Supporting Information

Dye Sensitized Core/ Active Shell Upconversion Nanoparticles for Optogenetics and Bioimaging Applications

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Spectroscopic and Transmission Electron Microscopy

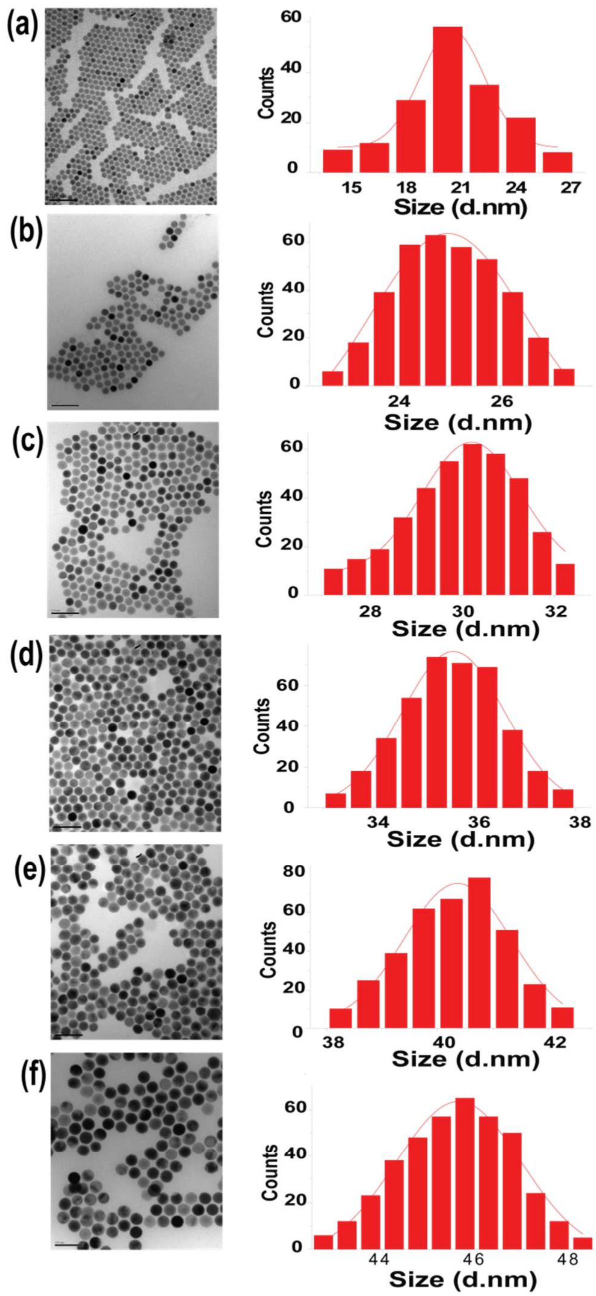

Figure S1. TEM images (left) and their corresponding size distributions (right) of (a) β-$NaYF_4$:20%Yb, 2%Er with the size 20.3 ± 1.6 nm, (b) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 24.9 ±1.5 nm, (c) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 30.2 ± 1.5 nm, (d) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 35.5 ± 1.2 nm, (e) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 40.4 ±1.1 nm, (f) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 45.6 ±1.5 nm. Scale bar: 100 nm.

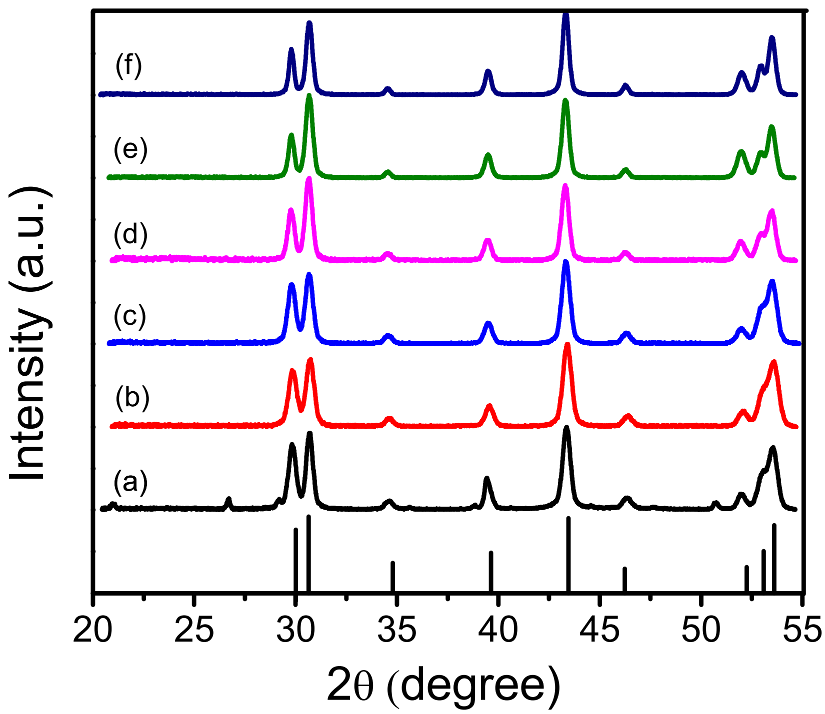

Figure S2. XRD patterns of (a) β-$NaYF_4$:20%Yb, 2%Er with the size 20.3 ± 1.6 nm, (b) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 24.9 ±1.5 nm, (c) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 30.2 ± 1.5 nm, (d) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 35.5 ± 1.2 nm, (e) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 40.4 ±1.1 nm, (f) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$ with the size 45.6 ±1.5 nm. The standard card of β-$NaYF_4$ (JCPDS: 16-0334) was given as a reference (bottom).

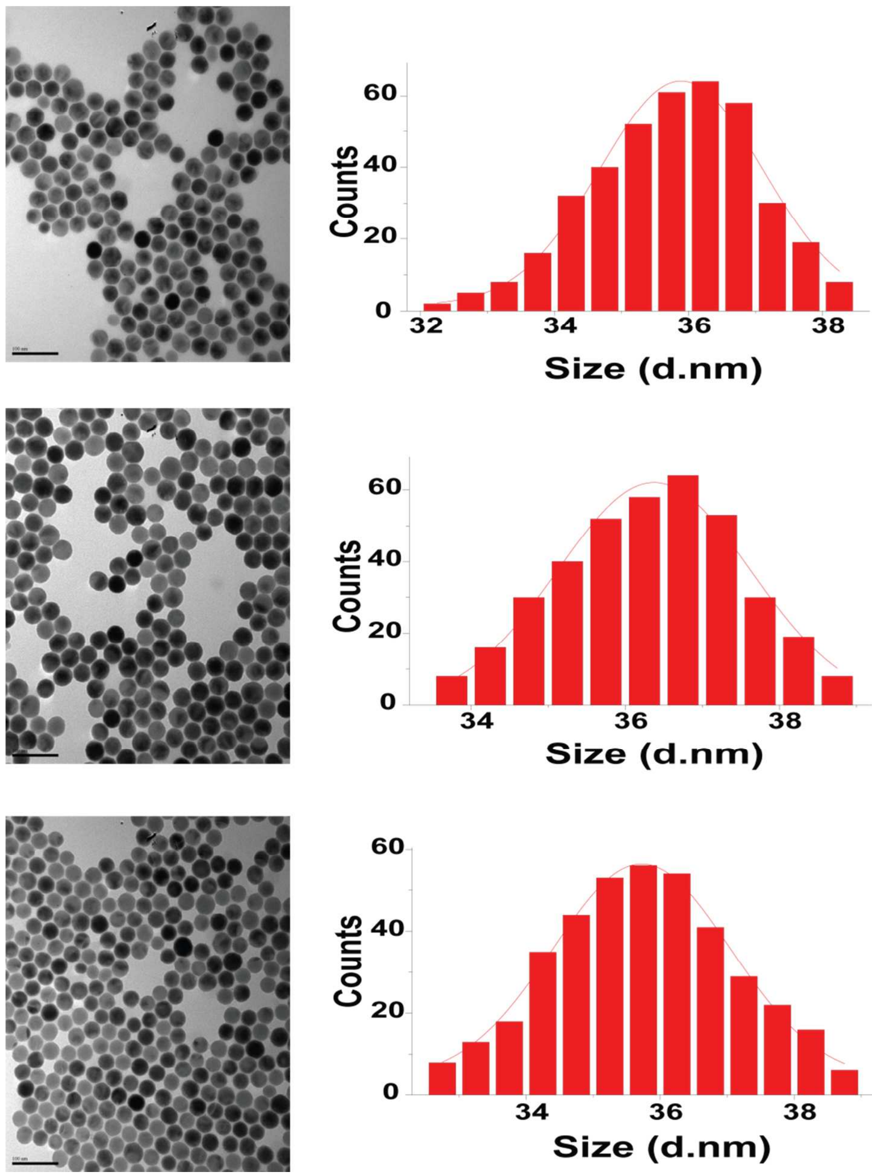

Figure S3. TEM images (left) and their corresponding size distributions (right) of (a) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$: 10%Yb with the size 35.9 ±1.4 nm, (b) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$: 30%Yb with the size 36.4 ±1.2 nm, (c) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$: 50%Yb UCNPs with the size 35.7 ±1.6 nm. Scale bar: 100 nm.

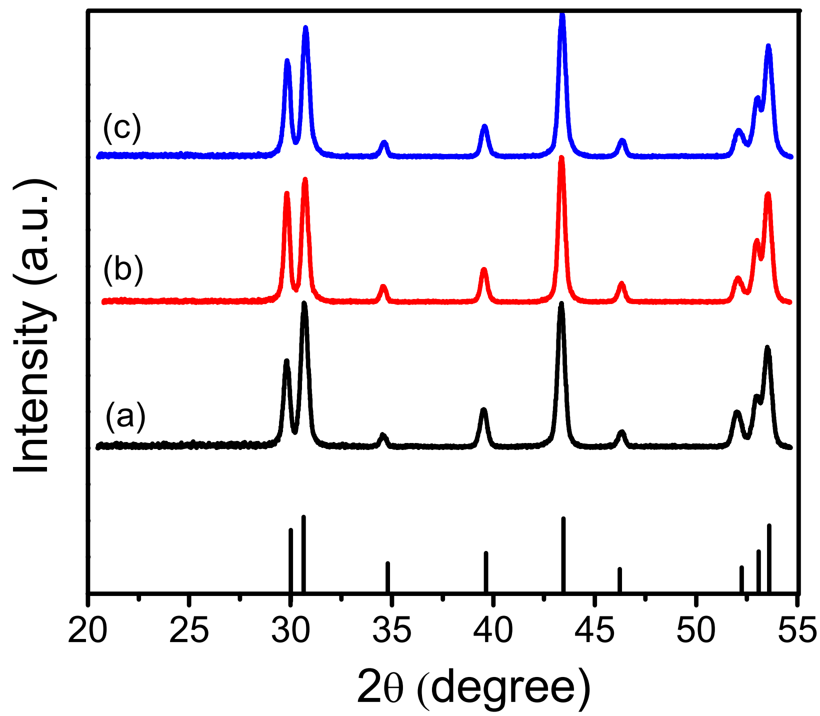

Figure S4. XRD patterns of (a) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$: 10%Yb with the size 35.9 ±1.4 nm, (b) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$: 30%Yb with the size 36.4 ±1.2 nm, (c) β-$NaYF_4$:20%Yb, 2%Er@β-$NaYF_4$: 50%Yb UCNPs with the size 35.7 ±1.6 nm. The standard card of β-$NaYF_4$ (JCPDS: 16-0334) was given as a reference (bottom).

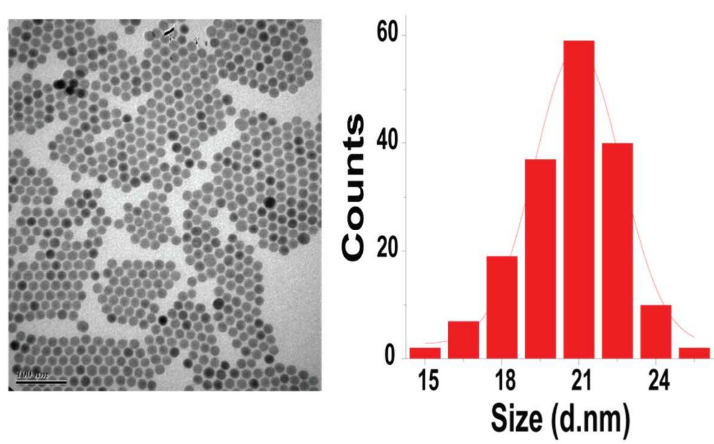

Figure S5. TEM images (left) and the corresponding size distribution (right) of β-$NaYF_4$:30%Yb, 2%Er with the size 20.9 ±1.4 nm. Scale bar: 100 nm.

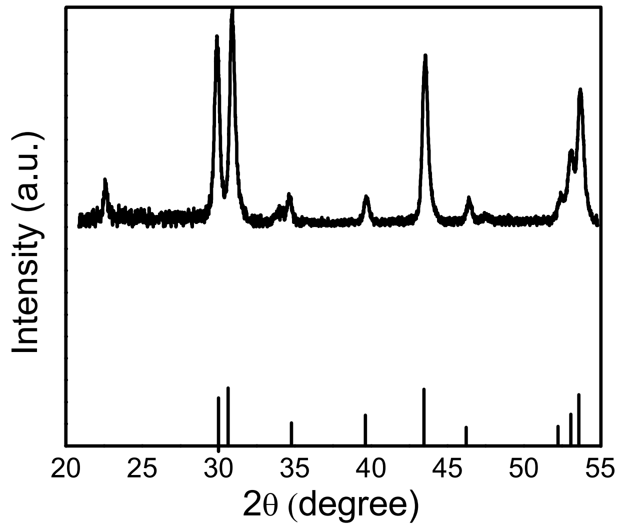

Figure S6. XRD pattern of β-$NaYF_4$:30%Yb, 2%Er with the size 20.9 ±1.4 nm. The standard card of β-$NaYF_4$ (JCPDS: 16-0334) was given as a reference (bottom).

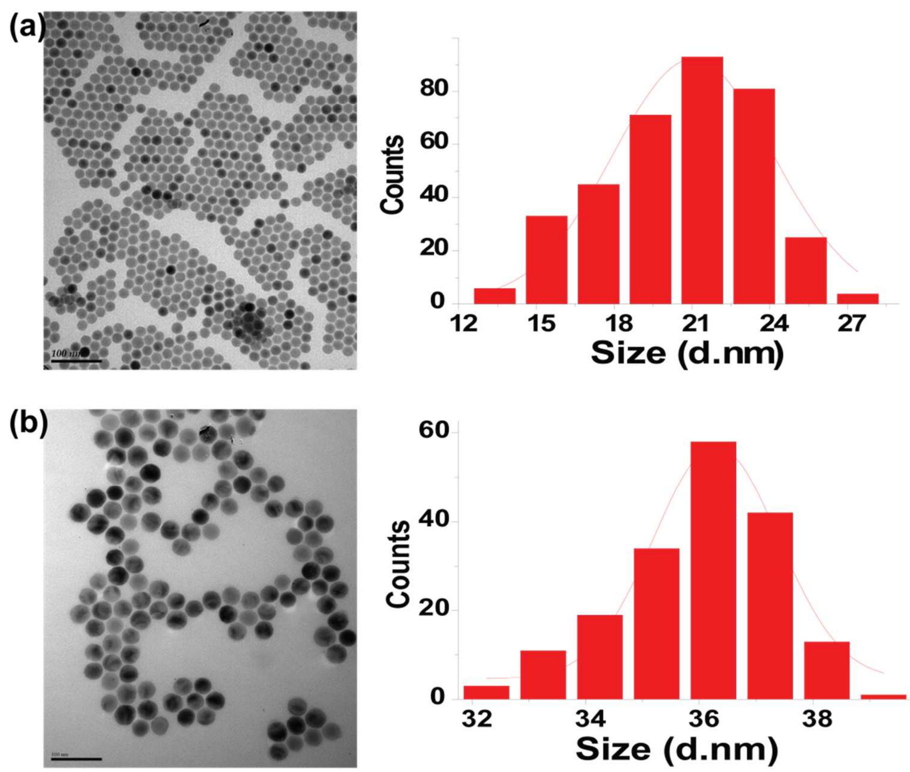

Figure S7. TEM images (left) and their corresponding size distributions (right) of (a) β-$NaYF_4$: 20%Yb with the size 21.0 ±1.1 nm, (b) β-$NaYF_4$: 20%Yb@β-$NaYF_4$:10%Yb with the size 36.2 ±1.4 nm. Scale bar: 100 nm.

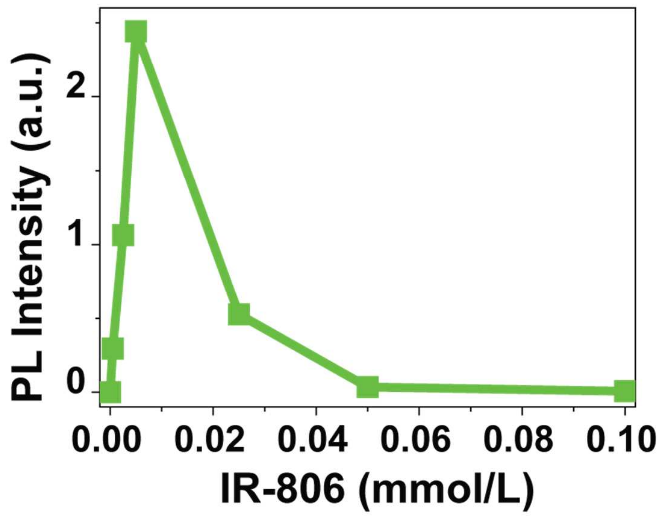

Figure S8. Emission intensity integrated in the range 500–700 nm of β-$NaYF_4$: 20%Yb, 2%Er NPs (0.1 μmol/L) as a function of increasing of IR-806 concentrations (0, 2, 4, 6, 25, 50, 100 μmol/L) (excited by 2 W/cm^2 800 nm, c.w. lasers).

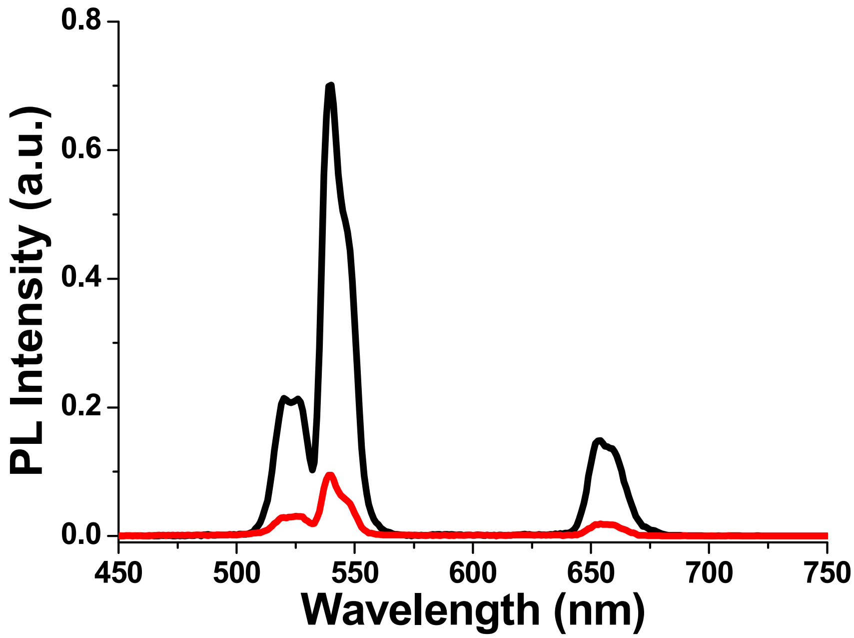

Figure S9. Emission spectrum of IR-806 sensitized β-$NaYF_4$:20%Yb, 2%Er@ $NaYF_4$:10%Yb and IR-806 sensitized β-$NaYF_4$:30%Yb, 2%Er (red line) UCNPs excited by 2 W/cm^2 800 nm, c.w. lasers.

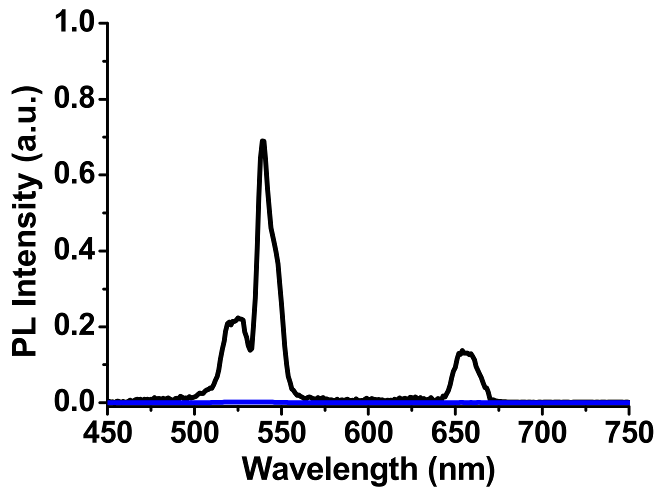

Figure S10. The emission spectrum of IR-806-sensitized β-$NaYF_4$: 20%Yb, 2%Er@β-$NaYF_4$: 10%Yb (black line) and IR-806/β-$NaYF_4$: 20%Yb@β-$NaYF_4$: 10%Yb (No Er Emitter) (blue line). Both samples were measured under 2 W/cm^2 800 nm c.w. laser excitation.

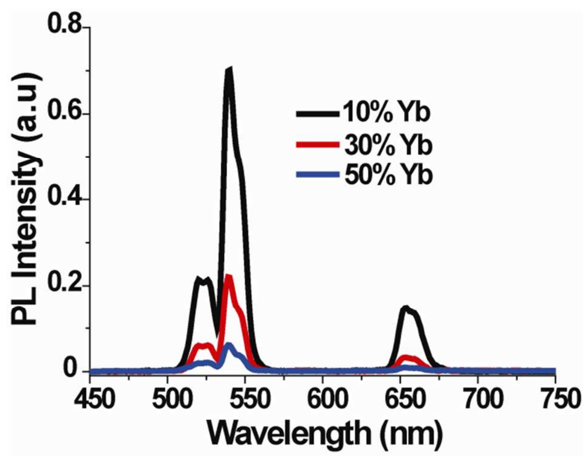

Figure S11. The emission spectrum of IR-806-sentized core/Yb^{3+}-shell UCNPs with different Yb^{3+} doping ratios. All of the samples were under 2 W/cm^2 800nm continuous wave laser excitation.

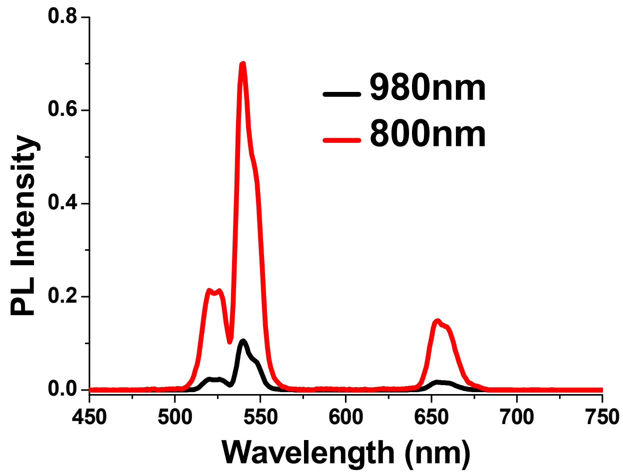

Figure S12. The emission spectra of IR-806-sentized core/Yb^{3+}-shell UCNPs under 2 W/cm^2 800 nm continuous wave laser excitation (red line) and the emission spectra of core/Yb^{3+}-shell UCNPs only under 2 W/cm^2 980 nm continuous wave laser excitation (black line).

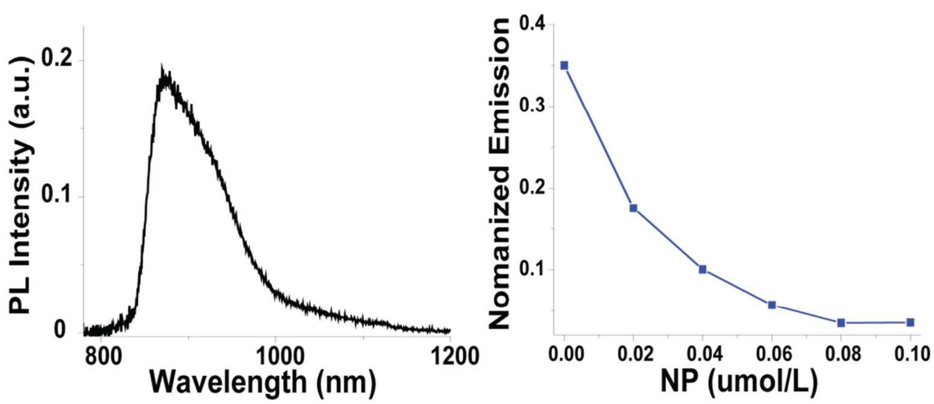

Figure S13. Emission spectrum of IR-806 (Final conc: 6 μmol/L in DCM) (left). The right depicts indicate that upon increasing concentration of β-$NaYF_4$: 20%Yb, 2%Er@ $NaYF_4$:10%Yb by adding NPs volume from 0 ml to 1 ml, (Final conc. 0, 0.02, 0.04, 0.06, 0.08, 0.1 μmol/L) the fluorescence intensity of IR-806 gradually decreased, suggesting the energy transfer occurs from IR-806 dye to the UCNPs. All of the samples were excited at 750 nm.

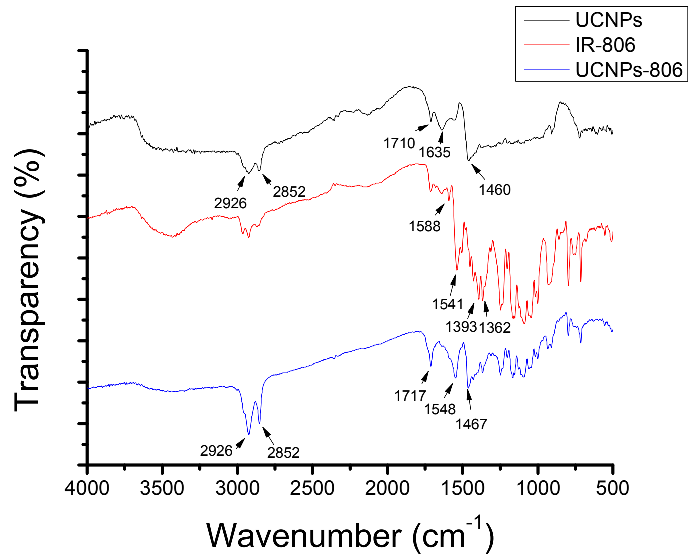

Figure S14. FT-IR spectrum of as-synthesized ~35 nm β-$NaYF_4$:20%Yb,2%Er/β-$NaYF_4$, 10%Yb UCNP with OA ligand coating, and IR806 dye and IR dye sensitized β-$NaYF_4$:20%Yb,2%Er/β-$NaYF_4$, 10%Yb UCNP. The peaks at 1710 and 1635 cm^{-1} of as-synthesized UCNPs are attributed to the resonance of the carboxyl groups while 2926 and 2852 cm^{-1} are attributed to the resonance of unsaturated OA ligands. After the partial ligand replacing by IR-806, the OA unsaturated peaks at 2926 and 2852 cm^{-1} remain, however, the peaks belong to carbonyl vibration are shifted to 1717 and 1548 cm^{-1}, which clearly show the binding of IR-806 to the UCNPs.

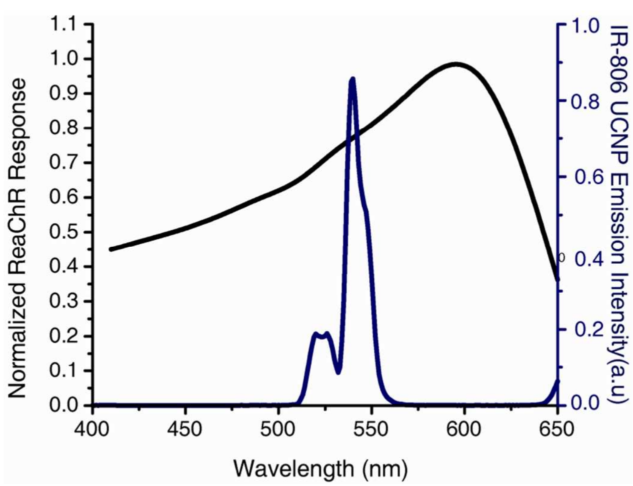

Figure S15. Overlaid Spectrum of the ReaChR light response curve (black curve) and an IR-806 dye sensitized β-$NaYF_4$:20%Yb,2%Er/β-$NaYF_4$, 10%Yb core/Yb^{3+}-shell UCNPs emission spectra under 800 nm continuous wave laser excitation. (blue curve)

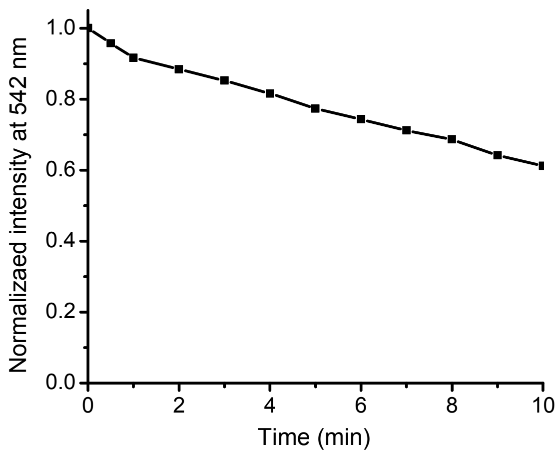

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Figure S16. The upconversion emission intensity at 542 nm of micelle encapsulated dye-sensitized β-$NaYF_4$:20%Yb,2%Er/β-$NaYF_4$, 10%Yb core/Yb^{3+}-shell UCNPs (0.1 μM) under continuous 800 nm CW (2 W/cm^2) irradiation .

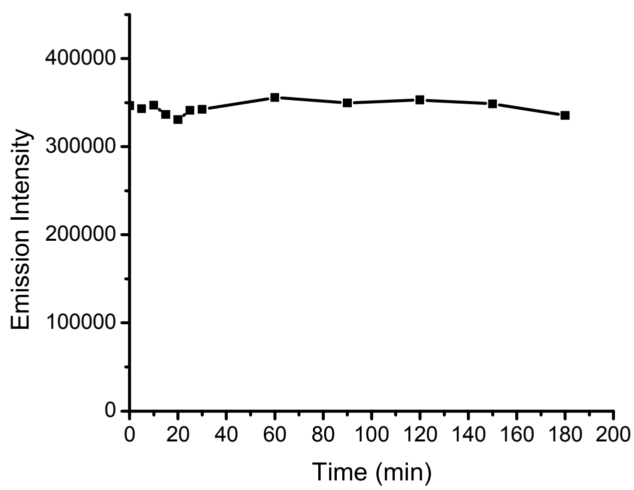

Figure S17. The upconversion emission at 542 nm of dye-sensitized β-$NaYF_4$:20%Yb,2%Er/β-$NaYF_4$, 10%Yb core/Yb^{3+}-shell UCNPs PMMA film soaked in PBS over the course of three hours. (2 W/cm^2 800 nm CW laser).

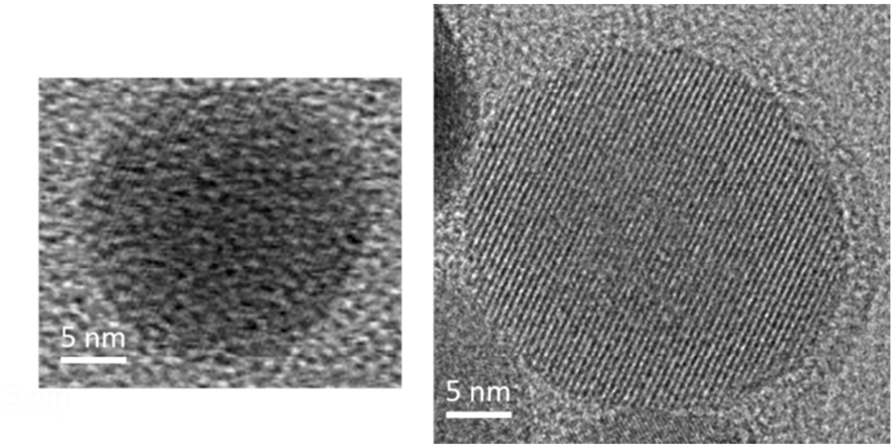

Figure S18. HR-TEMs of β-$NaYF_4$:20%Yb,2%Er (core, left) and β-$NaYF_4$:20%Yb,2%Er@ β-$NaYF_4$:10%Yb (core/Yb^{3+}-shell, right).

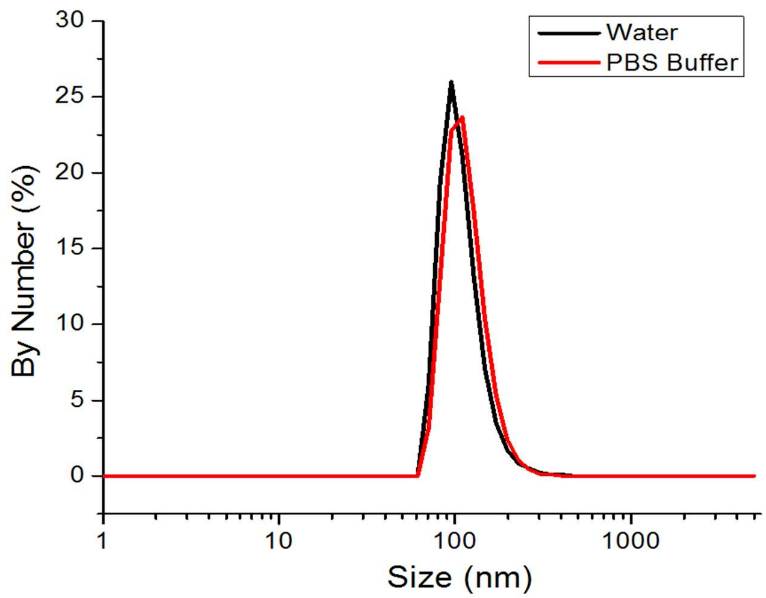

Figure S19. DLS data of micelle encapsulated dye-sensitized core/Yb^{3+}-shell UCNPs in water (black line) and PBS buffer (red line).

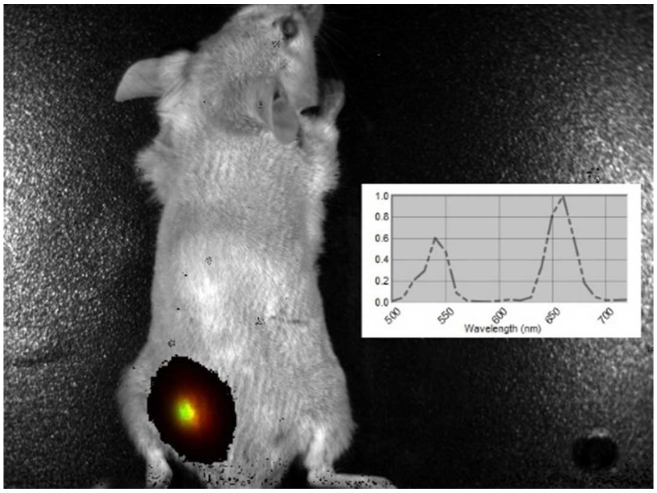

Figure S20. Overlaid image of a mouse with a subcutaneous injection of micelle encapsulated dye-sensitized core/Yb^{3+}-shell β-$NaYF_4$:20%Yb,2%Er@ β-$NaYF_4$:10%Yb UCNPs (50 μL, concentration 10 mg/mL), excitation wavelength 800 nm CW laser (1.0 W/cm^2) , and corresponding *in vivo* emission spectrum is in the inset.