

# Supporting Information

## **Tm<sup>3+</sup> mediated multicolor luminescence of NaYbF<sub>4</sub>:Er,Tm@NaYF<sub>4</sub> for advanced anti-counterfeiting**

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### **1. Experimental section**

#### **1.1 Materials.**

Ytterbium oxide (Yb<sub>2</sub>O<sub>3</sub>, 99.9%), erbium oxide (Er<sub>2</sub>O<sub>3</sub>, 99.5%), thulium acetate (Tm(Ac)<sub>3</sub>, 99.9%), yttrium oxide (Y<sub>2</sub>O<sub>3</sub>, 99.99%), 1-octadecene (ODE, > 90%), sodium trifluoroacetate (Na-TFA, 97%), sodium oleate (NaOA, 98%) was purchased from Shanghai Maclin Biochemical Technology Co., LTD. Oleic acid (OA, AR) was purchased from Shanghai Aladdin Biochemical Technology Co., LTD. Ammonium fluoride (NH<sub>4</sub>F, > 96%), hydrochloric solution (HCl, 36-38%), sodium hydroxide (NaOH, AR) were purchased from Chengdu Kelong Chemical Co., LTD. Anhydrous ethanol purchased from Chengdu Jinshan Chemical Reagent Co., LTD. Cyclohexane (≥ 99.7%) was purchased from Shanghai Titan Scientific Co., LTD. All chemicals are used as received without any further purification.

LnCl<sub>3</sub> (Ln = Y, Yb, Er) were prepared by dissolving the corresponding metal oxide in water containing an appropriate solution of hydrochloric solution, and then allowing the water to evaporate completely.

#### **1.2 General characterizations.**

The morphology and size of the as-prepared UCNPs were determined on JEOL 2100Plus transmission electron microscopy (TEM). Powder X-ray diffraction (XRD) data were obtained using a Shimadzu XRD-6100 diffractometer with Cu-Kα radiation (λ

= 1.5406 Å) at 40kV and 30 mA. The upconversion emission spectrums were recorded on an F-7000 instrument modified with a 980 nm laser. X-ray photoelectron spectroscopy (XPS) measurements were performed on the X-ray photoelectron spectrometer (Thermo Fisher Scientific) using an unmonochromated Al K $\alpha$  X-ray source. The absolute quantum yield (QY) was tested using the horiba Fluorolog-QM steady-state transient fluorescence phosphorescent spectrometer with the MDL-H-980/5W laser. During the test, the excitation power density was 78 W/cm<sup>2</sup> and the integration range was 300-800 nm.

The absorption spectrum was measured by the Shimazu 3600plus UV-VIS near-infrared spectroscopy. It is known that the optical path (b) is 1 cm, the concentration (c) of NaYbF<sub>4</sub>:30%Er,1%Tm@NaYF<sub>4</sub> is 15 g/L, and the absorbance (A) measured at the maximum absorption wavelength (980 nm) is 0.029. According to Lambert-Beer law ( $A = \alpha bc$ ), the optical absorption coefficient  $\alpha = A / (bc) = 0.029 / (1 \times 15) = 1.93 \times 10^{-3}$  L/(g·cm).

### **1.3 Synthesis of NaYbF<sub>4</sub>:x%Er,1%Tm (x = 2, 10, 30, 50, 99) core UCNPs.**

To synthesis the NaYbF<sub>4</sub>:x%Er,1%Tm, 1.5 mmol of the corresponding rare earth chloride salt was added to a 100 mL flask containing 9 mL OA and 22.5 mL ODE (Tm<sup>3+</sup> was derived from Tm (Ac)<sub>3</sub>). Under vacuum condition, the mixture was heated at 160 °C for 30 min and then cooled to 35 °C. Then, added 0.9895 g NaOA, 0.222 g NH<sub>4</sub>F and 0.02 g NaOH and stirred at room temperature for 30 min. The flask was again placed in a vacuum, the solution was heated to 100 °C and held for 15 min, and then the reaction solution was heated to 300 °C and held for 1h in the nitrogen atmosphere, and cooled to room temperature. The reaction solution was transferred to three centrifuge tubes containing a total of 90 mL ethanol, and then centrifuged at 7500 rpm for 10 min to precipitate the nanoparticles completely. The precipitate was dispersed in 12 mL cyclohexane, washed again with ethanol and centrifuged. Finally, the nanoparticles were dispersed in 15 mL cyclohexane.

### **1.4 Synthesis of NaYbF<sub>4</sub>:x%Er (x = 2, 10, 30, 50, 100) and NaYbF<sub>4</sub>:1%Tm core UCNPs.**

The synthesis method of NaYbF<sub>4</sub>:x%Er and NaYbF<sub>4</sub>:1%Tm core is similar to that

of NaYbF<sub>4</sub>:x%Er,1%Tm core, only the proportion of rare earth chloride salts of 1.5 mmol is adjusted accordingly.

### 1.5 Preparation of shell precursors.

Y-OA precursor: the mixture of YCl<sub>3</sub> (3.5 mmol), OA (14 mL) and ODE (21 mL) was placed in a 100 mL round-bottomed flask and heated for 2 h under vacuum magnetic stirring at 120°C to remove residual water and oxygen. Then a transparent Y-OA precursor solution (0.1 M) was obtained. Er-OA precursor: The synthesis of Er-OA (0.1 M) was carried out all the same as that of Y-OA except 3.5 mmol of ErCl<sub>3</sub> was used instead of 3.5 mmol of YCl<sub>3</sub>.

Na-TFA-OA precursor: the mixture of Na-TFA (18 mmol) and OA (45 mL) was placed in a 100 mL single-mouth flask and stirred magnetically under vacuum at room temperature for 3 h to remove residual water and oxygen. Colorless Na-TFA-OA precursor solution (0.4 M) was obtained.

### 1.6 Synthesis of core-shell or core-shell-shell UCNPs.

In a 50 mL three-way flask, 4 mL core nanoparticles, 3 mL OA and 7 mL ODE were added. The solution was stirred under vacuum and then heated to 80 °C to remove excess water and oxygen. After 30 min, the flask was filled with nitrogen and heated to 300 °C. The precursor solution was then injected in cycles, starting each cycle with the injection of Y-OA, waiting 15 min, ending with the injection of Na-TFA-OA, and immediately starting the next cycle. The amount of shell precursor solution required for each injection was shown in Table 1. After the final injection was completed, it was stored at 300 °C for 30 min and then quickly cooled to room temperature. The nanoparticles were washed in the same way as the core nanoparticles and finally redispersed in 4 mL of cyclohexane (15 mg/mL).

Table 1: Shell precursor injections.

Cycle Number	1	2	3	4	5	6	7	8
Y-OA (μL)	280	360	440	520	620	720	830	950
Na-TFA-OA (μL)	140	180	220	260	310	360	420	480

In the synthesis of NaYbF<sub>4</sub>:1%Tm@NaYF<sub>4</sub>:x%Er@NaYF<sub>4</sub>, the preparation method was the same as that of core-shell nanoparticles, except that the first 4 injections

were used as the inner shell and the last 4 injections were used as the shell. The volume of injected Y-OA and Er-OA precursor solutions was distributed in proportion to the elements, and the total volume remained unchanged.

### **1.7 Anti-counterfeiting.**

5  $\mu\text{L}$  of  $\text{NaYbF}_4:30\%\text{Er},1\%\text{Tm}@NaYF_4$ ,  $\text{NaYbF}_4:30\%\text{Er}@NaYF_4$ ,  $\text{NaErF}_4:1\%\text{Tm}@NaYF_4$ ,  $\text{NaYbF}_4:1\%\text{Tm}@NaYF_4$ , and  $\text{NaYbF}_4:10\%\text{Er},1\%\text{Tm}@NaYF_4$  were coated on the filter paper, and the luminescence images were taken under dark condition with a 980 nm laser. Similarly, the above five nanoparticles were applied to the painting with the word "UCL", and the luminescence images were taken under dark condition with a 980 nm laser. The letter "U" was drawn by  $\text{NaYbF}_4:30\%\text{Er},1\%\text{Tm}@NaYF_4$ , the letter "C" was drawn by  $\text{NaYbF}_4:30\%\text{Er}@NaYF_4$  and  $\text{NaErF}_4:1\%\text{Tm}@NaYF_4$ , and the letter "L" was drawn by  $\text{NaYbF}_4:1\%\text{Tm}@NaYF_4$  and  $\text{NaYbF}_4:10\%\text{Er},1\%\text{Tm}@NaYF_4$ .

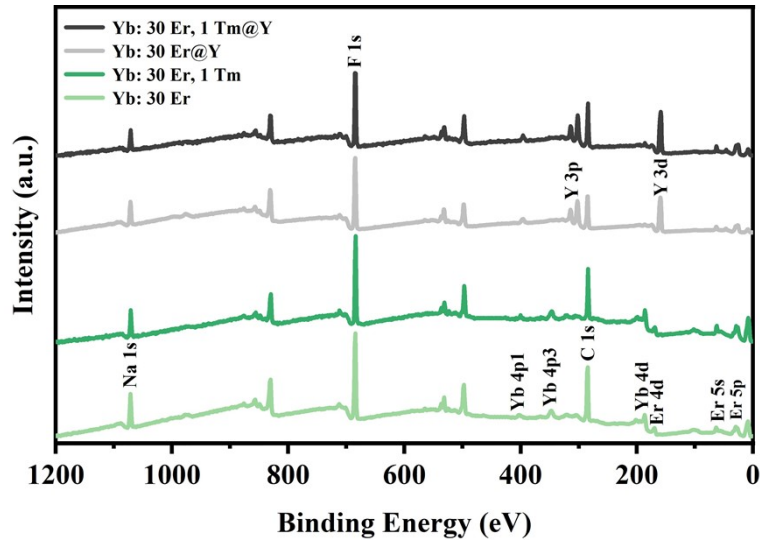


Figure S1. The XPS spectra of core (NaYbF<sub>4</sub>:30%Er,1%Tm (Yb:30Er,1Tm) and NaYbF<sub>4</sub>:30%Er (Yb:30Er)) and core-shell nanoparticles (NaYbF<sub>4</sub>:30%Er,1%Tm@NaYF<sub>4</sub> (Yb:30Er,1Tm@Y) and NaYbF<sub>4</sub>:30%Er@NaYF<sub>4</sub> (Yb:30Er@Y)).

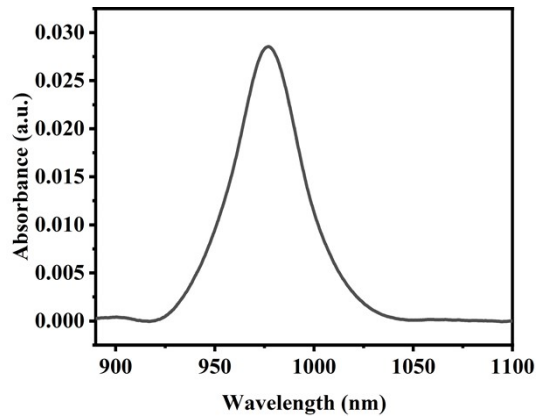


Figure S2. The absorption spectrum of NaYbF<sub>4</sub>:30%Er,1%Tm@NaYF<sub>4</sub>.

Table S2: The comparison of QY in this work with those in the references.

Sample	Size (nm)	QY (%)	Ref.
$\alpha$ -NaYbF <sub>4</sub> :2%Er@CaF <sub>2</sub>	~ 14	1.01 (34 W/cm <sup>2</sup> )	22
$\beta$ -NaYF <sub>4</sub> :20%Yb,2%Er,20%Gd@NaYF <sub>4</sub> :20%Gd	~ 16	0.8 (70 W/cm <sup>2</sup> )	31
$\beta$ -NaGdF <sub>4</sub> :20%Yb,2%Er@NaYF <sub>4</sub>	24.2	1.7 (420 W/cm <sup>2</sup> )	35
$\beta$ -NaYF <sub>4</sub> :33%Yb,5%Er@NaLuF <sub>4</sub>	~ 50	4.0 (63 W/cm <sup>2</sup> )	36
$\beta$ -NaYbF <sub>4</sub> :30%Er,1%Tm@NaYF <sub>4</sub>	22.15 × 45.46	1.19 (78 W/cm <sup>2</sup> )	This work

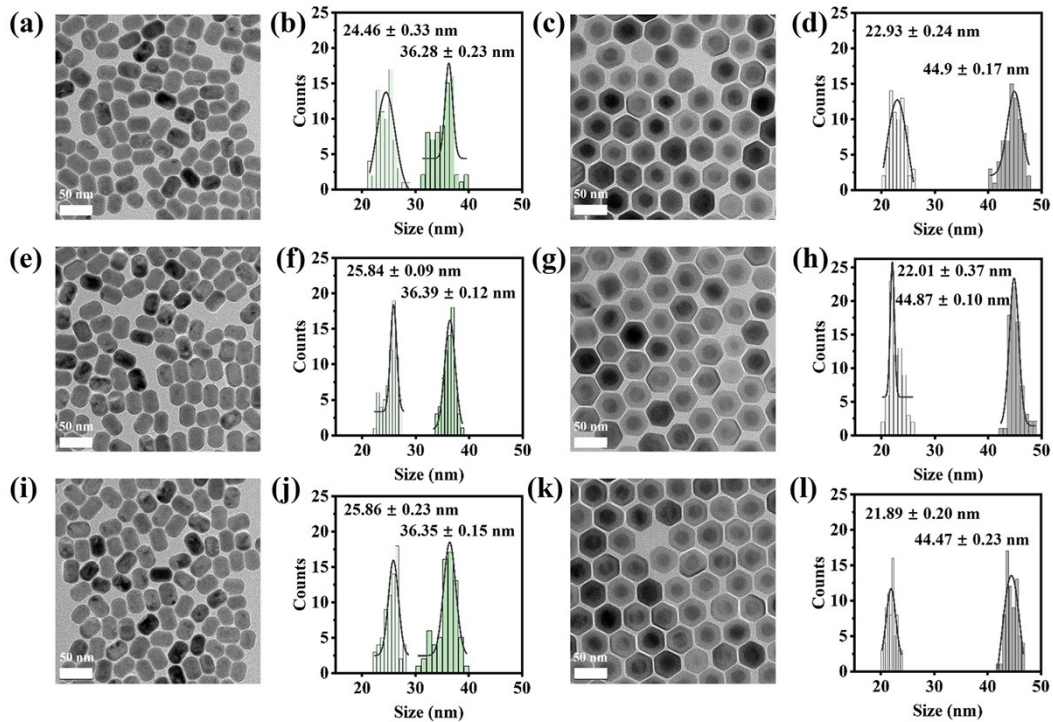


Figure S3. TEM images (first column) and size distributions (second column) of  $\text{NaYbF}_4:30\%\text{Er}$  (a, b),  $\text{NaErF}_4:1\%\text{Tm}$  (e, f), and  $\text{NaYbF}_4:1\%\text{Tm}$  (i, j) core nanoparticles. TEM images (third column) and size distributions (fourth column) of  $\text{NaYbF}_4:30\%\text{Er}@NaYF_4$  (c, d),  $\text{NaErF}_4:1\%\text{Tm}@NaYF_4$  (g, h), and  $\text{NaYbF}_4:1\%\text{Tm}@NaYF_4$  (k, l) core-shell nanoparticles.

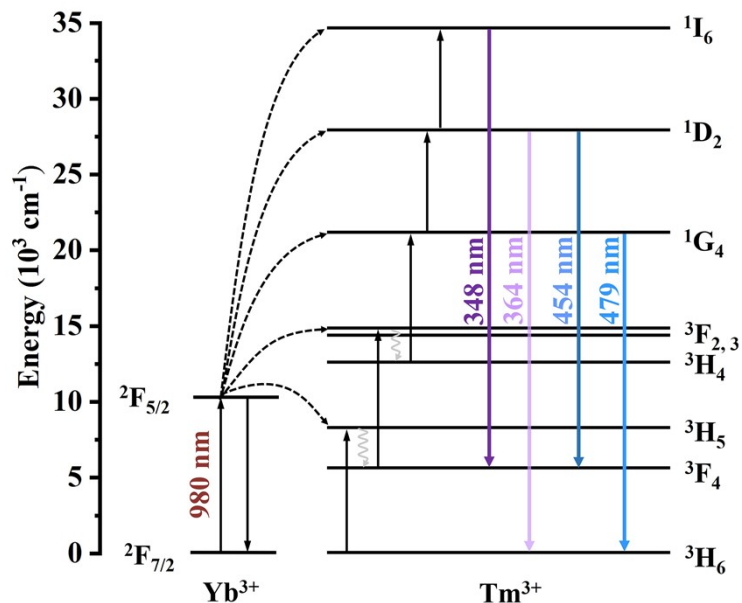


Figure S4. Energy level diagram of  $\text{NaYbF}_4:1\%\text{Tm}@NaYF_4$  nanoparticles.

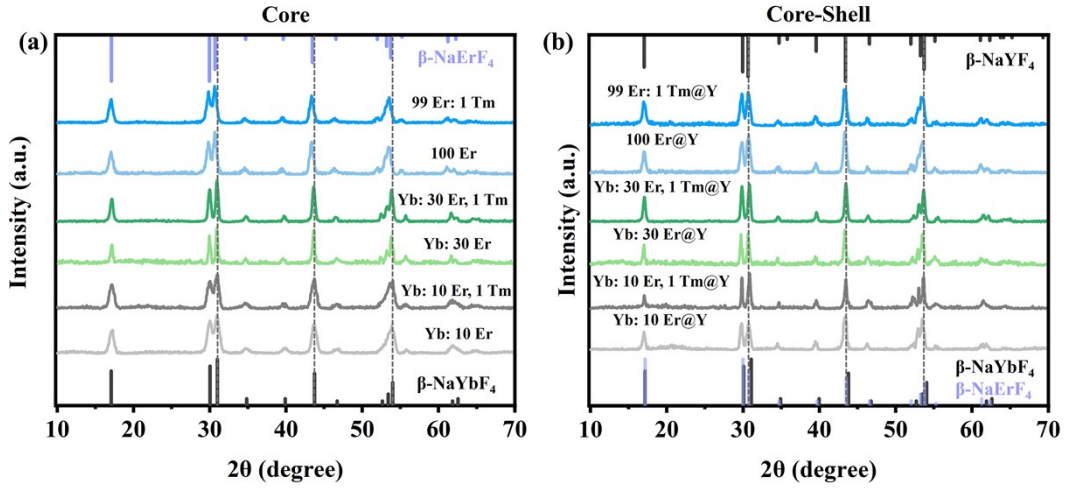


Figure S5. XRD patterns of (a) Yb:xEr ( $x = 10, 30, 100$ ), Yb:xEr,1Tm ( $x = 10, 30, 99$ ) core and (b) Yb:xEr@Y ( $x = 10, 30, 100$ ), Yb:xEr,1Tm@Y ( $x = 10, 30, 99$ ) core-shell. Three reference patterns corresponding to  $\beta\text{-NaYbF}_4$  (ICDD, PDF #00-027-1427),  $\beta\text{-NaErF}_4$  (ICDD, PDF #00-027-0689), and  $\beta\text{-NaYF}_4$  (ICDD, PDF #00-016-0334) were adopted.

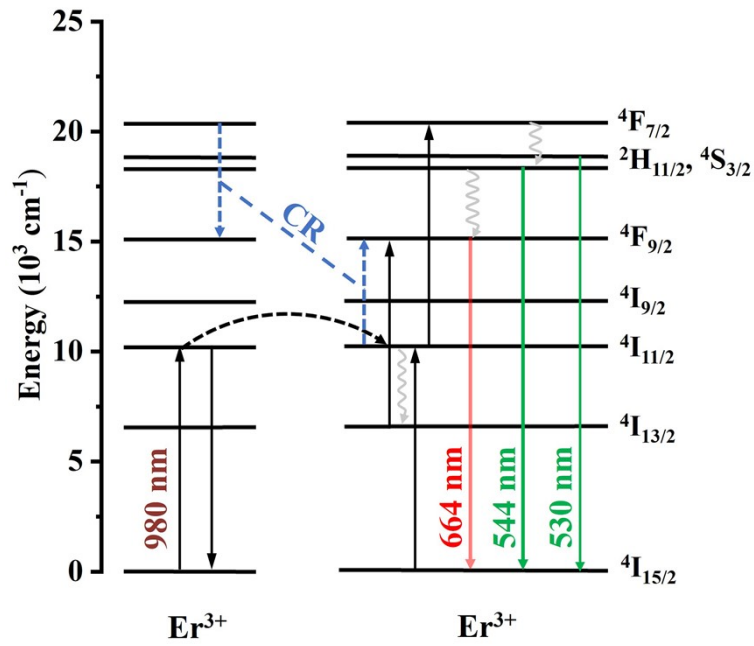


Figure S6. Energy level diagram of  $\text{NaErF}_4@NaYF_4$  (100Er@Y) nanoparticles.

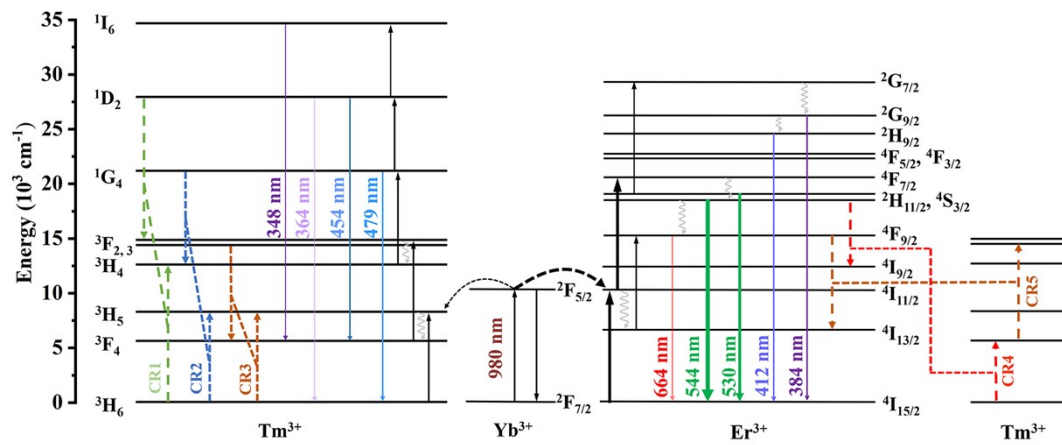


Figure S7. Energy level diagram of NaYbF<sub>4</sub>:2%Er,1%Tm@NaYF<sub>4</sub> (Yb:2Er,1Tm@Y) nanoparticles.

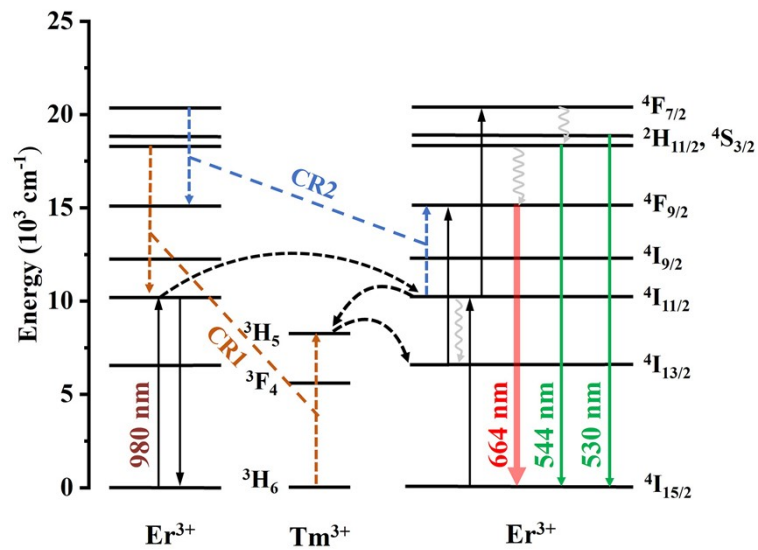


Figure S8. Energy level diagram of NaErF<sub>4</sub>:1%Tm@NaYF<sub>4</sub> (99Er:1Tm@Y) nanoparticles.



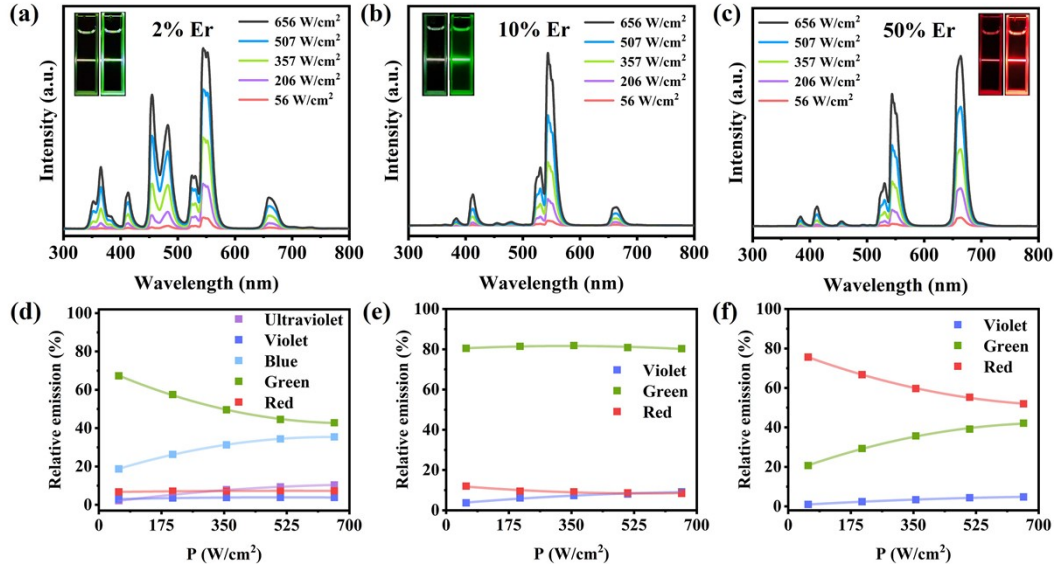


Figure S9. Emission spectra (top) and the relative emissions in different bands (bottom) of Yb:2Er, 1Tm@Y (a, d), Yb:10Er, 1Tm@Y (b, e), Yb:50Er, 1Tm@Y (c, f) UCNP systems with the increase of excitation power density (56 ~ 656 W/cm<sup>2</sup>). Inset in a, b, c: luminescence images of UCNP systems under 980 nm irradiation with the excited power density of 56 W/cm<sup>2</sup> (left) and 656 W/cm<sup>2</sup> (right).

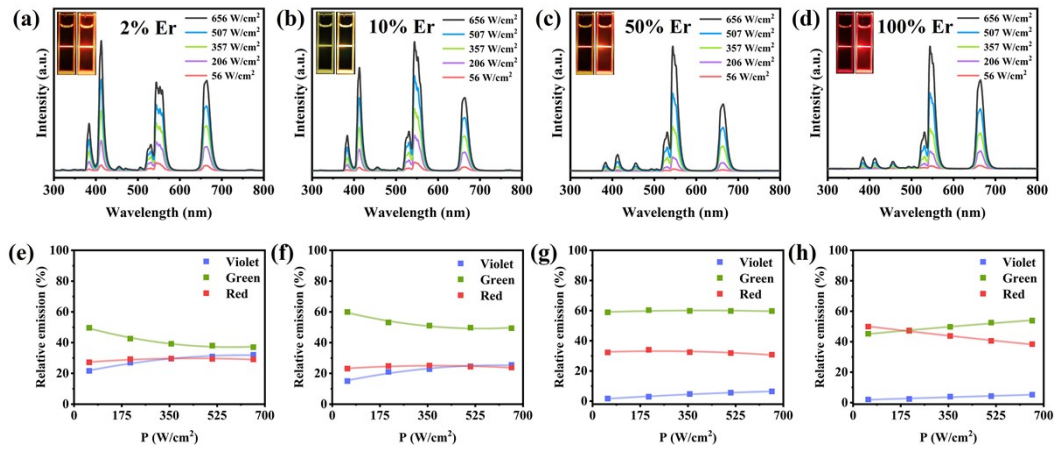


Figure S10. Emission spectra (top) and the relative emissions in different bands (bottom) of Yb:2Er@Y (a, e), Yb:10Er@Y (b, f), Yb:50Er@Y (c, g), 100Er@Y (d, h) UCNP systems with the increase of excitation power density (56 ~ 656 W/cm<sup>2</sup>). Inset in a, b, c, d: luminescence images of UCNP systems under 980 nm irradiation with the excited power density of 56 W/cm<sup>2</sup> (left) and 656 W/cm<sup>2</sup> (right).