

Electronic Supplementary Material (ESI) for Nanoscale.

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Supporting Information

Enhancing multiphoton upconversion emissions through confined energy migration in lanthanide-doped Cs₂NaYF₆ nanoplatelets

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I. Supplementary Materials & Methods

Chemicals and materials: $\text{Gd}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Y}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Yb}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Tm}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Tb}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Eu}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), oleic acid (OA) and 1-octadecene (ODE) were purchased from Sigma-Aldrich. Oleylamine (OAm), CsF (99.9%) and NaHCO_3 (99.9%) were purchased from Aladdin (Shanghai, China). $\text{NaAc} \cdot 3\text{H}_2\text{O}$ (AR), NH_4F (AR), ethyl acetate, methanol, ethanol and hexane were purchased from Sinopharm Chemical Reagent Co., China. Cs_2CO_3 (99.9%), Y_2O_3 (99.99%), Yb_2O_3 (99.99%), Tm_2O_3 (99.99%) were purchased from HWRK CHEM, China. All the chemical reagents were of analytical grade and used as received without further purification unless otherwise noted. Distilled water was used throughout the experiments.

Synthesis of $\text{Cs}_2\text{NaYF}_6:\text{Yb/Ln}$ NPs: $\text{Cs}_2\text{NaYF}_6:\text{Yb/Ln}$ (Ln = Tm, Gd, Eu, Tb) nanoplatelets (NPs) were synthesized via a modified high-temperature co-precipitation method. Typically, x (0.005 ~ 0.015) mmol of $\text{Ln}(\text{Ac})_3$, y (0.1 ~ 0.5 - x) mmol of $\text{Yb}(\text{Ac})_3$, (0.5 - x - y) mmol of $\text{Y}(\text{Ac})_3$ and 0.5 mmol of NaAc were mixed with 8 mL of OA, 4 mL of OAm and 8 mL of ODE in a 100-mL two-necked round-bottom flask. The resulting mixture was heated to 120 °C under N_2 flow with constant stirring for 30 min to remove the residual water and oxygen. After cooling down to room temperature (RT), 5 mL of methanol solution containing 3 mmol of CsF was added and the solution was stirred at 60 °C for 30 min. The resulting solution was heated to 320 °C under N_2 flow with vigorous stirring for 60 min, and then cooled down to RT. The obtained NPs were precipitated by addition of 20 mL of ethyl acetate. The product solution was centrifuged at 8000 rpm for 5 min. The supernatant was discarded, and the precipitated NPs were re-dispersed in 2 mL of hexane. By centrifugation at 5000 rpm for 5 min, the supernatant was precipitated with 4 mL ethyl acetate. The solution was centrifuged again at 12000 rpm for 5 min. The final NPs were obtained by discarding the supernatant. The size of these NPs can be tuned by varying the solvent ratio of OA, OAm and ODE under otherwise identical conditions. NPs with different doping concentrations and compositions were synthesized by adjusting the molar ratio of metal precursors under otherwise identical conditions.

Synthesis of $\text{Cs}_2\text{NaYF}_6:\text{Yb/Ln}$ powders: $\text{Cs}_2\text{NaYF}_6:\text{Yb/Ln}$ powders were prepared by a solid-state reaction method.¹ In a typical synthesis of $\text{Cs}_2\text{NaYF}_6:\text{Yb/Tm}$ powders, 5 mmol of Cs_2CO_3 , 2.5 mmol of NaHCO_3 , 2 mmol of Y_2O_3 , 15 mmol of NH_4F , 0.475 mmol of Yb_2O_3 and 0.025 mmol of Tm_2O_3 powders were mixed with 3 mL of acetone and ground thoroughly. The obtained mixture was heated at 150 °C for 7 h in muffle furnace and then sintered at 450 °C for 30 min in an air atmosphere. The heating rate was set at 5 °C·min⁻¹.

Synthesis of $\alpha\text{-NaYF}_4:\text{Ln}^{3+}$ NPs: $\alpha\text{-NaYF}_4:\text{Yb/Tm}$ NPs were synthesized via a solid-liquid-thermal-decomposition method.² Typically, 0.5 mmol of $\text{Y}(\text{Ac})_3$, 0.49 mmol of $\text{Yb}(\text{Ac})_3$, and 0.01 mmol of $\text{Tm}(\text{Ac})_3$ were mixed with 8 mL of OA and 12 mL of ODE in a 100-mL two-neck round-bottom flask. The resulting mixture was heated at 180 °C under N_2 flow with constant stirring for 20 min to form a

clear solution, then cooled down to RT. Thereafter, 2 mmol of NaHF₂ powder was added. The solution was heated to 260 °C under N₂ flow with vigorous stirring for 60 min. Subsequently, the mixture was allowed to cool down to RT. The obtained NPs were precipitated by addition of ethanol, collected by centrifugation, washed with ethanol and cyclohexane several times, and finally re-dispersed in cyclohexane.

Characterization: Powder X-ray diffraction (XRD) patterns of the samples were collected with an X-ray diffractometer (MiniFlex 600, Rigaku) with Cu K α 1 radiation ($\lambda = 0.154187$ nm). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were performed by using a TECNAI G² F20 TEM equipped with the energy dispersive X-ray (EDX) spectrum. Scanning electron microscope (SEM) measurement was performed by using a JSM6700F SEM. Upconversion (UC) emission spectra were carried out upon 980-nm excitation provided by a continuous-wave semiconductor laser diode (FLS980, Edinburgh). Time-resolved spectra and UC lifetimes were measured with a customized ultraviolet (UV) to mid-infrared steady-state and phosphorescence lifetime spectrometer (FSP980, Edinburgh) equipped with a tunable mid-band Optical Parametric Oscillator (OPO) pulse laser as the excitation source (410-2400 nm, 10 Hz, pulse width 5 ns, Vibrant 355II, OPOTEK) with the average power density of ~ 40 W/cm². Effective PL lifetimes (τ_{eff}) were calculated

$$\text{by: } \tau_{eff} = \frac{1}{I_{max}} \int_0^{\infty} I(t) dt$$

where $I(t)$ denotes the PL intensity as a function of time t , and I_{max} is the maximum PL intensity. All photoluminescence measurements were carried out at RT.

Determination of the upconversion quantum yields (UCQYs): Upconversion quantum yield (UCQY) measurements were conducted using the same experimental setup as following previously reported.³ These measurements include efficiency of upconversion from 980 nm excitation to emission in the visible. Briefly, a 980-nm diode laser (MDL-III-980-2W, Changchun New Industries Optoelectronics Tech Co., Ltd.) was used to excite UCL materials of this study. Excitation of the samples occurred within an integrating sphere (150 mm in diameter, Edinburgh Instruments), where samples were held in a cuvette dispersed in hexane or clamped in quartz tablets. Emitted light was collected from samples via a fiber optic spectrometer (QE65pro, Ocean Optics). An optical lens was used to collimate the laser beam and direct on the sample with a focus of 1 mm², and a laser powermeter (Model 1918-C, Newport) was applied to measure the excitation power on the sample. The UCQYs were then calculated by⁴

$$QY = \frac{N_e}{N_a} = \frac{L_s}{E_R - E_S}$$

where N_e and N_a are the photons emitted and absorbed, respectively; L_s is the emission intensity, E_R and E_S are the intensities of the excitation light in the presence of the pure Cs₂NaYF₆ NPs (reference) and the UCNP samples, respectively. The UCL emissions in the spectral region of 400-850 nm for Tm³⁺ were integrated for the QY determination. All the UCQYs for each sample were measured independently for at least three times under identical conditions to yield the average value and standard deviation.

II. Supplementary Table

Table S1. Comparison of UV emission for a variety of Yb³⁺, Tm³⁺-doped UC samples. Dopant concentration, nanoparticle size and power density of 980-nm laser are provided to address different measurement conditions, and UV/NIR ratio was determined based on the integrated UC luminescence (UCL) intensity of UV and NIR regions.

Samples	Size (nm)	Power Density (W/cm ²)	UV/NIR Ratio	Ref.
LiYbF ₄ :1%Tm	17	5	0.14	3
LiYF ₄ :20%Yb/1%Tm	/	5	0.01	3
NaYbF ₄ :1%Tm	/	5	0.02	3
NaYF ₄ :20%Yb/1%Tm	/	5	0.01	3
NaYF ₄ :17%Yb/1.2%Tm	30	140	0.01	5
LiLuF ₄ :20%Yb/0.5%Tm@LiLuF ₄	50	127	0.05	6
LiYbF ₄ :0.5%Tm@LiYF ₄	20	400	1	7
Sr _{1-x} Yb _x F _{2+x} :1%Tm@CaF ₂	11	250	0.13	8
		400	0.18	
NaYF₄:49%Yb/1%Tm	5	150	0.03	This work
Cs₂NaYF₆:49%Yb/1%Tm bulk	>1000	5	0.01	This work
		150	0.51	
Cs₂NaYF₆:49%Yb/1%Tm	11	5	0.24	This work
		150	1.20	

Table S2 PL lifetimes of Cs₂NaYF₆:Yb/Tm/Gd NPs with various doping concentration of Gd³⁺.

Gd ³⁺ concentration (mol %)	τ_{eff} of Tm ³⁺ (¹ I ₆ → ³ F ₄ , μs)	τ_{eff} of Gd ³⁺ (⁶ P _{7/2} → ⁸ S _{7/2} , ms)
0	163.96	/
10	102.27	1.61
20	78.46	5.12
30	59.89	7.03
40	50.47	2.97

III. Supplementary Figures

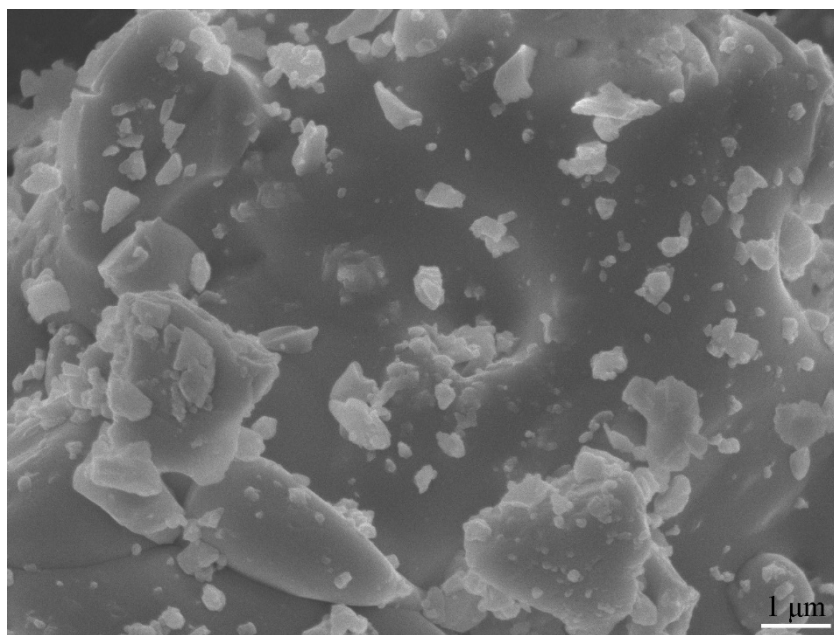


Figure S1. SEM image of the Cs₂NaYF₆:Yb/Tm bulk materials.

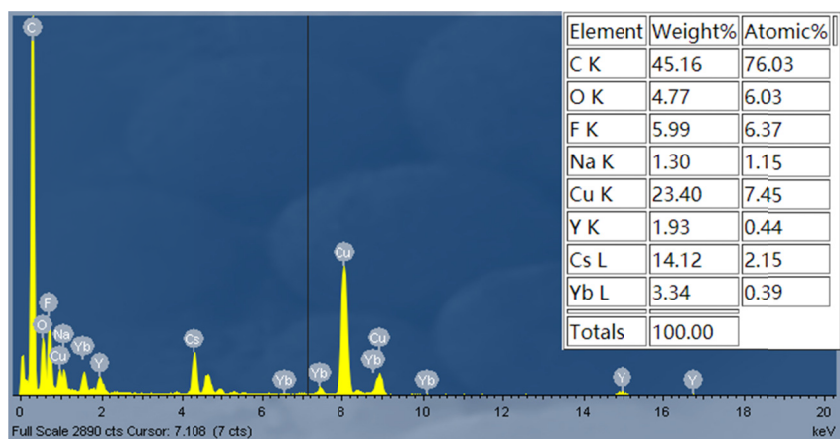


Figure S2. EDX spectrum of $\text{Cs}_2\text{NaYF}_6:\text{Yb/Tm}$ (49/1 mol%) NPs, revealing a molar ratio of approximately 1:3 for Cs^+/F^- in the as-prepared NPs. Tm^{3+} ion was not detected because of its low doping concentration (<1 mol%).

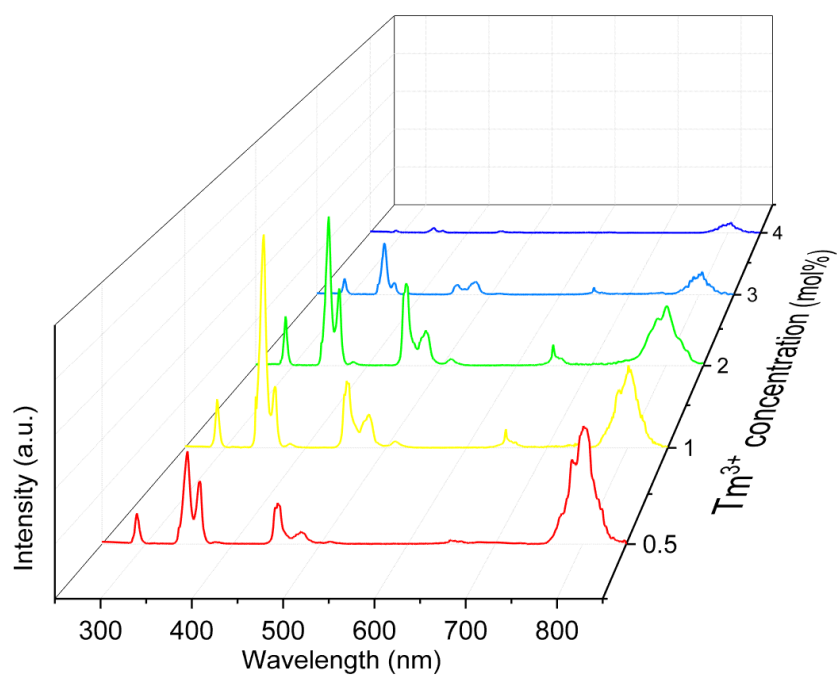


Figure S3. UCL spectra of the Cs₂NaYF₆:Yb/Tm (49/x mol%) NPs dispersed in hexane. A maximal UCL intensity of Tm³⁺ in the UV region can be achieved with the concentration of 1 mol% for Tm³⁺. At a higher doping concentration of Tm³⁺ (>2 mol%), the UCL intensity reduced significantly.

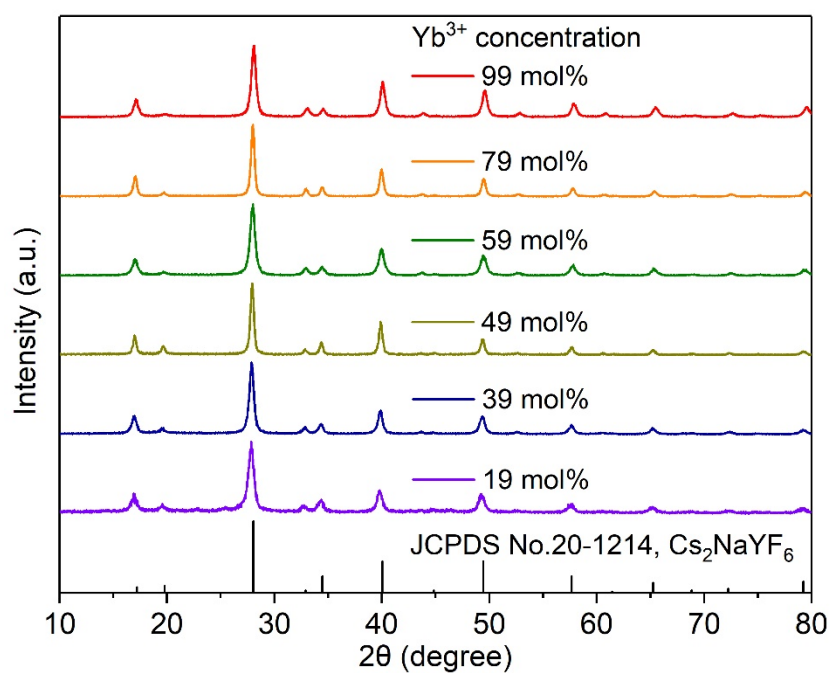


Figure S4. XRD patterns of Cs₂NaYF₆:Yb/Tm (x/1 mol%) NPs with different Yb³⁺ contents. All the diffraction peaks of the NPs are well consistent with the cubic Cs₂NaYF₆ (JCPDS No. 20-1214), which indicates that the obtained NPs are pure cubic phase without any impurity.

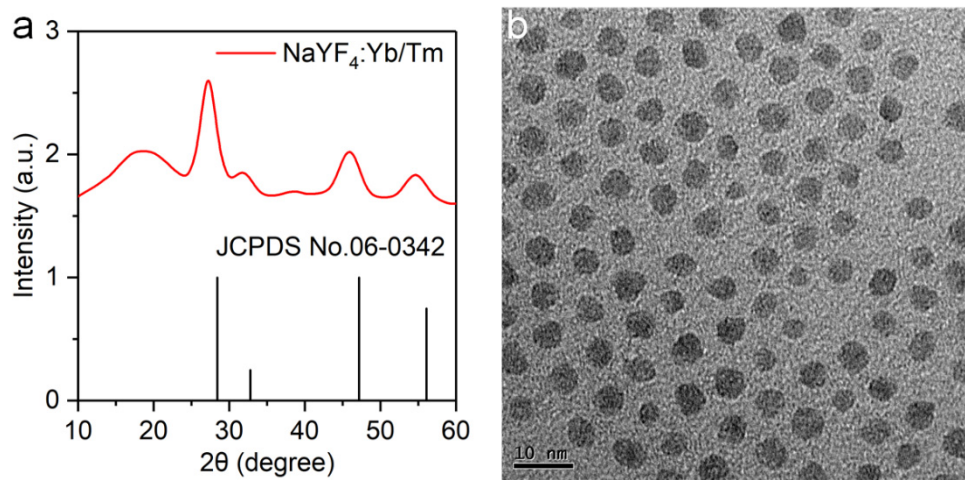


Figure S5. (a) XRD pattern of α -NaYF₄:Yb/Tm (49/1 mol%) nanocrystals. All the diffraction peaks match well with the α -NaYF₄ (JCPDS No. 06-0342). (b) TEM image of the α -NaYF₄:Yb/Tm nanocrystals.

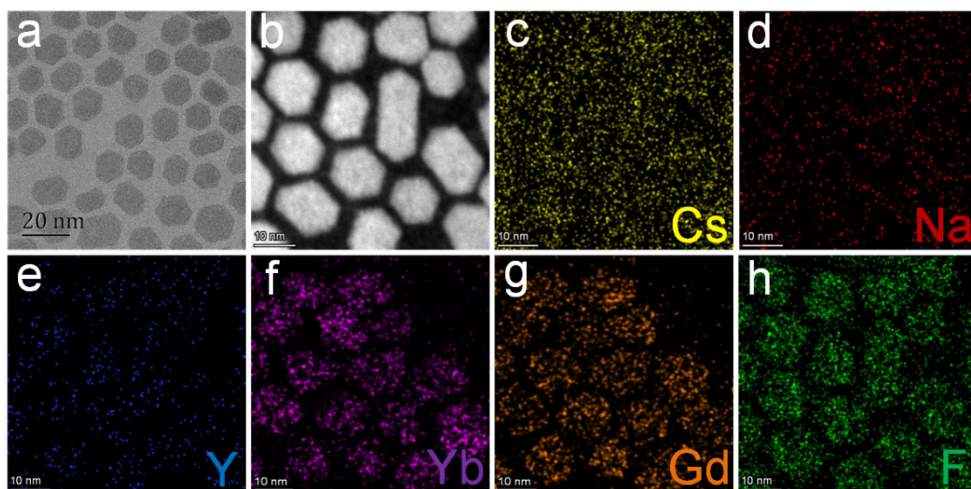


Figure S6. (a) Bright-field and (b) dark-field TEM images of $\text{Cs}_2\text{NaYF}_6:\text{Yb/Tm/Gd}$ (49/1/30 mol%) NPs. (c-h) EDX elemental mapping images of Cs, Na, Y, Yb, Gd and F in $\text{Cs}_2\text{NaYF}_6:\text{Yb/Tm/Gd}$ NPs (49/1/30 mol%). These results indicate that the Ln^{3+} dopants are homogeneously distributed among the as-prepared NPs.

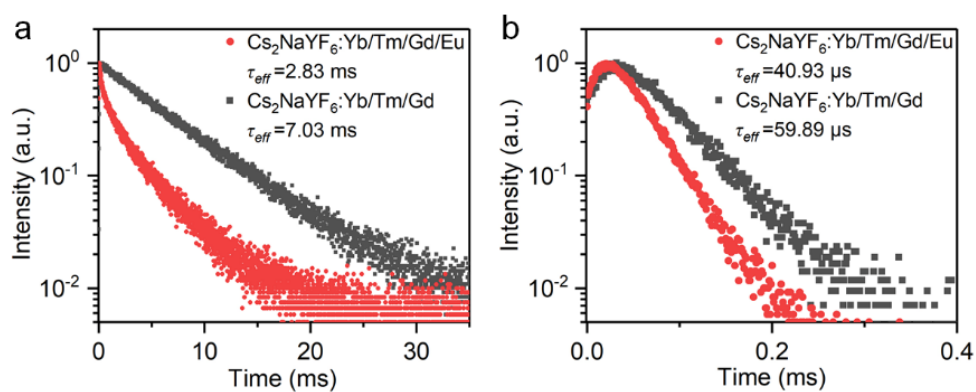


Figure S7. UCL decays of Gd^{3+} and Tm^{3+} in $\text{Cs}_2\text{NaYF}_6:\text{Yb/Tm/Gd}$ NPs (49/1/30 mol%) and $\text{Cs}_2\text{NaYF}_6:\text{Yb/Tm/Gd/Eu}$ NPs (49/1/30/10 mol%) by monitoring their emissions at 311 and 348 nm, which correspond to (a) ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ of Gd^{3+} and (b) ${}^1\text{I}_6 \rightarrow {}^3\text{F}_4$ of Tm^{3+} . It was determined that the photoluminescence lifetime of ${}^6\text{P}_{7/2}$ of Gd^{3+} and ${}^1\text{I}_6$ of Tm^{3+} were shortened after the doping of Eu^{3+} .

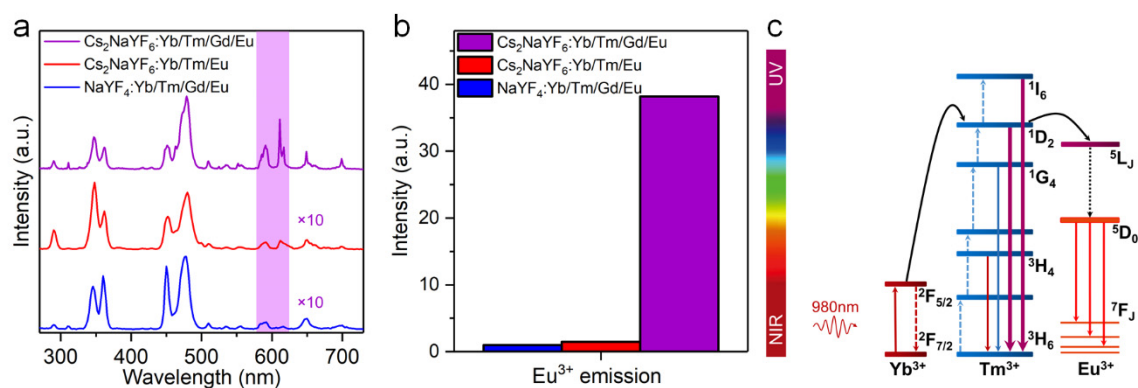


Figure S8. (a) UCL spectra of Cs₂NaYF₆:Yb/Tm/Gd/Eu (49/1/30/10 mol%), Cs₂NaYF₆:Yb/Tm/Eu (49/1/10 mol%) NPs, and α -NaYF₄:Yb/Tm/Gd/Eu (49/1/30/10 mol%) nanocrystals. It was found that the emissions of Eu³⁺ in both Cs₂NaYF₆:Yb/Tm/Eu and NaYF₄:Yb/Tm/Gd/Eu are rather weak. (b) Comparison of the integral emission intensity of Eu³⁺ peaking at 591 nm and 612 nm in the Cs₂NaYF₆:Yb/Tm/Gd/Eu, Cs₂NaYF₆:Yb/Tm/Eu NPs, and NaYF₄:Yb/Tm/Gd/Eu nanocrystals, with the relative integral intensities of 38.2, 1.5, and 1, respectively. (c) Schematic energy level diagram showing the energy transfer process of Yb³⁺, Tm³⁺ and Eu³⁺ in Cs₂NaYF₆:Yb/Tm/Eu.

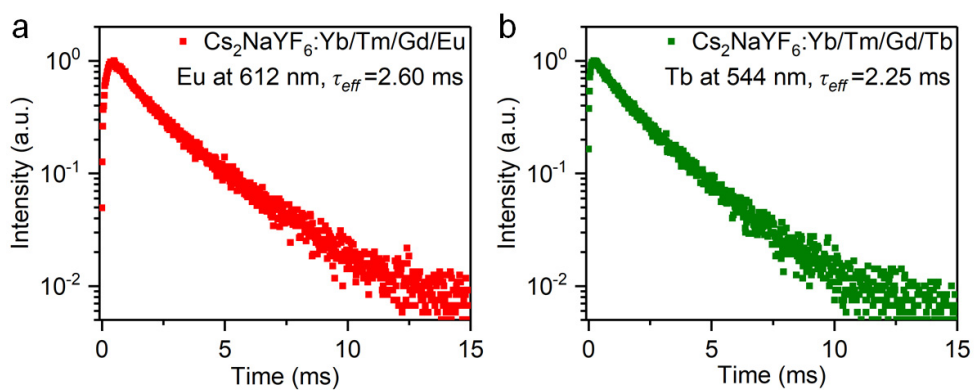


Figure S9. UCL decays of Eu^{3+} and Tb^{3+} in (a) $\text{Cs}_2\text{NaYF}_6:\text{Yb/Tm/Gd/Eu}$ and (b) $\text{Cs}_2\text{NaYF}_6:\text{Yb/Tm/Gd/Tb}$ NPs by monitoring their emissions at 612 and 544 nm, which correspond to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ of Eu^{3+} and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ of Tb^{3+} , respectively. The effective lifetimes for ${}^5\text{D}_0$ level of Eu^{3+} and ${}^5\text{D}_4$ level of Tb^{3+} in Cs_2NaYF_6 NPs were determined to be 2.60 ms and 2.25 ms, respectively.

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