Electronic Supplementary Material (ESI) for Analyst.

Supplementary material

Europium ion post-functionalized indium metal-organic frameworks hybrid system for fluorescence detecting aromatics

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Experimental Section

Materials and Reagents $Eu(NO_3)_3·6H_2O$ was obtained from the reaction, where Eu_2O_3 was dissolved in hot concentrated nitric acid. All the other chemicals were commercially available and all solvents were reagent grade without further purification. $In(NO_3)_3·6H_2O$ (408.93 g·mol^{-1}) and the ligand 2,2'bipyridine-5,5'-dicarboxylic acid (H_2bpydc, 244.20 g·mol^{-1}) were purchased from Aldrich, while N,N-dimethylformamide (DMF), ethyl alcohol, benzene, toluene, ethylbenzene, o-xylene, m-xylene, fluorobenzene, p-xylene, chlorobenzene, and bromobenzene were all purchased from TCI.

Physical characterization The record of powder X-ray diffraction patterns (PXRD) were performed with a Bruker D8 diffractometer under CuKa radiation and the data were collected within the 2θ within range of 5-50 ° at 40 mA and 40 kV with a scan speed of 0.10 s per step and a step size of 0.02 °. Fourier transform infrared spectra (FTIR) were harvested in the range of 4000-400 cm^{-1} within KBr pellets using a Nexus 912 AO446 infrared spectra radiometer. Scanning electronic microscope (SEM) images were carried out on a Hitachi S-4800 electron microscope. Thermogravimetric analysis (TGA) data was recorded on a Netzsch STA 449C system with a heating rate of 5 °C min^{-1} in air. The Nitrogen adsorption-desorption isotherms were performed on liquid nitrogen temperature, using a TriStar 3000 analyzer. BET surface areas were obtained by the Brunauer-Emmett-Teller method. The ultraviolet diffusion reflection spectra were calculated according to a B&WTEK BWS003 spectrophotometer. Luminescence excitation and emission spectra of the products were measured by an Edinburgh FLS920 phosphorimeter. Luminescence lifetime measurements were computed on an Edinburgh FLS920 phosphorimeter using a microsecond pulse lamp as excitation source. The outer luminescent quantum efficiency was determined employing an integrating sphere (150 mm diameter, $BaSO_4$ coating) from Edinburgh FLS920 phosphorimeter.

The detail and description of experiment

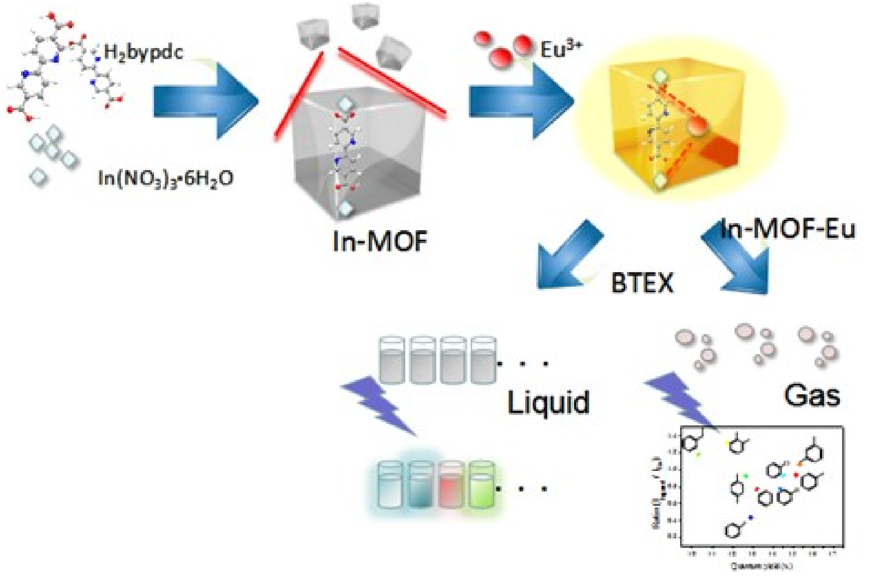
Preparation of In(OH)(bpydc) (In-MOF). In-MOF was synthesized depending upon the hydrothermal method. [26] $In(NO_3)_3·6H_2O$ (409.0 mg, 1.0 mmol) and H2bpydc (244.2 mg, 1.0 mmol) were transferred in DMF (20 mL) at room temperature and then sonicated for 30 min in a 40 mL solvothermal vessel. Subsequently, the mixture was

heated at 150 °C for 48 h. Through centrifugation and washing with DMF and acetonitrile for several times, the white product was then dried at 80 °C under vacuum environment for 8 h.

Preparation of In-MOF-Eu. The loading of lanthanide ions into In-MOF was performed by postsynthetic method.[13b] The mixture of 186.5 mg (0.5 mmol) of In-MOF and 114 mg (0.25 mmol) $Eu(NO_3)_3 \cdot 6H_2O$ in 25 mL DMF was stirred at 60 °C for 48 h in a Teflloncapped scintillation. The product was centrifuged and washed with DMF several times in order to remove residual Eu^{3+}. Finally, the resulted white powder was dried in vacuum environment at 80 °C for 12 h.

Luminescence sensing experiments. Powder samples of In-MOF-Eu served to detect a series of BTEX solvents at room temperature. In-MOF-Eu powders (3.0 mg) were directly impregnated into benzene, toluene, ethylbenzene, o-xylene, p-xylene, mxylene, F-benzene, Br-benzene and Cl-benzene (3 mL), respectively. After that, the mixtures were equilibrated thoroughly for 5 min by ultrasound processing. Then luminescence measurements were taken. In-MOF-Eu was used to detect a series of BTEX volatiles at room temperature. In-MOF-Eu (50 mg) was dispersed in 2 mL of ethanol and then the mixture was dropped on glass slides followed by drying in air. These glass slide was put in 10 mL vials which contained 3 mL BTEX solvent, afterwards, the vials were sealed up and put in a drying oven with 25 °C for 1 h. Then luminescence measurements were taken.

Preparation and application of test paper based on In-MOF-Eu. The filter papers were smeared with ethanol/In-MOF-Eu suspensions, and then exposed to air for drying to preparing fluorescence test paper. A series of BTEX solvents were dropped on test papers and then observed under the irradiation of UV light at λ_{ex} = 365 nm.



Scheme S1 Procedure for In-MOF and In-MOF-Eu hybrids. In-MOF-Eu is employed as fluorescent probe for the discrimination of BTEX in liquid or gas phase.

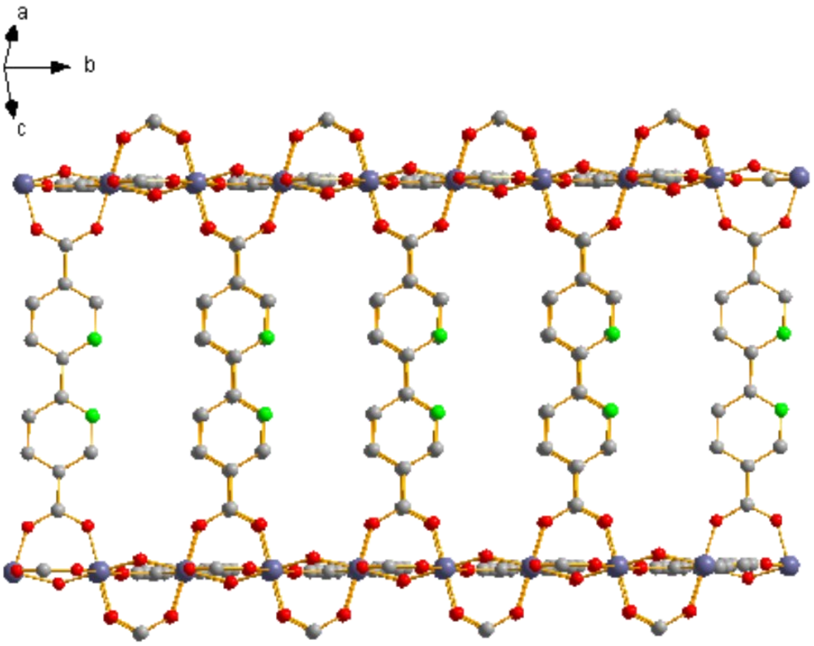


Fig. S1 The representative structure of In(OH)bpydc, in which the dark gray, green, red, light gray represent In, N, O and C atoms, respectively.

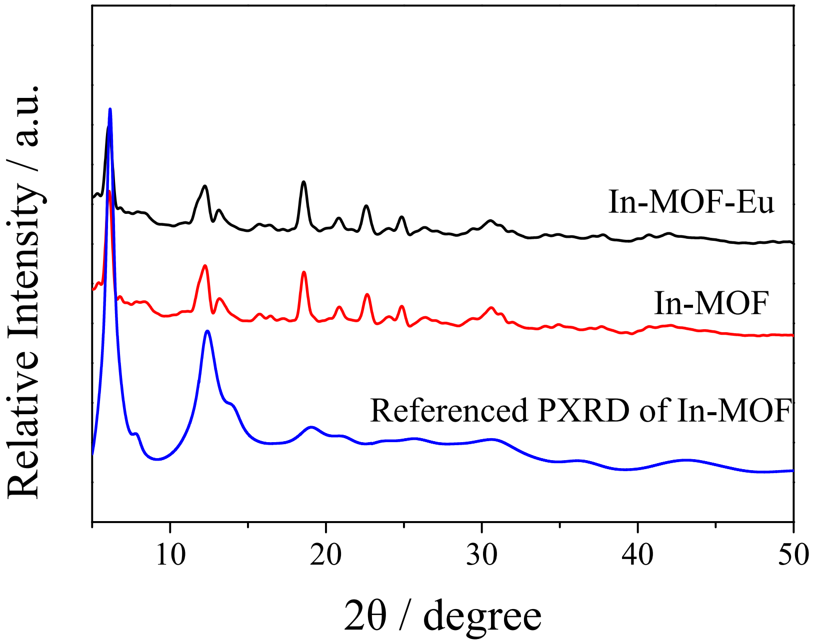


Fig. S2 The PXRD patterns of the In-MOF (red), In-MOF-Eu (black) and referenced one (blue)[1].

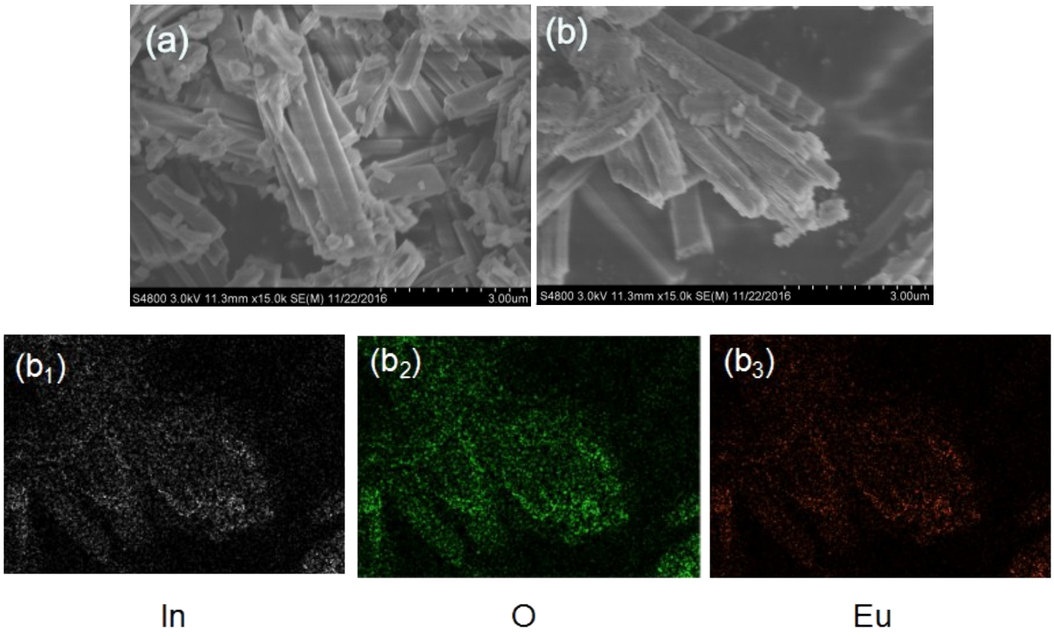


Fig. S3 SEM images of In-MOF (a), In-MOF-Eu (b) and elemental mapping of In-MOF-Eu (b_1-b_3).

Table. S1 Loading level of Eu^{3+} cations

Compounds	**In^{3+}**	**Eu^{3+}**
In-MOF-Eu	1	0.217
Solution after PSM	undetectable	1

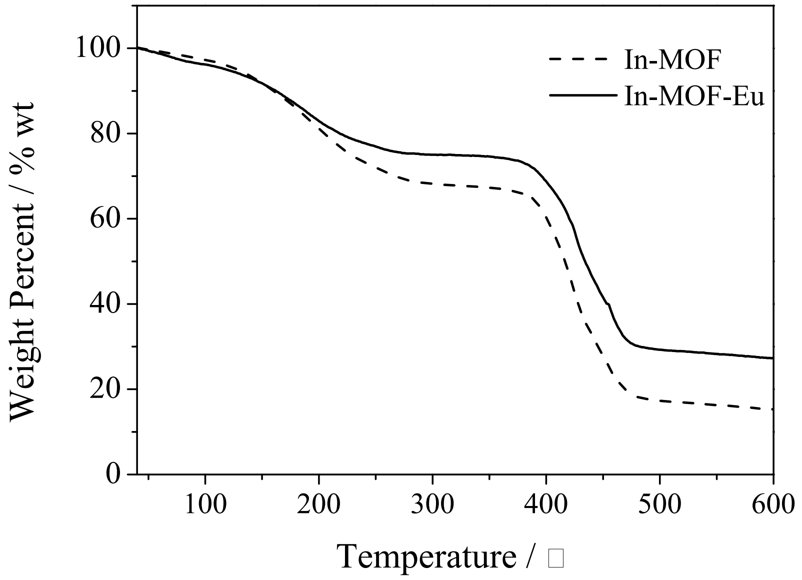


Fig. S4 Thermal gravimetric analysis (TGA) of In-MOF (dash line) and In-MOF-Eu (full line).

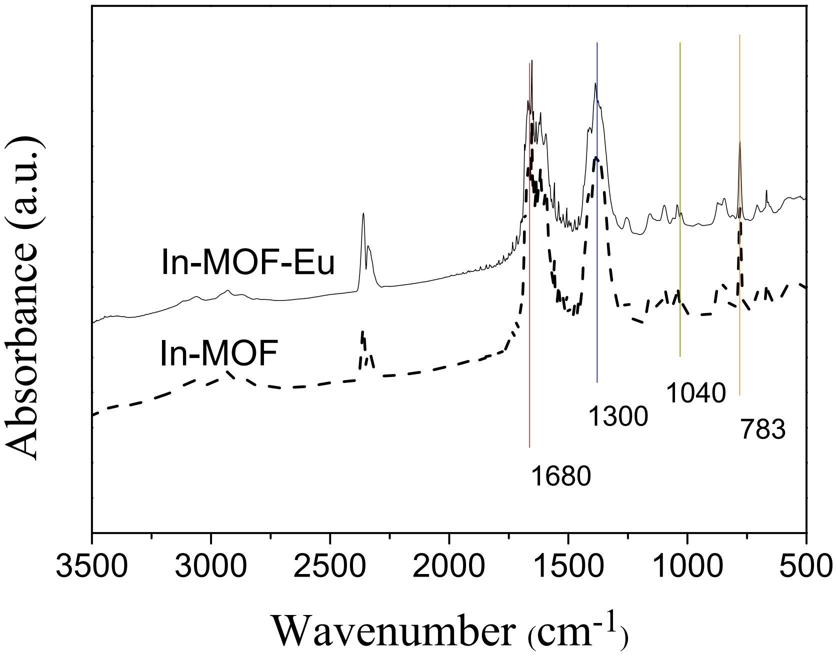


Fig. S5 Fourier transform infrared spectra (FT-IR) of In-MOF (dash line) and In-MOF-Eu (full line)

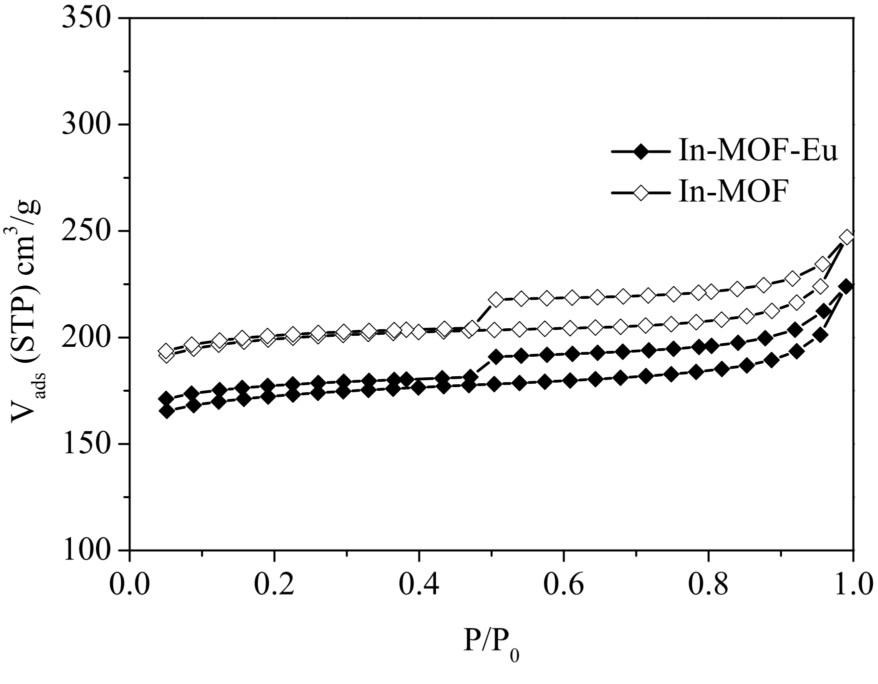


Fig. S6 The N_2 adsorption–desorption isotherms of In-MOF and In-MOF-Eu

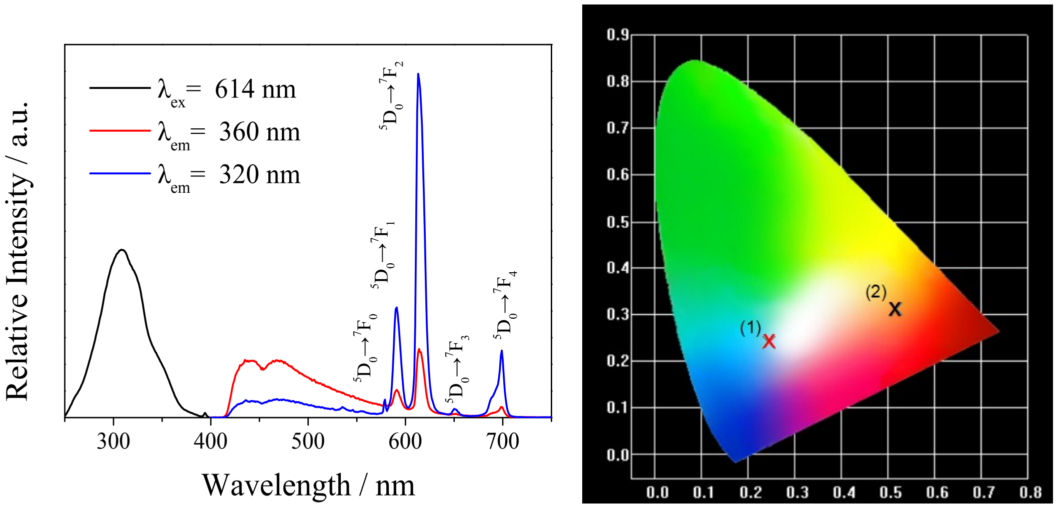


Fig. S7 The excitation and emission spectra of In-MOF-Eu dispersed in aqueous solution; the CIE chromaticity diagram of In-MOF-Eu excited at 360 nm (1, X = 0.24, Y = 0.24) and 320 nm (2, X = 0.52, Y = 0.31).

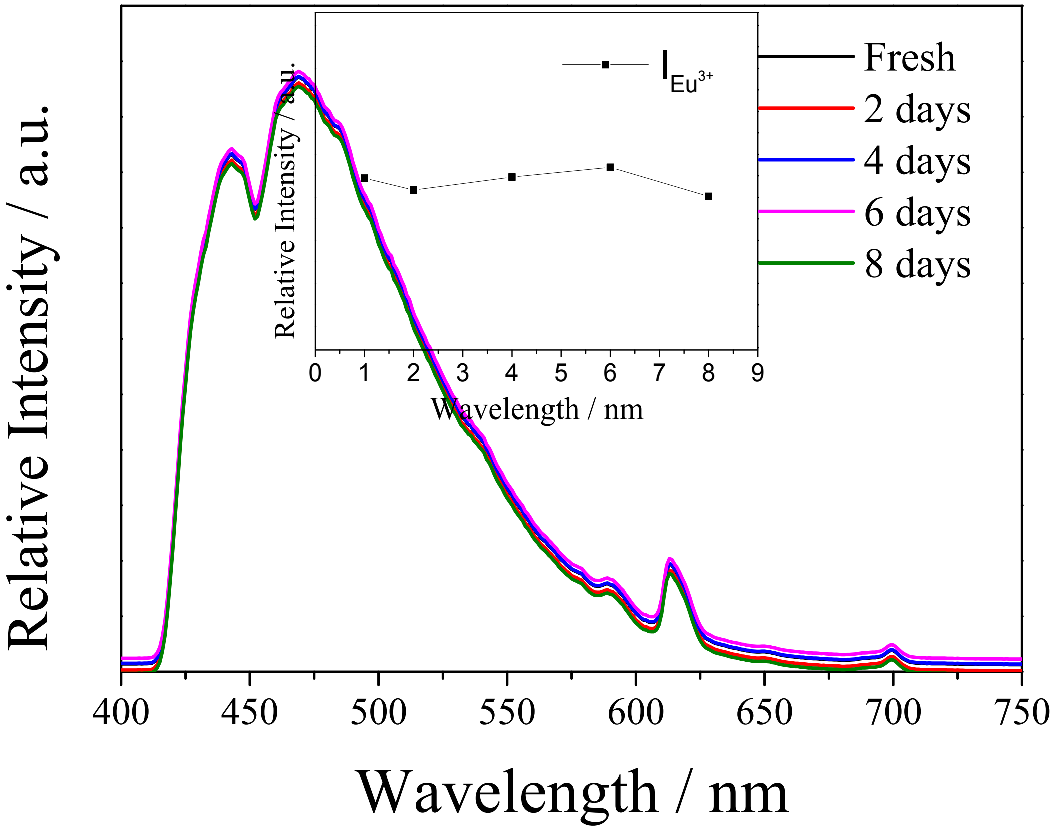


Fig. S8 Day-to-day fluorescence stability of In-MOF-Eu after immersing in benzene for several days and the inset is the corresponding relative intensity at λ_{em} = 616 nm.

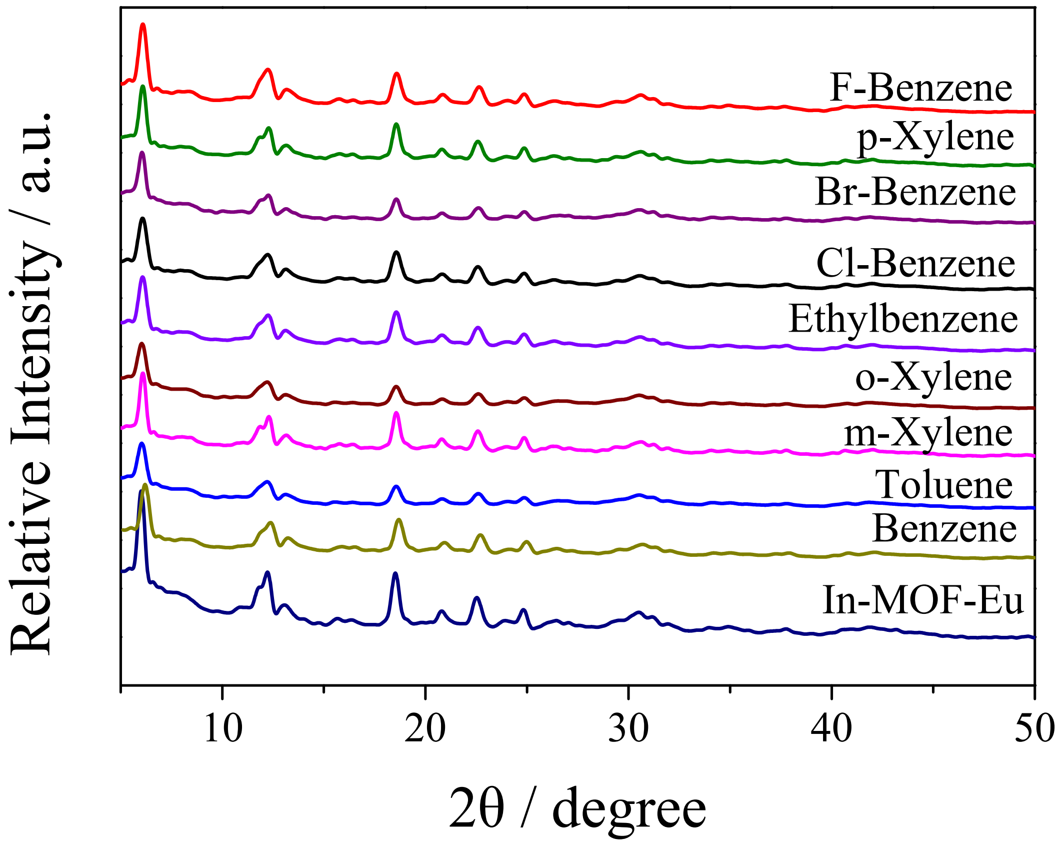


Fig. S9 Power X-ray diffraction (PXRD) pattern of In-MOF-Eu after dissolved in various BTEX.

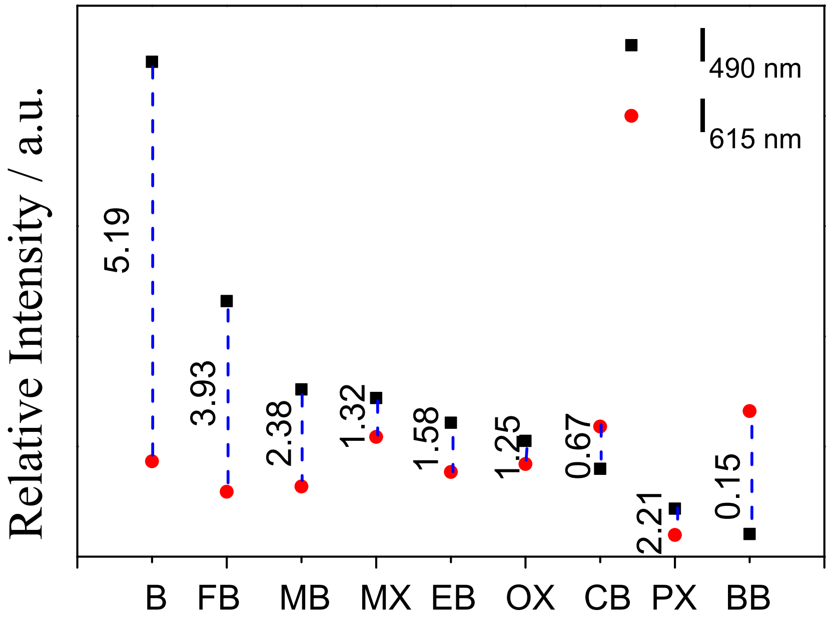


Fig. S10 Corresponding values of $I_{490\ nm}$ (I_{ligand}) and $I_{615\ nm}$ ($I_{Eu^{3+}}$) and ratio of I_{ligand} / $I_{Eu^{3+}}$ in BTEX.

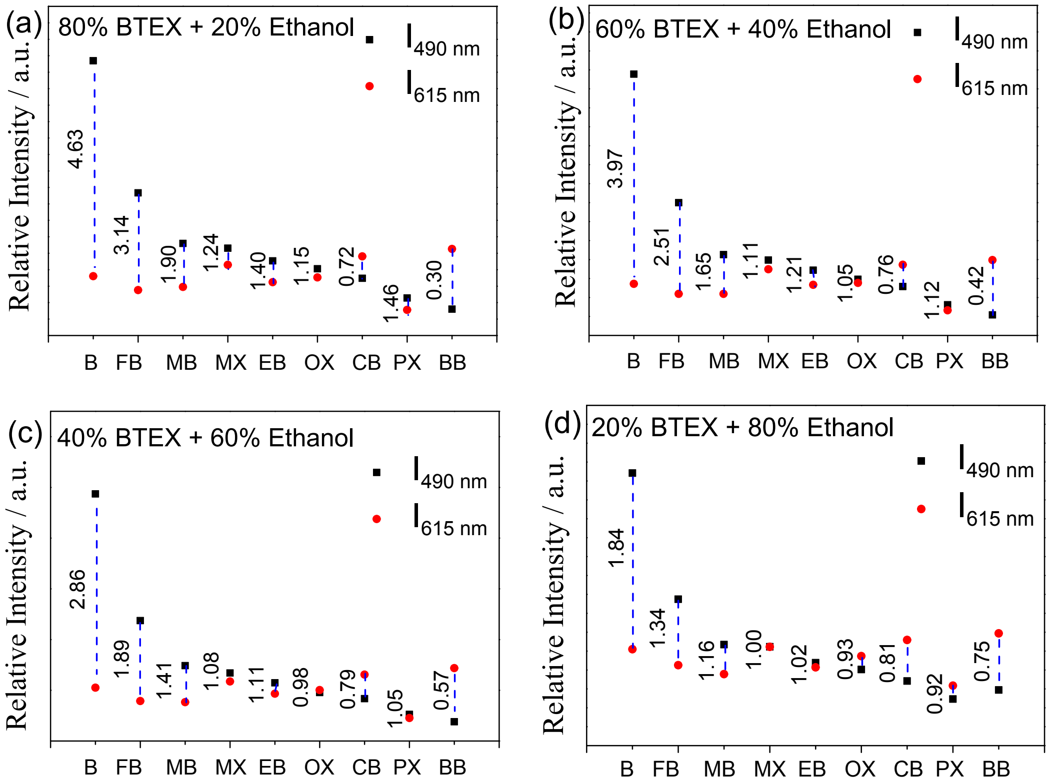


Fig. S11 Corresponding values of $I_{490\text{ nm}}$ (I_{ligand}) and $I_{615\text{ nm}}$ ($I_{\text{Eu}^{3+}}$) and ratio of I_{ligand} / $I_{\text{Eu3+}}$ in BTEX/ethanol solutions with different proportions.

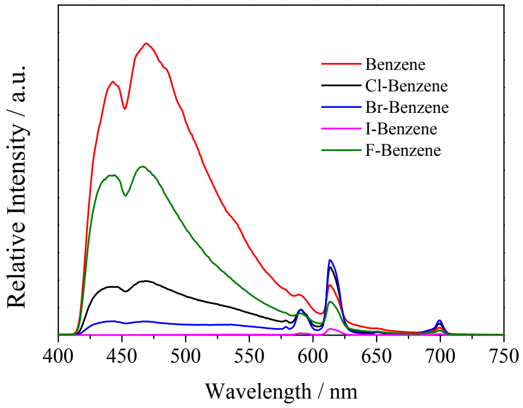


Fig. S12 Luminescence intensity of the In-MOF-Eu with X-Benzene (X = F, Cl, Br, I) excited at λ_{ex} = 360 nm.

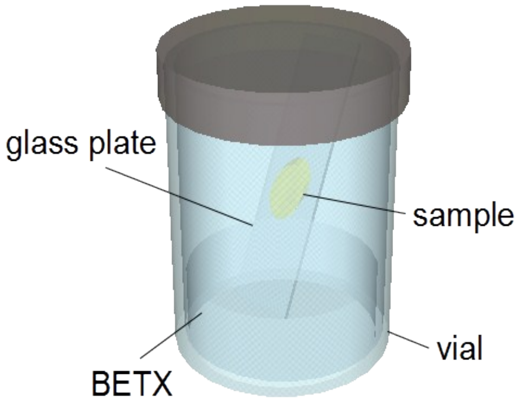


Fig. S13 The device for sensing BTEX volatiles.

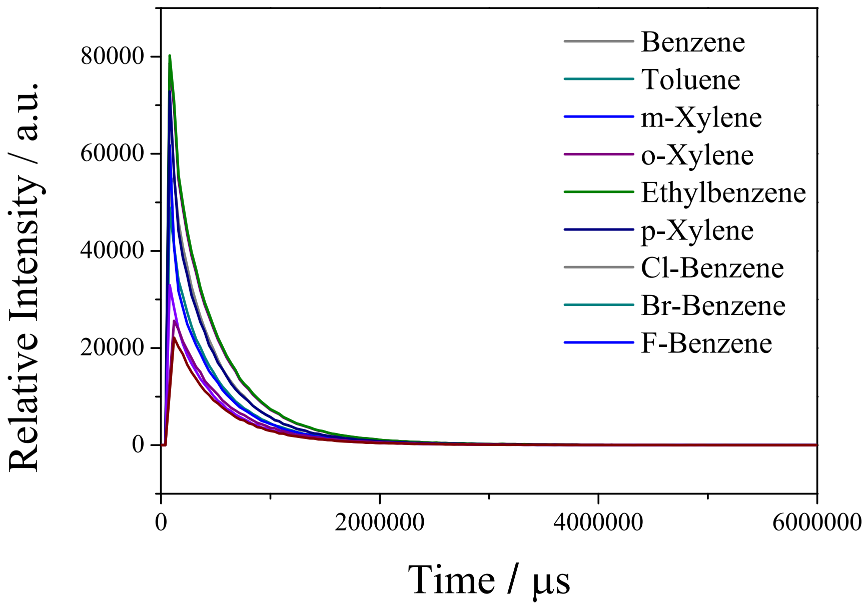


Fig. S14 The luminescence lifetime decay curves of In-MOF-Eu materials after vapour experiment in various BTEX.

Table S2 Lifetime and quantum yield of samples

	Time (µs)	η (%)
Benzene	564.38	17.21
Toluene	382.34	15.15
m-Xylene	405.32	15.33
o-Xylene	369.05	11.74
Ethylbenzene	351.83	10.31

p-Xylene	385.53	12.68
Cl-Benzene	420.34	14.53
Br-Benzene	381.36	10.32
I-Benzene	388.75	13.65
F-Benzene	412.36	16.38

1. Y. Zhou, B. Yan and F. Lei, *Chem. Commun. (Camb)*, 2014, **50**, 15235-15238.