Electronic Supplementary Information:

Utilizing amidation reaction to address the "cooperative effect" of carboxylic acid/amine on the size, shape and multicolor output of fluorides upconversion nanoparticles

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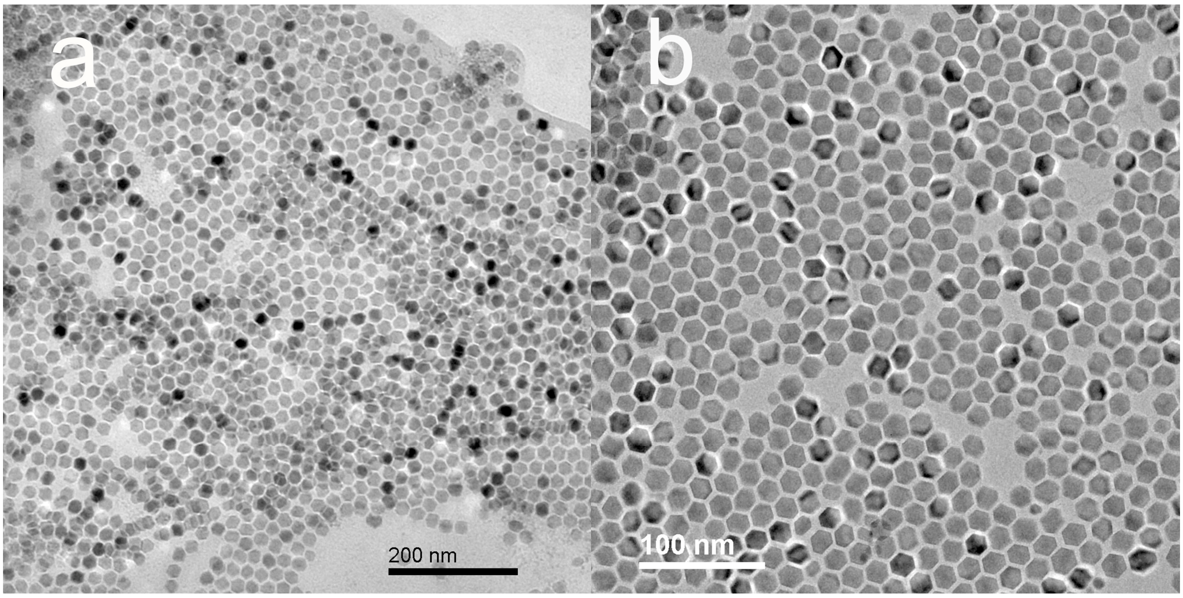
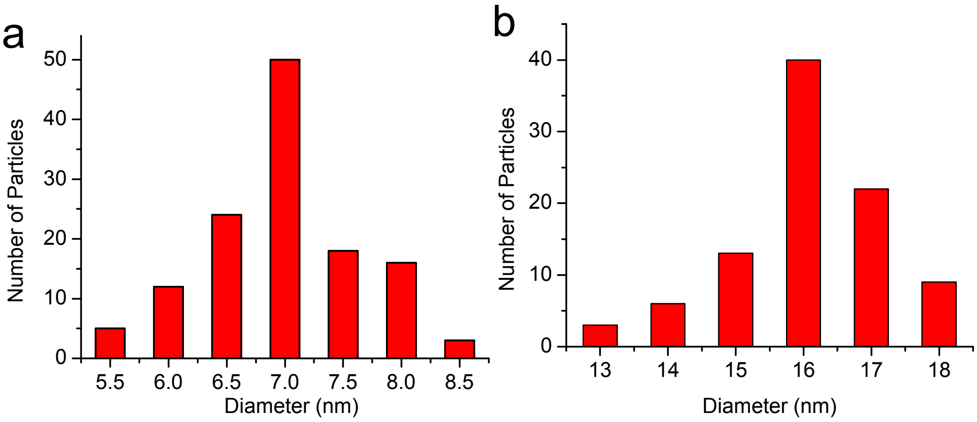


Fig. S1 TEM images of NaYF$_4$:20%Yb, 2%Er (a) and NaGdF$_4$:20%Yb, 2%Er (b) UCNPs prepared with molar ratios of OA/OM 25/30.



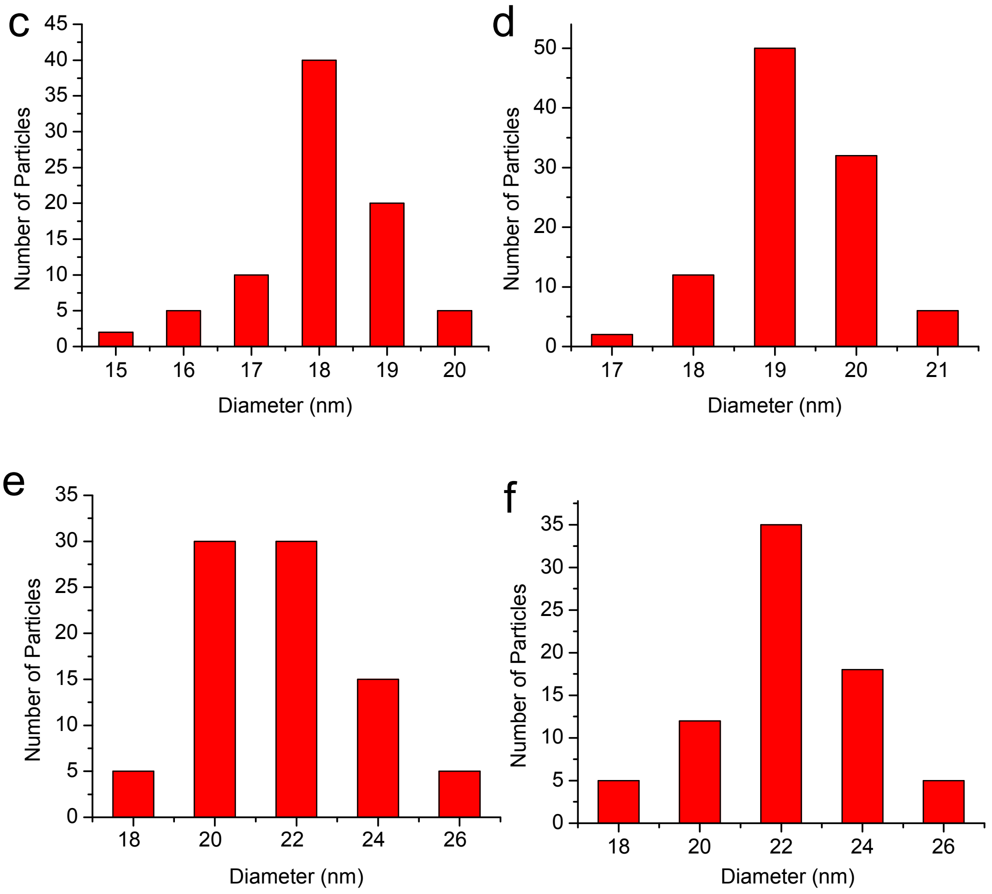


Fig. S2 Particle size distribution of the obtained NaYF4:20%Yb,2%Er nanoparticles with various ratio of OA/OM, a) 0/55; b) 15/40; c) 25/30; d) 27.5/27.5; e) 40/15; f) 55/0.

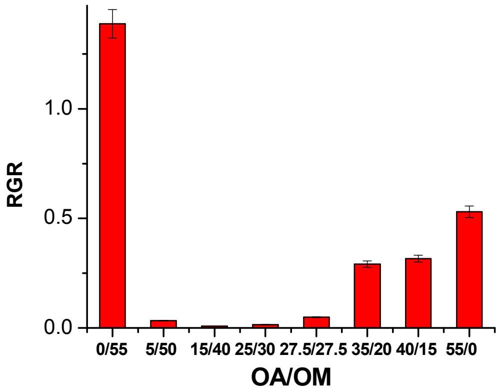


Fig. S3. Intensity ratio of green to red emissions (RGR) of NaYF$_4$:20%Yb,2%Er UCNPs prepared with various ratios of OA/OM.

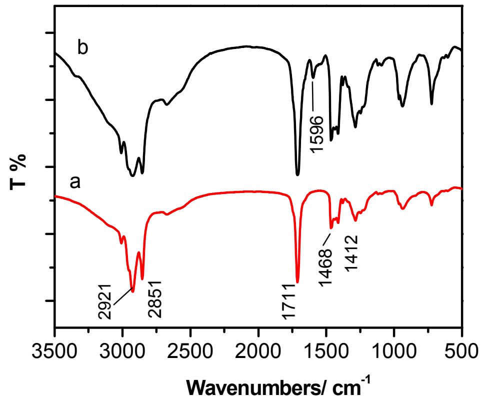


Fig. S4 FT-IR spectra of octadecylamine (OA, a), and mixture solution of $Y(CF_3COO)_3$ of 2 mmol and oleic acid (OA) of 110 mmol after maintaining at 120 °C for 30 min.

Effect of water

To examine the effect of water, a controlled experiment was carried out to synthesize $NaYF_4$: 20%Yb, 2%Er UCNPs by adding water in the thermolysis procedure (OA/OM, 40/15). When the temperature of the reaction solution was higher than 200 °C during heating, water (1.5 mL) was slowly added into the reaction solution. After the water was added, the reaction solution was continuously heated to 285 °C and aged for 1 h. Then, the solution was cooled to room temperature. The isolated $NaYF_4$:20%Yb, 2%Er UCNPs were characterized by upconversion fluorescence spectrometer. Because a large amount of water would be formed at 200 °C due to amidation reaction between OA and OM, water was added was slowly added into the reaction solution when the temperature was higher than 200 °C during heating. The result showed that the addition of water had no significant effect on the color emission (Fig. S5).

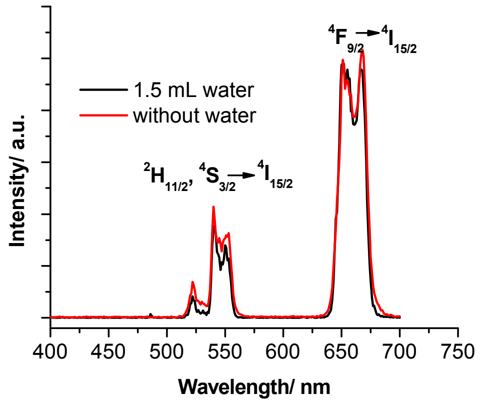


Fig. S5 Upconversion spectra of $NaYF_4$:20%Yb,2%Er UCNPs prepared with and without addition of water (OA/OM=40/15).

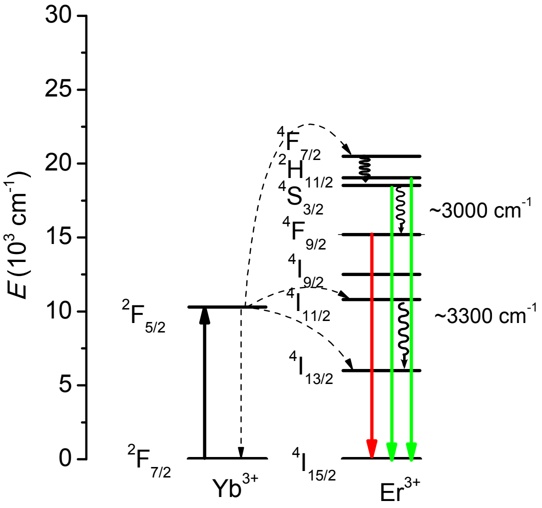


Fig. S6 The energy level diagrams of the Er^{3+} and Yb^{3+} dopant ions and upconversion mechanisms under excitation of 980 nm. The full, dotted, and curly arrows represent emission, energy transfer and multiphonon relaxation processes, respectively.

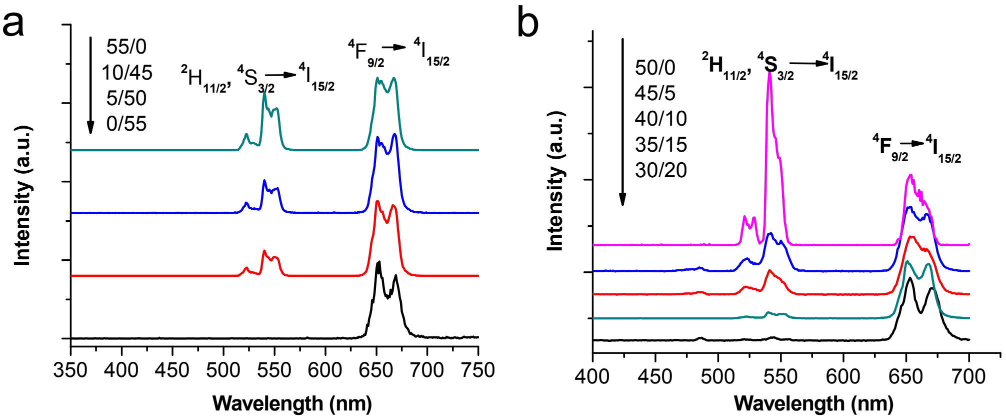


Fig. S7 Upconversion spectra of $NaYF_4$:20%Yb,2%Er nanoparticles (normalized to Er^{3+} 650 nm emission) prepared under different ratio of OA/OOA (a) and OM/OOA (b) (T = 285 °C, t = 1h).

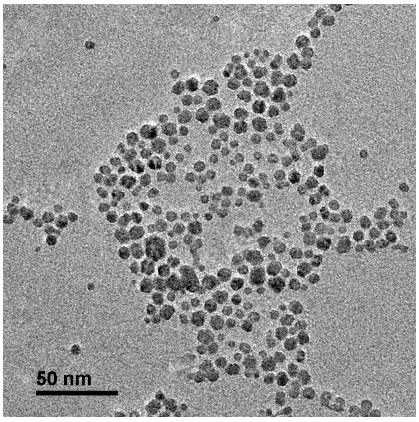


Fig. S8 TEM image of $NaYF_4$:20%Yb,2%Er nanoparticles prepared in pre-synthesized OOA.

Additionally, we found that the size of particles prepared in OA/OM mixture (27.5/27.5) was smaller than that of prepared in pre-synthesized OOA. This is due to the formation of rare earth ions-OA/OM complexes in reaction solution at the beginning stage of reaction (Fig.S4). The strong chelating interaction of earth ions-OA/OM complexes prevented nucleation and decreased the number of stable nuclei and finally, the size of particles increased. Therefore, the larger $NaYF_4$:20%Yb,2%Er nanoparticles were obtained in OA/OM mixture (27.5/27.5).

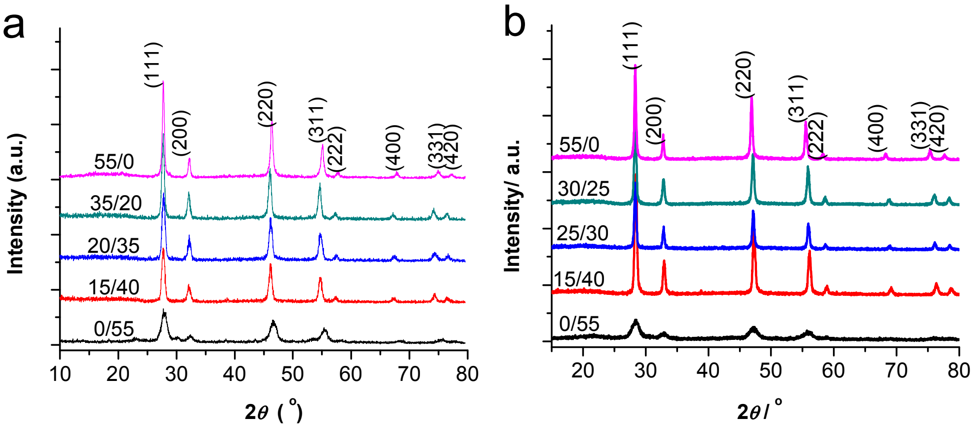


Fig. S9. XRD patterns of $NaGdF_4$: 20%Yb, 2%Er (a) and $NaLuF_4$: 20%Yb, 2%Er (b) UCNPs prepared with various ratios of OA/OM.

Synthesis of OOA

OOA was synthesized according to the previous report by heating a mixture of amine and carboxylic acid in the absence of any catalysis.[1] OA (14.1 g, 50 mmol) and octadecylamine (OM, 13.5 g, 50 mmol) were added into a flask at room temperature under stirring. The solution was heated to 100 °C and maintained for 15 min under reduced pressure to remove water and oxygen, during which time the flask was purged periodically with dry nitrogen. Subsequently, the temperature was raised to 230 °C reacting for 40 minutes under inert atmosphere. Then, the residual OA and OM were removed under reduced pressure at elevated temperature.

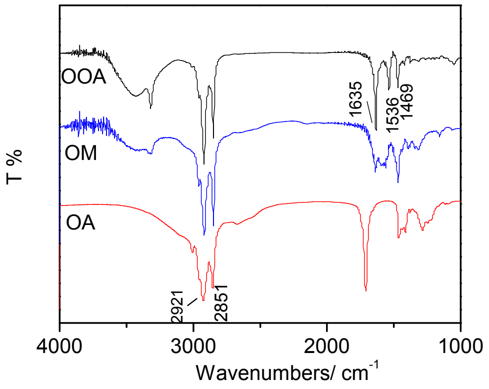
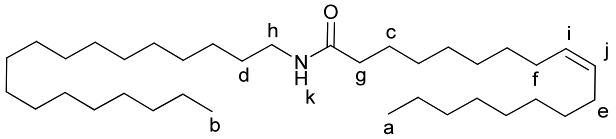


Fig. S10 IR spectra of OA, OM and as-prepared OOA.

Compared with the spectra of raw materials OA and OM, the IR spectrum of the product show two characteristic vibration peaks for alkyl-oleamide: 1635 cm^{-1} for C=O stretching and 1536 cm^{-1} for N-H bending, thus indicating the formation of *N*-octadecyloleamide (OOA). ^{1}H-NMR (400-MHz $CDCl_3$): δ_{ab} 0.88 (t, J= 6.6Hz,6H), δ 1.27 (m, 50H), δ_c 1.48 (m, J=6.6Hz, 2H), δ_d 1.62 (m, 2H), δ_{ef} 2.02 (m, 4H), δ_g 2.15(t, J=7.5Hz, 2H), δ_h 3.23 (q, 2H), δ_{ij} 5.34(m, 2H), δ_k 5.54 (s, 1H).



References:

1 B. S. Jursic and Z. Zdravkovski, *Synth. Commun.* 1993, **23**, 2761.