

Supporting Information

Wearable glove sensor for non-invasive organophosphorus pesticides detection based on double-signal fluorescence strategy

Xiao-Yu Xu, Bing Yan* and Xiao Lian

School of Chemical Science and Engineering, Tongji University, Siping Road 1239, Shanghai 200092, P. R. China

Experimental Section

Materials and methods

Barium nitrate ($\text{Ba}(\text{NO}_3)_2$) and 1,3,5-benzenetricarboxylic acid (BTB) ligand was purchased from Adamas. Citric acid (CA) was purchased from Aldrich. $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving oxides Eu_2O_3 in concentrated nitric acid (HNO_3) followed by evaporation and crystallization. All the other chemicals were commercially available reagents and used without further purification. Powder X-ray diffraction patterns (PXRD) were recorded with a Bruker D8 diffractometer under CuK α radiation. Fourier transform infrared (FTIR) spectra were collected on a Nexus 912 AO446 infrared spectrum radiometer in the spectral range of 400-4000 cm^{-1} using the KBr disk method. The UV-Vis absorption spectra were recorded on an Agilent 8453 UV-Vis spectrometer in the range of 190-1100 nm and the wavelength resolution of the instrument was 1 nm. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2010F electron microscope operated at 200 kV. The scanning electron microscope (SEM) images were recorded with a Hitachi S-4800 equipped with an energy dispersive X-ray spectrometer. The gas adsorption/desorption isotherms for N_2 at 77 K were carried out on a Tristar 3020 analyzer. Surface areas were calculated by the BET method. The measurement of metal ion was performed on Perkin Elmer 8300 ICP-OES. X-ray photoelectron spectra (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K α radiation ($h\nu = 1253.6$ eV). Thermogravimetric analysis (TGA) was measured using a Netsch STA 449C system at a heating rate of 15 K min^{-1} under nitrogen protection. The excitation/emission spectra and decays were recorded on an Edinburgh FLS920 fluorescence spectrophotometer equipped with both continuous (450 W) Xenon and pulsed flash lamps. The absolute external luminescent quantum efficiency was determined employing an

integrating sphere (150 mm diameter, BaSO₄ coating) from an Edinburgh FLS920 phosphorimeter.

Synthesis process

BaMOFs: A typical synthesis procedure of BaMOFs is prepared by using a modified procedure from the literature.^[16] Ba(NO₃)₂ (0.2 mmol, 0.052 g) and BTB (0.2 mmol, 0.087 g) were weighted to a 23 mL Teflon-lined stainless steel container and dissolved in 10 mL DMF. After being sonicated, the mixture was kept in oven at 100 °C for 120 h. When cooling to room temperature naturally, the colorless crystals were separated from the mixed dispersion by centrifugation (10000 rpm, 3 min) and washed with DMF.

EuMOFs: EuMOFs were synthesized via transmetallation in BaMOFs. 40 mg Eu(NO₃)₃ salt was dissolved in 10 mL DMF and added 60 mg of BaMOFs to the solution. After kept at room temperature for 30 h, the EuMOFs can be obtained.

Carbon dots (CDs): CDs were prepared directly by a simple hydrothermal method.^[17] 1.0507 g CA and 335 µL ethylenediamine were dissolved in 10 mL deionized water by sonicating for 10 min. Then, the mixture were transferred to a Teflon-lined stainless steel container (23 mL) and heated at 200 °C for 5 h to get well-dispersed CDs aqueous solutions. After purified, the dry CDs were obtained by lyophilization of the remaining aqueous solution.

EuMOFs/CDs@CMC and glove sensor: EuMOFs and dried CDs powder were added in an aqueous solution (2 mL) under ultrasonication. The mass ratio for EuMOFs and CDs adjusts to be 3.8, 4.7 and 12.5. 200 mg CMC powder was completely dissolved in 2 mL boiling water with continuously stirring. After cooled down to 40 °C, the solution of EuMOFs and CDs was added and homogenized. Then the CMC hydrogel loading with the fluorescence materials can be obtained. After aged for a few hours at room temperature, the hydrogel was then dropped into glass plate and covered with a glass slide. Hydrogel in the plate was then froze by liquid nitrogen, followed by freeze drying under 60 °C for 12 h. Finally, the prepared aerogel was cut to small wafer (1 cm diameter × 2 mm thickness) and fixed to the blue nitrile glove to construct the sensing glove.

CP sensing process

On solution: The fluorescent detection of CP was performed at room temperature in ethanol. 1 mg of as-prepared EuMOFs (or CDs) and 1 mL of 50 µM ethanol solution of CP were added into a 4.0 mL centrifuge tube and then the mixture was shaken thoroughly. Then the fluorescent spectra of the suspensions were recorded.

On surface of foods: The various target food surfaces were first rinsed with absolute ethanol, then distilled water and dried. Subsequently, the surface were contaminated using the CP compounds (100 µM in ethanol). A 500 µL aliquot of the CP solution was cast on the surface of thee fruits (apple and pear) and vegetables (green peppers and tomatoes) for two times.

Then the prepared glove sensor was worn for the sampling and detection steps. Swiping of these surfaces with the sensing finger was accomplished by abrasively rubbing them to mechanically collect analyte residues onto the attached CMC aerogel.

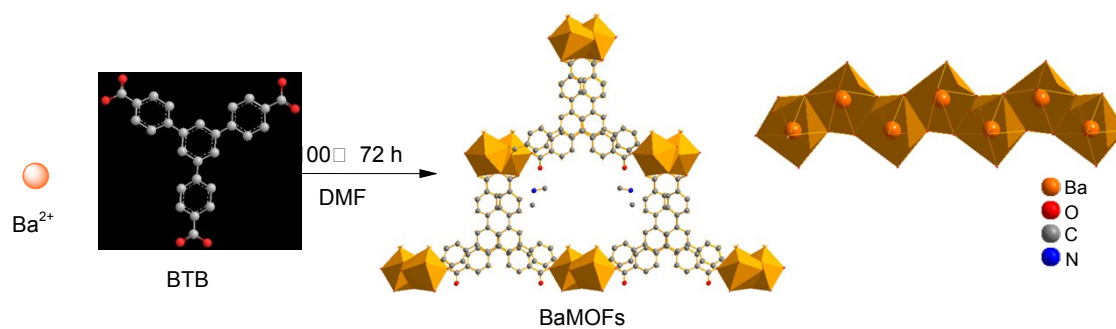


Fig. S1 The procedure to prepare BaMOFs through solvothermal reaction and Ba-O-Ba one-dimensional chain.

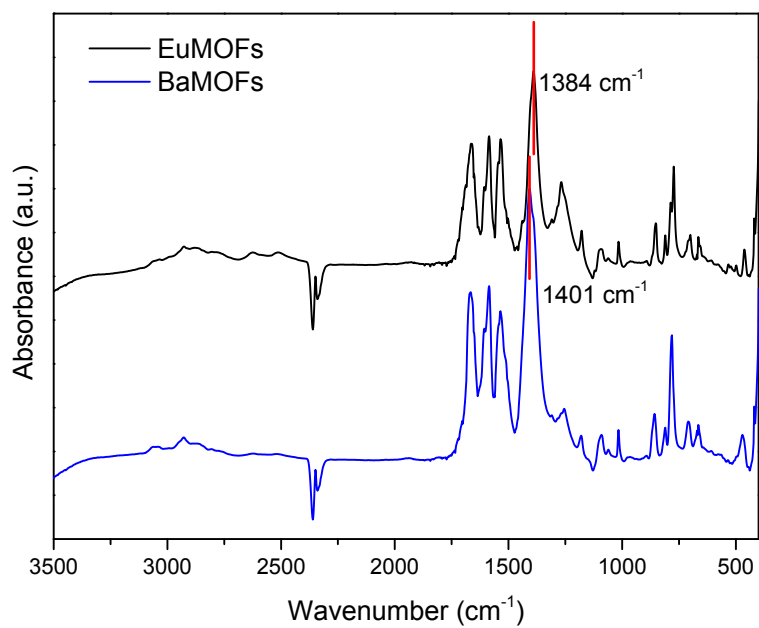


Fig. S2 FTIR spectra of BaMOFs and EuMOFs.

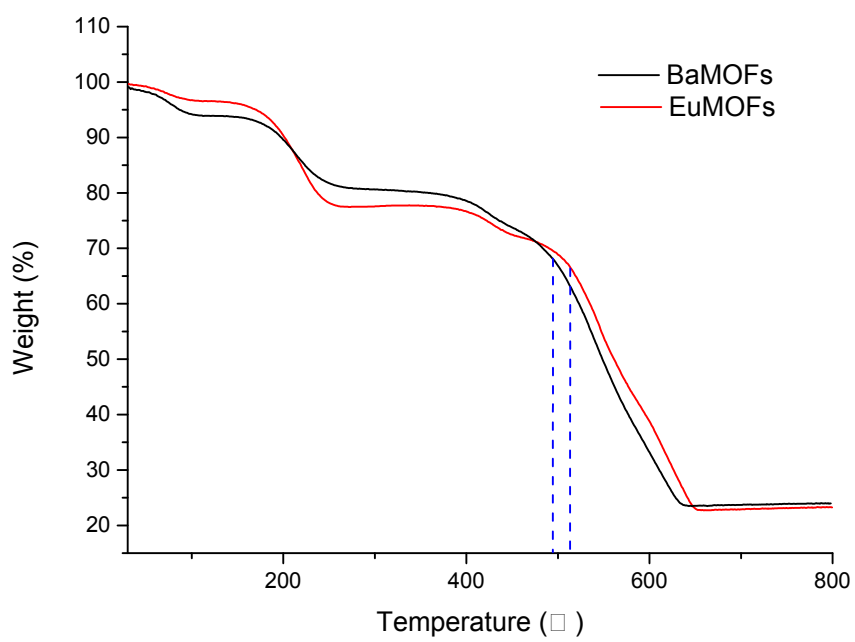


Fig. S3 Thermal gravimetric analysis (TGA) of BaMOFs and EuMOFs.

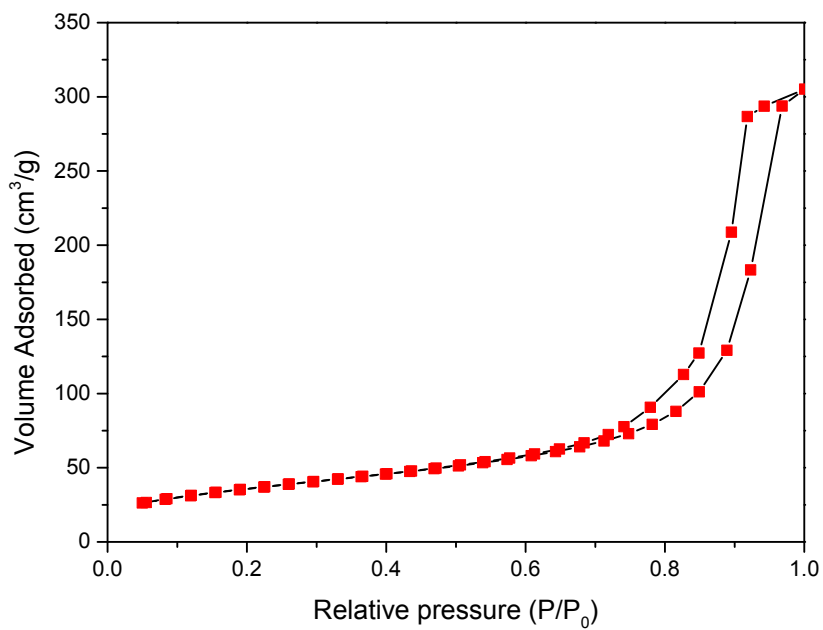


Fig. S4 N₂ adsorbing and desorption isotherms of as-synthesized EuMOFs.

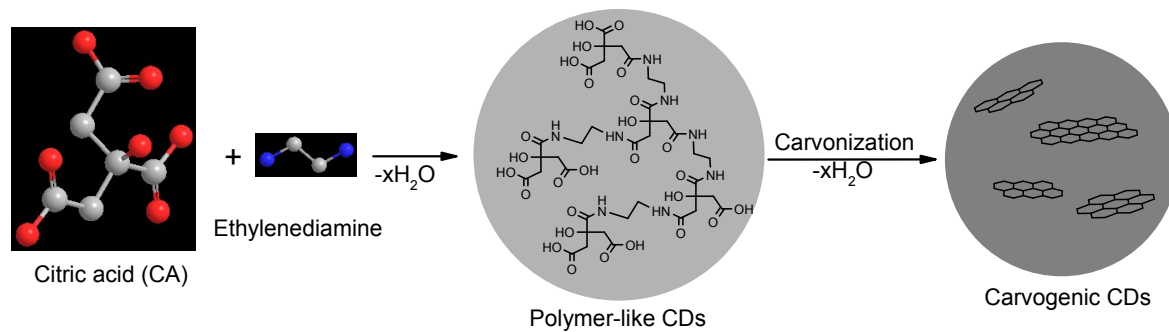


Fig. S5 A synthetic route using CA and ethylenediamine to form carvogenic CDs in aqueous solution.

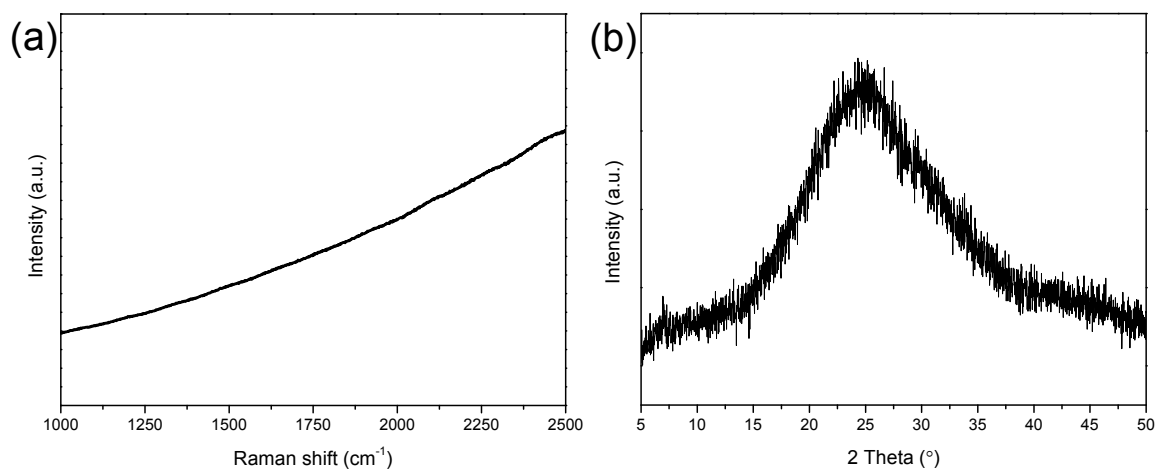


Fig. S6 (a) Raman spectrum and (b) PXRD pattern of synthesized CDs.

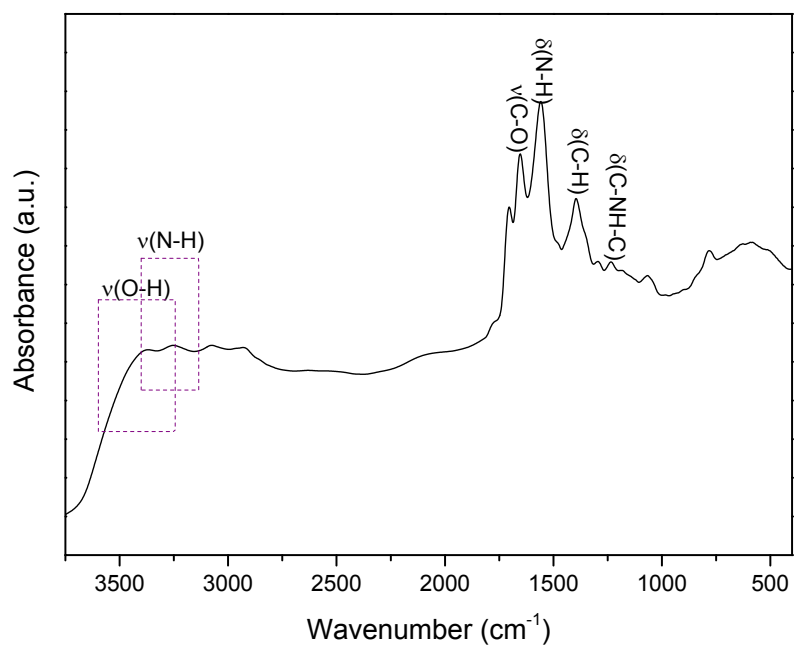


Fig. S7 FTIR spectra of CDs in the dry state.

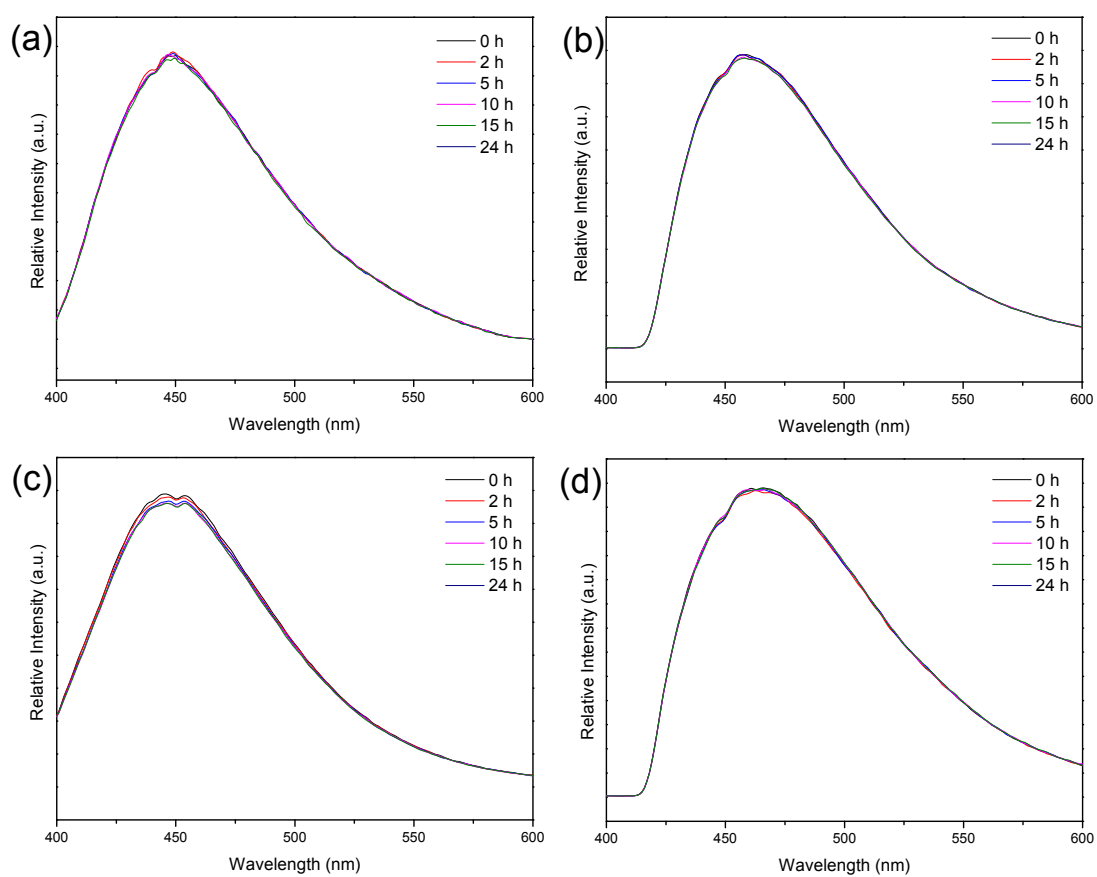


Fig. S8 Stability of fluorescent intensity of CDs solution in different solvents for 24 h: (a) H₂O; (b) methanol; (c) ethanol and (d) DMF, λ_{ex} =390 nm.

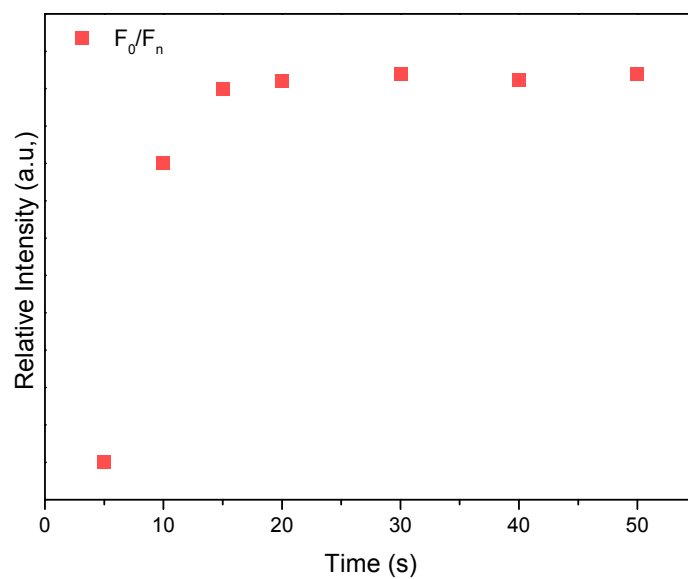


Fig. S9 Fluorescence response of EuMOFs ($\lambda_{\text{ex}}=313$ nm) with immersion time in the EtOH solution of CP (0.01 M), F_0 is the intensity of 614 nm at beginning and F_n is the intensity of 614 nm at different immersing times.

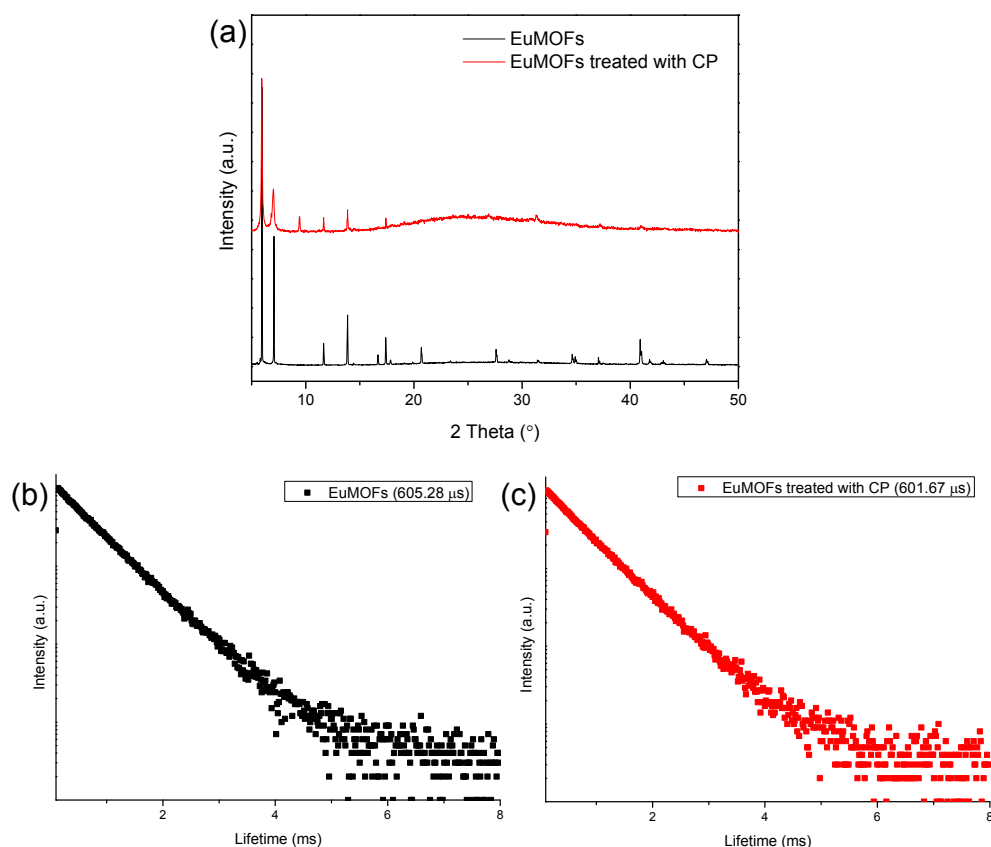


Fig. S10 (a) PXRD patterns of EuMOFs before and after treated with CP solution; the fluorescence decay curve of EuMOFs without (b) and with (c) CP, $\lambda_{\text{ex}}=313$ nm.

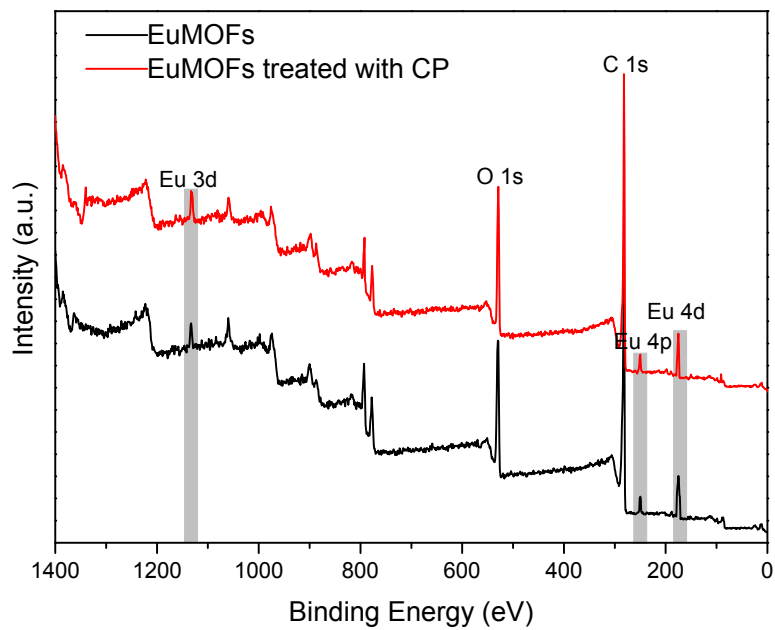


Fig. S11 XPS spectra of original EuMOFs and CP treated EuMOFs.

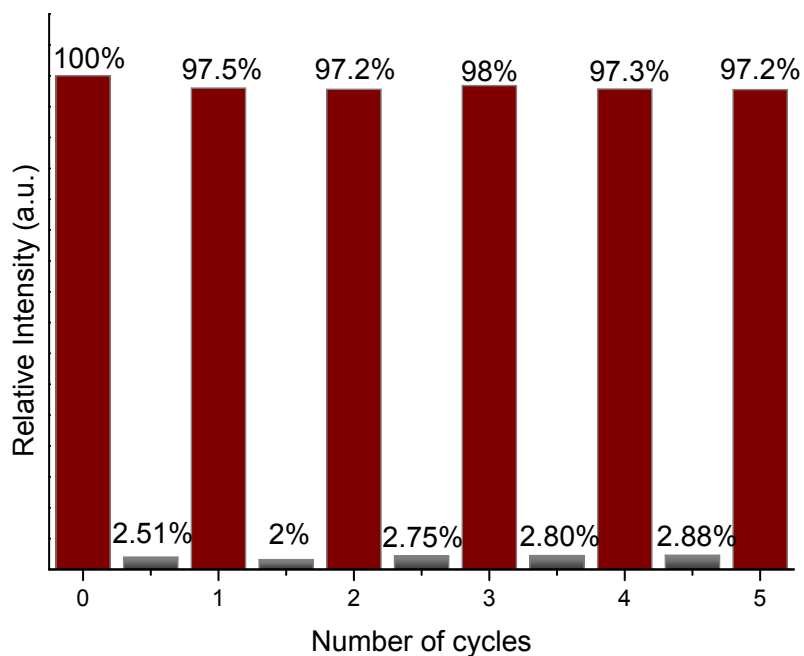


Fig. S12 Fluorescence intensity of EuMOFs at 614 nm during five consecutive quenching and regenerating cycles.

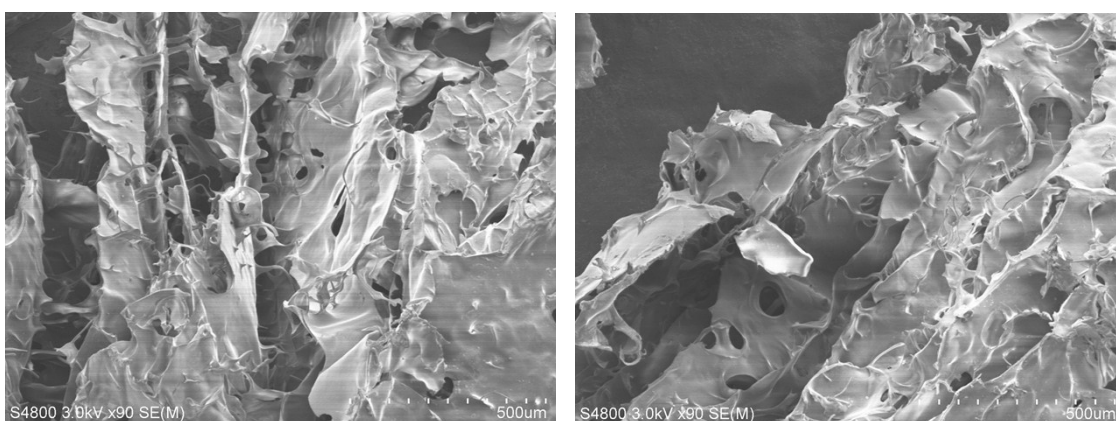


Fig. S13 TEM images of EuMOFs/CDs@CMC aerogel for three days storing.

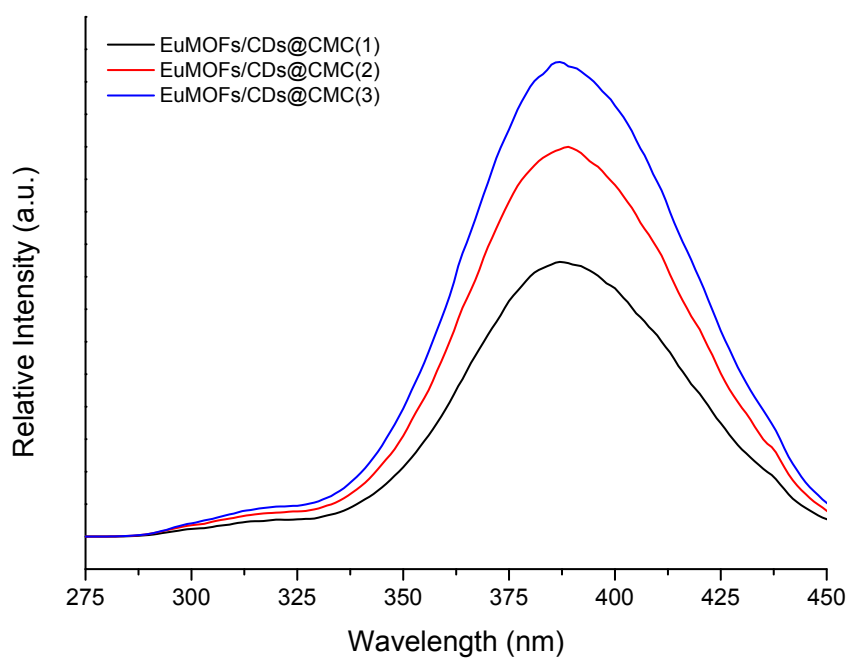


Fig. S14 The excitation wavelength of EuMOFs/CDs@CMC aerogel with different CDs loading mass.

Table S1 ICP-OES analysis for metal exchange process

Exchange time (h)	5	10	20	30
$P(M_{Eu}/M_{Ba})$ (%)	6.31	22.11	53.88	97.55

$S(M_{Eu}/M_{Ba} (\%))$	27.00	11.53	1.55	0.32
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M_{Eu} and M_{Ba} are amounts of Eu^{3+} and Ba^{2+} respectively; $P(M_{Eu}/M_{Ba})$ -relative molar ratio measured from powder using ICP-OES; $S(M_{Eu}/M_{Ba})$ -relative molar ratio measured from supernatant using ICP-OES.