Supporting Information

Tuning upconversion efficiency and spectrum of upconversion nanoparticles through surface decorating of organic dye

Meng Xue[a], Cong Cao[a,b], Xiaobo Zhou[a], Ming Xu[a], Wei Feng[a*], Fuyou Li[a*]

[a]Department of Chemistry & State Key Laboratory of Molecular Engineering of Polymers & Institute of Biomedicine Sciences & Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, 220 Handan Road, Shanghai 200433, P.R. China.

[b]Department of Materials Engineering, College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, P.R. China

E-mail: fengweifd@fudan.edu.cn and fyli@fudan.edu.cn

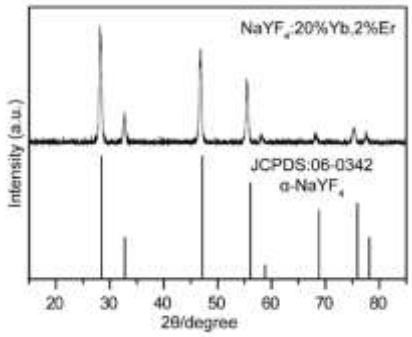


Figure S1: X-ray diffraction (XRD) pattern of $NaYF_4$:20%Yb,2%Er nanoparticles and the standard of cubic phase $NaYF_4$ (JCPDS card No. 06-0342).

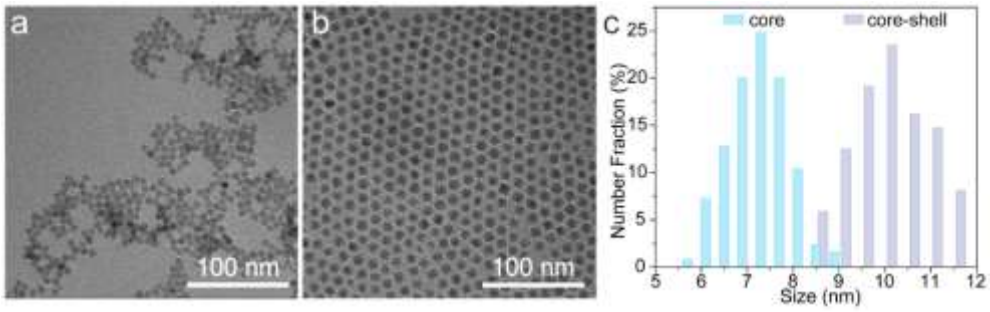


Figure S2: (a) Low-resolution TEM image of $NaYF_4$:20%Yb,2%Er NPs. (b) Low-resolution TEM image of $NaYF_4$:20%Yb,2%Er@CaF_2(1:2) NPs. (c) Particle size distribution of core $NaYF_4$:20%Yb,2%Er NPs and core-shell $NaYF_4$:20%Yb,2%Er@CaF_2(1:2) NPs. These data were obtained from the TEM images with more than 100 nanoparticles.

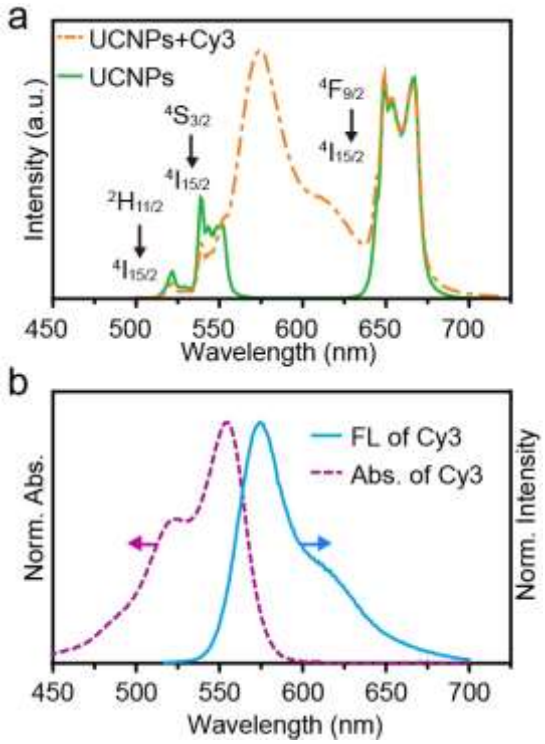


Figure S3: (a) Upconversion luminescence spectrum of $NaYF_4$:20%Yb,2%Er@CaF_2(1:2) with (orange dash line) and without (green solid line) Cy3-SO_3 in DMSO excited by a 980 nm laser. (b) Fluorescence (blue solid line, Ex: 488 nm) and absorption (purple dash line) spectrum of Cy3-SO_3 in DMSO.

We measured the upconversion luminescence spectrum of $NaYF_4$:20%Yb,2%Er@CaF_2(1:2) NPs with Cy3-SO_3 with different power density (Figure S4a) and converted the luminescence spectrum into CIE 1931 color coordinates (Table S1). The luminescence color changed with different pump power density.

Table S1: The luminescence color coordinates of $NaYF_4$:20%Yb,2%Er@CaF_2(1:2) NPs with different pump power density of the 980 nm laser.

	CIE x	CIE y
5 W/cm^2	0.5513	0.447
10 W/cm^2	0.5514	0.447
15 W/cm^2	0.5505	0.4478
20 W/cm^2	0.5503	0.448
25 W/cm^2	0.5491	0.4491
30 W/cm^2	0.5487	0.4495
35 W/cm^2	0.5481	0.4502

The dependence of the visible fluorescence intensity on the pump-laser power was calculated as shown in **Figure S4b**. In principle, the UCL emission intensity, I_{em}, is proportional to the power *n* of the near-infrared (NIR) exciting pump power. We found

that the n value of 539 and 575 nm is larger than that of 650 nm, which means the change tendency of emission intensity at 539, 575 and 650 nm with the exciting pump power are different. Because Cy3-SO_3 received energy from Er^{3+} ions ($^2H_{11/2}$ and $^4S_{3/2}$), the change tendency of emission at 575 nm (Cy3-SO_3) is the same with 539 nm (Er^{3+} ions). And the emission intensity at 539 nm increased more than 650 nm. So the color of the UCNPs-Cy3-SO_3 system will changed with the power density.

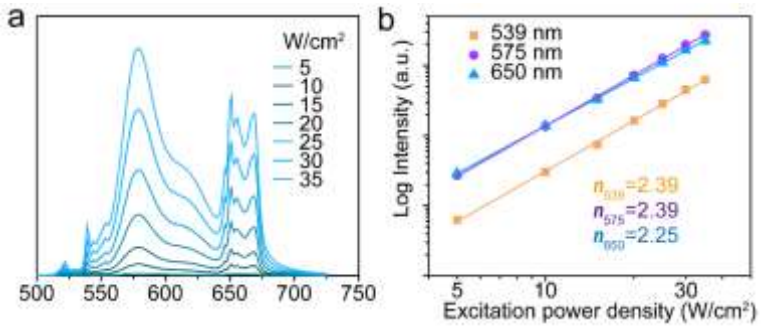


Figure S4: (a) Upconversion luminescence spectrum of 6.67 mM $NaYF_4$:20%Yb,2%Er@CaF_2(1:2) NPs with 5.33 μM Cy3-SO_3 in DMSO excited with different power density. (b) Log-log plots of luminescence emission of $NaYF_4$:20%Yb,2%Er@CaF_2(1:2) as a function of pump power of the 980 nm laser.

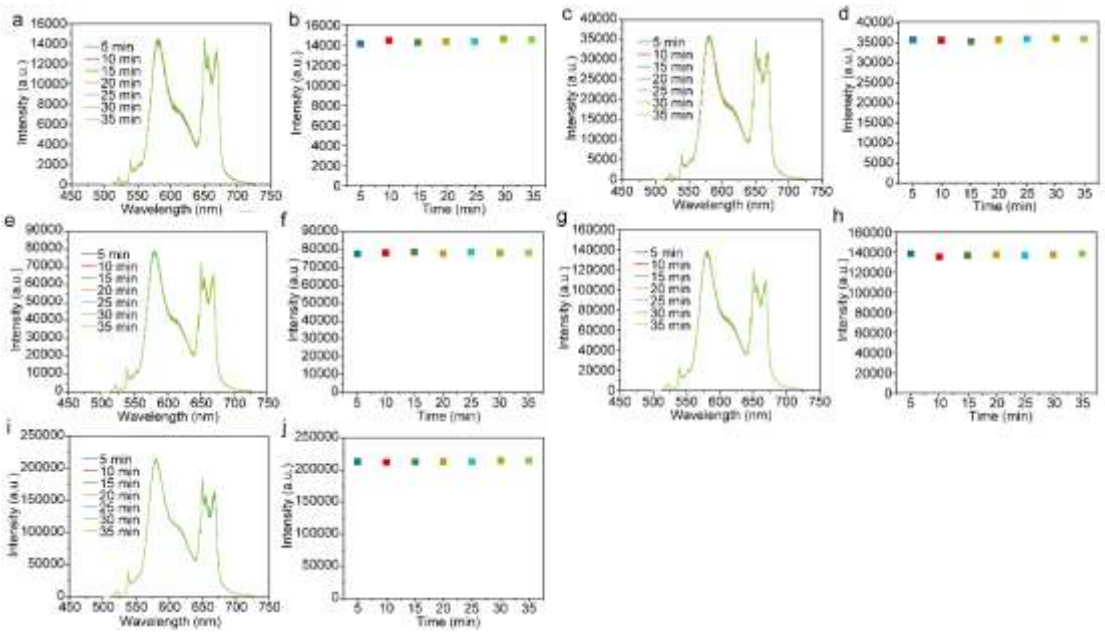


Figure S5: Changes in fluorescence spectra with 5.33 μM Cy3-SO_3 in 6.67 mM UCNPs DMSO solution and the fluorescence intensity of Cy3-SO_3 at 580 nm as a function of time with power density 10 W/cm^2 (a, b), 15 W/cm^2 (c, d), 20 W/cm^2 (e, f), 25 W/cm^2 (g, h), and 30 W/cm^2 (i, j), respectively. (Ex: 980 nm)

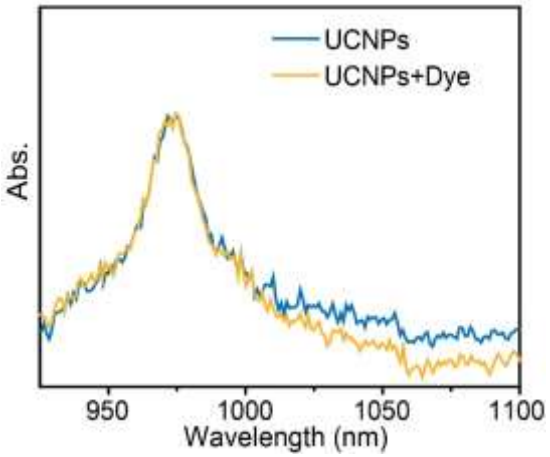


Figure S6: The absorption spectrum of $NaYF_4$:20%Yb,2%Er@CaF_2(1:2) with (orange) and without (blue) Cy3-SO_3 dye.

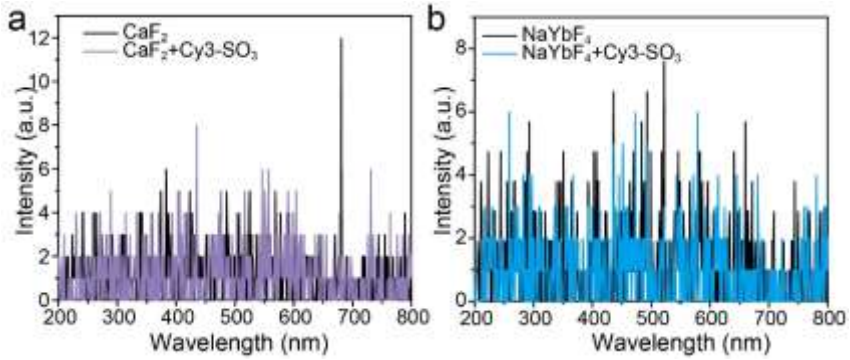


Figure S7: Upconversion luminescence spectrum of $NaYbF_4$ and CaF_2 with and without Cy3-SO_3 in DMSO excited by a 980 nm CW laser. The experiment condition was the same with the experiment condition in Figure 2.

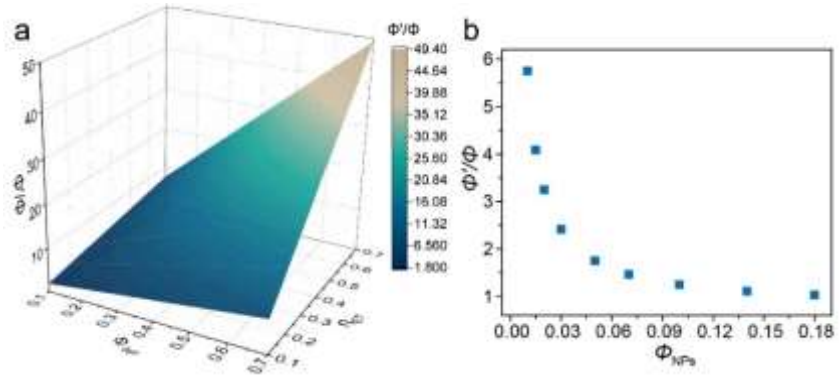


Figure S8: (a) The relationship of ϕ_{dye} and η_{ET} with ϕ'/ϕ. ϕ_{NPs} was assumed as 1%. (b) The relationship of ϕ_{UCNPs} with ϕ'/ϕ. ϕ_{dye} and η_{ET} were assumed as 20% and 25%, respectively.

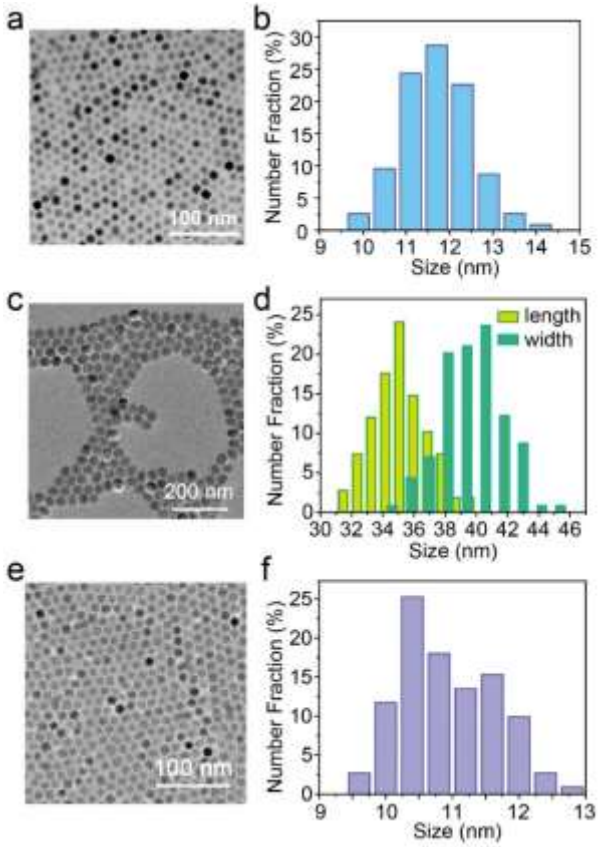


Figure S9: (a) Low-resolution TEM image of $NaYF_4$:20%Yb,2%Er@CaF_2(1:4) NPs. (b) Particle size distribution of $NaYF_4$:20%Yb,2%Er@CaF_2(1:4) NPs. (c) Low-resolution TEM image of $NaYF_4$:20%Yb,2%Er NPs. (d) Particle size distribution of $NaYF_4$:20%Yb,2%Er NPs. (e) Low-resolution TEM image of $NaYbF_4$:30%Tb@CaF_2:20%Tb NPs. (f) Particle size distribution of $NaYbF_4$:30%Tb@CaF_2:20%Tb NPs. These data were obtained from the TEM images with more than 100 nanoparticles.

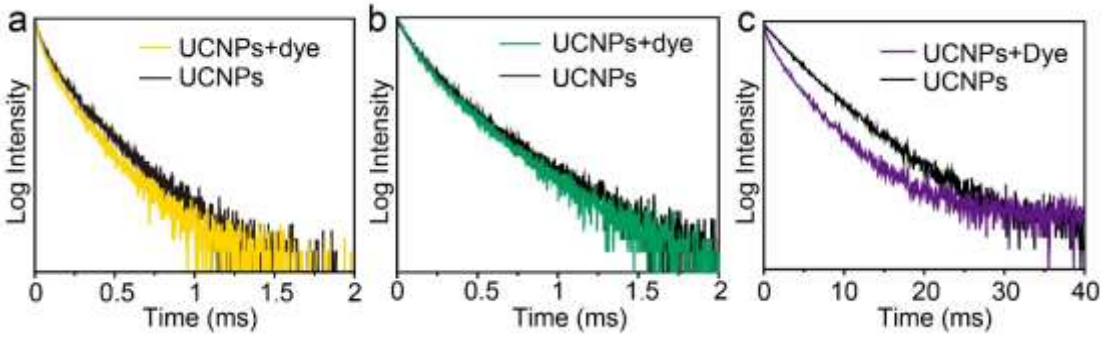


Figure S10: (a) Decay curves of Er^{3+} ions emission at 540 nm from $NaYF_4$:20%Yb,2%Er@CaF_2(1:4) NPs with and without Cy3-SO_3 in DMSO excited by a 488 nm pulse laser. (b) Decay curves of Er^{3+} ions emission at 540 nm from NaYF4:20%Yb,2%Er with and without Cy3-SO_3 in DMSO excited by a 488 nm pulse laser. (c) Decay curves of Tb^{3+} ions emission at 541 nm from $NaYbF_4$:30%Tb@CaF_2:20%Tb(1:2) NPs with and without Cy3-SO_3 in DMSO excited by a 488 nm pulse laser.

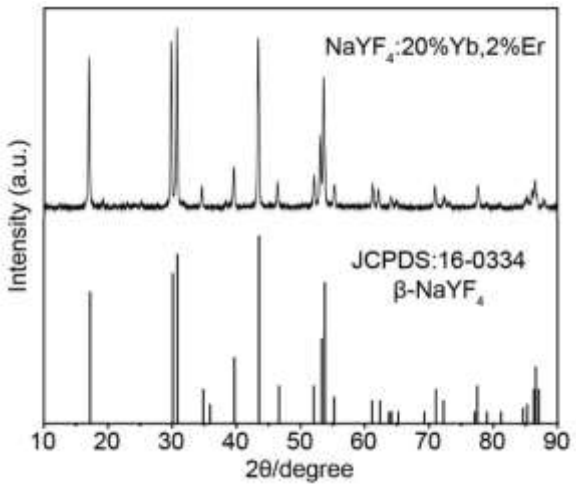


Figure S11: (a) X-ray diffraction (XRD) pattern of hexagonal $NaYF_4$:20%Yb,2%Er nanoparticles and the standard of hexagonal phase $NaYF_4$ (JCPDS card No. 16-0334).

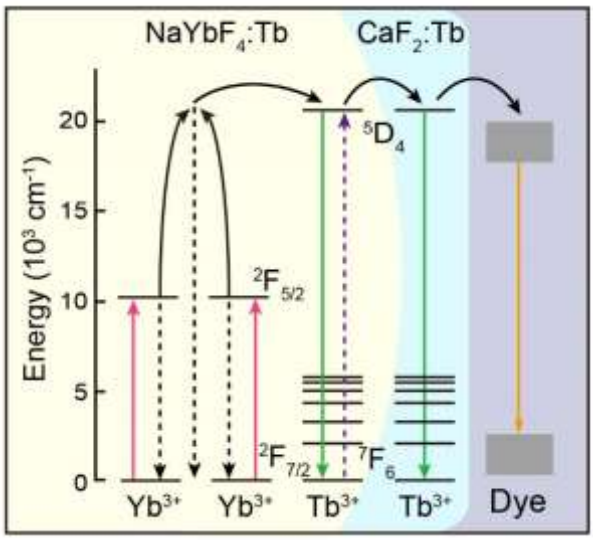
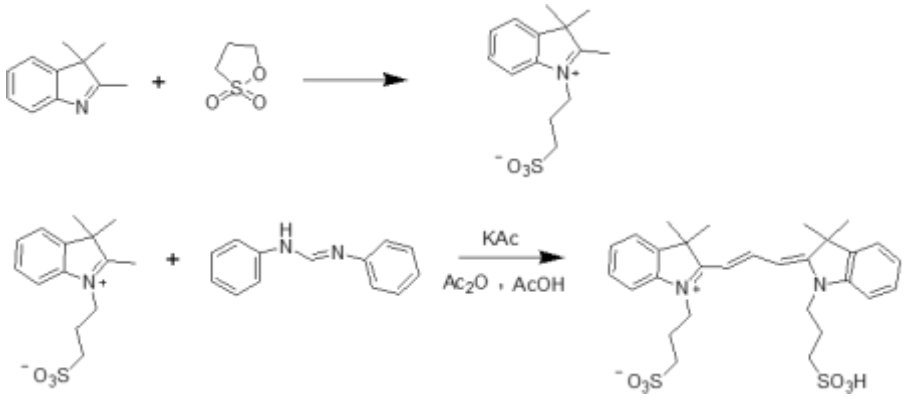


Figure S12: Part of energy level diagram of Yb^{3+} and Tb^{3+} doped $NaYbF_4$.



Scheme S1. Synthetic route of Cy3-SO_3.

Calculation of the number of Cy3-SO_3 dye on per nanoparticle

We mixed UCNPs (6.67 mM, 1500 μL) with 0 μL, 1 μL, 2 μL, 3 μL, 4 μL, 5 μL, 6 μL, 7 μL, 8 μL and 9 μL Cy3-SO_3 dye (10^{-3} M), respectively. Then the nanoparticles were centrifuged at 16500 rpm for 40 min. Take out the supernatant and measure the absorption spectra of supernatant. As shown in Figure S13, after centrifugation, there was no absorption peak of Cy3-SO_3 in the supernatant, indicating that no free dye exists in the supernatant, and all the dripped Cy3-SO_3 has attached to the UCNPs surface.

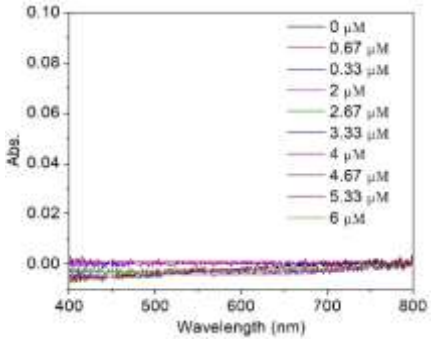


Figure S13: After centrifugation, changes in absorption spectra of supernatant with different addition of Cy3-SO_3 in UCNPs solution.

We consider the volume of $NaYF_4$ and $NaYF_4$:Yb,Er are approximately equal due to the low doping concentration of Yb^{3+} and Er^{3+} ions. The volume of $NaYF_4$ unit cell can be described as

$$V_{unit\ cell}=a^3=0.16\ nm^3$$

The volume of $NaYF_4$:Yb,Er is

$$V_{NP}=4/3*\pi*r^3=187.40\ nm^3$$

So one $NaYF_4$:Yb,Er nanoparticle has about 1171 unit cells. A unit cell contains 2 rare earth atoms. So one $NaYF_4$:Yb,Er nanoparticle has about 2342 rare earth atoms. Take 1500 μL UCNPs (6.67 mM) with 1 μL Cy3-SO_3 dye (10^{-3} M) in DMSO as example. 0.01 mmol UCNPs has 0.01 mmol rare earth ions which construct about $2.57*10^{15}$ nanoparticles. 1 μL Cy3-SO_3 (10^{-3} M) dye solution has $6.02*10^{14}$ dye molecule. So there is 0.23 dye attach on a nanoparticle. According to the concentration of UCNPs and Cy3-SO_3, we calculated the number of Cy3-SO_3 attached on per UCNPs shown in **Table S2**.

Table S2: The relationship between Cy3-SO_3 concentration and the number of Cy3-SO_3 on per UCNPs.

N_{dye}	0	0.23	0.46	0.69	0.92	1.15	1.38	1.61	1.84	2.07
c_{dye}(μM)	0.00	0.67	1.33	2.00	2.67	3.33	4.00	4.67	5.33	6.00