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

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ELECTRONIC SUPPLEMENTARY INFORMATION
Fig. S1: (A) Powder XRD (CuKα) patterns: (a) simulated from single crystal X-ray data of \([\text{Y}_{1.0}(\text{OBA})(\text{Ox})_{0.5}(\text{H}_2\text{O})_2]\), **Y-MOF** (CCDC: 659373)*, (b) **Y-MOF**, (c) **Y-MOF:Eu** (d) **Y-MOF:Tb**. *[C. –Y. Sun, X. –J. Zheng, X. –B.Chen, L.-C. Li and L. –P. Jin, *Inorganica Chimica Acta*, 2009, *362*, 325]. (B) Powder XRD (CuKα) patterns: (a) simulated from single crystal X-ray data of \([\text{Y}_{1.0}(\text{OBA})(\text{Ox})_{0.5}(\text{H}_2\text{O})_2]\), **Y-MOF** (CCDC: 659373)*, (b) **Y-MOF:Eu,Tb**.
Fig. S2: SEM images: (a) Y-MOF, (b) Y-MOF:Eu, (c) Y-MOF:Tb, (d) Y-MOF:Eu, Tb.
Fig. S3. Representative EDX plot of **Y-MOF:Eu,Tb**. Note the Y, Eu and Tb are in molar ratio of ~9:0.5:0.5.

### EDAX ZAF Quantification (Standardless)
Element Normalized

<table>
<thead>
<tr>
<th>Elem</th>
<th>Wt %</th>
<th>At %</th>
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<tbody>
<tr>
<td>Y L</td>
<td>81.88</td>
<td>89.59</td>
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<tr>
<td>EuL</td>
<td>8.16</td>
<td>5.14</td>
</tr>
<tr>
<td>TbL</td>
<td>9.96</td>
<td>5.27</td>
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Fig. S4: Thermogravimetric analysis (TGA) of Y-MOF in nitrogen atmosphere.
Fig. S5: Dotted line show excitation spectra (monitored at $\lambda_{em} = 365$ nm) of Y-MOF and solid lines represent the emission spectra of Y-MOF, Y-MOF:Eu, Y-MOF:Tb and Y-MOF:Eu,Tb dispersed in acetonitrile ($\lambda_{ex} = 275$ nm, filter: 515 nm cut-off for Y-MOF:Eu, filter: 430 nm cut-off for Y-MOF:Tb, filter: 430 nm cut-off for Y-MOF:Eu,Tb). All the spectra measured using PerkinElmer LS-55 spectrofluorometer. All the four suspensions in acetonitrile were prepared by sonicating the mixture of solvothermally synthesized Y-MOF, Y-MOF:Eu, Y-MOF:Tb and Y-MOF:Eu,Tb for 1 hour.
Fig. S6: Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of NT solution ($\lambda_{ex} = 275$ nm; filter: 515 nm cut-off). The final concentration of NT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu** for 1 hour.
Fig. S7: Emission spectra of Y-MOF:Eu dispersed in acetonitrile upon incremental addition of DNT solution ($\lambda_{ex} = 275$ nm; filter: 515 nm cut-off). The final concentration of DNT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu suspension in acetonitrile was prepared by sonicking the mixture of solvothermally synthesized Y-MOF:Eu for 1 hour.
Fig. S8: Emission spectra of \textit{Y-MOF:Eu} dispersed in acetonitrile upon incremental addition of NB solution ($\lambda_{ex} = 275$ nm; filter: 515 nm cut-off). The final concentration of NB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. \textit{Y-MOF:Eu} suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized \textit{Y-MOF:Eu} for 1 hour.
Fig. S9: Emission spectra of Y-MOF:Eu dispersed in acetonitrile upon incremental addition of DNB solution ($\lambda_{ex} = 275$ nm; filter: 515 nm cut-off). The final concentration of DNB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Eu for 1 hour.
Fig. S10: Emission spectra of Y-MOF:Eu dispersed in acetonitrile upon incremental addition of Phenol solution ($\lambda_{\text{ex}} = 275$ nm; filter: 515 nm cut-off). The final concentration of Phenol in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Eu for 1 hour.
Fig. S11: Emission spectra of Y-MOF:Eu dispersed in acetonitrile upon incremental addition of Toluene solution ($\lambda_{ex} = 275$ nm; filter: 515 nm cut-off). The final concentration of Toluene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Eu for 1 hour.
Fig. S12: Emission spectra of Y-MOF:Eu dispersed in acetonitrile upon incremental addition of Benzene solution ($\lambda_{\text{ex}} = 275$ nm; filter: 515 nm cut-off). The final concentration of Benzene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu suspension in acetonitrile was prepared by soninating the mixture of solvothermally synthesized Y-MOF:Eu for 1 hour.
Fig. S13: Plot of fraction of luminescence intensity of Y-MOF:Eu (at 614 nm) vs concentration of analytes. $I_0$ and I are luminescence intensity in absence and presence of analyte, respectively.
Fig. S14: Percentage of luminescence quenching with respect of $^5D_0 \rightarrow ^7F_2$ (at 614 nm) emission of Y-MOF:Eu with 100 μM of different analytes.
Fig. S15: Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of NT solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of NT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Tb** suspension in acetonitrile was prepared by sonicking the mixture of solvothermally synthesized **Y-MOF:Tb** for 1 hour.
Fig. S16: Emission spectra of \textbf{Y-MOF:Tb} dispersed in acetonitrile upon incremental addition of DNT solution ($\lambda_{\text{ex}} = 275$ nm; filter: 430 nm cut-off). The final concentration of DNT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. \textbf{Y-MOF:Tb} suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized \textbf{Y-MOF:Tb} for 1 hour.
Fig. S17: Emission spectra of Y-MOF:Tb dispersed in acetonitrile upon incremental addition of NB solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of NB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Tb suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Tb for 1 hour.
Fig. S18: Emission spectra of \textbf{Y-MOF:Tb} dispersed in acetonitrile upon incremental addition of DNB solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of DNB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. \textbf{Y-MOF:Tb} suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized \textbf{Y-MOF:Tb} for 1 hour.
Fig. S19: Emission spectra of Y-MOF:Tb dispersed in acetonitrile upon incremental addition of Phenol solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of Phenol in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Tb suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Tb for 1 hour.
Fig. S20: Emission spectra of Y-MOF:Tb dispersed in acetonitrile upon incremental addition of Toluene solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of Toluene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Tb suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Tb for 1 hour.
Fig. S21: Emission spectra of Y-MOF:Tb dispersed in acetonitrile upon incremental addition of Benzene solution ($\lambda_{\text{ex}} = 275$ nm; filter: 430 nm cut-off). The final concentration of Benzene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Tb suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Tb for 1 hour.
Fig. S22: Plot of fraction of luminescence intensity of Y-MOF:Tb (at 541 nm) vs concentration of analytes. $I_0$ and $I$ are luminescence intensity in absence and presence of analyte, respectively.
Fig. S23: Percentage of luminescence quenching with respect of $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (at 541 nm) emission of Y-MOF:Tb with 100 μM of different analytes.
Fig. S24: (A) Emission spectra of Y-MOF:Eu dispersed in acetonitrile upon the incremental addition of TNP solution in a mixture of 100 µM toluene and 100 µM benzene to Y-MOF:Eu solution ($\lambda_{ex} = 275$ nm; filter: 515 nm cut-off). All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Eu for 1 hour. The final added concentration of TNP, Benzene (B) and Toluene (T) are given below:

(a) 0 µM B + 0 µM T + 0 µM TNP, (b) 0 µM B + 100 µM T + 0 µM TNP, (c) 100 µM B + 100 µM T + 0 µM TNP, (d) 100 µM B + 100 µM T + 20 µM TNP, (e) 100 µM B + 100 µM T + 40 µM TNP, (f) 100 µM B + 100 µM T + 60 µM TNP, (g) 100 µM B + 100 µM T + 80 µM TNP, (h) 100 µM B + 100 µM T + 100 µM TNP.

(B) Bar diagram showing the overall luminescence intensity after the sequential addition of the analytes as mentioned in Figure (A).
Fig. S25: Emission spectra of Y-MOF:Eu,Tb dispersed in acetonitrile upon incremental addition of TNP solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of TNP in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu,Tb suspension in acetonitrile was prepared by sonicking the mixture of solvothermally synthesized Y-MOF:Eu,Tb for 1 hour.
Fig. S26: Emission spectra of $\text{Y-MOF:Eu,Tb}$ dispersed in acetonitrile upon incremental addition of NT solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of NT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. $\text{Y-MOF:Eu,Tb}$ suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized $\text{Y-MOF:Eu,Tb}$ for 1 hour.
Fig. S27: Emission spectra of Y-MOF:Eu,Tb dispersed in acetonitrile upon incremental addition of DNT solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of DNT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu,Tb suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Eu,Tb for 1 hour.
Fig. S28: Emission spectra of Y-MOF:Eu,Tb dispersed in acetonitrile upon incremental addition of NB solution (λ_ex = 275 nm; filter: 430 nm cut-off). The final concentration of NB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu,Tb suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Eu,Tb for 1 hour.
Fig. S29: Emission spectra of Y-MOF:Eu, Tb dispersed in acetonitrile upon incremental addition of DNB solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of DNB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu,Tb suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized Y-MOF:Eu,Tb for 1 hour.
Fig. S30: Emission spectra of Y-MOF:Eu, Tb dispersed in acetonitrile upon incremental addition of Phenol solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of Phenol in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu,Tb suspension in acetonitrile was prepared by sonicking the mixture of solvothermally synthesized Y-MOF:Eu,Tb for 1 hour.
Fig. S31: Emission spectra of Y-MOF:Eu,Tb dispersed in acetonitrile upon incremental addition of Toluene solution ($\lambda_{ex} = 275$ nm; filter: 430 nm cut-off). The final concentration of Toluene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu,Tb suspension in acetonitrile was prepared by sonication the mixture of solvothermally synthesized Y-MOF:Eu,Tb for 1 hour.
Fig. S32: Emission spectra of Y-MOF:Eu,Tb dispersed in acetonitrile upon incremental addition of Benzene solution (\(\lambda_{\text{ex}} = 275\) nm; filter: 430 nm cut-off). The final concentration of Benzene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. Y-MOF:Eu,Tb suspension in acetonitrile was prepared by sonicking the mixture of solvothermally synthesized Y-MOF:Eu,Tb for 1 hour.
Fig. S33: Plot of fraction of luminescence intensity of \textbf{Y-MOF:Eu,Tb (at 541 nm)} vs concentration of analytes. \( I_0 \) and \( I \) are luminescence intensity in absence and presence of analyte, respectively.
Fig. S34: Percentage of luminescence quenching with respect of $^5\text{D}_4 \rightarrow \text{^7F}_5$ of Tb$^{3+}$ ions (at 541 nm) emission of Y-MOF:Eu,Tb with 100 μM of different analytes.
Fig. S35. (a) Plot of $I_0/I$ of Y-MOF:Eu (at 614 nm) vs concentration of analytes in lower concentration range of analytes (upto 20 μM). $I_0$ and I are luminescence intensity in absence and presence of analyte, respectively (b) Plot of $I_0/I$ of Y-MOF:Eu (at 541 nm) vs concentration of analytes in lower concentration range of analytes (upto 20 μM). $I_0$ and I are luminescence intensity in absence and presence of analyte, respectively.
Fig. S36. Stern-Volmer plots of analytes in higher concentration range of analytes (upto 100 μM) for Y-MOF:Eu.