

Electronic Supplementary Information

Experimental details

Reagents: $\text{Gd}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), $\text{Y}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), $\text{Yb}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), $\text{Nd}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), $\text{Tm}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), NaOH, (>98%), NH_4F , (>98%), 1-octadecene (90%), oleic acid (90%), were all purchased from Sigma-Aldrich. Absolute ethanol (99.85%), methyl alcohol (99.99%), and cyclohexane (99.9%) were purchased from VWR International. All chemicals were used as received without further purification.

Synthesis of core nanoparticles: The core layer nanoparticle was synthesized on the basis of a previous literature method.^[1] Typically, 4 ml of lanthanide acetates in water solution (0.2 M) was firstly added into a 50 ml round-bottom flask. Then 8 ml of OA and 12 ml of ODE was added into the flask under stirring. The flask was heated at 175 °C for 60 min followed by cooling down to 45 °C. After that, appropriate amount of NH_4F and NaOH in methanol solution was added into the flask and being stirred for 120 min. The mixture was then heated to 285 °C in argon atmosphere for 90 min, followed by cooling down to the room temperature. The resultant nanoparticles were collected by addition of ethanol and centrifugation at 6000 rpm for 3 min. The obtained product was washed with ethanol for 3 times and re-dispersed in cyclohexane.

Synthesis of core-shell nanoparticles: The pre-synthesized core nanoparticles were used as seeds for the epitaxial growth of the shell layer. In a typical experiment, 4 ml of lanthanide acetates in water solution (0.2M), 8 ml of OA, and 12 ml of ODE were added into a 50 ml flask and heated to 175 °C for 60 min under stirring. Then the flask was cooled down to 45 °C, followed by injection of NH_4F and NaOH in methanol solution. After being stirred for 120 min to get rid of the methanol, the flask was heated to 285 °C in argon atmosphere for 90 min with constant stirring. After cooling down to room temperature, the products were collected, washed, and re-

dispersed in cyclohexane.

Synthesis of core-shell-shell nanoparticles: The synthetic process of the core-shell-shell nanoparticles was the same as that for the core-shell nanoparticles, except that yttrium acetate was used as shell precursor and pre-synthesized core-shell nanoparticles were used as seeds.

Synthesis of ligand-free nanoparticles: The obtained nanoparticles were extracted by centrifugation and re-dispersed in 8 ml of HCl solution (0.1 M). The mixture was kept still overnight to remove the organic ligand on the surface. Then the clear colloid was centrifuged at 14000 rpm for 30 min to collect the ligand-free NaGdF₄:Yb/Tm@NaGdF₄:Nd@NaYF₄ nanoparticles. The product was finally dispersed in 4 mL deionized water.

Characterization: Transmission electron microscopy (TEM) measurements were conducted on a JEOL-JEM 2100F transmission electron microscope operating at an acceleration voltage of 200 kV. High angle annular dark-field imaging (HAADF) measurement was carried out on an FEI aberration-corrected Titan G2 80-200 Chemi transmission electron microscope. The X-ray diffraction (XRD) analysis were accomplished on a Bruker AXS D2 phaser with a graphite-monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The photoluminescence spectra were acquired on a Hitachi F-4600 spectrophotometer equipped with a R3788 photomultiplier tube as well as a 980 nm diode laser. The decay curves of nanoparticles in water dispersion were recorded on an Edinburgh FLSP980 spectrometer equipped with a pulsed 980nm laser. The effective lifetimes were determined by

$$\tau_{eff} = \frac{1}{I_0} \int_0^{\infty} I(t) dt$$

where I_0 and $I(t)$ represents the maximum luminescence intensity and luminescence intensity at time t after cutoff of the excitation light, respectively. All optical measurements were carried out at room temperature and under identical condition.

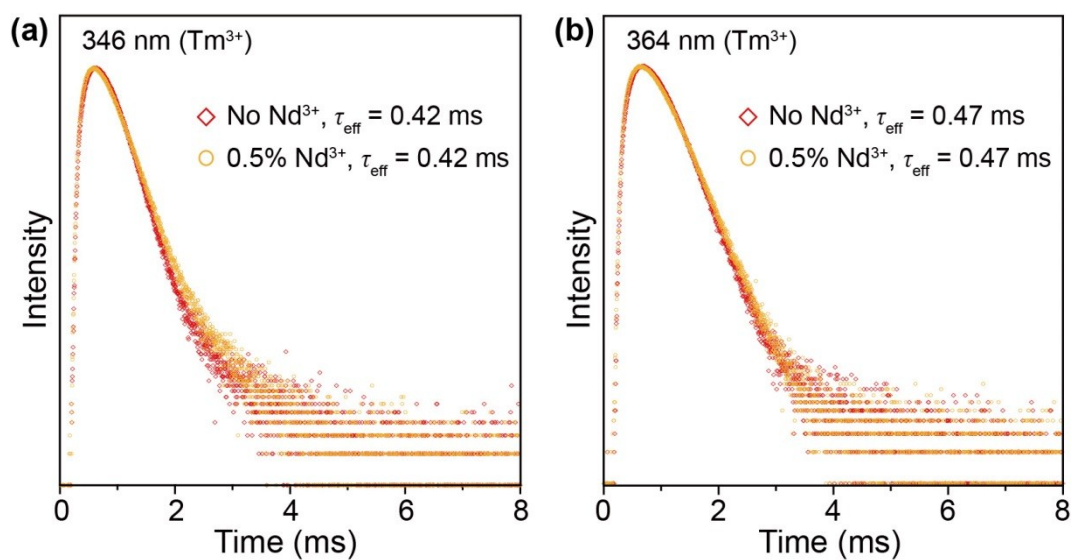


Figure S1. Time decay curves of Tm^{3+} at (a) 346 nm and (b) 364 nm in the $\text{NaGdF}_4\text{:Yb/Tm@NaGdF}_4\text{@NaYF}_4$ and the $\text{NaGdF}_4\text{:Yb/Tm@NaGdF}_4\text{:Nd (0.5%)@NaYF}_4$ nanoparticles. The samples were all excited at 980 nm. The lifetime of Tm^{3+} is essentially not affected by the Nd^{3+} dopants, thus ruling out direct energy transfer from Tm^{3+} to Nd^{3+} .

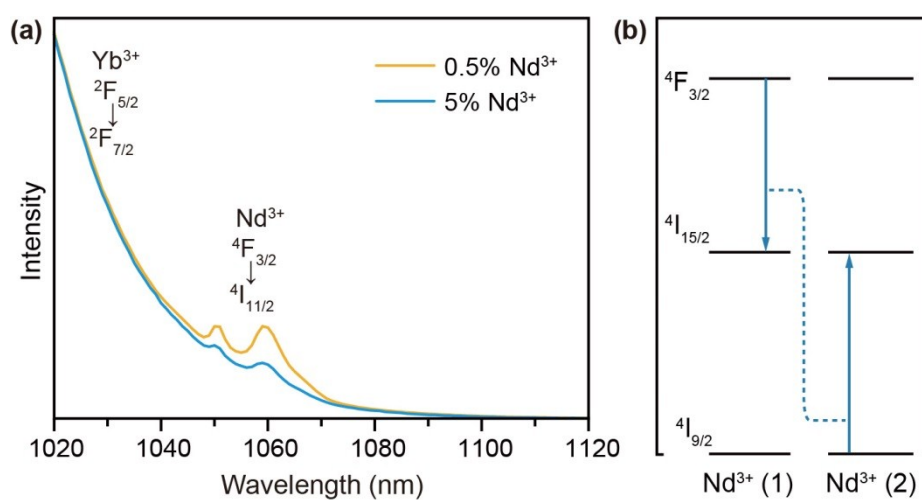


Figure S2. Concentration quenching of NIR emission of Nd^{3+} . (a) NIR emission spectra of $\text{NaGdF}_4\text{:Yb/Tm@NaGdF}_4\text{:Nd@NaYF}_4$ nanoparticles with 0.5% and 5% Nd^{3+} in the inner shell layer. (b) Simplified energy level diagram showing cross-relaxation between Nd^{3+} dopants.

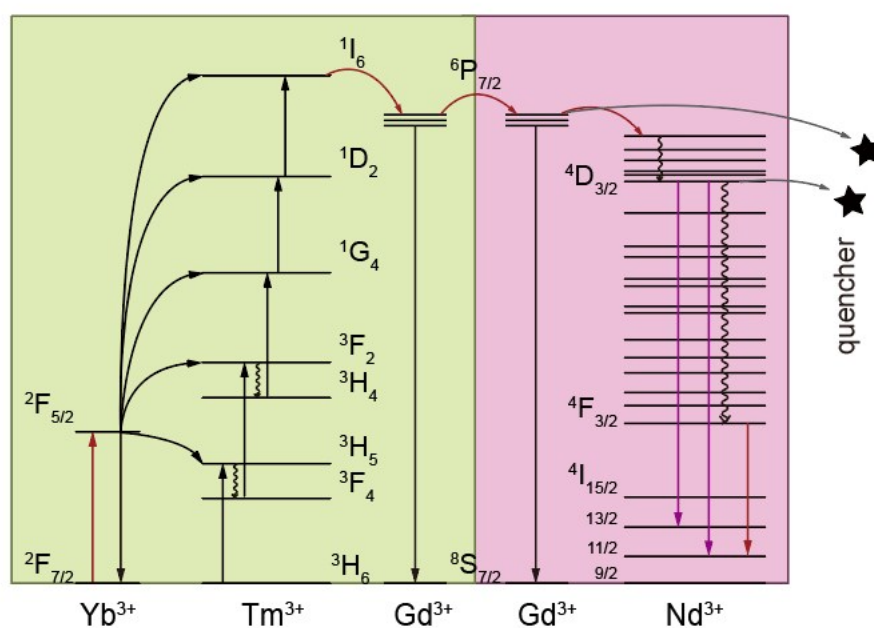


Figure S3. Proposed energy transfer mechanisms in NaGdF₄:Yb/Tm@NaGdF₄:Nd nanoparticles. Without the protection of NaFY₄ shell, excitation energy is readily dissipated by surface quenchers.

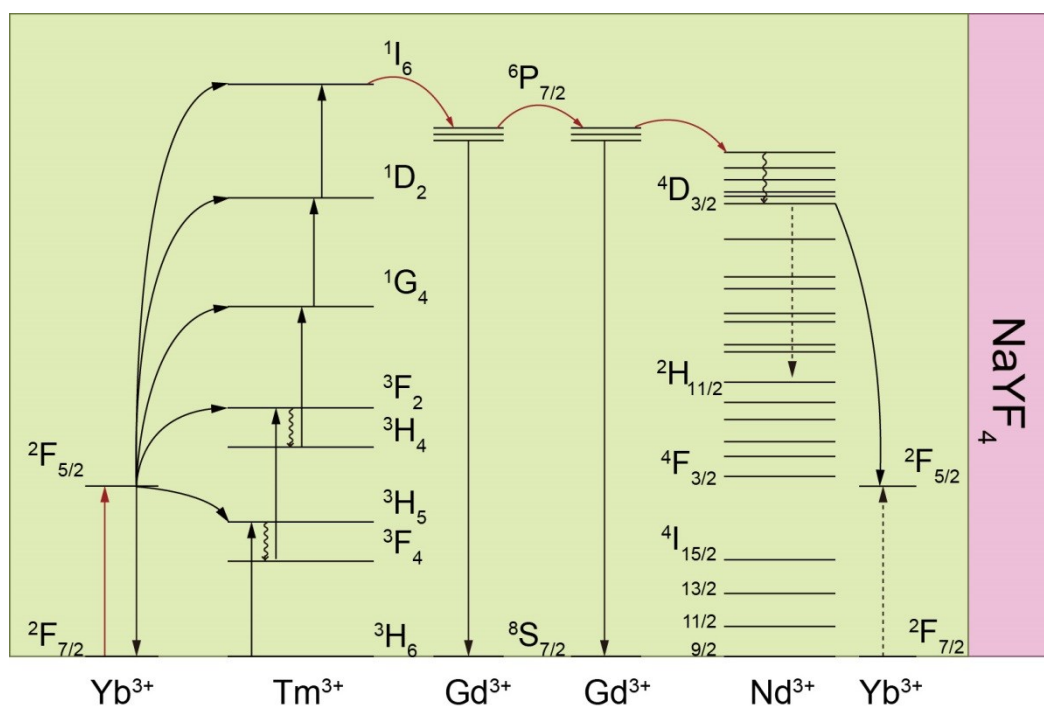


Figure S4. Proposed energy transfer mechanisms in $\text{NaGdF}_4:\text{Yb}/\text{Tm}/\text{Nd}@/\text{NaYF}_4$ nanoparticles. When Yb^{3+} , Tm^{3+} , and Nd^{3+} is homogenously doped, energy transfer from Nd^{3+} to Yb^{3+} occurs that quenches Nd^{3+} emissions.

Reference:

- 1 Q. Su, S. Han, X. Xie, H. Zhu, H. Chen, C. K. Chen, R. S. Liu, X. Chen, F. Wang and X. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 20849-20857.