Electronic Supplementary Information

Hypersensitive ratiometric temperature sensing in a bimetallic lanthanide metal-organic framework

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Section S1. Materials and Methods

Materials and reagents

All chemicals and solvents obtained from suppliers were used without further purification. All solvents were analytical grade reagent.

X-ray crystallography

SCXRD measurements were performed using a Rigaku XtaLAB Pro diffractometer with Cu-Kα radiation (λ = 1.54184 Å) and Mo-Kα radiation (λ = 0.71073 Å). Data collection and reduction were performed using *CrysAlis*^{Pro}. The structures were solved using intrinsic phasing methods (SHELXT-2015) and refined by full-matrix least squares on F^2 using OLEX2, which utilizes the SHELXL-2018/3 module. All atoms were refined anisotropically, and all hydrogen atoms were placed in their calculated positions with idealized geometries, and they possessed fixed isotropic displacement parameters. Appropriate restraints and/or constraints were applied to the geometry, and the atomic displacement parameters of the atoms in the MOF were determined.

Characterization

Single-crystal X-ray diffraction measurements of HPU-99 was performed on a Rigaku XtaLAB Pro diffractometer with Cu-Kα radiation (λ = 1.54184 Å) at 152 K. Elemental analyses of C, H, O, and N were performed on a FLASH2000 elemental analyzer. Powder X-ray diffraction (PXRD) data were performed at room temperature in air using a SmartLab diffractometer (Cu-Kα; λ = 1.54178 Å). Data were collected in the 2θ range of 5-50°. FT-IR spectra were recorded using a Bruker ALPHA II FT-IR spectrometer in the wavenumber range from 4000 to 400 cm^{-1}. UV-vis absorption spectra (solid) were recorded on a HITACHI UH4140 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo ESCALAB 250XI spectrometer. Transmission electron microscopy (TEM) images were obtained using a JEOL2100 electron microscope operated at 300 kV. TEM specimens were prepared by depositing one or two drops of the sample solutions onto carbon-coated copper grids. Scanning electron microscopy (SEM) measurement was carried out using Merlin Compact. Thermogravimetric (TG) analyses of the as-synthesized samples were performed on a STA449F3 thermal analyzer from room temperature to 1200 ℃ at a heating rate of 10 ℃/min under nitrogen atmosphere. Steady-state photoluminescence (PL) spectra of solutions and powder were recorded on an Edinburgh FLS1000 fluorescence spectrometer using a xenon lamp as the excitation source. The fluorescence lifetime was determined using an Edinburgh FLS1000 fluorescence spectrometer and the absolute fluorescence quantum yield in the solid state was measured using an integrating sphere on the same fluorescence spectrometer. The low-temperature spectra were also measured on Edinburgh FLS1000 fluorescence spectrometer. Inductively coupled plasma optical emission spectrometer (ICP-OES) analyses of the pre-process samples were performed on a Agilent 5110 analyzer. The 10 mg dried sample was digested with 0.05 mL concentrated nitric acid and then diluted with 19.95 mL deionized water. After ultrasonic treatment for 20 minutes, a stable solution to be analyzed was obtained by filtration membrane.

Experimental

Preparation of $\{[Eu_4(ebdc)_6(DMF)_{2.75}(H_2O)_7]\}_n$ (denoted as HPU-99)

HPU-99 was synthesized by the solvothermal method and its typical synthesis process was as follows. First, the ligand 5-ethynyl-isophthalic acid (0.05 mmol, 9.51 mg) was dissolved in 2.5 mL DMF by ultrasound for 3 minutes to obtain a light yellow solution and set aside. $Eu(NO_3)_3{\cdot}6H_2O$ (0.05 mmol, 22.30 mg) was dissolved in 2.5 mL deionized water and then was added to the above mentioned ligand solution. The resulting mixture was transferred to a 25 mL stainless steel reactor, kept in the air blowing drying oven under a temperature of 100 °C for 48 h, cooled to room temperature naturally, and colorless plate crystals were obtained. Finally, HPU-99 was obtained by extraction and filtration, washed with DMF for three times, and dried in vacuum at 60 ℃ overnight. (60% yield, based on Eu). Elemental analysis (found, %; based on $C_{68.25}H_{57.25}Eu_4N_{2.75}O_{33.75}$): C, 40.99 ; H, 2.28 ; N, 1.38; O, 18.15.

Preparation of Eu_xTb_{1-x}-HPU-99 (x = 0, 0.05, 0.1, 0.2, 0.3)

Tb-HPU-99 was prepared by the solvothermal method, and the synthesis steps and reaction conditions were basically the same as those of HPU-99. It was only necessary to replace the metal salt $Eu(NO_3)_3{\cdot}6H_2O$ with equal molar amount $Tb(NO_3)_3{\cdot}6H_2O$.

For the synthesis of Eu_xTb_{1-x}-HPU-99 (x = 0.05, 0.1, 0.2, 0.3), the metallic salts $Eu(NO_3)_3{\cdot}6H_2O$ were replaced by $Eu(NO_3)_3{\cdot}6H_2O$ and $Tb(NO_3)_3{\cdot}6H_2O$ corresponding to the molar ratio, other conditions remained unchanged.

Preparation of Ag NCs@HPU-99

Ag NCs@HPU-99 compound was prepared by a solution infiltration method. Prepare an aqueous solution of silver nitrate with a concentration of 0.08 $mmol{\cdot}mL^{-1}$ and put 2.5 mL into a brown screw-topped glass bottle for later use. HPU-99 (15 mg) was dispersed in 1.5 mL of DMF solvent and treated with ultrasound for 5 minutes. The suspension was then slowly added to the above silver nitrate solution and the spiral glass vial was sealed. The mixture was incubated for 24 h preserved in dark place at room temperature, followed by suction filtration and washed thoroughly with a large amount of deionized water, and dried in vacuum at 50 ℃ overnight before performing characterization.

Section S2. Supplementary Figures

HPU-99

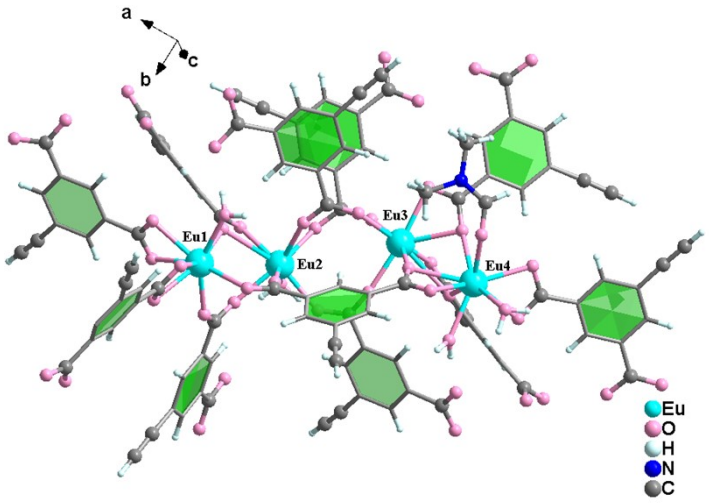

Figure S1 The coordinated environments of Eu^{3+}. Atom color codes: turquiose, Eu; pink, O; gray, C; pale blue, H; and blue, N.

PXRD

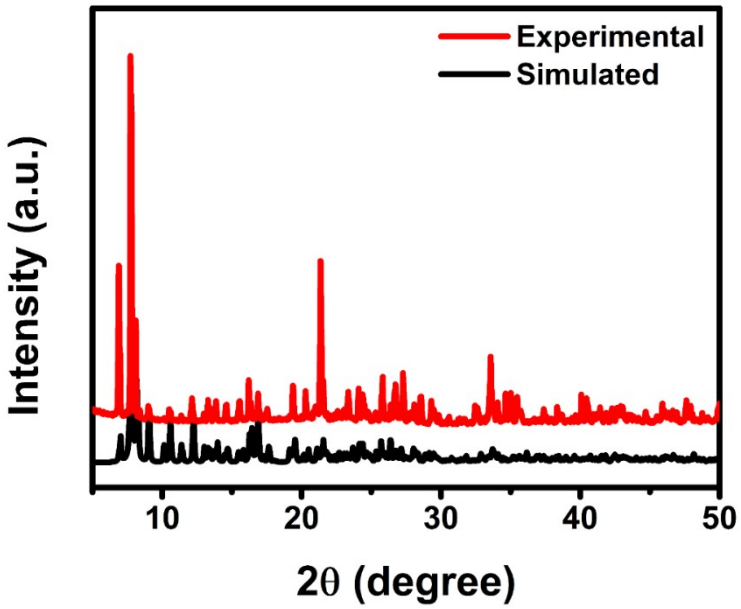

Figure S2 Powder XRD patterns of HPU-99.

FT-IR

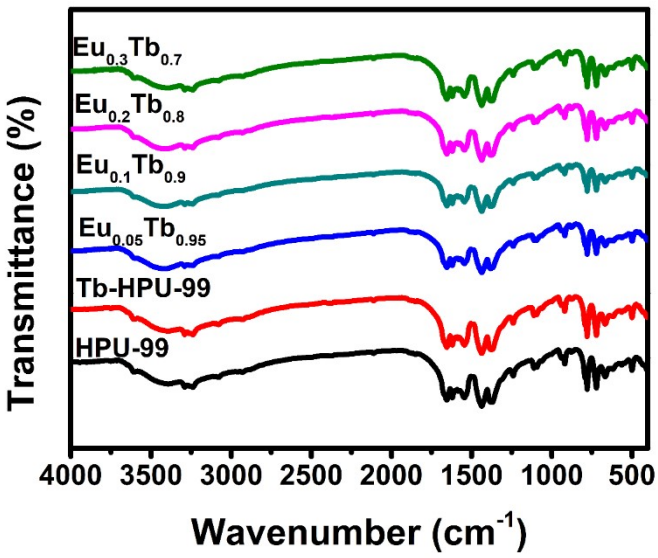

Figure S3 FT-IR spectra of HPU-99 and Eu_xTb_{1-x}-HPU-99 (x = 0, 0.05, 0.1, 0.2, 0.3).

SEM

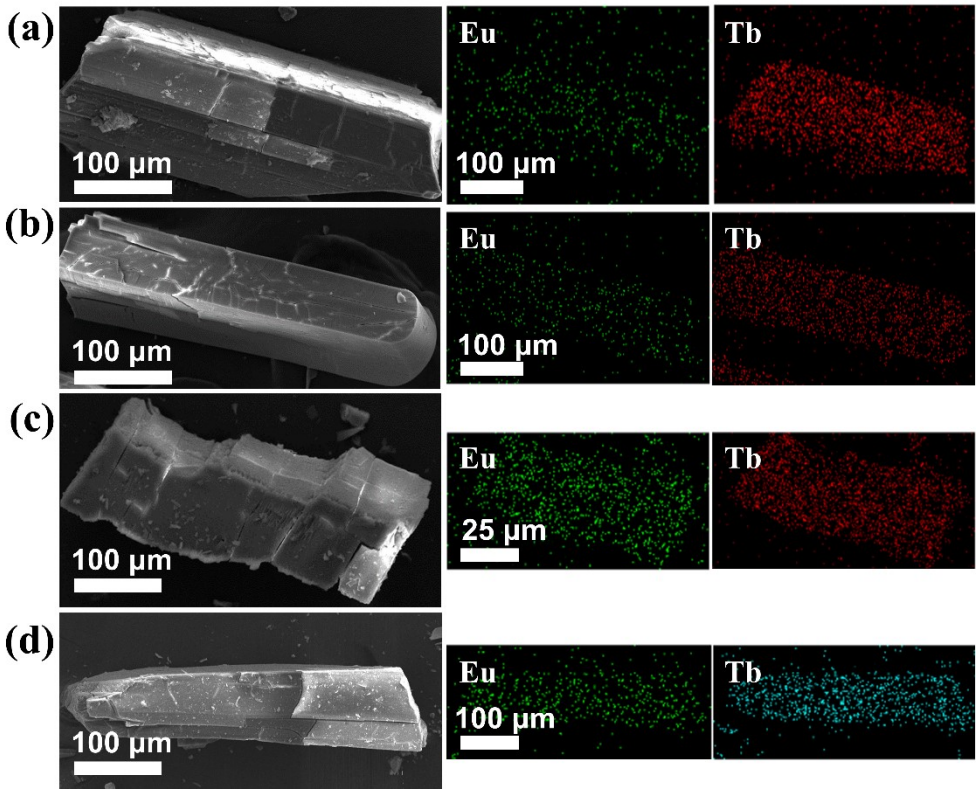

Figure S4 SEM images (left) and EDX mapping of (a) $Eu_{0.05}Tb_{0.95}$-HPU-99, (b) $Eu_{0.1}Tb_{0.9}$-HPU-99, (c) $Eu_{0.2}Tb_{0.8}$-HPU-99, (d) $Eu_{0.3}Tb_{0.7}$-HPU-99. The corresponding elemental distributions of Eu (middle) and Tb (right).

TG

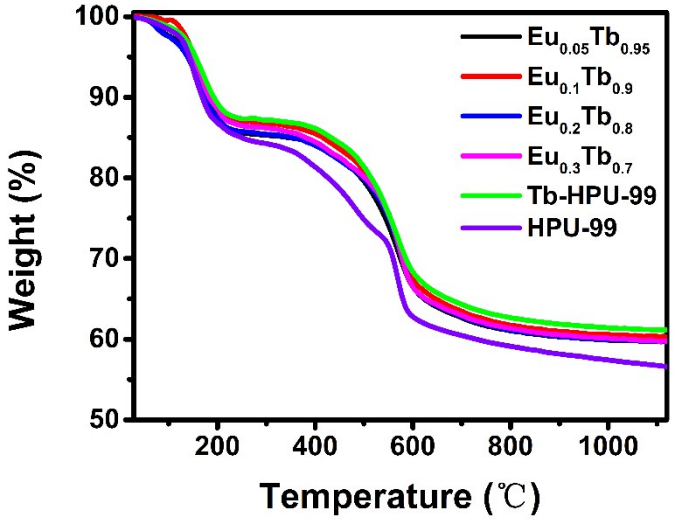

Figure S5 TGA plots of HPU-99 and Eu_xTb_{1-x}-HPU-99 (x = 0, 0.05, 0.1, 0.2, 0.3).

Emission

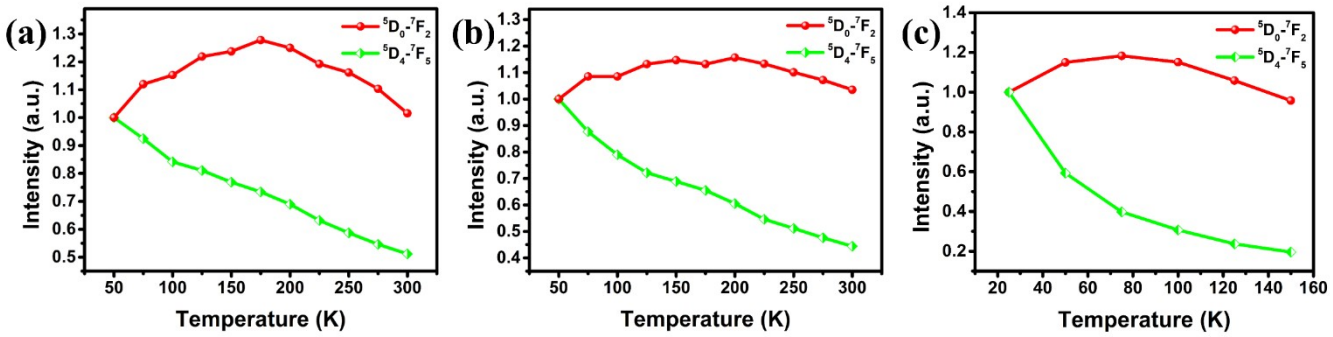

Figure S6 Temperature-dependent intensity of Eu^{3+} ($^5D_0$-$^7F_2$) transition and Tb^{3+} ($^5D_4$-$^7F_5$) transition of (a) $Eu_{0.05}Tb_{0.95}$-HPU-99, (b) $Eu_{0.1}Tb_{0.9}$-HPU-99 and (c) $Eu_{0.2}Tb_{0.8}$-HPU-99.

Lifetime

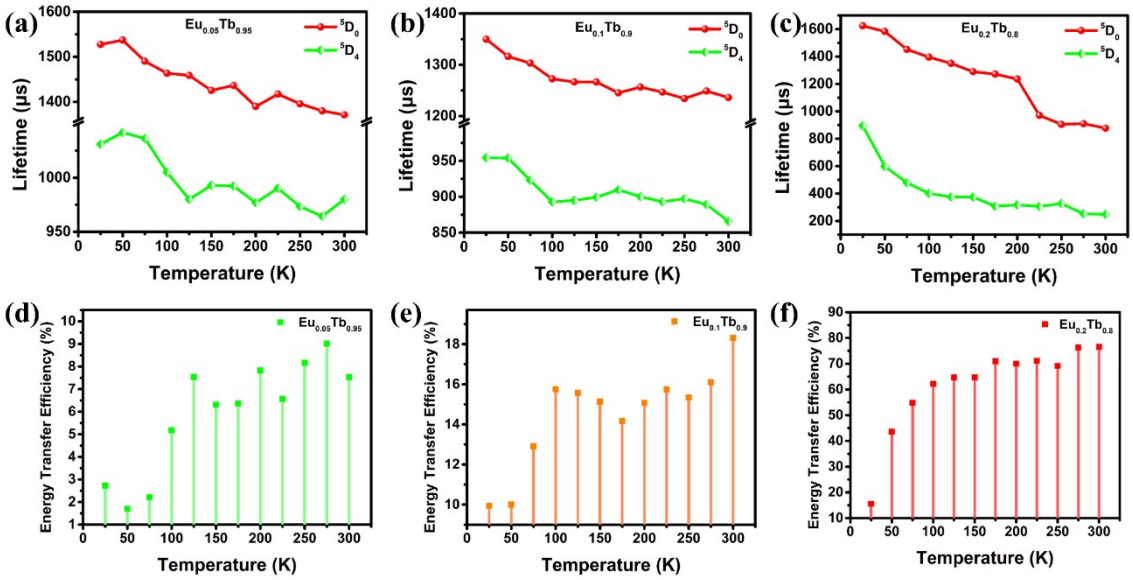

Figure S7 The Eu^{3+} ($^5D_0$) and Tb^{3+}($^5D_4$) lifetimes for (a) $Eu_{0.05}Tb_{0.95}$-HPU-99, (b) $Eu_{0.1}Tb_{0.9}$-HPU-99 and (c) $Eu_{0.2}Tb_{0.8}$-HPU-99 in the range of 25 to 300 K, the energy transfer efficiency from Tb^{3+} to Eu^{3+}within (d) $Eu_{0.05}Tb_{0.95}$-HPU-99, (e) $Eu_{0.1}Tb_{0.9}$-HPU-99 and (f) $Eu_{0.2}Tb_{0.8}$-HPU-99.

Reversibility

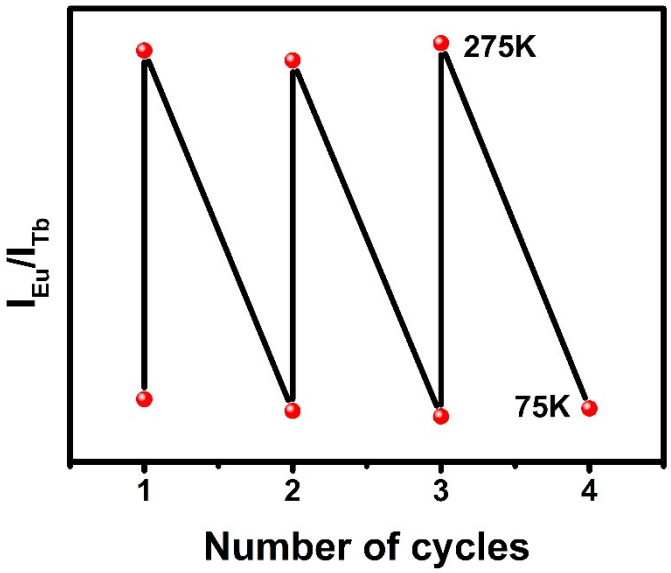

Figure S8 The reversible changes of emission intensity ratio of Eu^{3+} ($^5D_0$-$^7F_2$) to Tb^{3+} ($^5D_4$-$^7F_5$) of $Eu_{0.05}Tb_{0.95}$-HPU-99 by the alternative thermo-cycles in the range of 75 K and 275 K.

PXRD

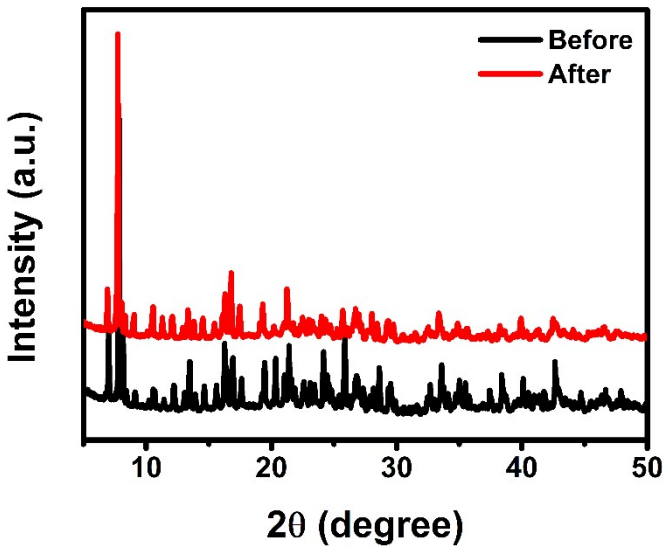

Figure S9 PXRD patters of $Eu_{0.05}Tb_{0.95}$-HPU-99 before and after three thermo-cycles in the range of 75 K and 275 K.

XPS

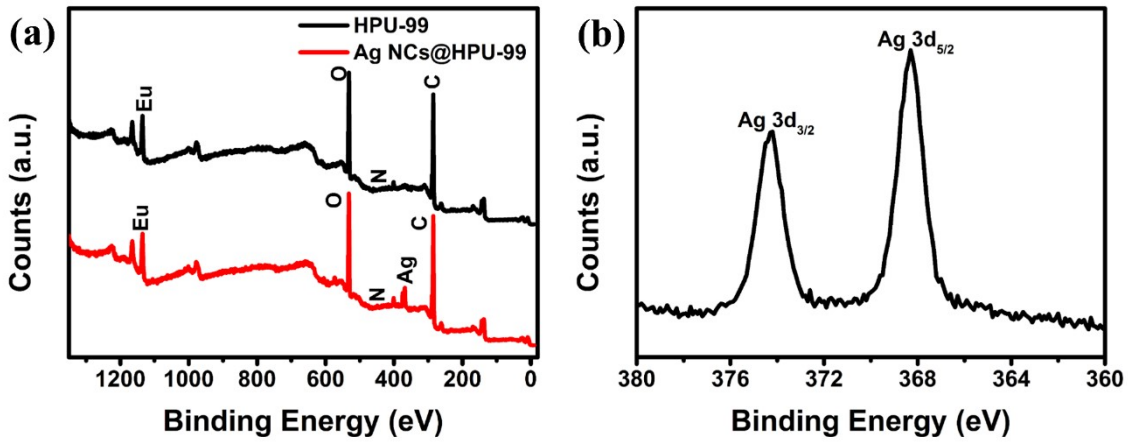

Figure S10 (a) XPS spectra of HPU-99 and Ag NCs@HPU-99. (b) XPS analysis of Ag 3d region for Ag NCs@HPU-99.

SEM

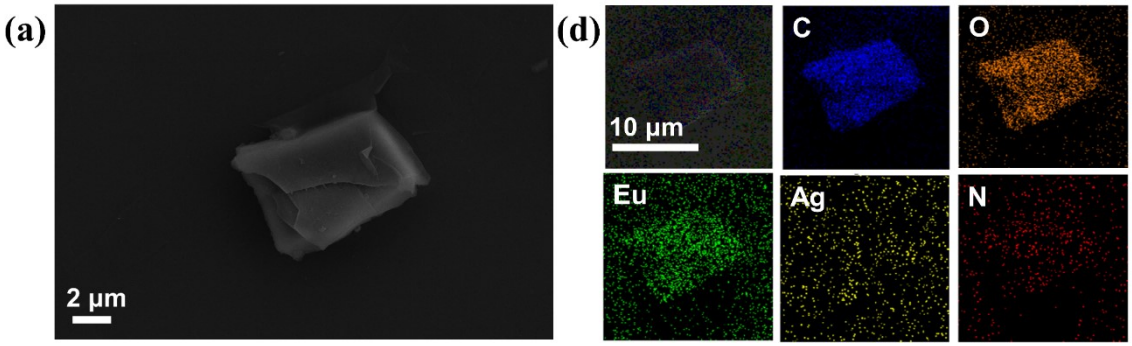

Figure S11 (a) SEM images of Ag NCs@HPU-99. (b) The corresponding elements EDX mapping of Ag NCs@HPU-99.

TG

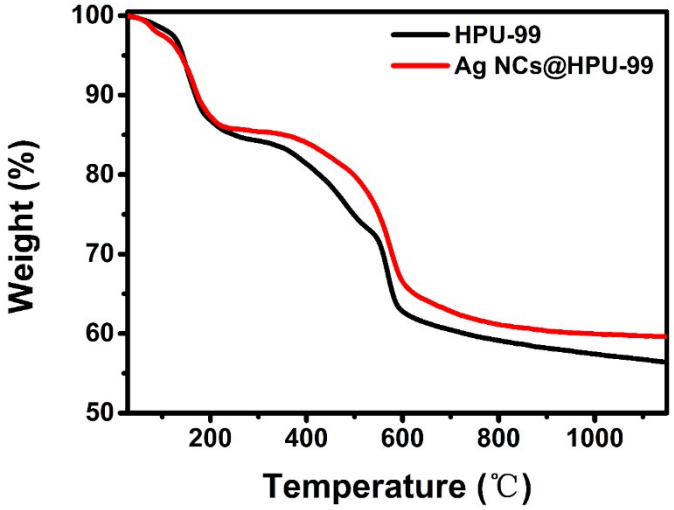

Figure S12 TGA plots of HPU-99 (black) and Ag NCs@HPU-99 (red) under nitrogen.

PL

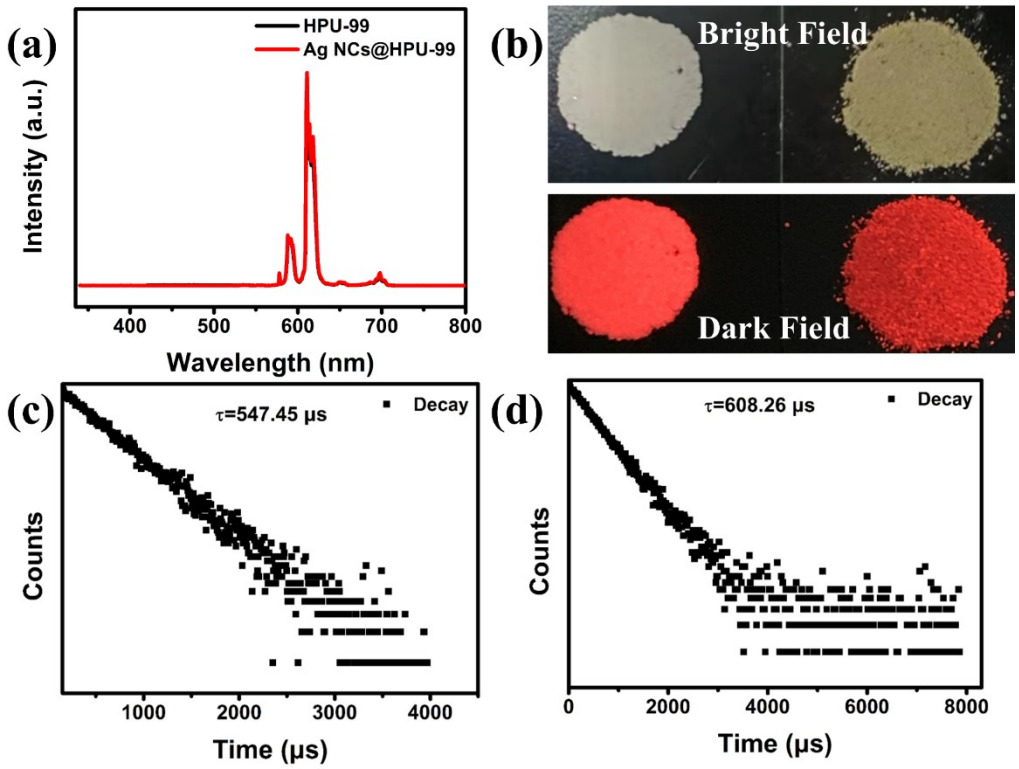

Figure S13 (a) Fluorescent and emission spectra obtained for HPU-99 and Ag NCs@HPU-99 (λ_{ex} = 314 nm). (b) Photograph of HPU-99 and Ag NCs@HPU-99 under natural light and 365 nm UV lamp. Fluorescence lifetime spectra obtained for (c) HPU-99 and (d) Ag NCs@HPU-99 at room temperature.

Section S3. Supplementary Tables

Table S1 Crystallographic data collection and refinement result for HPU-99

	HPU-99
CCDC number	2292095
Empirical formula	$C_{68.25}H_{57.25}Eu_4N_{2.75}O_{33.75}$
Formula weight	2063.75
Temperature (K)	152.00
Wavelength (Å)	1.34138
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	13.6608(10)
b (Å)	43.285(3)
c (Å)	13.8948(11)
α (°)	90
β (°)	105.598(2)
γ (°)	90
V (Å^3)	7913.4(10)
Z	4
ρ_{calc} (g/cm^3)	1.732
F(000)	4032
Goodness-of-fit on F^2	1.058
Final R indices [I>2σ(I)]	R_1 = 0.0471, wR_2 = 0.1233
R indices [all data]	R_1 = 0.0495, wR_2 = 0.1247

Table S2 Bond lengths for HPU-99.

Eu1-O3[1]	2.447(4)	Eu3-O1	2.281(4)
Eu1-O4[1]	2.468(4)	Eu3-O9	2.315(4)
Eu1-O6	2.344(4)	Eu3-O15[3]	2.772(4)
Eu1-O7[2]	2.469(4)	Eu3-O16[3]	2.342(4)
Eu1-O8[2]	2.468(4)	Eu3-O17	2.313(3)
Eu1-O14	2.393(4)	Eu3-O19[4]	2.431(4)
Eu1-O23	3.042(7)	Eu3-O20[4]	2.519(4)
Eu1-O24	2.441(5)	Eu3-O21	2.312(4)
Eu1-O28	2.410(4)	Eu4-O11[3]	2.490(4)
Eu2-O2	2.299(6)	Eu4-O12[3]	2.450(4)
Eu2-O5	2.310(4)	Eu4-O15[3]	2.448(4)
Eu2-O10	2.332(4)	Eu4-O20[4]	2.479(4)
Eu2-O13	2.358(4)	Eu4-O21	2.581(4)
Eu2-O14	2.835(4)	Eu4-O22	2.538(4)
Eu2-O18	2.380(3)	Eu4-O26	2.421(4)
Eu2-O23	2.360(7)	Eu4-O27	2.428(4)
Eu2-O25	2.457(5)	Eu4-O35	2.377(4)

Symmetry codes: [1]1+x, +y, +z; [2]1/2+x, 3/2-y, 1/2+z; [3]-1+x, +y, +z; [4]1-x, 1-y, 1-z.

Table S3 The feed composition ratios and molar ratios after reaction of Eu^{3+} and Tb^{3+} ions in Eu_xTb_{1-x}-HPU-99 measured by ICP

Samples	Eu/Tb (%) ratio used in the reaction	Eu/Tb (%) ratio calculated from ICP	
		Eu^{3+}	Tb^{3+}
Tb-HPU-99	0:100	0	100
$Eu_{0.05}Tb_{0.95}$-HPU-99	0.05:0.95	0.0551	0.9426
$Eu_{0.1}Tb_{0.9}$-HPU-99	0.1:0.9	0.1076	0.9084
$Eu_{0.2}Tb_{0.8}$-HPU-99	0.2:0.8	0.2073	0.8018
$Eu_{0.3}Tb_{0.7}$-HPU-99	0.3:0.7	0.2953	0.6925
HPU-99	100:0	100	0

Table S4 Lifetimes and Quantum yields of Eu_xTb_{1-x}-HPU-99 at room temperature (x = 1, 0, 0.05, 0.1, 0.2, 0.3) and energy transfer efficiency from Tb^{3+} to Eu^{3+}

Samples	Lifetime τ (μs)/λ_{em}[(a)] (nm)	Quantum yields (%)	Energy transfer efficiency[(b)] from Tb^{3+} to Eu^{3+}
HPU-99	547.45	17.60	—
Tb-HPU-99	1059.83	54.03	—
$Eu_{0.05}Tb_{0.95}$-HPU-99	941.79; 1035.54	50.03	11.14%
$Eu_{0.1}Tb_{0.9}$-HPU-99	863.57; 935.43	43.43	18.52%
$Eu_{0.2}Tb_{0.8}$-HPU-99	744.61; 796.10	31.51	29.74%
$Eu_{0.3}Tb_{0.7}$-HPU-99	644.99; 705.74	24.67	39.14%

(a) wavelength of the emission peak (Eu^{3+}, $^5D_0$-$^7F_2$; Tb^{3+}, $^5D_4$-$^7F_5$)

The energy transfer efficiency formula[(b)] between donor and acceptor:

$$E = 1 - \frac{\tau_{da}}{\tau_d} \quad (1)$$

where τ_{da} and τ_d are the donor's excited-state lifetime in the presence and absence of the acceptor, respectively.

Table S5 ICP analyses for HPU-99 and Ag NCs@HPU-99.

Samples	Amount of Eu^{3+}	Amount of Ag^{+}
HPU-99	26.0%	0
Ag NCs@HPU-99	28.8%	4.53%