Supporting Information for the manuscript

A Luminescent Nanoscale Metal-Organic Framework for Sensing of Nitroaromatic Explosives

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Experimental Section

The methylammonium salt of H_2BDC was synthesized by dissolving H_2BDC(0.0060mol, 1.000 g) in methylamine(12.4 ml, 40wt% in water) and dried under reduced pressure. Then the salt was dissolved in distilled water to form a 0.1M solution.

The nanoscale **MOF 1** were synthesized through the microemulsion method at room temperature, according to Lin's work.[1] Firstly, two microemulsion systems contain cetyltrimethylammonium bromide(CTAB)(0.91g, 2.5mmol),1-hexanol(3.13ml, 0.025mol) and iso-octane(45.87ml, 0.2771mol) were stirred respectively for 30min. Two aqueous solutions of $EuCl_3.6H_2O$(0.225ml, 0.1M) and the methylammoium salt of H_2BDC(0.225ml, 0.1M) were added to the microemulsion systems respectively, after stirred for 30min, the microemulsions termed to be transparent. Then the two microemulsions were mixed together and stirred vigorously for another 2hr at room temperature. The microemulsion was centrifugated at 3000rpm for 5min to give the nanorods. The nanorods were washed and redispersed in ethanol by sonificated for 5min and centrifugated again by the same method. This centrifugation and redispersement was repeated for twice and finally give the ethanol solution of nanoscale **MOF 1**. The PXRD sample was prepared by drying the ethanol solution of **MOF 1** under 40 ^oC overnight. TGA showed that there are two weight loss during the heating process, as indicated in Figure S1, they are 7.72% in the range of 110-170^oC and 47.02% in the range of 430-590 ^oC, corresponding with the loss of four coordinated water molecules(calc.8.3%) and the loss of organic ligands (calc.56.7%) respectively.

Elemental Analysis was performed on a ThermoFinnigan Flash EA 1112. The concentration of the ethanol solution of the $Eu(BDC)_{1.5}(H_2O)_2$ nanorods is 150μg/ml. The dispersion/deposition cycles were repeatedly done by immersing the MOF-1 in 150ppm ethanol solution of DNT for 1d and then centrifuged by 8000rmp/min. The nanorods of $Eu(BDC)_{1.5}(H_2O)_2$ do not undergo degradation during a number of dispersion/deposition cycles in 150ppm ethanol solution of DNT, as indicated in Figure S21, the PXRD patterns remain the same in this process.

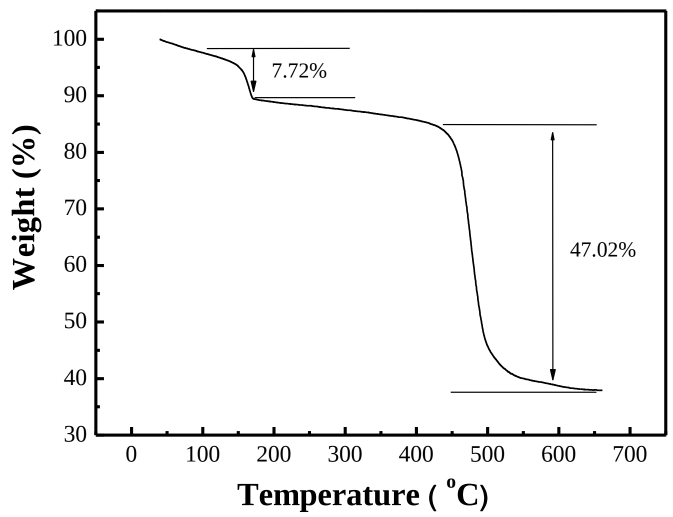


Figure S1. The TGA curve of nanoscale **MOF 1**

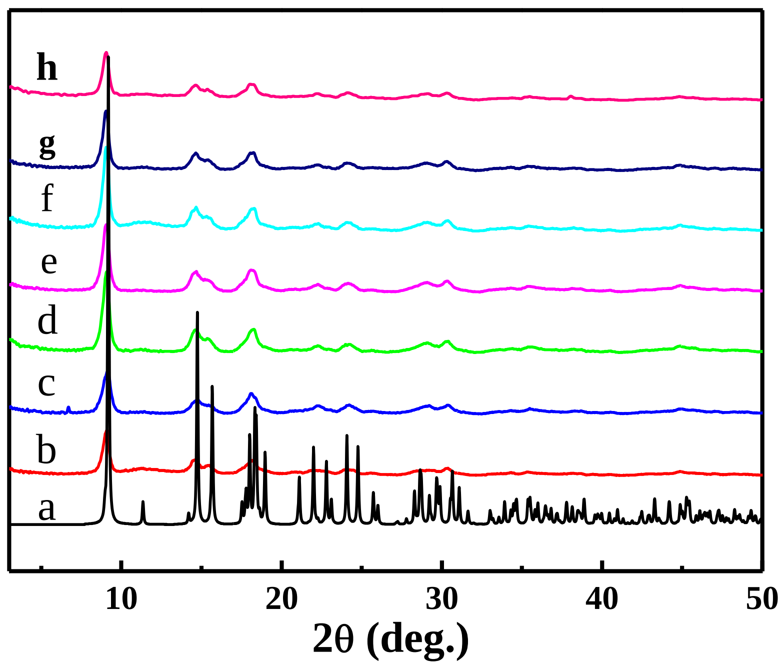


Figure S2 Powder X-ray diffraction patterns of a) simulated from the X-ray single structure of $Tb(BDC)_{1.5}(H_2O)_2$, b) the origin ethanol solution of $Eu(BDC)_{1.5}(H_2O)_2$, and the diffraction patterns obtained after the introduction of various solvents: c) toluene, d) *p*-xylene, e) phenol, f) nitrobenzene, g) 2,4-DNT and h) TNT.

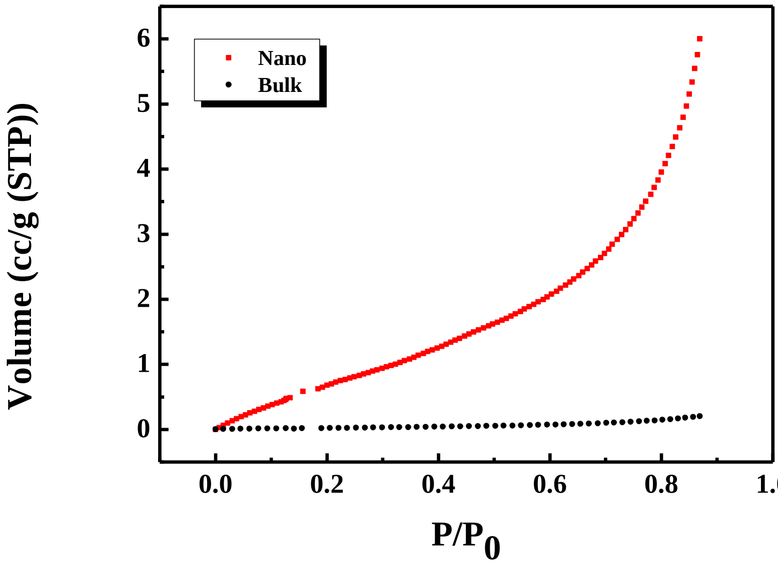


Figure S3   Ethanol vapor sorption isotherms of nano-sized (red) and bulk (black) **MOF 1** at 295 K.

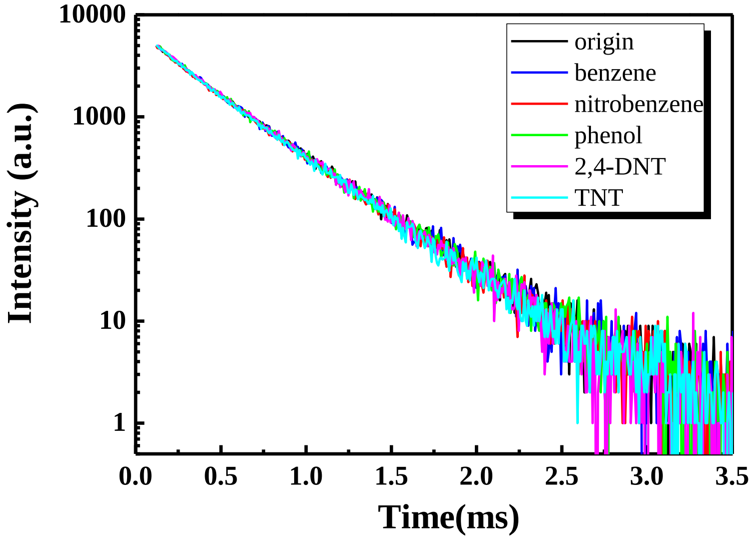


Figure S4   PL decay curves of **MOF 1** in ethanol solution with the concentration of 150 ppm of different solvents (excited: 315nm; monitored:617nm)

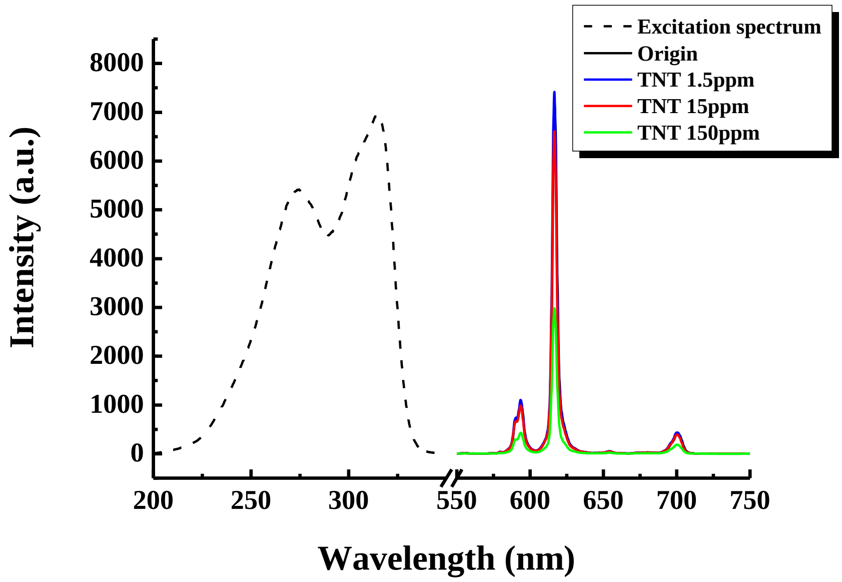


Figure S5 The excitation (dotted) and PL spectra(solid) of the dispersed **MOF 1** with the addition of different concentration of TNT, monitored and excited at 617 and 315 nm, respectively.

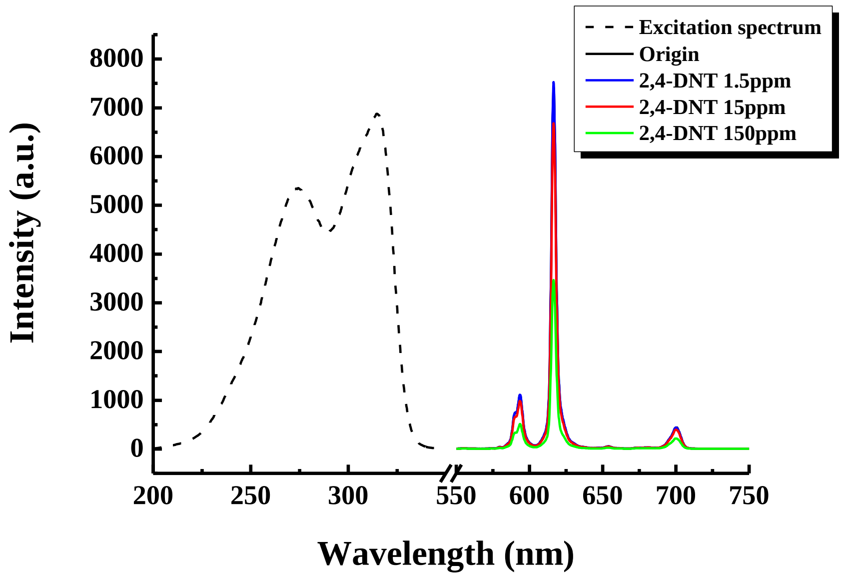


Figure S6 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of *2,4*-DNT, monitored and excited at 617 nm and 315 nm, respectively.

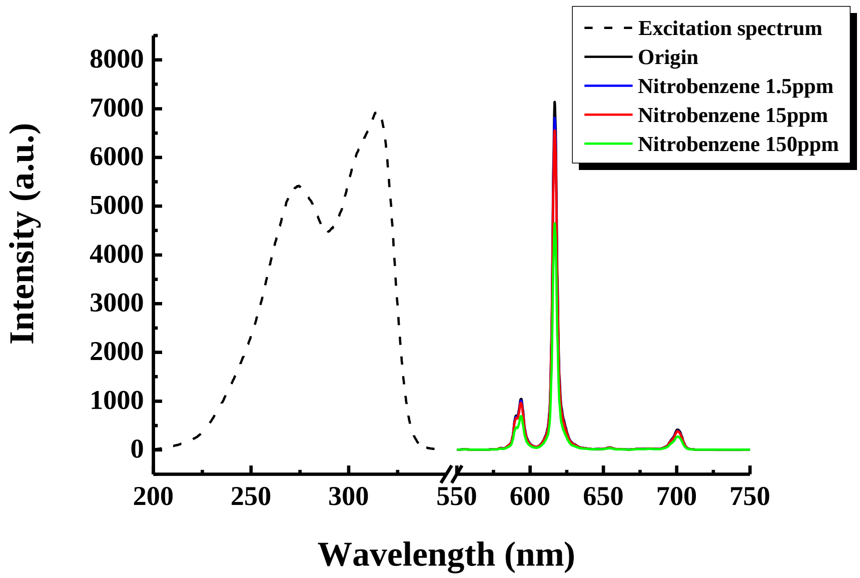


Figure S7 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of nitrobenzene, monitored and excited at 617 nm and 315 nm, respectively.

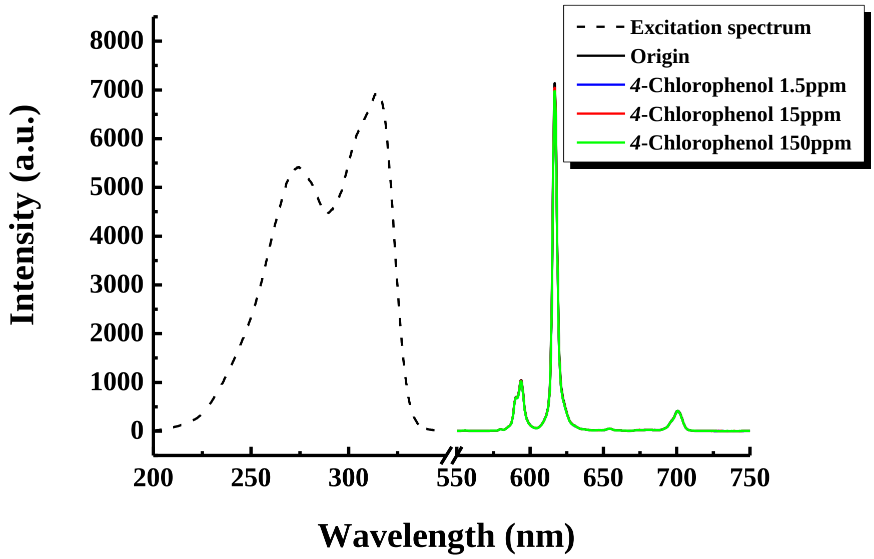


Figure S8 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of *4*-chlorophenol, monitored and excited at 617 nm and 315 nm, respectively.

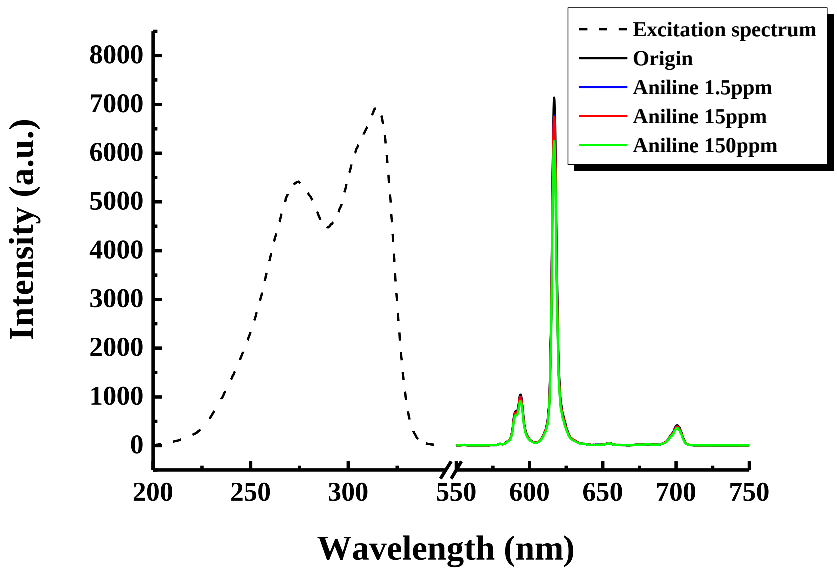


Figure S9 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of aniline, monitored and excited at 617 nm and 315 nm, respectively.

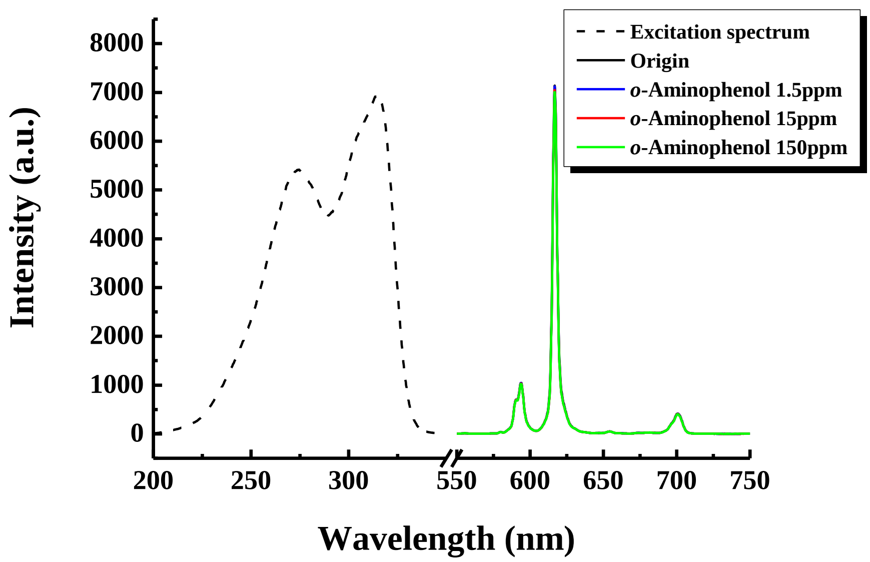


Figure S10 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of *o*-aminophenol, monitored and excited at 617 nm and 315 nm, respectively.

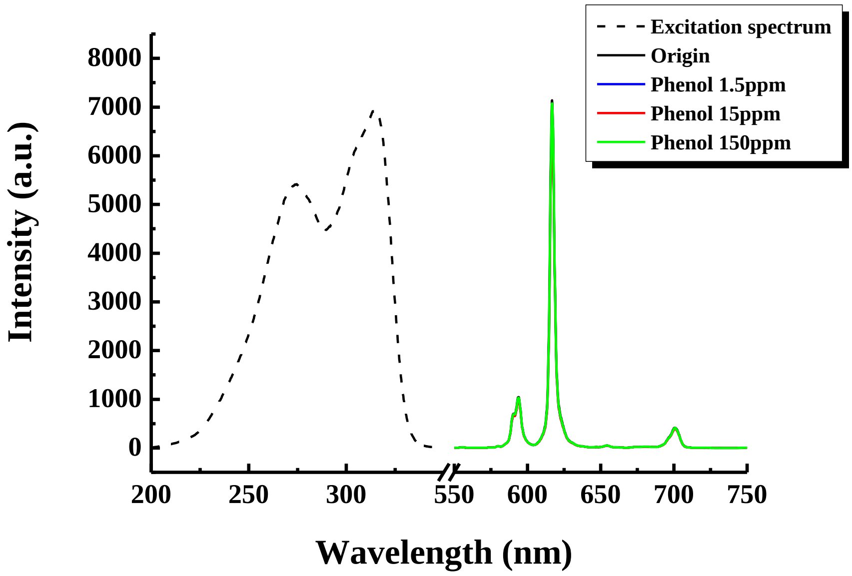


Figure S11 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of phenol, monitored and excited at 617 nm and 315 nm, respectively.

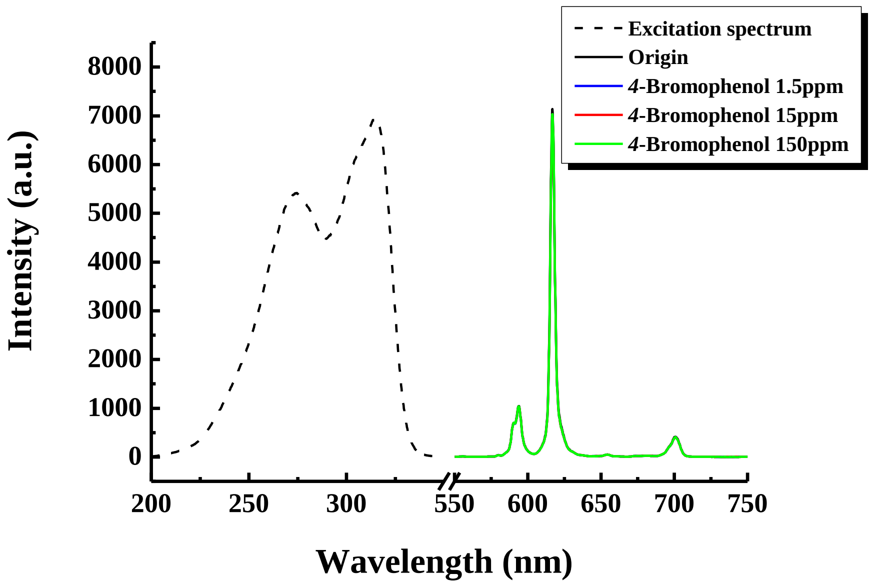


Figure S12 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of *4*-bromophenol, monitored and excited at 617 nm and 315 nm, respectively.

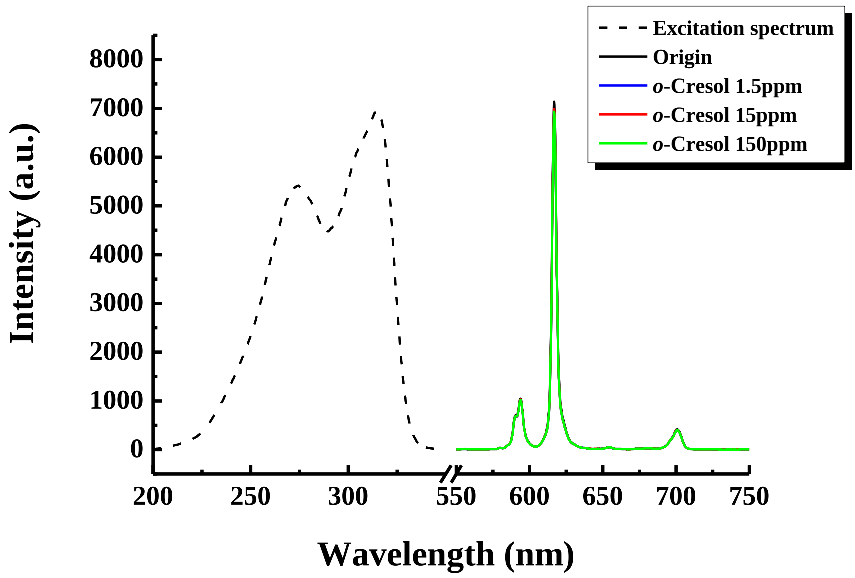


Figure S13 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of *o*-cresol, monitored and excited at 617 nm and 315 nm, respectively.

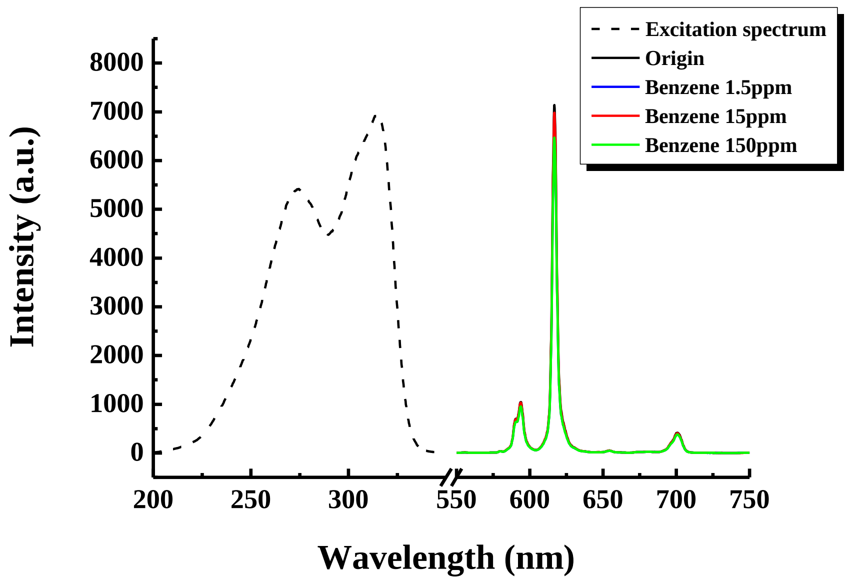


Figure S14 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of benzene, monitored and excited at 617 nm and 315 nm, respectively.

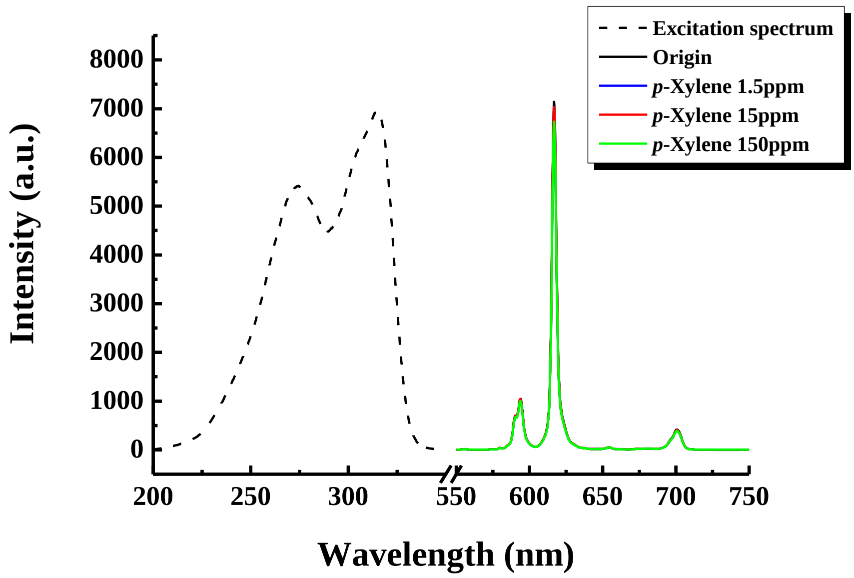


Figure S15 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of *p*-xylene, monitored and excited at 617 nm and 315 nm, respectively.

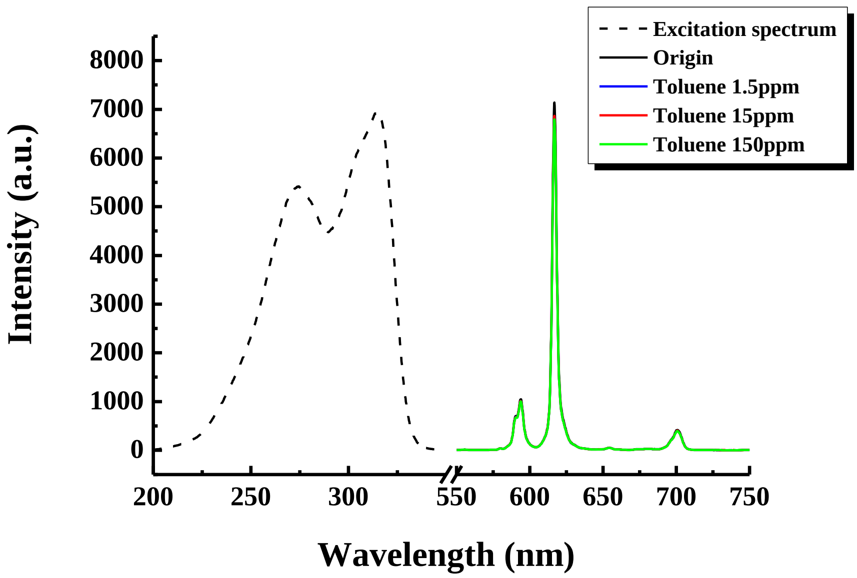


Figure S16 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of toluene, monitored and excited at 617 nm and 315 nm, respectively.

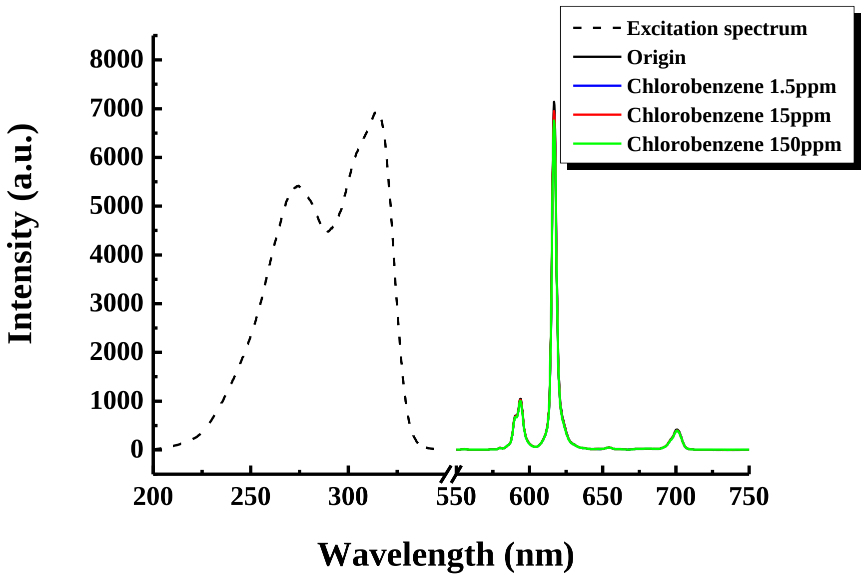


Figure S17 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of chlorobenzene, monitored and excited at 617 nm and 315 nm, respectively.

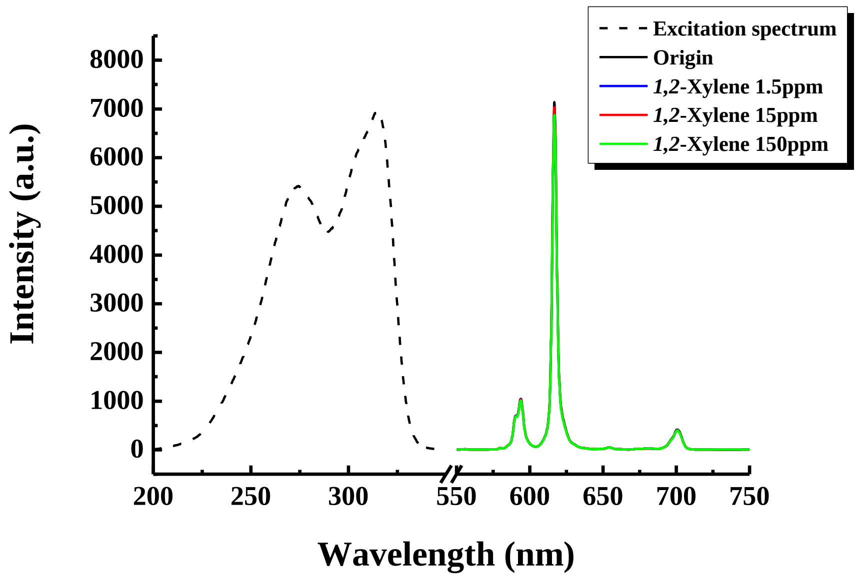


Figure S18 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of *1,2*-xylene, monitored and excited at 617 nm and 315 nm, respectively.

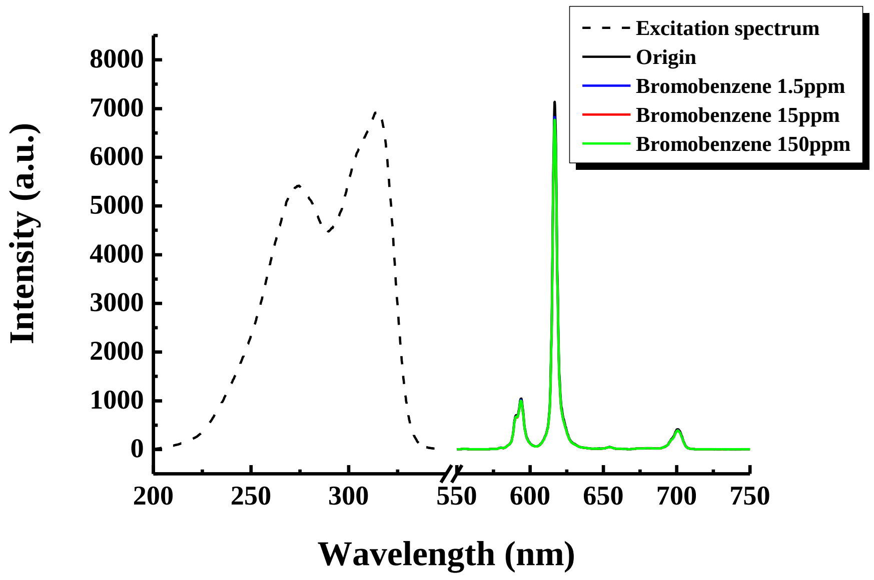
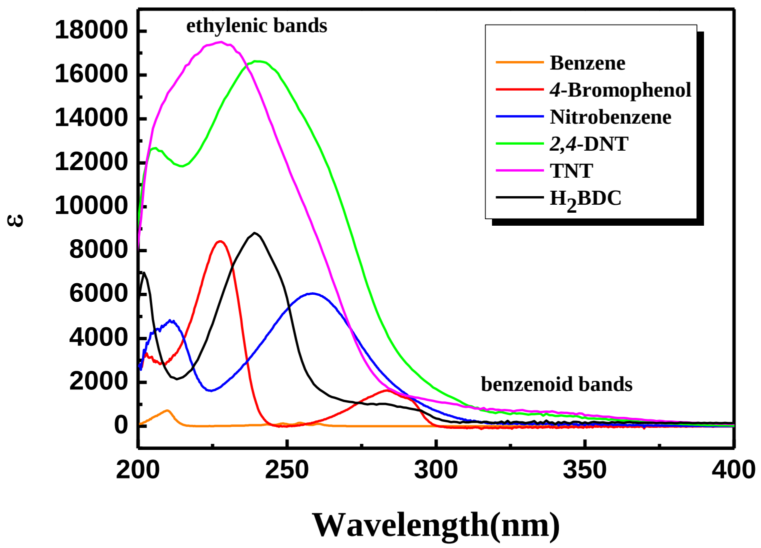


Figure S19 The excitation (dotted) and PL spectra (solid) of the dispersed **MOF 1** with the addition of different concentration of bromobenzene, monitored and excited at 617 nm and 315 nm, respectively.

a)



b)

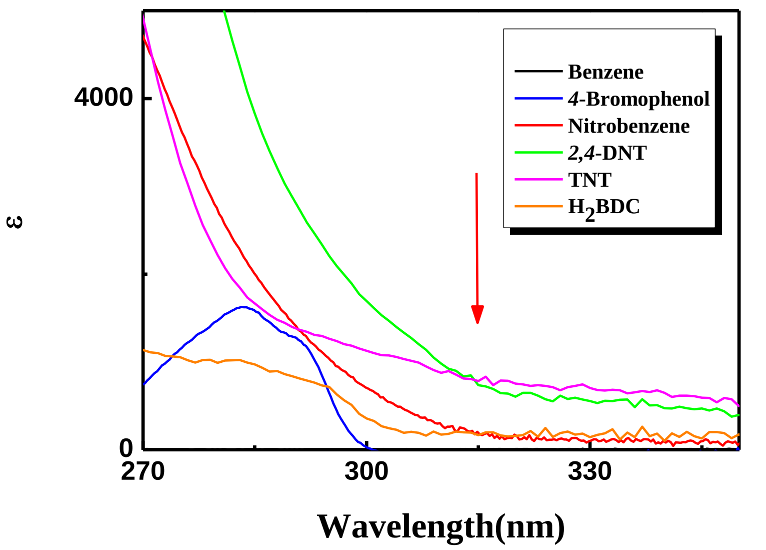


Figure S20 a) UV-Vis spectra and b) selected and magnified area of the UV-Vis spectra of ligand H_2BDC and different solvents.

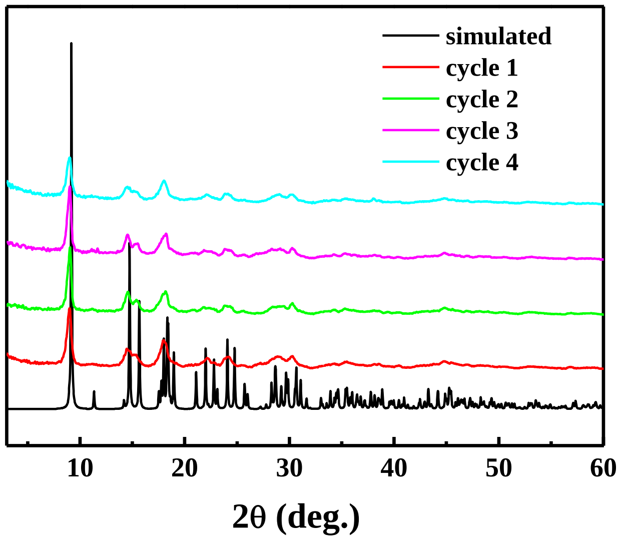


Figure S21 PXRD of $Eu(BDC)_{1.5}(H_2O)_2$ as a function of the number of the dispersion/deposition cycles.

Table S1 Fluorescence lifetime of **MOF 1** and dispersed **MOF 1** in ethanol solution with the concentration of 150 ppm of different solvents (excited: 315nm; monitored: 617nm).

solvent	Fluorescence lifetime (μs)
MOF 1	344.06±1.02
Benzene	344.30±1.08
p-Xylene	344.88±0.91
1,2-Xylene	341.53±0.92
Bromobenzene	340.72±0.98
Chlorobenzene	344.51±0.85
Toluene	345.76±0.89
Phenol	348.69±1.16
4-Bromophenol	342.86±1.09
4-Chlorophenol	340.19±1.05
o-Cresol	344.30±1.15
Nitrobenzene	341.72±0.99
2,4-DNT	340.80±0.95
TNT	336.04±0.88

Table S2 Molar extinction coefficient of H_2BDC and different analytes at 315nm.

Solvent	ε (315nm)
Benzene	~0
Toluene	~0
Chlorobenzene	~0
Bromobenzene	~0
1,2-Xylene	~0
P-Xylene	~0
Phenol	~0
4-Bromophenol	~0
o-Cersol	~0
o-Aminophenol	~0

Aniline	~0
Nitrobenzene	179
2,4-DNT	736
TNT	782
H_2BDC	165

Reference

1 W.J. Rieter, K.M.L. Taylor, H.Y. An, W. Lin, W. Lin, *J. Am. Chem. Soc.* **2006**, *128*, 9024.