Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

The preferred upconversion pathway for the red emission of lanthanide-doped upconverting nanoparticles, $NaYF_4$:Yb^{3+},Er^{3+}

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EXPERIMENTAL DETAILS

Synthesis of hexagonal phase core/shell $NaYF_4$:Yb^{3+},Er^{3+}/$NaYF_4$ UCNPs. Hexagonal phase core/shell upconverting nanoparticles (UCNPs) were synthesized by using the previously reported methods with some modifications.[1] For hexagonal phase core UCNPs, pre-prepared Y-oleate (0.78 mmol), Yb-oleate (0.20 mmol), Er-oleate (0.02 mmol) complexes were mixed with oleic acid (8 ml) and 1-octadecene (15 ml) in a 100 ml three-neck round bottom flask. The reaction mixture was heated to 100°C under vacuum with stirring for 30 min., and then cooled to room temperature. NaOH (2.5 mmol) and NH_4F (4 mmol) were dissolved in methanol (10 ml), and slowly added into the reaction vessel under Ar. It was aged for 30 min at 50°C. To remove methanol, it was heated to 100°C under vacuum with stirring for 30 min. Then it was heated to 300°C at a constant heating rate of 3.3°C min^{-1}, and then kept at that temperature for 2 h under Ar. After Cooling down to room temperature, UCNPs were precipitated by adding ethanol and retrieved by centrifugation 3 times. The purified core UCNPs were dispersed in hexane.

For hexagonal phase core/shell UCNPs, pre-prepared Y-oleate (0.5 mmol) was mixed with oleic acid (6 ml) and 1-octadecene (15 ml) in a 100 ml three-neck round bottom flask. The reaction mixture was heated to 100°C under vacuum with stirring for 30 min, and then cooled to room temperature. A solution of hexagonal phase core UCNPs in hexane (1 mmol) was injected to the reaction vessel. The mixture was heated to 80°C under vacuum with stirring for 30 min to remove hexane, and then cooled to room temperature. NaOH (1 mmol) and NH_4F (1.6 mmol) were dissolved in methanol, and slowly added into the reaction vessel under Ar. After aging for 30 min. at 50°C, it was heated to 100°C under vacuum with stirring for 30 min to remove methanol. Then it was heated to 300°C at a constant heating rate of 3.3°C min^{-1}, and then kept at that temperature for 1 h under Ar. The resulting solution was then cooled to room temperature. The core/shell UCNPs were precipitated by adding ethanol and retrieved by centrifugation 3 times. The purified hexagonal phase core/shell UCNPs were dispersible in many organic solvents such as hexane and chloroform.

UCNPs characterization. The synthesized UCNPs were characterized by transmission electron microscope (TEM), XRD and inductive coupled plasma atomic emission spectroscopy (ICP-AES). TEM images were captured by JEOL EM-2010 TEM, which was operated at 200 kV (Figure 1S). XRD patterns were obtained (Figure S2) with Rigaku D/Max-3C diffractometer, equipped with a rotating anode and a Cu-Kα radiation source (l=0.15418 nm). The composition and concentration of UCNPs were analyzed by ICP-7500 (Shimadzu ICP-AES), and the results for the core and core/shell UCNPs are summarized in Table S1.

Emission spectra of UCNPs. The UCNPs in *n*-hexane (100 nM) were excited by 980-nm CW lasers (AC1401-0600-0980-SM, EM4) and 488-nm CW laser (LBX-488-100-CIR-PP, Oxxius). The emission was collected by an objective and detected by HR2000+ spectrometer (Ocean optics). The exposure time was set 100 ms for most measurements in this study, and laser power was varied for power dependence measurement.

Time-resolved emission of UCNPs. The UCNP solution in *n*-hexane (100 nM) was excited by pulsed 980-nm or 488-nm laser generated by Nd:YAG laser (GCR-150, 355 nm, pulse width (FWHM) 7 ns)-pumped optical parametric oscillator (OPO). The emission was spectrally dispersed by a monochromator (250IS, chromex) and detected at 525, 540, 655 nm by a photomultiplier tube (H3177, Hamamatsu) and the temporal profile was obtained by a digital oscilloscope.

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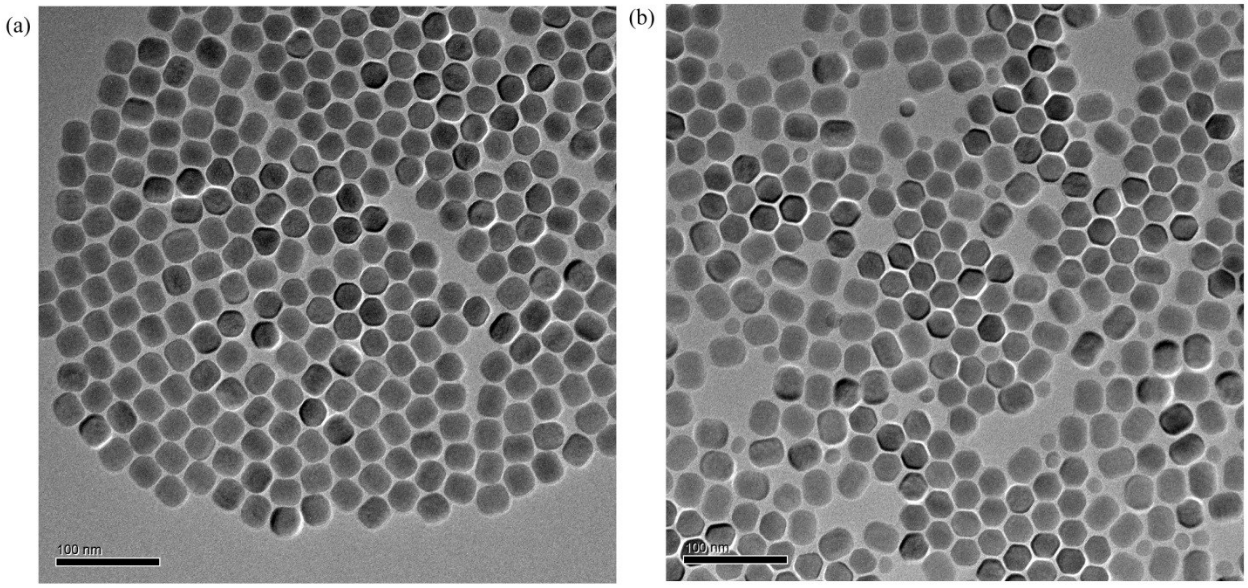

Figure S1. TEM image of (a) NaYF$_4$:Yb^{3+},Er^{3+} core nanoparticles and (b) NaYF$_4$:Yb^{3+},Er^{3+}/NaYF$_4$ core/shell nanoparticles (Yb^{3+} 12%, Er^{3+} 1.2%).

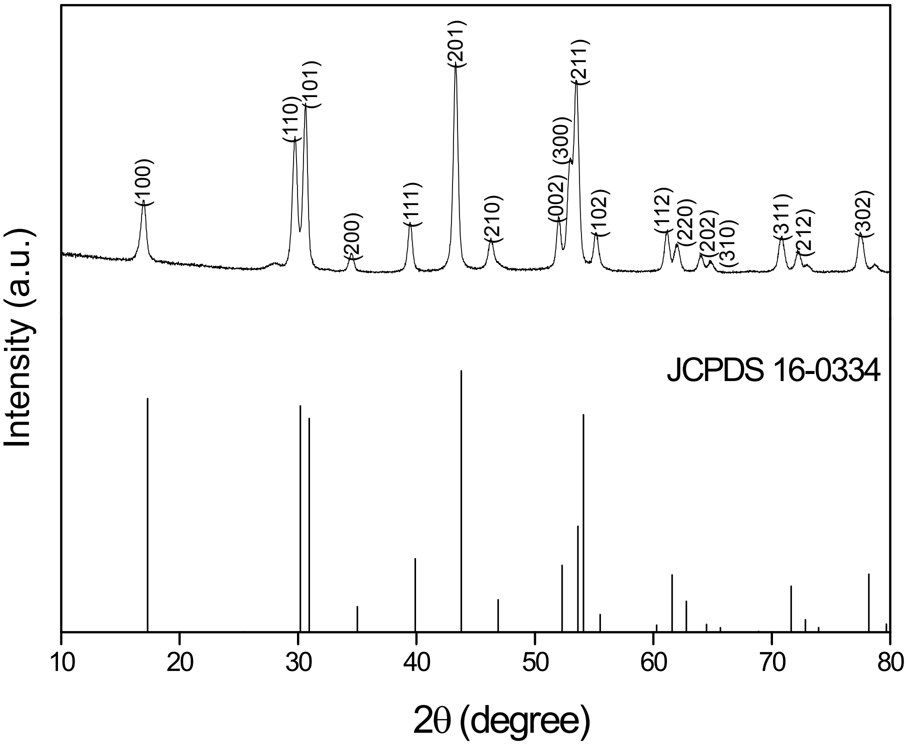

Figure S2. The powder X-ray diffraction (XRD) pattern of UCNPs (upper). The peak positions match the standard pattern whose JCPDS file number is 16-0334 (lower), representing a well-known reference for hexagonal phase $NaYF_4$.[2–4] In the hexagonal phase, an ordered array of F^- ions provides two types of cation sites: one occupied by Na^+ and the other occupied randomly by RE^{3+} and Na^+.[2] This structure can be written as $Na(Y_{1.5}Na_{0.5})F_6$, which gives total elemental ratio of Na^+:Y^{3+}:F^- =1:1:4. The slight peak shift from the standard pattern could be explained by the 'doping' effect: the cationic radii of Yb^{3+} (100.8 pm) and Er^{3+} (103 pm) are different from that of Y^{3+} (104 pm) and this difference might lead to the lattice distortion of the hexagonal $NaYF_4$ matrices.

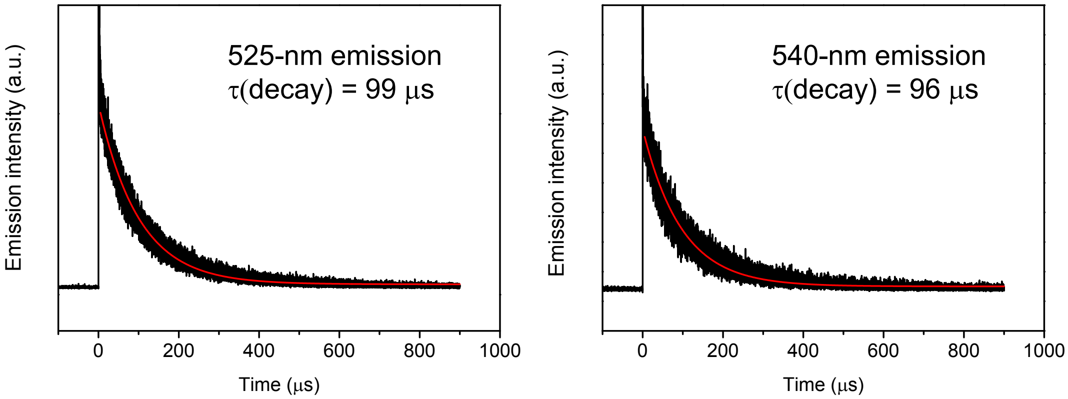

Figure S3. Time-resolved emission spectra of UCNPs at the green bands (525 and 540 nm). The excitation wavelength was 488 nm. The red band (655 nm) was not be detected with reasonable signal-to-noise ratio. The time constants were obtained by fitting the experimental curves to I(t) = A exp(-t/τ(decay)) + const. There was no rise component in both data.

Table S1. Elemental compositions of core and core/shell UCNPs analyzed with ICP-AES

Core NPs	Y (mol%)	Yb (mol%)	Er (mol%)
Molar Ratio (%)	79.5	18.6	1.9

Core/Shell NPs	Y (mol%)	Yb (mol%)	Er (mol%)
Molar Ratio (%)	87.8	11.1	1.2