Electronic Supplementary Material (ESI) for RSC Advances.

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

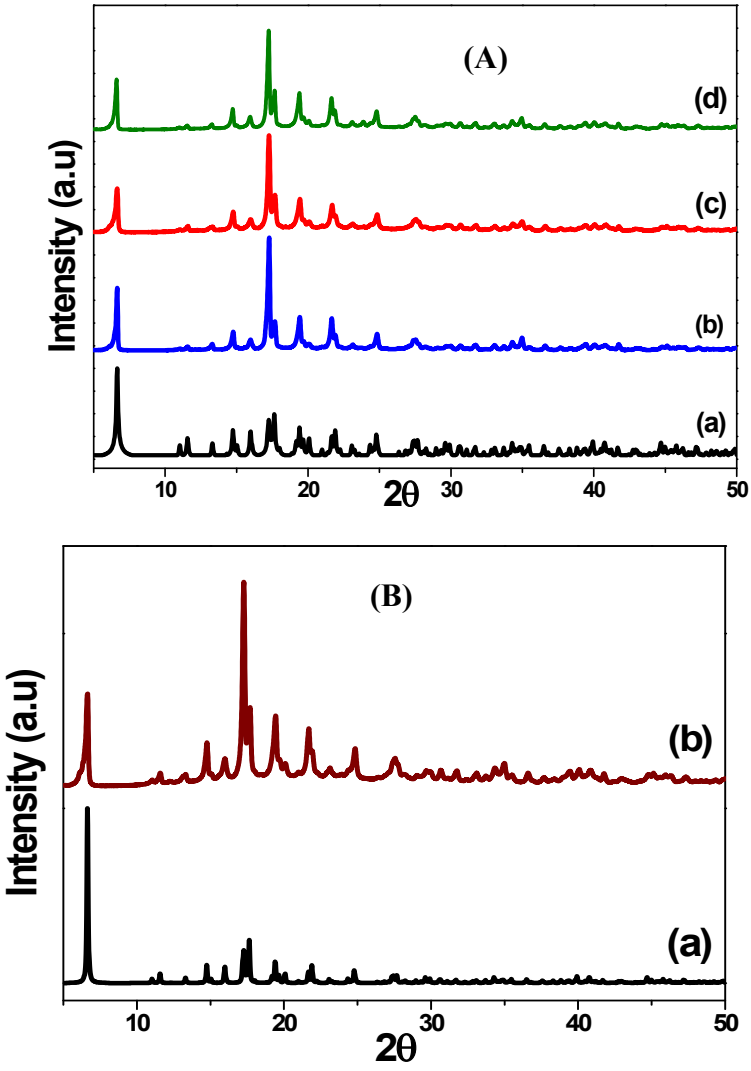
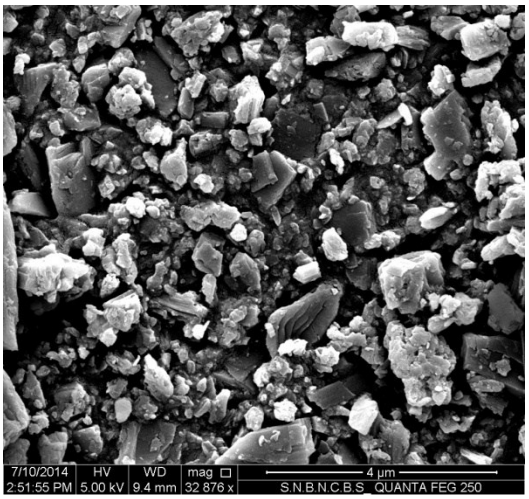
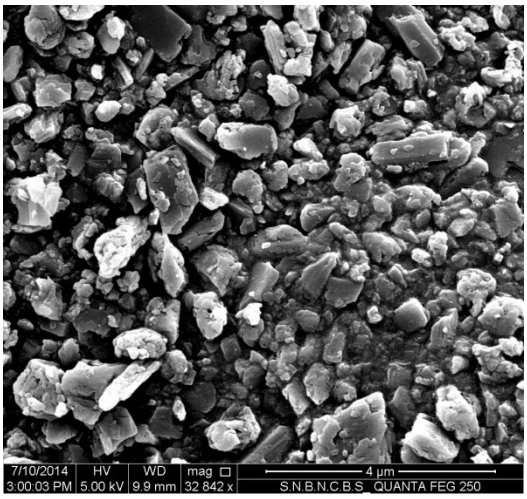


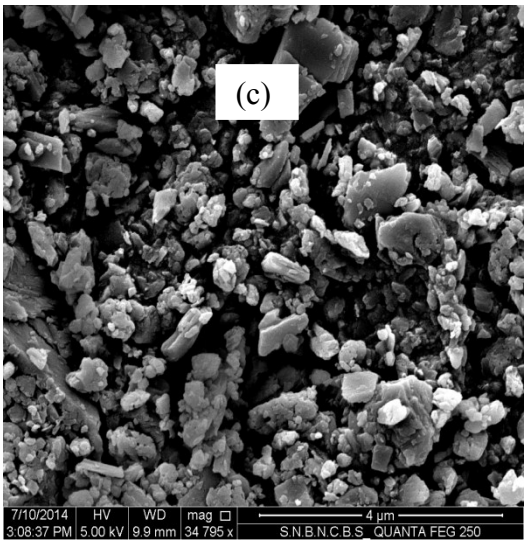
Fig. S1: (A) Powder XRD (CuKα) patterns: (a) simulated from single crystal X-ray data of $[Y_{1.0}(OBA)(Ox)_{0.5}(H_2O)_2]$, **Y-MOF** (CCDC: 659373)*, (b) **Y-MOF**, (c) **Y-MOF:Eu** (d) **Y-MOF:Tb**. *[C. –Y. Sun, X. –J. Zheng, X. –B.Chen, L.-C. Li and L. –P. Jin, *Inorganica Chimica Acta,* 2009, **362**, 325]. (B) Powder XRD (CuKα) patterns: (a) simulated from single crystal X-ray data of $[Y_{1.0}(OBA)(Ox)_{0.5}(H_2O)_2]$, **Y-MOF** (CCDC: 659373)*, (b) **Y-MOF:Eu,Tb.**



(a)



(b)



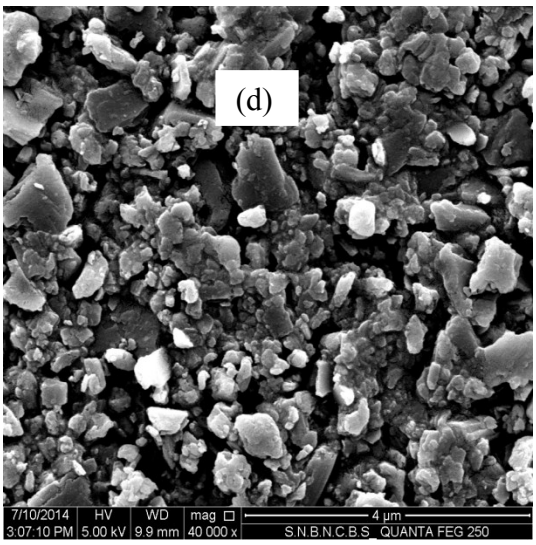
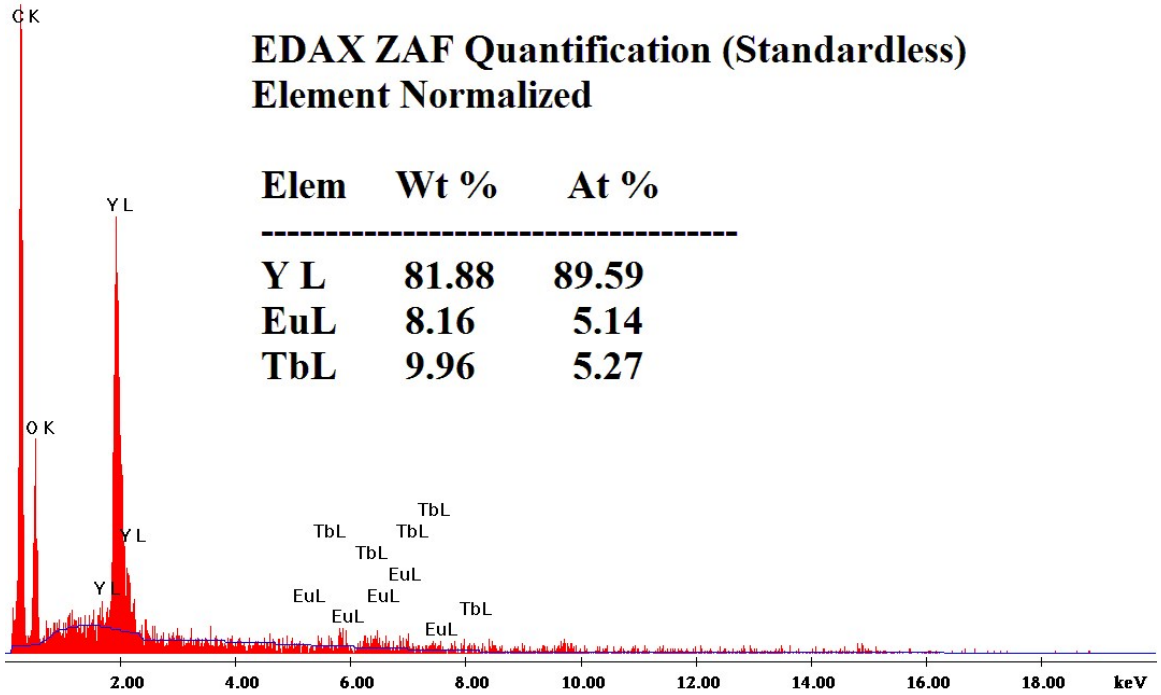


Fig. S2: SEM images: (a) **Y-MOF,** (b) **Y-MOF:Eu**, (c) **Y-MOF:Tb**, (d) **Y-MOF:Eu, Tb.**



EDAX ZAF Quantification (Standardless)
Element Normalized

Elem	Wt %	At %
Y L	81.88	89.59
EuL	8.16	5.14
TbL	9.96	5.27

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.

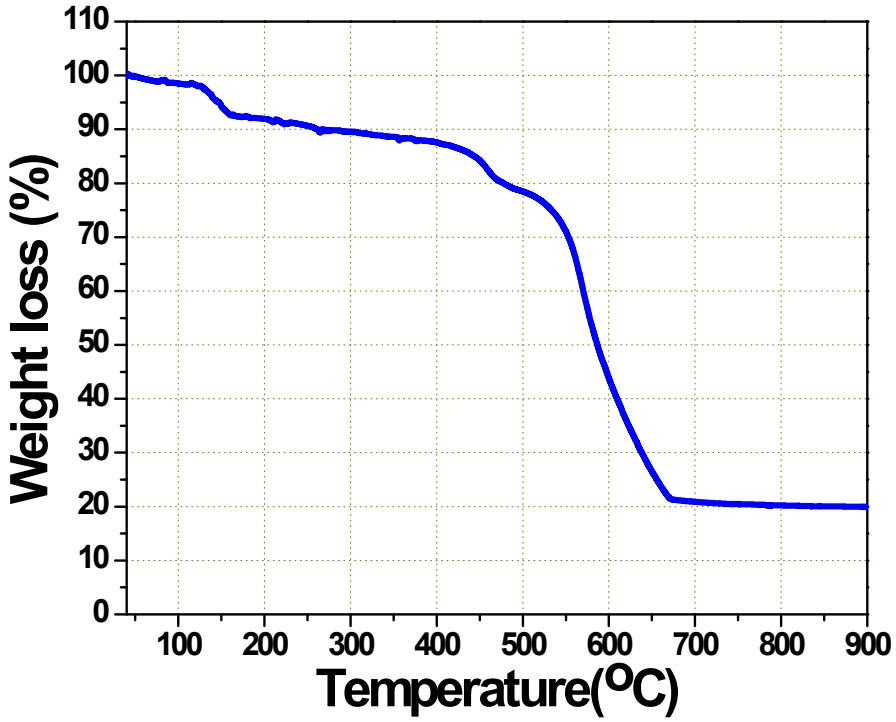


Fig. S4: Thermogravimetric analysis (TGA) of **Y-MOF** in nitrogen atmosphere.

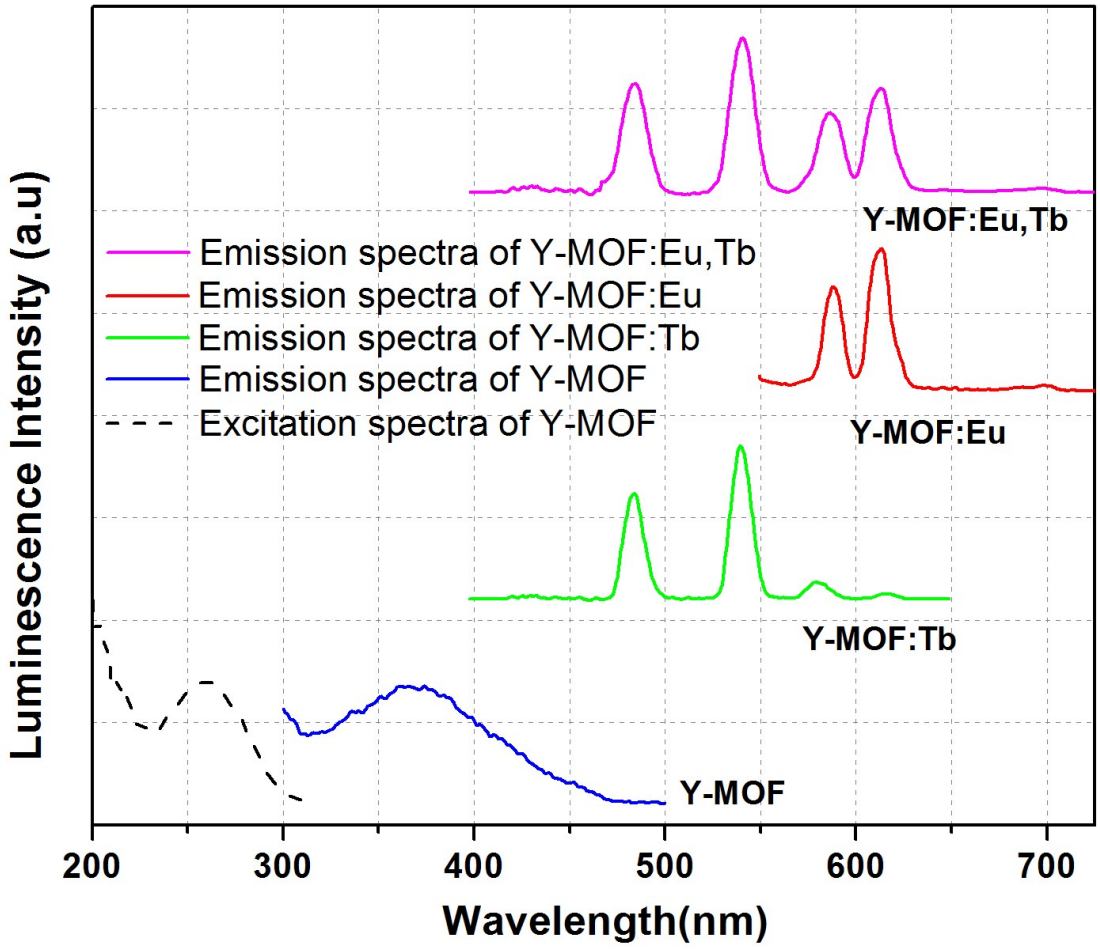


Fig. S5: Dotted line show excitation spectra (monitored at λ_{em} = 365 nm) of **Y-MOF** and solid lines represent the emission spectra of **Y-MOF**, **Y-MOF:Eu**, **Y-MOF:Tb** and **Y-MOF:Eu,Tb** dispersed in acetonitrile (λ_{ex} = 275 nm, filter: 515 nm cut-off for **Y-MOF:Eu**, filter: 430 nm cut-off 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.

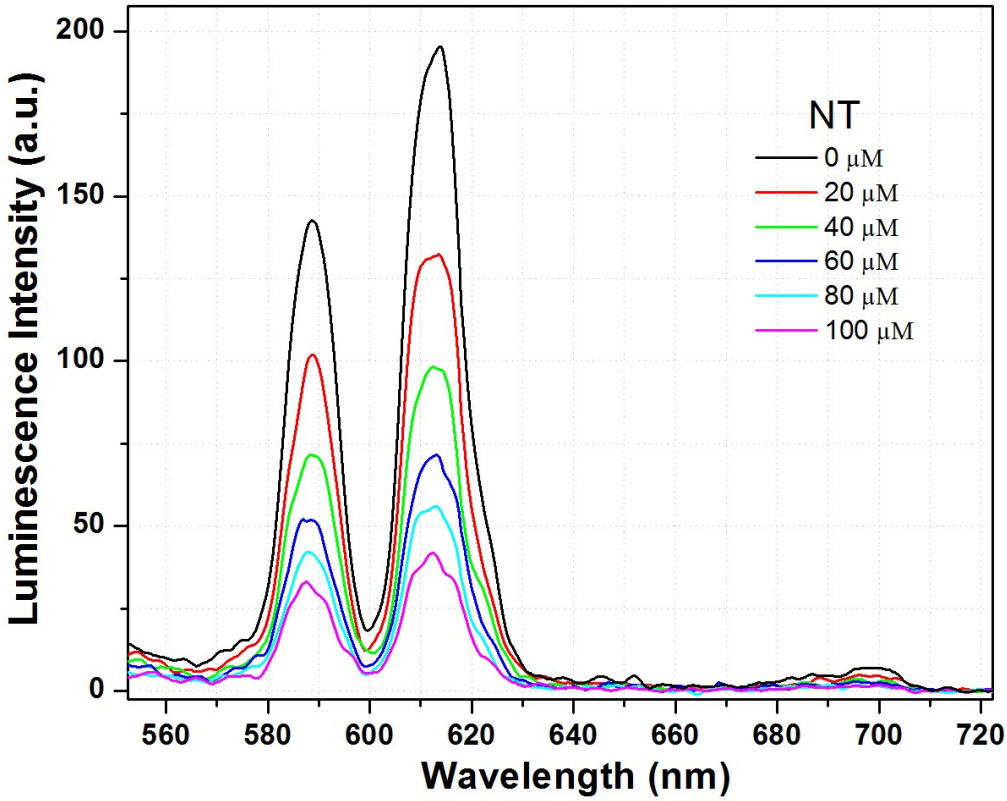


Fig. S6: Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of NT solution (λ_{ex} = 275 nm; filter: 515 nm cut-off). The final concentration of NT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu** for 1 hour.

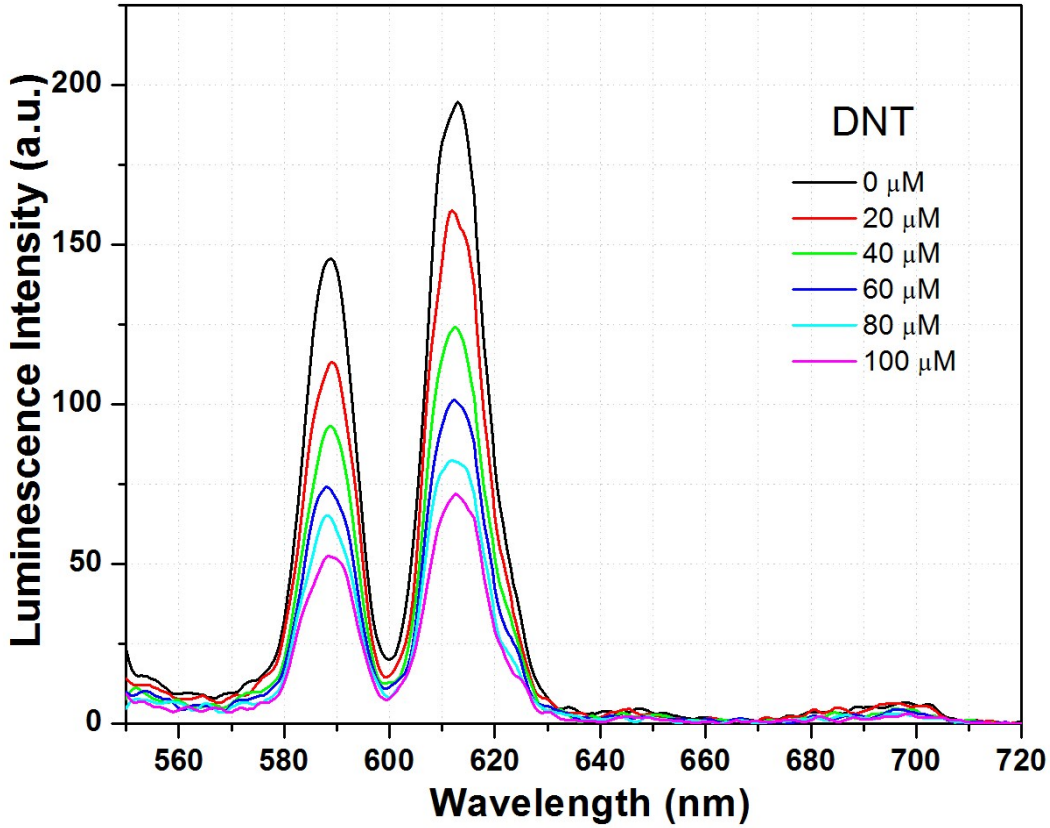


Fig. S7: Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of DNT solution (λ_{ex} = 275 nm; filter: 515 nm cut-off). The final concentration of DNT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu** for 1 hour.

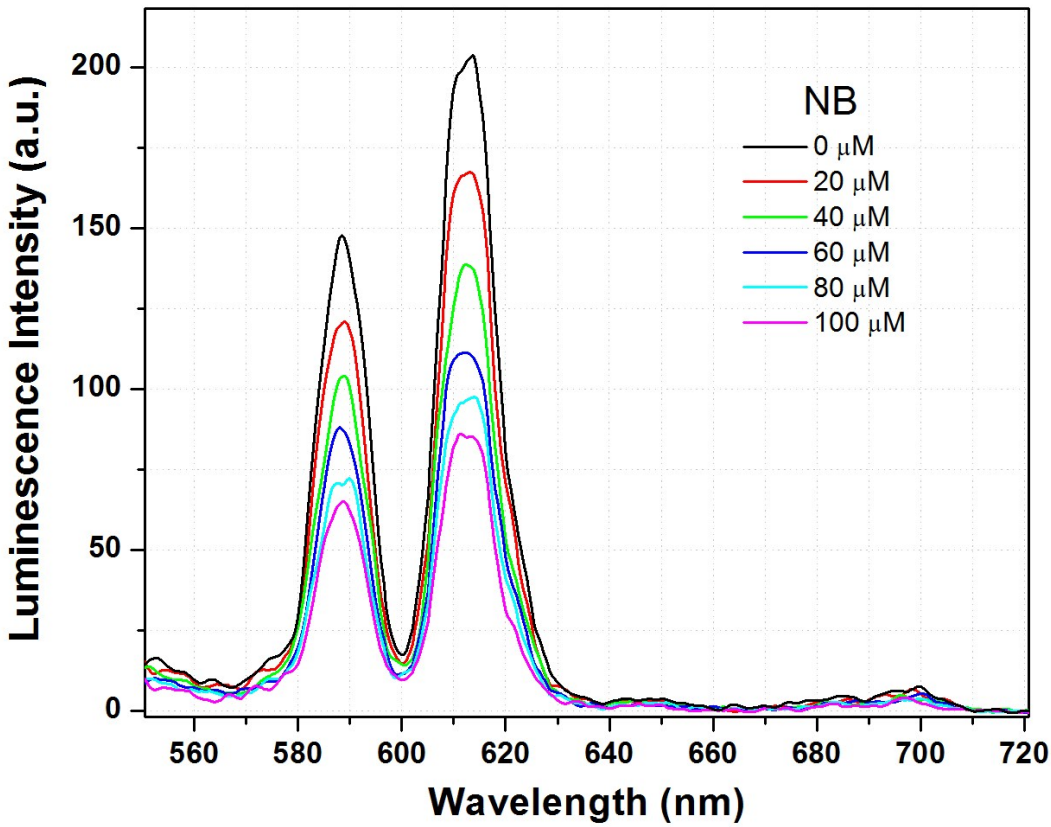


Fig. S8: Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of NB solution (λ_{ex} = 275 nm; filter: 515 nm cut-off). The final concentration of NB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu** for 1 hour.

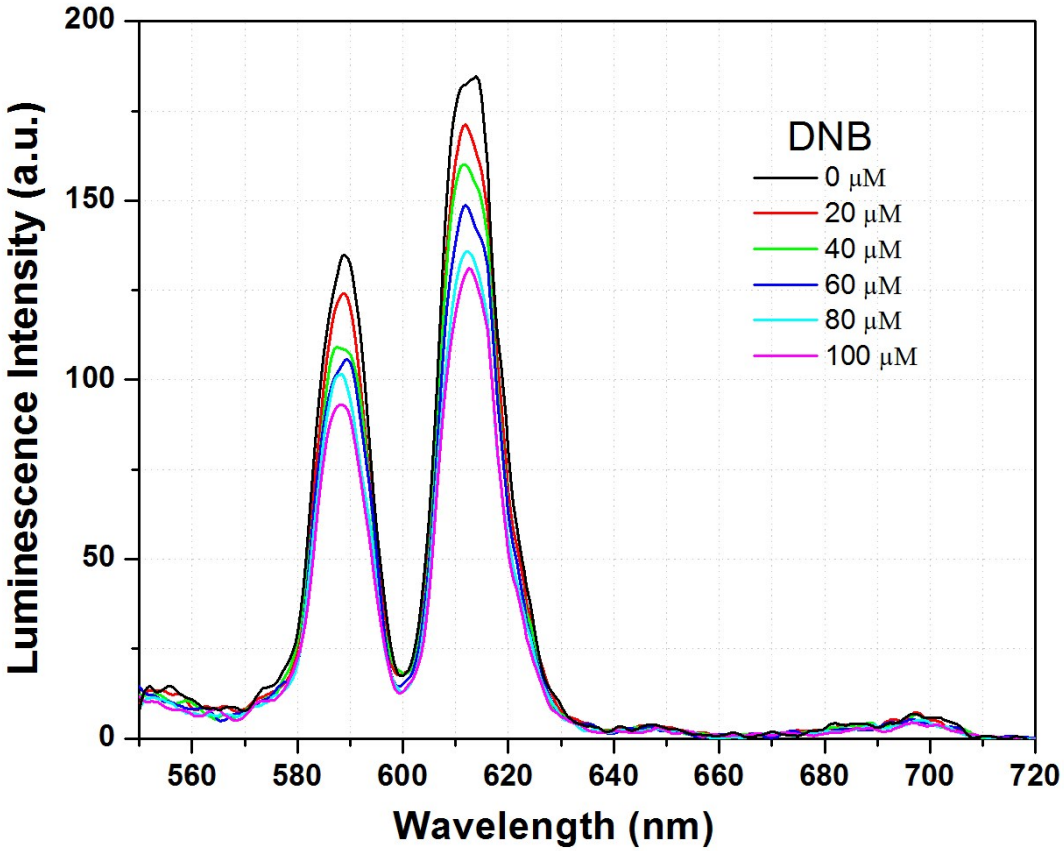


Fig. S9: Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of DNB solution (λ_{ex} = 275 nm; filter: 515 nm cut-off). The final concentration of DNB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu** for 1 hour.

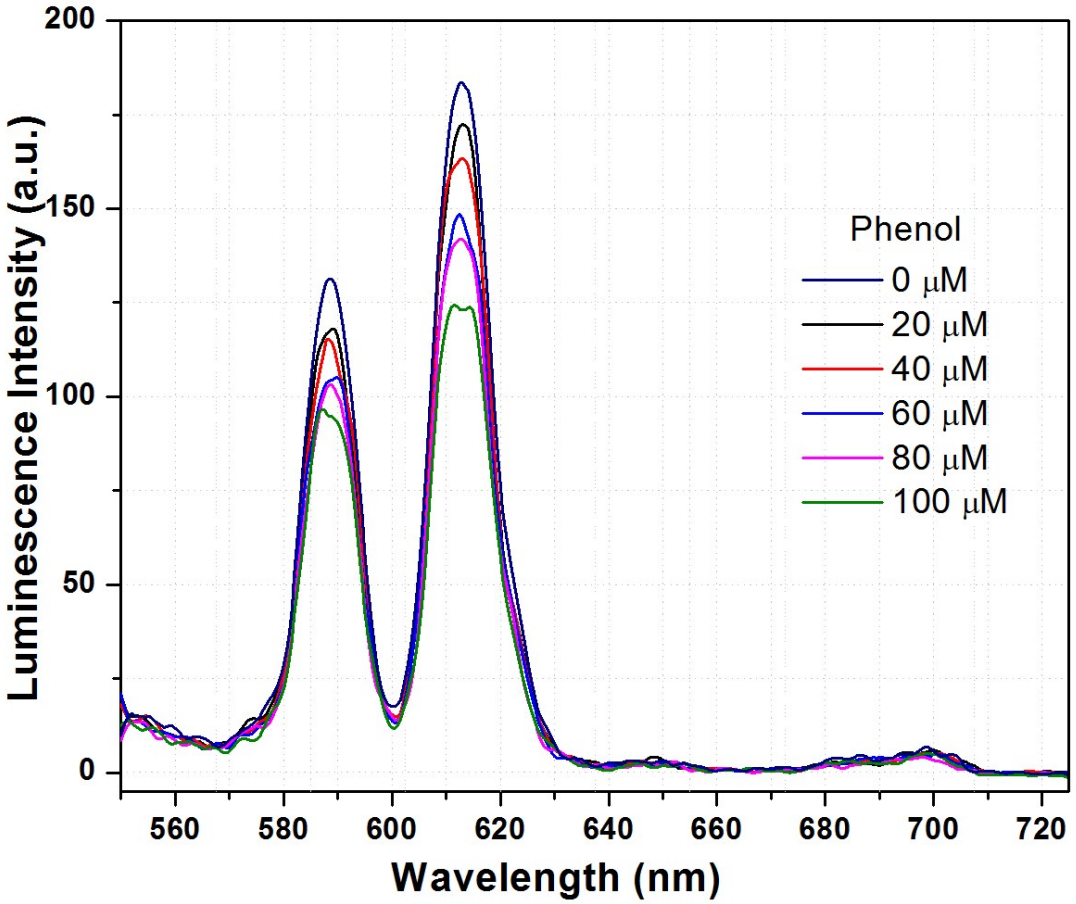


Fig. S10: Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of Phenol solution (λ_{ex} = 275 nm; filter: 515 nm cut-off). The final concentration of Phenol in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu** for 1 hour.

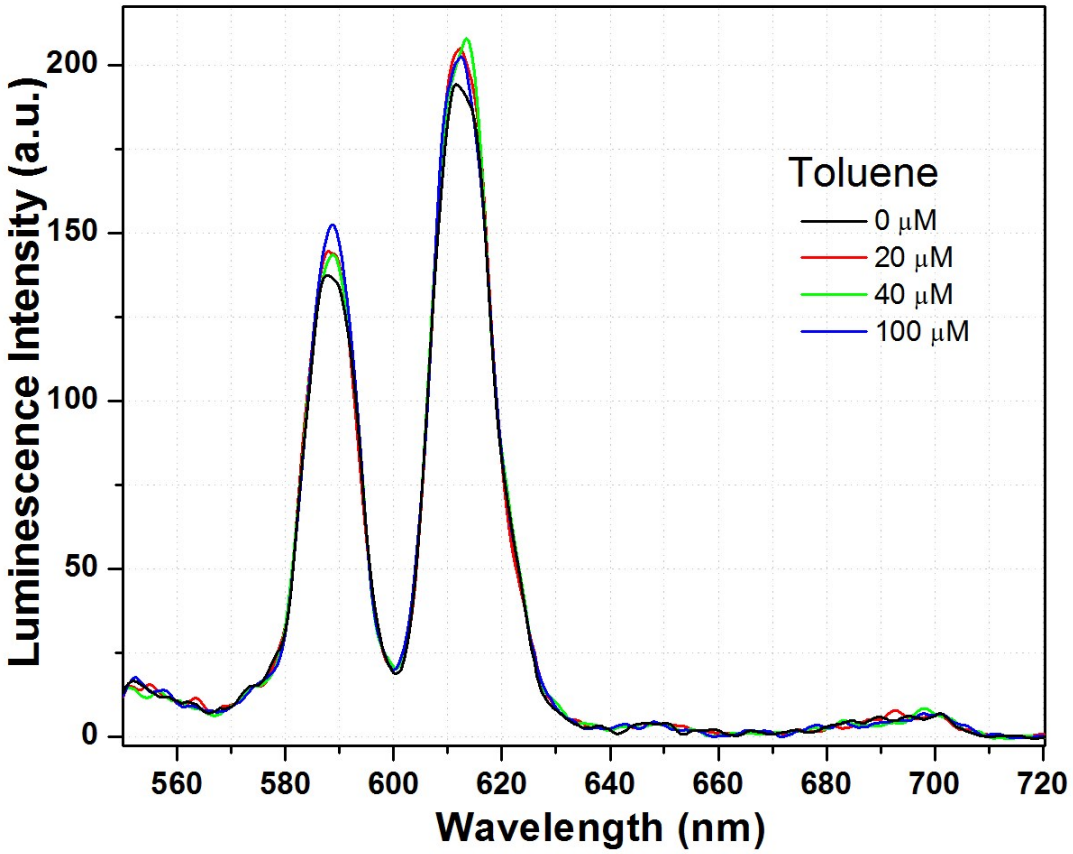


Fig. S11: Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of Toluene solution (λ_{ex} = 275 nm; filter: 515 nm cut-off). The final concentration of Toluene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu** for 1 hour.

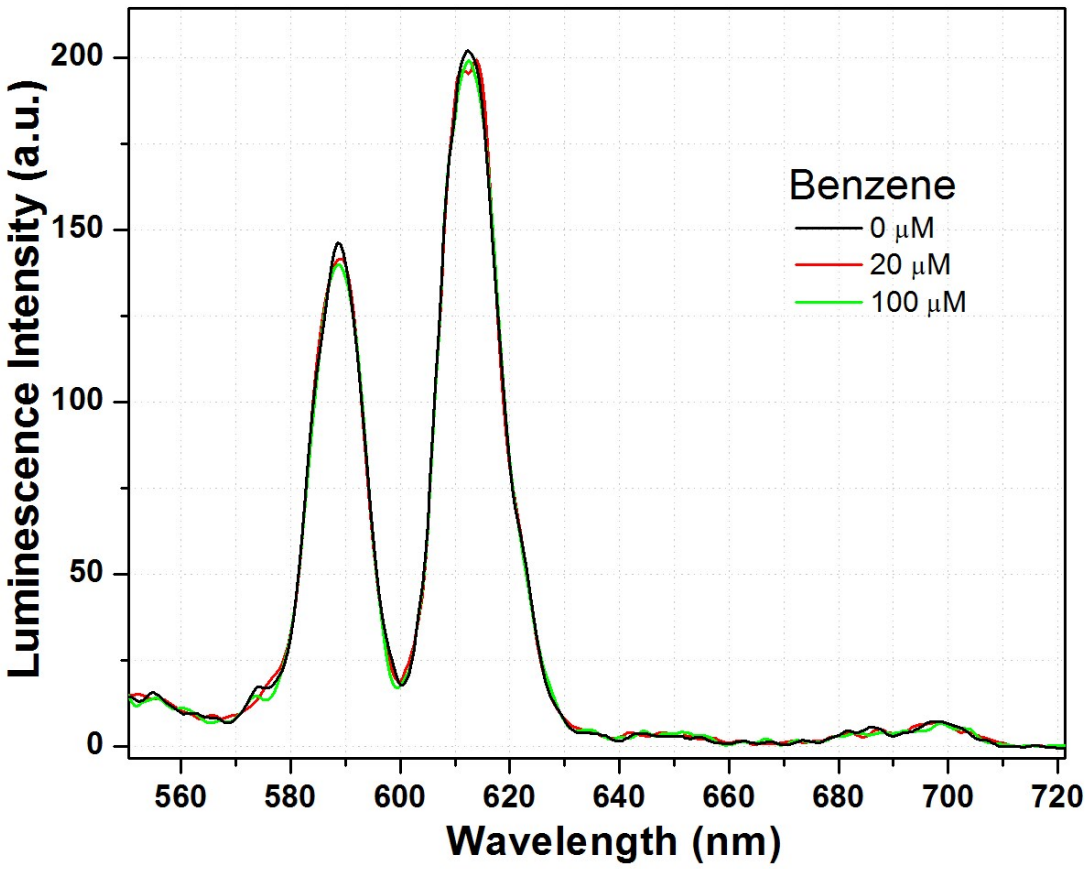


Fig. S12: Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon incremental addition of Benzene solution (λ_{ex} = 275 nm; filter: 515 nm cut-off). The final concentration of Benzene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu** for 1 hour.

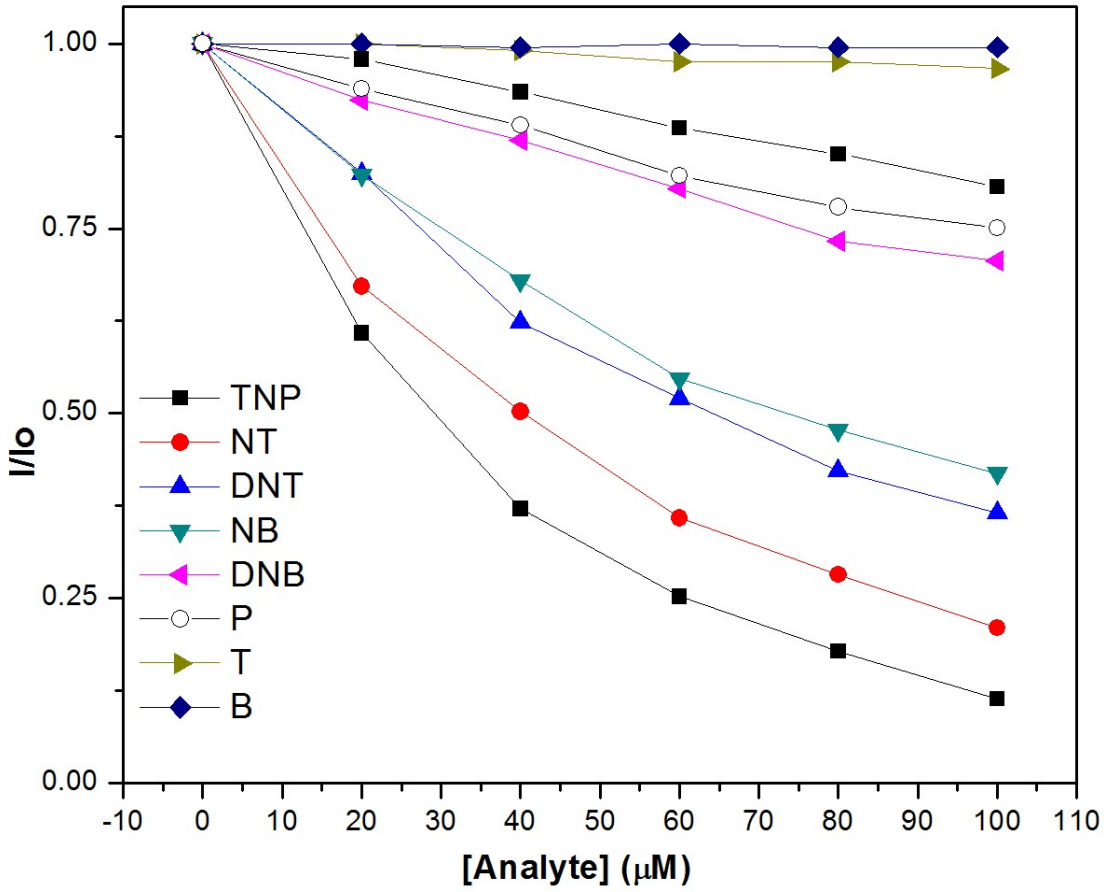


Fig. S13: Plot of fraction of luminescence intensity of **Y-MOF:Eu (at 614 nm)** vs concentration of analytes. I_0 and I are luminescence intensity in absence and presence of analyte, respectively

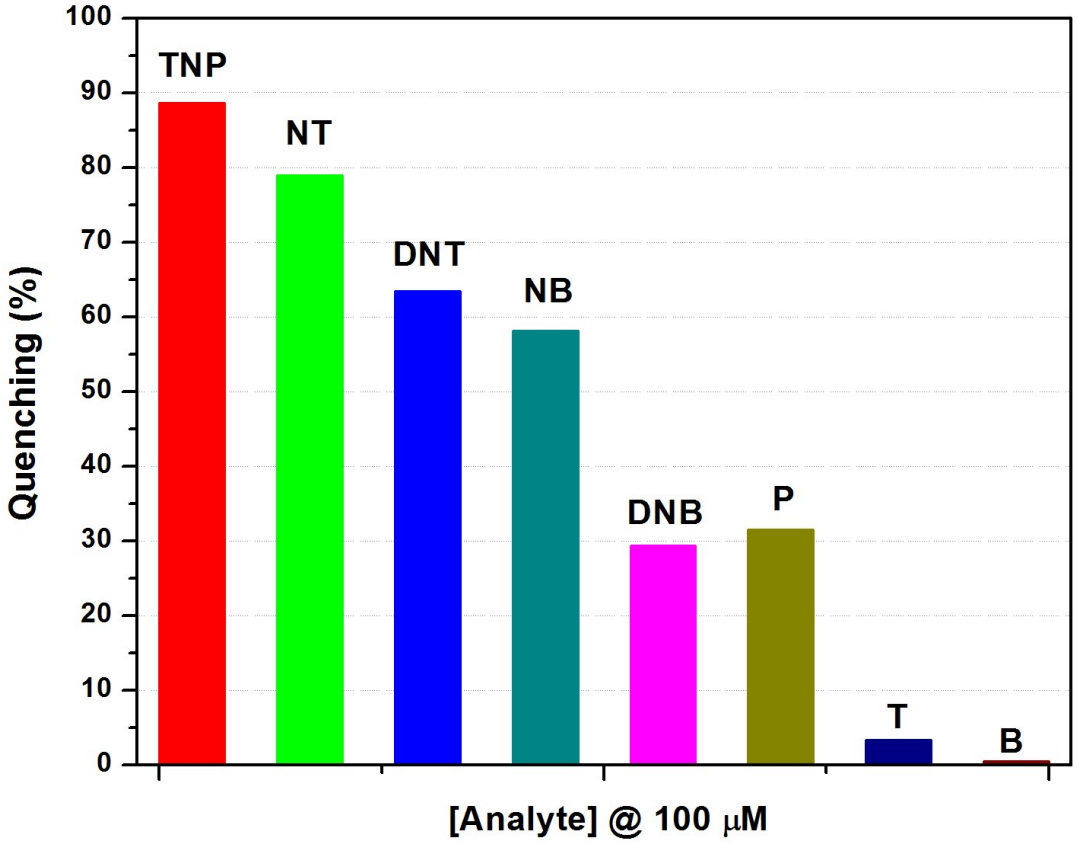


Fig. S14: Percentage of luminescence quenching with respect of $^5D_0 \rightarrow {}^7F_2$ (**at 614 nm**) emission of **Y-MOF:Eu** with 100 μM of different analytes.

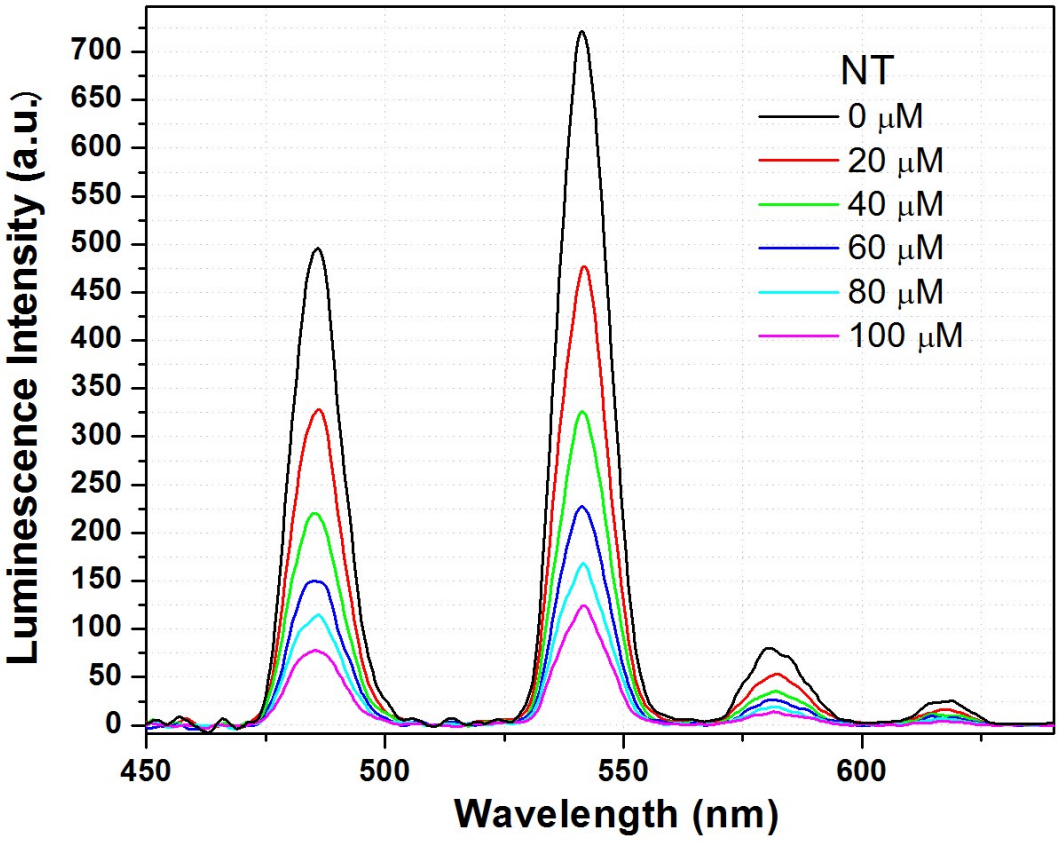


Fig. S15: Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of NT solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of NT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Tb** for 1 hour.

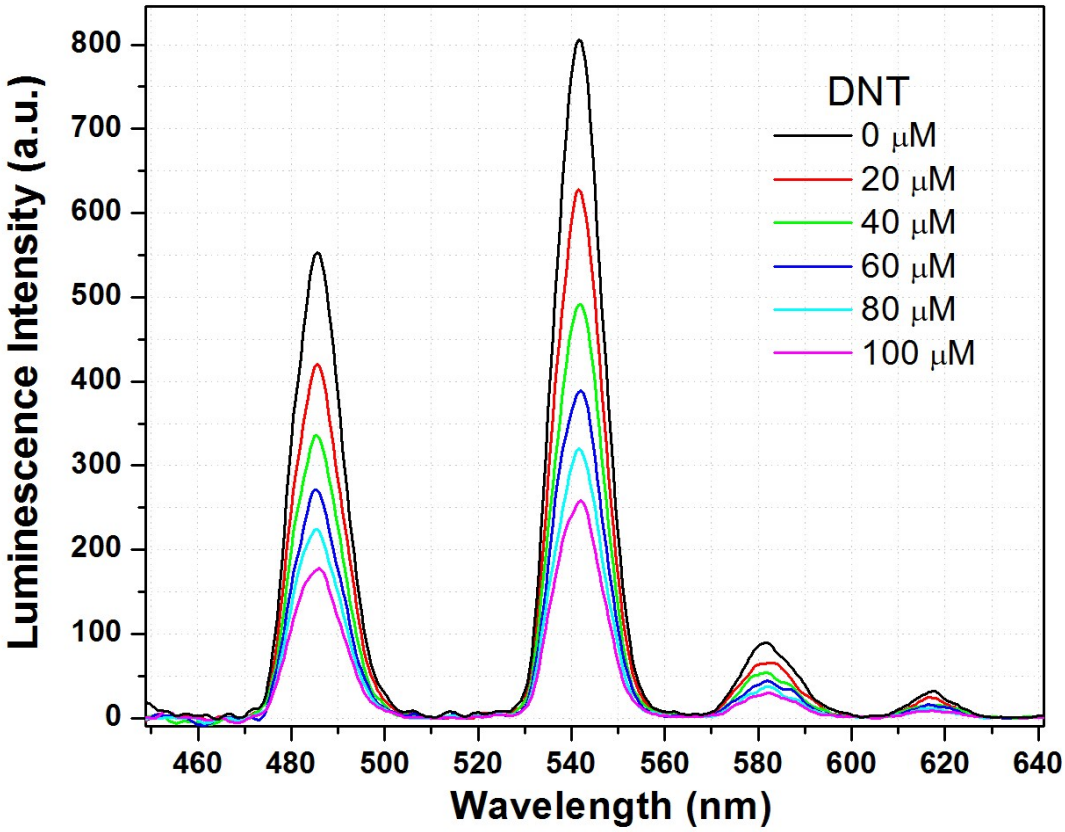


Fig. S16: Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of DNT solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of DNT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Tb** for 1 hour.

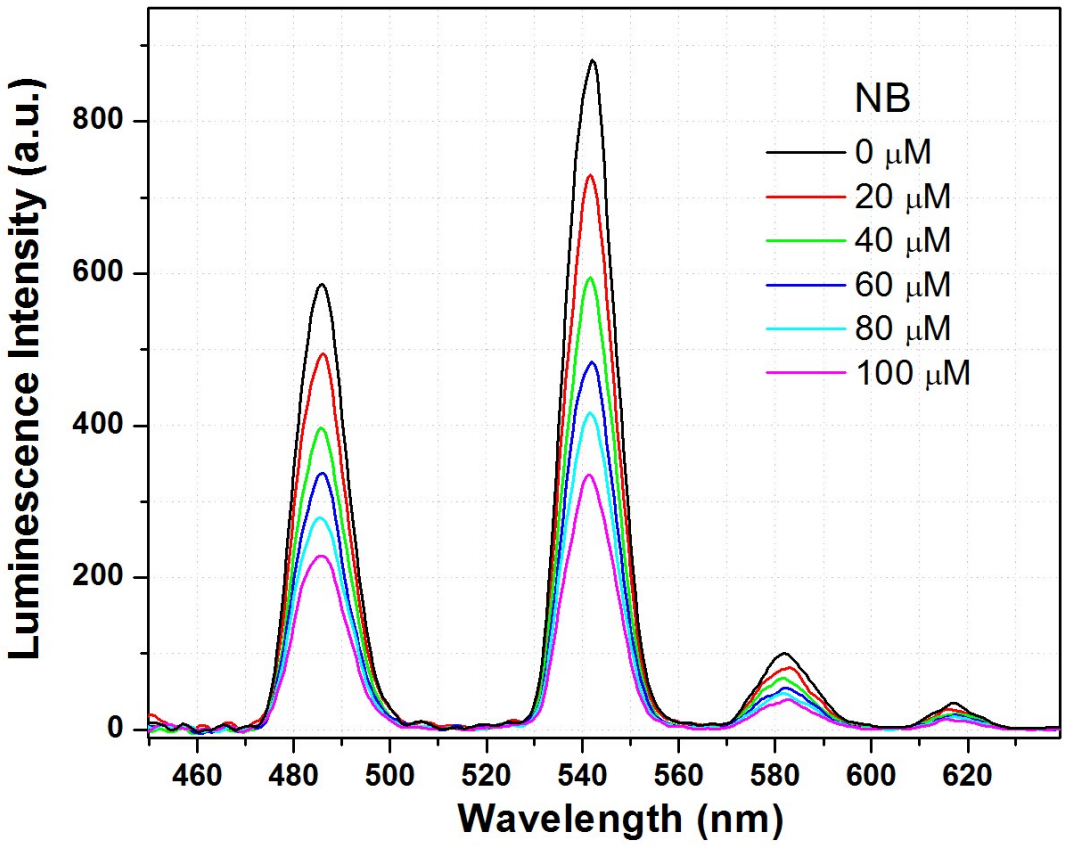


Fig. S17: Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of NB solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of NB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Tb** for 1 hour.

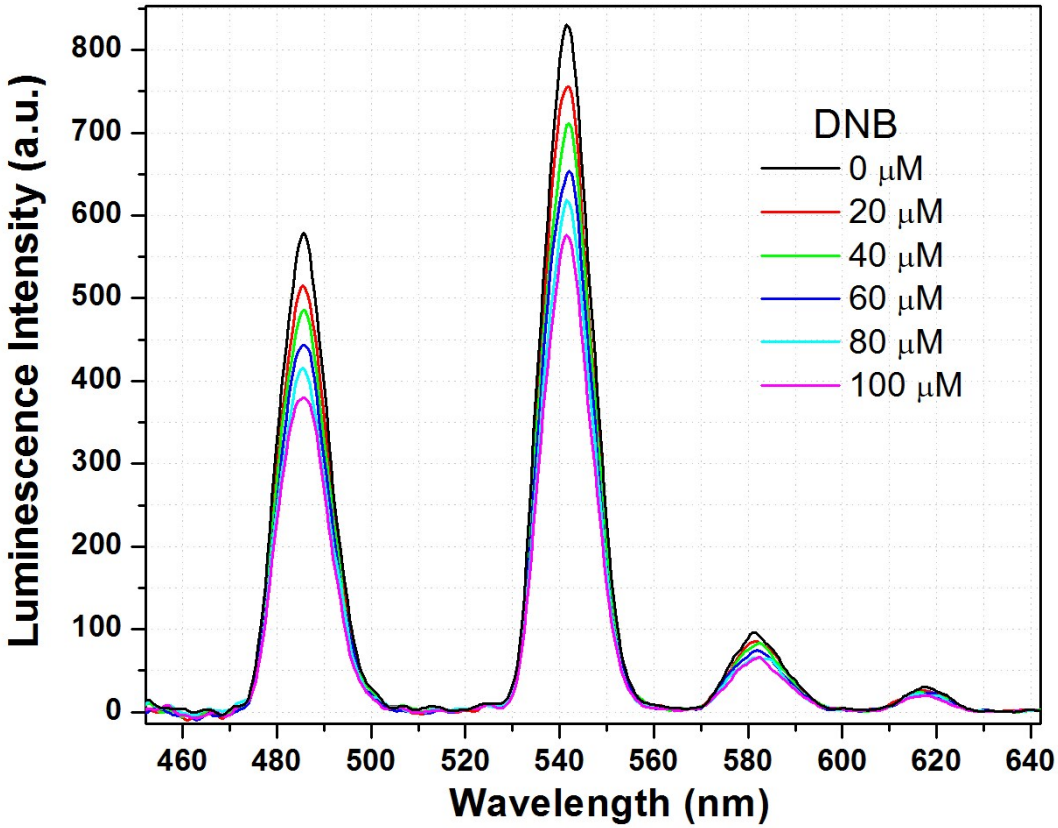


Fig. S18: Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of DNB solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of DNB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Tb** for 1 hour.

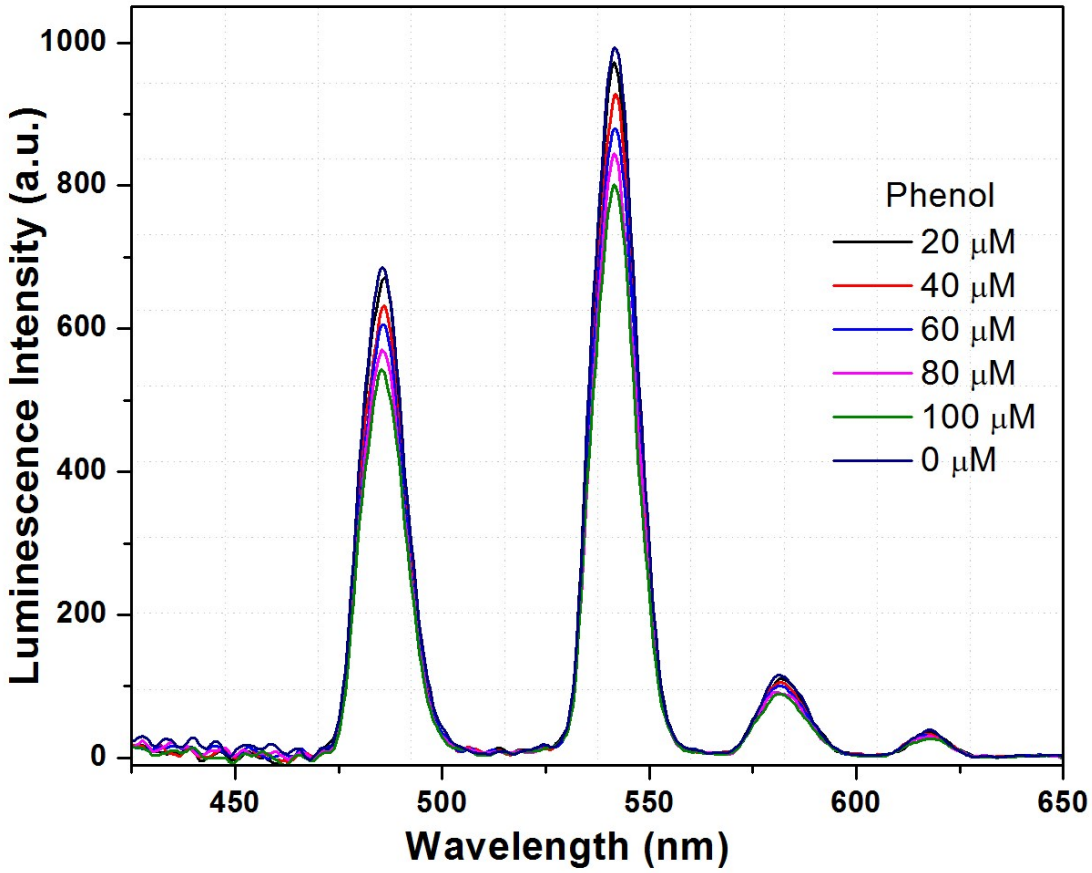


Fig. S19: Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of Phenol solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of Phenol in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Tb** for 1 hour.

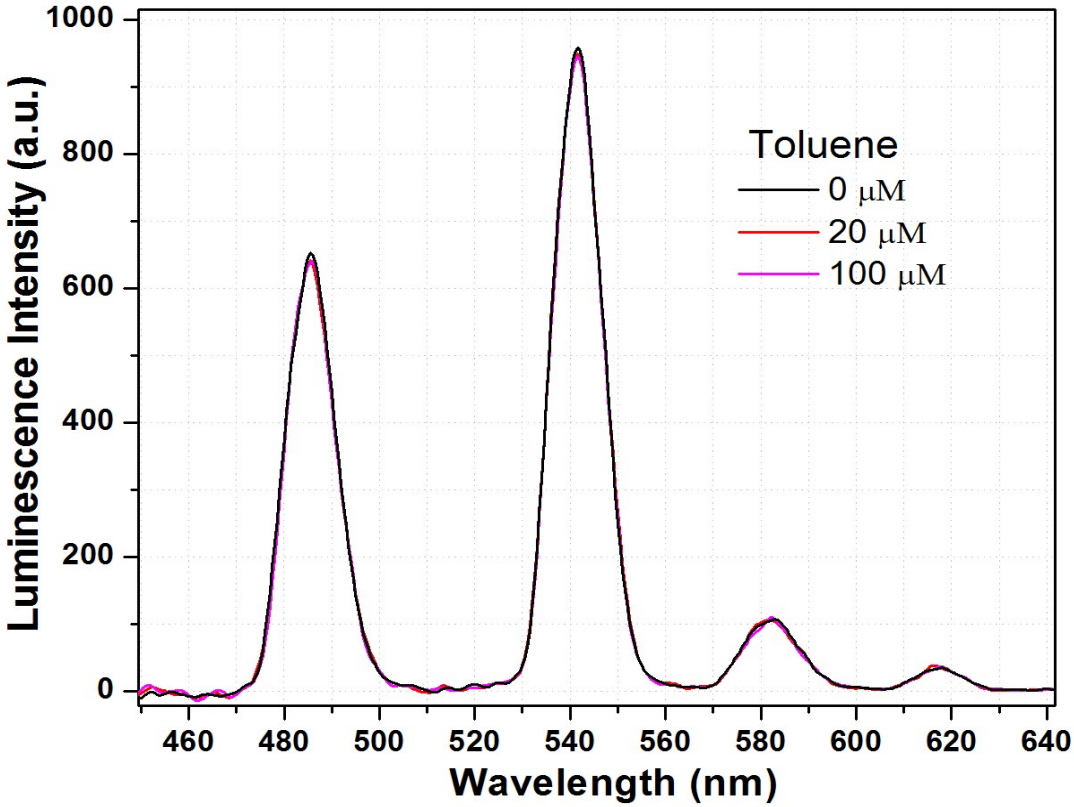


Fig. S20: Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of Toluene solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of Toluene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Tb** for 1 hour.

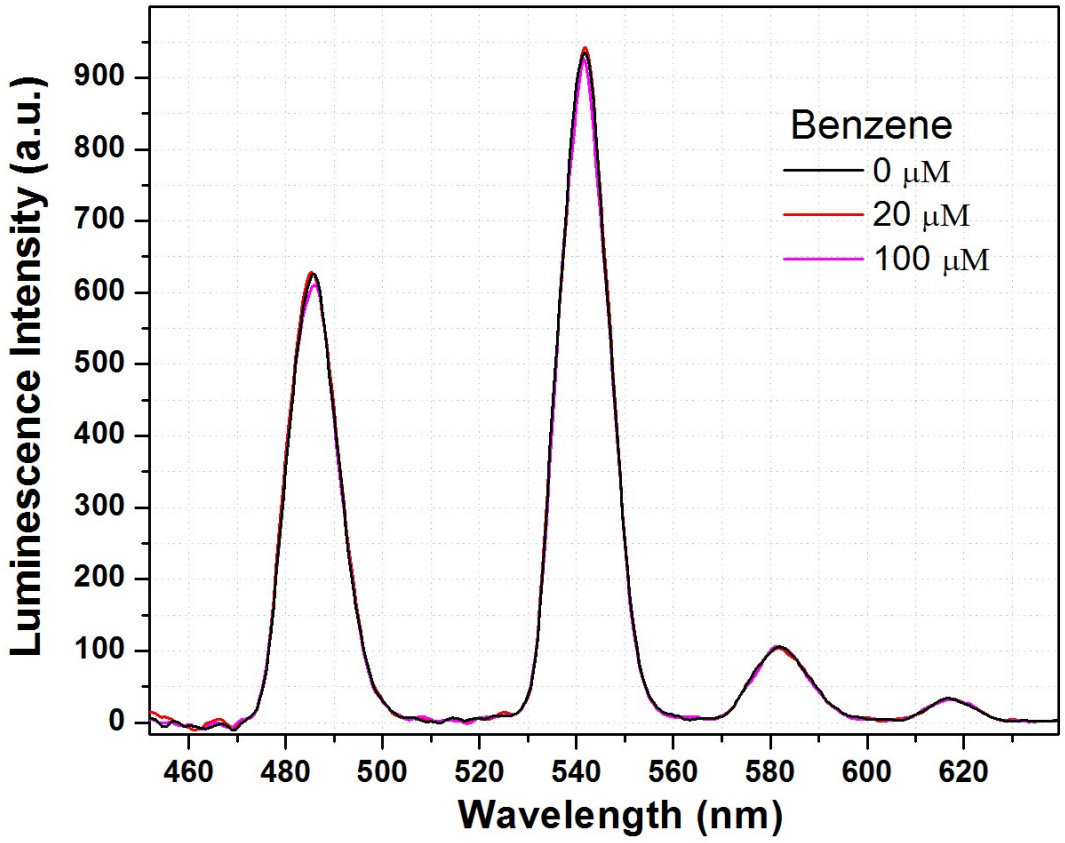


Fig. S21: Emission spectra of **Y-MOF:Tb** dispersed in acetonitrile upon incremental addition of Benzene solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of Benzene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Tb** for 1 hour.

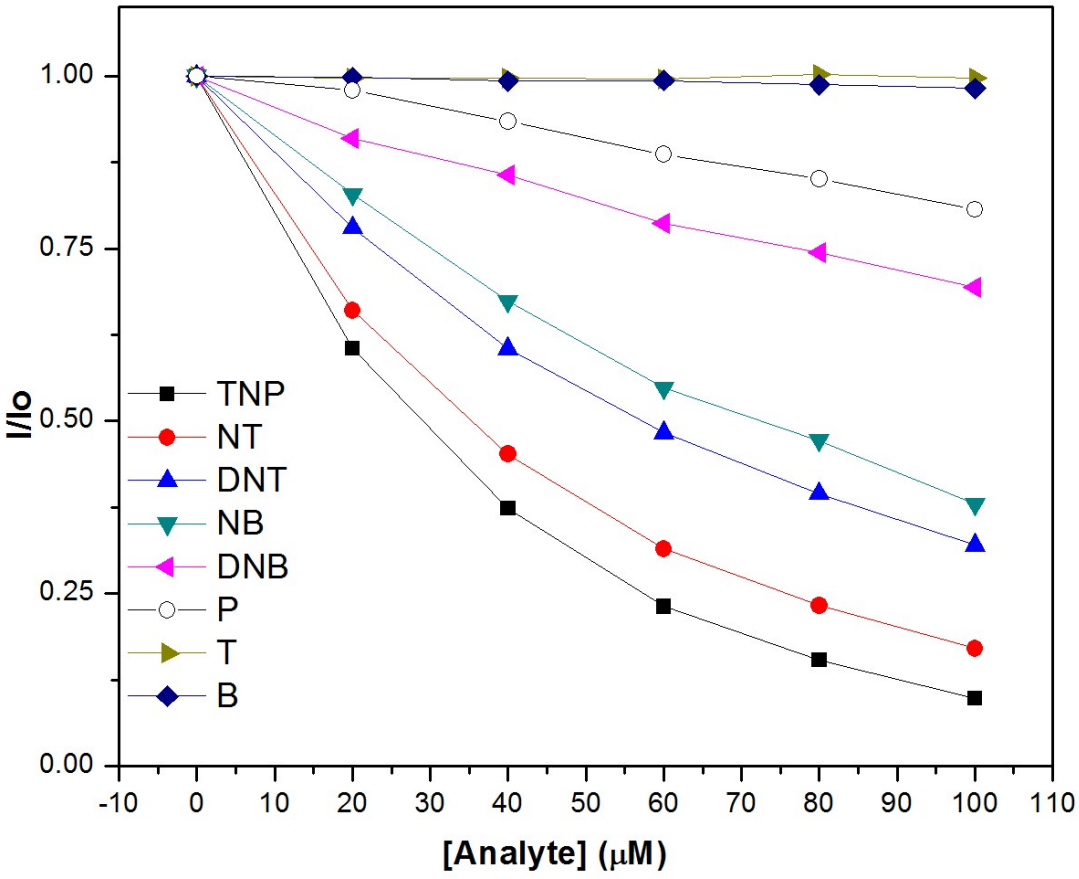


Fig. S22: Plot of fraction of luminescence intensity of **Y-MOF:Tb (at 541 nm)** vs concentration of analytes. I_0 and I are luminescence intensity in absence and presence of analyte, respectively.

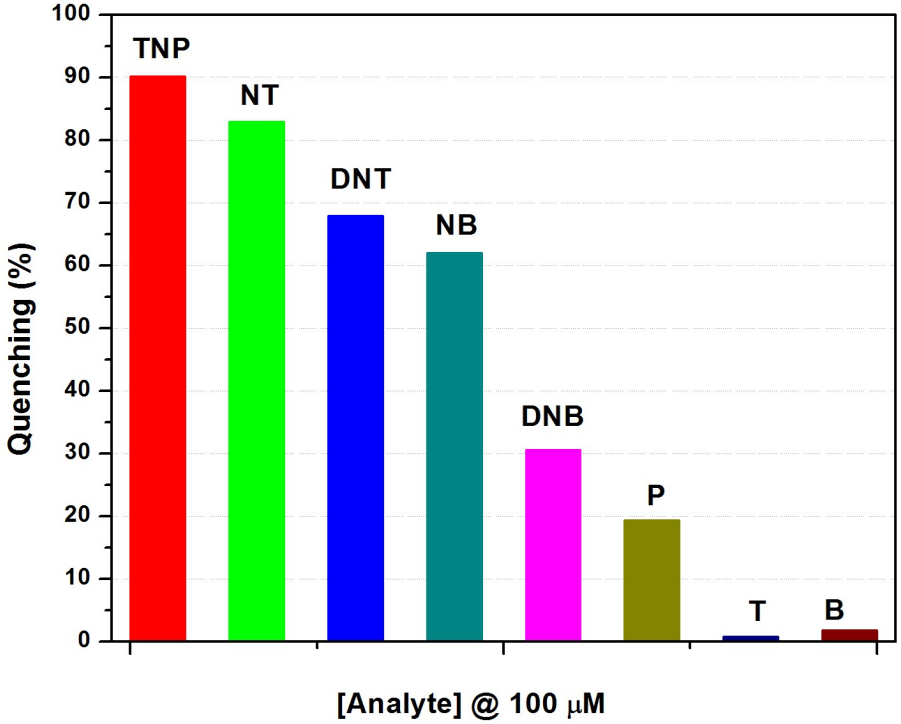


Fig. S23: Percentage of luminescence quenching with respect of $^5D_4 \rightarrow {}^7F_5$ (**at 541 nm**) emission of **Y-MOF:Tb** with 100 μM of different analytes.

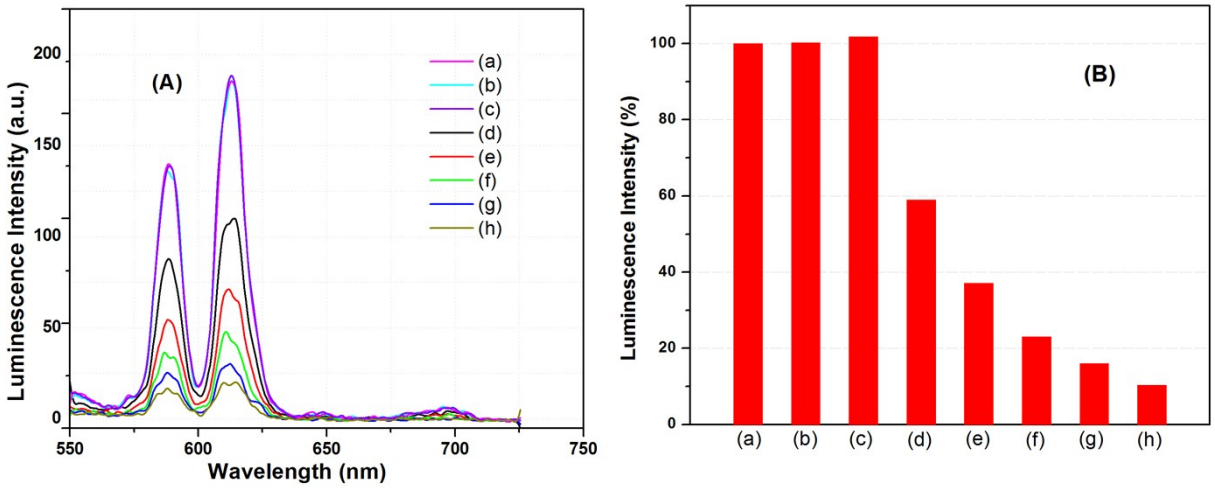


Fig. S24: (A) Emission spectra of **Y-MOF:Eu** dispersed in acetonitrile upon the incremental addition of TNP solution in a mixture of 100 μM toluene and 100 μM benzene to **Y-MOF:Eu** solution (λ_{ex} = 275 nm; filter: 515 nm cut-off). All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **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).

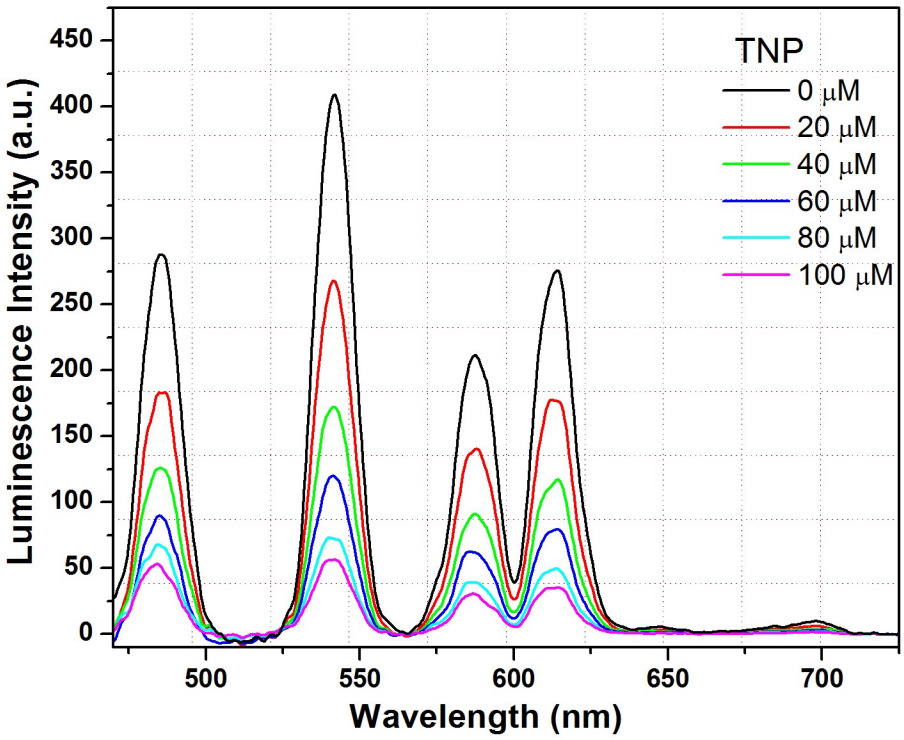


Fig. S25: Emission spectra of **Y-MOF:Eu,Tb** dispersed in acetonitrile upon incremental addition of TNP solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of TNP in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu,Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu,Tb** for 1 hour.

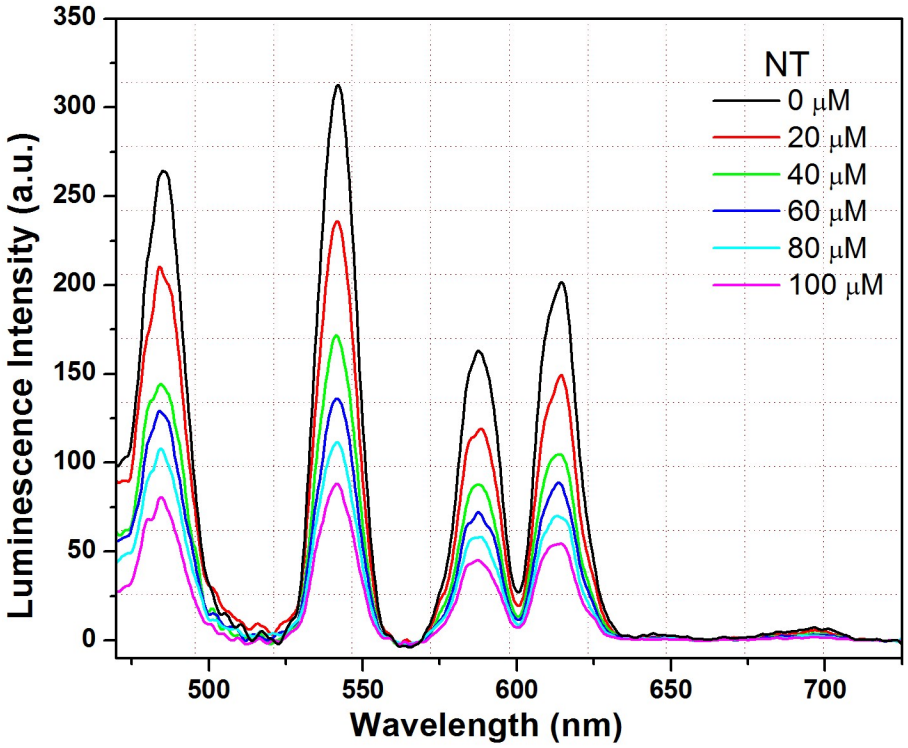


Fig. S26: Emission spectra of **Y-MOF:Eu,Tb** dispersed in acetonitrile upon incremental addition of NT solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of NT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu,Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu,Tb** for 1 hour.

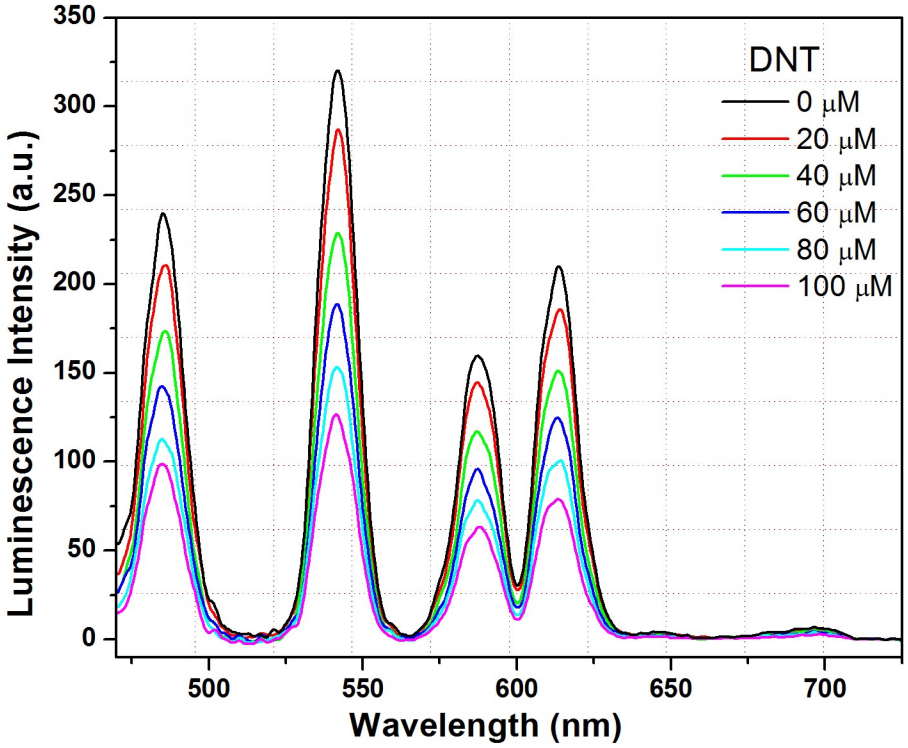


Fig. S27: Emission spectra of **Y-MOF:Eu,Tb** dispersed in acetonitrile upon incremental addition of DNT solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of DNT in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu,Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu,Tb** for 1 hour.

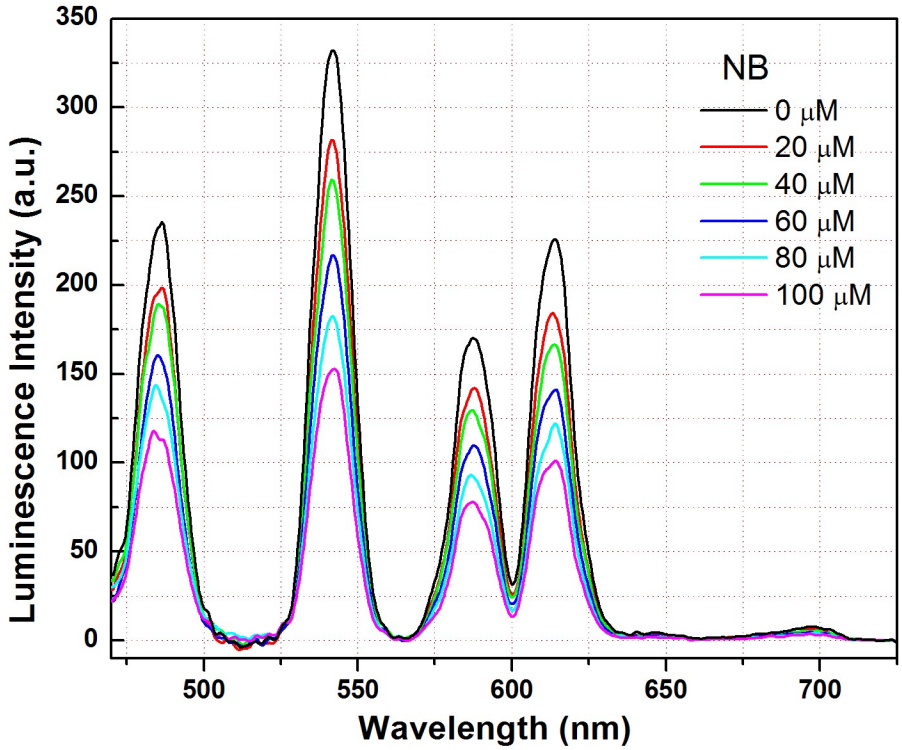


Fig. S28: Emission spectra of **Y-MOF:Eu,Tb** dispersed in acetonitrile upon incremental addition of NB solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of NB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu,Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu,Tb** for 1 hour.

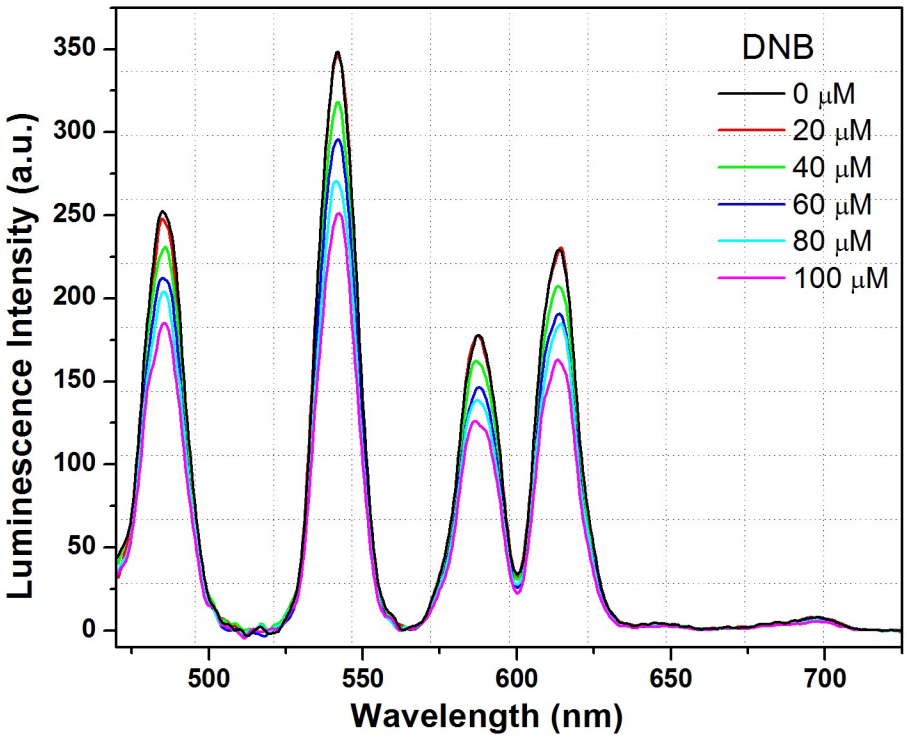


Fig. S29: Emission spectra of **Y-MOF:Eu, Tb** dispersed in acetonitrile upon incremental addition of DNB solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of DNB in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu,Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu,Tb** for 1 hour.

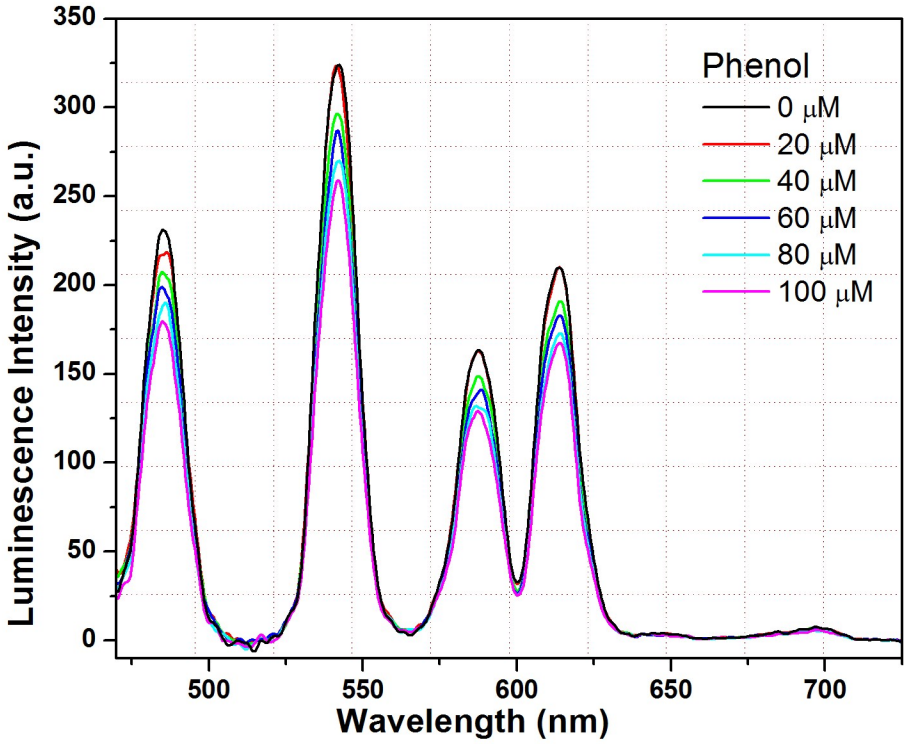


Fig. S30: Emission spectra of **Y-MOF:Eu, Tb** dispersed in acetonitrile upon incremental addition of Phenol solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of Phenol in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu,Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu,Tb** for 1 hour.

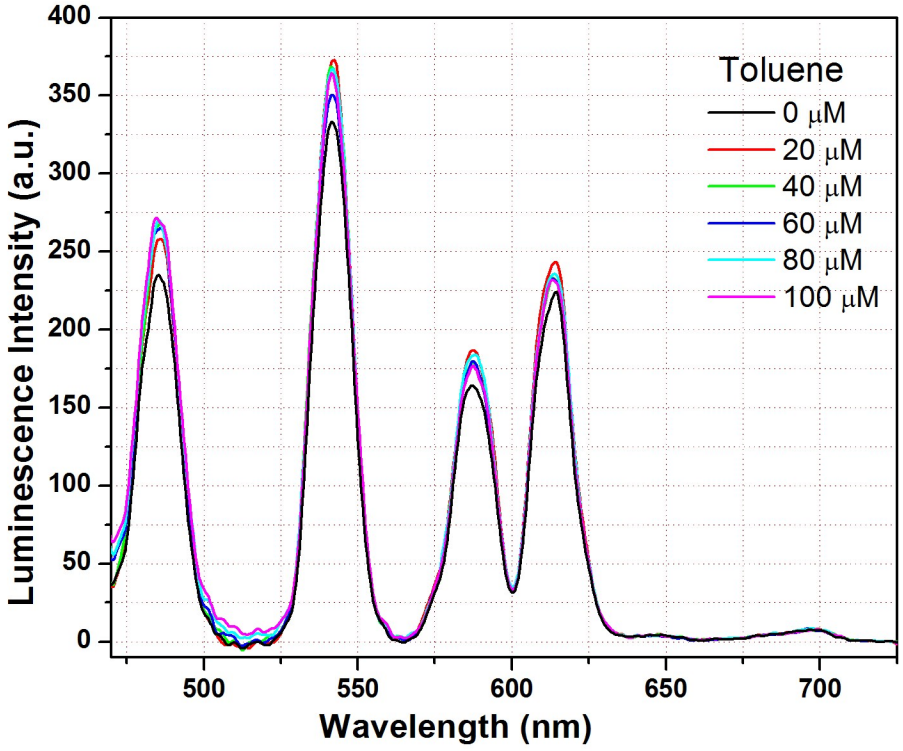


Fig. S31: Emission spectra of **Y-MOF:Eu,Tb** dispersed in acetonitrile upon incremental addition of Toluene solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of Toluene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu,Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu,Tb** for 1 hour.

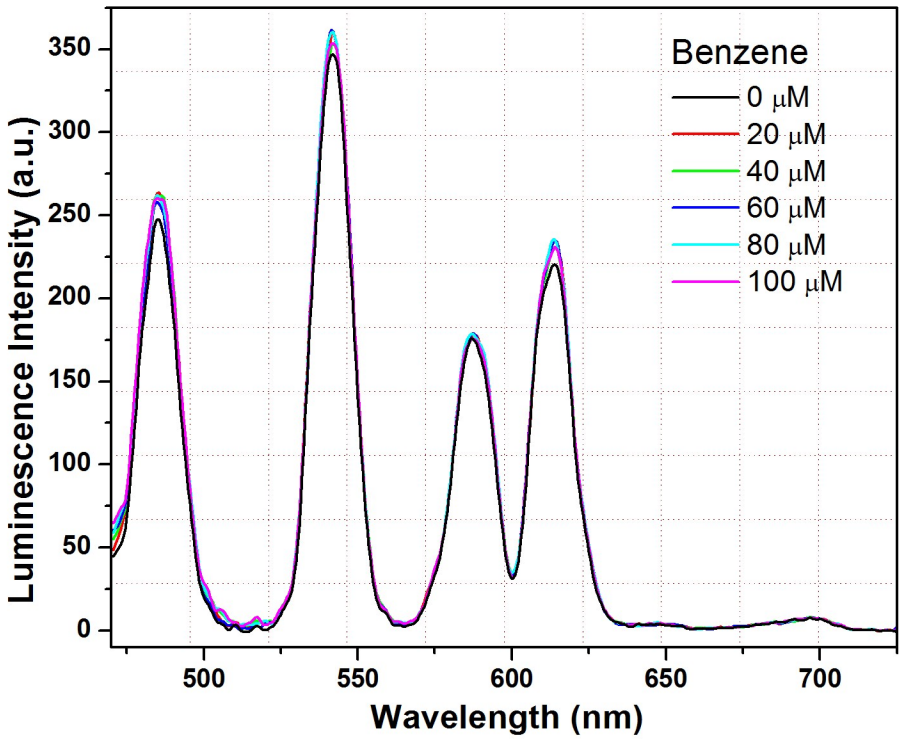


Fig. S32: Emission spectra of **Y-MOF:Eu,Tb** dispersed in acetonitrile upon incremental addition of Benzene solution (λ_{ex} = 275 nm; filter: 430 nm cut-off). The final concentration of Benzene in the medium is indicated in the legend. All the spectra are measured using PerkinElmer LS-55 spectrofluorometer. **Y-MOF:Eu,Tb** suspension in acetonitrile was prepared by sonicating the mixture of solvothermally synthesized **Y-MOF:Eu,Tb** for 1 hour.

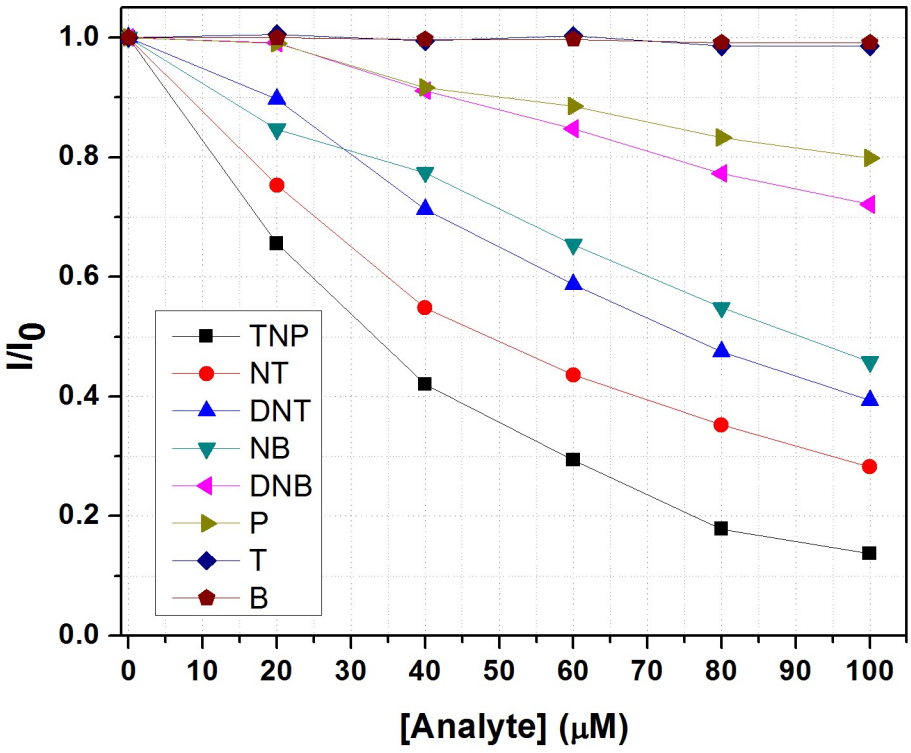


Fig. S33: Plot of fraction of luminescence intensity of **Y-MOF:Eu,Tb (at 541 nm)** vs concentration of analytes. I_0 and I are luminescence intensity in absence and presence of analyte, respectively.

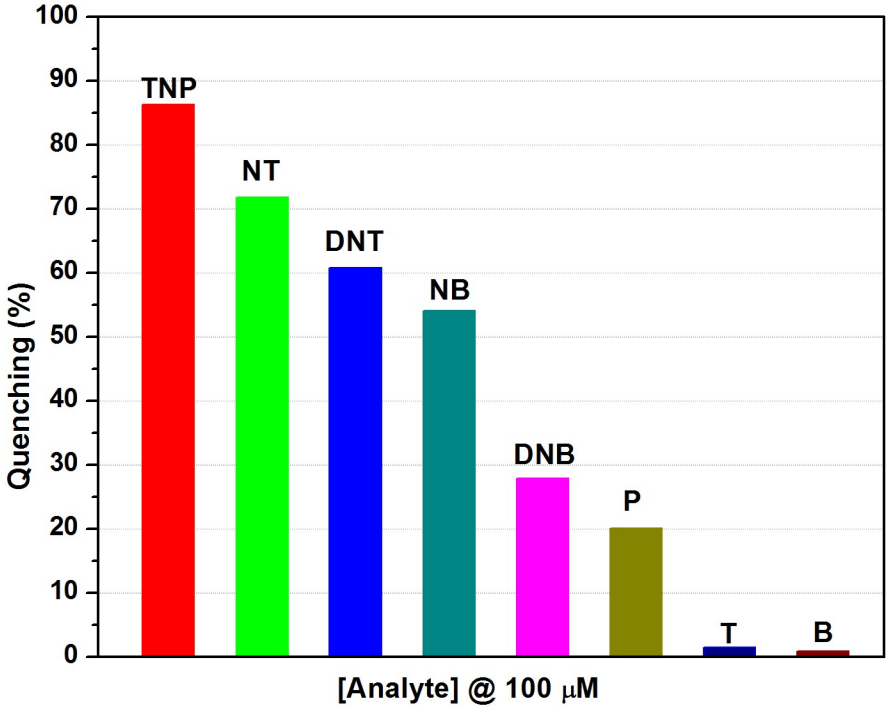
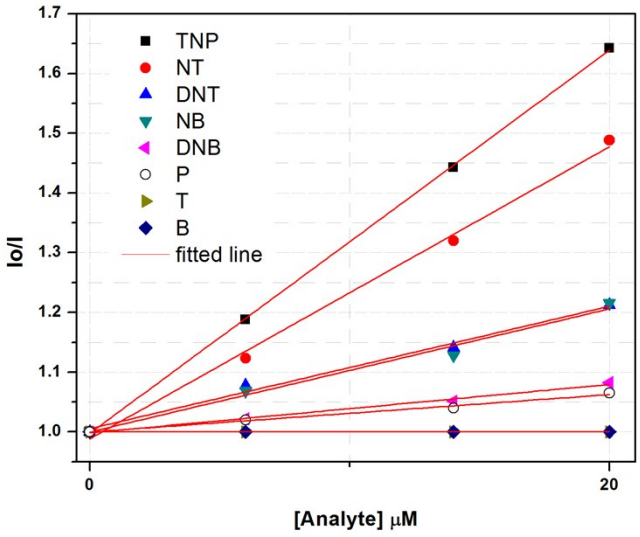
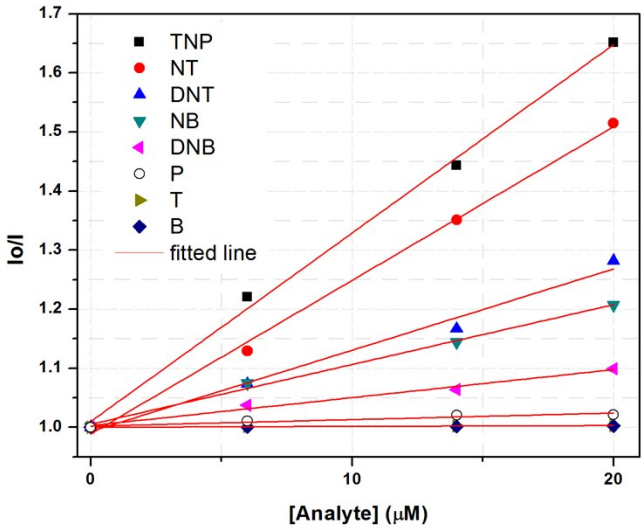


Fig. S34: Percentage of luminescence quenching with respect of $^5D_4 \rightarrow {}^7F_5$ of Tb^{3+} ions (**at 541 nm**) emission of **Y-MOF:Eu,Tb** with 100 μM of different analytes.



(a)



(b)

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.

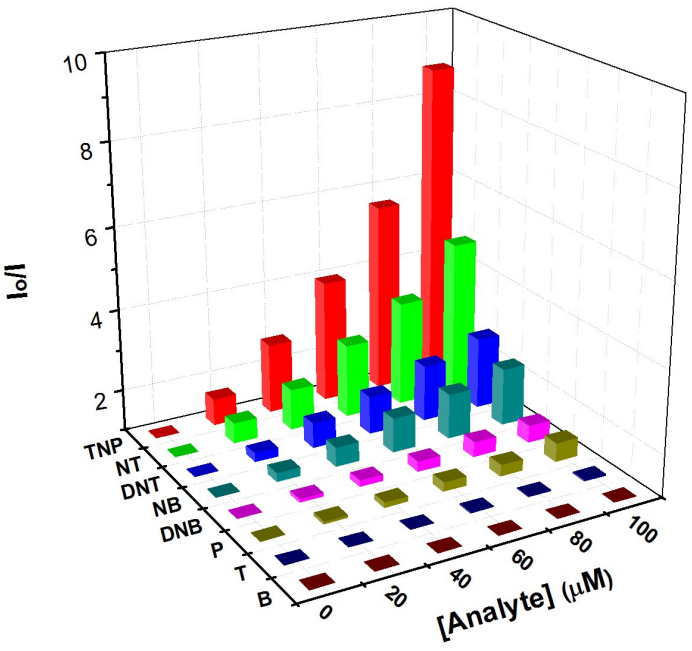


Fig. S36**.** Stern-Volmer plots of analytes in higher concentration range of analytes (upto 100 μM) for **Y-MOF:Eu.**