

Electronic Supplementary Information (ESI)

Photoinduced *versus* spontaneous host-guest electron transfer within a MOF and chromic/luminescent response

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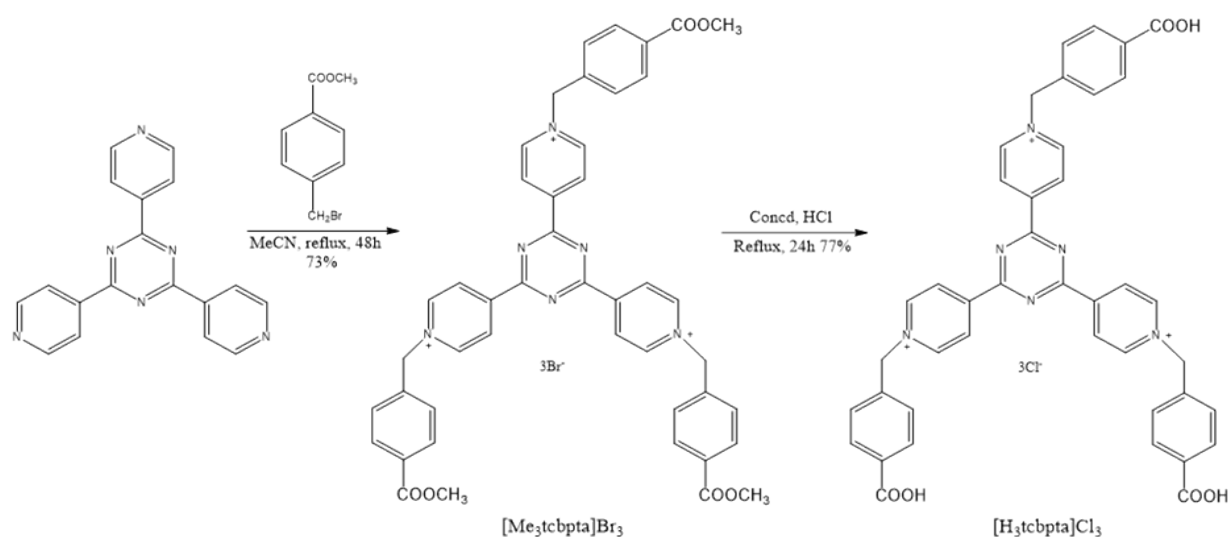
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Materials. All the reagents and solvents employed were commercially available and used without further purification.

Preparation of [H₃tcbpta]Cl₃

The synthetic route is shown in Scheme S1. 4-(bromomethyl)benzoate methyl ester (0.80 g, 3.5 mmol) was added to a suspension of 2,4,6-tris(4-pyridyl)-1,3,5-triazine (0.312 g, 1.0 mmol) in 50 ml acetonitrile. The mixture was refluxed for 36 h. As the reaction progressed, the mixture gradually changed from gray to yellow. After the reaction, the mixture was cooled to room temperature and filtered. The filter cake was rinsed with CH₃CN (10 ml × 5) and then dried in a vacuum oven. The ester [Me₃tcbpta]Br₃ was obtained in a yield of 77%. ¹H NMR (400 MHz, DMSO-d₆, δ): 9.69 (d, J = 4.5, 6H), 9.57 (d, J = 5.5, 6H), 8.12 (d, J = 5.7, 6H), 7.91 (d, J = 6.0, 6H), 6.10 (s, 6H), 3.98 (s, 9H). A solution of 1.0 mmol [Me₃tcbpta]Br₃ (0.76 g) in hydrochloric acid (40 ml, 6mol/L) was refluxed for 24 h. The solution was cooled to room temperature and then kept in the refrigerator for 4 h. The yellow solid was collected by filtration, washed with ice water, and dried in a vacuum oven, giving the salt [H₃tcbpta]Cl₃. Yield: 76%. ¹H NMR (400 MHz, DMSO-d₆, δ): 9.73 (d, J = 5.2, 6H), 9.59 (d, J = 6.0, 6H), 8.16 (d, J = 6.0, 6H), 7.97 (d, J = 6.0, 6H), 6.17 (s, 6H).



Scheme S1. Synthesis of ligand [H₃tcbpta]Cl₃

Synthesis of [Eu₂(tcbpta)(ndc)(H₂O)₇Cl]Cl₃·4H₂O·EtOH (1)

EuCl₃·6H₂O (37 mg, 0.1 mmol), H₂ndc (2.7 mg, 0.012 mmol) and [H₃tcbpta]Cl₃ (10.0 mg, 0.012 mmol) were mixed in H₂O-EtOH-CH₃CN (5 ml, v/v/v = 1/1/3). The suspension was ultrasonicated for 20 min and transferred to a 15 ml Teflon-lined stainless-steel reactor, and the

reactor was kept at 120 °C in an oven for 50 h. After cooling to room temperature, the pale-yellow crystals were isolated by filtration, wash with ethanol, dried in air. The yield was about 46% based on [H₃tcbpta]Cl₃. Anal. calc. for C₅₆H₆₄N₆Cl₄Eu₂O₂₂: C, 40.86; H, 3.61; N, 4.98. Found: C, 41.15; H, 3.95; N, 5.18 %. IR (KBr, cm⁻¹): 3302s, 1669s, 1615m, 1582m, 1529s, 1418s, 1219w, 1067w, 875m, 808m, 742m, 516w.

Preparation of the MOF-PVDF mixed matrix membrane

A grinded sample of **1** (75 mg) was dispersed in 2 mL ethanol with sonication for 10 min, and 1.0 g of PVDF (polyvinylidene fluoride) solution (5 wt% in DMF) was added. The mixture was sonicated for 30 min to give a slurry, which was cast onto a glass substrate and dried at 70 °C in an oven. The membrane thus obtained has MOF: PVDF = 1.5:1 (w/w).

Physical measurements

Powder X-ray diffraction (PXRD) patterns was recorded at room temperature on a Rigaku D/Max-2500 diffractometer at 35 kV, 25 mA for a Cu-target K α irradiation (λ = 1.5418 Å) tube and a graphite monochromator in a 2 θ range of 5-30°. FT-IR spectra were recorded from KBr pellets in the range 500-4000 cm⁻¹ on a Nicolet NEXUS 670 spectrophotometer. ¹H NMR spectra were recorded on a Bruker Advance 300 MHz spectrometer. Electron-spin resonance (ESR) signals were recorded on a Bruker Elexsys 580 spectrometer with a 100 kHz magnetic field in the X band at room temperature. UV-vis diffuse reflectance spectra were recorded on a HIMADZU UV-2700 spectrometer. BaSO₄ were used as references and the ground power of a sample was coated. Fluorescence spectra were recorded on a Hitachi F-4500 spectrofluorometer. TGA-DTG was performed on a STA 449 F3 Simultaneous Thermal Analyzer under air atmosphere at 10°C/min in the temperature range of 25°C-800 °C.

Photochromic experiments

A CEL-HXUV300 300W xenon lamp system (Ceaulight, China) equipped with an IR filter was used for photochromic studies. The distance between the sample and the Xe lamp was set at 15 cm. The solid-state UV-vis diffusive reflectance and luminescence spectra were recorded using the same sample after irradiation for the given time.

Luminescence sensing experiments

The MOF-PVDF mixed matrix membrane was sealed in gas chamber, and the O₂/NH₃ was injected with different concentration. In the recovery experiment for NH₃, the membrane is

rinsed with acetone and then dried for the next run.

DFT calculations

The orbital calculations were performed using the DMol³ module in the Materials Studio software package.^{1, 2} The PW91 local functional and the DNP 4.4 basis set were adopted in the calculations. The π - π stacking model of 2,4,6-tris(N-methylpyridinium-4-yl)-s-triazine and H₂ndc were obtained from the single crystal structure of **1**.

Crystal structure determination

Single-crystal X-ray diffraction measurement was recorded at 100 K on a Bruker D8 VENTURE diffractometer (Cu-K α radiation, λ = 1.54184 Å) equipped with a graphite monochromator. The structure was solved by direct methods with SHELX-2014 program and refined using a full-matrix least-squares refinement on F².³ Non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbons were added geometrically and refined isotropically with the riding model. The solvent molecules were determined from elemental analysis and thermogravimetric measurements. The charges of the cationic framework were balanced with chloride ions. The chloride ions in the pores of the compound were located, some of chloride ions were disordered over two positions with refined occupancies. The solvent molecules were removed using the “SQUEEZE” protocol of the PLATON program.⁴ The crystallographic data reported in this paper are presented in Table S1.

Table S1. Crystal data and structure refinement for **1**.

Compound	1
Empirical formula	C ₅₄ H ₅₀ Cl ₄ Eu ₂ N ₆ O ₁₇
Formula mass	1500.72
Crystal system	Triclinic
Space group	<i>P</i> -1
a (Å)	13.3224(5)
b (Å)	16.8341(5)
c (Å)	17.0487(8)
α (°)	105.416(3)
β (°)	108.352(4)
γ (°)	106.645(3)
V (Å ³)	3199.5(2)
Z	2
T/K	100.01(10)
D _{calcd} (g.cm ⁻³)	1.558
μ (mm ⁻¹)	7.379
<i>F</i> (000)	1492
θ range collected	3.280 to 67.684
R ₁ , wR ₂ (I > 2 σ (I))	0.1322,0.2571
GOF	1.006

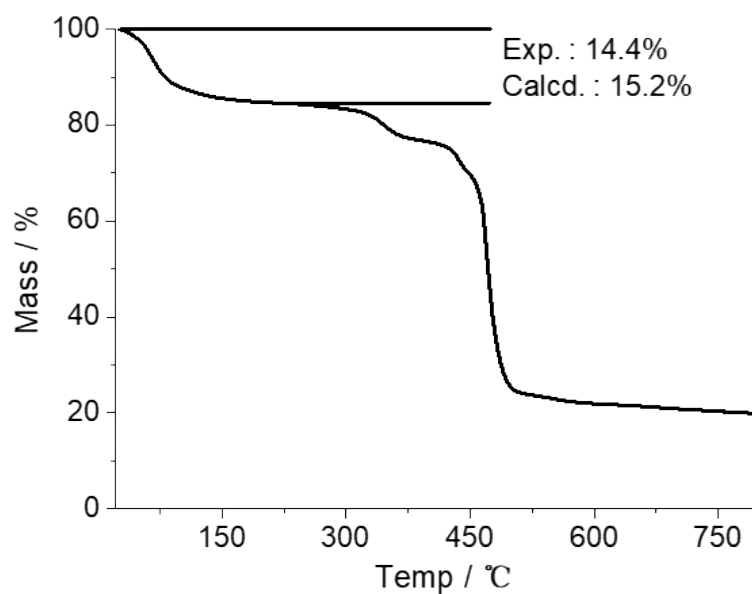


Fig. S1 Thermogravimetric plot of **1** from room temperature to 800 °C under air atmosphere. The weight loss ~14.4 % upon heating to 150 °C corresponds to the release of solvent molecules (calcd. 15.2 %).

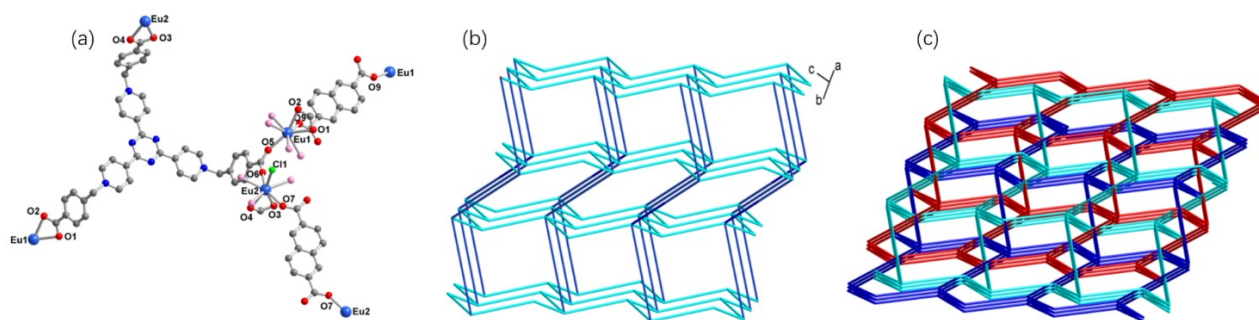


Fig. S2 (a) Coordination environments of the ligands and metal centers. The water oxygens are shown in pink and other oxygens in red. Hydrogen atoms are not shown. (b) Topological representation of the framework. (c) Topological representation of the 3-fold interpenetration.

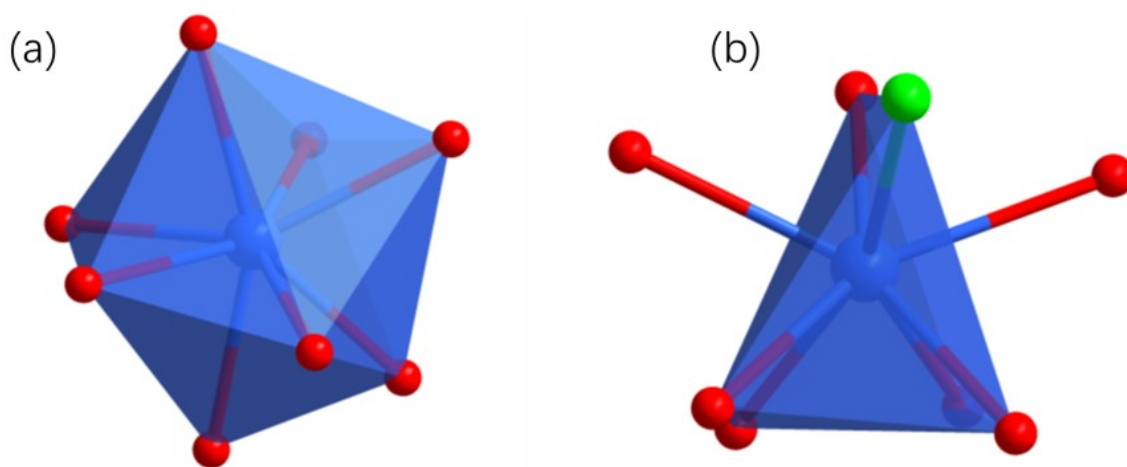


Fig. S3 Coordination polyhedron of Eu1(a) and Eu2(b).

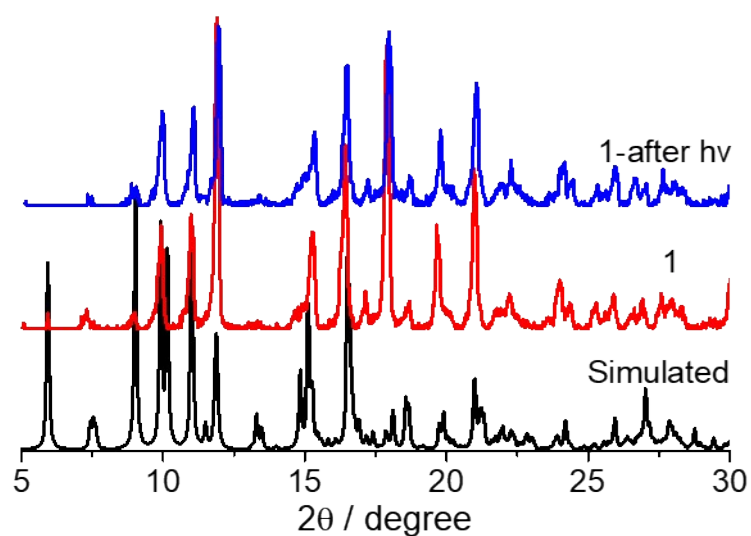


Fig. S4 PXRD profiles of **1** before and after Xe light irradiation.

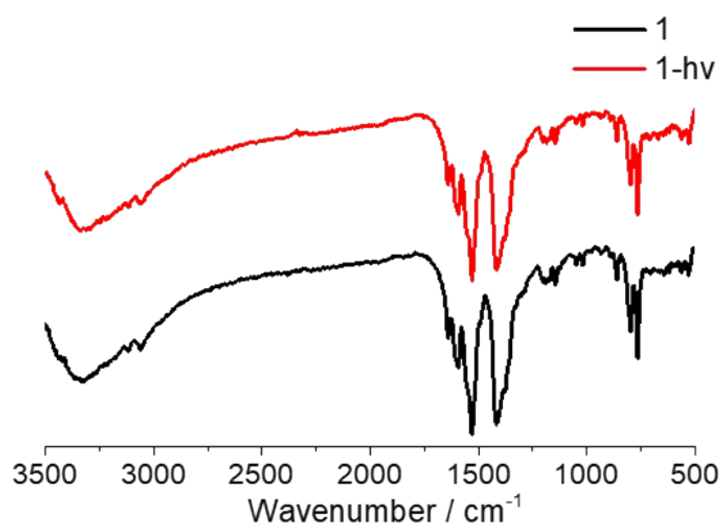


Fig. S5 IR spectra of **1** before and after Xe light irradiation.

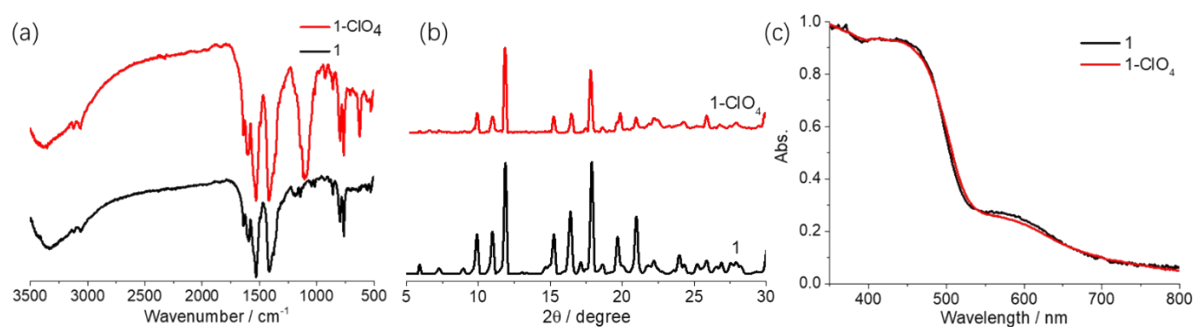


Fig. S6 IR spectra, PXRD profiles and UV-vis spectra of **1** and **1-ClO₄** respectively.

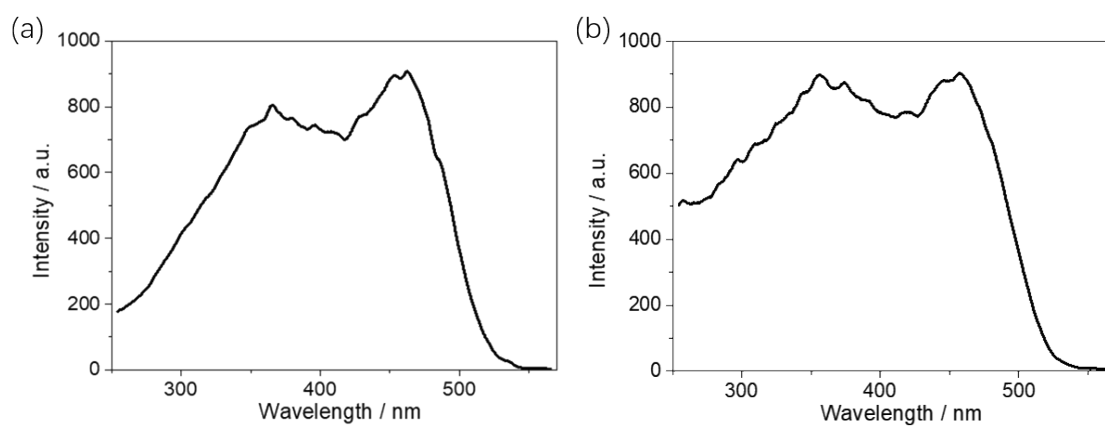


Fig. S7 Solid-state excitation spectra of **1** (a) and **1-ClO₄** (b).

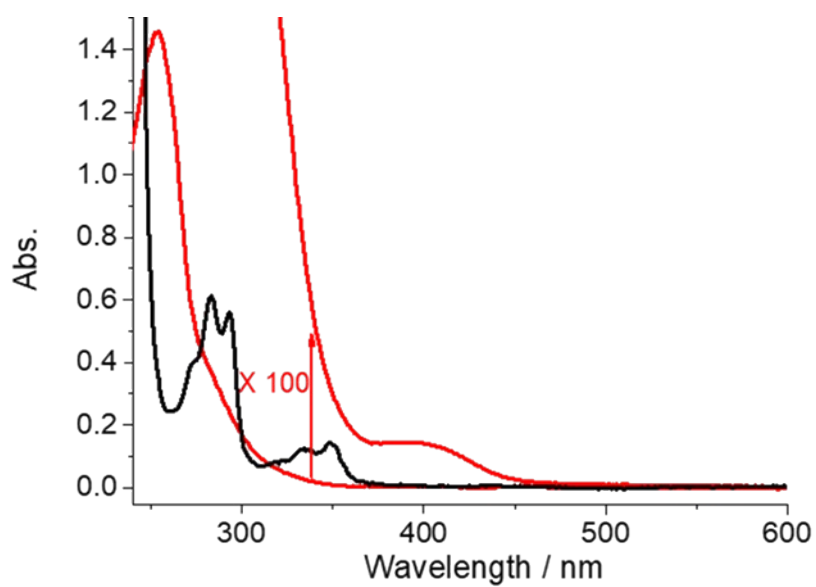


Fig. S8 UV-vis absorption spectra of H₃tcapta (red lines) and H₂ndc (black line) in acetonitrile-water solution.

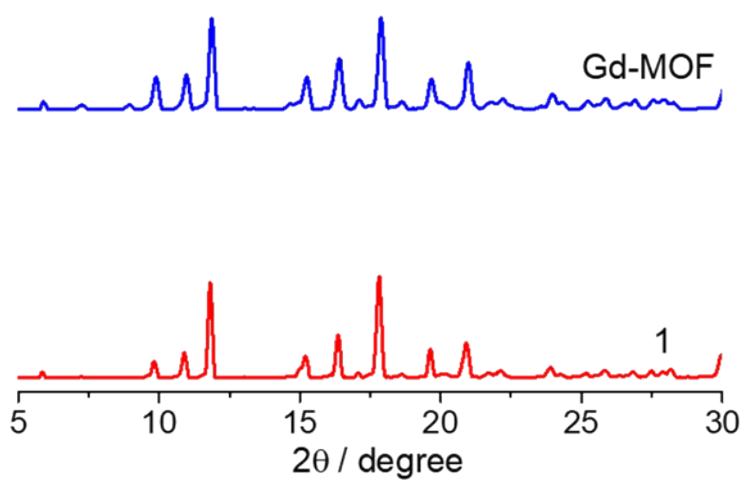


Fig. S9 PXRD profiles of **1** and the Gd(III) counterpart.

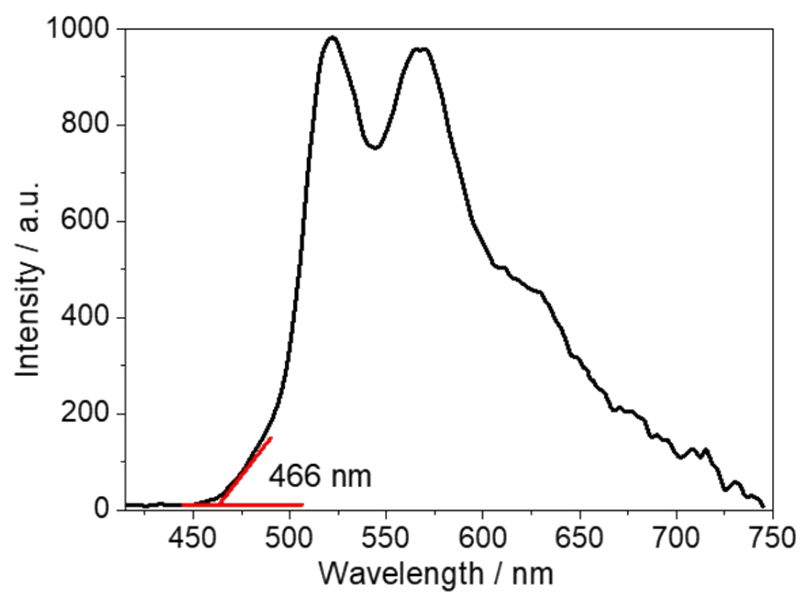


Fig. S10 Phosphorescence spectrum of the Gd(III) MOF at 77 K.

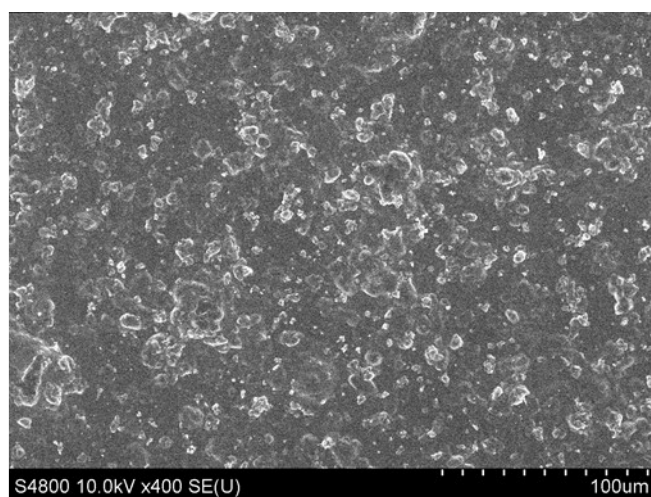


Fig. S11 SEM image of the 1-PVDF membrane.

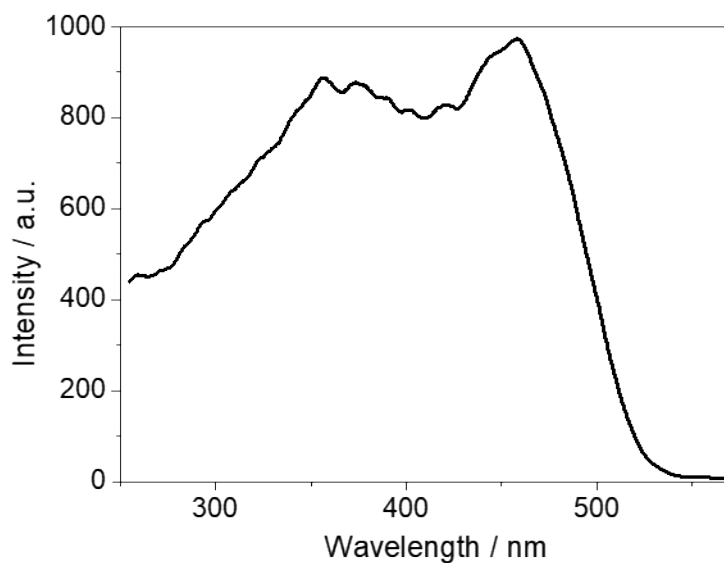


Fig. S12 Solid-state excitation spectra of the **1**-PVDF membrane.

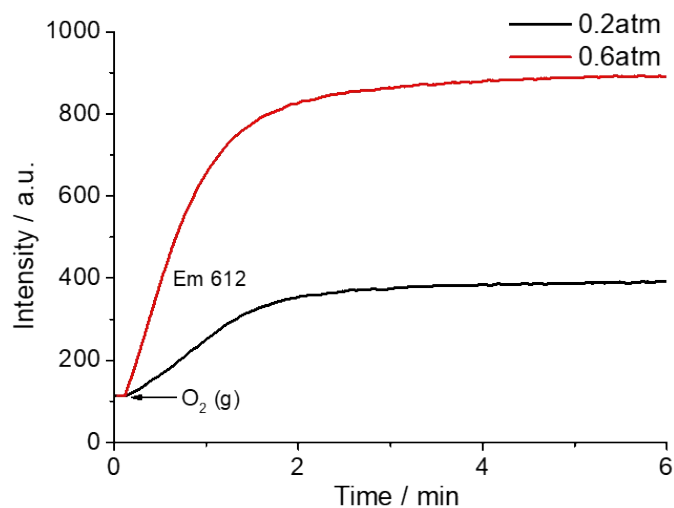


Fig. S13 Variation of luminescence (emission at 612 nm) with time of **1a**-PVDF membrane when adding O₂.

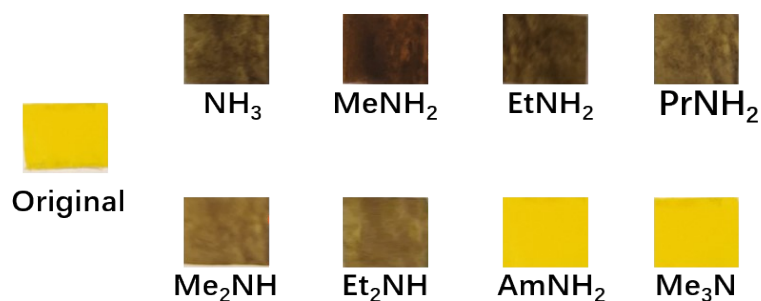


Fig. S14 The photos show the **1**-PVDF membrane before and after exposure to different amines.

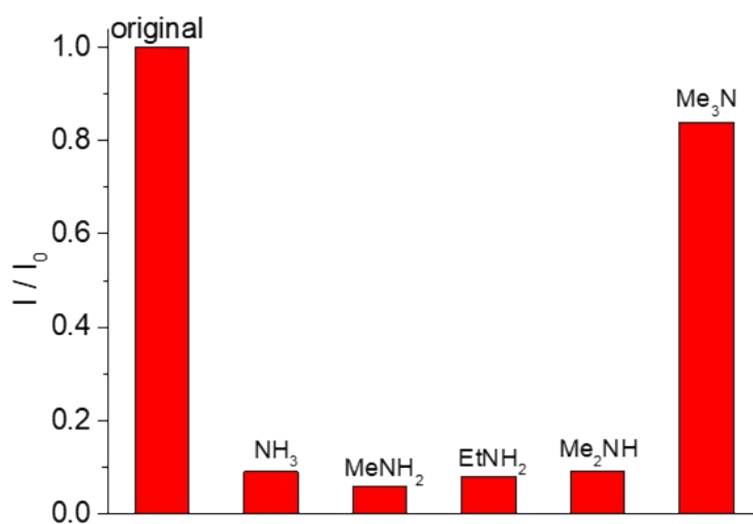


Fig. S15 The relative intensity at 612 nm for the **1**-PVDF membrane before and after exposure to various amine vapors.

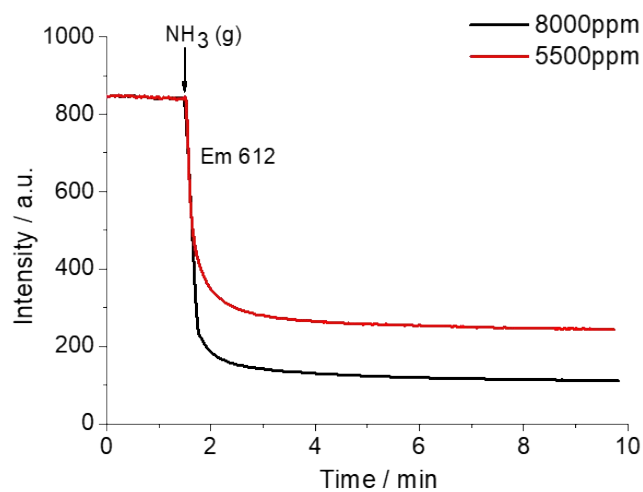


Fig. S16 Variation of the emission intensity of **1**-PVDF at 612 nm with time when adding NH_3 .

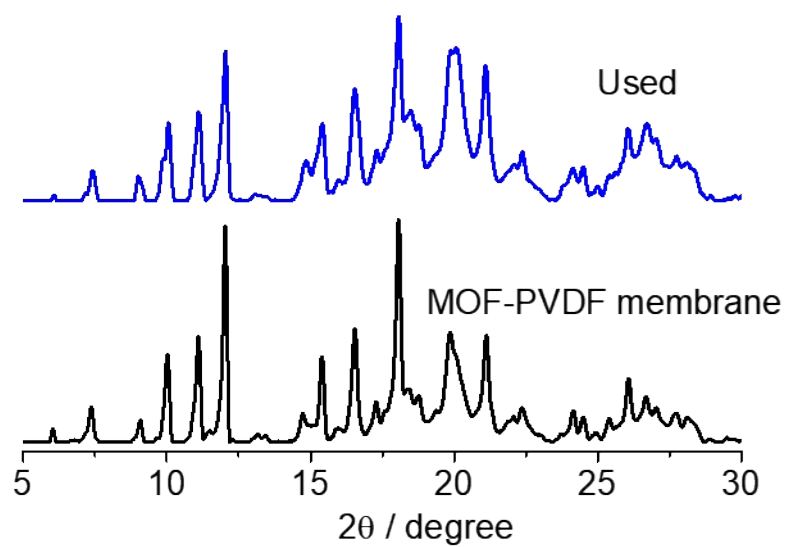


Fig. S17 PXRD profiles of the **1**-PVDF membrane before and after 5 cycles of NH_3 -sensing.

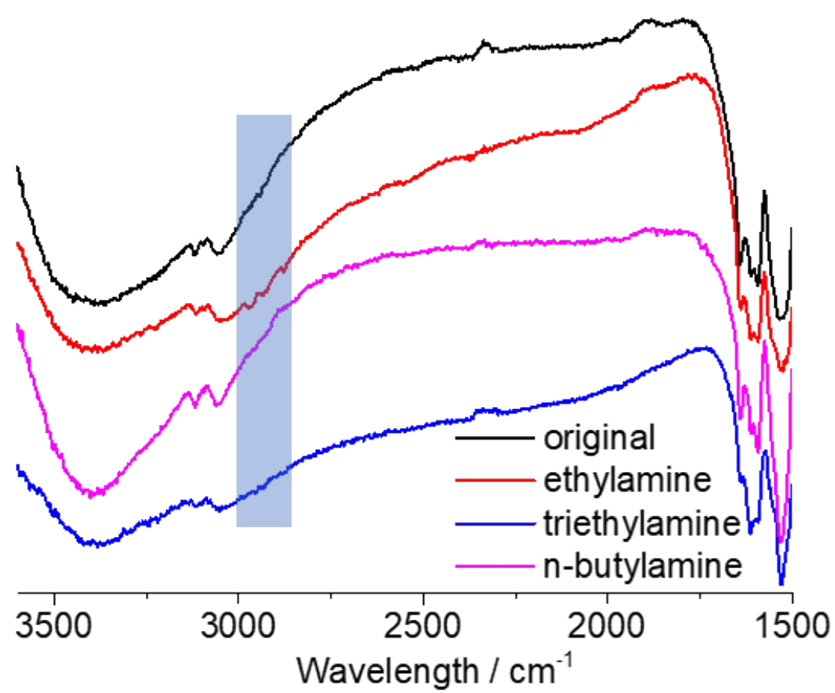


Fig. S18 IR spectra of **1** before and after fuming with different amines.

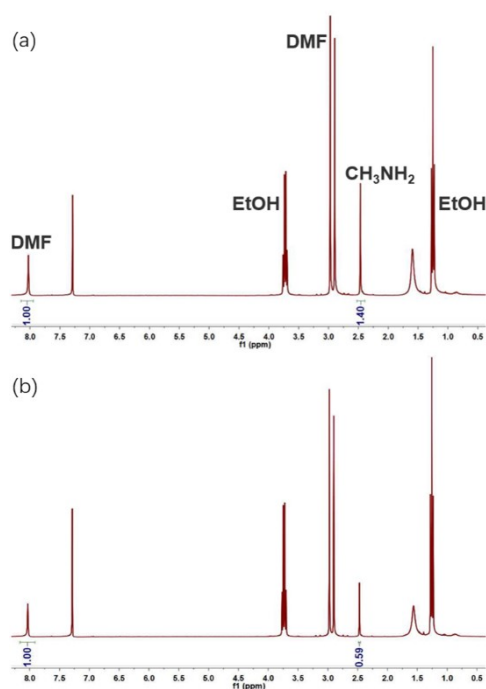


Fig. S19 ^1H NMR spectra of Methylamine/ CDCl_3 solutions before (a) and after (b) addition of the MOF. (150 mg MOF was added to the mixture containing 15.0 ml CD_3Cl , 75.0 μL Methylamine/ethanol solution (25.0 wt%), 100 μL N, N-Dimethylformamide (DMF) as internal standard and stir for 2h, then take the supernatant for ^1H NMR test).

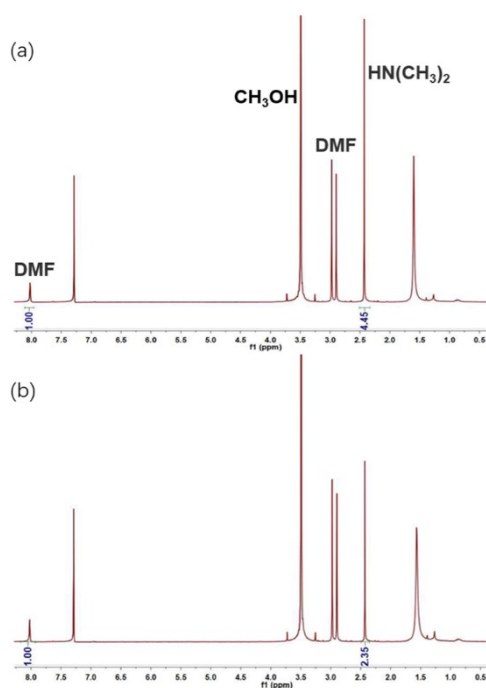


Fig. S20 ^1H NMR spectra of Dimethylamine/ CDCl_3 solutions before (a) and after (b) addition of the MOF. (300 mg MOF was added to the mixture containing 15.0 ml CD_3Cl , 475 μL Dimethylamine/methanol solution (2.00 mol/L), 100 μL DMF as internal standard and stir for 2h, then take the supernatant for ^1H NMR test).

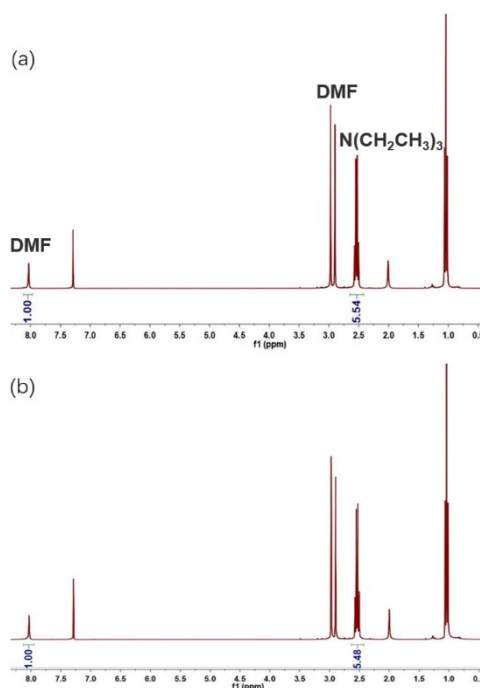


Fig. S21 ^1H NMR spectra of Triethylamine / CDCl_3 solutions before (a) and after (b) addition of the MOF. (300 mg MOF was added to the mixture containing 15.0 ml CD_3Cl , 165 μL Triethylamine, 100 μL DMF as internal standard and stir for 2h, then take the supernatant for ^1H NMR test).

References

1. B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules, *J. Chem. Phys.*, 1990, **92**, 508-517.
2. B. Delley, From molecules to solids with the DMol³ approach, *J. Chem. Phys.*, 2000, **113**, 7756-7764.
3. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3-8.
4. A. L. Spek, PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 9-18.