

Electronic supporting information

Dual-Mode Multi-Color Circularly Polarized Luminescent MOFs from a Facile Approach of Chiral Induction

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1. Experimental Procedures

1.1 Materials.

All the reagents and solvents were used as received. Milli-Q water (18.2 M Ω cm) was used in all the experiments. 1, 3, 5-tris(4-carboxyphenyl)benzene (>98%, high-performance liquid chromatography (HPLC)), L-phenylalanine (>98%, HPLC), D-phenylalanine (>98%, HPCL), L-valine (98.0%, T), D-valine (98.0%, T), L-alanine (99.0%), D-alanine (99.0%), (PVP K 15 (average molecular weight, 10000), 1-octadecene (90%, GC), and oleic acid (>99%, GC) were purchased from TCI Development Co., Ltd. Eu(NO₃)₃·6H₂O (99.99%), Tb(NO₃)₃·5H₂O (99.9%) and NH₄F (99.99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. TmCl₃·6H₂O (99.9%), YCl₃·6H₂O (99.99%), and YbCl₃·6H₂O (99.9%) were purchased from Alfa Aesar.

1.2 Characterizations.

UV-visible spectra were recorded on a Hitachi U-4150 spectrophotometer, and CD spectra were obtained on a JACSO J-1500 spectrophotometer. Fluorescence spectra were measured on Edinburgh FS5 fluorescence spectra using a Xe lamp as the excitation source. UC luminescence spectra were recorded using a Zolix Omni- λ 500i monochromator with a photomultiplier tube (PMT-R 928) using an external excitation source (980 nm multimode diode laser; MDL-III-980, maximum power: 2W, central wavelength: 980 \pm 10 nm, Changchun New Industry Optoelectronic Technology Co. Ltd). CPL spectra were detected on JASCO CPL-200 spectrophotometer with a Xe lamp and an external excitation source, 980 nm semiconductor laser. Fluorescence lifetime measurements were obtained on a HORIBA Scientific Nanolog FL3-Ihr320 spectrofluorometer using multichannel scaling (MCS). X-ray diffraction (XRD) was achieved on Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu/K α radiation ($\lambda = 1.5406 \text{ \AA}$). TEM images were recorded using an FEI Tecnai G2 20 A-TWIN microscope (200 kV), and the samples were dropped on carbon-coated Cu grids and then evaporated under ambient conditions before the TEM measurements. Fourier-transform infrared spectra were collected on a PerkinElmer Spectrum ONE B spectrometer in the attenuated total reflectance mode. Focused ion beam/scanning electron microscopy dual-beam system (FIB/SEM) was performed using Nova200 Nanolab microscope,

beam current of Ga⁺: 30 pA@30 kV, SEM setup with an accelerating voltage of 10 kV and current of 0.21 Na (UHR mode). Prior to the SEM experiments, a thin layer of Pt was coated onto the samples on silicon wafers to increase contrast. Thermogravimetric analyses (TGA) were carried out with a Diamond TG/DTA analyzer under a nitrogen atmosphere with a heating rate of 10 °C·min⁻¹. Nitrogen adsorption isotherm was tested on a ASAP2460 instrument at 77 K.

1.3 Synthesis

1.3.1 Preparation of chiral Eu-MOFs.

Chiral Ln-MOFs were prepared according to the previously reported method with some modifications¹. Typically, a mixture of 0.44 mmol chiral induction reagents (*L/D*-phenylalanine, *L/D*-valine, and *L/D*-alanine, respectively) and triethylamine (100 μL) were dissolved in 8.88 mL mixed solution of methanol/H₂O (1: 1, v/v) and stirred for 15 min. After that, 1.11 mL mixed solution (methanol/H₂O = 1: 1, v/v) of Eu(NO₃)₃·6H₂O (57.9 mg, 0.13 mmol) was dropwise added. The solution was stirred for 30 min, then the precursors were collected by centrifugation (7000 rpm, 10 min) and washed twice with 5 mL water. The collected precursors were resolved in 5 mL mixed solution of DMF/methanol/ water (5.75: 5.75: 1, v/v), then the solution (DMF/methanol/ water = 5.75: 5.75: 1, 5 mL) of 1, 3, 5-tris(4-carboxyphenyl)benzene (54.8 mg, 0.13 mmol) was gradually added. The reaction was carried out by stirring at room temperature for 1.5 h. The precipitates were collected by centrifugation (7000 rpm, 5 min) and repeatedly centrifugal washing with 7 mL of DMF two times and redispersed in 7 mL of methanol. The suspension liquid was sonicated for 30 min and the precipitates were collected by centrifugation. Finally, the collected powder was dried in a vacuum at 80 °C.

1.3.2 Preparation of chiral Tb-MOFs.

All the procedures were the same as preparation for chiral Eu-MOFs except for Eu(NO₃)₃·6H₂O was replaced by Tb(NO₃)₃·5H₂O (56.5 mg, 0.13 mmol).

1.3.3 Preparation of L / D -Phe-Eu_xTb_{1-x}-MOFs ($x = 0.001, 0.003, 0.005, 0.007, 0.01, 0.02, 0.04$).

All the procedures were the same as preparation for chiral Eu MOFs except for Eu(NO₃)₃·6H₂O was replaced by a mixture of Eu(NO₃)₃·6H₂O and Tb(NO₃)₃·5H₂O with a certain proportion, and the chiral induction reagents were L / D -phenylalanine.

1.3.4 Preparation of L / D -Phe-Eu \supset UCNPs composites.

A mixture of L / D -phenylalanine (73.4 mg, 0.44 mmol) and triethylamine (100 μ L) was dissolved in 8.88 mL mixed solution of methanol/H₂O (1: 1, v/v) and stirred for 15 min. After that, 1.11 mL mixed solution (methanol/H₂O = 1: 1, v/v) of Eu(NO₃)₃·6H₂O (57.9 mg, 0.13 mmol) was dropwise added. The solution was stirred for 30 min, then the precursors were collected by centrifugation (7000rpm, 10min) and washed twice with 5 mL water. The collected precursors were resolved in 5 mL mixed solution of DMF/methanol/ water (5.75: 5.75: 1, v/v), then the solution (DMF/methanol/ water = 5.75: 5.75: 1, 5 mL) of 1, 3, 5-tris(4-carboxyphenyl)benzene (54.8 mg, 0.13 mmol) and PVP-modified UCNPs (10 mg, 1mg/mL in reaction system) was gradually added. The reaction was carried out by stirring at room temperature for 1.5 h. The precipitates were collected by centrifugation (7000 rpm, 5 min) and repeatedly centrifugal washing with 7 mL of DMF two times and redispersed in 7 mL of methanol. The suspension liquid was sonicated for 30 min and the precipitates were collected by centrifugation. Finally, the collected powder was dried in a vacuum at 80 °C.

1.3.5 preparation of L / D -Phe-Tb \supset UCNPs composites.

All the procedures were the same as the preparation of L / D -Phe-Eu \supset UCNPs composites except for Eu(NO₃)₃·6H₂O was replaced by Tb(NO₃)₃·5H₂O (56.5 mg, 0.13 mmol).

1.3.6 Preparation of L / D -Phe-Eu_{0.003}Tb_{0.997} \supset UCNPs composites ($x=0.003$).

All the procedures were the same as the preparation of L / D -Phe-Eu \supset UCNPs composites except for Eu(NO₃)₃·6H₂O was replaced by a mixture of Eu(NO₃)₃·6H₂O (0.0004 mmol) and Tb(NO₃)₃·5H₂O (0.1296 mmol).

1.3.7 Upconversion nanoparticles (UCNPs).

The OA-coated UCNP-Tm (NaYF₄:20% Yb, 1% Tm) were synthesized according to the previously reported method². In a typical procedure, the mixture of 1.38 mg (0.005 mmol) of TmCl₃·6H₂O, 38.75 mg (0.1 mmol) of YbCl₃·6H₂O, 119.83 mg (0.395 mmol) of YCl₃·6H₂O, 6 mL of oleic acid and 10 mL of 1-octadecene was added in a three-neck flask and degassed under N₂ flow for 1 h. After that, it was heated to 160 °C with N₂ flow to remove moisture until a transparent solution was observed, and then cooled down to room temperature. The methanol solution of NH₄F (2.5 mmol, 5 mL) and 5 mL of methanol containing 20 mg NaOH were dropped into the reacted solution, respectively. The mixture was heated to 50 °C 30 min and 110 °C 30 min in a vacuum to remove methanol. Finally, the solution was fast heated to 300 °C and kept for 1 h under N₂ atmosphere, then cooled down to room temperature naturally. Then 30 mL of ethanol was added to precipitate the produces. The samples were collected by centrifugation (10000 rpm, 10 min) and washed with ethanol/hexane (1: 1, v/v) for three times. The obtained UCNPs were dried in a vacuum at room temperature.

The mixture of 0.8 mmol OA-coated UCNP-Tm (NaYF₄: 20% Yb, 1% Tm), 242.6 mg (0.8 mmol) of YCl₃·6H₂O, 6 mL of oleic acid, and 10 mL of 1-octadecene was added in a three-neck flask and degassed under N₂ flow for 1 h. After that, it was heated to 160 °C with N₂ flow to remove moisture until a transparent solution was observed, and then cooled down to room temperature. The methanol solution of NH₄F (3.2 mmol, 5 mL) and 5 mL of methanol containing 80 mg NaOH were dropped into the reacted solution, respectively. The mixture was heated to 50 °C 30 min and 110 °C 30 min in a vacuum to remove methanol. Finally, the solution was fast heated to 300 °C and kept for 1 h under N₂ atmosphere, then cooled down to room temperature naturally. Then 30 mL of ethanol was added to precipitate the produces. The samples were collected by centrifugation (10000 rpm, 10 min) and washed with ethanol/hexane (1: 1, v/v) for three times. The obtained UCNPs NaYF₄: Yb/Tm@NaYF₄ with core-shell structure was dried in a vacuum at room temperature.

The obtained UCNPs powder was dispersed in 20 ml of chloroform (0.5 mg/ml). A solution of PVP (62.5 mg, Mw = 10,000) in chloroform (10 ml) was then added. After the mixture was stirred for 24 h, the PVP-modified UCNPs were precipitated with n-hexane and collected by centrifugation. The sample was cleaned with chloroform/hexane (1:1 v/v) to remove the excess free PVP. Finally, the PVP-modified UCNPs were dried in a vacuum at room temperature.

2. Results and Discussions (Fig. S1-S16)

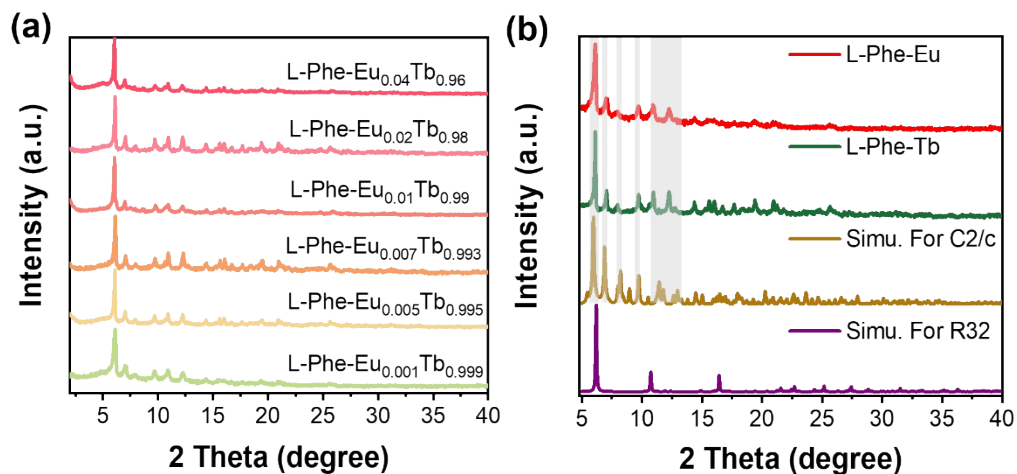


Fig. S1 (a) XRD of L-Phe-Eu_{0.001}Tb_{0.999}, L-Phe-Eu_{0.005}Tb_{0.995}, L-Phe-Eu_{0.007}Tb_{0.993}, L-Phe-Eu_{0.01}Tb_{0.99}, L-Phe-Eu_{0.02}Tb_{0.98}, L-Phe-Eu_{0.04}Tb_{0.96}. (b) XRD of L-Phe-Eu, L-Phe-Tb, the simulated patterns of various Eu and Tb MOFs were added for comparison³.

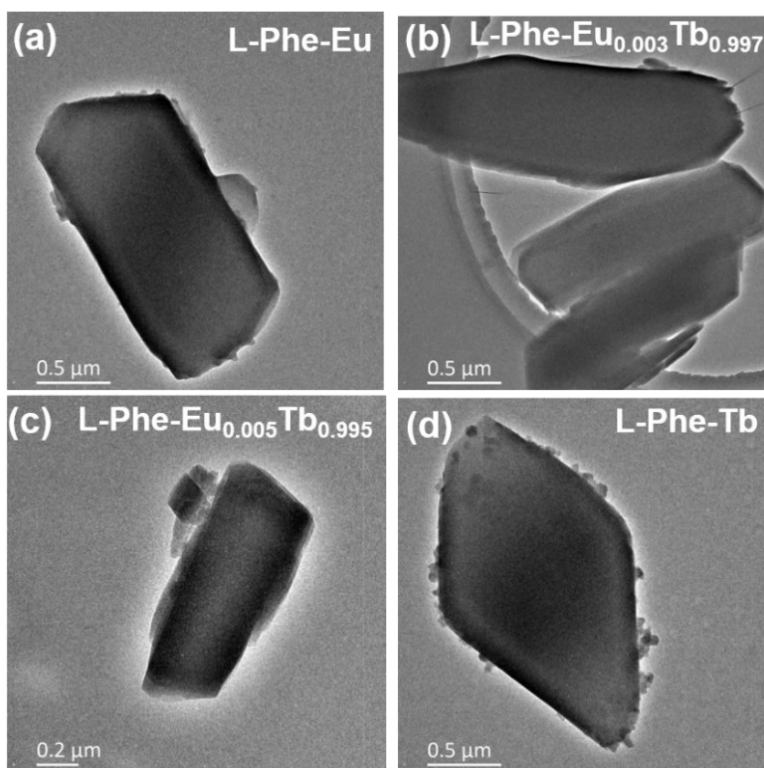


Fig. S2 TEM images of L-Phe-Eu, L-Phe-Eu_{0.003}Tb_{0.997}, L-Phe-Eu_{0.005}Tb_{0.995}, L-Phe-Tb.

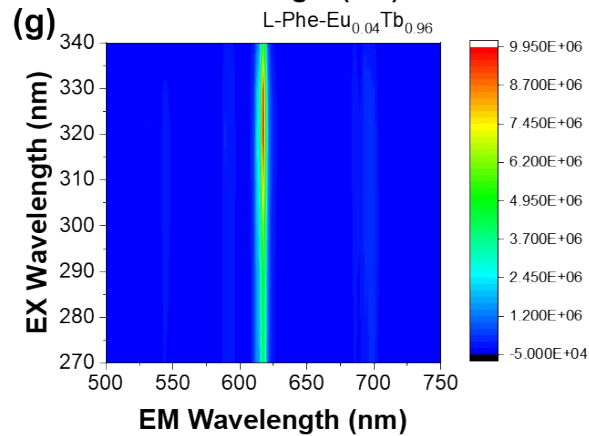
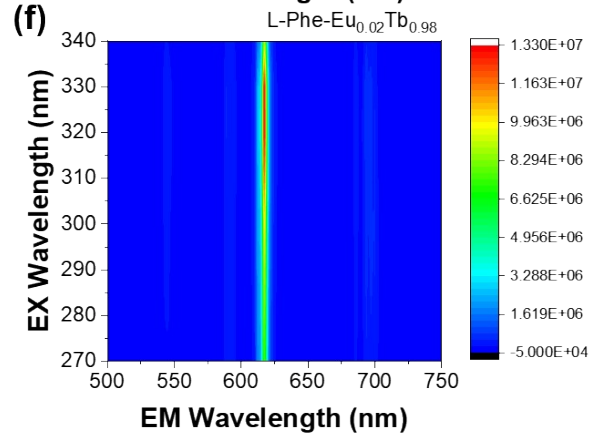
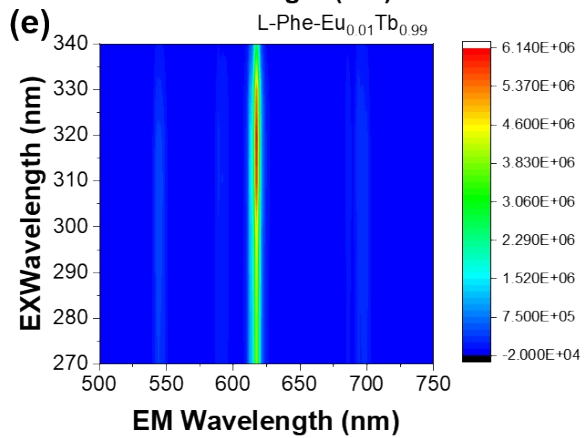
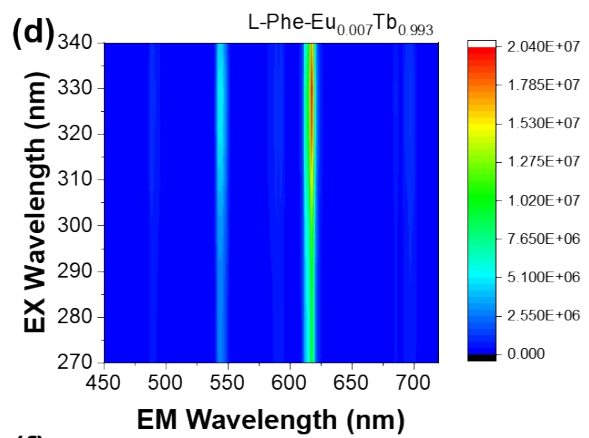
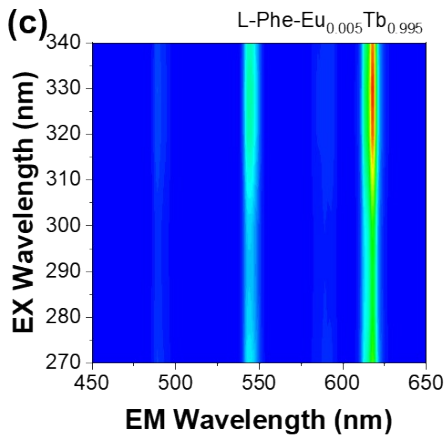
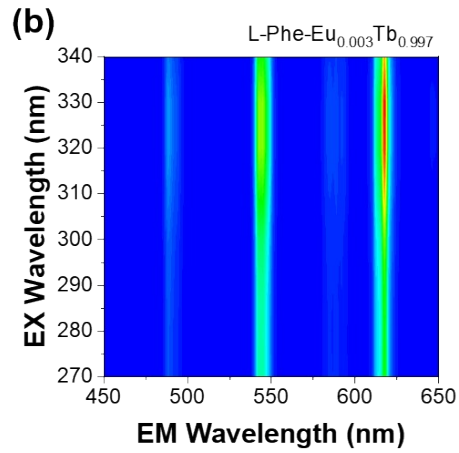
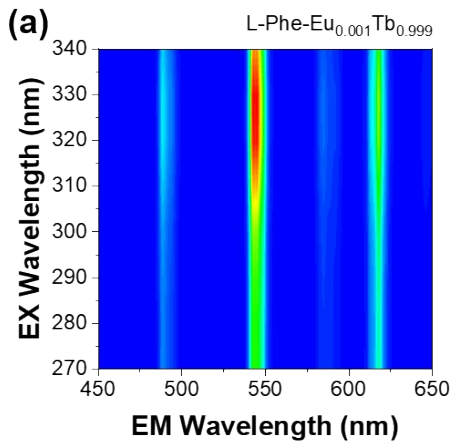


Fig. S3 The excitation-emission matrix spectrums of (a) L-Phe-Eu_{0.001}Tb_{0.999}, (b) L-Phe-Eu_{0.003}Tb_{0.997}, (c) L-Phe-Eu_{0.005}Tb_{0.995}, (d) L-Phe-Eu_{0.007}Tb_{0.993}, (e) L-Phe-Eu_{0.01}Tb_{0.99}, (f) L-Phe-Eu_{0.02}Tb_{0.98}, (g) L-Phe-Eu_{0.04}Tb_{0.96}.

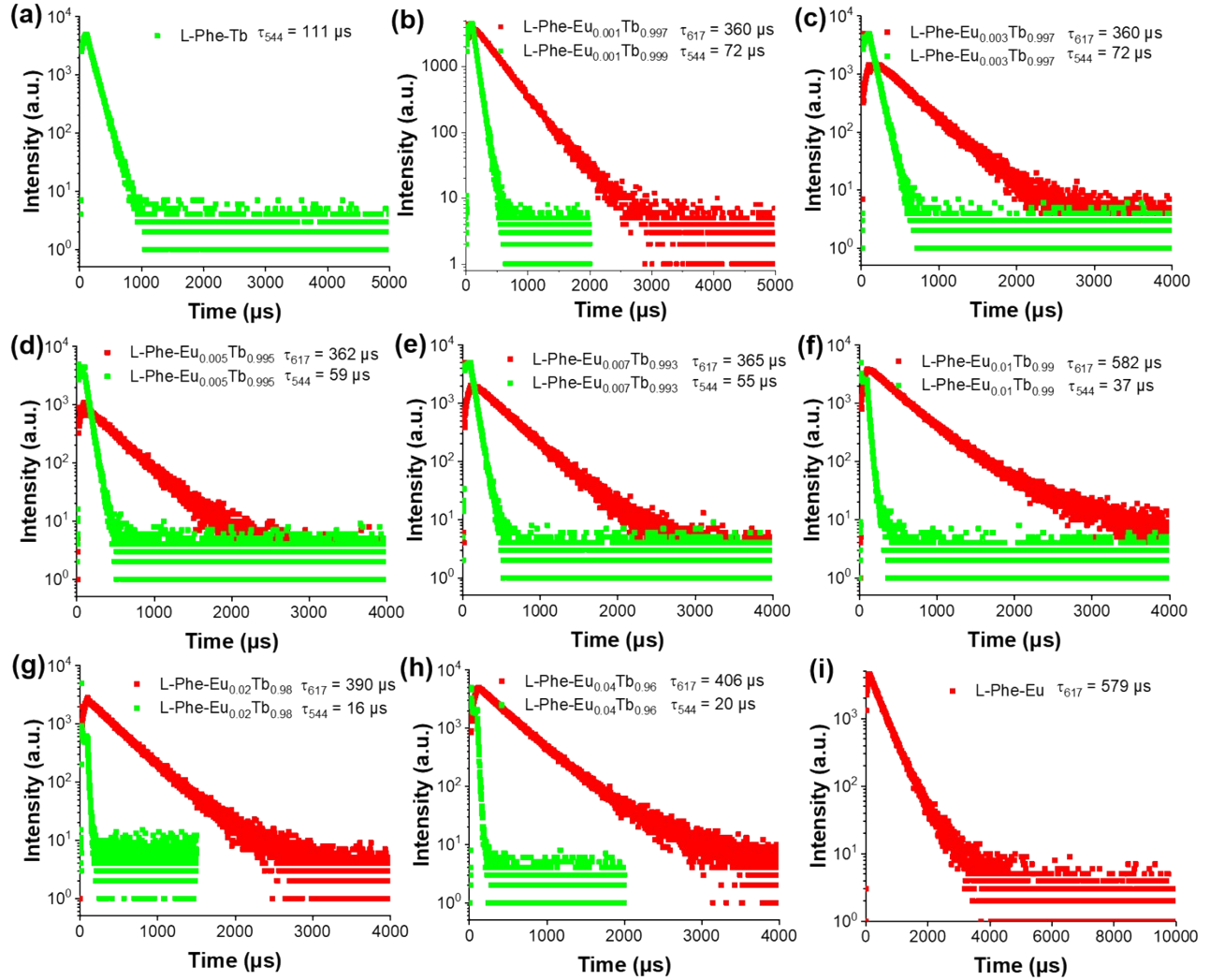


Fig. S4 Luminescent decay of (a) L-Phe-Tb (b) L-Phe-Eu_{0.001}Tb_{0.999}, (c) L-Phe-Eu_{0.003}Tb_{0.997}, (d) L-Phe-Eu_{0.005}Tb_{0.995}, (e) L-Phe-Eu_{0.007}Tb_{0.993}, (f) L-Phe-Eu_{0.01}Tb_{0.99}, (g) L-Phe-Eu_{0.02}Tb_{0.98}, (h) L-Phe-Eu_{0.04}Tb_{0.96}, (i) L-Phe-Eu powder monitored at 617, and 544 nm, respectively. (Excitation wavelength = 360 nm, L-Phe-Tb powder was only monitored at 544 nm and L-Phe-Eu powder was only monitored at 617 nm.)

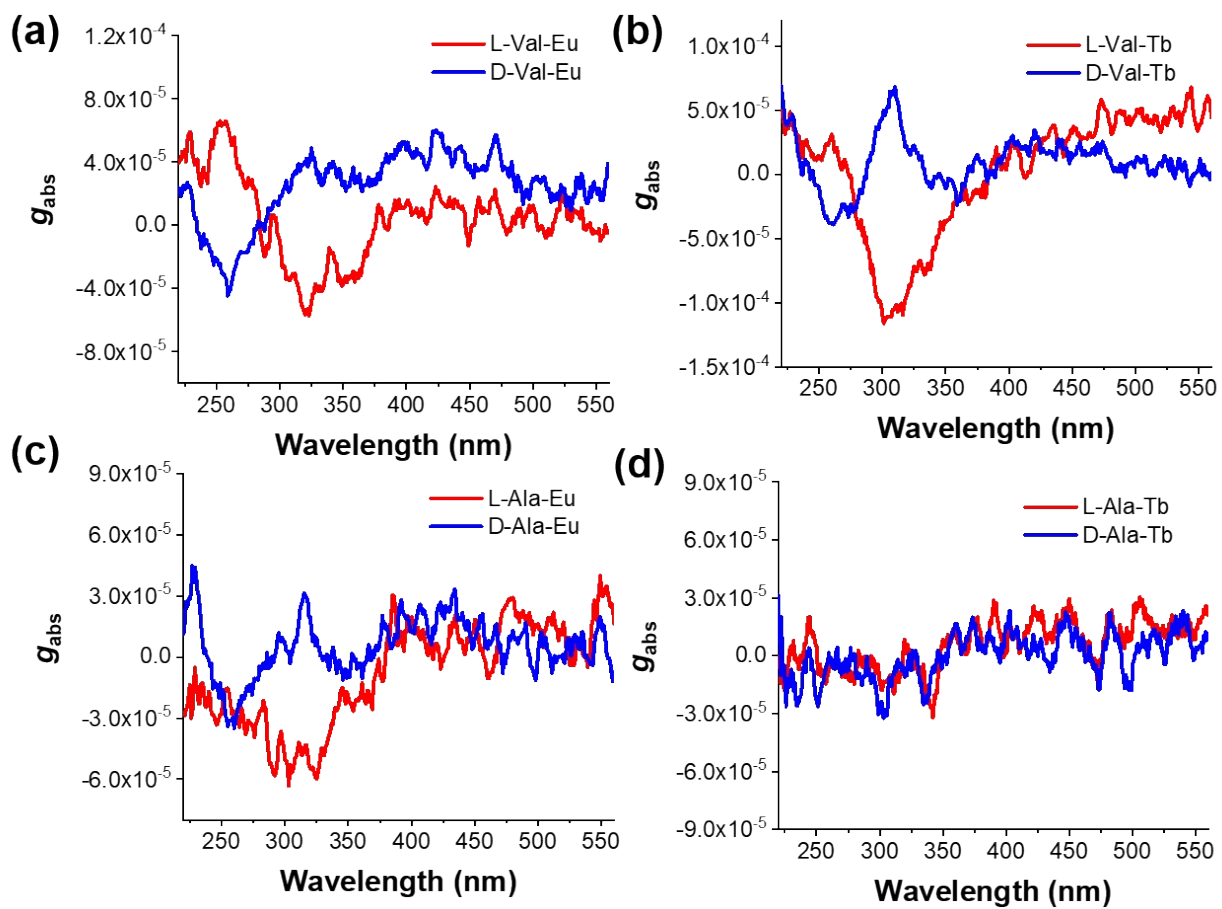


Fig. S5 g_{abs} spectra of (a) L/D -Val-Eu, (b) L/D -Val-Tb, (c) L/D -Ala-Eu, (d) L/D -Ala-Tb powder dispersed in methanol.

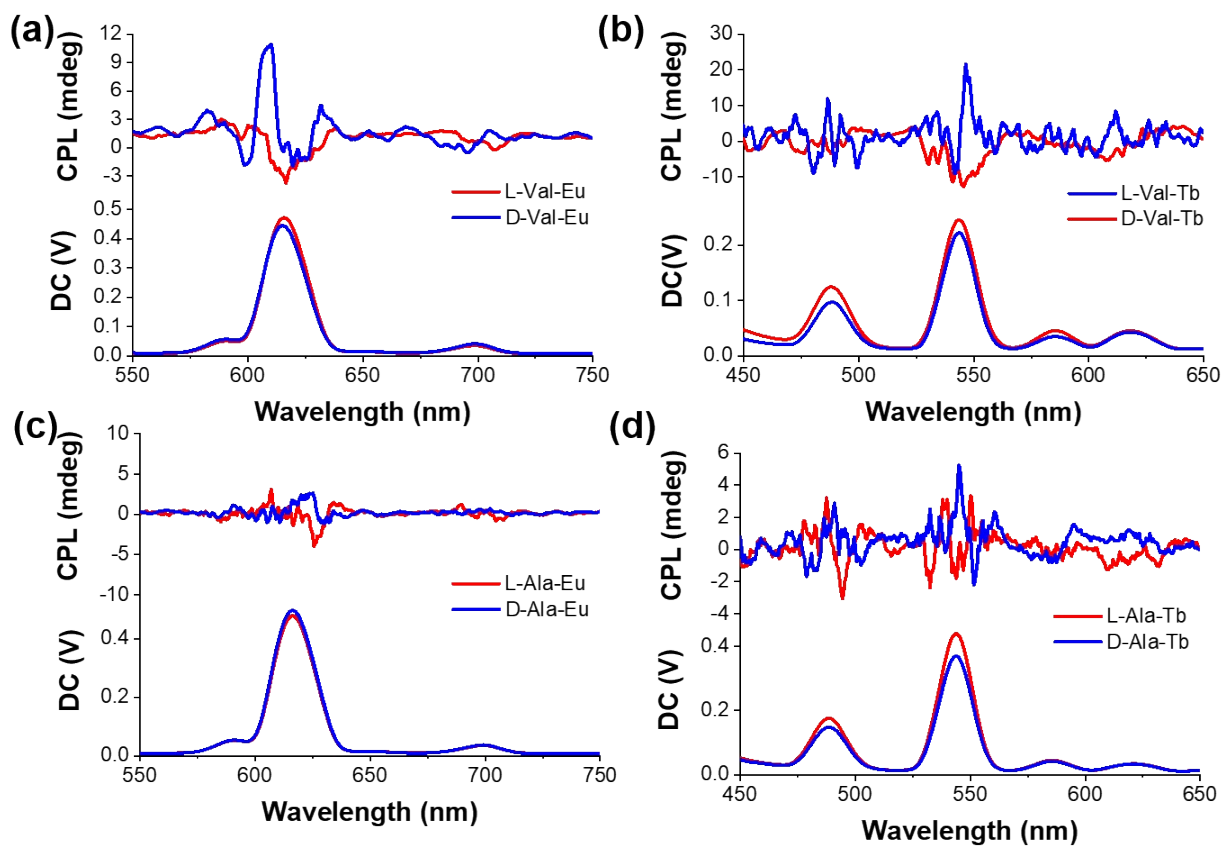


Fig. S6 CPL spectra of (a) L/D -Val-Eu, (b) L/D -Val-Tb, (c) L/D -Ala-Eu, (d) L/D -Ala-Tb powder excited by 347 nm Xe lamp.

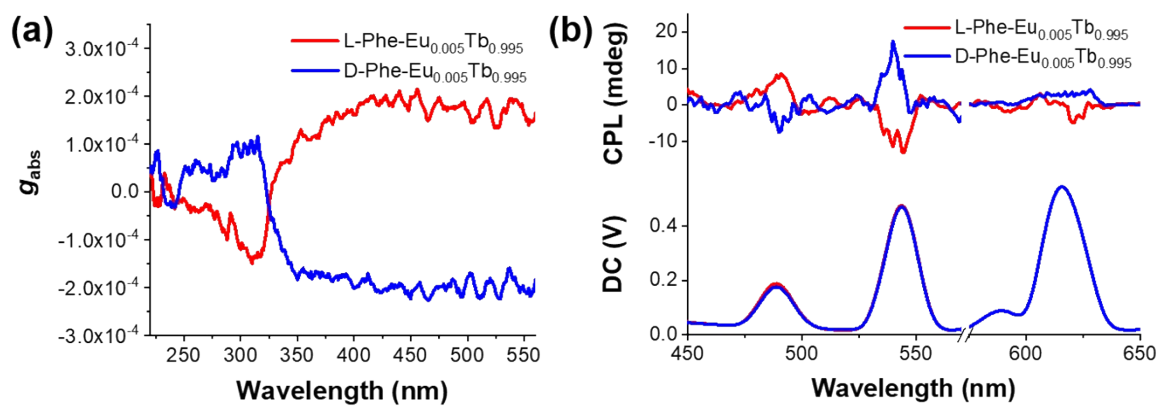


Fig. S7 (a) g_{abs} spectra of L/D-Phe-Eu_{0.005}Tb_{0.995} powder dispersed in methanol, (b) CPL spectra of L/D-Phe-Eu_{0.005}Tb_{0.995} powder excited by 347 nm Xe lamp.

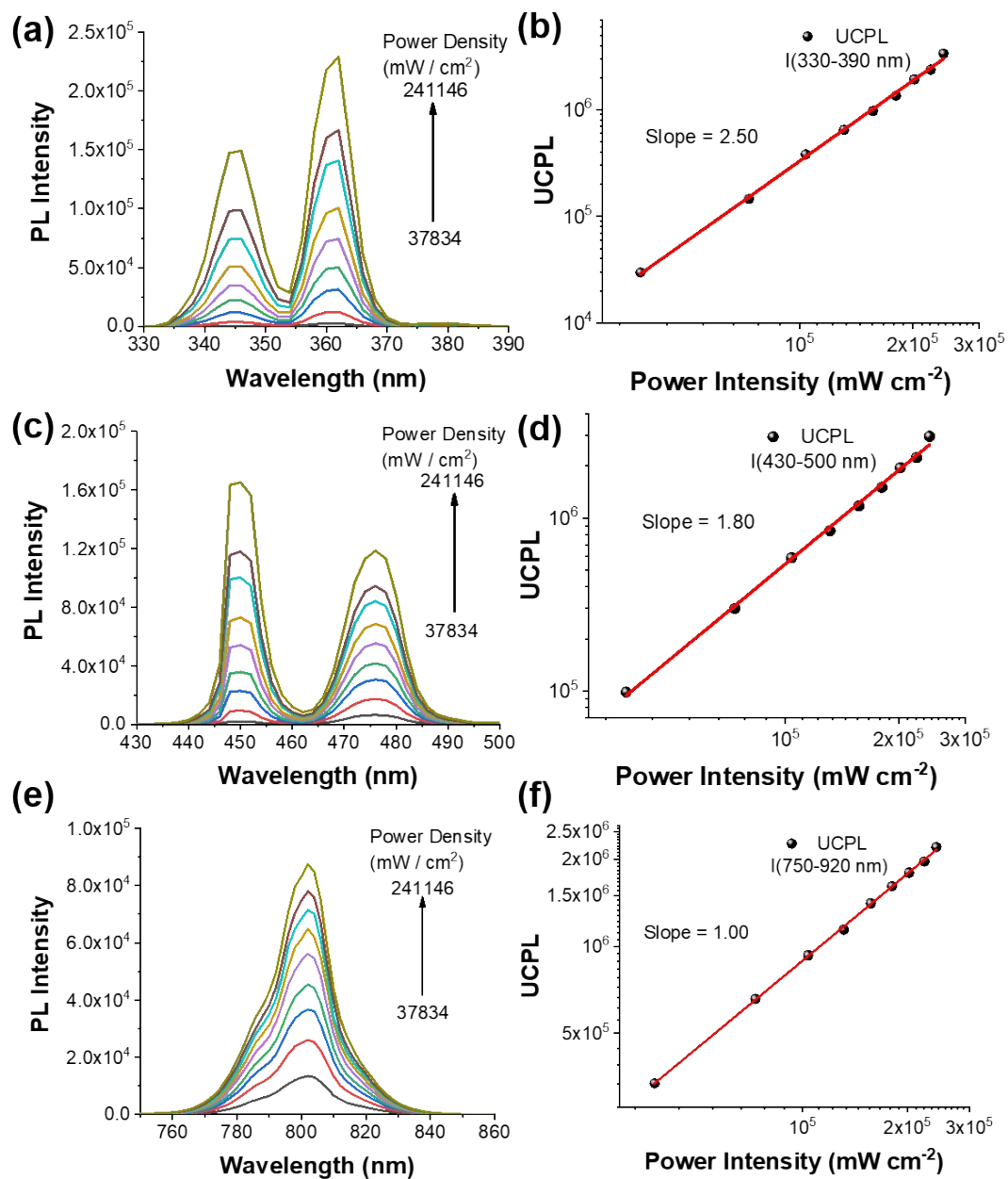


Fig. S8 Upconversion emission spectra of UCNPs of (a) 330-390 nm, (c) 430-500 nm, (e) 750-860 nm dispersed in chloroform (0.5 mg/mL) with different incident power densities of 980 nm laser. Double-logarithmic plots of the UC emission intensity (b) 330-390 nm, (d) 430-500 nm, (f) 750-860 nm of UCNPs as a function of excitation intensity of the 980 nm laser.

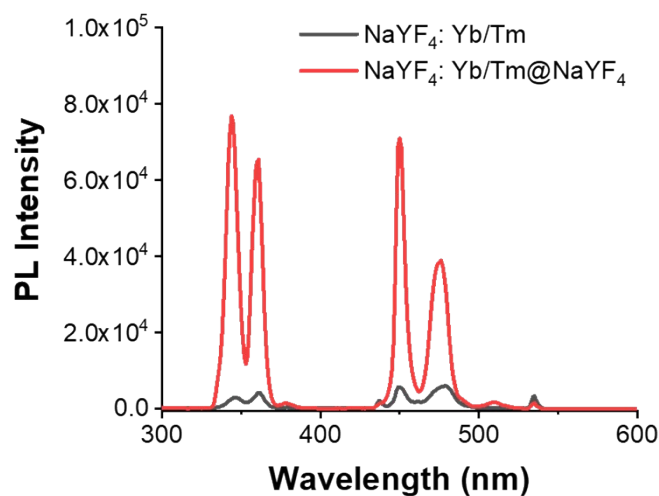


Fig. S9 Upconversion emission of NaYF₄: Yb/Tm and core-shell NaYF₄: Yb/Tm@NaYF₄ (this work) dispersed in chloroform (0.5 mg/mL) excited by 980 nm laser (power density: 49936 mW/cm²). The emission intensity of core-shell NaYF₄: Yb/Tm@NaYF₄ was highly improved compared to NaYF₄: Yb/Tm, attributing to reducing surface defects.

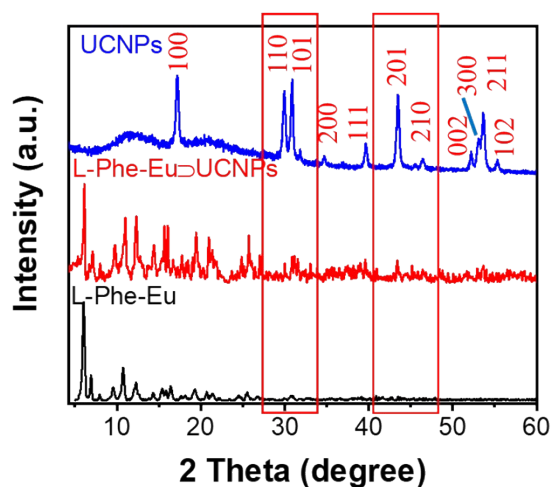


Fig. S10 XRD patterns of core-shell NaYF₄: Yb/Tm@NaYF₄ UCNPs, L-Phe-Eu@UCNPs and L-Phe-Eu.

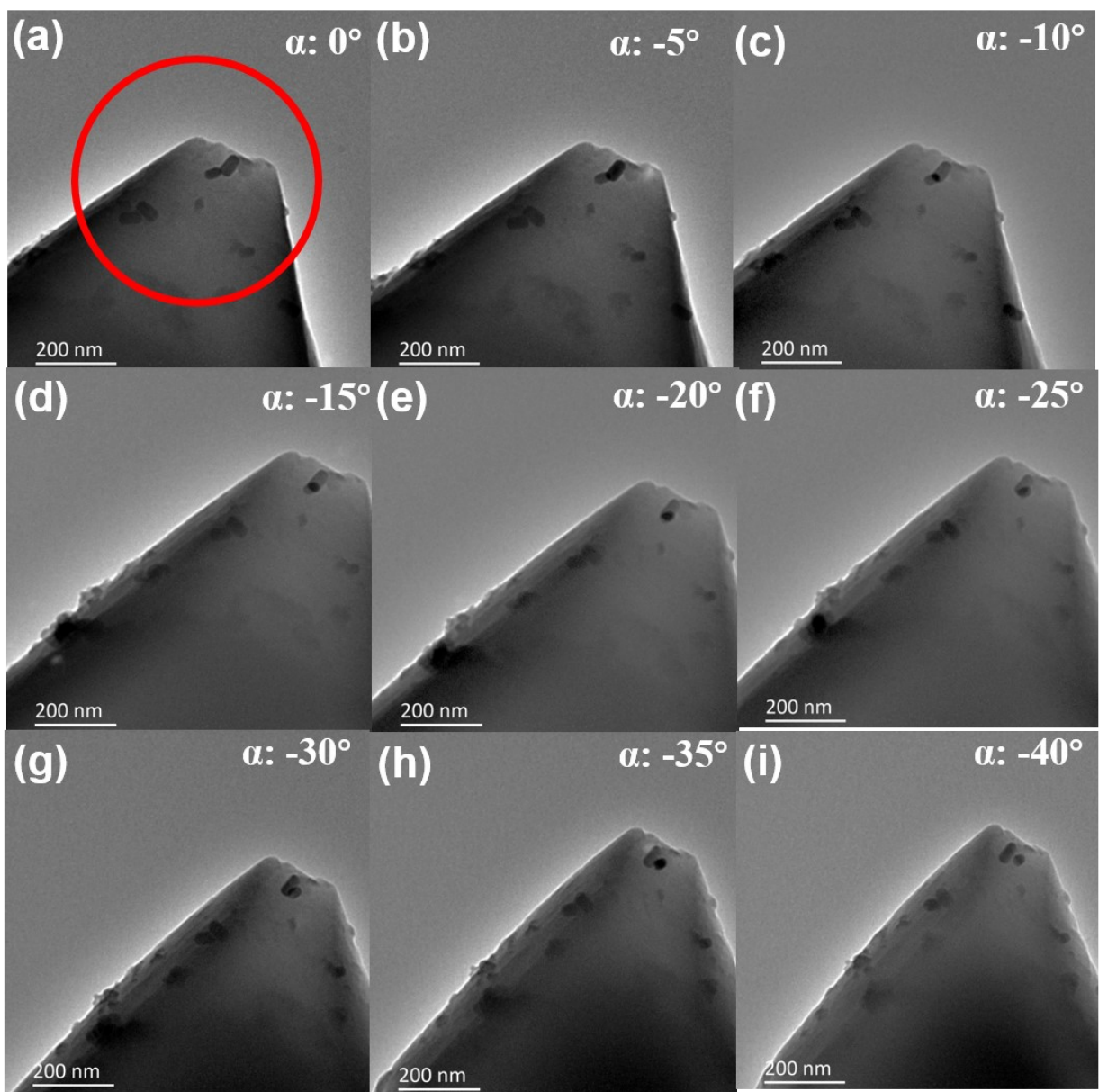


Fig. S11 TEM image of L-Phe-Eu@UCNPs of copper mesh with (a) 0° , (b) -5° , (c) -10° , (d) -15° , (e) -20° , (f) -25° , (g) -30° , (h) -35° , (i) -40° .

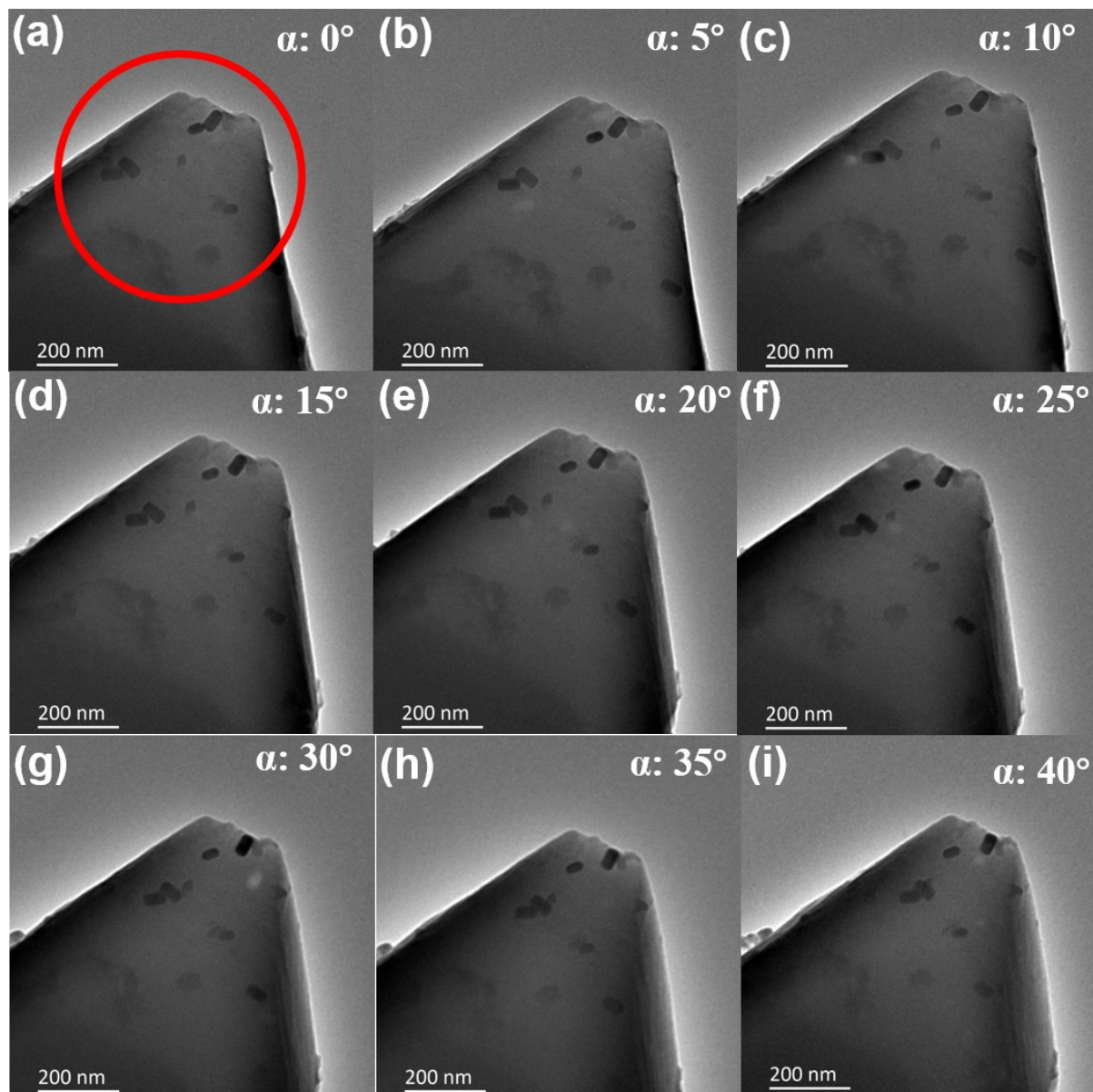


Fig. S12. TEM image of L-Phe-Eu@UCNPs of copper mesh with (a) 0° , (b) -5° , (c) -10° , (d) -15° , (e) -20° , (f) -25° , (g) -30° , (h) -35° , (i) -40° .

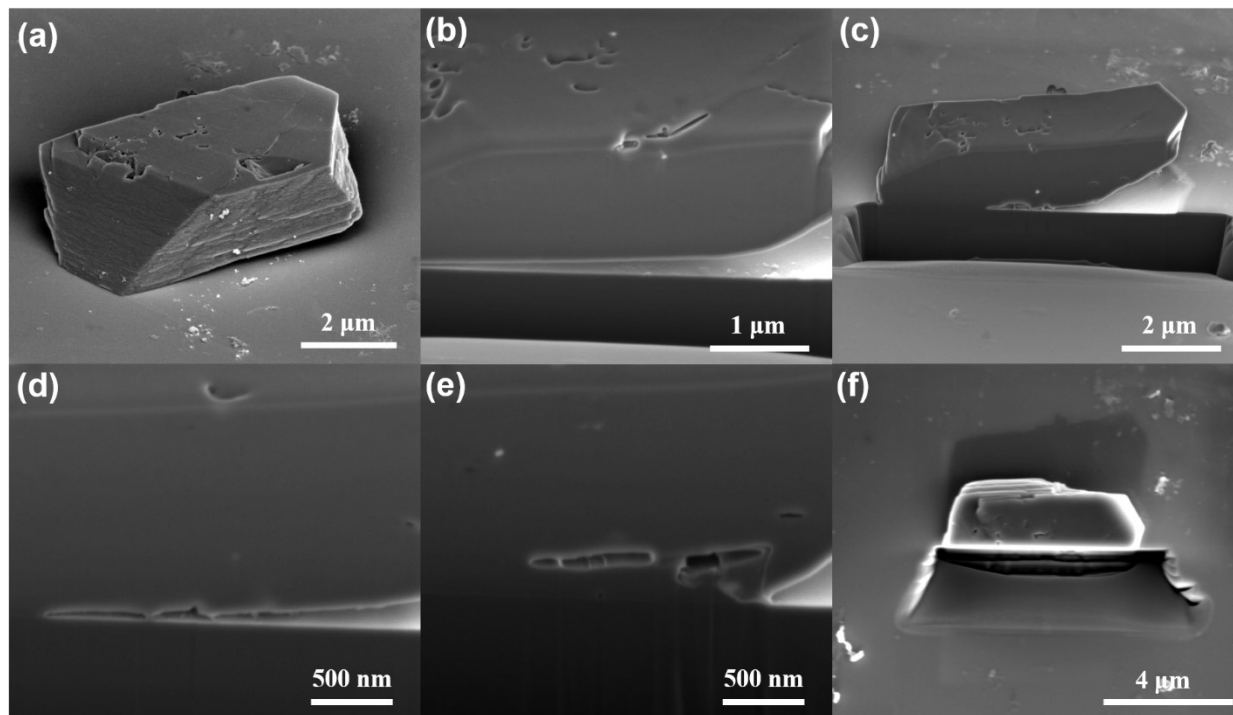


Fig. S13 Images of SEM/FIB dual beam system of L-Phe-Eu \supset UCNPs. (a) SEM image of L-Phe-Eu \supset UCNPs, tilt: 52°, (b-e) SEM image of L-Phe-Eu \supset UCNPs after FIB cutting, tilt: 52°, (f) Top view of L-Phe-Eu \supset UCNPs after FIB cutting, tilt: 0°.

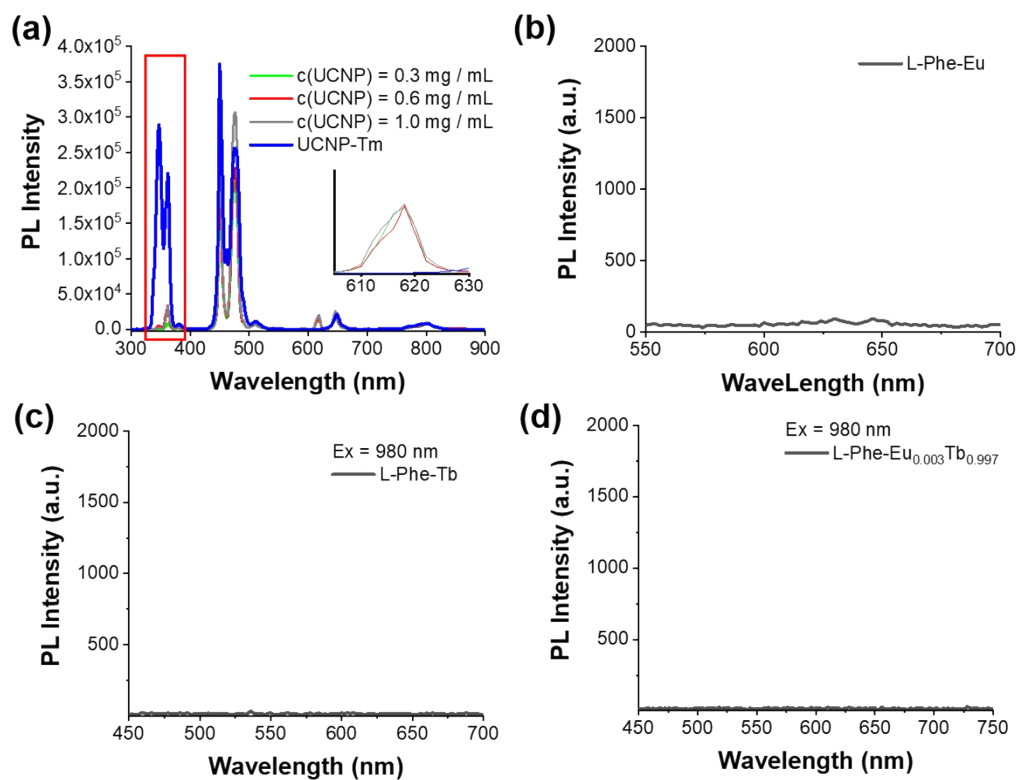


Fig. S14 (a) Upconversion emission of UCNP powder, L-Phe-Eu \supset UCNP powder with excitation of 980 nm laser. (c(UCNP) represents with the concentrations of PVP- modified in the reaction system.) Upconversion emission of (b) L-Phe-Eu, (c) L-Phe-Tb, (d) L-Phe-Eu_{0.003}Tb_{0.997} powder without encapsulation of UCNP excited by 980 nm (power density: 42547 mW/cm²).

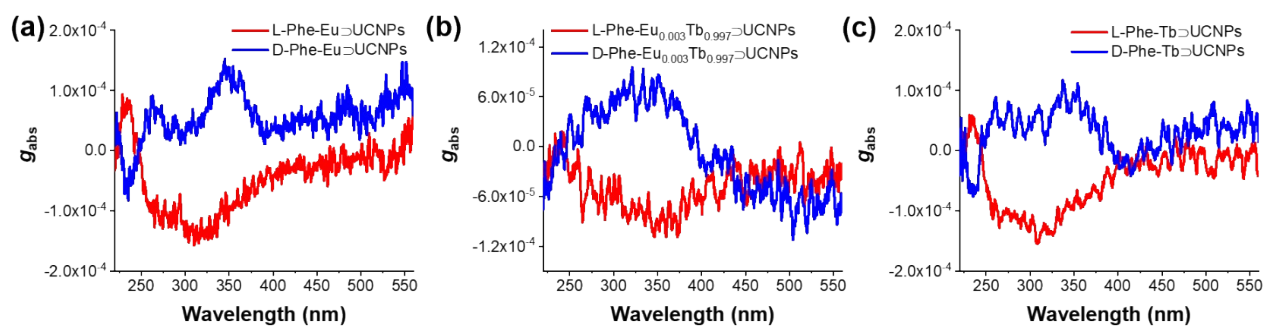


Fig. S15 g_{abs} of L-Phe-Eu \supset UCNPs, L-Phe-Eu_{0.003}Tb_{0.997} \supset UCNPs, L-Phe-Tb \supset UCNPs powders dispersed in methanol.

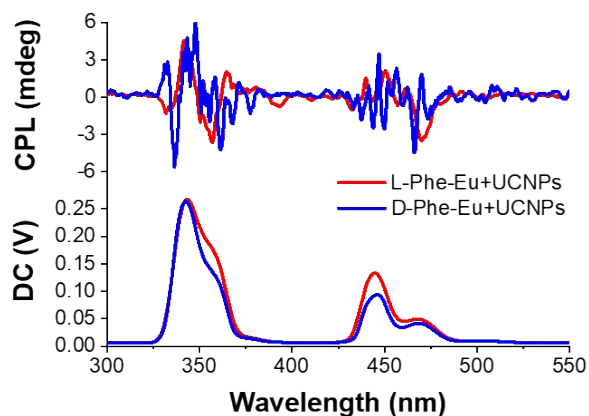


Fig. S16 Upconversion CPL spectra of the composites prepared by physical adsorption upon excitation of 980 nm. CPL spectra of PVP modified upconversion nanoparticles (PVP-UCNPs) and L-/D-Phe-Eu dispersed in PMMA upon irradiation with 980 nm laser. [PVP-UCNPs] = 2 wt % in PMMA, [L-/D-Phe-Eu] = 5 wt% in PMMA, PMMA was 100 mg/mL in chloroform. Composite layers were cast onto the surface of a quartz substrate and annealed at 50°C.

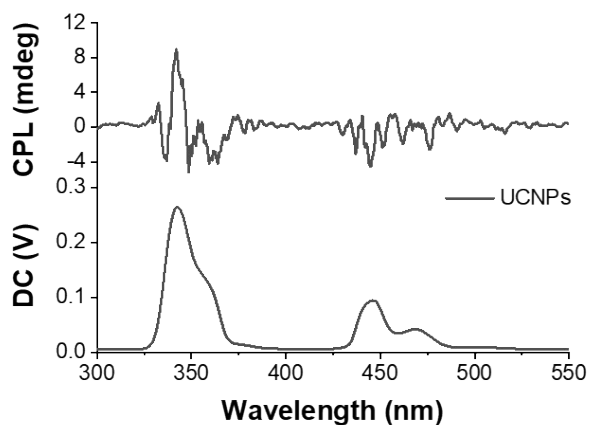


Fig. S17 Upconversion CPL spectra of PVP-UCNPs powder upon excitation of 980 nm.

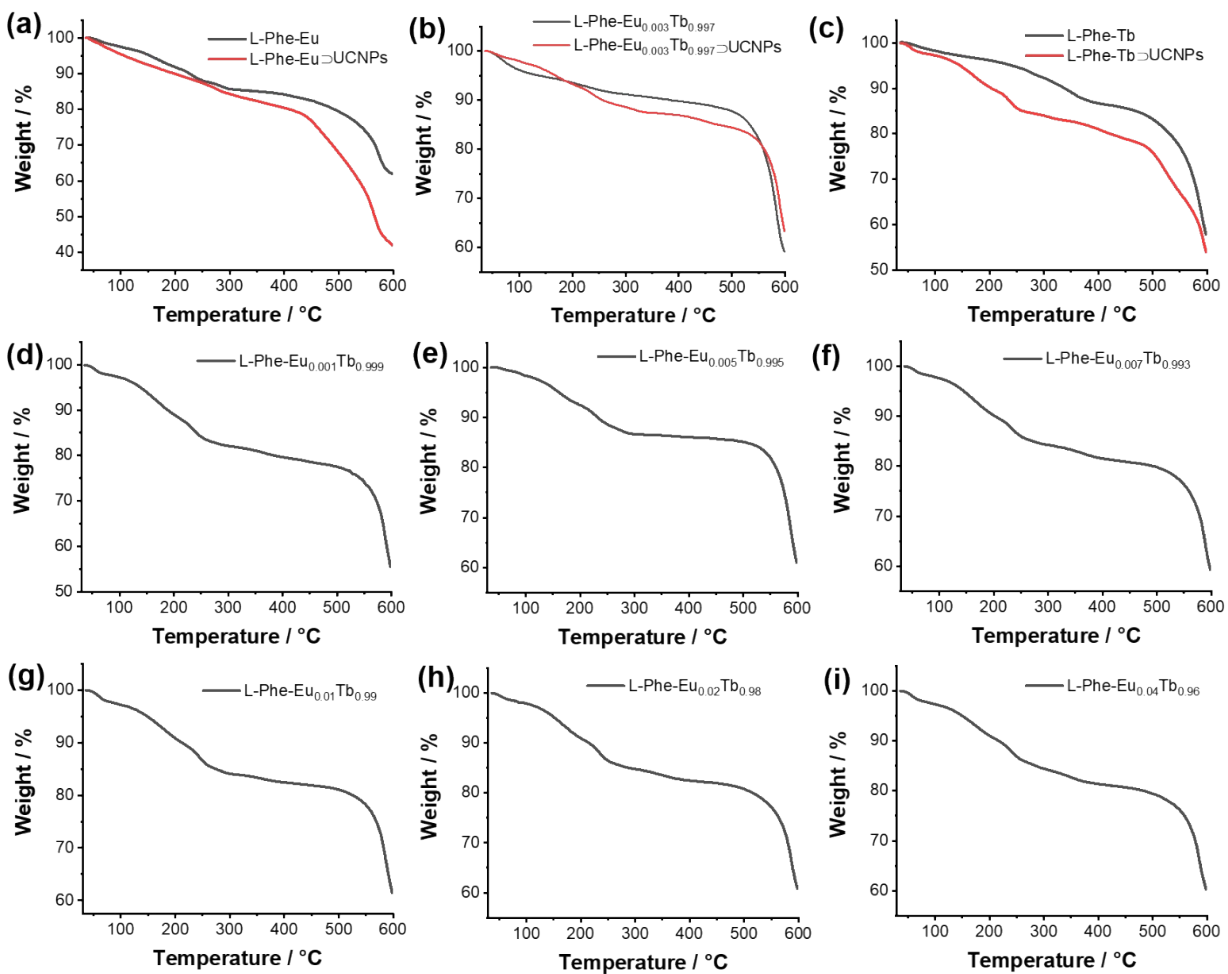


Fig. S18 Thermogravimetric analyses curves of (a) L-Phe-Eu (black line), L-Phe-Eu \supset UCNPs (red line), (b) L-Phe-Eu_{0.003}Tb_{0.997} (black line), L-Phe-Eu_{0.003}Tb_{0.997} \supset UCNPs (red line), (c) L-Phe-Tb (black line), L-Phe-Tb \supset UCNPs (red line), (d) L-Phe-Eu_{0.001}Tb_{0.999}, (e) L-Phe-Eu_{0.005}Tb_{0.995}, (f) L-Phe-Eu_{0.007}Tb_{0.993}, (g) L-Phe-Eu_{0.01}Tb_{0.99}, (h) L-Phe-Eu_{0.02}Tb_{0.98}, (i) L-Phe-Eu_{0.04}Tb_{0.96}.

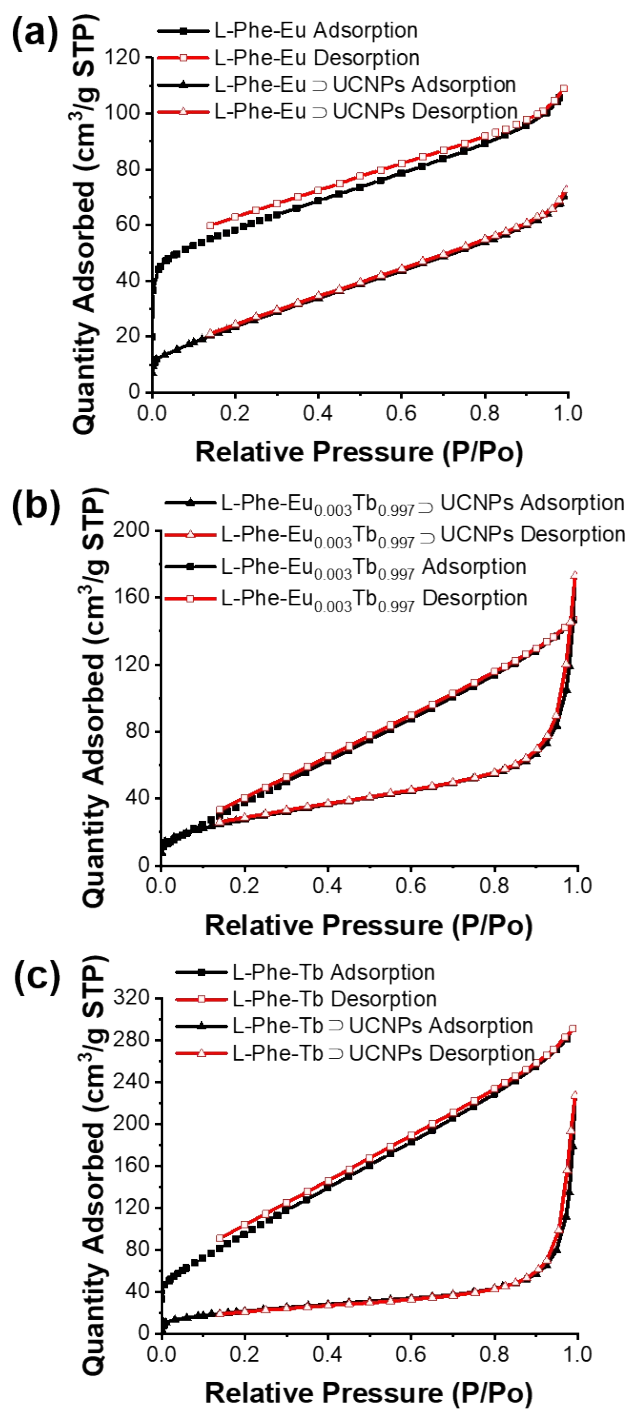


Fig. S19 Nitrogen adsorption isotherm of (a) L-Phe-Eu, L-Phe-Eu \supset UCNPs, (b) L-Phe-Eu_{0.003}Tb_{0.997}, L-Phe-Eu_{0.003}Tb_{0.997} \supset UCNPs, (c) L-Phe-Tb, L-Phe-Tb \supset UCNPs measured at 77 K.

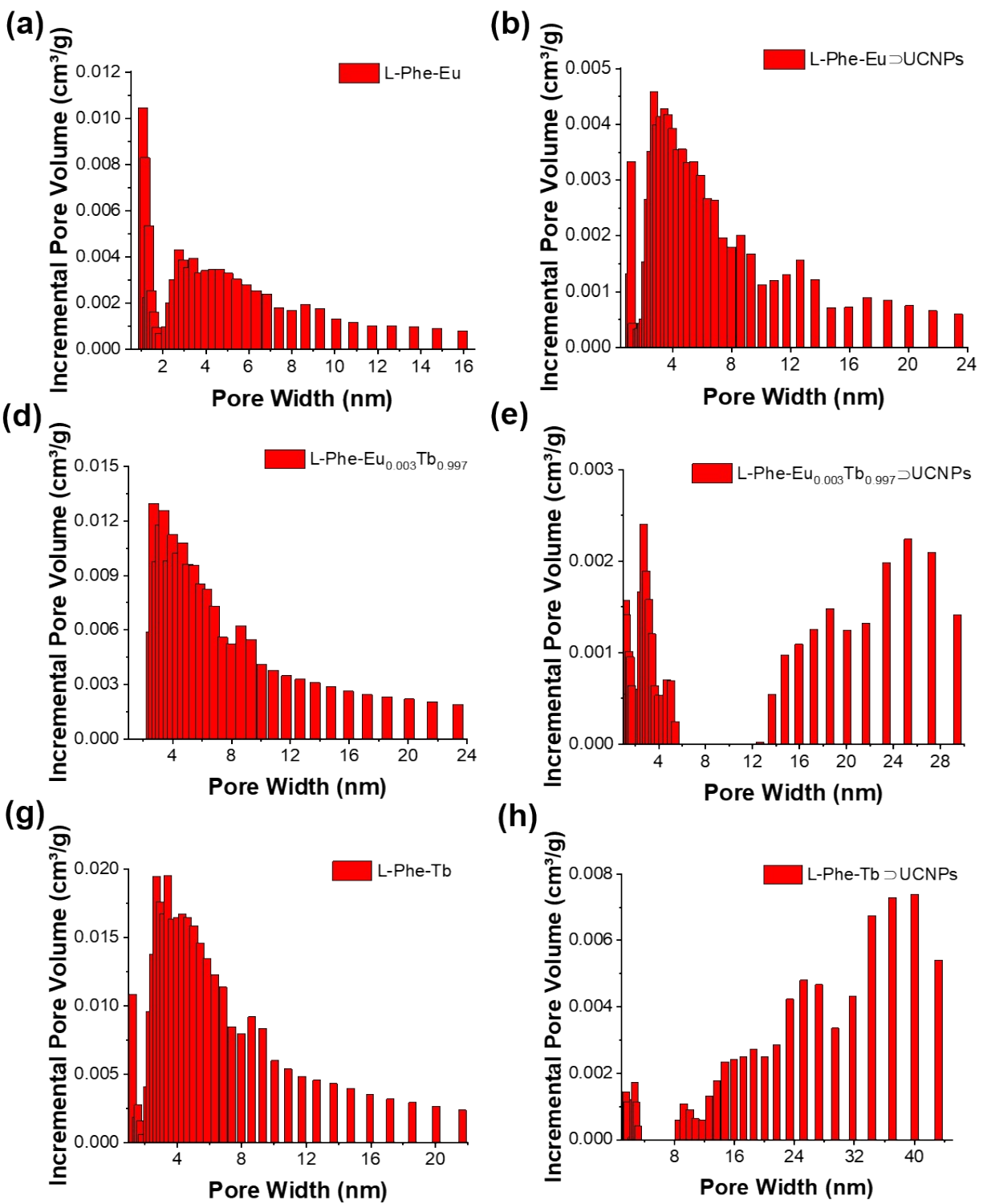


Fig. S20 The pore size distributions of (a) L-Phe-Eu, (b) L-Phe-Eu \supset UCNPs, (c) L-Phe-Eu_{0.003}Tb_{0.997}, (d) L-Phe-Eu_{0.003}Tb_{0.997} \supset UCNPs, (e) L-Phe-Tb, (f) L-Phe-Tb \supset UCNPs measured at 77 K.

Table S1. Porosity measurements of Ln-MOFs and Ln-MOFs \supset UCNPs

	BET surface area (m ² ·g ⁻¹)	Desorption average pore diameter (nm)
L-Phe-Eu	209.21	3.22
L-Phe-Eu \supset UCNPs	94.92	4.89
L-Phe-Eu _{0.003} Tb _{0.997}	195.55	4.66
L-Phe-Eu _{0.003} Tb _{0.997} \supset UCNPs	103.35	10.81
L-Phe-Tb	402.85	4.48
L-Phe-Tb \supset UCNPs	80.12	18.61

3. Reference

1. T. Yamada, T. Eguchi, T. Wakiyama, T. Narushima, H. Okamoto and N. Kimizuka, *Chem. - Eur. J.*, 2019, **25**, 6698-6702.
2. J.-C. Boyer, L. A. Cuccia and J. A. Capobianco, *Nano. Lett.*, 2007, **7**, 847-852.
3. H. Xu, B. Zhai, C. S. Cao and B. Zhao, *Inorg. Chem.*, 2016, **55**, 9671-9676.