-1}$  for **Y-MOF:Tb**. Using these materials ppm level detection of nitro explosives have been achieved.

## Introduction

The increasing number of terrorist attack using different explosives in several countries has brought risk in our daily life. Among the commercially available diverse explosive chemicals, nitroaromatics are extensively used.<sup>1</sup> Therefore, the selective detection of commercially available nitroexplosives is a matter of security concern in the defence sector.<sup>2</sup> Nitro aromatics such as 2,4,6-trinitrophenol (TNP), 2,4-dinitro toluene (DNT), 1,3-dinitro benzene (DNB) are common ingredients of explosives.<sup>3</sup> Moreover, nitroaromatics remain as key energetic materials for the preparation of landmines and improvised explosive devices (IED).<sup>4</sup> Beside these, TNP are used in glass, match, fireworks, dye, and lather industries.<sup>5,6</sup> More importantly, these nitroaromatics has adverse affect on human being.<sup>7</sup> Therefore, the detection of nitroaromatics is of high significance for both security and environmental pollution control in the present decade.<sup>8</sup> Recent nitroexplosive detection methods consists of detection by trained canines,<sup>9</sup> surface enhanced Raman spectroscopy,<sup>10</sup> ion mobility spectrometry,<sup>11</sup> gas chromatography coupled with mass spectrometry,<sup>12</sup> electron capture detection,<sup>13</sup> various imaging techniques<sup>14</sup> etc. These methods are generally expensive, time consuming and often not easily accessible. Therefore, some less expensive methods need to be developed so that rapid and precise detection is possible as well.

Recently, luminescence based detection methods have been considered as one of the most excellent, sensitive and reliable method in the detection of nitroaromatics,<sup>15</sup> as this method possesses several advantages like high simplicity, selectivity, portability, short response time and could be used in both solution and solid state.<sup>16</sup> Variety of materials including nanomaterials, conjugated polymers, supramolecular polymers and metal complexes have been used for the luminescence based detection of nitroaromatics.<sup>17</sup> However, their widespread use is restricted due to the multistep processing, stability and lack of molecular organization.<sup>18</sup>

Metal-organic frameworks (MOFs) are relatively a new class of hybrid crystalline materials with diverse structural type and tunable pore size constructed by the connectivity of metal ions or metal clusters and organic ligands. It has attracted rigorous attention in recent past due to their structural chemistry<sup>19</sup> and diverse application in gas storage,<sup>20</sup> gas separation,<sup>21</sup> catalysis,<sup>22</sup> magnetism,<sup>23</sup> sensing,<sup>24</sup> drug delivery,<sup>25</sup> proton conductivity<sup>26</sup>. Recently, metal-organic frameworks, especially Zn and Cd based, have been developed as new kind of materials for the detection of nitroexplosives using ligand centred emission.<sup>27</sup> But ligand centred based luminescence detectors have small stokes shifts, which prevent the naked eye detection of nitroaromatic explosives as the colour differences between emission and excitation light are very little. For this purpose, few lanthanide based MOFs, especially europium and terbium containing, have been used for the detection of nitroaromatic

explosives.<sup>28</sup> Metal-organic materials of these lanthanides ions generally shows distinct luminescence through antenna effect where organic ligands function as sensitizer.<sup>29</sup> In this process, the organic ligands is excited to the singlet state, from which fraction of the energy is transferred to the triplet state of ligands through inter system crossing. The excited state of ligands transfer the energy to the metal centers, resulting metal centered luminescence. The detection of nitroexplosives through naked eye is still challenging as the pure lanthanide based metal-organic frameworks shows lower quenching efficiency owing to the occurrence of self quenching.<sup>28a</sup>

For these purpose, we have synthesized two  $\text{Eu}^{3+}/\text{Tb}^{3+}$  doped micron sized yttrium based metal-organic frameworks,  $[\text{Y}_{0.9}\text{Eu}_{0.1}(\text{OBA})(\text{Ox})_{0.5}(\text{H}_2\text{O})_2]$ , **Y-MOF:Eu** and  $[\text{Y}_{0.9}\text{Tb}_{0.1}(\text{OBA})(\text{Ox})_{0.5}(\text{H}_2\text{O})_2]$ , **Y-MOF:Tb**, respectively, through hydrothermal process and their luminescence based nitro explosives detections are extensively studied. Upon the exposure of UV light, **Y-MOF:Eu** gives highly intense visible red emission and **Y-MOF:Tb** gives highly intense visible green emission. These luminescence of **Y-MOF:Eu** and **Y-MOF:Tb** are quenched so quickly and efficiently that an instant visible colour change is observed in the presence of explosive nitroaromatics such as 2,4,6-trinitrophenol (TNP), 4-nitrotoluene (NT), 2,4-dinitro toluene (DNT), nitrobenzene (NB) and 1,3-dinitro benzene (DNB) in acetonitrile. These two compounds can detect TNP, NT, DNT, NB and DNB even in very low concentration (0 - 20  $\mu\text{M}$ ) range. The observed  $K_{\text{SV}}$  (quenching constant) values in  $\text{M}^{-1}$  are  $3.21 \times 10^4$  for TNP,  $2.44 \times 10^4$  for NT,  $1.02 \times 10^4$  for DNT and  $1.03 \times 10^4$  for NB in case of **Y-MOF:Eu** and  $3.19 \times 10^4$  for TNP,  $2.60 \times 10^4$  for NT,  $1.37 \times 10^4$  for DNT and  $1.01 \times 10^4$  for NB in case of **Y-MOF:Tb**. These observed  $K_{\text{SV}}$  values are among the list of best values known for metal-organic frameworks. These values indicate both the compounds are effective detectors for nitroaromatics. In this article, we present the synthesis, characterization of **Y-MOF**, **Y-MOF:Eu** and **Y-MOF:Tb** and nitroaromatics detection behaviours of **Y-MOF:Eu** and **Y-MOF:Tb**.

## Experimental Section

### Materials

The chemicals needed for the synthesis of the metal-organic compounds,  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich, 99.9%),  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 99.9%),  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (Sigma-Aldrich, 99.9%), 4,4'-Oxybis(benzoic acid) (Sigma-Aldrich, 99%), Oxalic acid dihydrate (Merck, 99%) and NaOH (Merck, 97%) were used as received. The chemical used for the detection experiments, acetonitrile (99.8%), 2,4,6-trinitrophenol (TNP) (98%), 1,3-dinitrobenzene (DNB) (97%), 2,4-dinitrotoluene (DNT) (97%), nitrobenzene (NB) (99%), 4-nitrotoluene (NT) (99%) and benzene(B) (99%), Toluene (99%) and Phenol (99%) were used as received from Sigma-Aldrich without further purification. The water used was double distilled and filtered through a Millipore membrane.

### Synthesis and initial characterizations

**Y-MOF** was hydrothermally synthesized from a mixture of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1915 g, 0.5 mmol), 4,4'- Oxybis(benzoic acid) (0.1304 g, 0.5 mmol), Oxalic acid (0.0637 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and  $\text{H}_2\text{O}$  (10 ml, 555.55 mmol). The mixture was continuously stirred for 30 minutes prior to heating at 150° C for 5

days in a 23 ml Teflon-linked stainless steel autoclave. After the mixture was cooled to room temperature, yellow crystals of compound **Y-MOF** were collected after filtration and washing with sufficient quantity of water. The starting pH value and the final pH value after the reaction were 1 and 3, respectively. Similar procedure has also been used for the synthesis of the **Y-MOF:Eu** and **Y-MOF:Tb**. For **Y-MOF:Eu**, a mixture of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1724 g, 0.45 mmol),  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.0223 g, 0.05 mmol), 4,4'-Oxybis(benzoic acid) (0.1304 g, 0.5 mmol), Oxalic acid (0.0637 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and  $\text{H}_2\text{O}$  (10 ml, 555.55 mmol) and for **Y-MOF:Tb**, a mixture of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1724 g, 0.45 mmol),  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.0217 g, 0.05 mmol), 4,4'- Oxybis(benzoic acid) (0.1304 g, 0.5 mmol), Oxalic acid (0.0637 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and  $\text{H}_2\text{O}$  (10 ml, 555.55 mmol) were used for the hydrothermal treatment. Additionally, another compound  $[\text{Y}_{0.9}\text{Eu}_{0.05}\text{Tb}_{0.05}(\text{OBA})(\text{Ox})_{0.5}(\text{H}_2\text{O})_2]$ , **Y-MOF:Eu,Tb**, were synthesized using a mixture of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1724 g, 0.45 mmol),  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.0112 g, 0.025 mmol),  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.0108 g, 0.025 mmol), 4,4'- Oxybis(benzoic acid) (0.1304 g, 0.5 mmol), Oxalic acid (0.0637 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and  $\text{H}_2\text{O}$  (10 ml, 555.55 mmol) to check the effect of the presence of both the metals (**Eu** and **Tb**). The products were analyzed by powder X-ray diffraction (XRD) in the  $2\theta$  range 5-50° using  $\text{Cu K}\alpha$  radiation (Rigaku, MiniFlex II). The powder XRD patterns of all the synthesized compounds being entirely consistent with the simulated XRD pattern generated based on the structures determined using the single-crystal XRD of **Y-MOF** synthesized by Jin and co-workers (see ESI, Fig. S1).<sup>30</sup>

Leaching test using water as solvent was performed. In this experiment 500 mg sample (**Y-MOF:Eu/Y-MOF:Tb**) has been taken in 50 mL water in round bottom flask and stirred for 72 hrs. Then the sample has been decanted and tested for the presence of Eu/Tb ions using UV-Vis absorption spectrometer and luminescence spectrometer. The results do not show spectra corresponding to the Ln ions. Hence, no leaching of Ln ions occurred from the synthesized single crystalline MOFs. It also indicates the compounds are completely insoluble in water.

### Instrumentations

The sizes of the synthesized compounds were investigated using scanning electron microscope (QUANTA FEG250, FEI). Energy-dispersive X-ray analyses (EDX) were performed to investigate the ratio of Eu and Y in **Y-MOF:Eu** and Tb and Y in **Y-MOF:Tb** and Y, Eu and Tb in **Y-MOF:Eu,Tb** using EDAX, QUANTA 200. The inductively coupled plasma (ICP) analysis of the above three mixed metal compounds were carried out on Thermo-iCap 6000 Series spectrometer. The thermogravimetric analysis (TGA) of the compounds were carried out (Perkin-Elmer Diamond) in nitrogen atmosphere (flow rate 20 mL/min) in the temperature range 40-900 °C (heating rate 10 °C/min).

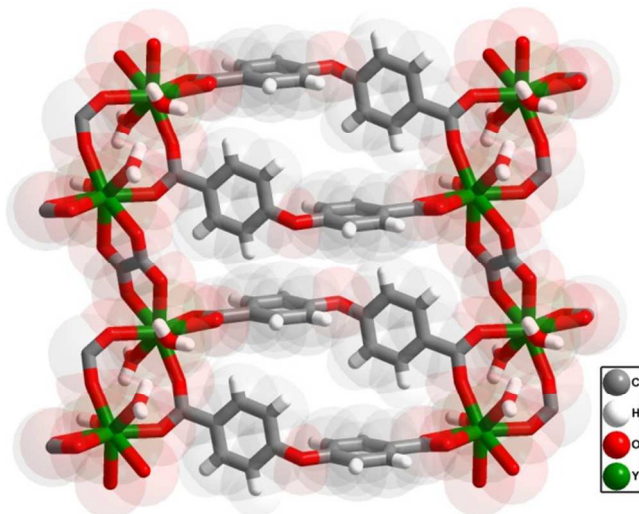
### Photoluminescent based detection measurements

The photoluminescence properties of the compounds dispersed in acetonitrile were investigated at room temperature. The dispersions were prepared by introducing 2 mg of individual compound into 2.00 mL acetonitrile and ultrasonic agitation for 1 hour followed by diluted to 10 mL before measuring the spectra. Photoluminescent spectra were measured using a PerkinElmer LS-55 spectrofluorometer. The analytes were added into the dispersion using micro pipette. UV-Vis spectra of analytes in acetonitrile solvent were studied using Shimadzu UV 3101PC spectrophotometer.

## Results and Discussion

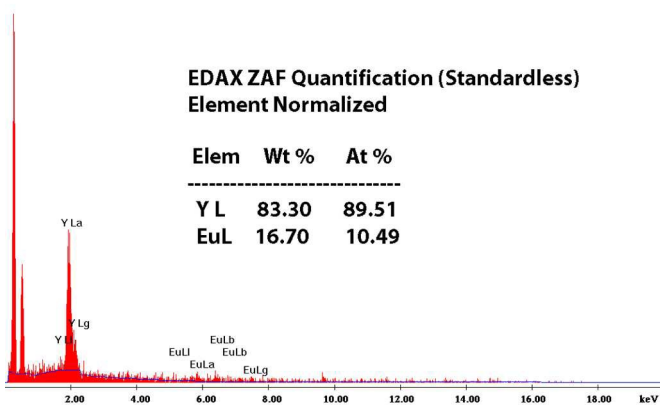
### Structure and morphology

Structure of **Y-MOF** is composed of  $Y^{3+}$  ions, 4,4'-Oxybis(benzoate) (OBA) ligands, oxalates (Ox) and coordinated water molecules. The  $Y^{3+}$  ions are connected by the carboxylate groups of OBA and Ox to form one dimensional structure. The one dimensional structures are further connected by aromatic part of the OBA units resulting in two dimensional structures (Figure 1). The structure of **Y-MOF** has been determined earlier by Jin and co-workers.<sup>30</sup>

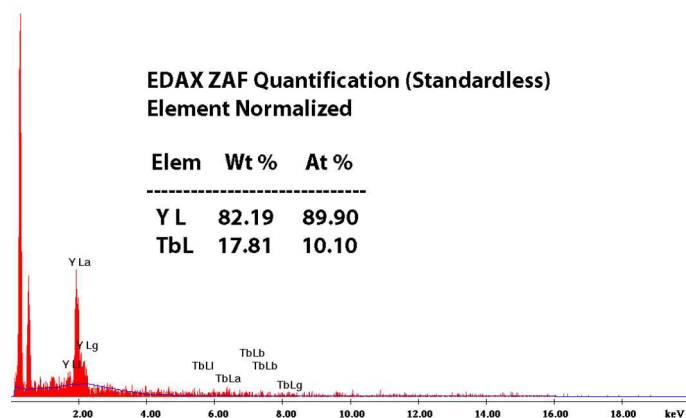


**Fig. 1.** View of two-dimensional connectivity between  $Y^{3+}$  ions and ligands in  $[Y_{1.0}(OBA)(Ox)_{0.5}(H_2O)_2]$ , [OBA = 4,4'- Oxybis(benzoic acid), Ox = Oxalate], **Y-MOF**.

The powder sample of **Y-MOF**, **Y-MOF:Eu**, **Y-MOF:Tb** and **Y-MOF:Eu,Tb** were analyzed using scanning electron microscopy (SEM) to evaluate the sizes. The size of powder grains are in micron regime (see ESI, Fig. S2). The EDX analysis on several crystals shows the presence of Y and Eu/Tb with molar ratio of ~9:1 in **Y-MOF:Eu** and **Y-MOF:Tb** (Figure 2) and the presence of Y, Eu and Tb with molar ratio of ~9:0.5:0.5 in **Y-MOF:Eu,Tb** (See ESI, Fig. S3). The ICP analysis shows the atom percentages of metals as Y 89.37% and Eu 10.63% in **Y-MOF:Eu**; Y 89.56% and Tb 10.44% in **Y-MOF:Tb**; Y 89.26%, Eu 5.41% and Tb 5.33% in **Y-MOF:Eu,Tb**.



(a)

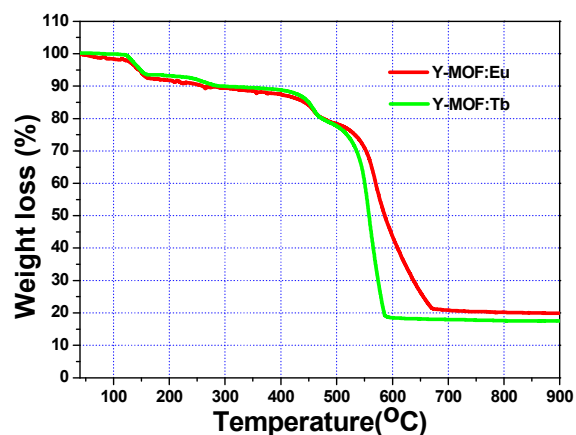


(b)

**Fig. 2.** Representative EDX plot: (a) **Y-MOF:Eu**, (b) **Y-MOF:Tb**. Note the Y and Eu/Tb are in molar ratio of ~9:1

### Thermal Properties

Thermogravimetric analysis is performed on the three compounds. The TGA studies of **Y-MOF**, **Y-MOF:Eu** and **Y-MOF:Tb** shows weight loss in three distinct steps. The first weight loss of 8.2 % (calculated 8.3%) upto 160 °C for **Y-MOF:Eu** and 7.7% (calculated 8.3%) for **Y-MOF:Tb** may be due to the removal of - the coordinated water molecules. The second weight loss of 10.8% (calculated 10.5%) in the range of 400-470 °C for **Y-MOF:Eu** and 11.8% (calculated 10.5%) for **Y-MOF:Tb** is probably due to the decomposition of coordinated oxalate moiety. The final weight loss of 60.3% (calculated 59.2%) for **Y-MOF:Eu** and 62.2% (calculated 61.5) for **Y-MOF:Tb** leads to the decomposition of the framework (Figure 3). Similar result is also obtained for **Y-MOF** (see ESI, Fig. S4).



**Fig.3.** Thermogravimetric analysis (TGA) of **Y-MOF:Eu** and **Y-MOF:Tb** in nitrogen atmosphere.

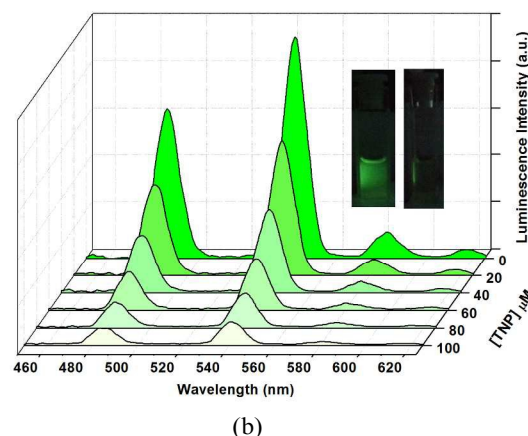
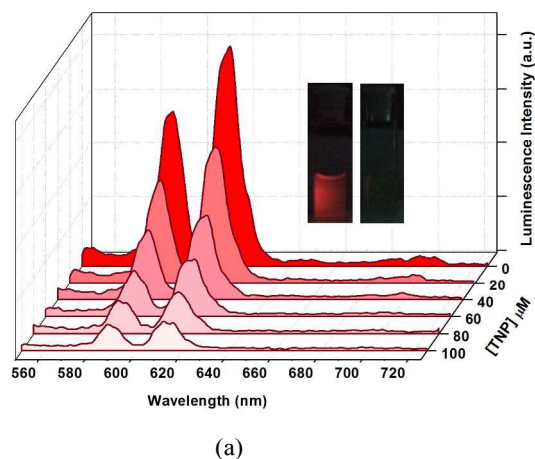
### Photoluminescence properties

The photoluminescence studies of **Y-MOF**, **Y-MOF:Eu**, **Y-MOF:Tb** and **Y-MOF:Eu,Tb** are performed using their dispersions in acetonitrile (see ESI, Fig. S5). The luminescence spectrum of compound **Y-MOF** shows emission at 367 nm upon excitation at 275 nm. This ligand centred emission can be assigned to intra-ligand electronic transitions. Luminescence spectrum of **Y-MOF:Eu** shows strong red emission in the visible region upon excitation at 275 nm. The emission bands observed at 589, 614, 649 and 697 nm can be assigned to the  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_2$ ,  $^5D_0 \rightarrow ^7F_3$  and  $^5D_0 \rightarrow ^7F_4$  transitions, respectively, based on OBA sensitized  $Eu^{3+}$  centered emission. The emission at lower wavelength regions observed for intra-ligand transitions of aromatic dicarboxylates are excluded by using appropriate cut-off filters. Similarly, **Y-MOF:Tb** exhibits strong green emission in the visible region upon excitation at 275 nm. The emission bands observed at 486, 541, 583 and 618 nm can be assigned to the  $^5D_4 \rightarrow ^7F_6$ ,  $^5D_4 \rightarrow ^7F_5$ ,  $^5D_4 \rightarrow ^7F_4$  and  $^5D_4 \rightarrow ^7F_3$  transitions, respectively. The strong emissions of **Y-MOF:Eu** and **Y-MOF:Tb** promoted us to investigate their potential application for the detection of nitroaromatic explosives.

### Nitroaromatic Explosives Detections

To explore the potential application of **Y-MOF:Eu** and **Y-MOF:Tb** towards detection of trace amount of nitroaromatics explosives, luminescence quenching titrations were performed by gradual addition of analytes to **Y-MOF:Eu/Y-MOF:Tb** dispersed in acetonitrile. The change in luminescence intensity (monitored at 614 nm for **Y-MOF:Eu** and at 541 nm for **Y-MOF:Tb**) with the increasing addition of TNP (upto 100  $\mu M$ ) in **Y-MOF:Eu** and **Y-MOF:Tb** are shown in Figure 4a and 4b, respectively.

The visible red emission of **Y-MOF:Eu** and green emission of **Y-MOF:Tb** on UV exposure gradually loses their intensity and these visible emissions almost switch off upon the addition of 100  $\mu M$  of TNP solution when nearly 90% quenching of their initial intensity occurs.



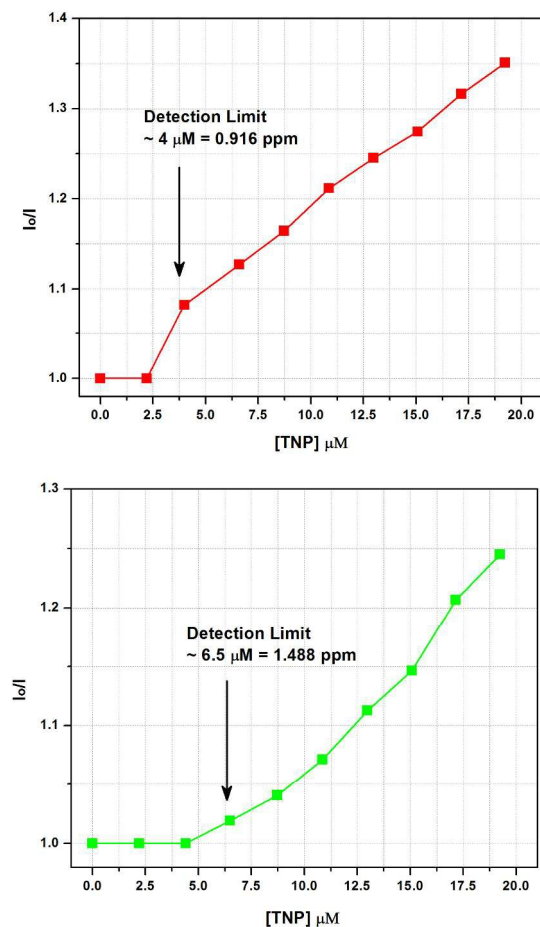
**Fig. 4.** (a) Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of TNP solution ( $\lambda_{ex} = 275$  nm). Inset: a photograph showing the original luminescence of **Y-MOF:Eu** sample and the quenched one in presence of 100  $\mu M$  TNP. (b) Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of TNP solution ( $\lambda_{ex} = 275$  nm). Inset: a photograph showing the original luminescence of **Y-MOF:Tb** sample and the quenched one in presence of 100  $\mu M$  TNP.

Motivated by the high quenching effect, we have also performed luminescence quenching titration using ultralow concentration of TNP so as to get the value of the detection limit of TNP. As can be seen from figure 5, the luminescence quenching can be clearly detected at as low as 4  $\mu M$  concentration in case of **Y-MOF:Eu** and 6.5  $\mu M$  in case of **Y-MOF:Tb**.

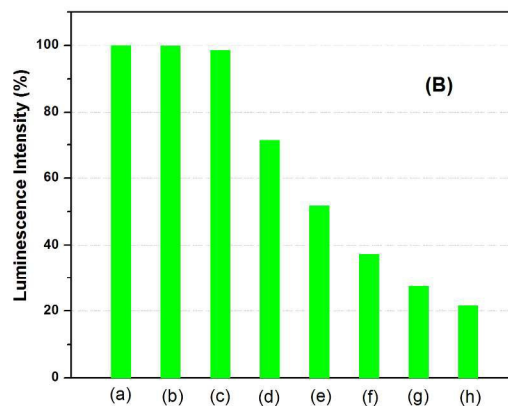
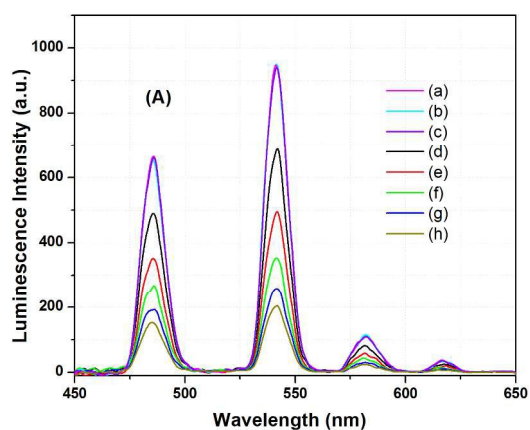
The quenching effect of TNP inspired us to further investigate the possibility of detecting other nitro explosives in detail. For this purpose luminescence quenching titrations were also performed with other aromatic compounds such as 4-nitro toluene (NT), 2,4-dinitro toluene (DNT), nitro benzene (NB), 1,3-dinitro benzene (DNB), Phenol (P), Toluene (T) and benzene (B) (see ESI, Fig.S6 – S12). Among these, NT shows nearly 81% luminescence quenching upon the addition of 100  $\mu M$  solution in **Y-MOF:Eu**. In case of DNT, NB and DNB, the quenching are 63.6%, 58.2% and 31.0%, respectively, upon the incremental addition of 100  $\mu M$  of respective analytes to **Y-MOF:Eu** dispersed in acetonitrile. Phenol shows a little quenching behaviour. Whereas benzene and toluene show negligible quenching behaviour (see ESI, Fig.S13 – S14). All of these luminescence titrations were also performed in the case of **Y-MOF:Tb** (see ESI, Fig.S15 – S23). The two compounds show similar sensitivity orders for nitroaromatics, that is, for both **Y-MOF:Eu** and **Y-MOF:Tb**, the luminescence quenching efficiencies of TNP and NT are significantly higher than those of other nitroaromatics. The order of quenching efficiency for the selected analytes is TNP > NT > DNT > NB > DNB > P > T > B for both **Y-MOF:Eu** and **Y-MOF:Tb**. These results indicate that both the compounds are effective detectors for nitroaromatic explosives.

It is very important to check the selectivity of TNP detection in presence of non-quenchable aromatics like benzene, toluene as these aromatics usually remain as impurity along with nitroaromatics explosives. For this purpose, we have added 100

$\mu\text{M}$  toluene followed by  $100 \mu\text{M}$  benzene to both **Y-MOF:Eu** and **Y-MOF:Tb** prior to stepwise addition of TNP solution. The luminescence spectra and the bar diagram of the overall quenching in the case **Y-MOF:Tb** are shown in figure 6 (see ESI Fig. S24, for **Y-MOF:Eu**). The quenching efficiency of TNP almost remains unaltered in presence of benzene and toluene for both the MOFs.

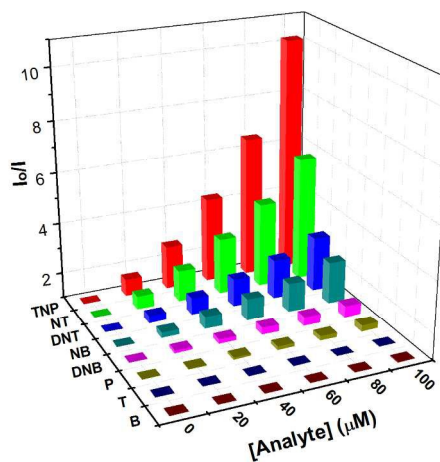


**Fig. 5.** Luminescence quenching vs concentration of TNP plot indicating the detection limit [**Y-MOF:Eu** (top) and **Y-MOF:Tb** (down)] (where  $I_0$  = luminescence intensity in absence of analyte,  $I$  = luminescence intensity with incremental addition of TNP).



**Fig. 6.** (A) Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon the incremental addition of TNP solution in presence of  $100 \mu\text{M}$  toluene and  $100 \mu\text{M}$  benzene ( $\lambda_{\text{ex}} = 275 \text{ nm}$ ). (B) Corresponding bar diagram showing the luminescence intensity (monitored at  $541 \text{ nm}$ ) after the sequential addition of the analytes. The composition and concentration of the system were as follows: (a) **Y-MOF:Tb** in acetonitrile, (b) a +  $100 \mu\text{M}$  Toluene, (c) b +  $100 \mu\text{M}$  B, (d) c +  $20 \mu\text{M}$  TNP, (e) c +  $40 \mu\text{M}$  TNP, (f) c +  $60 \mu\text{M}$  TNP, (g) c +  $80 \mu\text{M}$  TNP, (h) c +  $100 \mu\text{M}$  TNP.

The luminescence quenching titrations have also been carried out using **Y-MOF:Eu,Tb** in presence of all the analytes. The details studies shows the similar trend of quenching as observed in **Y-MOF:Eu** and **Y-MOF:Tb**. (see ESI, Fig. S25 – S34). The differences in quenching efficiency can be quantitatively analysed by fitting the experimental data to the Stern–Volmer (SV) equation:  $(I_0/I) = K_{\text{sv}}[A] + 1$ , where  $I_0$  is the initial luminescence intensity without the analyte,  $I$  represents the luminescence intensity with the analyte having molar concentration  $[A]$ , and  $K_{\text{sv}}$  is the Stern–Volmer quenching constant ( $\text{M}^{-1}$ ). In the lower concentration range (upto  $20 \mu\text{M}$ ) for all the nitroaromatic explosives a linear increase in  $(I_0/I)$  was observed (see ESI Fig. S35). In the higher concentration range, the SV plot diverged from linearity and began to bend upwards in case TNP, NT, DNT, and NB for both the MOFs (Fig. 7 and ESI Fig. S36).



**Fig. 7.** Stern-Volmer plots of analytes in higher concentration range of analytes (upto  $100 \mu\text{M}$ ) for **Y-MOF:Tb**.

The observed linear variation in the lower concentration range are mainly due to the static quenching, whereas the steep curves at higher concentration are probably due to dynamic quenching. The static quenching can be attributed due to the ground state interaction between the analytes and the MOFs. The dynamic quenching is mainly due to the energy and electron transfer processes between the analytes and the MOFs. Besides these mechanisms, the absorption of excitation light by the analyte itself may also contribute to the quenching effect.

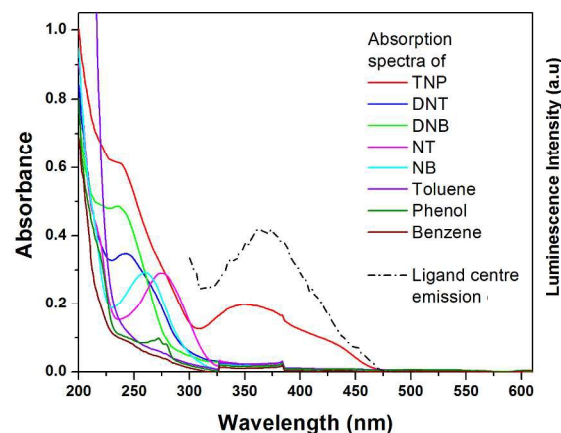
Fitting of linear part of plots allows the determination of the quenching constants ( $K_{sv}$ ). The observed  $K_{sv}$  values for different analytes are summarised in Table 1. These large  $K_{sv}$  values revealed extremely high sensitivity towards the nitro aromatics. So, it can be said that **Y-MOF:Eu** and **Y-MOF:Tb** are among the best effective luminescence based metal-organic framework for nitro aromatics, especially for TNP and NT. The higher quenching efficiency of **Y-MOF:Eu** and **Y-MOF:Tb** in the lower concentrations is due to static quenching. Static quenching arises due to molecular level interactions between analytes and MOFs. Apart from the static quenching, the mechanism of the ligand sensitized metal centered luminescence quenching of **Y-MOF:Eu** and **Y-MOF:Tb** in presence of nitro aromatics are due to the reduction of excitation energy through the absorption of the excitation energy by the analytes by competing with the antenna ligands and transfer of electron from the antenna ligand excited state to the LUMO of the analytes.

**Table 1.** Summary of the observed Stern-Volmer quenching constants ( $K_{sv}$ ) values for **Y-MOF:Eu** and **Y-MOF:Tb**

Analyte	<b>Y-MOF:Eu</b> [ $K_{sv}$ ( $M^{-1}$ )]	<b>Y-MOF:Tb</b> [ $K_{sv}$ ( $M^{-1}$ )]
TNP	$3.21 \times 10^4$	$3.19 \times 10^4$
NT	$2.44 \times 10^4$	$2.60 \times 10^4$
DNT	$1.02 \times 10^4$	$1.37 \times 10^4$
NB	$1.03 \times 10^4$	$1.01 \times 10^4$
DNB	$0.41 \times 10^4$	$0.47 \times 10^4$
P	$0.31 \times 10^4$	$0.11 \times 10^4$

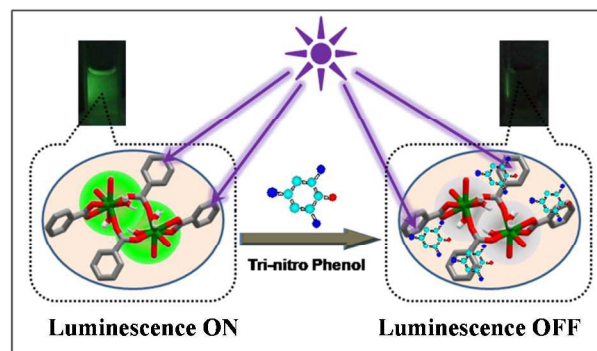
The absorption spectra of the analytes in acetonitrile contains useful information to explain the observed luminescence quenching. TNP, NT, DNT and NB have some absorbance around 275nm. NT has absorption band situated exactly at 275 nm which suggest that, both the processes (absorption of excitation energy and ligand-analyte electron transfer) in this case is highly favourable compared to the other nitroaromatics explosives. In addition TNP has another absorption band around 350 nm which is nicely overlapped with the ligand centred emission spectrum (Fig. 8). This overlap supports the possibility of resonance energy transfer from the ligand centre of **Y-MOF:Eu** and **Y-MOF:Tb** to the TNP which also results the quenching of metal centre emission. For these reasons, TNP has higher quenching efficiency compared to NT. On the other hand DNT and NB have nearly equal absorbance at 275 nm and they show

similar quenching behaviour. DNB has a small absorption tail near to 275 nm and show less quenching effect.



**Fig. 8.** Absorption spectra of all the eight analytes in acetonitrile (Conc. = 20  $\mu$ M). Black dash-dotted curve is the ligand centre emission spectrum of **Y-MOF** which is nicely overlapped with the second absorption band (~350 nm) of TNP.

From the observed experimental results, the luminescence response of **Y-MOF:Tb** in presence and absence of nitroaromatics explosives and the mechanism of quenching can be demonstrated schematically as in Fig. 9. By absorption of UV light the antenna ligand get excited, then the energy transfer from the ligand to  $Tb^{3+}$  centre occurs resulting the green luminescence emission. When nitroaromatics explosives (TNP is shown in Fig. 9) are present in the close proximity of the MOF through molecular level interaction with the ligand, the excess energy from the ligand is transferred to the nitroaromatic molecules through energy or electron transfer processes. As a consequence, the energy transfer from ligand to the metal centre is reduced, resulting the luminescence quenching. Quenching of red emission of **Y-MOF:Eu** by nitroaromatics can also be explained using similar schematic diagram.



**Fig. 9.** Schematic of the ligand-sensitized metal-centered luminescence phenomenon of the **Y-MOF:Tb** in the absence of TNP (left side) and in the presence of TNP (right side).

## Conclusions

In conclusion, two lanthanide doped luminescent micron sized metal-organic materials- **Y-MOF:Eu** and **Y-MOF:Tb** have been designed and synthesized through isomorphous substitution technique using a yttrium based two dimensional metal-organic framework (MOF) **Y-MOF**, as structural basis. These materials demonstrate high sensitive detection of TNP, NT, NB, DNB and DNT in acetonitrile through the quenching of ligand sensitized  $\text{Eu}^{3+}/\text{Tb}^{3+}$  centered luminescence. Details experimental studies explained that static quenching as well as the excitation energy absorption and electron transfers are the mechanisms for the luminescence quenching in presence of nitroaromatics. In case of TNP, additionally, the resonance energy transfer mechanism plays a major role. Possibility of several quenching mechanisms makes these materials more sensitive towards nitro explosives. More importantly, the large Stokes shift makes these two materials useful as naked eye detectors using UV light.

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