Electronic Supplementary Information (ESI)

Bifunctional luminescent europium metal-organic framework for highly selective sensing of nitrobenzene and 4-aminophenol †

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Materials and general methods

All solvents and starting materiels for synthesis were purchased commercially and were used as received. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 advanced automated diffractometer with Cu-K_α radiation. Luminescencespectra for the solid samples and liquid samples were investigated with a Hitachi F-4500 fluorescence spectrophotometer and Varian Cary Eclipse Fluorescence spectrophotometer, respectively.

Preparation of $(DMA)_2[Eu_6(\mu_3\text{-}OH)_8(BPDC)_6]\cdot x(solvent)$:

A solution of $Eu(NO_3)_3\cdot 6H_2O$ (9 mg, 0.0225 mmol), H_2BPDC (5 mg, 0.0225 mmol), 2-Fluorobenzoic acid (95.2 mg 0.675 mmol), DMF (2 ml) and EtOH (0.5 ml) was prepared in a 20 ml scintillation vial stirred in a glass vial for ca. 20 mins at room temperature which was heated in an oven to 378 K for 36 hours in a preheated oven, followed by slow cooling (5 K h^{-1}) to room temperature. The colorless polyhedral crystals of 1 were obtained and washed with DMF and air-dried(yield: ca. 53%). The counter cation $(CH_3)_2NH_2^+$ is generated via decomposition of the DMF solvent. EA. Calcd for $C_{88}H_{72}Eu_6O_{32}N_2$: C, 40.95; H, 2.81; N, 1.09. Found: C, 39.56; H, 2.31; N, 1.12. FT-IR (KBr pellets): 3426 (s), 2930 (w), 1668 (vs), 1604 (s), 1542 (m), 1405 (vs), 1252 (m), 1172 (m), 1094 (m), 844 (m), 772 (m), 664 (w), 553 (m) cm^{-1}.

Experimental details for the anti-interference ability of Eu-MOF

The powder sample of Eu-MOF (24 mg) was suspended in methanol (100 mL). Treated by ultrasonication and then aged to generate stable suspensions before the fluorescence study. Some aromatic compounds with the same concentrations of 70 ppm were added to the methanol suspension of Eu-MOF, and the corresponding emission spectra were monitored. With the subsequent addition of 70 ppm nitrobenzene into the parallel tests, the corresponding emission spectra were monitored.

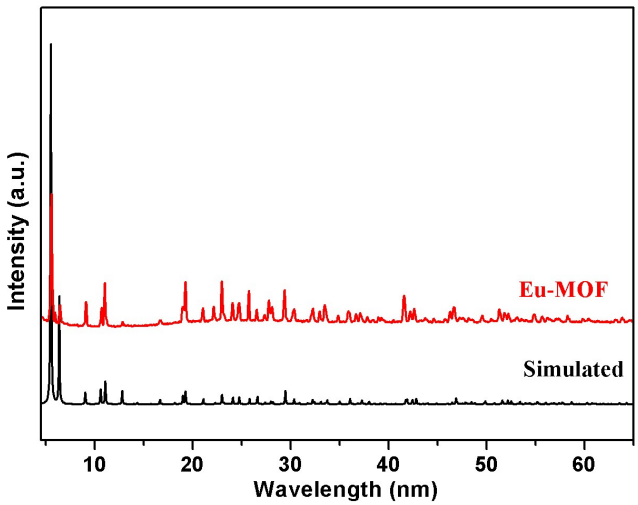

Fig. S1 PXRD pattern of **Eu-MOF**

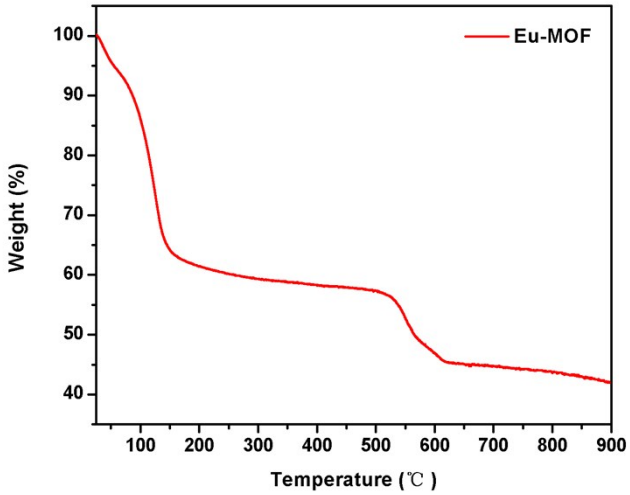

Fig. S2 The thermal stability of Eu-MOF was examined by thermogravimetric analysis (TGA) in the temperature range of 25-900 ^{o}C with a heating rate of 5 ^{o}C min^{-1} under N_2 atmosphere.

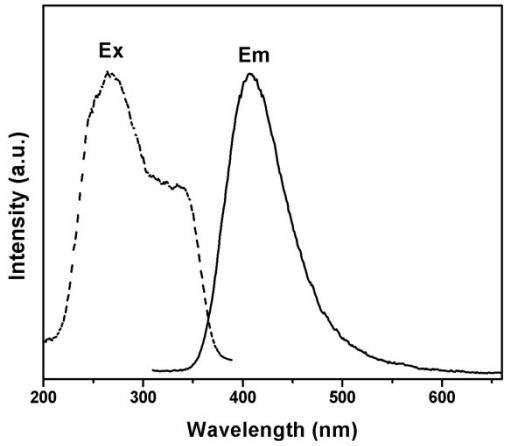

Fig. S3 Excitation (λ_{ex} = 264 nm) and emission (λ_{em} = 407 nm) spectra of H_2BPDC in the solid state at room temperature.

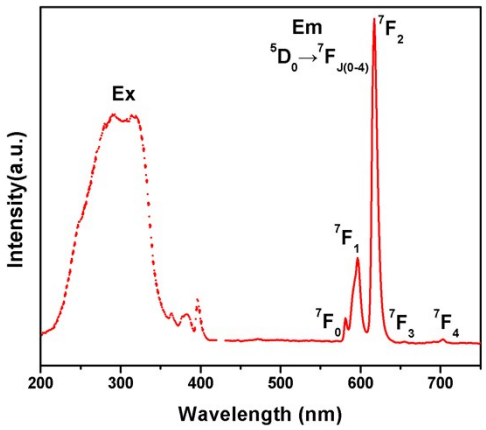

Fig. S4 Excitation (λ_{ex} = 317 nm) and emission (λ_{em} = 615 nm) spectra of **Eu-MOF** in the solid state at room temperature.

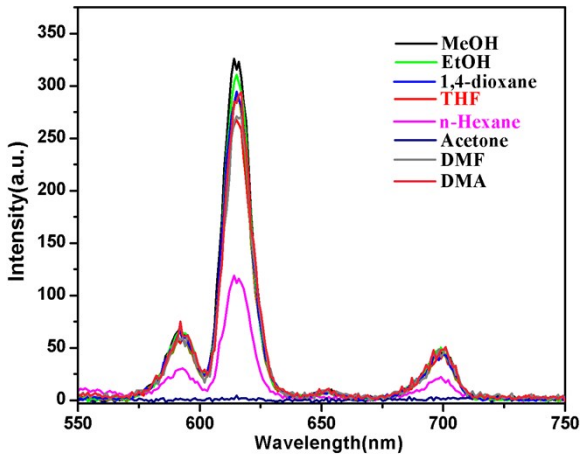

Fig. S5 Emission spectra of **Eu-MOF** (5 mg) at room temperature in different solvents (5 mL) (λ_{ex} = 317 nm).

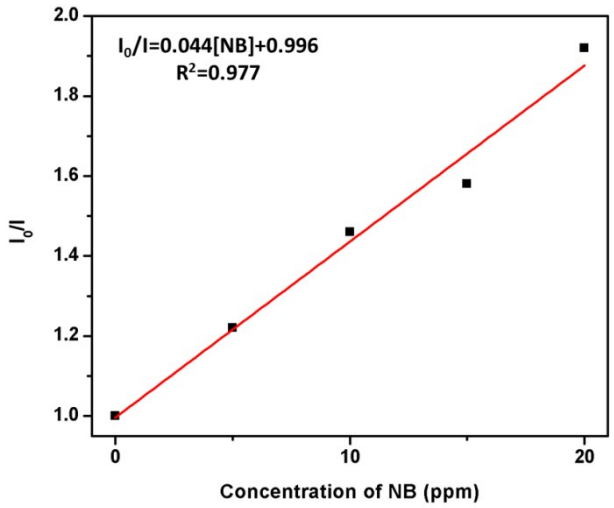

Fig. S6 The luminescent intensity (I_0/I) *versus* the NB concentration.

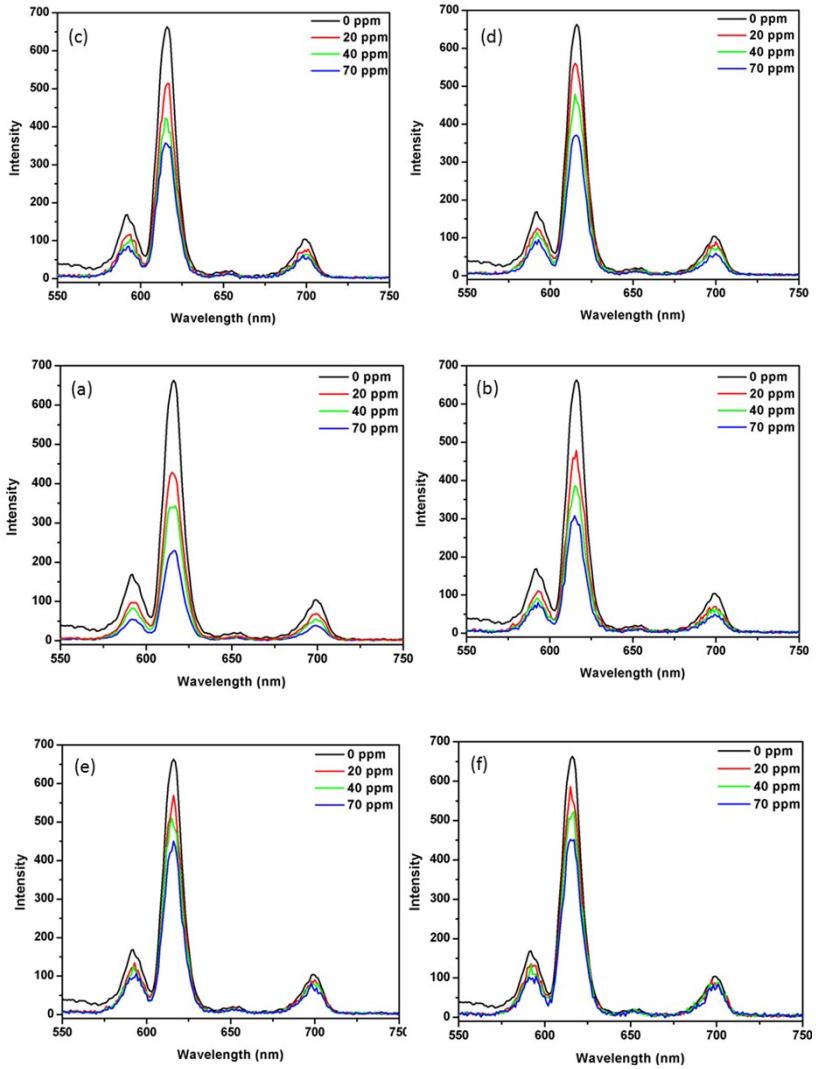

Fig.S7 The luminescent intensity of Eu-MOF in different concentration of nitro compounds (a) p-NP, (b) 4-NP, (c) DNP, (d)o-NP , (e) p-ND, (f) 3,5-DB (λ_{ex} = 317 nm).

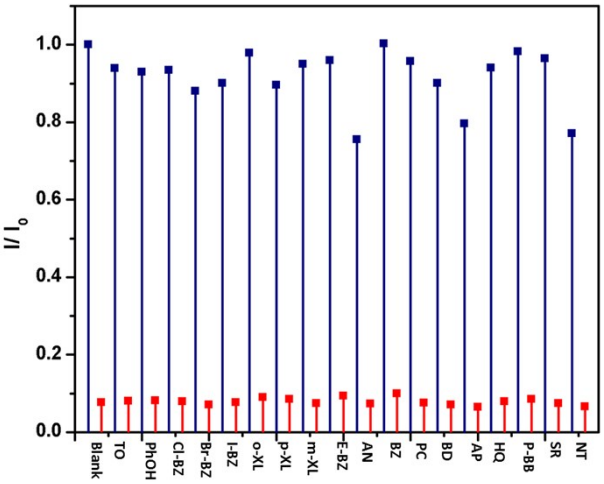

Fig. S8 Luminescence intensity ratio histograms of **Eu-MOF** dispersed in methanol with the addition of different aromatic compounds (blue) and subsequent addition of NB (red) (λ_{ex}= 317 nm).

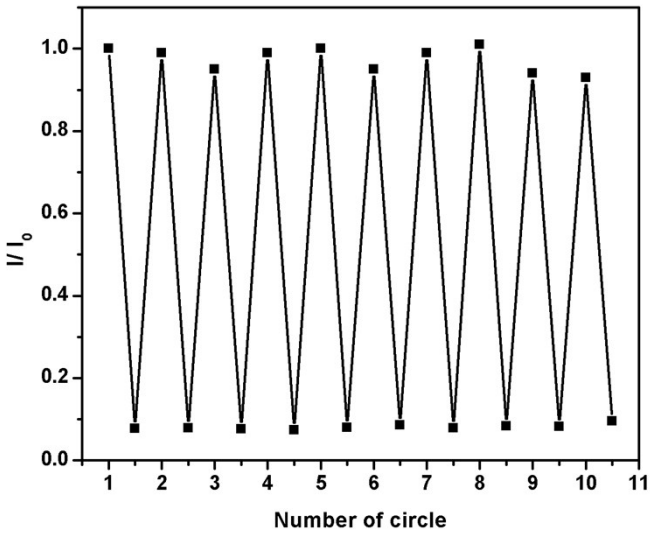

Fig. S9 Reproducibility of the quenching ability of **Eu-MOF** dispersed in methanol to NB (λ_{ex}= 317 nm).

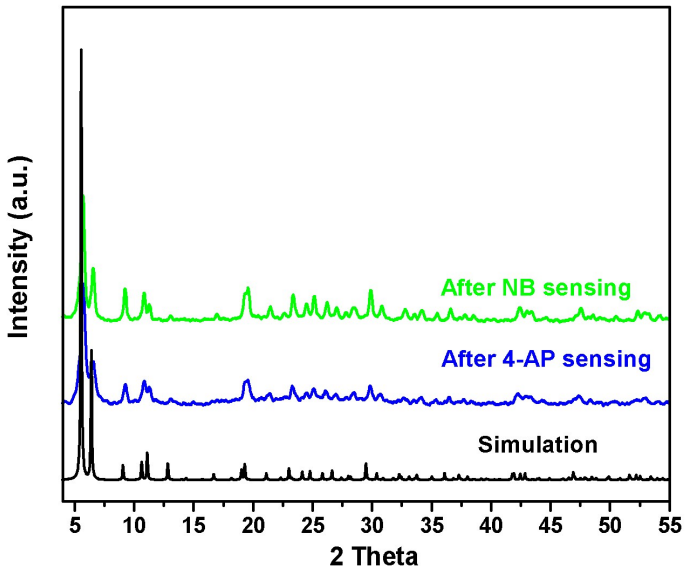

Fig. S10 The PXRD patterns of **Eu-MOF**: the samples after 10 quenching cycles.

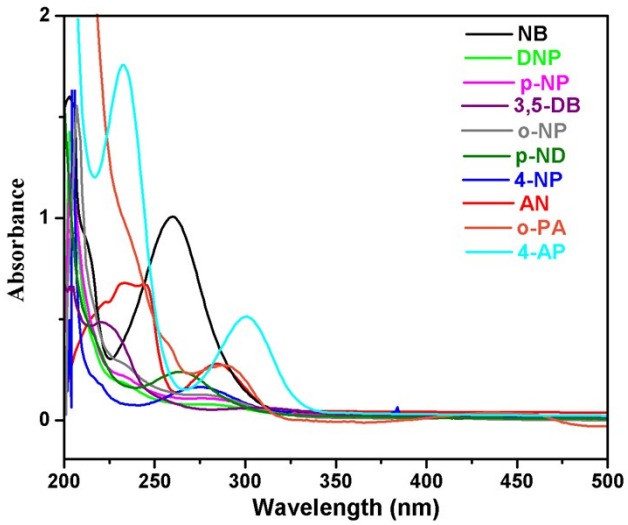

Fig. S11 The UV-vis absorption spectra of NB, DNP, p-NP, 4-NP, o-NP, 3, 5-DB, p-ND, AN, o-PA and 4-AP in methanol.

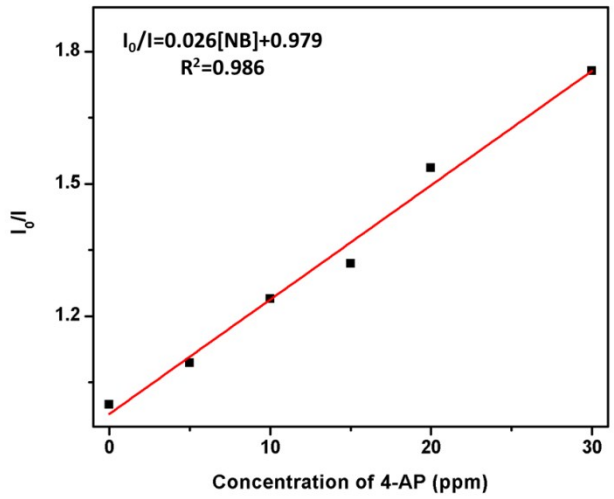

Fig. S12 The luminescent intensity (I_0/I) *versus* the 4-AP concentration.

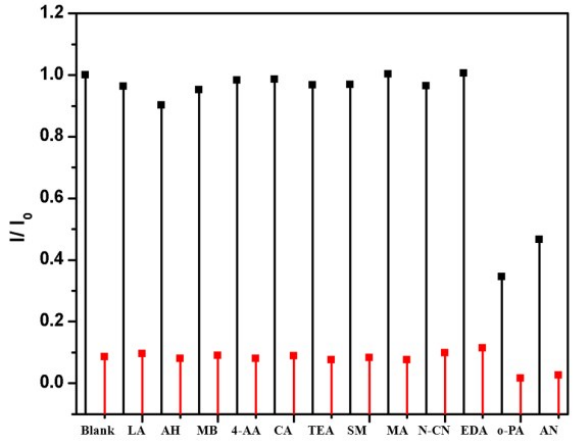

Fig. S13 Luminescence intensity ratio histograms of **Eu-MOF** dispersed in methanol with the addition of different organic amines (black) and subsequent addition of 4-AP (red) (λ_{ex}= 317 nm).

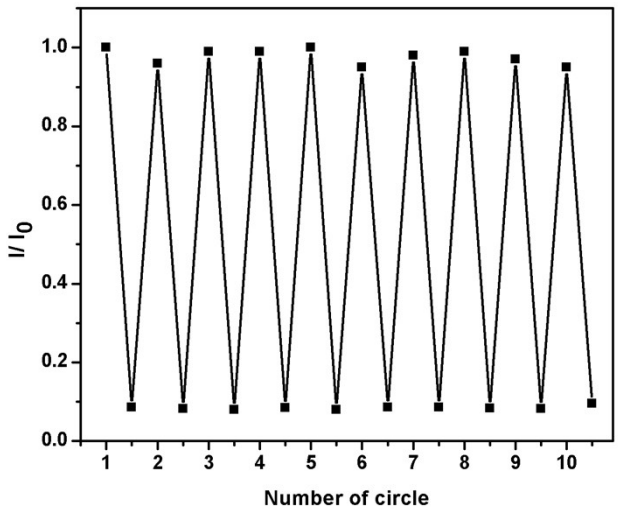

Fig. S14 Reproducibility of the quenching ability of **Eu-MOF** dispersed in methanol to 4-AP (λ_{ex}= 317 nm).

Table S1 Summary of the quenching efficiency of luminescent MOF sensors for NB[a]

MOF	Quantity(mg)/solvent (mL)	NB concentration	Quenching efficiency	Ref.
$[Tb(L_1)_{2/3}(L_2)_{1/2}(H_2O)_2]\cdot 2H_2O$	3 mg/5 mL	1000 ppm	60 %[a]	[1]
$\{[(UO_2)_2(H_2TTHA)(H_2O)]\cdot 4,4'\text{-bipy}\cdot 2H_2O\}_n$	2 mg/3 mL	1000 ppm	90 %[b]	[2]
$Mg_4(L)(DMF)_4(H_2O)_4(DMF)_{0.5}$	5 mg/3 mL	1500 ppm	100 %	[3]
$[Eu(L)_{1.5}(DEF)]_n$	3 mg/5 mL	970 ppm	100 %	[4]
$[Cd_3(NTB)_2(DMA)_3]\cdot 2DMA$	[c]/3 mL	600 ppm	79 %	[5]
UiO-66-NH_2	0.25 mg/5 mL	100	95.4 %	[6]
$[Zn_3(HL)_2(fma)_2]\cdot DMA\cdot H_2O$	0.3 mg/3 mL	300 ppm	92 %	[7]
$[Zn_2(trz)_2(bpdc)]\cdot DMA$	3 mg/3 mL	500 ppm	89 %	[8]
Tb^{3+}@NENU-522	3 mg/3 mL	2000 ppm	100 %	[9]
$[Tb(HL)(H_2O)_4]\cdot H_2O$	5 mg/5 mL	615 ppm	>95 %	[10]
$[Cd(ppvppa)(1,4\text{-NDC})]_n$	2 mg/2 mL	800 ppm	94 %	[11]
$Cd_{2.5}Na(NTB)_2(DMF)_4]\cdot 3DMF$	0.3 mg/3 mL	500 ppm	83 %	[12]
$[NH_2(CH_3)_2]_2[Cd_{17}(L)_{12}(\mu_3\text{-}H_2O)_4(DMF)_2(H_2O)_2]$	5 mg/5 mL	100 ppm	92.5 %	[13]
$([Cd_2L\cdot H_2O)_2]\cdot DMF\cdot H_2O)n$	5 mg/5 mL	500 ppm	>95 %	[14]
$[Tb(mtpc)_{1.5}(DMA)(H_2O)]\cdot 2H_2O$	0.4 mg/5 mL	150ppm	87.9 %	Our previous work [15]
$(DMA)_2[Y_9(\mu_3\text{-}OH)_8(\mu_2\text{-}OH)_3BTB_6]_n\cdot(solv)_x$	1.8 mg/5 mL	60 ppm	93.1 %	Our previous work[16]
(DMA)2[Eu6(μ3-OH)8(BPDC)6]·x(solvent)	1.2 mg/5 mL	70 ppm	92.3 %	This work

[a] The values were estimated from the literature[1]. [b] The values were estimated from the literature [2].

[c] The quantity of MOF is missed in literature [5].

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