Electronic Supplementary Material (ESI) for Nanoscale Advances.

Electronic Supplementary Material

Single-Particle Förster Resonance Energy Transfer from Upconversion Nanoparticles to Organic Dyes

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Results and Discussion

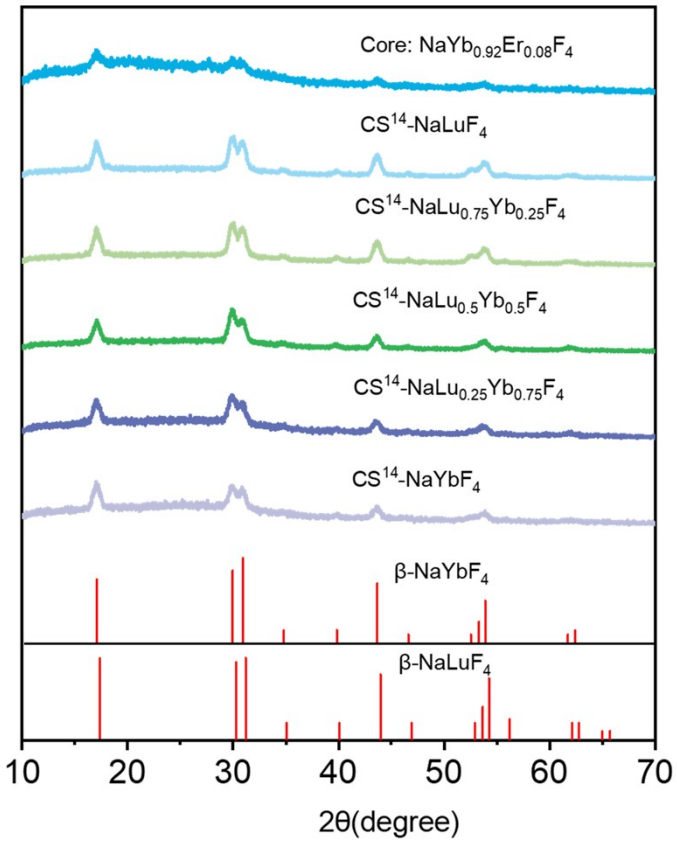

Figure S1. X-Ray Powder Diffraction (XRD) data of the core $NaYb_{0.92}Er_{0.08}F_4$, core-shell $NaYb_{0.92}Er_{0.08}F_4$@$NaLu_{1-x}Yb_xF_4$ (x=0, 0.25, 0.5, 0.75 and 1) UCNPs. The XRD pattern is consistent with the hexagonal (β-) $NaREF_4$ crystal pattern.

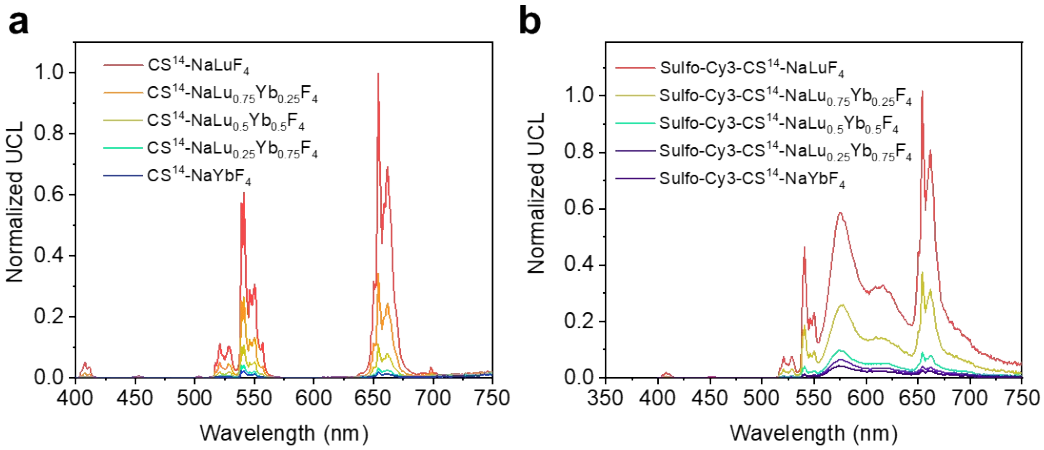

Figure S2. The normalized upconversion emission spectra of $NaYb_{0.92}Er_{0.08}F_4$@$NaLu_{1-x}Yb_xF_4$ (x=0, 0.25, 0.5, 0.75 and 1) UCNPs (a) without and (b) with sulfo-Cy3 (4.00 μM) under 980 nm laser irradiation at 63 W/cm^2, the emission intensity at 654 nm of CS^{14}-$NaLuF_4$ and sulfo-Cy3-CS^{14}-$NaLuF_4$ (the red emission peak of Er^{3+}) in (a) and (b) was normalized to unity, respectively.

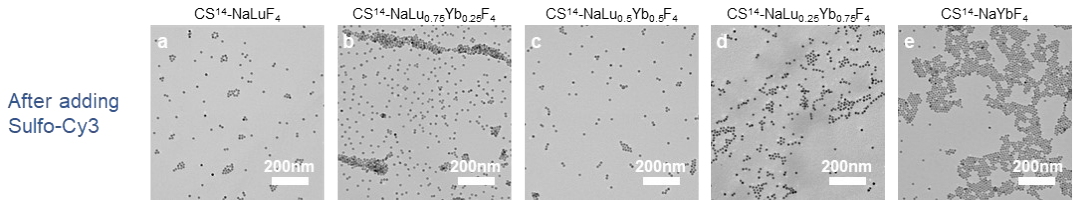

Figure S3. TEM images of sulfo-Cy3 modified CS UCNPs $NaYb_{0.92}Er_{0.08}F_4@NaLu_{1-x}Yb_xF_4$ (x=0, 0.25, 0.5, 0.75 and 1).

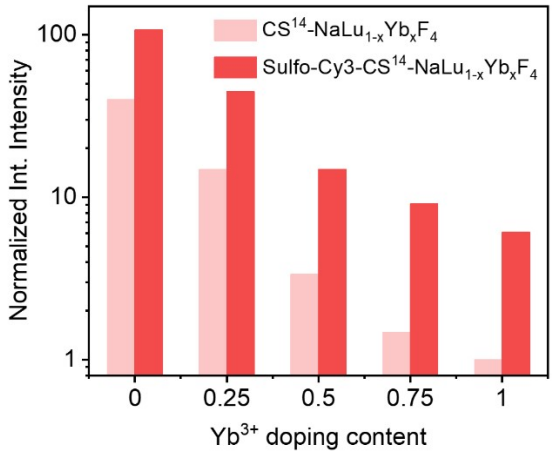

Figure S4. The integrated intensity of $NaYb_{0.92}Er_{0.08}F_4@NaLu_{1-x}Yb_xF_4$ (x=0, 0.25, 0.5, 0.75 and 1) UCNPs with and without sulfo-Cy3 at dye concentration of 4.00 μM (λ_{ex} = 980 nm, 63W/cm^2), the intensity of $NaYb_{0.92}Er_{0.08}F_4@NaLu_{1-x}Yb_xF_4$ without sulfo-Cy3 was normalized to unity.

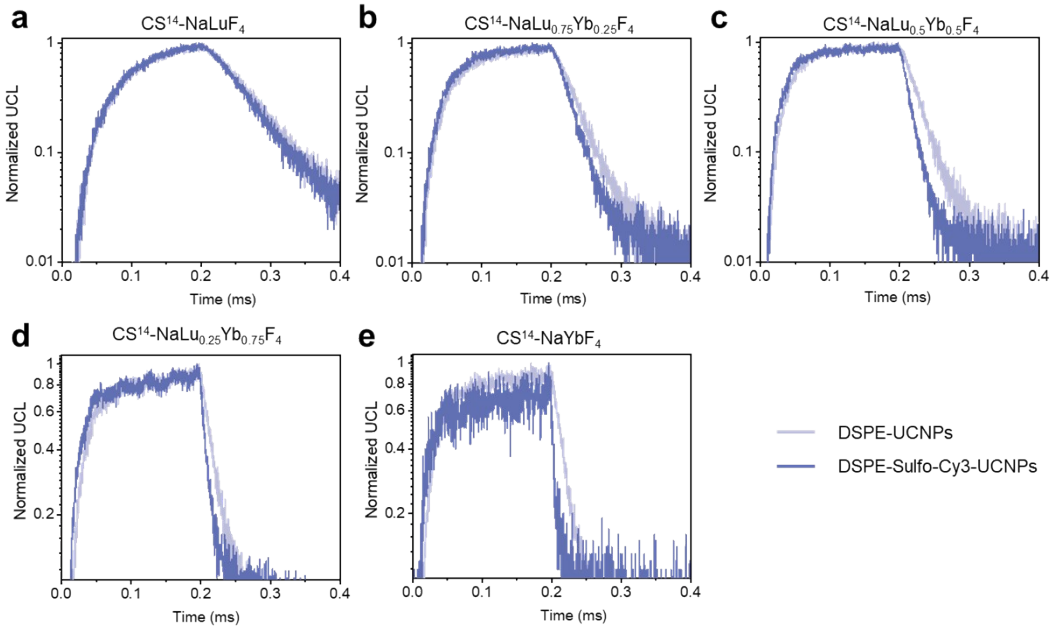

Figure S5. Normalized luminescence kinetic response data of UCNPs before and after the addition of dye sulfo-Cy3. The composition of UCNPs were (a) CS^{14}-$NaLuF_4$, (b) CS^{14}-$NaLu_{0.75}Yb_{0.25}F_4$, (c) CS^{14}-$NaLu_{0.5}Yb_{0.5}F_4$, (d) CS^{14}-$NaLu_{0.25}Yb_{0.75}F_4$, (e) CS^{14}-

$NaYbF_4$, respectively. Particles dispersed in chloroform were excited at 980 nm and the luminescence kinetics of the green upconversion emission around 541 nm were recorded. The fitted decay lifetimes are presented in the **Table S1**.

Table S1. The resulting decay lifetimes of green ($^2H_{11/2} \rightarrow {}^4I_{15/2}$, 541 nm) emission of Er^{3+}, obtained from exponential fitting of decay curves in **Figure S5**.

	CS^{14}-$NaLuF_4$	CS^{14}-$NaLu_{0.75}Yb_{0.25}F_4$	CS^{14}-$NaLu_{0.5}Yb_{0.5}F_4$	CS^{14}-$NaLu_{0.25}Yb_{0.75}F_4$	CS^{14}-$NaYbF_4$
τ_{UCNPs} (μs)	55.05	27.00	22.84	18.41	19.01
$\tau_{Sulfo\text{-}Cy3\text{-}UCNPs}$ (μs)	51.26	19.81	12.59	9.20	4.95

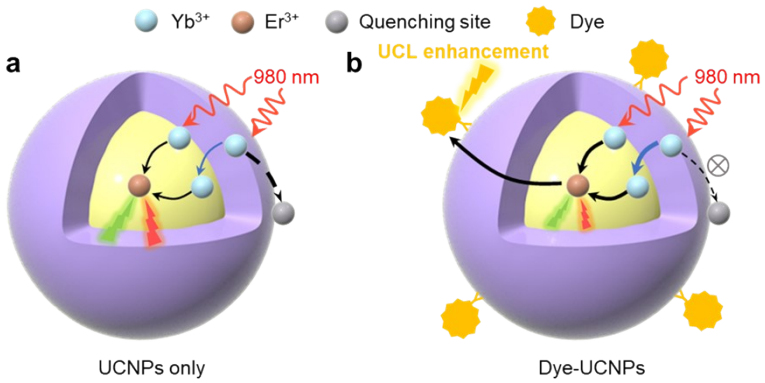

Figure S6. Schematic energy transfer of active-shelled CS UCNPs (a) without and (b) with dye, right: active-shelled UCNPs irradiated under 980 nm. For the UCNPs only, the excited state Yb^{3+} was severely quenched through the fast nonradiative transition to the surface quencher. After the dye coordination, dye added a new energy dissipation pathway to the energy donor Er^{3+}, thus, more excited Yb^{3+} tend to transfer energy to Er^{3+} and subsequently enrich the dye molecules on the surface by FRET energy transfer process, decreasing the ratio of nonradiative transition in the active-shelled UCNPs.

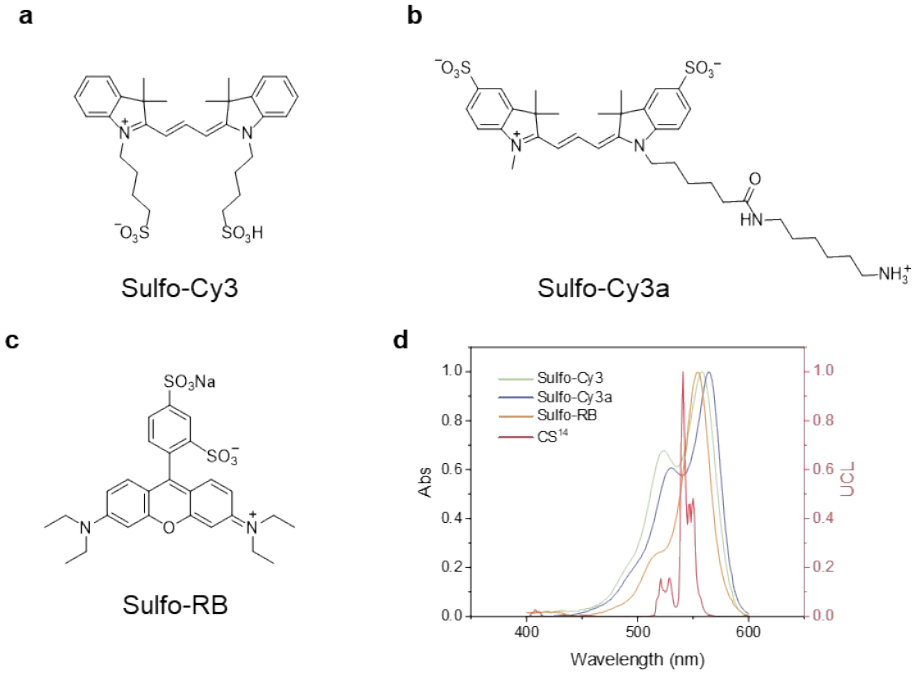

Figure S7. Molecular structure of (a) sulfo-Cy3, (b) sulfo-Cy3-amine (abbreviated to sulfo-Cy3a) and (c) sulfo-rhodamine B (abbreviated to sulfo-RB). (d) Normalized absorption sulfo-Cy3 (green), sulfo-Cy3-amine (blue) and sulfo-rhodamine B (yellow), normalized emission spectra of $NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ UCNPs (red) from 400-600 nm, the maximum UCL intensities of $NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ UCNPs and the maximum absorbance of dyes were normalized to unity, respectively.

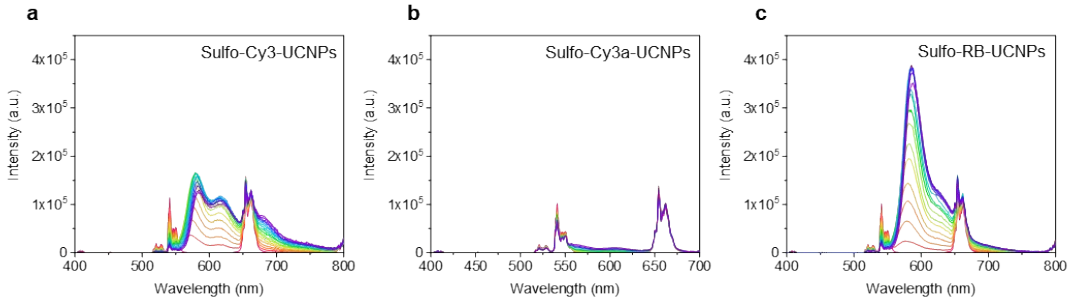

Figure S8. Upconversion emission spectra of CS $NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ UCNPs emission enhanced by the dye titration of (e) sulfo-Cy3 (0-10.7 μM), (f) sulfo-Cy3-amine (0-6.67 μM) and (g) sulfo-rhodamine B (0-10.7 μM) under 980 nm laser irradiation at 63 W/cm^2

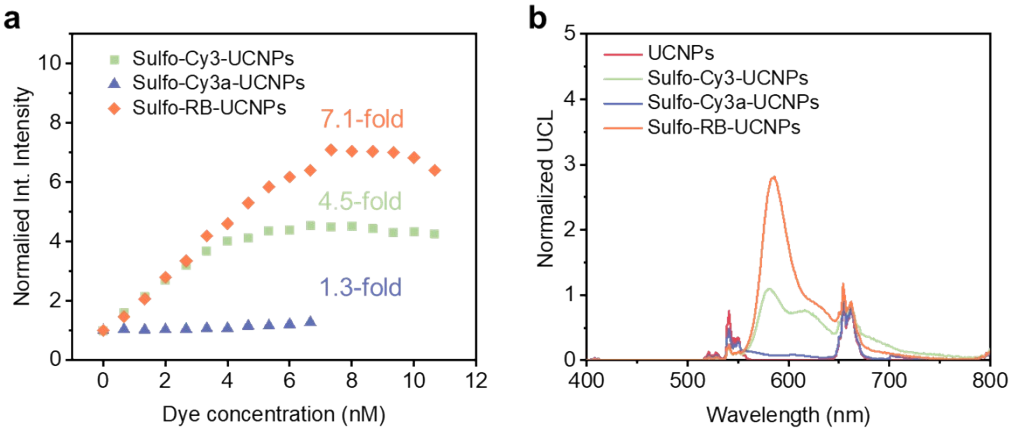

Figure S9. (a) Integrated UCL intensity of FRET-enhanced upconversion in UCNPs as a function of dye concentration. The integrated emission of UCNPs without dye were normalized to unity. (b) Normalized upconversion emission spectra of $NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ UCNPs emission enhanced by sulfo-Cy3, sulfo-Cy3-amine and sulfo-rhodamine B at optimal dye concentration (λ_{ex} = 980 nm, 63 W/cm^2). The emission intensity at 654 nm of UCNPs (the red emission peak of Er^{3+}) was normalized to unity. The optimal dye concentrations used were those with the maximum emission in the dye titration curves of (a).

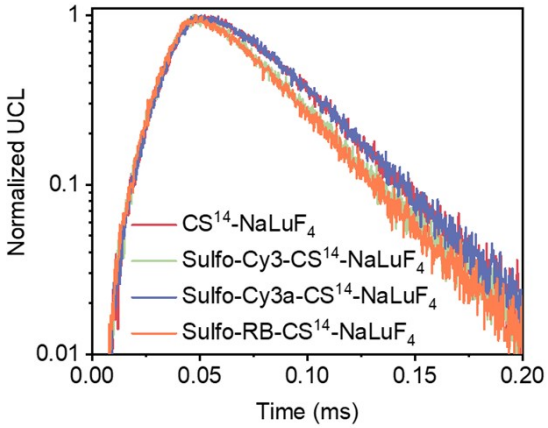

Figure S10. Normalized luminescence kinetic response data of CS^{14}-$NaLuF_4$ UCNPs before and after the addition of three different dyes. Particles dispersed in chloroform were excited at 980 nm and the luminescence kinetics of the green upconversion emission around 541 nm were recorded. The fitted decay lifetimes are presented in the **Table S2**. Note: the pulse width using in this test was shorter than that for **Figure S5**, resulting in the shorter lifetime and less significant kinetic response.

Table S2. The resulting decay lifetimes of green ($^2H_{11/2}\rightarrow {}^4I_{15/2}$, 541 nm) emission of Er^{3+}, obtained from exponential fitting of decay curves in **Figure S10**.

	CS^{14}-$NaLuF_4$	Sulfo-Cy3-CS^{14}-$NaLuF_4$	Sulfo-Cy3a-CS^{14}-$NaLuF_4$	Sulfo-RB-CS^{14}-$NaLuF_4$
τ (μs)	35.02	34.36	35.45	34.06

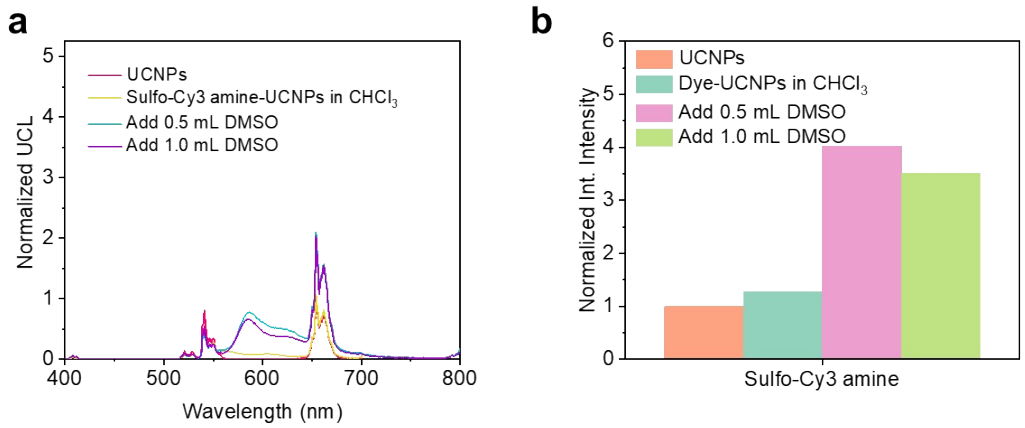

Figure S11. (a) Upconversion emission spectra of bare CS UCNPs, sulfo-Cy3-amine-UCNPs without and with the addition of 0.5 mL or 1.5 mL DMSO under 980 nm laser irradiation at 63 W/cm^2, the emission intensity at 541 nm of bare UCNPs was normalized to unity. (b) The corresponding integrated intensity histogram.

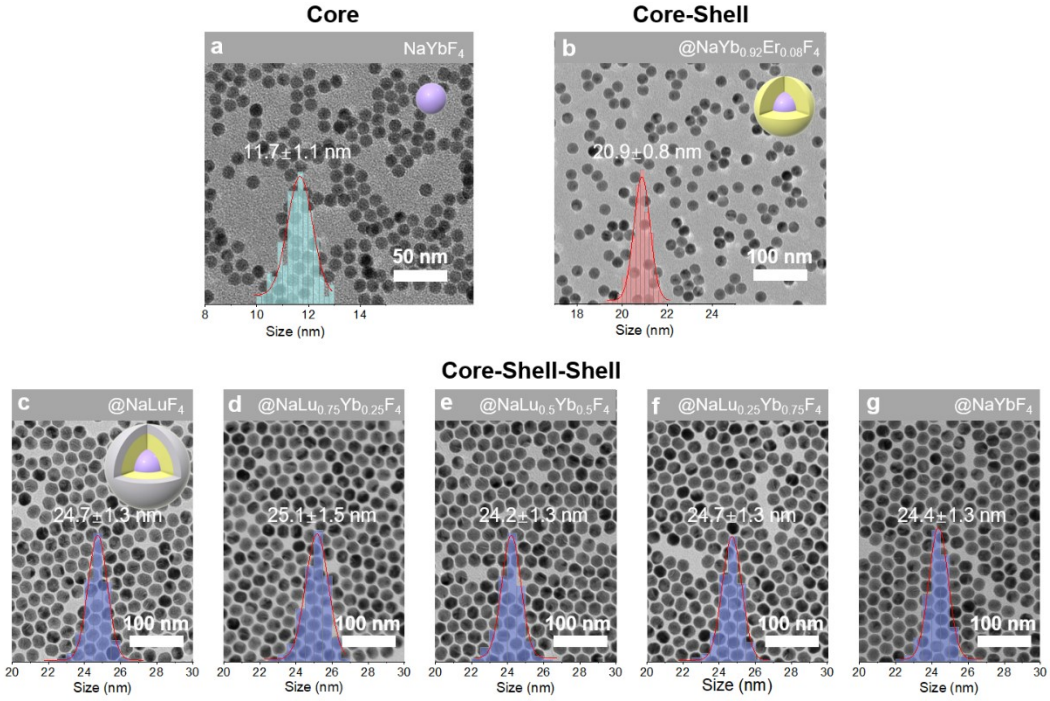

Figure S12. TEM images and size distributions of the as-prepared (a) core $NaYbF_4$ (~11 nm), (b) core-shell $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$ (~21 nm), (c-d) core-shell-shell $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaLu_{1-x}Yb_xF_4$ (x=0, 0.25, 0.5, 0.75 and 1) (~25 nm) UCNPs with various Yb^{3+} doping contents in the outermost shell.

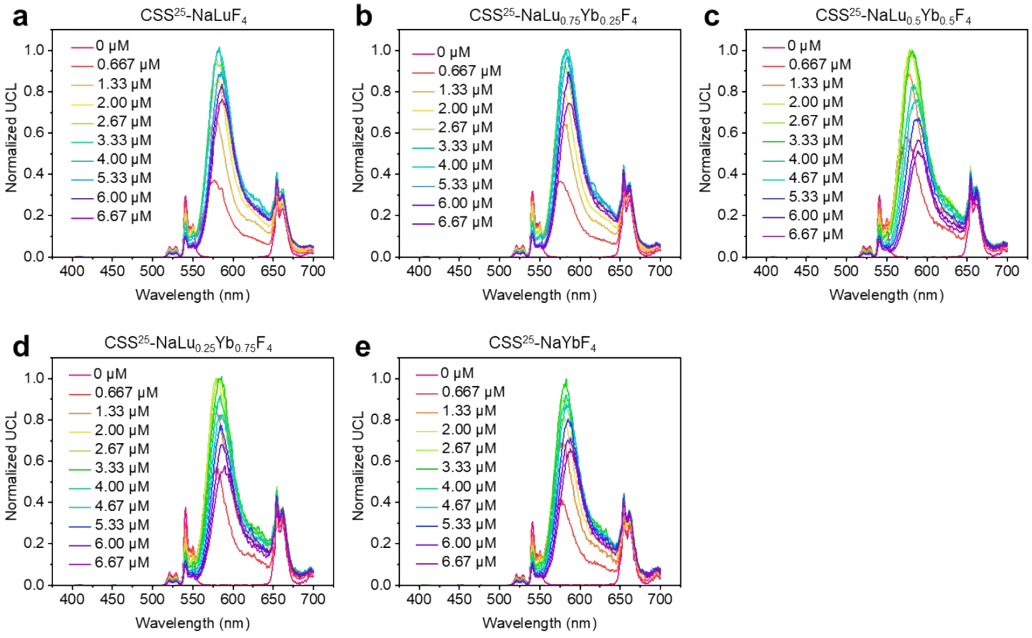

Figure S13. Upconversion emission spectra of $NaYbF_4@NaYb_{0.92}Er_{0.08}F_4@NaLu_{1-x}Yb_xF_4$ (x=0, 0.25, 0.5, 0.75 and 1) CSS UCNPs emission enhanced by the dye titration of sulfo-rhodamine B under 980 nm laser irradiation at 63 W/cm^2, the maximum emission intensities at 587 nm of sulfo-RB-UCNPs (at the optimal concentration of sulfo-RB) in each panel were normalized to unity, respectively.

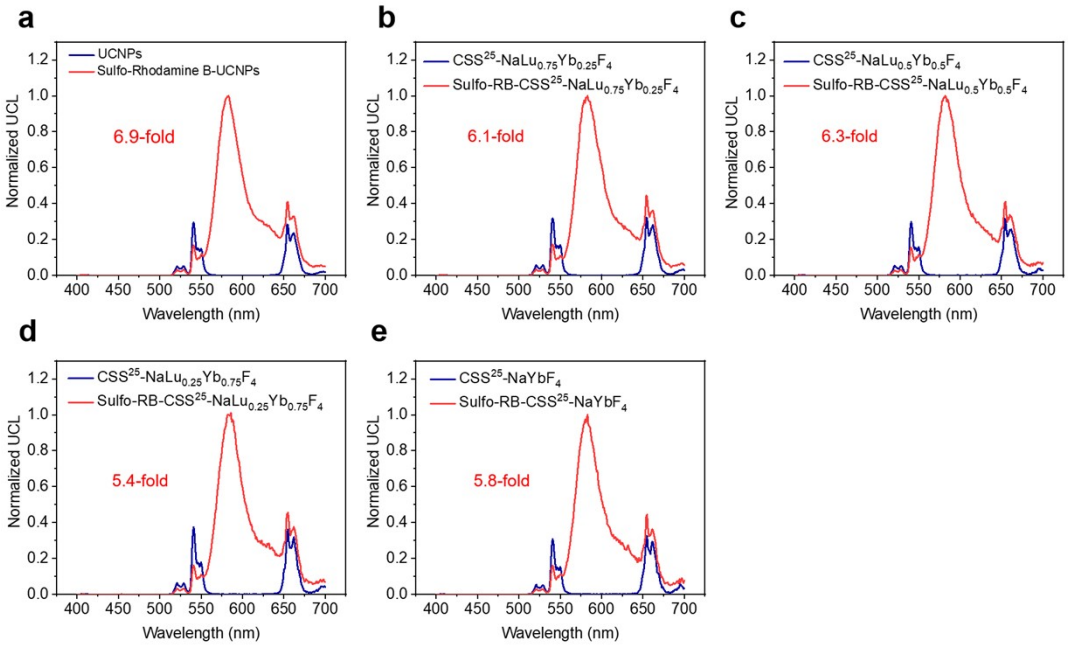

Figure S14. Normalized upconversion emission spectra of $NaYbF_4@NaYb_{0.92}Er_{0.08}F_4@NaLu_{1-x}Yb_xF_4$ (x=0, 0.25, 0.5, 0.75 and 1) CSS UCNPs with and without sulfo-RB at dye concentration of 3.33 μM (λ_{ex} = 980 nm, 63 W/cm^2) in $CHCl_3$, the emission intensities at 587 nm of sulfo-UCNPs (the emission peak of sulfo-RB) were normalized to unity, respectively.

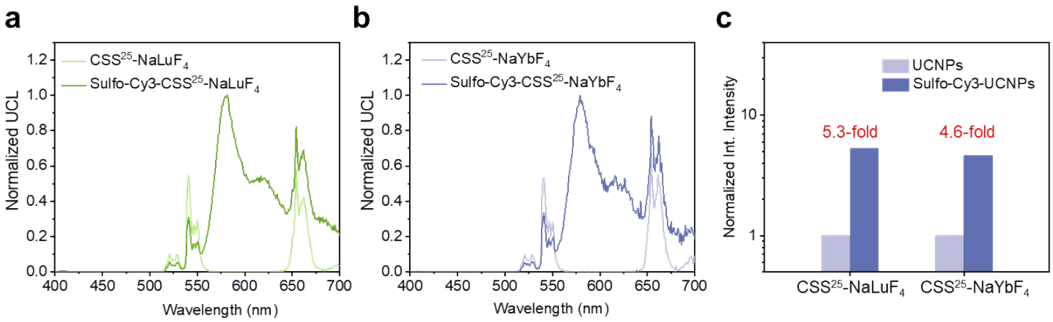

Figure S15. The upconversion of larger UCNPs enhanced by sulfo-Cy3. (a) Normalized upconversion emission spectra of $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ CSS UCNPs with and without sulfo-Cy3 at dye concentration of 3.33 μM (λ_{ex} = 980 nm, 63 W/cm^2) in $CHCl_3$. (b) Normalized upconversion emission spectra of $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaYbF_4$ CSS UCNPs with and without sulfo-Cy3 at dye concentration of 3.33 μM (λ_{ex} = 980 nm, 63 W/cm^2) in $CHCl_3$, the emission intensity at 576 nm of sulfo-Cy3-UCNPs (the emission peak of sulfo-Cy3) in (a) and (b) was normalized to unity, respectively. (c) The integrated intensity of $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ and $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaYbF_4$ UCNPs with and without sulfo-Cy3 at dye concentration of 3.33 μM (λ_{ex} = 980 nm, 63W/cm^2), their corresponding intensities without sulfo-Cy3 were normalized to unity, respectively.

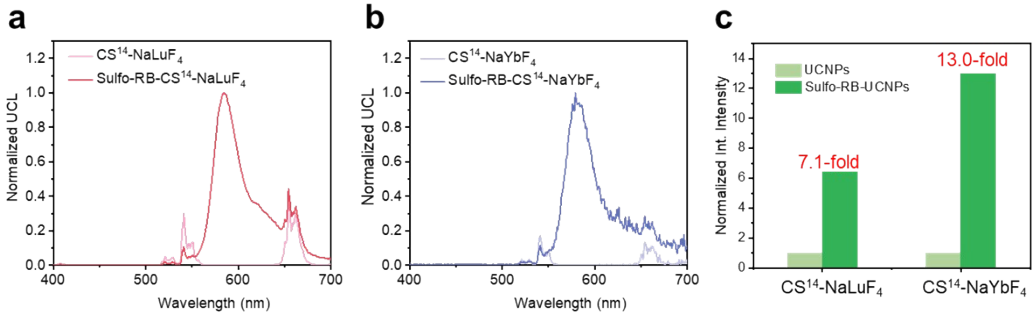

Figure S16. The upconversion of smaller UCNPs enhanced by sulfo-rhodamine B. (a) Normalized upconversion emission spectra of $NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ CSS UCNPs with and without sulfo-rhodamine B at dye concentration of 5.33 μM (λ_{ex} = 980 nm, 63 W/cm^2) in $CHCl_3$. (b) Normalized upconversion emission spectra of $NaYb_{0.92}Er_{0.08}F_4$@$NaYbF_4$ CSS UCNPs with and without sulfo-rhodamine B at dye concentration of 3.33 μM (λ_{ex} = 980 nm, 63 W/cm^2) in $CHCl_3$, the emission intensity at 587 nm of sulfo-RB-UCNPs (the emission peak of sulfo-RB) in (a) and (b) was normalized to unity, respectively. (c) The integrated intensity of $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ and $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaYbF_4$ UCNPs with and without sulfo-RB at optimal dye concentration (λ_{ex} = 980 nm, 63W/cm^2), their corresponding intensities without sulfo-RB were normalized to unity, respectively.

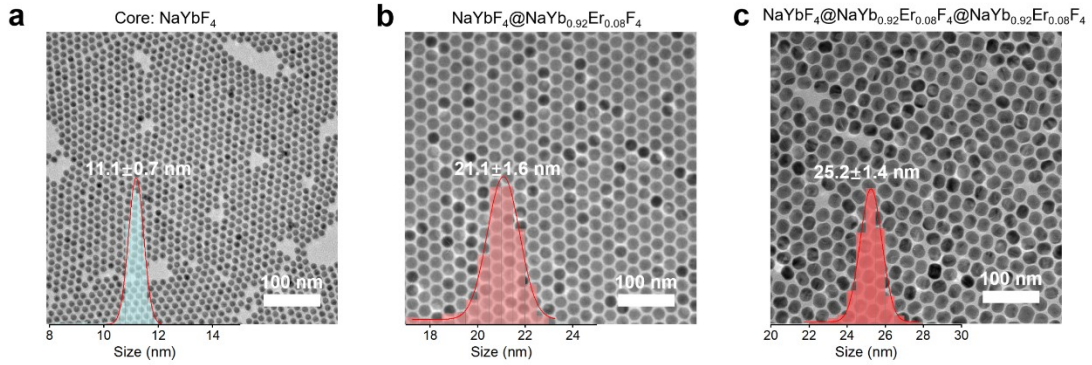

Figure S17. TEM images and size distributions of the as-prepared (a) core $NaYbF_4$ (~11 nm), (b) core-shell $NaYbF_4@NaYb_{0.92}Er_{0.08}F_4$ (~21 nm), (c) core-shell-shell $NaYbF_4@NaYb_{0.92}Er_{0.08}F_4@NaYb_{0.92}Er_{0.08}F_4$ (~25 nm) UCNPs (CSS^{25}-$NaYb_{0.92}Er_{0.08}F_4$).

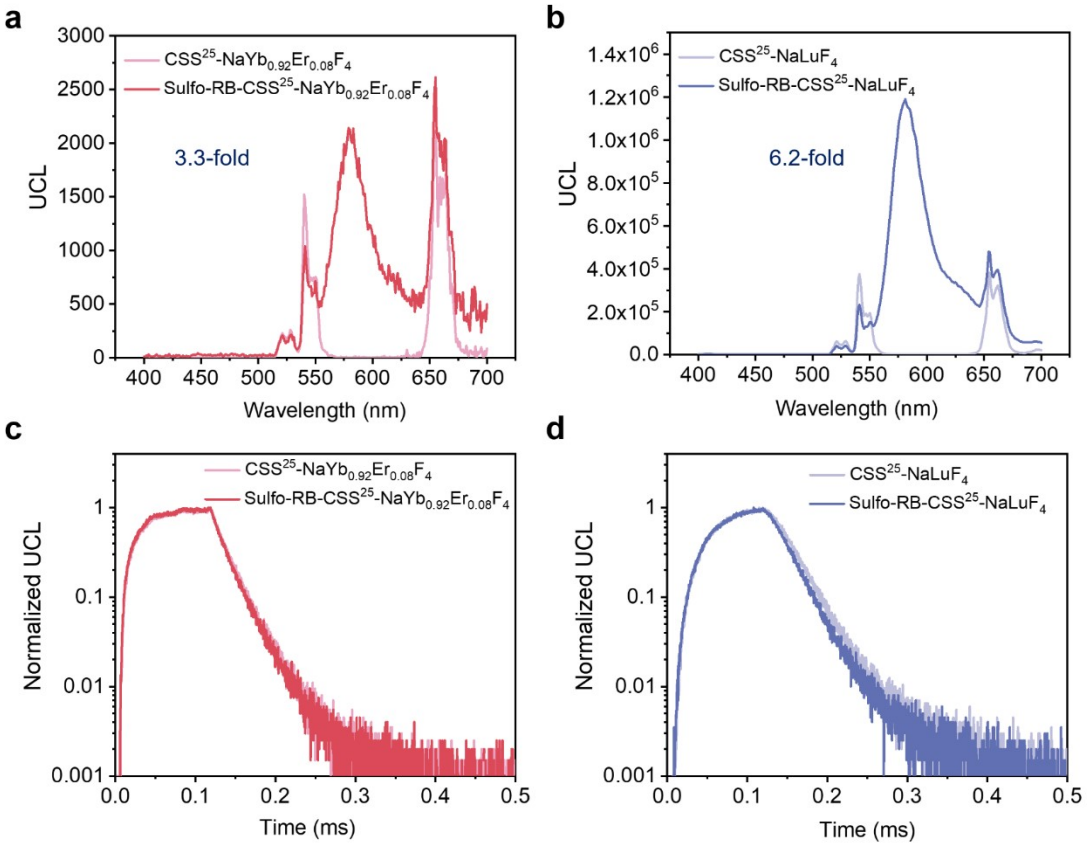

Figure S18. The FRET-enhanced upconversion of CSS^{25}-$NaYb_{0.92}Er_{0.08}F_4$ and CSS^{25}-$NaLuF_4$ UCNPs. Upconversion emission spectra of (a) CSS^{25}-$NaYb_{0.92}Er_{0.08}F_4$ and (b) CSS^{25}-$NaLuF_4$ UCNPs with and without sulfo-rhodamine B at dye concentration of 3.33 μM (λ_{ex}=980 nm, 150 W/cm^2). Normalized luminescence kinetic response data of (c) CSS^{25}-$NaYb_{0.92}Er_{0.08}F_4$ and (d) CSS^{25}-$NaLuF_4$ UCNPs with and without sulfo-rhodamine B at dye concentration of 3.33 μM. Particles dispersed in chloroform were excited at 980 nm and the luminescence kinetics of the green upconversion emission around 541 nm were recorded. The fitted decay lifetimes are presented in the **Table S3**.

Table S3. The resulting decay lifetimes of green ($^2H_{11/2} \rightarrow {}^4I_{15/2}$, 541 nm) emission of Er^{3+}, obtained from exponential fitting of decay curves in **Figure S18**.

	CSS^{25}-$NaYb_{0.92}Er_{0.08}F_4$	CSS^{25}-$NaLuF_4$
τ_{UCNPs} (μs)	20.39	28.56
$\tau_{Sulfo\text{-}RB\text{-}UCNPs}$ (μs)	18.95	26.17

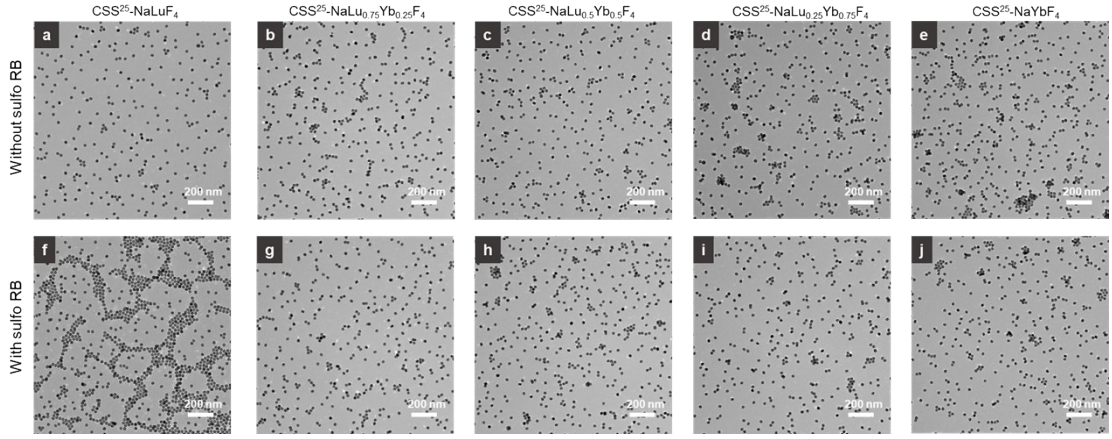

Figure S19. TEM images of (a-e) DSPE-UCNPs and (f-j) DSPE-Sulfo-RB-UCNPs of CSS $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaLu_{1-x}Yb_xF_4$ (x= 0, 0.25, 0.5, 0.75 and 1).

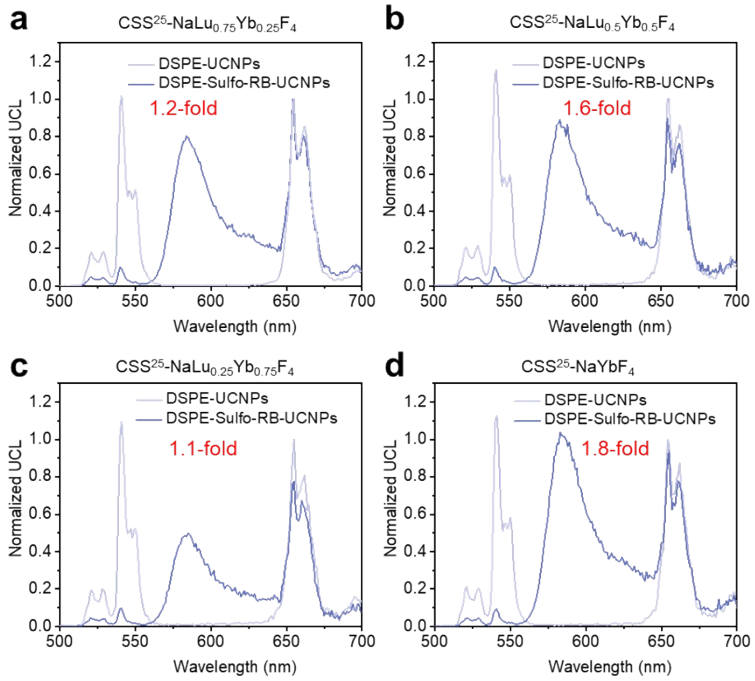

Figure S20. Normalized upconversion spectra of DSPE-UCNPs $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaLu_{1-x}Yb_xF_4$ (x=0.25, 0.5, 0.75 and 1) in ethanol and DSPE-Sulfo-RB-UCNPs with 18.00 μM sulfo-RB, the emission intensities at 654 nm of DSPE-UCNPs (the red emission peak of Er^{3+}) were normalized to unity, respectively.

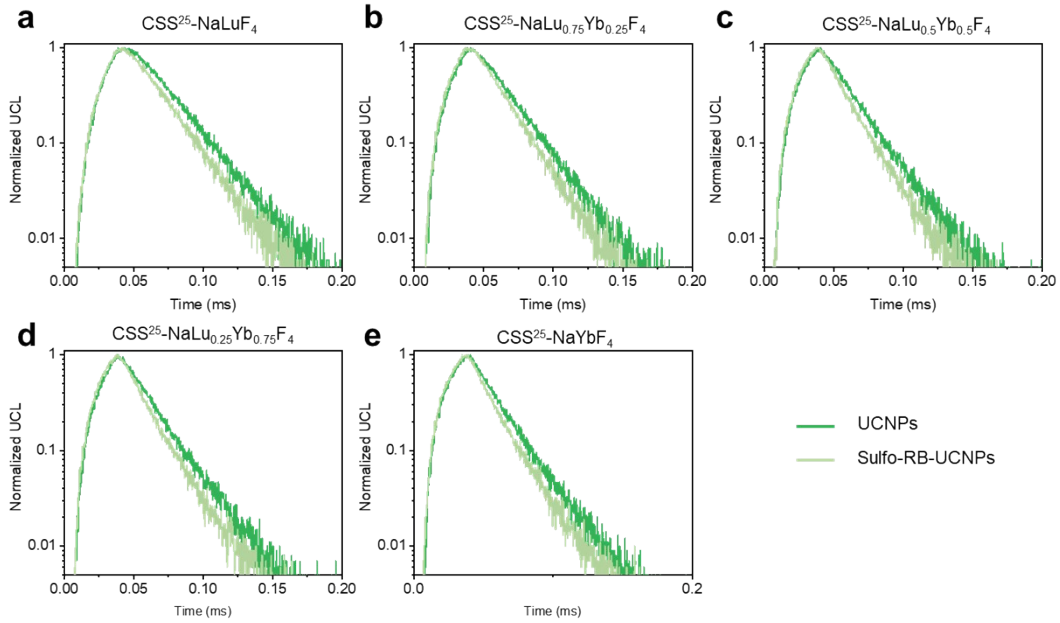

Figure S21. Normalized luminescence kinetic response data of UCNPs the before and after addition of dyes sulfo-rhodamine B. The composition of UCNPs were (a) CSS^{25}-$NaLuF_4$, (b) CSS^{25}-$NaLu_{0.75}Yb_{0.25}F_4$, (c) CSS^{25}-$NaLu_{0.5}Yb_{0.5}F_4$, (d) CSS^{25}-$NaLu_{0.25}Yb_{0.75}F_4$, (e) CSS^{25}-$NaYbF_4$. Particles dispersed in chloroform were excited at 980 nm and the luminescence kinetics of the green upconversion emission around 541 nm were recorded. The fitted decay lifetimes are presented in the **Table S4**. Note: the pulse width using in this test was shorter than that for **Figure S18**, resulting in the shorter lifetime.

Table S4. The resulting decay lifetimes of green ($^2H_{11/2}\rightarrow {}^4I_{15/2}$, 541 nm) emission of Er^{3+}, obtained from exponential fitting of decay curves in **Figure S21**.

	CSS^{25}-$NaLuF_4$	CSS^{25}-$NaLu_{0.75}Yb_{0.25}F_4$	CSS^{25}-$NaLu_{0.5}Yb_{0.5}F_4$	CSS^{25}-$NaLu_{0.25}Yb_{0.75}F_4$	CSS^{25}-$NaYbF_4$
τ_{UCNPs} (μs)	24.61	21.61	20.49	20.41	20.07
$\tau_{Sulfo\text{-}RB\text{-}UCNPs}$ (μs)	21.24	18.67	17.51	17.30	17.40

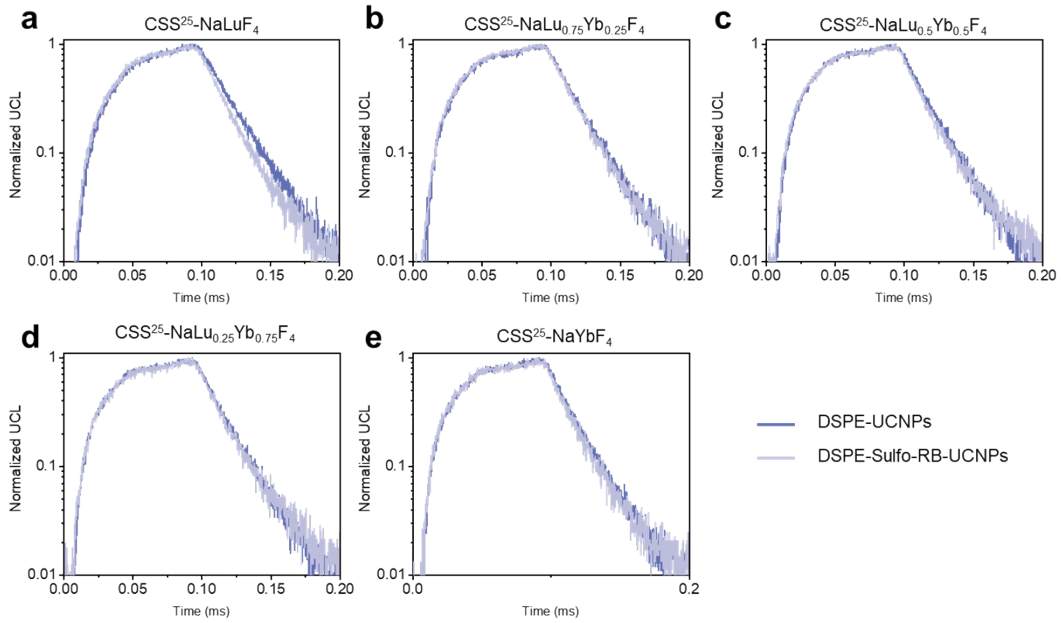

Figure S22. Normalized luminescence kinetic response data of DSPE-UCNPs before and after the addition of dyes sulfo-rhodamine B. The composition of UCNPs were (a) CSS^{25}-$NaLuF_4$, (b) CSS^{25}-$NaLu_{0.75}Yb_{0.25}F_4$, (c) CSS^{25}-$NaLu_{0.5}Yb_{0.5}F_4$, (d) CSS^{25}-$NaLu_{0.25}Yb_{0.75}F_4$, (e) CSS^{25}-$NaYbF_4$. Particles dispersed in EtOH were excited at 980 nm and the luminescence kinetics of the green upconversion emission around 541 nm were recorded. The fitted decay lifetimes are presented in the **Table S5**.

Table S5. The resulting decay lifetimes of green ($^2H_{11/2} \rightarrow {}^4I_{15/2}$, 541 nm) emission of Er^{3+}, obtained from exponential fitting of decay curves in **Figure S22**.

	CSS^{25}-$NaLuF_4$	CSS^{25}-$NaLu_{0.75}Yb_{0.25}F_4$	CSS^{25}-$NaLu_{0.5}Yb_{0.5}F_4$	CSS^{25}-$NaLu_{0.25}Yb_{0.75}F_4$	CSS^{25}-$NaYbF_4$
$\tau_{DSPE\text{-}UCNPs}$ (μs)	21.58	20.22	19.54	19.85	19.78
$\tau_{DSPE\text{-}Sulfo\text{-}RB\text{-}UCNPs}$ (μs)	18.38	18.13	17.09	17.36	17.07

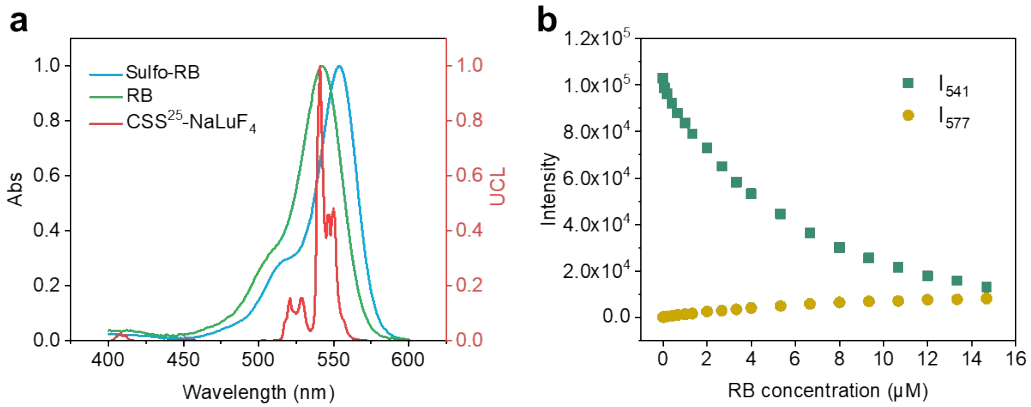

Figure S23. (a) Normalized absorption sulfo-rhodamine B (blue line) and rhodamine B (green line), normalized emission spectra of CSS $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ UCNPs (red line) from 400-600 nm, the maximum UCL intensities of CSS $NaYbF_4$@$NaYb_{0.92}Er_{0.08}F_4$@$NaLuF_4$ UCNPs and the maximum absorbance of dyes were normalized to unity, respectively. (b) The intensity of emission peak of rhodamine B at 577 nm and the green emission peak of Er^{3+} in DSPE-RB-UCNPs with the concentration of rhodamine B varied from 0 to 14.67 μM.

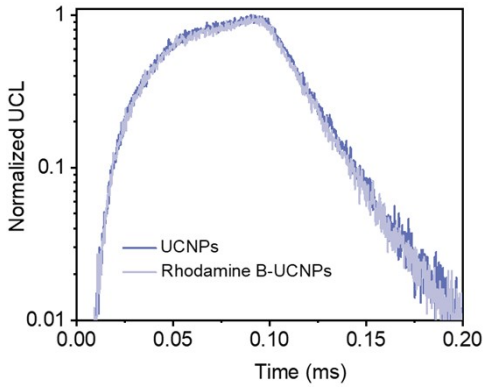

Figure S24. Normalized luminescence kinetic response data of DSPE-CSS[25]-$NaLuF_4$ before and after the addition of dye rhodamine B. Particles dispersed in EtOH were excited at 980 nm and the luminescence kinetics of the green upconversion emission around 541 nm were recorded. The fitted decay lifetimes are presented in the **Table S6.** Note: the pulse width using in this test was the same as that for **Figure S22** for fair comparison.

Table S6. The resulting decay lifetimes of green ($^2H_{11/2} \rightarrow {}^4I_{15/2}$, 541 nm) emission of Er^{3+}, obtained from exponential fitting of decay curves in **Figure S24**.

	UCNPs	Rhodamine B-UCNPs
τ (μs)	20.74	20.41

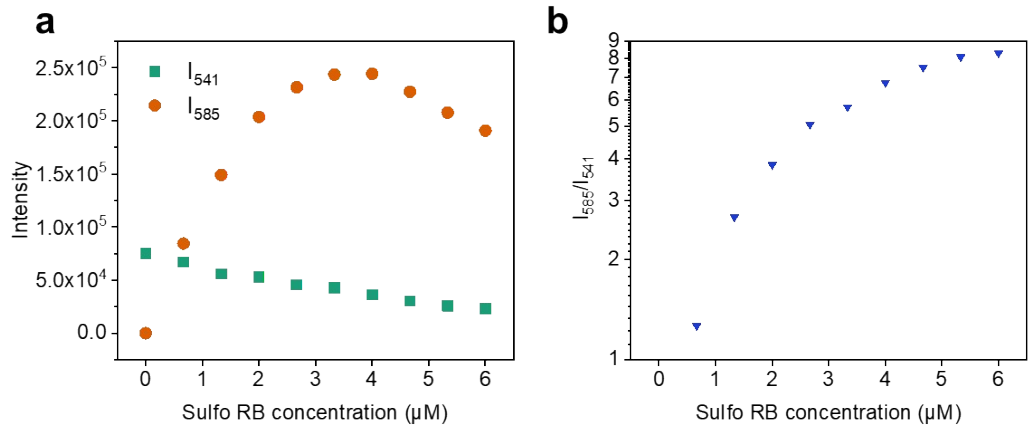

Figure S25. The intensity of emission peak of sulfo-rhodamine B at 585 nm and the green emission peak of Er in sulfo-RB-UCNPs ($CHCl_3$) with the concentration of sulfo-rhodamine B varied from 0 to 6 μM. (b) The corresponding I_{585}/I_{541} ratio versus the sulfo-rhodamine B concentration in sulfo-RB-UCNPs.

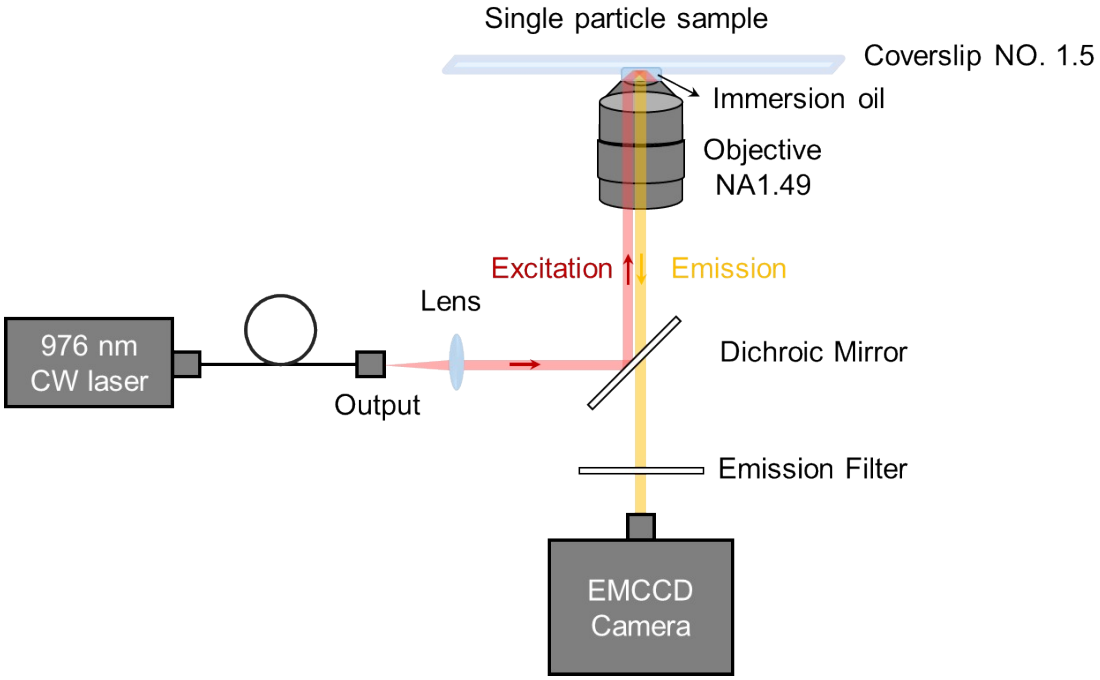

Figure S26. Schematic illustration of the TIRF (Total internal reflection fluorescence) microscopy used for single particle measurement. Single-particle characterization was done using a lab constructed microscope system equipped with wide field epi-illumination of a 976 nm fiber laser through a Nikon 100× NA 1.49 Oil objective. The upconversion signal was recorded on EMCCD (Andor, iXon 897) with a 750 Shortpass emission filter (Chroma, ET750sp-2p8), and the Light Red Bandpass (Chroma, ET645/75m) filter was further added for the measurement of red emission.