Supporting Information

Optimal fluorescence and photosensitivity properties of dual-functional $NaYb_{1-x}F_4:Tm^{3+}{}_x$ nanoparticles for applications in imaging guided photodynamic therapy

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I. Theoretically investigate intensity of 800 nm emission

In order to understand the change of the 800 nm emission theoretically, rate equations in the steady states based on the process of energy transitions are proposed as follows:

$$\frac{\mathrm{d}N_1}{\mathrm{d}t}=0=W_0N_{\mathrm{Yb1}}N_0-W_1N_{\mathrm{Yb1}}N_1-\frac{N_1}{\tau_1} \tag{1}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t}=0=W_1N_{\mathrm{Yb1}}N_1-W_2N_{\mathrm{Yb1}}N_2-\frac{N_2}{\tau_2} \tag{2}$$

$$\frac{\mathrm{d}N_{\mathrm{Yb1}}}{\mathrm{d}t}=0=\rho\sigma_{\mathrm{Yb}}N_{\mathrm{Yb0}}-W_0N_{\mathrm{Yb1}}N_0-W_1N_{\mathrm{Yb1}}N_1-W_2N_{\mathrm{Yb1}}N_2-\frac{N_{\mathrm{Yb1}}}{\tau_{\mathrm{Yb1}}} \tag{3}$$

where N_{i} (i= 0, 1, 2) are population densities of the $^3H_6$, $^3F_4$ and $^3H_4$ states of the Tm^{3+} ions, respectively; N_{Yb0} and N_{Yb1} are the population densities of ground and exited states of Yb^{3+}, respectively; τ_{x} are the decay times of relevant levels; W_{i} are the energy transfer rates from the excited state of Yb^{3+} to the N_{i} levels of Tm^{3+}; ρ denotes the laser photon number density; σ_{Yb} is the absorption cross section of Yb^{3+}.

In the steady state rate equation above, all terms involving upconversion process in Eq. S3 would be neglected due to their contribution being much less than that of the pump laser. Meanwhile, the upconversion terms $W_1N_{\mathrm{Yb1}}N_1$ in Eq. S1 and $W_2N_{\mathrm{Yb1}}N_2$ in Eq. S2 are also neglected owning to the fact that the rates of energy transmission in the upconversion processes are much less than the decay rates of relevant energy levels. In this way, the population densities N_2 and the 800 nm emission intensity can be described as below (Eq. S4 and Eq. S5):

$$N_2=\rho^2\sigma_{Yb}^2W_0W_1N_0(N_{Yb0}\tau_{Yb1})^2\tau_1\tau_2 \tag{4}$$

$$I_{800}=\frac{N_2}{\tau_2}=\rho^2\sigma_{Yb}^2W_0W_1N_0(N_{Yb0}\tau_{Yb1})^2\tau_1 \tag{5}$$

Ⅱ. Morphology and structural characteristics

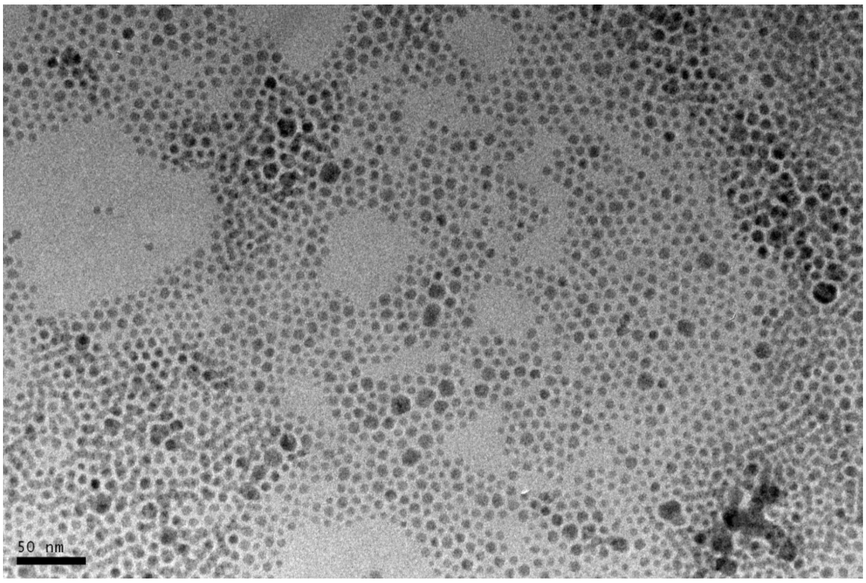

Figure S1. A low magnification TEM of $NaYb_{99\%}F_4:Tm^{3+}{}_{1\%}$.

Statistical report			
Distribution/nm	Mean/nm	Amount	Freq.
4-4.6	4.3	4	2.21%
4.6-5.2	4.9	10	5.52%
5.2-5.8	5.5	28	15.47%
5.8-6.4	6.1	32	17.68%
6.4-7	6.7	44	24.31%
7-7.6	7.3	27	14.92%
7.6-8.2	7.9	22	12.15%
8.2-8.8	8.5	5	2.76%
8.8-9.4	9.1	7	3.87%
9.4-10	9.7	2	1.1%

Table S1. Statistical report for particle size distribution

Total	181
Max./nm	9.72
Min./nm	4.09
Mean/nm	6.68

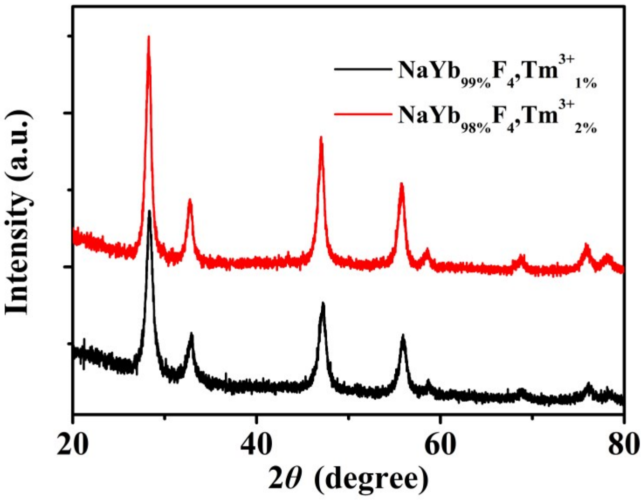

Figure S2. XRD patterns of $NaYb_{1-x}F_4:Tm^{3+}_x$ with x=1% and 2%

Ⅲ. The 800 nm upconversion fluorescence spectra

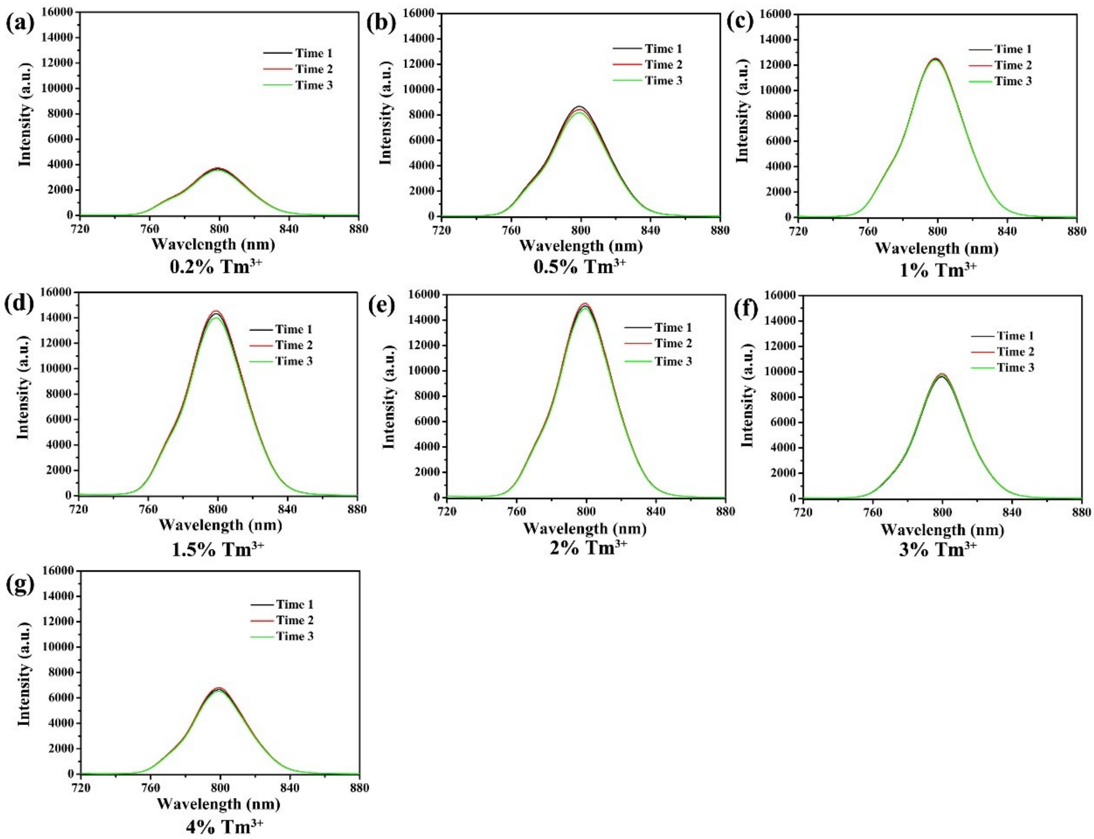

Figure S3. The 800 nm upconversion fluorescence spectra in $NaYb_{1-x}F_4$:$Tm^{3+}{}_x$ NPs.

(a) corresponding to Tm^{3+} concentration of 0.2%

(b) corresponding to Tm^{3+} concentration of 0.5%

(c) corresponding to Tm^{3+} concentration of 1%

(d) corresponding to Tm^{3+} concentration of 1.5%

(e) corresponding to Tm^{3+} concentration of 2%

(f) corresponding to Tm^{3+} concentration of 3%

(g) corresponding to Tm^{3+} concentration of 4%

Ⅳ. DPBF absorbance spectra

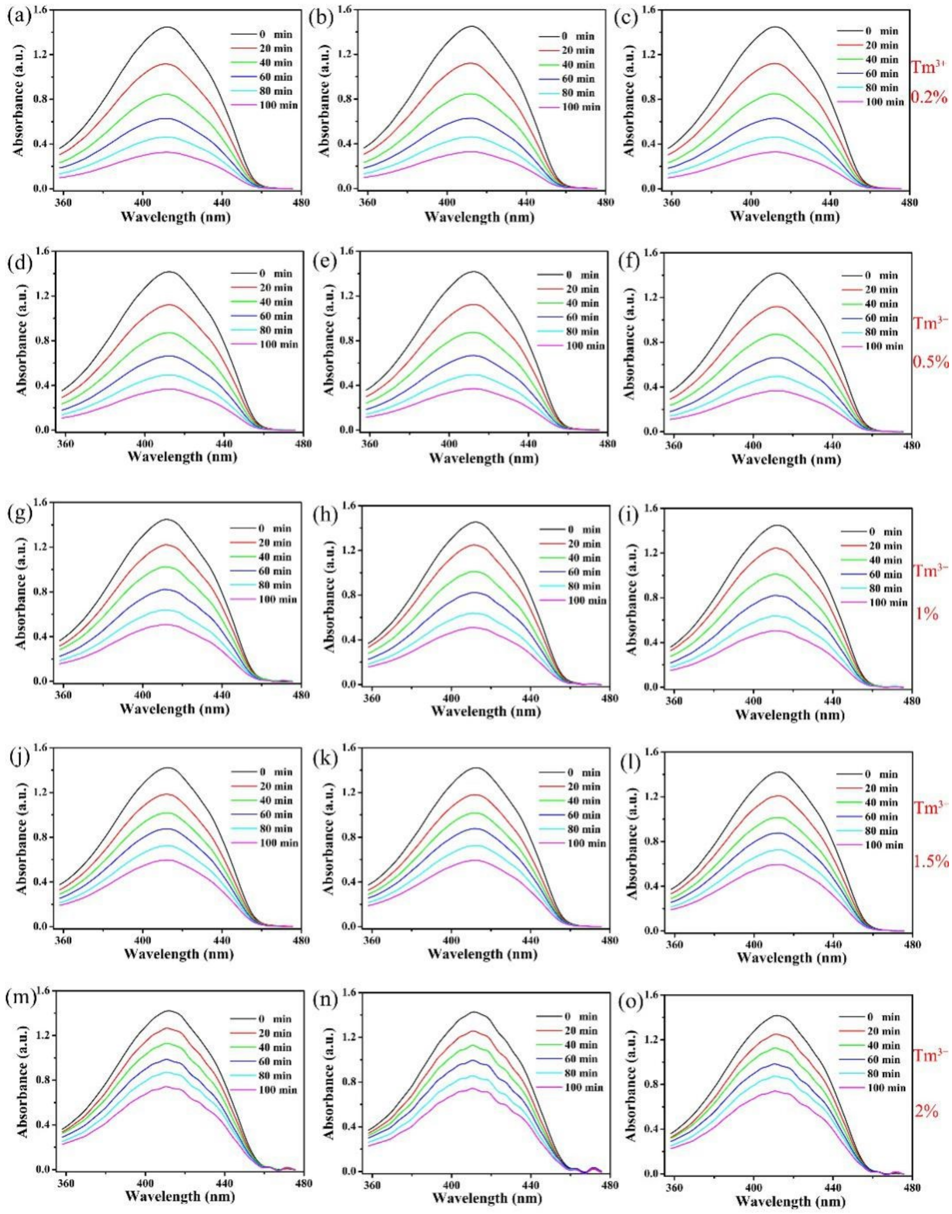

Figure S4. The 1,3-diphenylisobenzofuran (DPBF) absorbance spectra in solutions with $NaYb_{1-x}F_4:Tm^{3+}_x$ NPs.

(a),(b),(c) corresponding to Tm^{3+} concentration of 0.2%

(d),(e),(f) corresponding to Tm^{3+} concentration of 0.5%

(g),(h),(i) corresponding to Tm^{3+} concentration of 1%

(j),(k),(l) corresponding to Tm^{3+} concentration of 1.5%

(m),(n),(o) corresponding to Tm^{3+} concentration of 2%