

Supporting Information for

**White-Light-Emitting Lanthanide Metallohydrogel with Multi-Stimuli
Responsiveness Using for Environmental Sensing and Anti-Counterfeit**

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1. Experimental Section

1.1 Materials

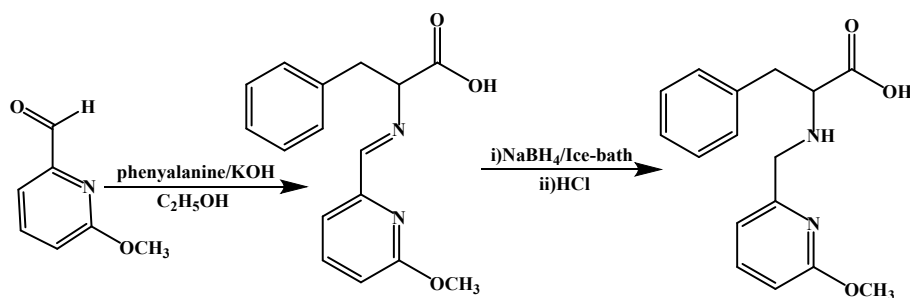
6-methoxypicolinaldehyde, L-phenylalanine and sodium borohydride (NaBH_4) were purchased from Aladin Reagent (Shanghai, China). All the other salts were of analytical grade, which includes KOH , Na_2CO_3 , CaCl_2 , $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, MgCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$, MnSO_4 , KCl , NaCl , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 6\text{H}_2\text{O}$. All chemicals were used without further purification.

1.2 Instruments

^1H NMR data were obtained on Bruker 500 MHz spectrometer in D_2O . The mass spectra were collected on G2-XS QTOF mass spectrometry. FT-IR spectra were obtained on a Perkin-Elmer Spectrum GX. Fluorescence measurements were recorded on a F-7000, Hitachi fluorescence spectrometer. Isothermal titration calorimetry (ITC) experiments were carried out on a Microcal VP-ITC microcalorimeter. Scanning electron microscope (SEM) images and Transmission electron microscope (TEM) images were obtained on a FEI HELIOS NanoLab 600i SEM (America) and a FEI Titan microscope (America), respectively.

1.3 Synthesis of MPF

Adding an aqueous solution of L-phenylalanine (10 mmol) containing 10 mmol potassium hydroxide to a flask, and then the ethanol solution of 6-methoxypicolinaldehyde (10 mmol) was dripped to the system. The mixture was stirred at $50\text{ }^\circ\text{C}$ for 4 h and then cooled in an ice bath. 6 mmol sodium borohydride was added to the mixed solution and kept stirring for 5 h. Finally, the reaction mixture was neutralized to nearly neutral with HCl . The resulted solid was filtered off, and washed with the mixture of ethanol and water, and then dried.



Scheme S1 The synthetic route of MPF.

1.4 Fluorescence studies

Fluorescence spectra were obtained on a fluorescence spectrometer (F-7000, Hitachi). The emission spectra of MPF, MPF-Eu, MPF-Tb and MPF-Eu/Tb were measured by diluting the fresh gel 50 times ($\lambda_{\text{ex}} = 295$ nm, ex slit 10 nm, em slit 10 nm, voltage 550 V). For Job's plot, the total concentration of MPF and Ln^{3+} were kept constant (the total concentration of MPF and Ln^{3+} ($\text{Eu}^{3+}/\text{Tb}^{3+}=7:3$) was 1 mM) and their mole fractions varied in the range of 0-1. In Ln^{3+} titration, 5 μL Ln^{3+} (0.1 M) was added to MPF solution (20 mM) continuously until the concentration of Ln^{3+} reached 10 mM. During the temperature responsive fluorescence test, the diluted gels were first incubated in water bath or ice bath to a certain temperature (0-60 °C) before fluorescence detection and then were transferred quickly to the detection tank for testing. The responsiveness for various metal ions of WLE hydrogel was tested. The fluorescence spectra were obtained by adding various metal ions (10 mM) to diluted MPF-Eu_{0.7}/Tb_{0.3} gels. Unless otherwise indicated, the excitation wavelength of fluorescence detection mentioned in this paper is 295 nm.

Quantum yield (QY) is defined as the ratio of the emitted photons to the absorbed photons, and was measured by a spectrofluorometer (FLS1000). An integrating sphere was mounted on the spectrofluorometer with the entrance and exit ports located in 90° geometry. The sample was located in the center of the integrating sphere. All the recorded spectroscopic data were corrected for the spectral responses of both the spectrofluorometer and the integrating sphere. The responses of the detecting systems (integrating sphere, monochromators and detectors) in photon flux were determined using a calibrated tungsten lamp. QY is calculated by the following equation:

$$\eta = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} = \frac{L_{\text{sample}}}{E_{\text{reference}} - E_{\text{sample}}} \quad (1)$$

where η represents QY, L_{sample} the emission intensity, $E_{\text{reference}}$ and E_{sample} the intensities of the excitation light not absorbed by the reference and the sample respectively. The precursor glass was used as the standard reference. The difference in integrated areas between the sample and the reference represents the number of the absorbed photons. The photons emitted were determined by integrating the area of the emission band. The quantum yield is obtained through directly from the

software that comes with the instrument (Edinburgh FLS1000).

Fluorescence lifetime test was performed on Edinburgh FLS1000 spectrofluorometer. The test condition: Excitation light source (μF), Intensity (100), $\lambda_{\text{ex}} = 295 \text{ nm}$, Bandwidth (1 nm), Detector (PMT-900), Monitored emission wavelength (420 nm, 550 nm, 620 nm). The average fluorescence lifetime was calculated using 3 order exponentials (shown in the equation 2).

$$\tau = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3} \quad (2)$$

1.5 ITC studies

Isothermal titration calorimetry (ITC) measurements were performed on a Microcal VP-ITC microcalorimeter (GE Life Sciences). MPF and Ln^{3+} (Eu^{3+} or Tb^{3+}) solutions are completely degassed in a Thermo Val instrument (Microcal). In the titration experiment, Ln^{3+} (1 mM) solution was injected into $\sim 1.5 \text{ mL}$ of MPF (15 mM) for 25 consecutive injections (2 μL for the first injection and 10 μL for the subsequent injection) with a 150 sec interval between each injection. The reaction cell was continuously stirred at 502 rpm and the heat change was recorded at 25 °C. The data were analyzed in Origin 9.0 software (GE Life Sciences), the combined isotherm was fitted into a unit point model, and net reaction heat was obtained from the integration of the calorimetric traces.

1.6 EPR studies

Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300 spectrometer (X-band) equipped with a Bruker ER4141VTM liquid N_2 system. The samples were transferred to quartz EPR tubes (Wilmad, 707-SQ) and frozen in liquid N_2 . The spectra were then measured at 100 K, with a frequency of 9.238 GHz, center field of 3000 G, sweep width of 1100 G, microwave power 1 mW, modulation frequency, 100 kHz and modulation amplitude of 3.0 G. The EPR studies were performed for Cu^{2+} , MPF-Eu/Tb, MPF-Eu/Tb + various metal ions including Cu^{2+} .

MPF (5 mM) pH = 10	Eu (NO ₃) ₃ (5 mM)	[Tb (NO ₃) ₃] (5 mM)	Glycerol (50%)	CuSO ₄ (5 mM)	Other metal ions (5 mM)
200 μL	70 μL	30 μL	75 μL	-	-
200 μL	70 μL	30 μL	75 μL	-	[Pb ²⁺] 100 μL
200 μL	70 μL	30 μL	75 μL	-	[Bb ²⁺] 100 μL
200 μL	70 μL	30 μL	75 μL	-	[Zn ²⁺] 100 μL
200 μL	70 μL	30 μL	75 μL	-	[Mg ²⁺] 100 μL
200 μL	70 μL	30 μL	75 μL	-	[K ⁺] 100 μL
200 μL	70 μL	30 μL	75 μL	-	[La ³⁺] 100 μL
200 μL	70 μL	30 μL	75 μL	-	[Li ⁺] 100 μL
200 μL	70 μL	30 μL	75 μL	-	[Na ⁺] 100 μL
200 μL	70 μL	30 μL	75 μL	100 μL	-
0	0	0	75 μL	100 μL	H ₂ O 300 μL

2. Supplementary Figures

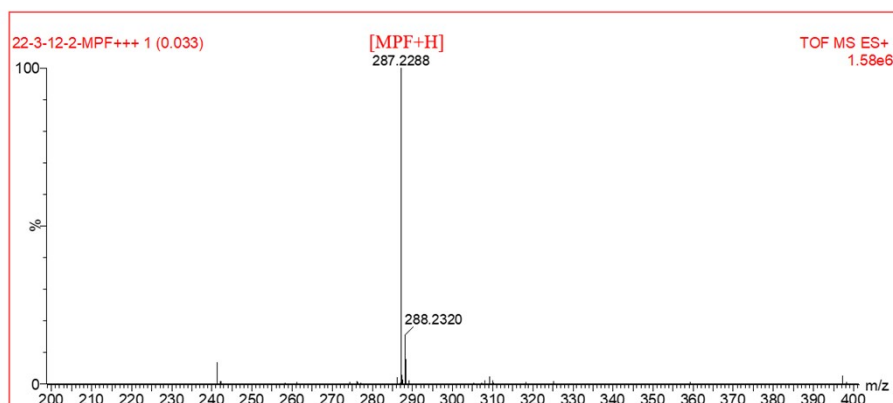


Fig. S1 ESI-MS spectra of compound MPF, Calculated: 286.3 Da; Observed: 287.2 Da ([MPF +H]).

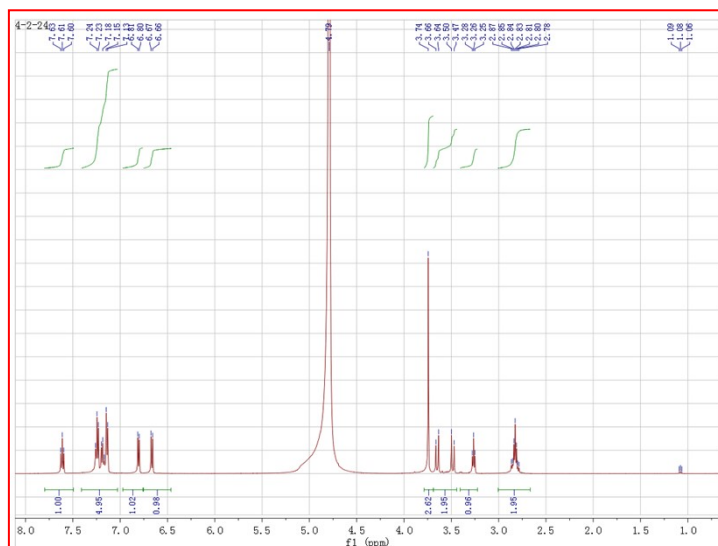


Fig. S2 ^1H NMR spectrum of MPF in D_2O . ^1H NMR (500 MHz, D_2O) δ 7.61 (d, $J = 6.0$ Hz, 1H), 7.21-7.26 (m, 5H), 6.80 (d, $J = 7.0$ Hz, 1H), 6.67 (d, $J = 7.0$ Hz, 1H), 3.74 (s, 3H), 3.56 (dd, $J = 80, 10.0$ Hz, 2H), 3.26 (t, $J = 6.5$ Hz, 1H), 2.83 (m, 2H), 1.08 (t, $J = 7.0$ Hz, 1H).

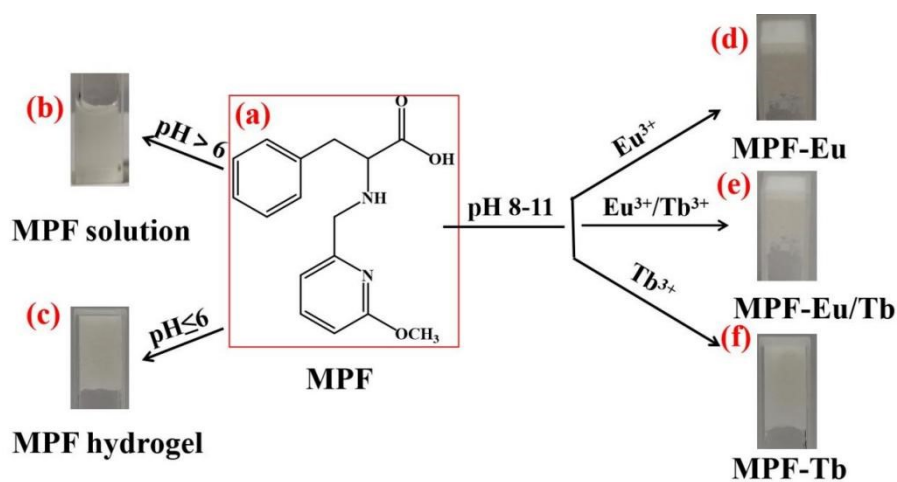


Fig. S3 (a) The molecular structure of MPF, (b) (c) (d) (e) (f) Photos under sunlight of MPF solution, MPF hydrogel, MPF-Eu, MPF-Eu_{0.7}/Tb_{0.3}, and MPF-Tb metallogels. ($C_{\text{MPF}} = 0.1$ M, the molar ratio of MPF and Ln^{3+} is 2:1.)

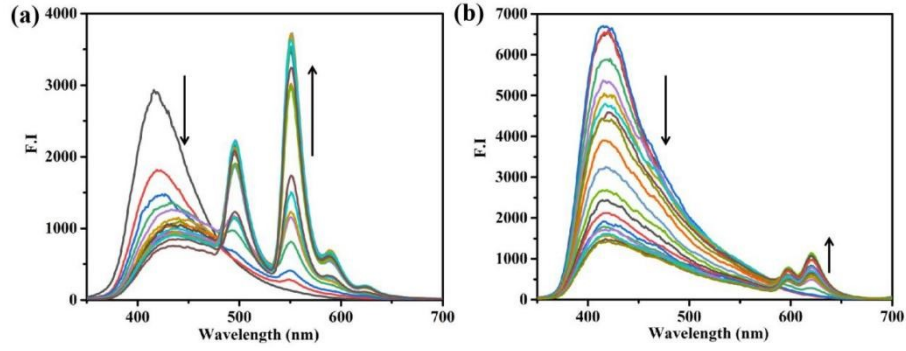


Fig. S4 Fluorescence spectra of MPF changed with the concentrations of (a) Tb^{3+} and (b) Eu^{3+} . ($\lambda_{ex} = 295$ nm).

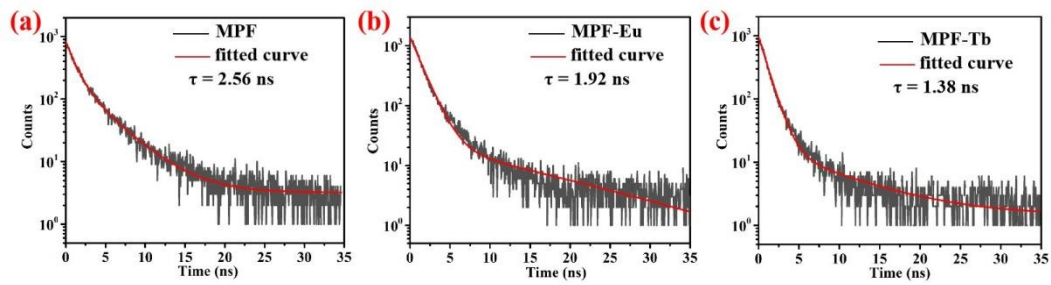


Fig. S5 Fluorescent decay curves of MPF, MPF-Eu, MPF-Tb xerogels at emission wavelength 420 nm ($\lambda_{ex} = 295$ nm).

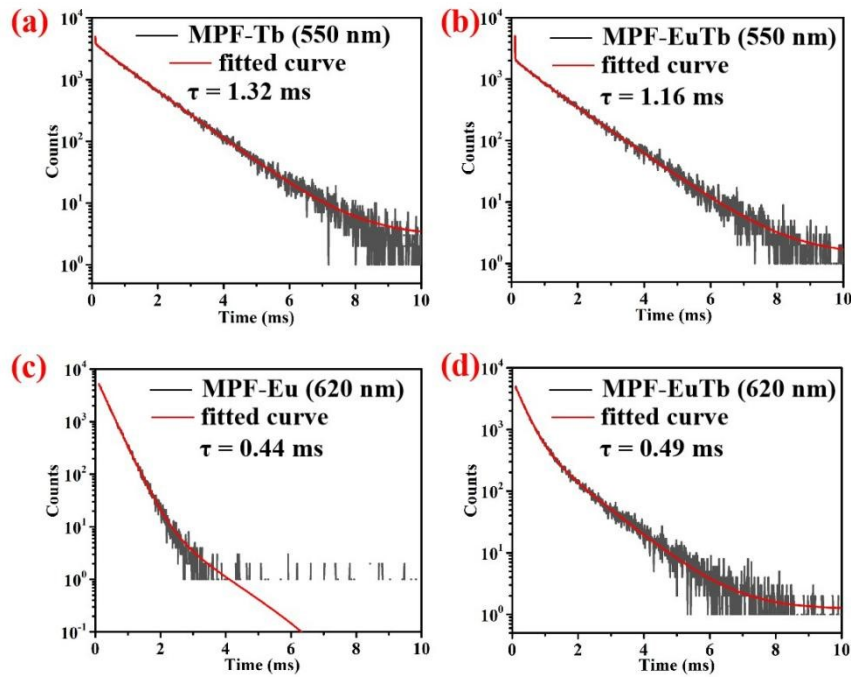


Fig. S6 Fluorescent decay curves with emission wavelength 550 nm ((a) MPF-Tb, (b) MPF- $Eu_{0.7}/Tb_{0.3}$ xerogel) and 620 nm (c) MPF-Eu, (d) MPF- $Eu_{0.7}/Tb_{0.3}$ xerogel). ($\lambda_{ex} = 295$ nm)

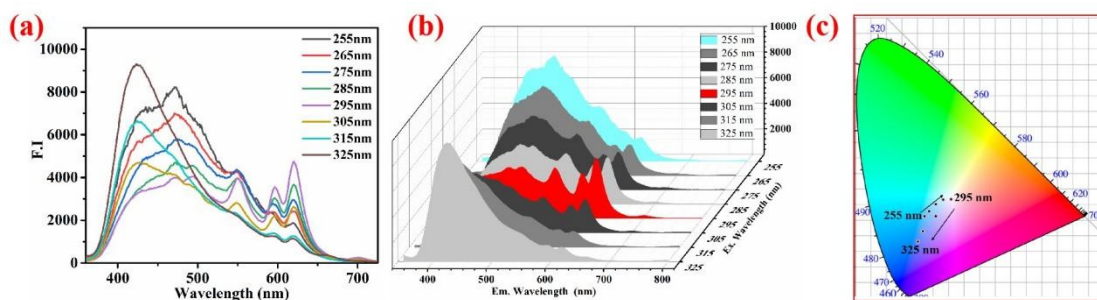


Fig. S7 (a) The fluorescence spectra of WLE hydrogel MPF-Eu_{0.7}/Tb_{0.3} at different excitation wavelengths. (b) The fluorescence emission spectra, (c) the CIE chromaticity diagram of MPF-Eu/Tb at different excitation wavelengths (255 nm, 265 nm, 275 nm, 285 nm, 295 nm, 305 nm, 315 nm, 325 nm).

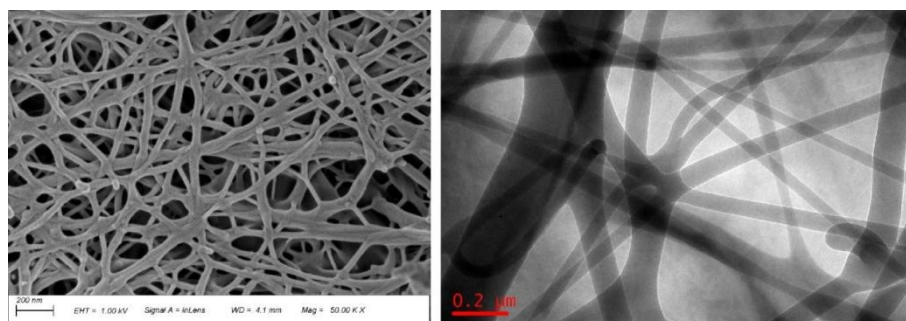


Fig. S8 SEM and TEM images of MPF hydrogel.

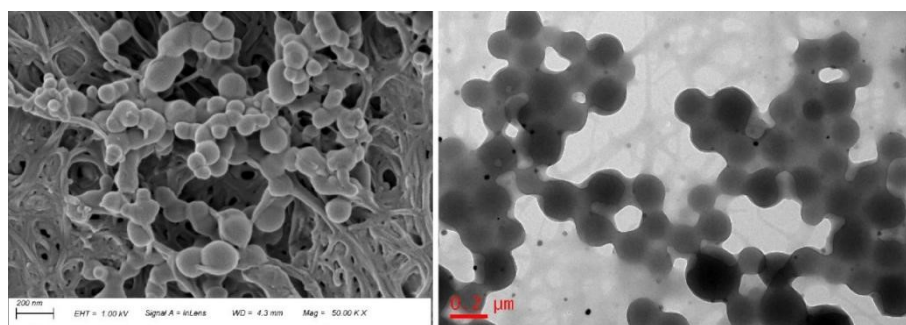


Fig. S9 SEM and TEM images of MPF-Eu xerogel.

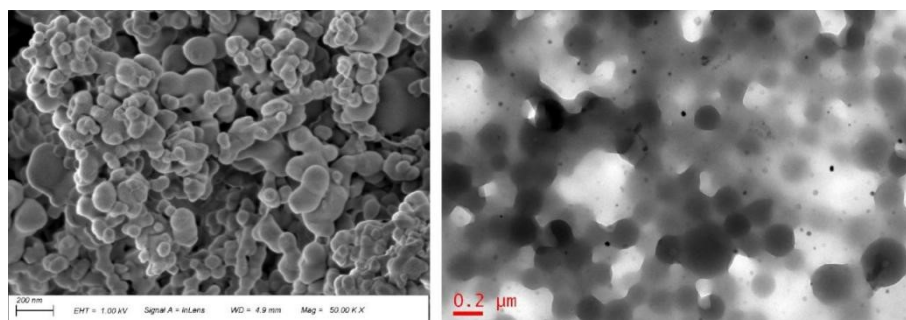


Fig. S10 SEM and TEM images of MPF-Tb xerogel.

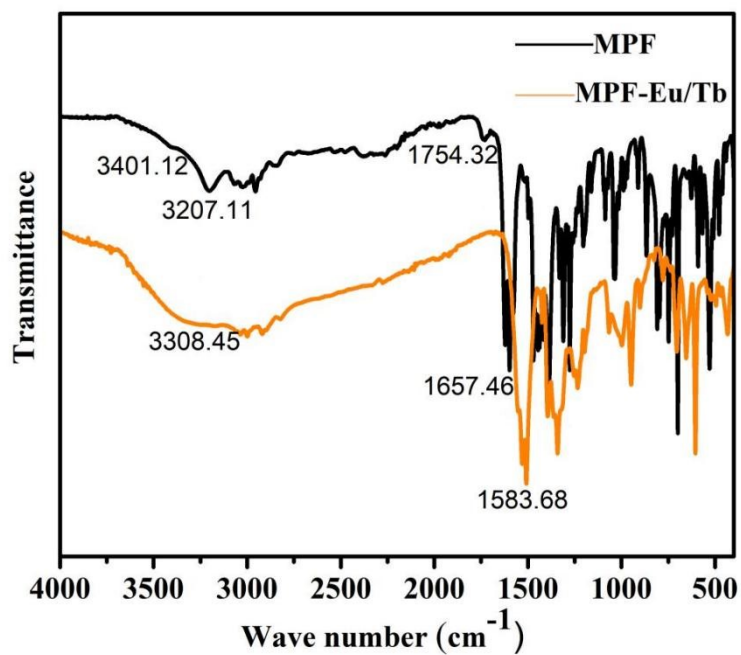


Fig. S11 FT-IR spectra of MPF and MPF-Eu_{0.7}/Tb_{0.3} xerogels.

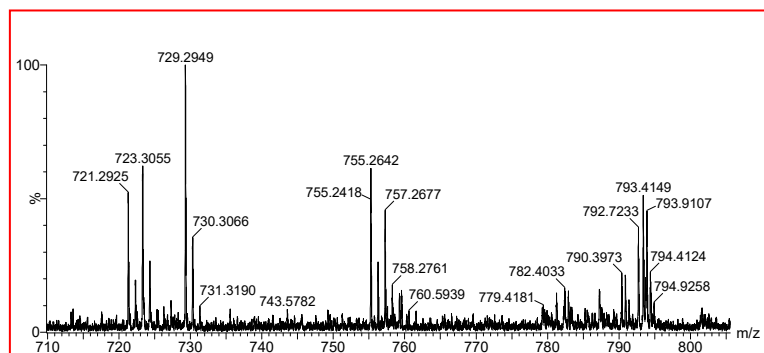


Fig. S12 ESI-MS spectra of MPF-Eu_{0.7}/Tb_{0.3} complex, Calculated: 722.2 Da ([Eu(MPF)₂]) and 729.2 Da ([Tb(MPF)₂]); Observed: 723.3 Da ([Eu(MPF)₂]+H) and 730.3 Da ([Tb(MPF)₂]+H).

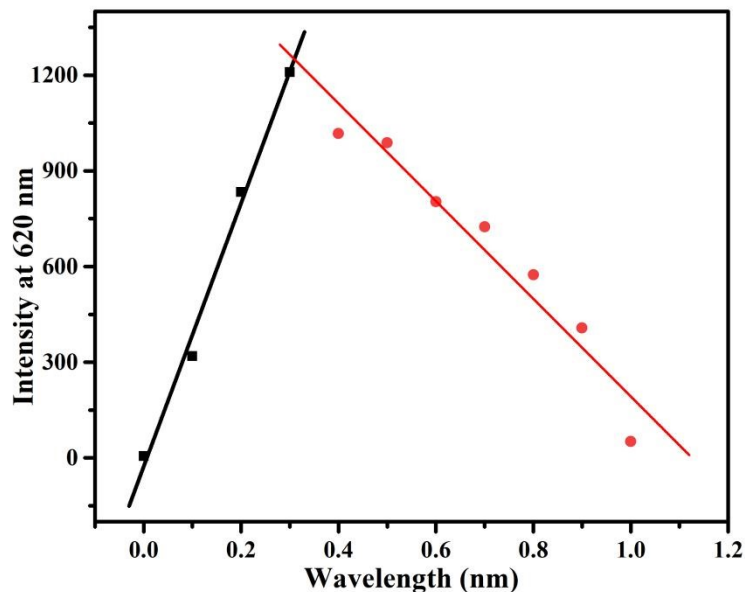


Fig. S13 A Job's plot for determining the binding stoichiometry between MPF and Ln^{3+} (the total concentration of MPF and Ln^{3+} ($\text{Eu}^{3+}/\text{Tb}^{3+}=7:3$) was 1 mM).

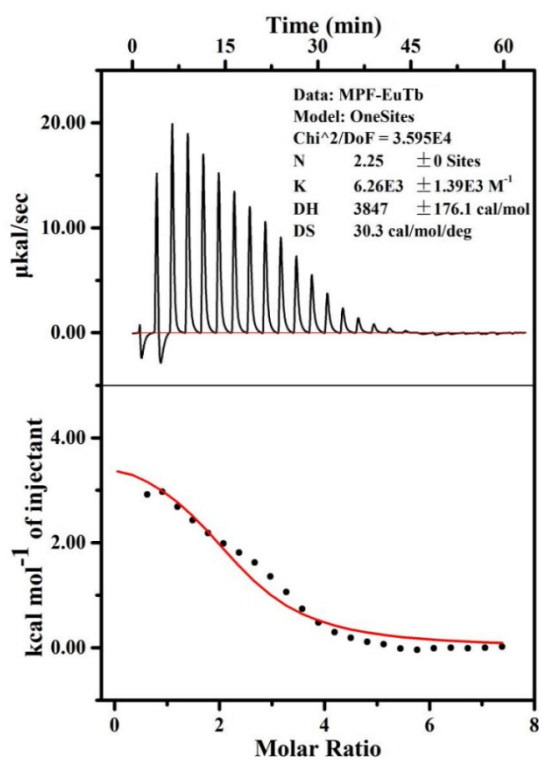


Fig. S14 Microcalorimetric titration of MPF with Eu^{3+} and Tb^{3+} in water at 298.15 K. (Top) Raw ITC data for 25 sequential injections (10 μL per injection) of MPF solution (10.0 mM) into $\text{Eu}^{3+}/\text{Tb}^{3+}$ (7:3) mixing solution (0.5 mM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

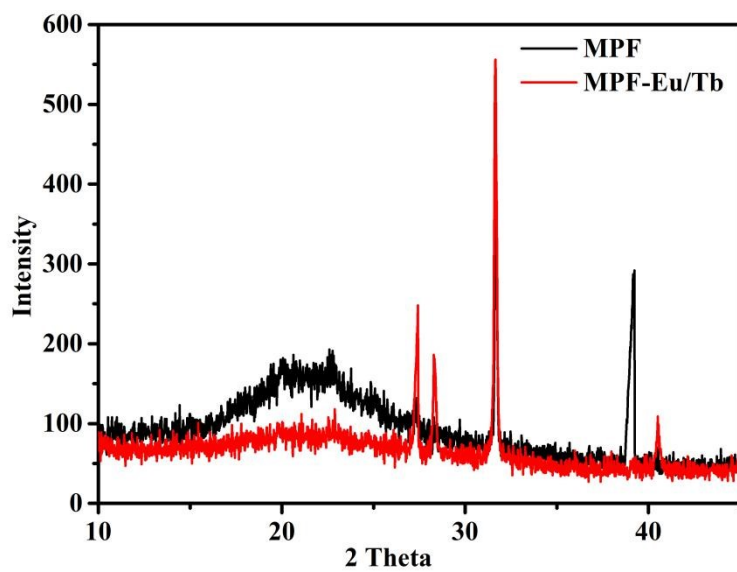


Fig. S15 XRD patterns of MPF and MPF-Eu_{0.7}/Tb_{0.3} xerogels.

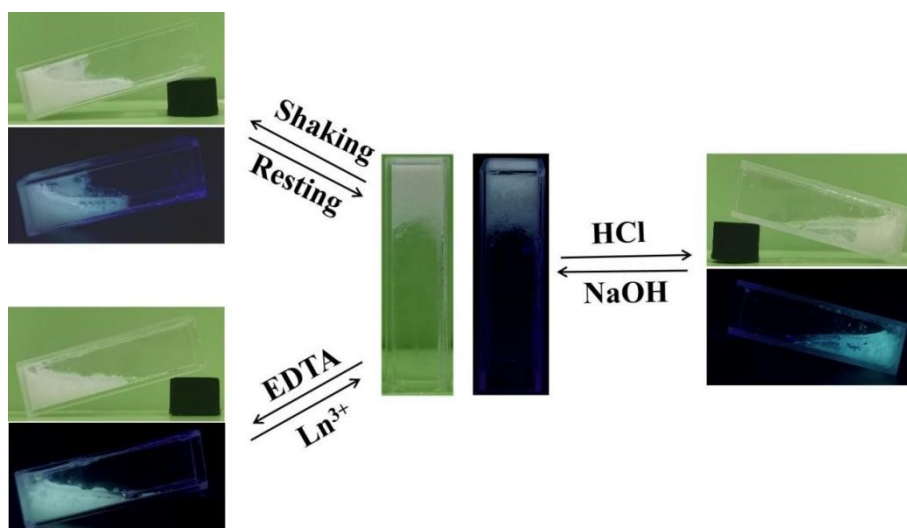


Fig. S16 The photos of WLE hydrogel MPF-Eu_{0.7}/Tb_{0.3} responsive for various stimuli.

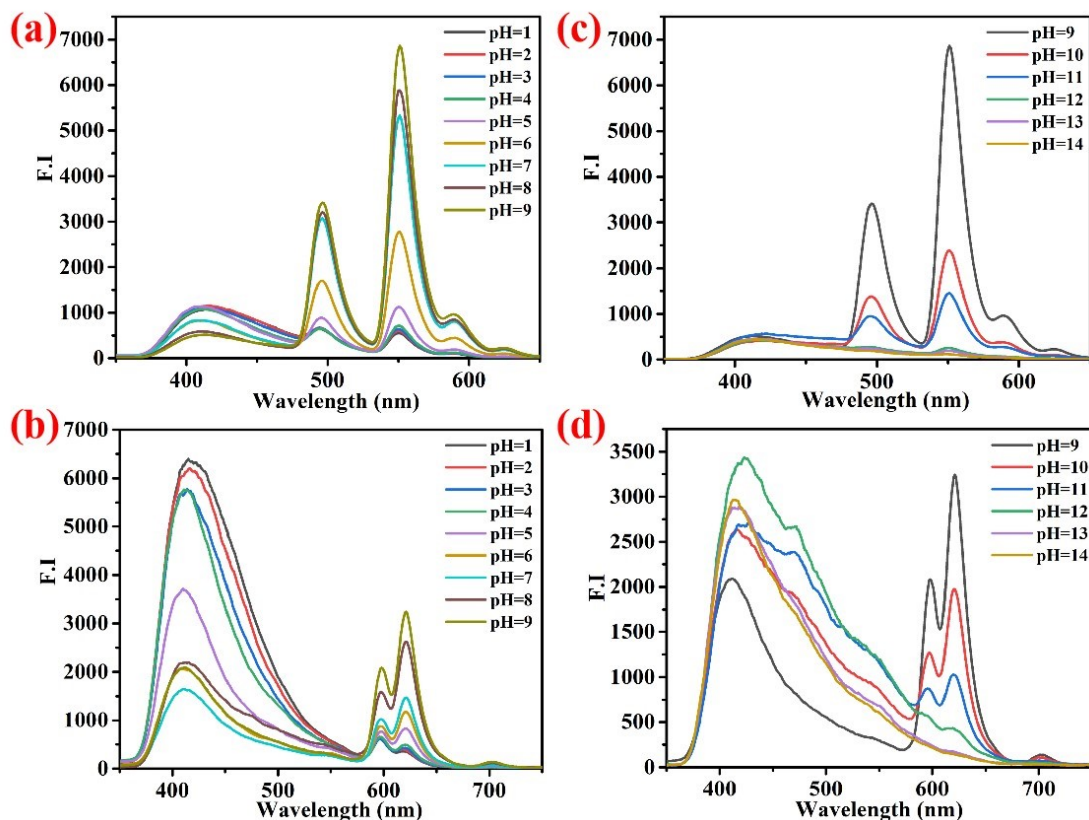


Fig. S17 The fluorescence spectra of diluted MPF-Tb (a)(c) and MPF-Eu (b)(d) metallohydrogels at different pH values.

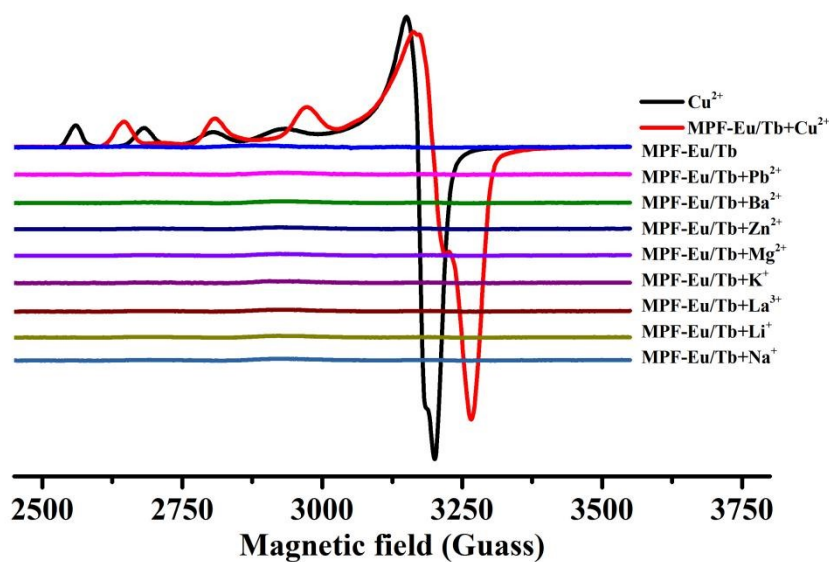


Fig. S18 EPR spectra of Cu^{2+} , MPF-Eu/Tb, MPF-Eu/Tb + Cu^{2+} , MPF-Eu/Tb + other metal ions (Pb^{2+} , Ba^{2+} , Zn^{2+} , Mg^{2+} , K^+ , La^{3+} , Li^+ , Na^+). The spectra were measured at 100 K, with a frequency of 9.238 GHz, microwave power of 1 mW, and modulation amplitude of 3.0 G.

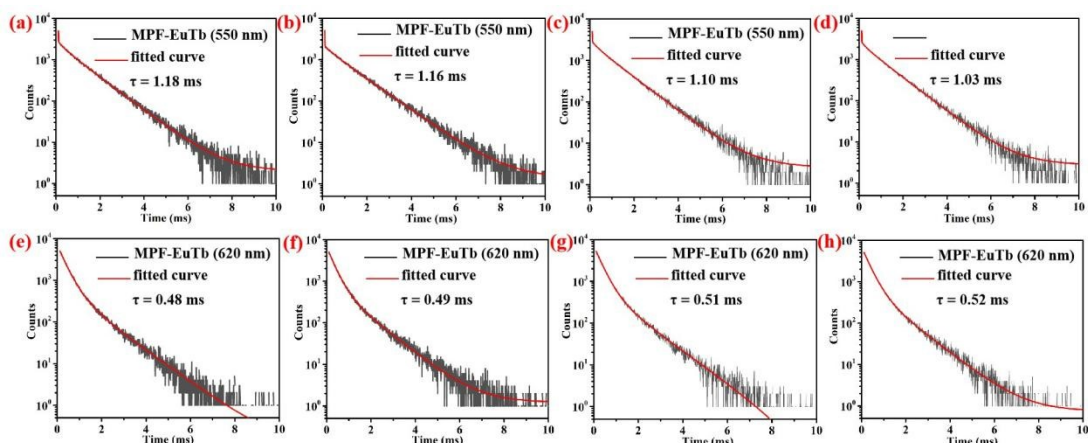


Fig. S19 Fluorescent decay curves of MPF-Eu_{0.7}/Tb_{0.3} xerogel with emission wavelength 550 nm and 620 nm at different temperature (273 K (a,e), 298 K (b,f), 313 K (c,g), 333 K (d,h)) ($\lambda_{\text{ex}} = 295$ nm).

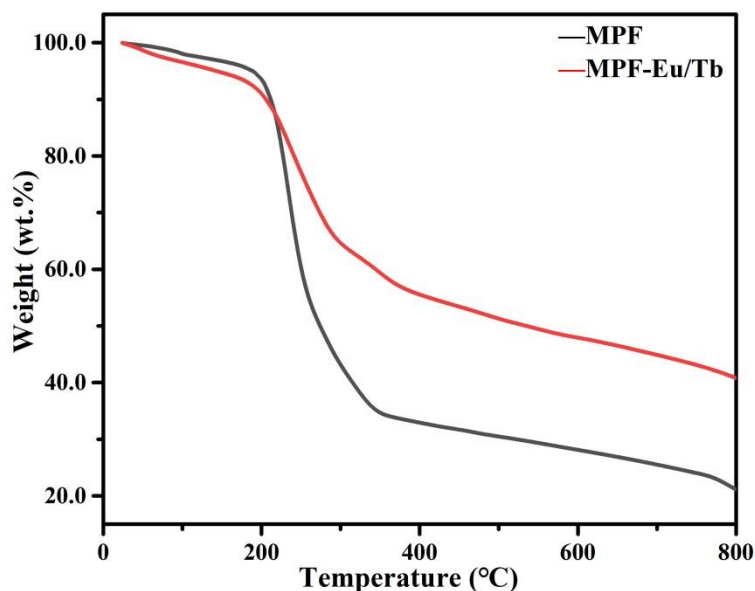


Fig. S20 Thermogravimetric analysis (TGA) thermogram of MPF and MPF-Eu_{0.7}/Tb_{0.3}. Thermal analysis system in a dynamic nitrogen atmosphere (heating rate: 10°C/min, MPF and MPF-Eu/Tb, mass 1-3 mg, temperature range from room temperature up to 800°C).

The thermogravimetric analysis (TGA) curve (Fig. S20) of MPF and MPF-Eu/Tb xerogels showed that these gels proceeded in three stages. The similar mass loss about 8% at the first stage (25°C-200°C) was due to the loss of absorbed water. At the second stage (25°C-200°C), the weight loss of MPF and MPF-Eu/Tb was 58% and 33%, respectively. When the temperature was 800°C, the residual mass of MPF was 21.1%, while that of Eu_{0.7}/Tb_{0.3} was 40.8%. These results indicated that the thermal stability of WLE hydrogel was better than MPF gel, which also showed that this material was reliable in the general environment.



Fig. S21 Digital images of the handwritten symbols of “USC” using MPF-Eu, MPF-Tb, and MPF-Eu_{0.7}/Tb_{0.3} gel as luminescence ink read under 254 nm UV irradiation.