Electronic Supplementary Material (ESI) for ChemComm.

Intense upconversion red emission from Gd-doped $NaErF_4$:Tm-based core/shell/shell nanocrystals under 980 and 800 nm near infrared light excitations

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Experimental Section

Materials. NaOH (99.99%), $ErCl_3 \cdot 6H_2O$ (99.9%), $TmCl_3 \cdot 6H_2O$ (99.99%), $GdCl_3 \cdot 6H_2O$ (99%), $Ca(CH_3COO)_2 \cdot xH_2O$ (≥99%), $YCl_3 \cdot 6H_2O$ (99.99%), $NdCl_3 \cdot 6H_2O$ (99.9%), $YbCl_3 \cdot 6H_2O$ (99.9%), NH_4F (≥99.99%), oleic acid (OA, technical grade 90%), and 1-octadecene (ODE, technical grade 90%) were purchased from Sigma-Aldrich.

Synthesis of core upconversion nanophosphors (UCNPs). The UCNPs were synthesized with slight modification of previously reported method.[S1,S2] One mmol of $RECl_3 \cdot 6H_2O$ [RE: rare earth and RE = Er (99.5% - x%), Tm (0.5%), and Gd (x% = 0, 10, and 30%)] was mixed with 6 mL of OA and 15 mL of ODE in a three-neck flask and the mixed solution was heated to 150 °C and retained for 40 min. After the solution was cooled to 60 °C, NaOH (2.5 mmol) and NH_4F (4 mmol) dissolved methanol (MeOH) solution (10 mL) was added to the reaction solution and stirred for 40 min. Then, MeOH was removed and the mixed solution was heated to 320 °C and kept for 1 h in Ar gas atmosphere. After

finishing the heat-treatment, the synthesized $NaErF_4$:Tm(0.5%),Gd(0, 10, and 30%) UCNPs were washed with ethanol (EtOH) several times and then dispersed in cyclohexane (10 mL).

Synthesis of core/shell (C/S) UCNPs. One mmol of $RECl_3 \cdot 6H_2O$ [RE = Y (100%) for $NaYF_4$ shell, Y (80%), Nd (20%) for $NaYF_4$:Nd shell, Y (80%), Ca (20%) for $NaYF_4$:Ca shell, and Y (70%), Ca (20%), Yb (10%) for $NaYF_4$:Ca,Yb shell] was mixed with 6 mL of OA and 15 mL of ODE in a three-neck flask and the mixed solution was heated to 150 °C and retained for 40 min. After the solution was cooled to 60 °C, 10 mL of core UCNP solution was added to the reaction flask followed by addition of NaOH (2.5 mmol) and NH_4F (4 mmol) dissolved MeOH solution (10 mL). The mixed solution was stirred for 40 min at 50 °C. Then, MeOH was removed and the mixed solution was heated to 320 °C and kept for 1 h in Ar gas atmosphere. After finishing the heat-treatment, the synthesized C/S UCNPs were washed with EtOH several times and then dispersed in cyclohexane (10 mL).

Synthesis of core/shell/shell (C/S/S) UCNPs. One mmol of $RECl_3 \cdot 6H_2O$ [RE = Y (50%), Nd (40%), and Yb (10%)] was mixed with 6 mL of OA and 15 mL of ODE in a three-neck flask and the mixed solution was heated to 150 °C and retained for 40 min. After the solution was cooled to 60 °C, 10 mL of $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%) C/S UCNP solution was added to the reaction flask followed by addition of NaOH (2.5 mmol) and NH_4F (4 mmol) dissolved MeOH solution (10 mL). The mixed solution was stirred for 40 min at 50 °C. Then, MeOH was removed and the mixed solution was heated to 320 °C and kept for 1 h in Ar gas atmosphere. After finishing the heat-treatment, the synthesized $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNPs were washed with EtOH several times and then dispersed in cyclohexane (10 mL).

Synthesis of ligand-free core/shell/shell (C/S/S) UCNPs. The ligand-free C/S/S UCNPs (LF-C/S/S UCNPs) were prepared by adopting the previously reported method with slight modification.[S1] Typically, the oleate-capped C/S/S UCNPs in cyclohexane were precipitated by adding EtOH and then the precipitated C/S/S UCNPs were redispersed in 0.5 mL of $CHCl_3$. The oleate-capped C/S/S UCNP $CHCl_3$ solution was mixed with 2 M HCl solution (0.25 mL) and the mixed solution was

ultrasonicated for 5 min. Then, the solution was centrifuged at 16,500 rpm for 20 min to collect the LF-C/S/S UCNPs. The LF-C/S/S UCNPs were dispersed in 1 mL of deionized (DI) water after washing with EtOH several times.

Characterization. Transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) images for the UCNP samples were obtained by using Tecnai G^2 F20 transmission electron microscope under operation at 200 kV. Absorption and photoluminescence (PL) spectra were obtained by using Perkin-Elmer lambda25 spectrometer and Hitachi F-7000 spectrophotometer, respectively. To acquire PL spectra, 980 and 800 nm continuous wave diode lasers were coupled with the Hitachi F-7000 spectrophotometer. Laser powers were set to be 2 W and the quartz cuvette (1 cm × 1 cm, Hellma QS cell) containing the UCNP solution was placed in the sample holder equipped in the F-7000 spectrophotometer. The concentrations of the UCNP solutions were adjusted in order that the absorbance values around 978 nm (for $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition in the Er^{3+}) or 654 nm (for $^4I_{15/2} \rightarrow {}^4F_{9/2}$ transition in the Er^{3+}) were identical. Scanning transmission electron microscopy (STEM) image and energy dispersive X-ray spectroscopy (EDS) spectra and maps were obtained by using Talos X-200F transmission electron microscope under operation at 200 kV. X-ray diffraction (XRD) patterns were acquired by using Bruker D8-Advance under operation at 45 kV and 40 mA. Photographs were obtained by using a Cannon 600D digital camera. The absolute UC quantum yields (QYs) were obtained by measuring UCNPs' emission spectra and unabsorbed laser emission spectra using an integrating sphere and PL/PLE-500 PL measurement system (PSITD-ETMAX co. ltd., Korea) equipped with a charge-coupled device (CCD) detector (Hamamatsu S10420, Back-thinned, 2D type).[S3] The absolute UC QYs were obtained by calculation as UC QY = (the number of emitted photons from the C/S/S UCNPs)/(the number of photons absorbed by the C/S/S UCNPs) = $(L_{sample})/(A_{ref} - A_{sample})$ where L_{sample} is the integrated UC PL intensity of the sample, A_{ref} and A_{sample} are the integrated intensities of the excitation NIR light which is not absorbed by the reference and sample, respectively.[S3]

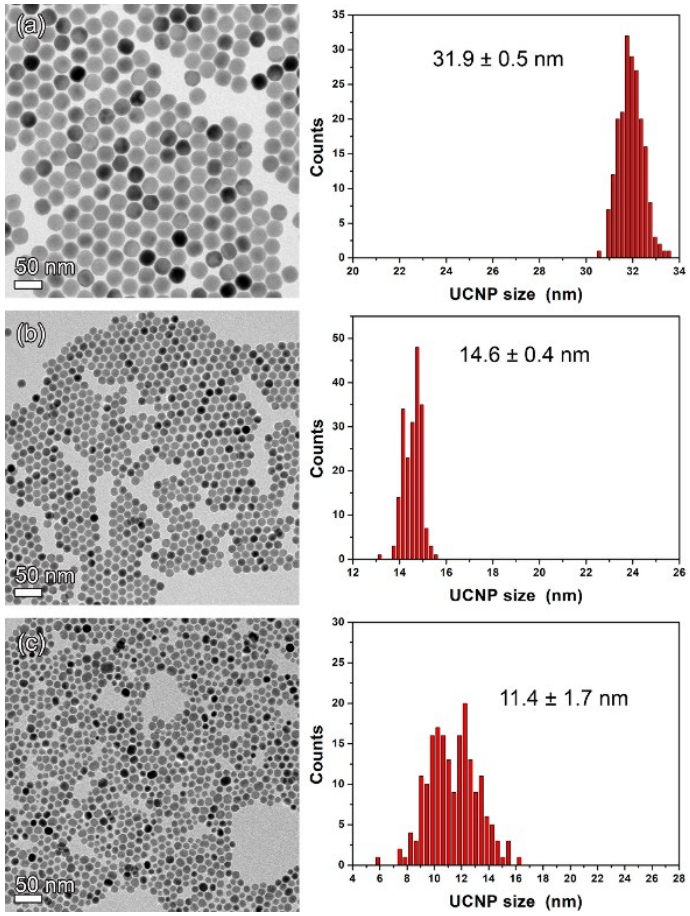

Figure S1. TEM images (left) and size distributions (right) of (a) $NaErF_4$:Tm(0.5%) UCNPs, (b) $NaErF_4$:Tm(0.5%),Gd(10%) UCNPs, and (c) $NaErF_4$:Tm(0.5%),Gd(30%) UCNPs.

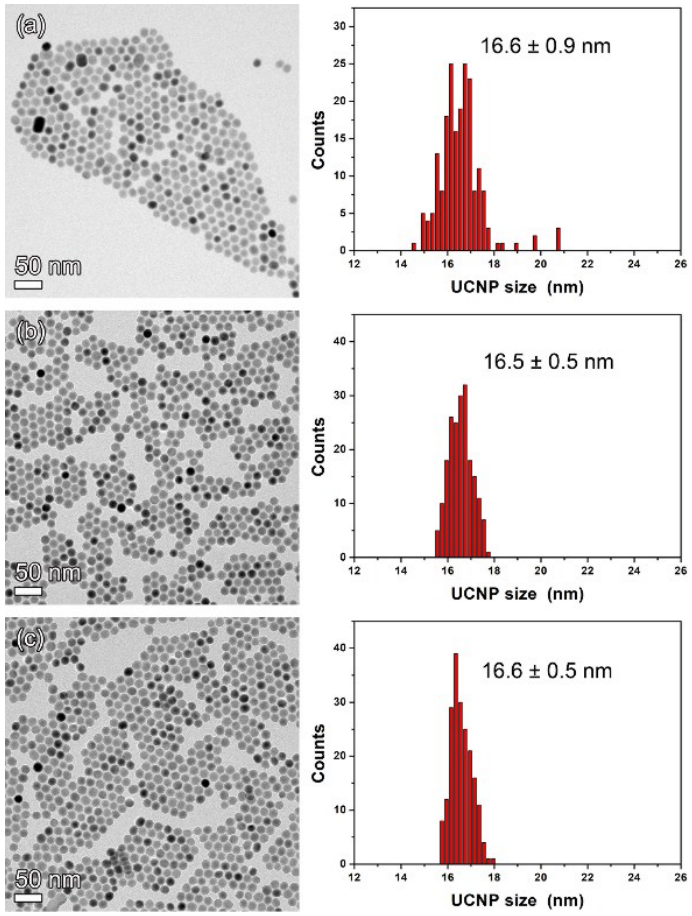

Figure S2. TEM images (left) and size distributions (right) of (a) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$ C/S UCNPs, (b) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%) C/S UCNPs, and (c) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Nd(20%) C/S UCNPs.

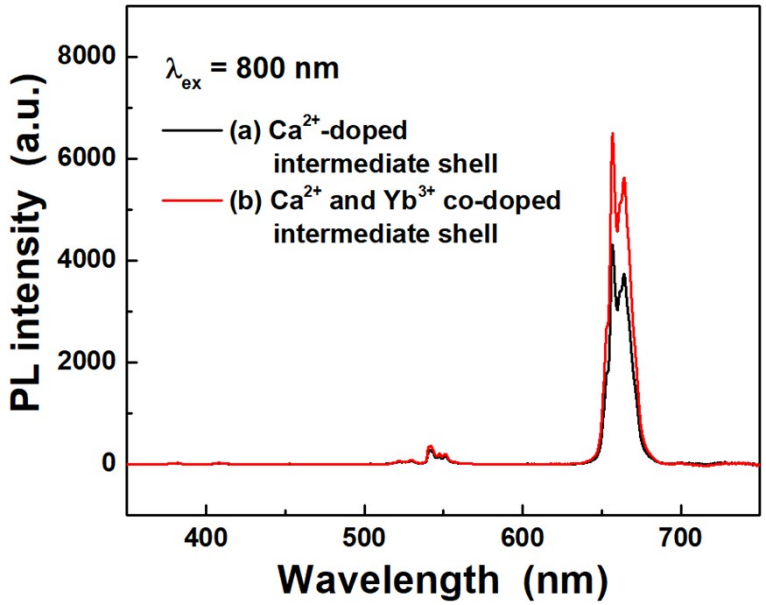

Figure S3. PL spectra of (a) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%)/$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNPs and (b) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%) /$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNPs under excitation with 800 nm NIR light.

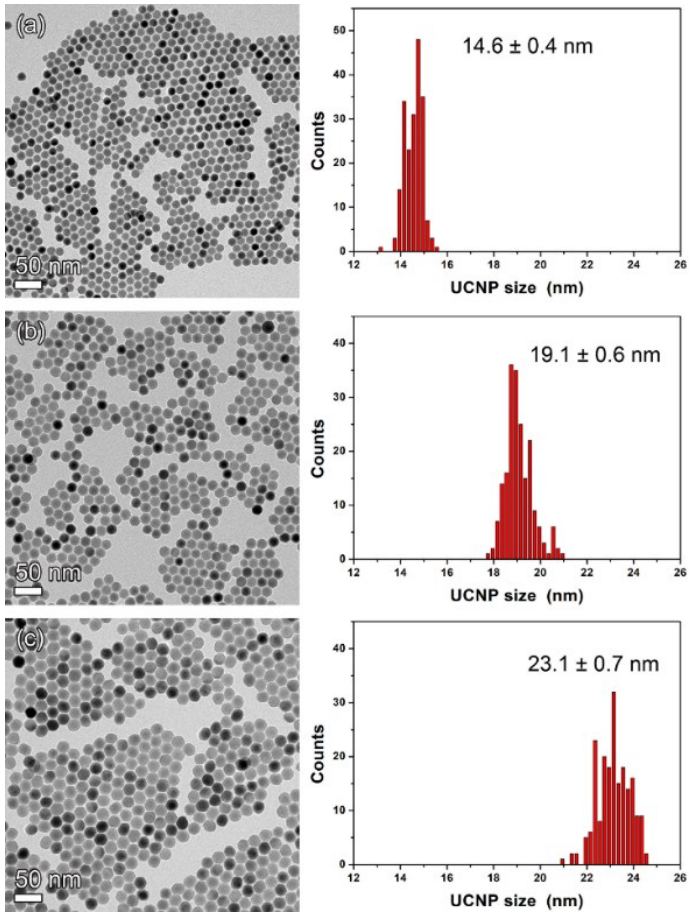

Figure S4. TEM images (left) and size distributions (right) of (a) $NaErF_4$:Tm(0.5%),Gd(10%) core UCNPs, (b) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%) C/S UCNPs, and (c) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNPs.

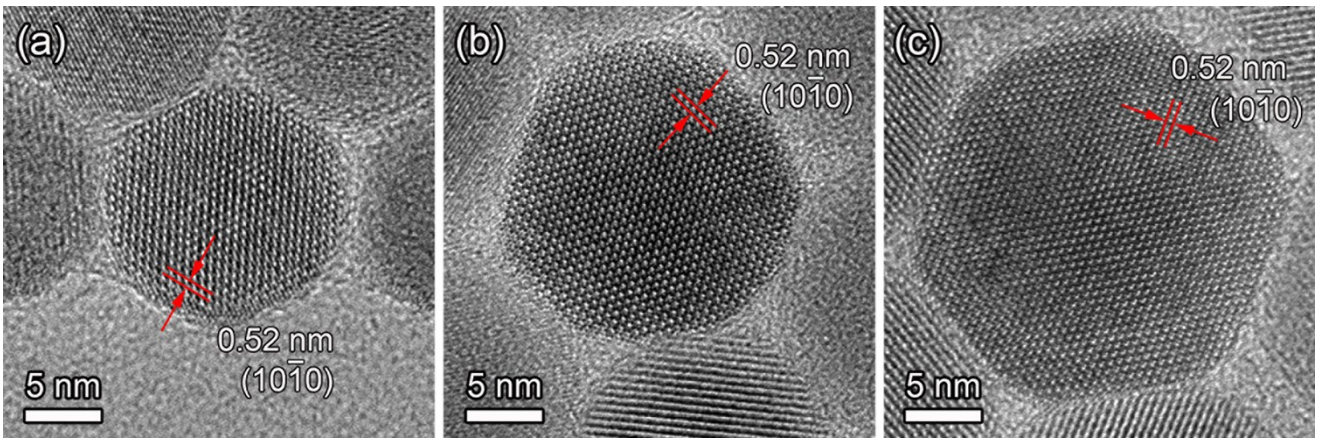

Figure S5. HR-TEM images of (a) $NaErF_4$:Tm(0.5%),Gd(10%) core UCNPs, (b) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%) C/S UCNPs, and (c) $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNPs.

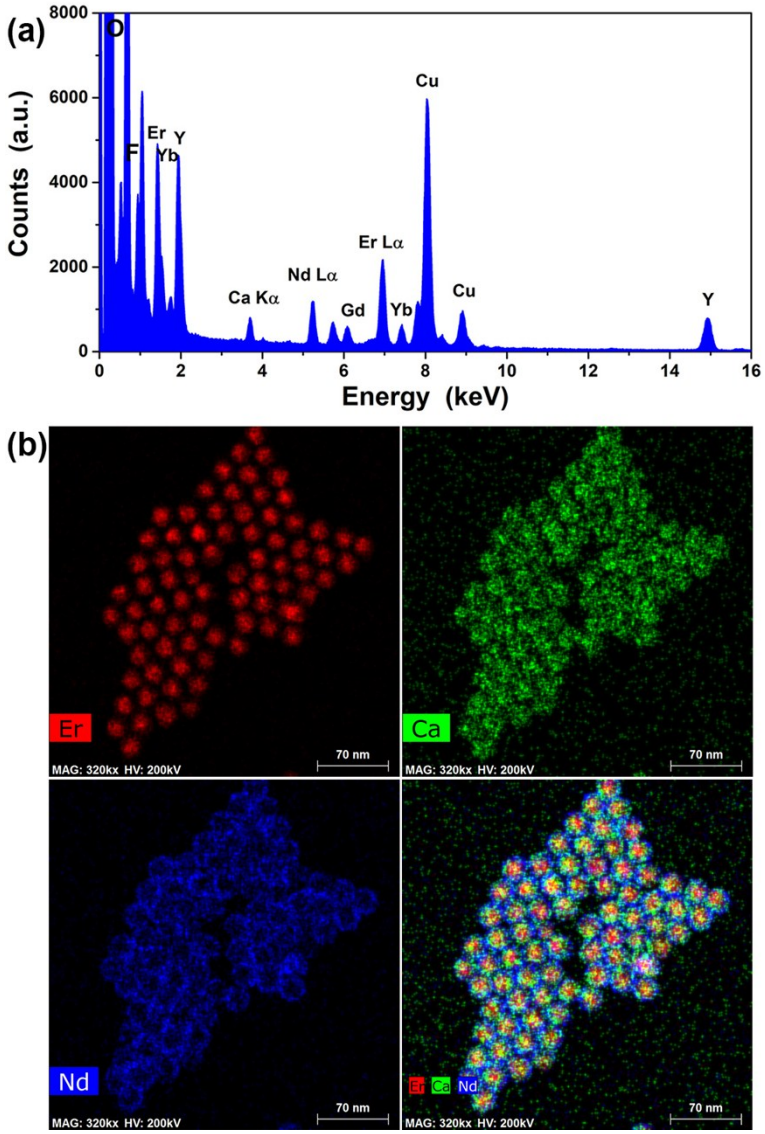

Figure S6. (a) EDS spectrum and (b) EDS maps for $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNPs. The composite EDS map was generated by superposing Er Lα map (red), Ca Kα map (green), and Nd Lα map (blue).

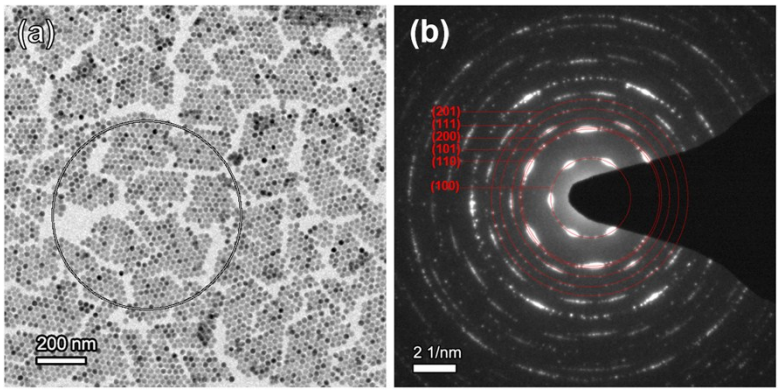

Figure S7. (a) TEM image and (b) selected area electron diffraction (SAED) pattern of the C/S/S UCNPs. The SAED pattern was obtained for the area indicated with a solid circle in the TEM image.

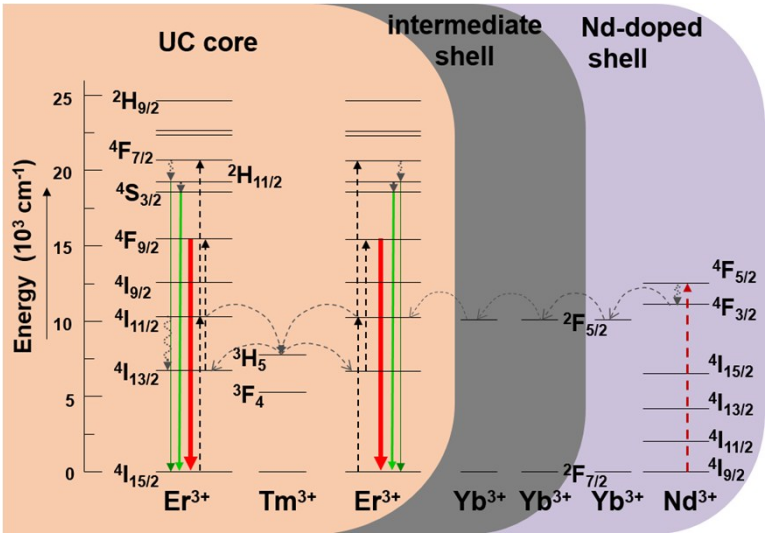

Figure S8. Schematic energy level diagram showing UC luminescence mechanism of the $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNPs.

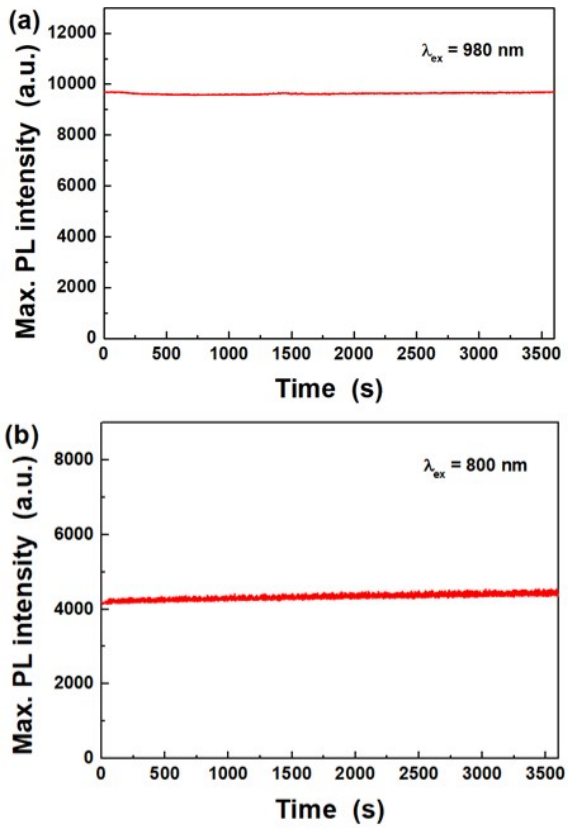

Figure S9. Maximum PL intensities of the $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNPs under continuous irradiations with (a) 980 nm and (b) 800 nm NIR lasers (laser power = 2 W).

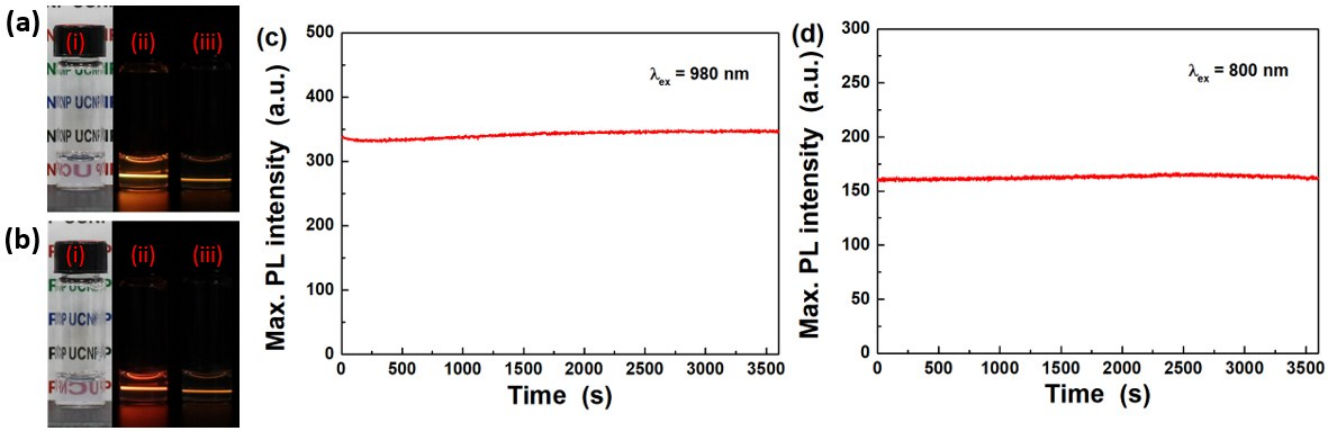

Figure S10. (a and b) Photographs of ligand-free $NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%) C/S/S UCNP DI water solution (pH 6.5) taken at (a) just after the synthesis and (b) 6 days later after the synthesis [(i) indoor light condition, (ii) 980 nm NIR light irradiation condition, and (iii) 800 nm NIR light irradiation condition]. (c and d) Maximum PL intensities of the ligand-free C/S/S UCNPs dispersed in DI water against continuous irradiations with (c) 980 nm and (d) 800 nm NIR lasers (laser power = 2 W). Although the ligand-free C/S/S UCNPs were stable in DI water, when the ligand-free C/S/S UCNPs were dispersed in phosphate buffered saline (PBS) solution (pH 7.4) instead of DI water, the solution was not clear. Thus, further surface functionalization is necessary for bio-related applications.

Table S1. Absolute UC QYs of red-emitting $NaErF_4$-based UCNPs under excitation with 980 nm NIR light.

Composition	Average Particle Size	Laser Power	QY (%)	Remark
$NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%), Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%)	23.1 nm	16 W cm^{-2}	1.9	This work
$NaErF_4$:Tm(0.5%)/$NaYF_4$	28.6 nm	2 W	0.78	Ref. S2
$NaErF_4$/$NaLuF_4$	33.8 nm	10 W cm^{-2}	5.2	Ref. S4

Table S2. Absolute UC QYs of red-emitting $NaErF_4$-based UCNPs under excitation with 800 nm NIR light.

Composition	Average Particle Size	Laser Power	QY (%)	Remark
$NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%), Yb(10%)/$NaYF_4$:Nd(40%),Yb(10%)	23.1 nm	17 W cm^{-2}	0.06[a]	This work

[a]The measured UC QY is comparable to the previously reported value for the $NaYF_4$:Nd,Yb/$NaYF_4$:Yb,Tm/$NaYF_4$/$NaYF_4$:Yb,Ho,Ce/$NaYF_4$ core/multi-shell UCNPs (0.09%) under 808 nm NIR light excitation.[S5]

References

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