Supporting Information

Photoinduced-electron-transfer-driven Surface Modification to Regulate Adsorption Behaviour in A Pyridinium-decorated Metal−Organic Framework

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Section 1. Experimental section

1.1 Materials and instruments

All chemicals and reagents were obtained from commercial sources and used without further purification. Infrared spectrum (IR) was measured from KBr pellet on a Nicolet iS10 FT-IR spectrometer. Powder X-ray diffraction (PXRD) pattern was recorded with a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ=1.54056 Å). Thermogravimetric analysis (TGA) was collected on a Mettler Toledo TGA/DSC 1/1100 analyzer in a flowing air atmosphere at a heating rate of 20 °C min^{-1} from 25 to 1000 °C. UV-Vis spectral measurement was carried out at room temperature by using a PE Lambda 900 spectrometer. Elemental analysis (C, H, N) was performed using a Vario EL III CHNOS elemental analyzer. Electron spin resonance (ESR) signal was collected with a JES-FA200 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a ULVAC PHI Quantera SXM X-ray photoelectron spectrometer using Al Kα radiation (X-ray beam spot 200 μm). Energy-dispersive spectroscopy (EDS) measurement was performed on a JSM-7500F scanning electron microscope. Vapor-phase adsorption isotherm was measured with an Intelligent Gravimetric Sorption Analyzer IGA100B from the Hiden Corporation. N_2 and CO_2 adsorption isotherms were measured on a Quantachrome Instrument ASiQMVH002-5. The activated samples of **Eu-TPC** were heated at 100 °C under vacuum environment for 5 h. The weight changing curve and PXRD pattern reveal that all the coordinated and guest water molecules ($10H_2O$ of per formula unit) are removed completely and the open channels still remain after activation (Figure S26-S27).

1.2 Synthesis

Ligand: $H_3TTTPCBr_3$ were synthesized according to the previously reported literature.[1]

Eu-TPC: $H_3TTTPCBr_3$ (40.00 mg, 0.06 mmol) was dissolved in distilled water (5 mL) and the pH value was adjusted to 7 with 0.1 mol/L NaOH solution. $Eu(NO_3)_3{\cdot}6H_2O$ (44.61 mg, 0.10 mmol) was added to the solution, then sealed in a 25 mL glass bottle after stirring for 20 minutes. The glass bottle was heated at 90 °C for 3 days and then cooled to room temperature gradually. After being filtered, the filtrate was allowed to stand at room temperature for slow evaporation. Colourless block crystals were obtained within a few days. The yield is about 60% based on Eu.

Reference:

[1] G.-Q. Kong, C.-D. Wu, *Cryst. Growth Des*. 2010, **10**, 4590.

1.3 X-ray crystallographic analysis

The X-ray diffraction data of **Eu-TPC** was collected on a Gemini A Ultra diffractometer with graphite monochromated Mo Kα radiation (λ= 0.71073 Å) at room temperature. The absorption correction was performed by using the multi-scan program and the structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXL-2016 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms except those attached to coordinated water molecules were calculated in ideal positions and refined by riding on their respective carbon atoms, while the hydrogen atoms of the coordinated water molecules were first determined by difference Fourier map and then fixed at the calculated positions. The guest molecules and dissociative NO_3^- anions in the pore of **Eu-TPC** cannot be modeled properly for their high disorder, and its formula is derived from the crystallographic data combined with energy-dispersive spectroscopy (EDS), infrared spectrum (IR), thermogravimetric analysis (TGA) and elemental analysis.

Table S1. Crystal Data and Structural Refinement Parameters of **Eu-TPC**

Compound name	**Eu-TPC**
Structural formula	$[Eu(TTTPC)(H_2O)_2]\cdot 2NO_3\cdot Br\cdot 8H_2O$
Empirical formula	$EuBrO_{22}N_5C_{30}H_{47}$
Formula weight	1061.58
Temperature (K)	293
Crystal system	Triclinic
Space group	*P-1*
a (Å)	9.5744(3)
b (Å)	12.8702(6)
c (Å)	18.8207(9)
α (°)	107.276(4)
β (°)	98.664(3)
γ (°)	97.376(3)
Volume (Å^3)	2152.14(17)
Z	2
D_{calcd} (g/cm^3)	1.638
Absorption coefficient (mm^{-1})	2.471
F(000)	1072
Reflections collected/unique	20984/10196 (R_{int}=0.0316)
GOOF on F^2	1.102
R_1, wR_2 ($I > 2\sigma(I)$)	0.0635, 0.1856
R_1, wR_2 (all date)	0.0763, 0.1963

Table S2 Elemental analyses of **Eu-TPC**, **Eu-TPC-I$_2$** and **Eu-TPC-365 nm-I$_2$**

Compound	Empirical formula	Calculated (%)			Experiment (%)		
		C	N	H	C	N	H
Eu-TPC	$[Eu(TTTPC)(H_2O)_2]\cdot 2NO_3\cdot Br\cdot 8H_2O$	33.94	6.60	4.46	33.95	6.80	4.47
Eu-TPC-I$_2$	$[Eu(TTTPC)(H_2O)_2]\cdot 2NO_3\cdot Br\cdot 6H_2O\cdot 0.25I_2$	33.08	6.43	3.98	33.26	6.52	4.34
Eu-TPC-365 nm-I$_2$	$[Eu(TTTPC)(H_2O)_2]\cdot 2NO_3\cdot Br\cdot 6H_2O\cdot 0.05I_2$	34.70	6.75	4.17	34.95	6.66	4.03

Section 3. Additional Data and Figures

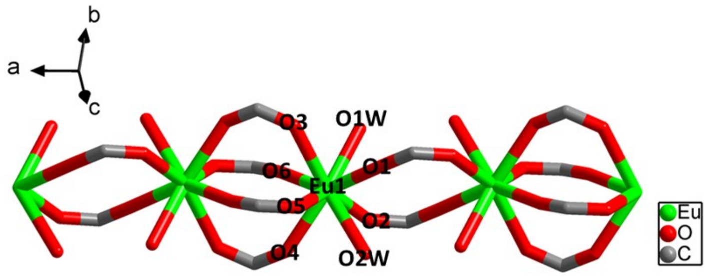

Fig. S1 The 1D $[Eu(COO)_3(H_2O)_2]_n$ chain in **Eu-TPC.**

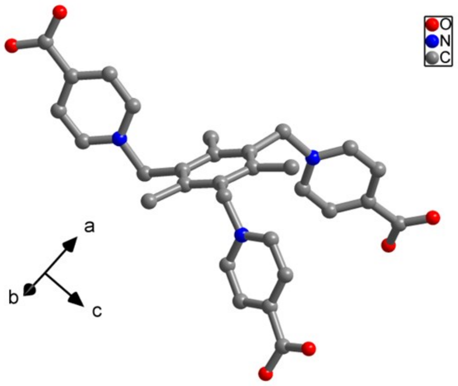

Fig. S2 The chair-shaped configuration of TTTPC ligand in **Eu-TPC**.

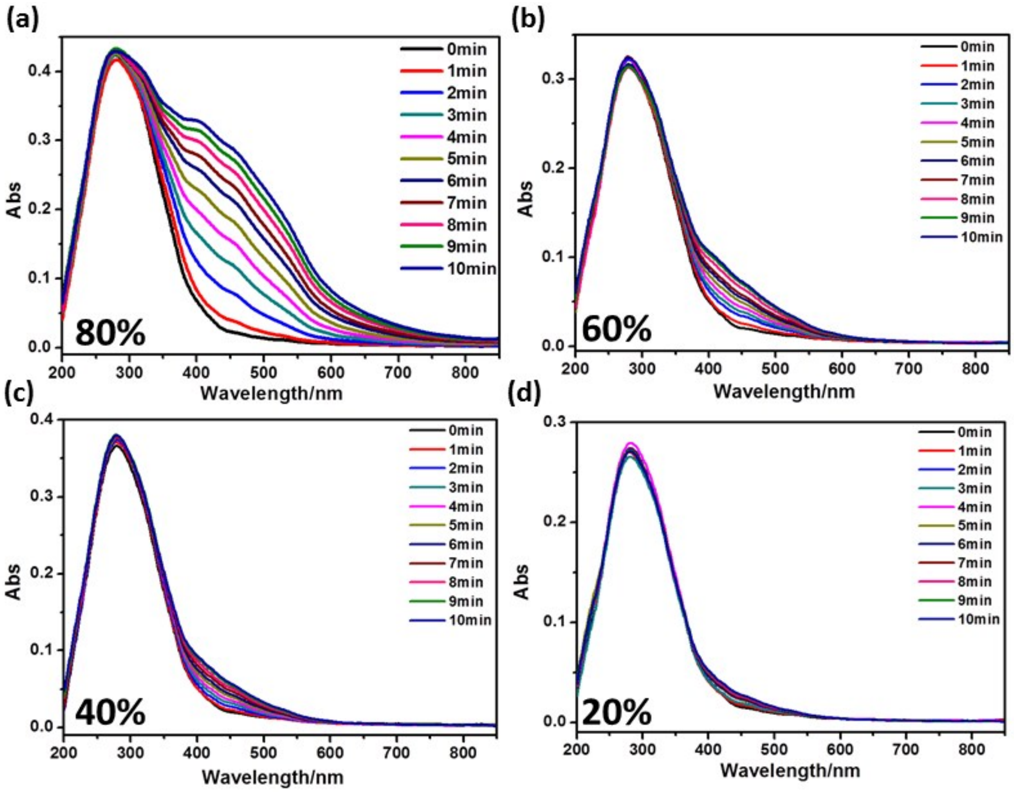

Fig. S3 The UV-Vis absorption spectra of **Eu-TPC** after the irradiation of 365 nm light in 80% power (a), 60% power (b), 40% power (c) and 20% power (d).

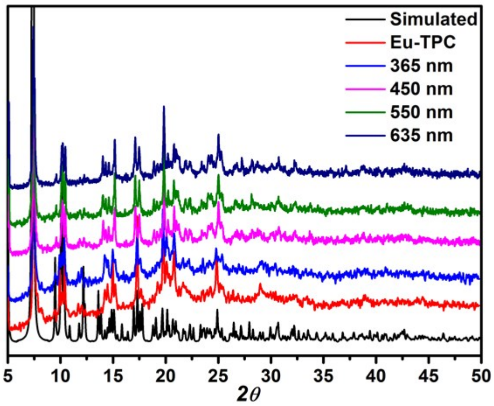

Fig. S4 PXRD patterns of **Eu-TPC** before and after the irradiation of 365 nm, 450 nm, 550 nm and 635 nm. In comparison with the simulated pattern, some peaks are not presented due to the effect of crystal orientation.

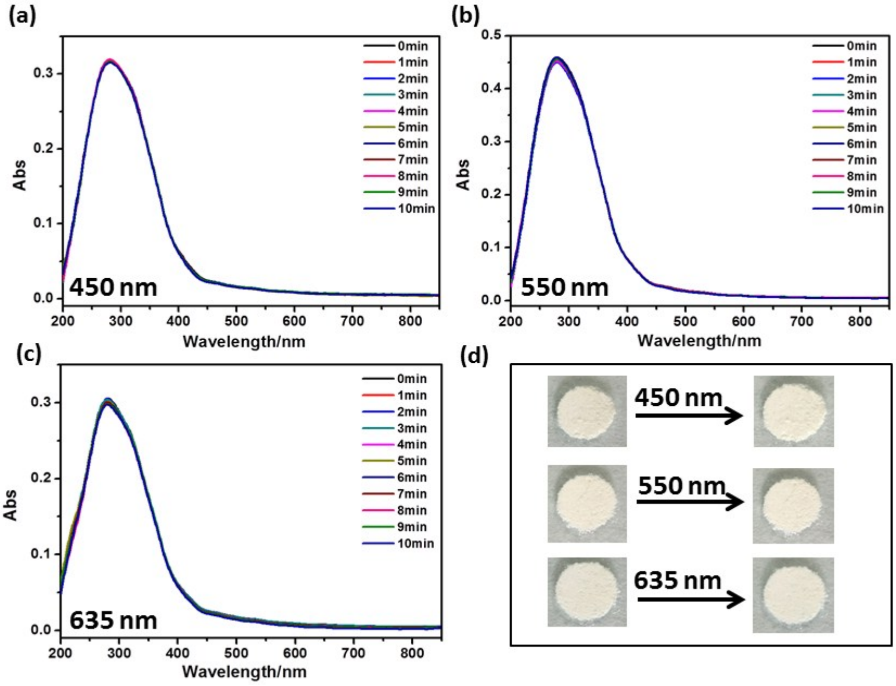

Fig. S5 The UV-Vis absorption spectra of **Eu-TPC** after the irradiation of 450 nm light (a), 550 nm light (b) and 635 nm light (c). The color development of **Eu-TPC** before and after 450 nm light, 550 nm light and 635 nm light, respectively (d).

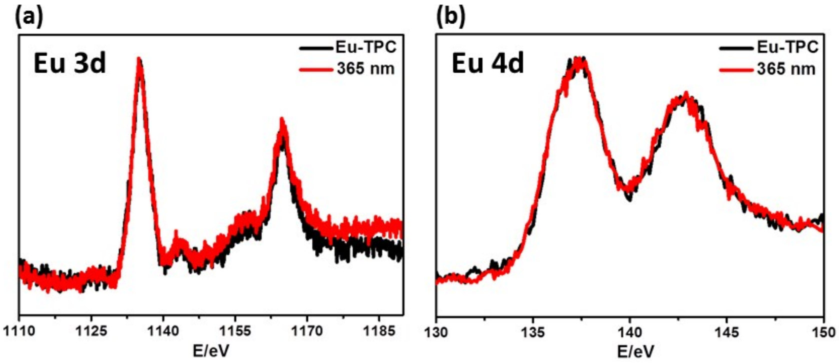

Fig. S6 XPS core-level spectra of Eu-3d (a) and Eu-4d (b) in **Eu-TPC** before and after 365 nm light irradiation.

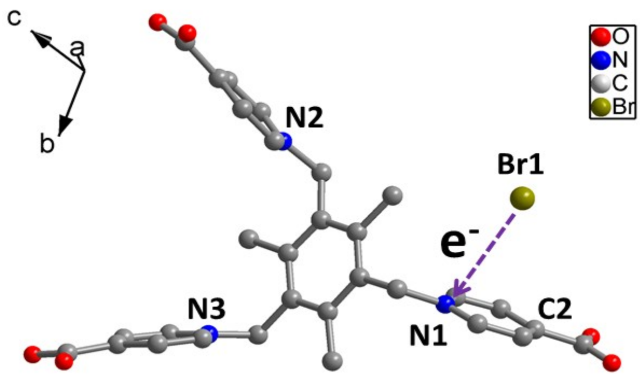

Fig. S7 The orientation diagram of Br- ion and TTTPC ligand in **Eu-TPC**.

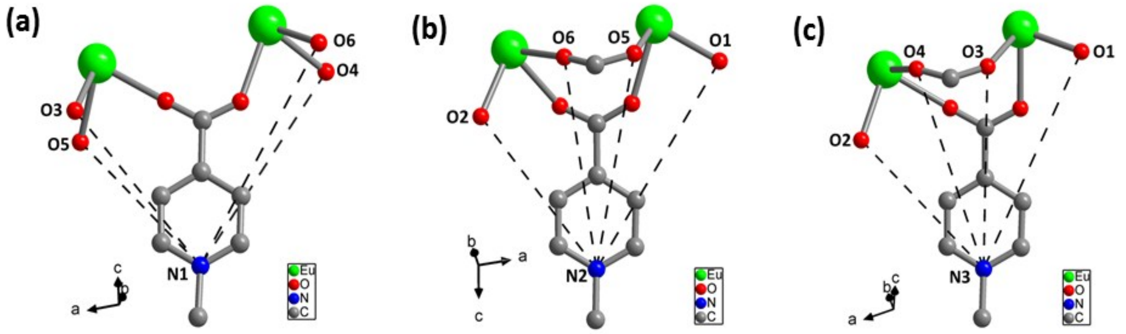

Fig. S8 (a) The distance between the positively charged pyridinium N1 atom and surrounding carboxylate O atoms in **Eu-TPC** ($d_{O3\cdots N1}$ = 5.73 Å, $d_{O4\cdots N1}$ = 7.20 Å, $d_{O5\cdots N1}$ = 5.63 Å, $d_{O6\cdots N1}$ = 7.19Å). (b) The distance between the positively charged pyridinium N2 atom and surrounding carboxylate O atoms in **Eu-TPC** ($d_{O1\cdots N2}$ = 7.15 Å, $d_{O2\cdots N2}$ = 5.78 Å, $d_{O5\cdots N2}$ = 6.79 Å, $d_{O6\cdots N2}$ = 6.49 Å). (c) The distance between the positively charged pyridinium N3 atom and surrounding carboxylate O atoms in **Eu-TPC** ($d_{O1\cdots N3}$ = 7.37 Å, $d_{O2\cdots N3}$ = 5.49 Å, $d_{O3\cdots N3}$ = 6.49 Å, $d_{O4\cdots N3}$ = 6.66 Å).

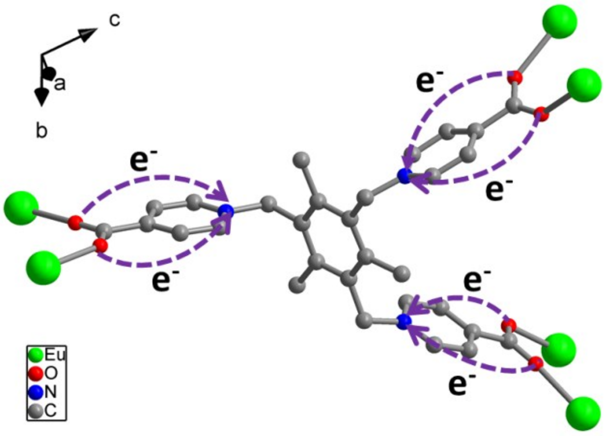

Fig. S9 The intramolecular conjugated pathways for PET reaction in **Eu-TPC**.

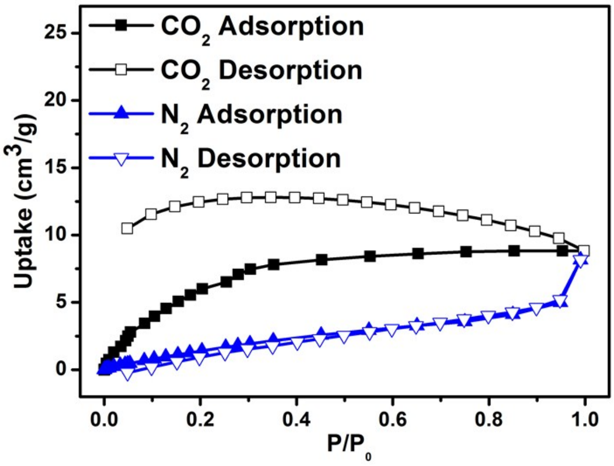

Fig. S10 The isotherms of **Eu-TPC** toward CO_2 (273.15 K, uptake: 8.82 cm^3/g) and N_2 (77 K, uptake: 8.16 cm^3/g). The slight floatation of the CO_2 desorption isotherm is caused by the measurement deviation due to its low adsorption uptake.

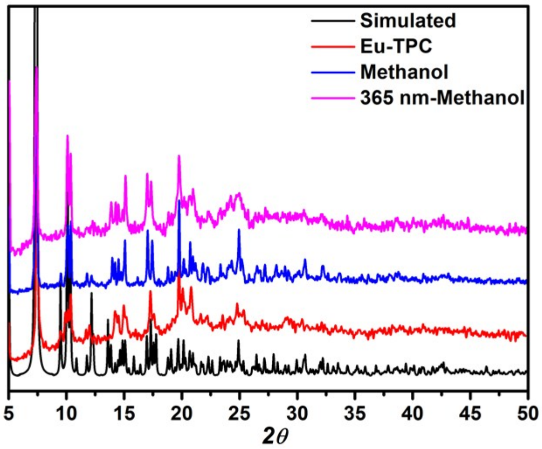

Fig. S11 PXRD patterns of **Eu-TPC** (red), original sample after methanol adsorption (blue) and coloured sample after methanol adsorption (pink).

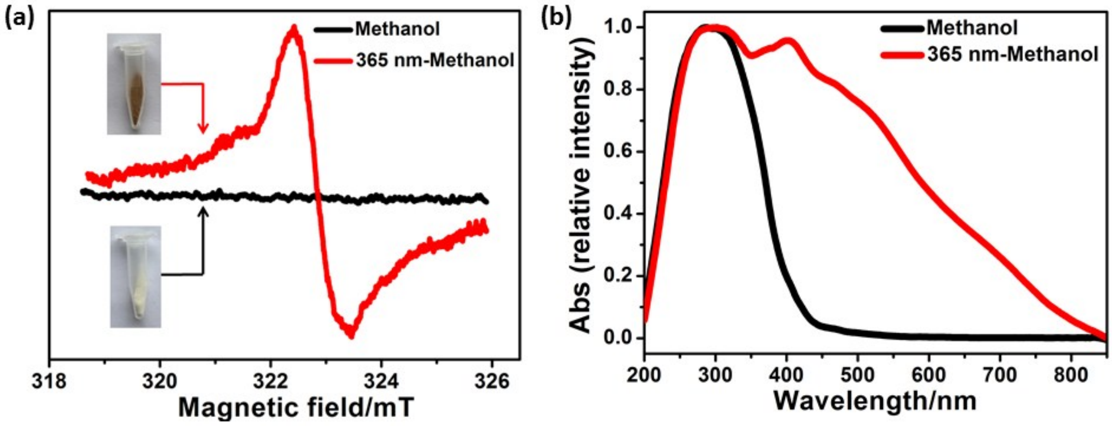

Fig. S12 (a) ESR spectra of original sample after methanol adsorption and coloured sample after methanol adsorption. (b) UV-Vis absorption spectra of original sample after methanol adsorption and coloured sample after methanol adsorption.

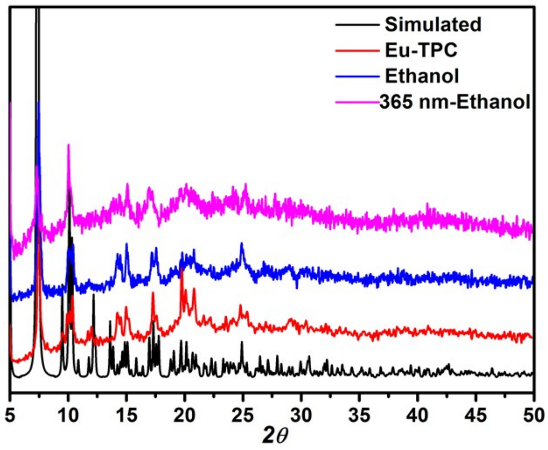

Fig. S13 PXRD patterns of **Eu-TPC** (experimental: red; simulated: black), original sample after ethanol adsorption (blue) and coloured sample after ethanol adsorption (pink).

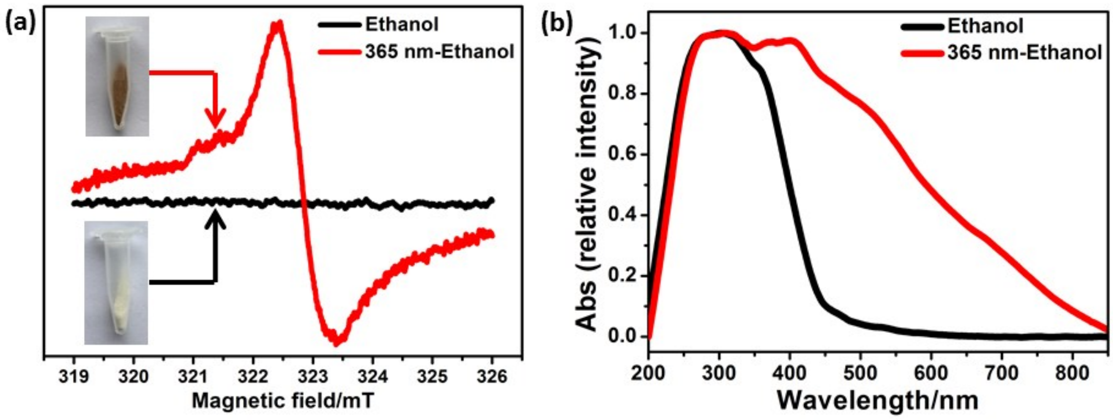

Fig. S14 (a) ESR spectra of original sample after ethanol adsorption and coloured sample after ethanol adsorption. (b) UV-Vis absorption spectra of original sample after ethanol adsorption and coloured sample after ethanol adsorption.

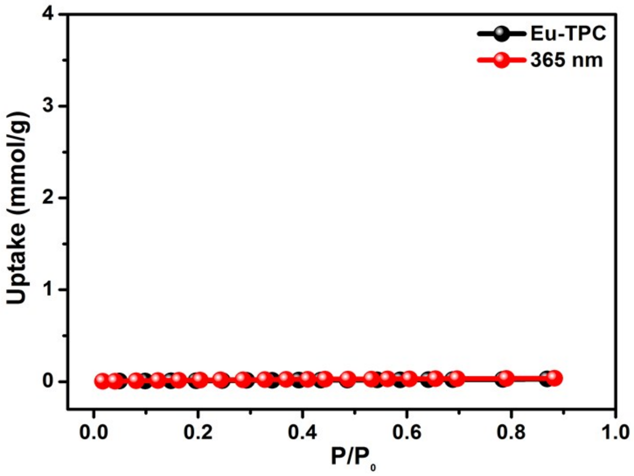

Fig. S15 The adsorption isotherms of **Eu-TPC** toward cyclohexane before and after the irradiation of 365 nm light.

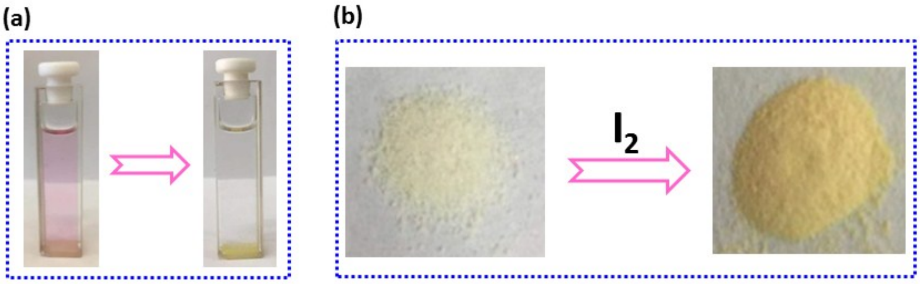

Fig. S16 (a) The color change of the cyclohexane solution of I_2 before and after encountering **Eu-TPC**. (b) The color change of **Eu-TPC** before and after I_2 adsorption.

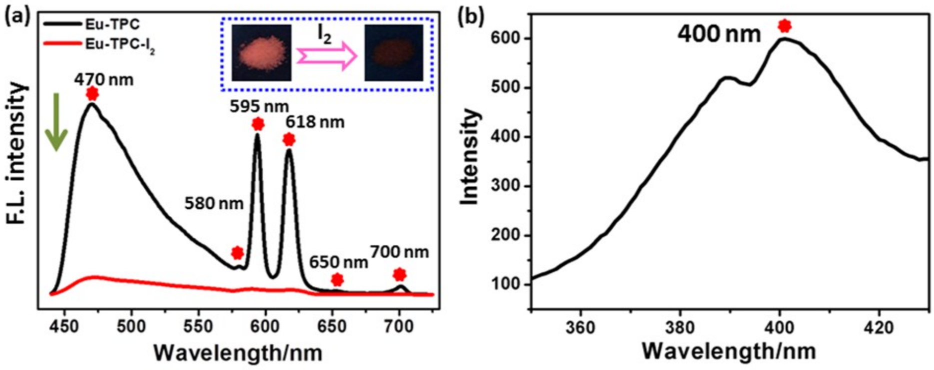

Fig. S17 (a) The fluorescence emission of **Eu-TPC** before and after I_2 adsorption. (b) The excitation spectrum (λ_{ex} = 400 nm) of **Eu-TPC**.

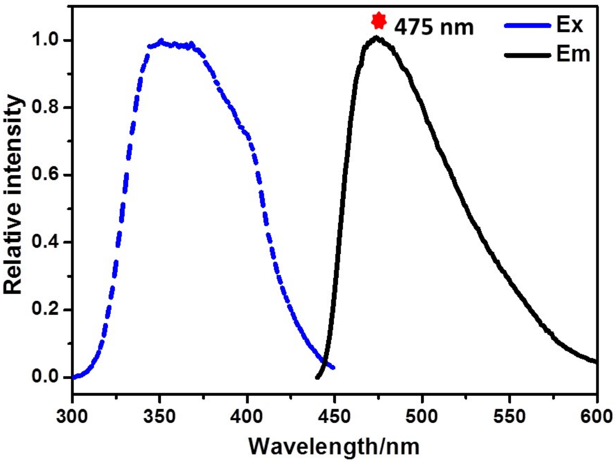

Fig. S18 The fluorescence excitation (blue, λ_{ex} = 350 nm) and emission (black, λ_{em} = 475 nm) spectra of $H_3TTTPBr_3$ measured in an aqueous solution (1×10^{-3} mol L^{-1}) which was adjusted to pH = 7 with 0.1 mol L^{-1} NaOH solution.

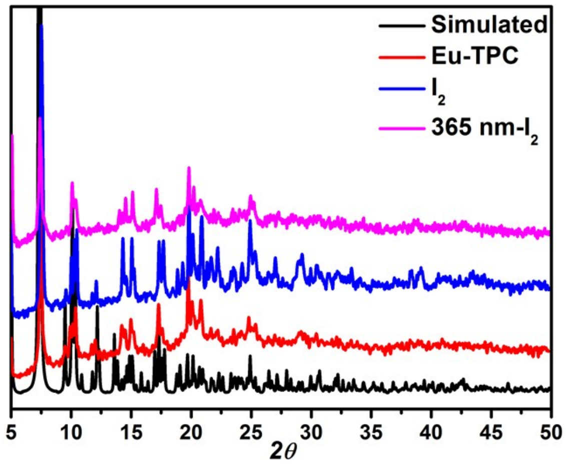

Fig. S19 PXRD patterns of **Eu-TPC** (red), original sample after I_2 adsorption (blue) and coloured sample after I_2 adsorption (pink).

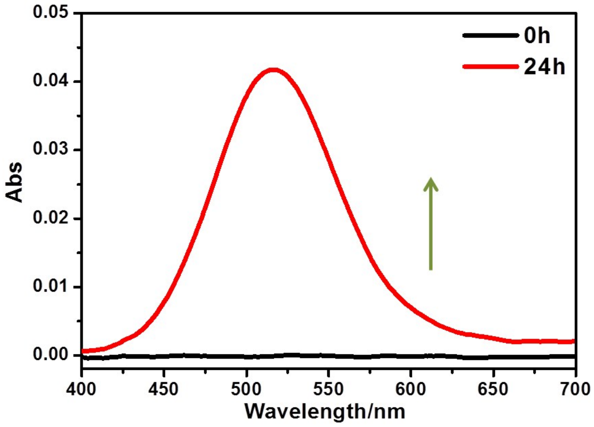

Fig. S20 UV-Vis absorption spectra monitored with time during the release process of I_2 in CCl_4 solvent.

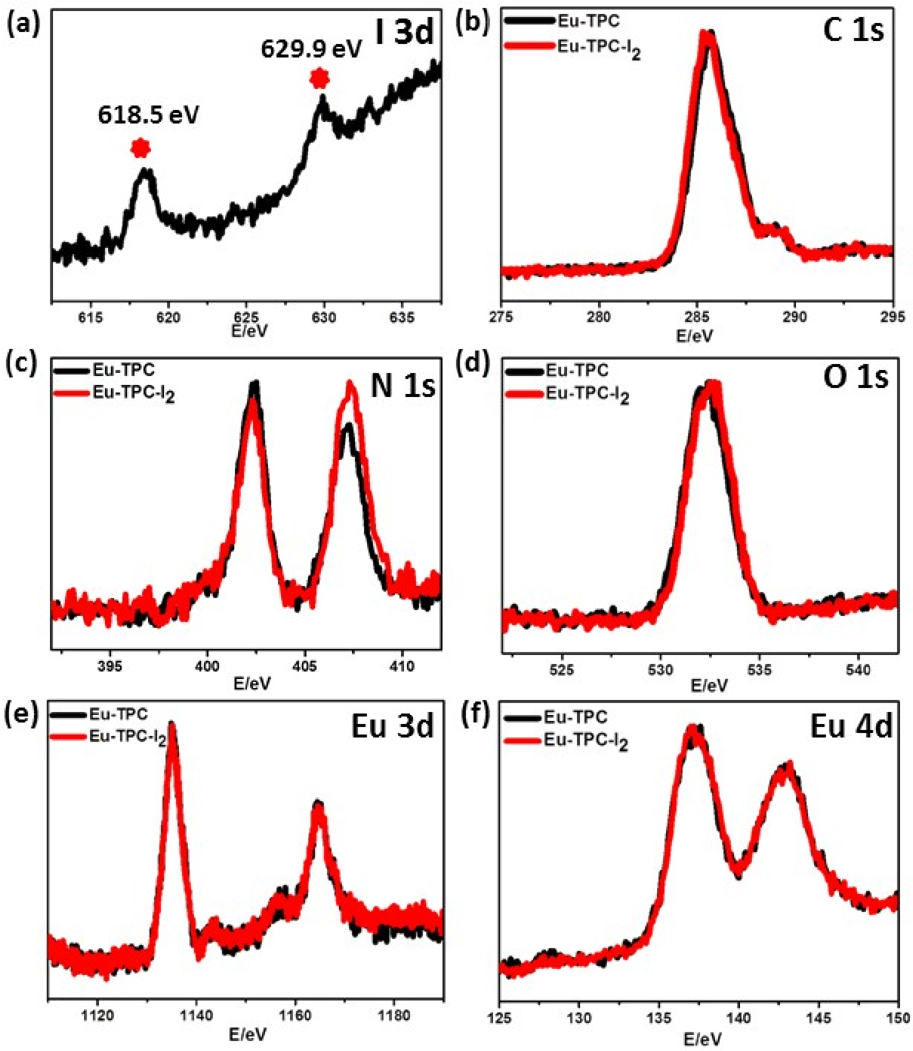

Fig. S21 XPS core-level spectra of I 3d (a), C 1s (b), N 1s (c), O 1s (d), Eu 3d (e) and Eu 4d (f) in **Eu-TPC** after I_2 adsorption.

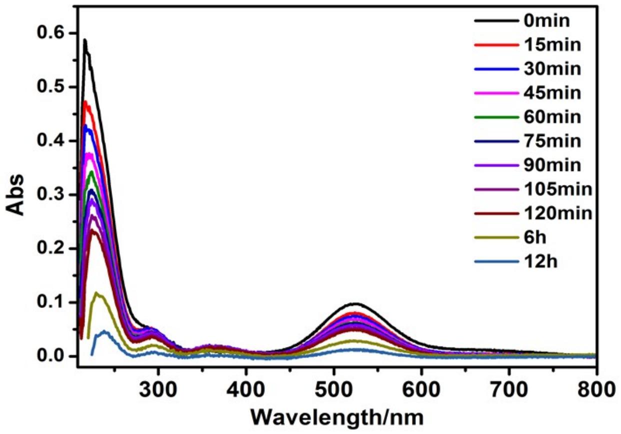

Fig. S22 Sequential UV−Vis absorption spectra of I_2 in cyclohexane solution (1×10^{-4} mol/L, 3 mL) in the presence of **Eu-TPC** (20 mg) irradiated by 365 nm light for 3 h.

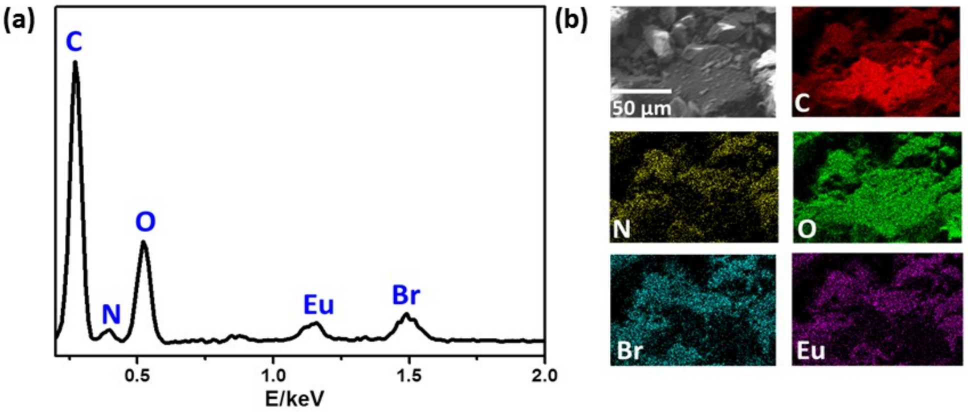

Fig. S23 (a) The EDS spectrum of **Eu-TPC**. (b) The EDS mapping of the existing elements in **Eu-TPC**.

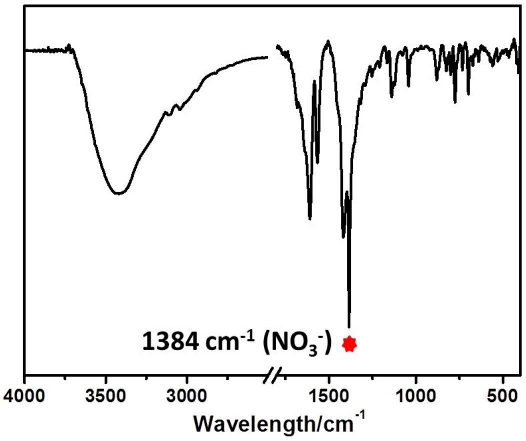

Fig. S24 The IR spectra of **Eu-TPC**. The characteristic peak at 1384 cm^{-1} can confirm the existence of NO_3^- anion in the structure.

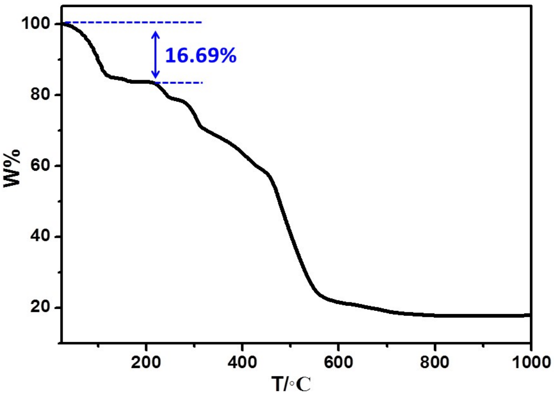

Fig. S25 TGA curve of **Eu-TPC**. It reveals a weight loss of 16.69% from 25 to 215 °C corresponding to the release of two coordinated and eight dissociative water molecules in the lattice (calcd: 16.97%), and then the framework collapses upon further heating.

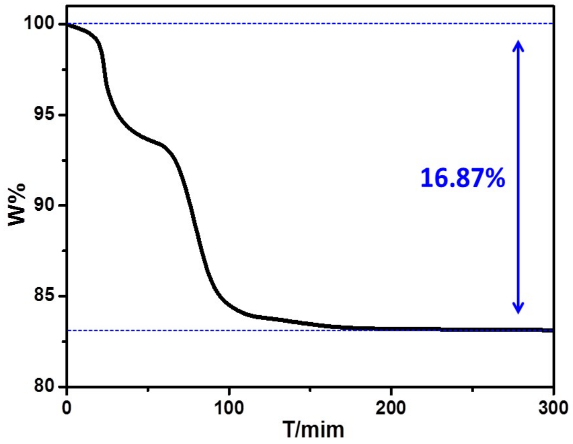

Fig. S26 Weight changing curve of **Eu-TPC** alone with time in vacuum environment. It shows that all the coordinated and dissociative water molecules (10H_2O, 16.87 %, Cal: 16.97 %) in the open channels are lost when placed in vacuum environment at 100 ºC for 5 h.

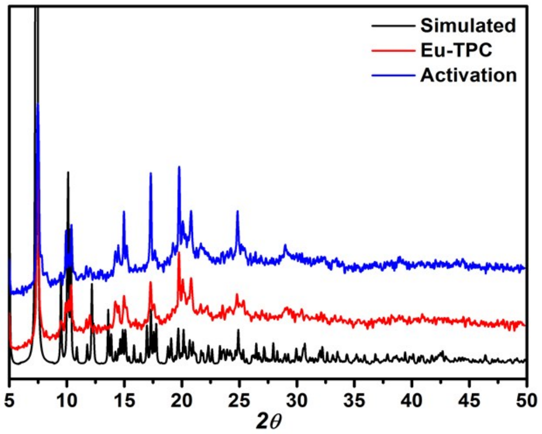

Fig. S27 PXRD patterns of **Eu-TPC** before and after heated at 100 ˚C for 5 h in vacuum.