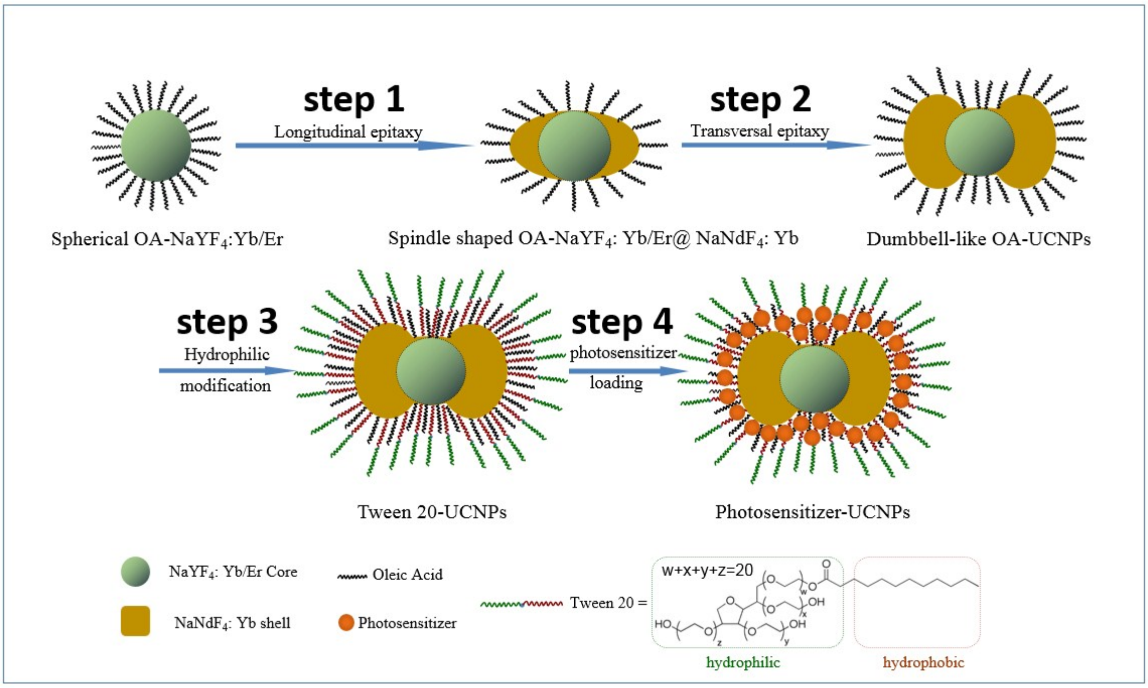
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Nd^{3+} Sensitized Dumbbell-like Upconversion Nanoparticles for Photodynamic Therapy Application

Bing Xu, Xiao Zhang, Wenjuan Huang, Yijun Yang, Ying Ma, Zhanjun Gu, Tianyou Zhai, Yuliang Zhao



Scheme S1. Schematic illustrating the preparation of dumbbell-like $NaYF_4$: Yb/Er@$NaNdF_4$: Yb core–shell nanostructures (not to real scale) for photosensitizer loading used in PDT (Photodynamic Therapy).

Table S1. Differentials of main crystal indices belonging to β-$NaYF_4$, β-$NaYbF_4$ and β-$NaNdF_4$ crystal

crystal indices	β-$NaYF_4$ x_1(nm)	β-$NaYbF_4$ x_2(nm)	β-$NaNdF_4$ x_3(nm)	δ_1(%)	δ_2(%)
(001)	0.353	0.347	0.371	5.13	1.70
(110)	0.297	0.296	0.305	2.70	0.34
(100)	0.515	0.513	0.528	2.52	0.39
(101)	0.29	0.287	0.304	4.72	1.03
(201)	0.208	0.206	0.215	3.37	0.96

$\delta_1 = |x_1 - x_3| / x_1$; $\delta_2 = |x_1 - x_2| / x_1$

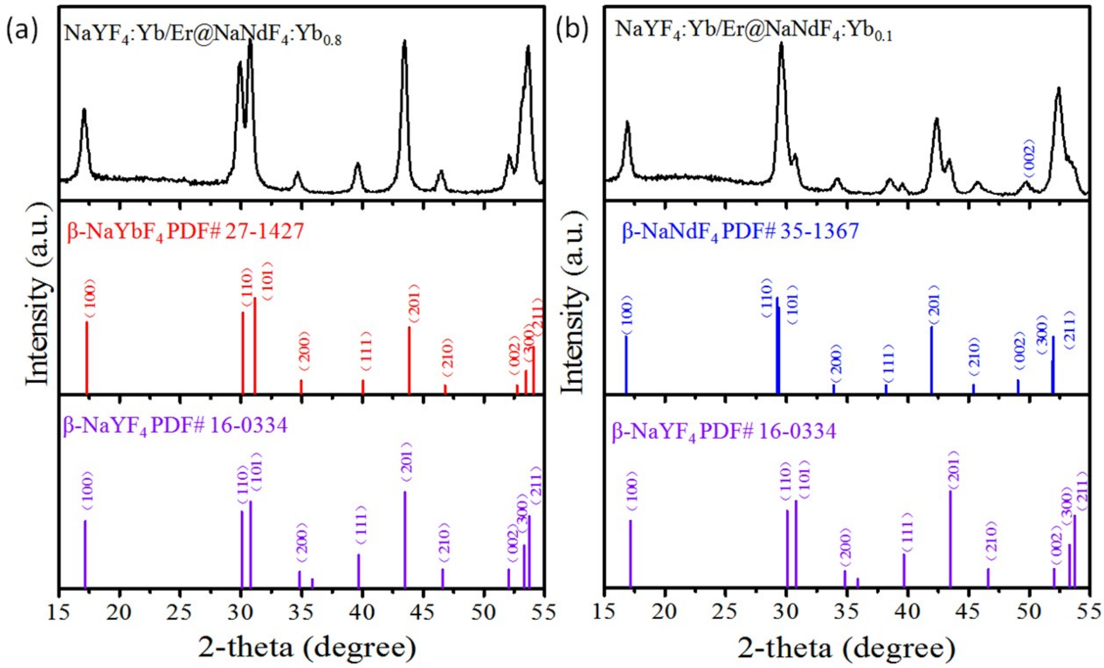


Figure S1. (a) XRD patterns of spherical $NaYF_4$:Yb/Er @ $NaNdF_4$:$Yb_{0.8}$, standard β-$NaYbF_4$ and β-$NaYF_4$ crystals. (b) XRD patterns of dumbbell-like $NaYF_4$:Yb/Er@$NaNdF_4$:$Yb_{0.1}$, standard β-$NaNdF_4$ and β-$NaYF_4$ crystals.

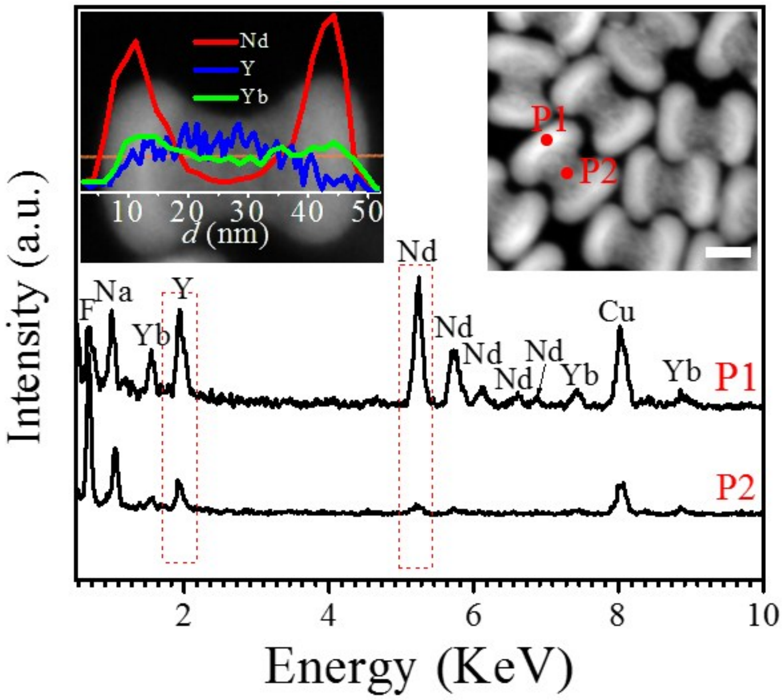


Figure S2. EDX spectra collected from P1 located at the dumbbell ends and P2 located in the center of the dumbbell, respectively. Inset (left) EDX line-scan profile showing the distribution of Nd^{3+}, Y^{3+}, Yb^{3+} ions along the *c* axis of a dumbbell-like $NaYF_4$:Yb/Er@$NaNdF_4$:$Yb_{0.1}$ nanocrystal. The right inset is STEM image of the dumbbell-like $NaYF_4$: Yb/Er@ $NaNdF_4$: $Yb_{0.1}$ nanoparticles (scale bar is 20 nm).

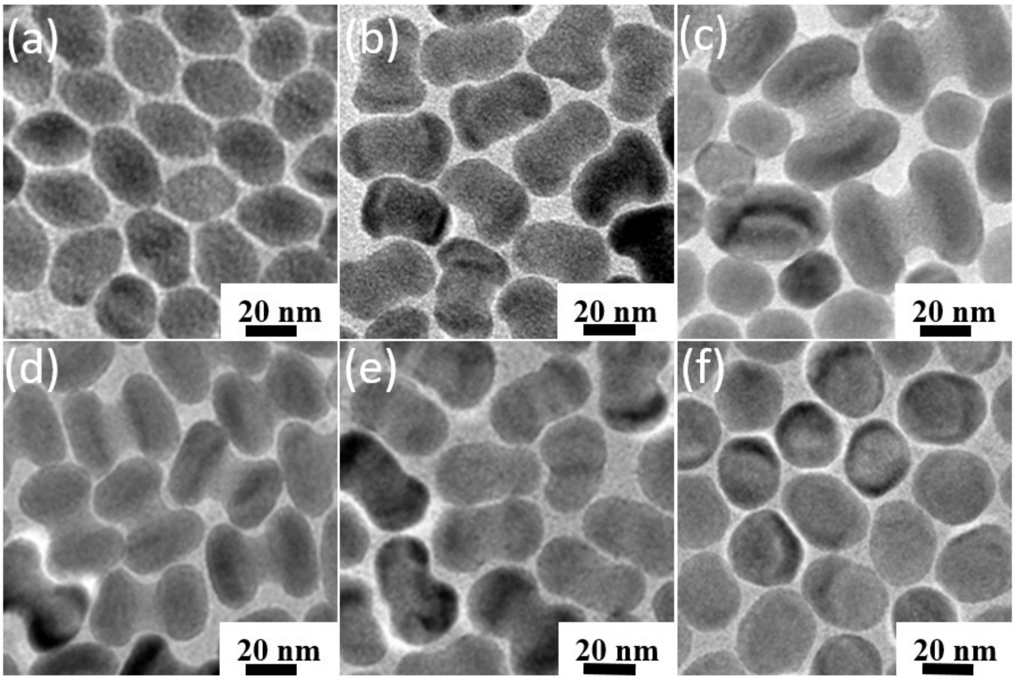


Figure S3. (a-c) TEM images of $NaYF_4$:Yb/Er @ $NaNdF_4$: $Yb_{0.1}$ nanoparticles with different ratios of core/shell: 1:0.25, 1:0.5, 1:1.5, respectively. (d-f) TEM images of $NaYF_4$:Yb/Er@$NaNd_{1-x}F_4$:Yb_x nanoparticles with different Yb^{3+} doping contents in the $NaNdF_4$:Yb shell: x= 0, 0.3, 0.8, respectively.

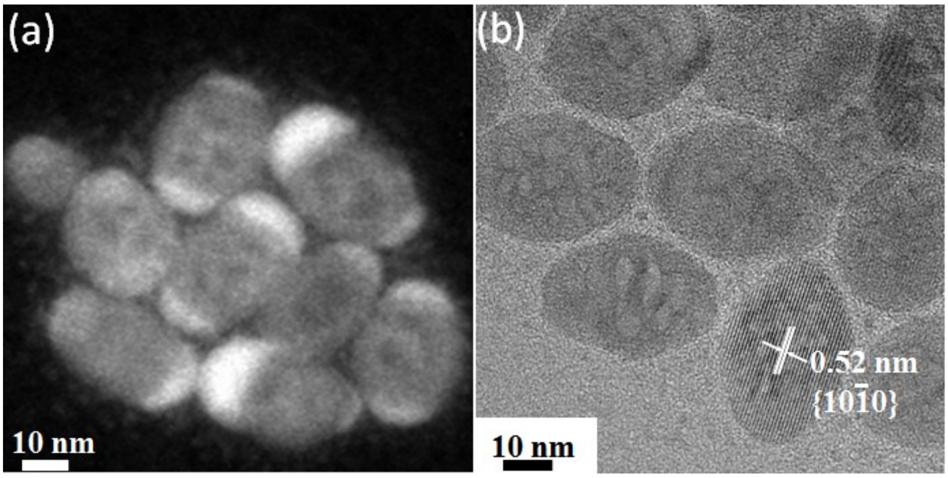


Figure S4. (a) HAADF image and (b) HRTEM image of the spindle shaped $NaYF_4$: Yb/Er@ $NaNdF_4$: $Yb_{0.1}$ nanoparticles (molar ratio of core/shell is 1:0.25).

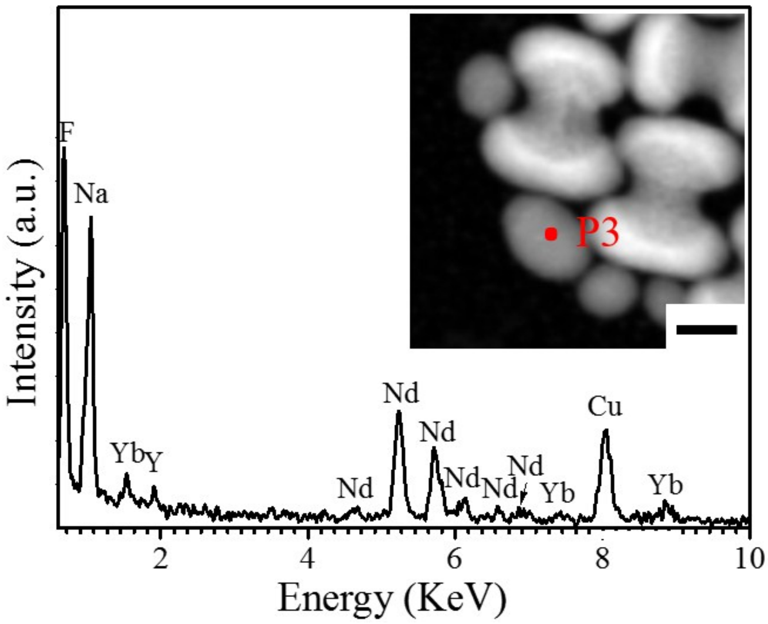


Figure S5. EDX spectrum of small individually nucleated $NaNdF_4$ nanoparticles in the $NaYF_4$:Yb/Er@$NaNdF_4$:$Yb_{0.1}$ sample (molar ratio of core/shell is 1:1.5) and (inset) the corresponding STEM image (Scale bar is 20 nm).

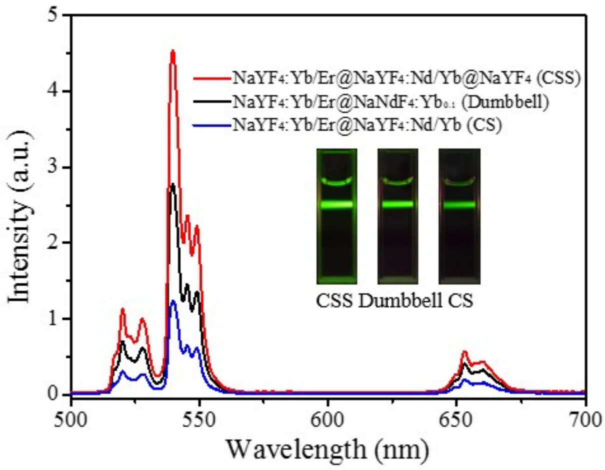


Figure S6. Upconversion emission spectra of dumbbell-like $NaYF_4$: Yb/Er @ $NaNdF_4$: Yb, $NaYF_4$: Yb/Er@$NaYF_4$: Nd core-shell and $NaYF_4$: Yb/Er @ $NaYF_4$: Nd @ $NaYF_4$ core-shell-shell nanoparticles (10 mg mL^{-1}) under 808 nm laser excitation (1.5 W cm^{-2}) dispersed in cyclohexane and (inset) the corresponding photographs of luminescent intensity.

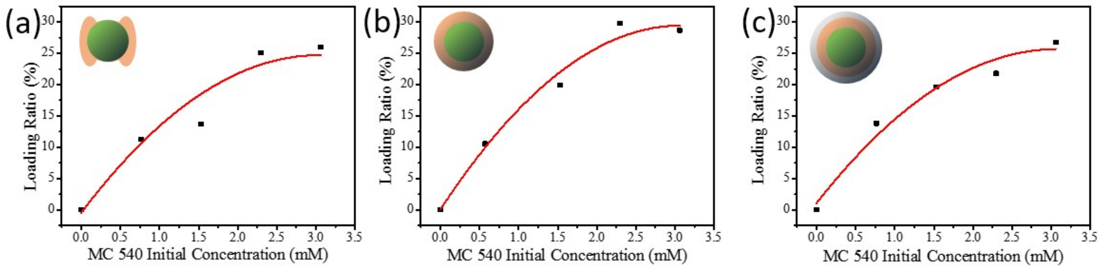


Figure S7. MC540 loading percentages of (a) dumbbell-like, (b) core-shell, (c) core-shell-shell Tween20-UCNPs with different concentration of MC540 aqueous solution.

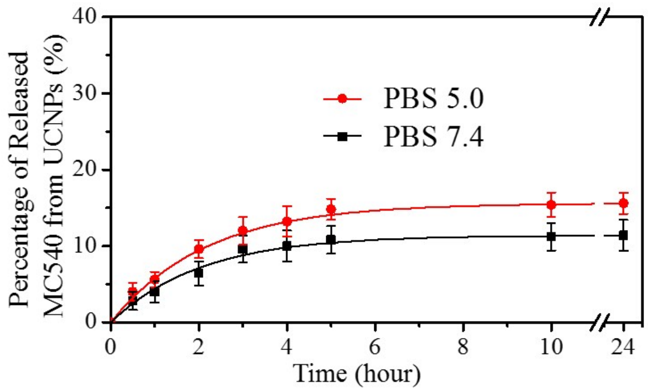


Figure S8 Stability of dumbbell-like MC540-UCNPs in PBS medium. After 24 h stirring, less than 20% of the MC540 was detached from the UCNPs. More photosensitizers release was observed at a slightly acidic pH. Error bars were based on standard deviations of triplicated samples. Similar results were obtained from the core-shell and core-shell-shell MC540-UCNPs.

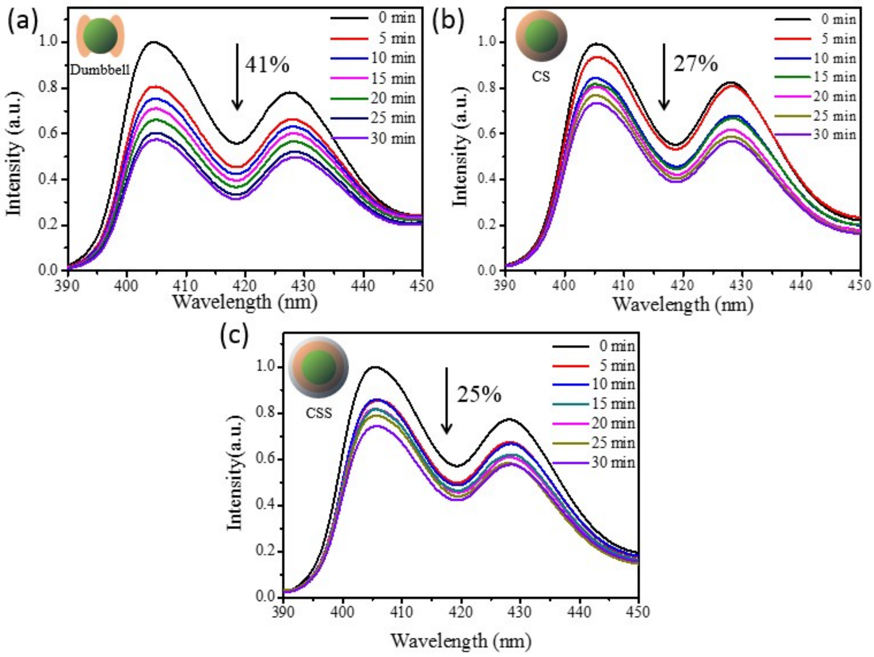


Figure S9. (a-c) Absorption spectra measured every 5 minutes of ABDA (10 μM) incubated with MC540-dumbbell, MC540-CS, MC540-CSS UCNPs in aqueous dispersion irradiated by 808 nm laser (1.5 W cm^{-2}), respectively.

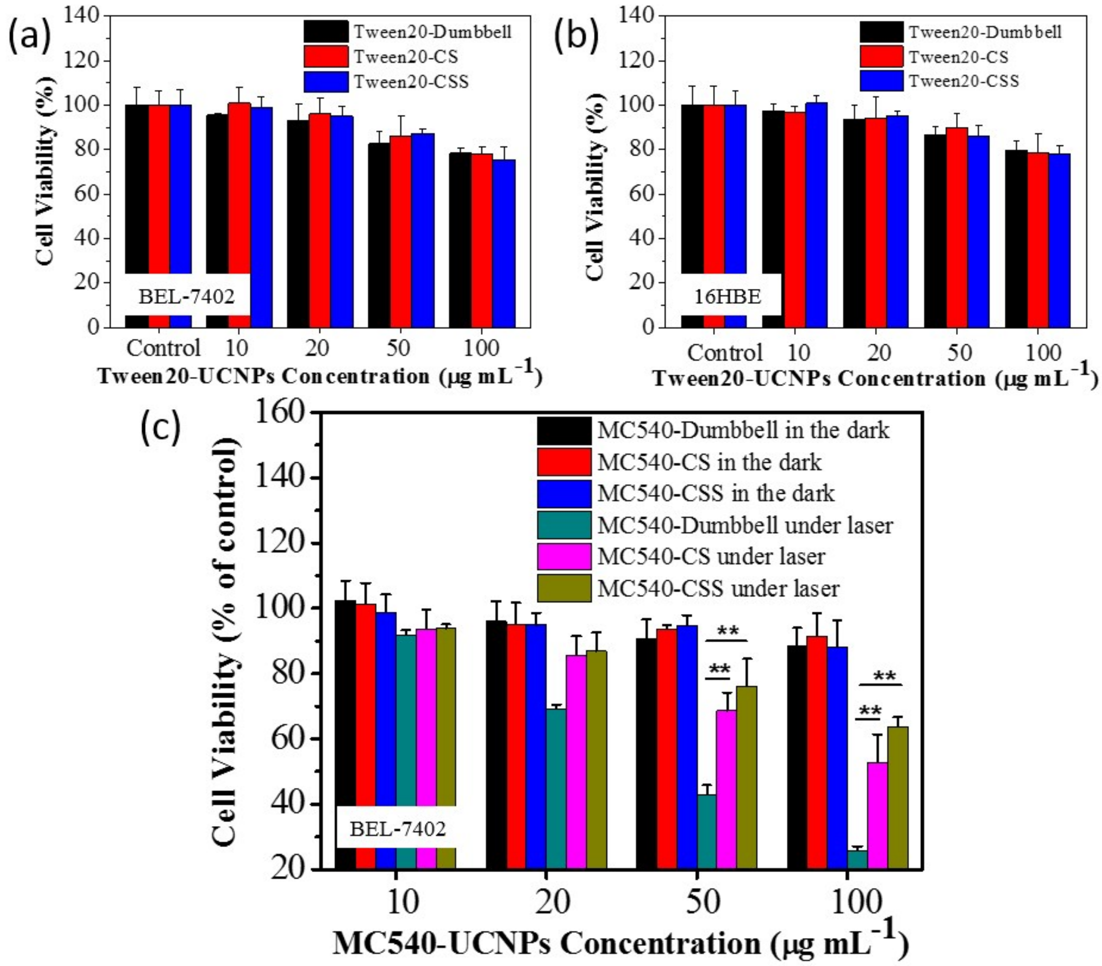


Figure S10. Cell viability of (a) BEL-7402 cells and (b) 16HBE cells incubated with different concentrations of Tween20-UCNPs after 12 h in the dark. Error bars were based on triplicate samples. (c) Cell viability of BEL-7402 cells incubated with different concentrations of MC540-UCNPs under 20 min 808 nm laser exposure (0.65 W cm^{-2}). Error bars were based on triplicate samples. ** $P < 0.01$.

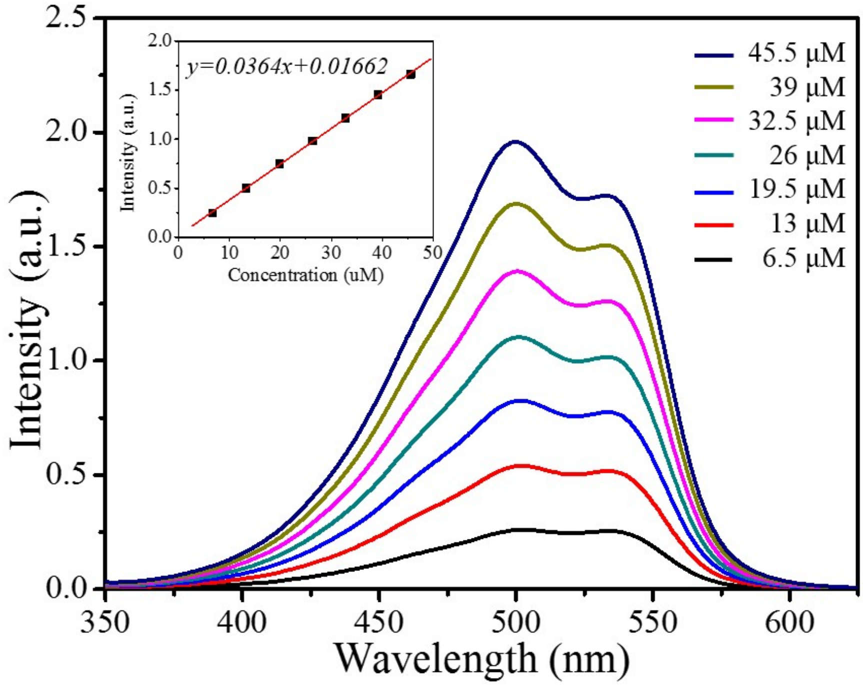


Figure S11. The absorbance curve of the MC540 water solution under different concentrations and (inset) the relationship between MC540 concentration and absorption at 540 nm wavelength.

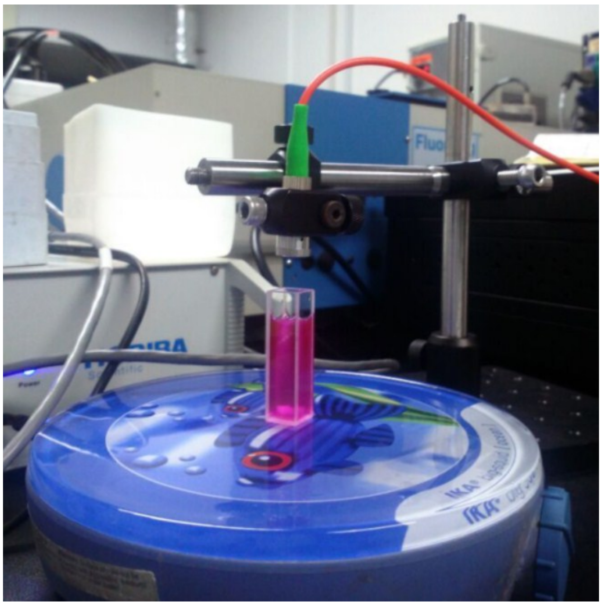


Figure S12. Photograph of the experimental setup for irradiation under 808 nm laser.