Electronic Supplementary Information

A facile and general approach for the multicolor tuning of lanthanide-ion doped $NaYF_4$ upconversion nanoparticles within a fixed composition

Wenbin Niu, Suli Wu and Shufen Zhang

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116012, China

FT-IR analysis: We could observe that oleamide showed two strong characteristic absorption bands around 3361 cm^{-1} and 3194 cm^{-1} ascribed to the intense asymmetric and symmetric stretching vibrations of N-H ($-CONH_2$) of amide group, which were stronger than that of OM (Fig. S1a). As the ratio of oleamide/OM increased in reaction solution, the absorption band around 1580 cm^{-1} attributed to the N-H bending vibrations of amine group was gradually broadened in the samples of isolated $NaYF_4$:20%Yb, 2%Er upconversion nanoparticles. It indicated the increase of the relative content of oleamide in surface ligands. These results were in agreement with ^1H-NMR analysis (Fig. 3). Furthermore, the N-H vibrational energy of amide group approaches to the energy level difference between green ($^2H_{11/2}$, $^4S_{3/2}$) and red ($^4F_{9/2}$) levels (about 3000 cm^{-1}, Fig. S3) of Er^{3+} ion. Therefore, the green emissions of $NaYF_4$:20%Yb,2%Er upconversion nanoparticles decreased with the rise of the relative content of oleamide bonded onto nanoparticle surface, because amide group quenched the green ($^2H_{11/2}$, $^4S_{3/2}$) levels and populated the red ($^4F_{9/2}$) levels of excited Er^{3+} ion.

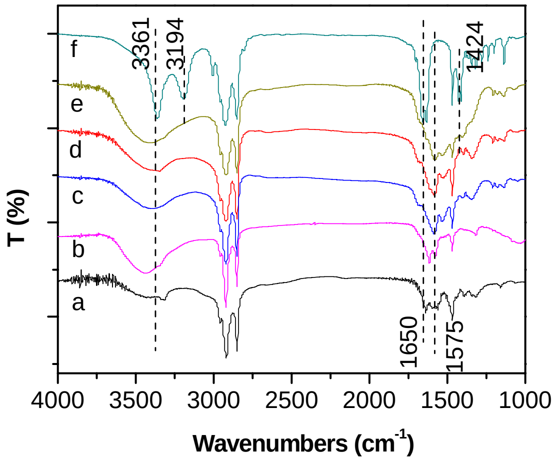

Fig. S1 FT-IR spectra of octadecylamine (OM, a), oleamide (f), and isolated $NaYF_4$:20%Yb,2%Er upconversion nanoparticles prepared with various ratios of oleamide/OM (b, 0/50; c, 2.5/47.5; d, 5/45; e, 7.5/42.5).

Effect of the molar ratio of one coordinating ligand: Fig. S2 shows the upconversion spectra of $NaYF_4$:20%Yb,2%Er nanoparticles prepared with various ratios of OM/octadecene and oleamide/octadecene. We can observe that the intensity ratio of green to red emissions did not vary obviously with the increasing of coordinating ligands. These results indicate that the change of one coordinating ligand concentration in reaction solution could not lead to multicolor output.

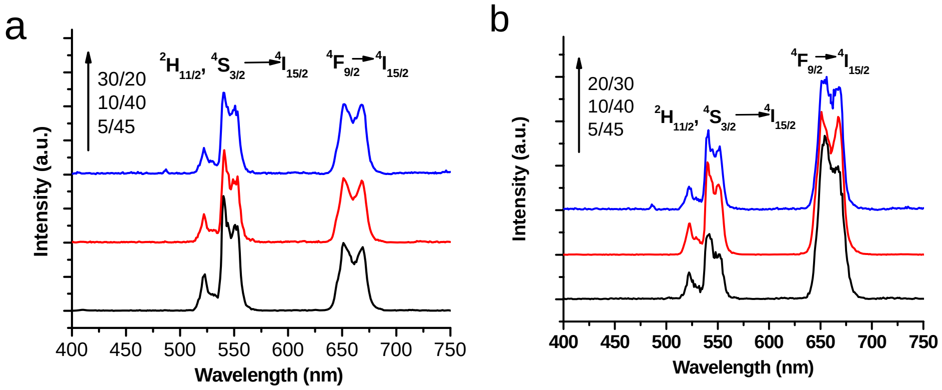

Fig. S2 Upconversion spectra of $NaYF_4$:20%Yb,2%Er nanoparticles prepared with various ratios of OM/octadecene (a) and oleamide/octadecene (b) (T = 285 °C, t = 1h).

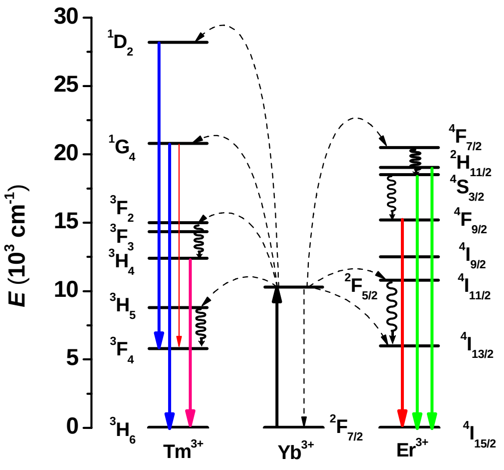

Fig. S3 The energy level diagrams of the Er^{3+}, Tm^{3+} and Yb^{3+} dopant ions and upconversion mechanisms under excitation of 980 nm. The full, dotted, and curly arrows represent emission, energy transfer and multiphonon relaxation processes, respectively.

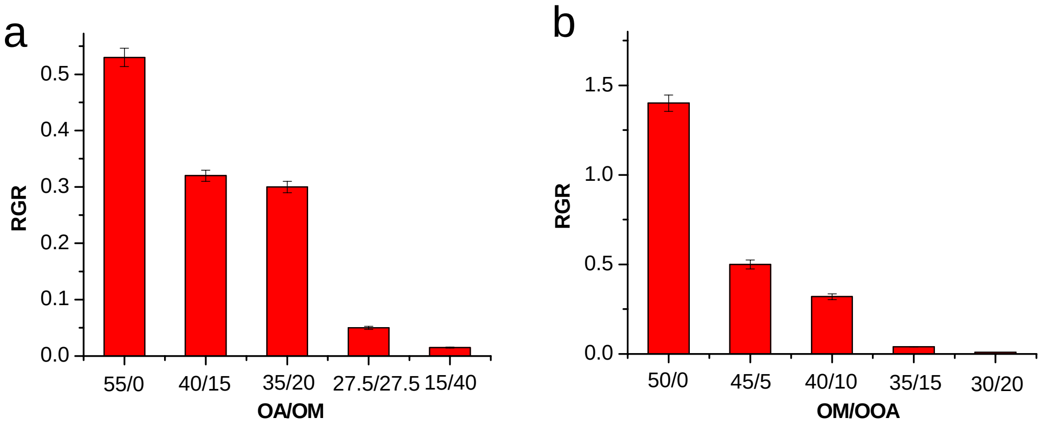

Fig. S4 RGR of $NaYF_4$:20%Yb,2%Er UCNPs prepared under different OA/OM and OM/OOA.

Effect of OA/OOA on the multicolor output of $NaYF_4$:20%Yb,2%Er UCNPs: It clearly shows that the green emissions of $^2H_{11/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and RGR of $NaYF_4$:20%Yb,2%Er UCNPs decreased gradually as the concentration of oleic acid decreased in reaction solution, which results in different color output. Similar to the results of samples prepared in a mixture of oleamide/OM, OA/OM as well as OM/OOA, color output can also be tuned in a mixture of OA/OOA.

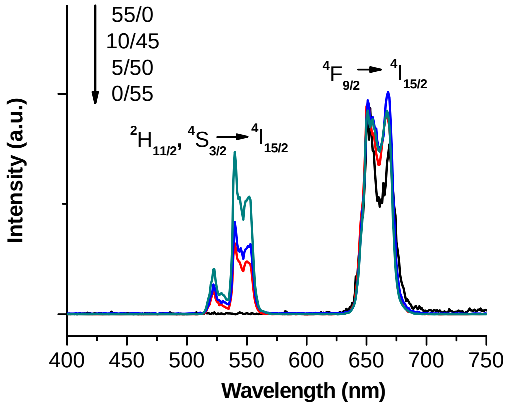

Fig. S5 Upconversion spectra of $NaYF_4$:20%Yb,2%Er nanoparticles (normalized to Er^{3+} 650 nm emission) prepared under different ratio of OA/OOA (T = 285 °C, t = 1h).

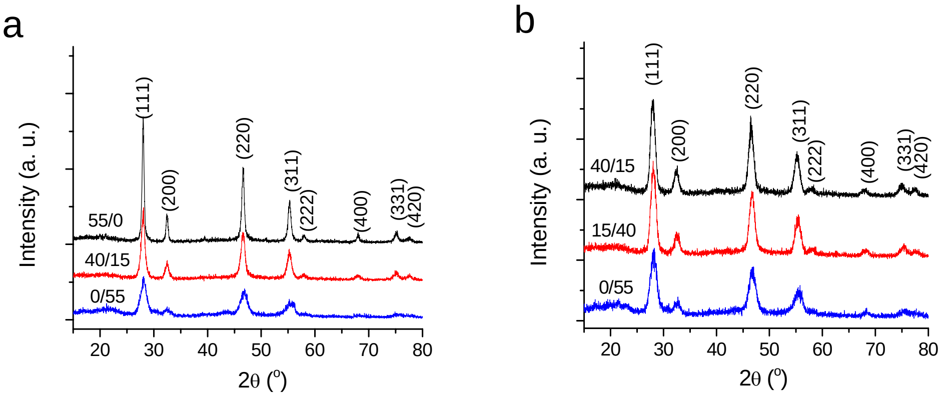

Fig. S6 XRD patterns of $NaYF_4$:2%Yb,2%Ho (a) and $NaYF_4$:2%Yb,0.5%Tm (b) UCNPs prepared under different OA/OM (T = 280 °C, t= 1h).

Synthesis of OOA: 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.

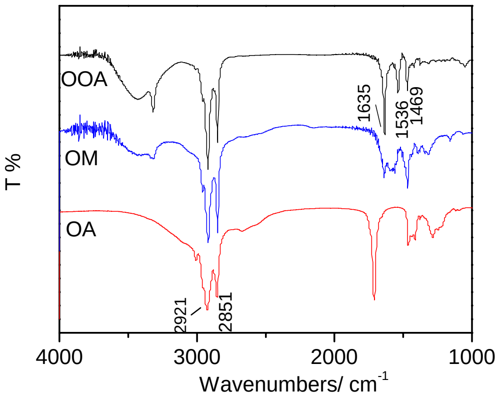

Fig. S7 IR spectra of OA, OM and as-prepared OOA.

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).