

Electronic Supplementary Information (ESI) for

**Colloidal Synthesis and Blue Based Multicolor Upconversion Emissions of Size and Composition Controlled Monodisperse Hexagonal NaYF<sub>4</sub>:Yb,Tm Nanocrystals**

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**Table S1: Synthesis Conditions of Size-controlled Monodisperse  $\beta$ -NaYF<sub>4</sub>:Yb,Tm Nanocrystals**

| No. | Precursor (mmol)      |                                                        | Solvent (mmol) |    |     | Temp. (°C) | Time (min) | Product  |           |            |
|-----|-----------------------|--------------------------------------------------------|----------------|----|-----|------------|------------|----------|-----------|------------|
|     | CF <sub>3</sub> COONa | RE                                                     | OA             | OM | ODE |            |            | Phase    | Size (nm) | Shape      |
| 1   | 1                     | 1 (RE(CF <sub>3</sub> COO) <sub>3</sub> ) <sup>a</sup> | 10             | 10 | 20  | 300        | 30         | $\alpha$ | < 10      | polyhedral |
| 2   | 1                     | 1 ( $\alpha$ -NaYF <sub>4</sub> :Yb,Tm) <sup>b</sup>   | 20             | /  | 20  | 320        | 30         | $\beta$  | ~25       | sphere     |
| 3   | 1                     | 1 ( $\alpha$ -NaYF <sub>4</sub> :Yb,Tm) <sup>b</sup>   | 20             | /  | 20  | 320        | 45         | $\beta$  | ~50       | prism      |
| 4   | 1                     | 1 ( $\alpha$ -NaYF <sub>4</sub> :Yb,Tm) <sup>b</sup>   | 20             | /  | 20  | 330        | 45         | $\beta$  | ~150      | plate      |

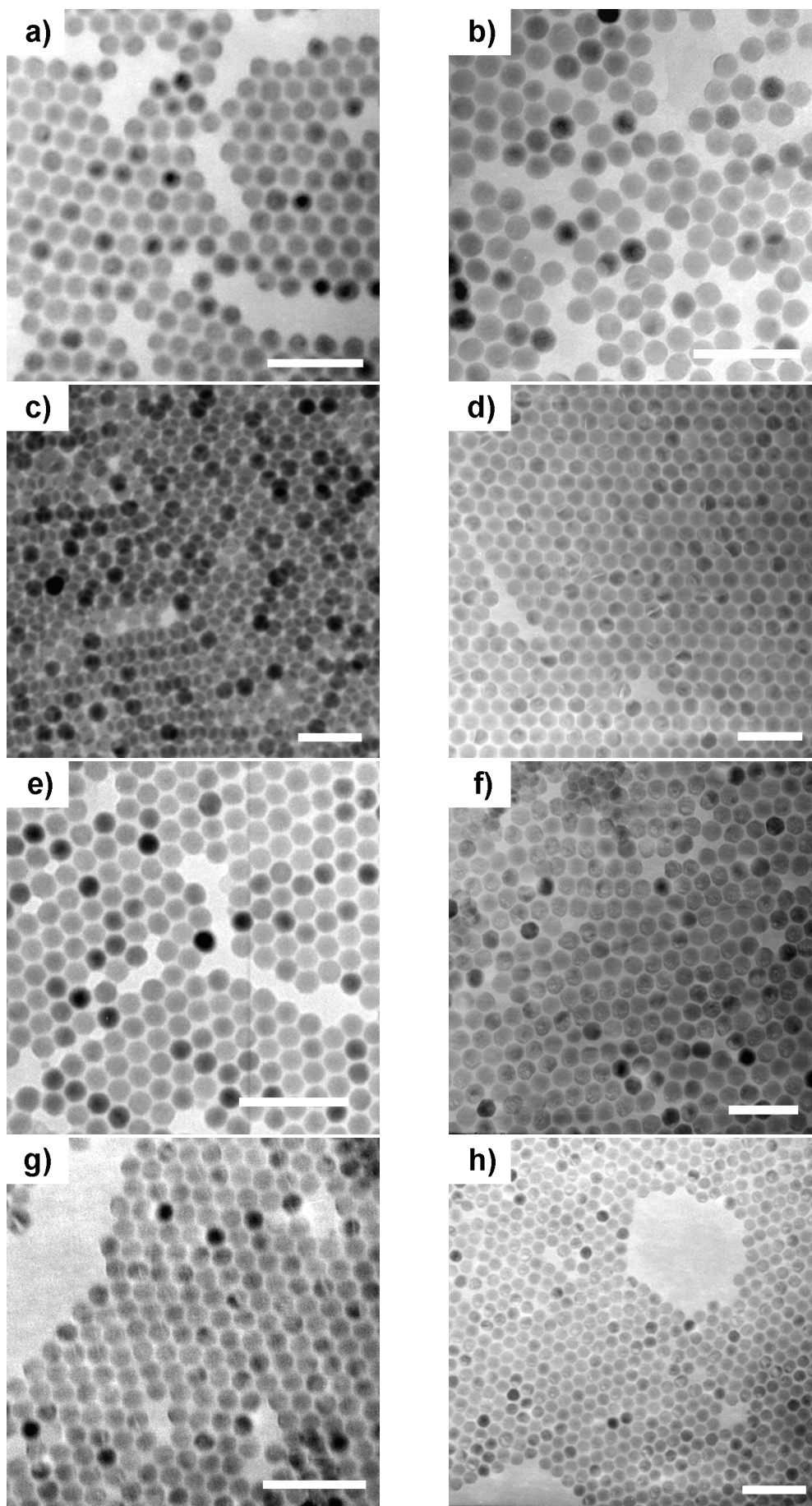
<sup>a</sup> Total amount of Y(CF<sub>3</sub>COO)<sub>3</sub>, Yb(CF<sub>3</sub>COO)<sub>3</sub>, and Tm(CF<sub>3</sub>COO)<sub>3</sub> with different molar ratios.

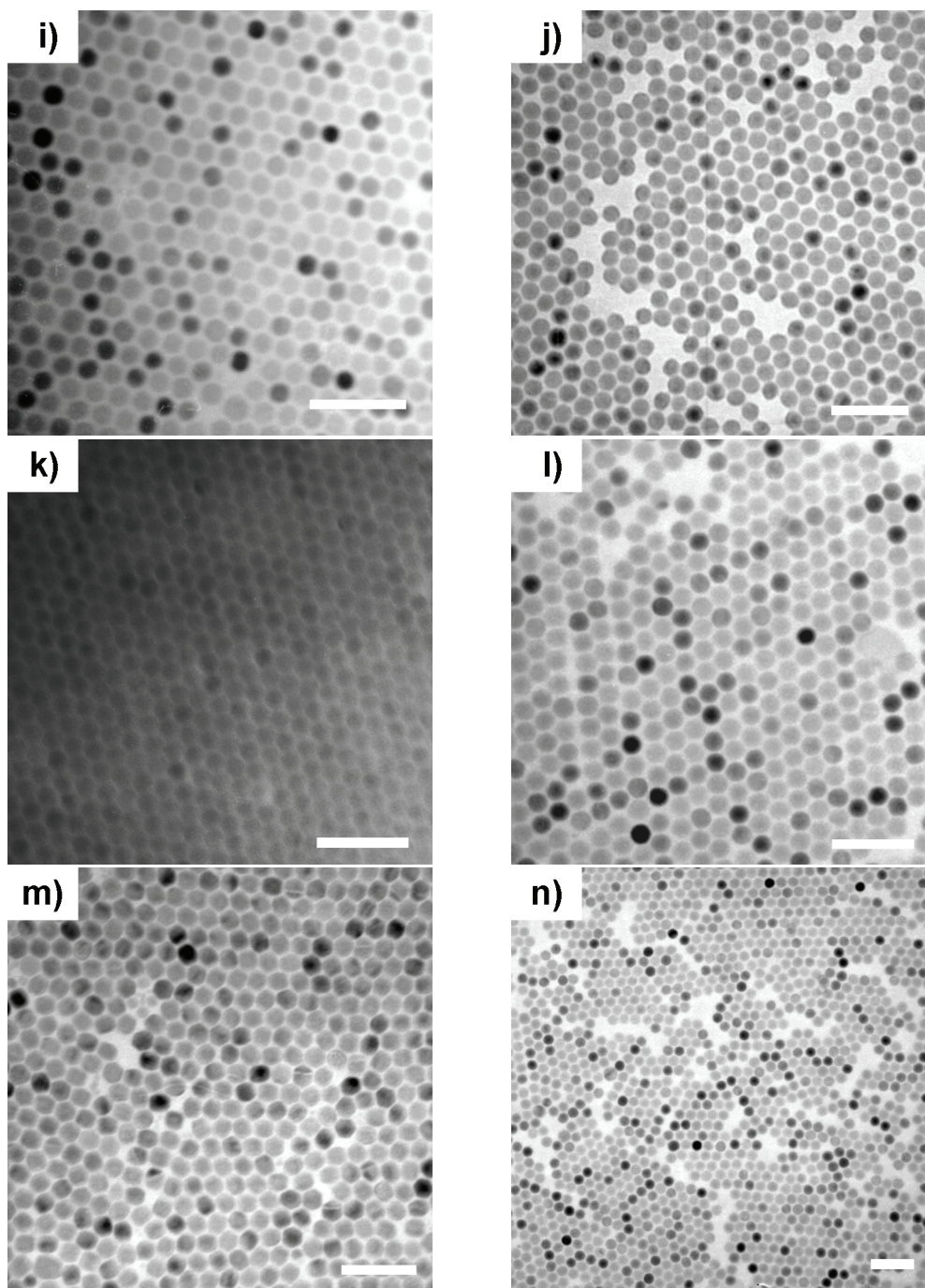
<sup>b</sup> 1 mmol as-prepared fresh  $\alpha$ -NaYF<sub>4</sub>:Yb,Tm nanocrystals with different doping concentrations of Yb<sup>3+</sup> and Tm<sup>3+</sup>.

**Table S2: EDS Analysis Results of Different Selected Areas of  $\beta$ -NaYF<sub>4</sub>:Yb,Tm Nanocrystals**

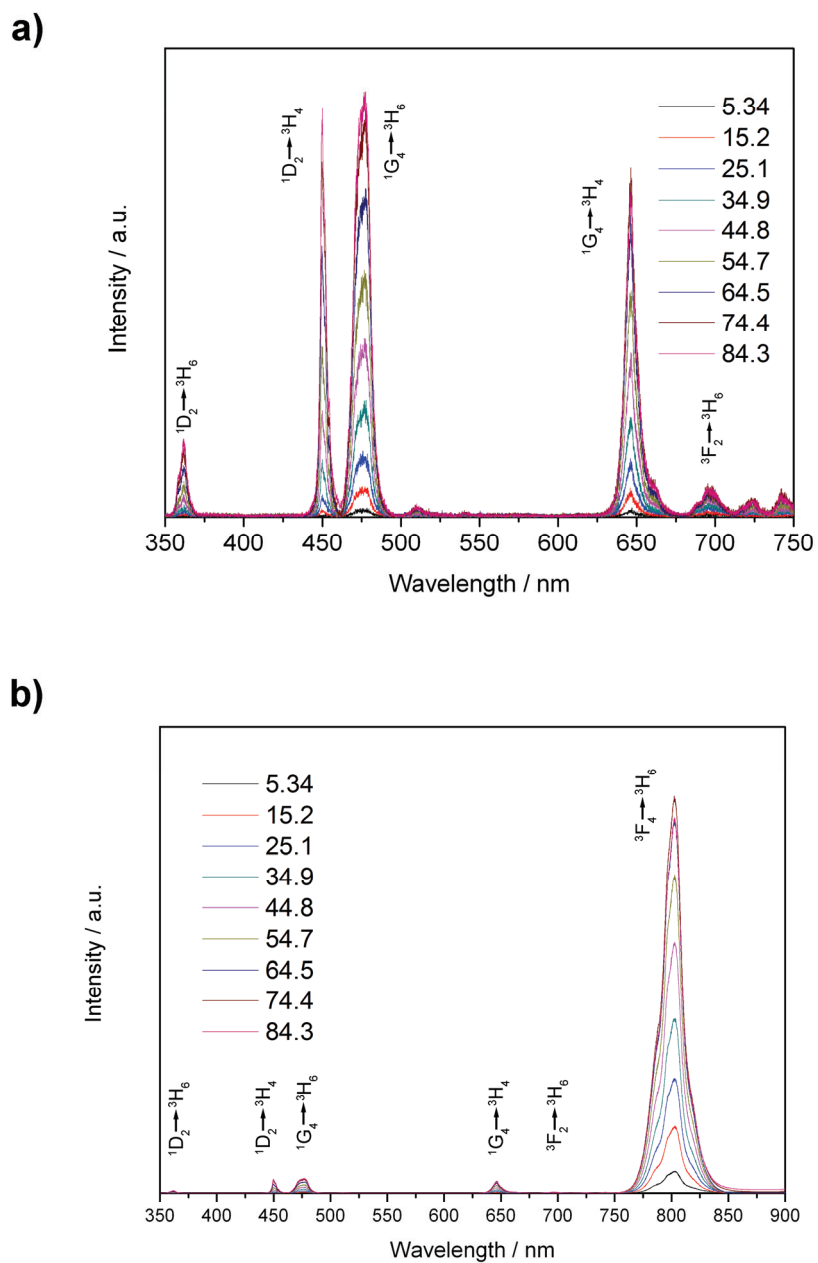
| No. | Molar ratio <sup>a</sup> |     | Size (nm)  | Area <sup>b</sup> | EDS results (atomic ratio) |      |       |
|-----|--------------------------|-----|------------|-------------------|----------------------------|------|-------|
|     | Yb%                      | Tm% |            |                   | Y%                         | Yb%  | Tm%   |
| 1   | 30                       | 0.5 | 23.9 ± 0.8 | a                 | 67.0                       | 32.4 | 0.6   |
|     |                          |     |            | b                 | 68.0                       | 32.0 | trace |
|     |                          |     |            | c                 | 69.6                       | 29.1 | 1.3   |
| 2   | 30                       | 0.5 | 47.3 ± 1.7 | a                 | 69.1                       | 29.7 | 1.2   |
|     |                          |     |            | b                 | 69.5                       | 30.6 | trace |
|     |                          |     |            | c                 | 69.4                       | 30.1 | 0.5   |
| 3   | 30                       | 0.5 | ~150 × 70  | a                 | 68.5                       | 31.0 | 0.5   |
|     |                          |     |            | b                 | 69.1                       | 30.2 | 0.7   |
|     |                          |     |            | c                 | 66.8                       | 32.5 | 0.7   |

<sup>a</sup> Molar ratio of reactants, <sup>b</sup> three independently selected areas on the copper grid for each sample.



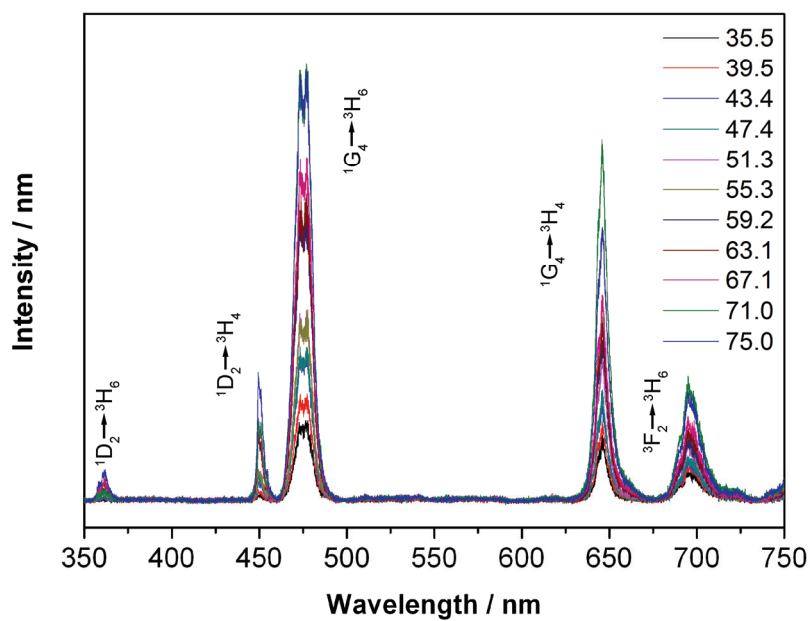


**Figure S1.** TEM images of as-prepared  $\beta$ -NaYF<sub>4</sub>:Yb,Tm nanocrystals with different concentrations of Yb and Tm. (a) – (d) 30% Yb, and 0.2/1/2%/5% Tm, respectively; (e) – (i) 20% Yb, and 0.2/0.5/1/2/5% Tm, respectively; (j) – (n) 40% Yb, and 0.2/0.5/1/2/5% Tm, respectively. The length of the white scale bar in these figures is 100 nm.

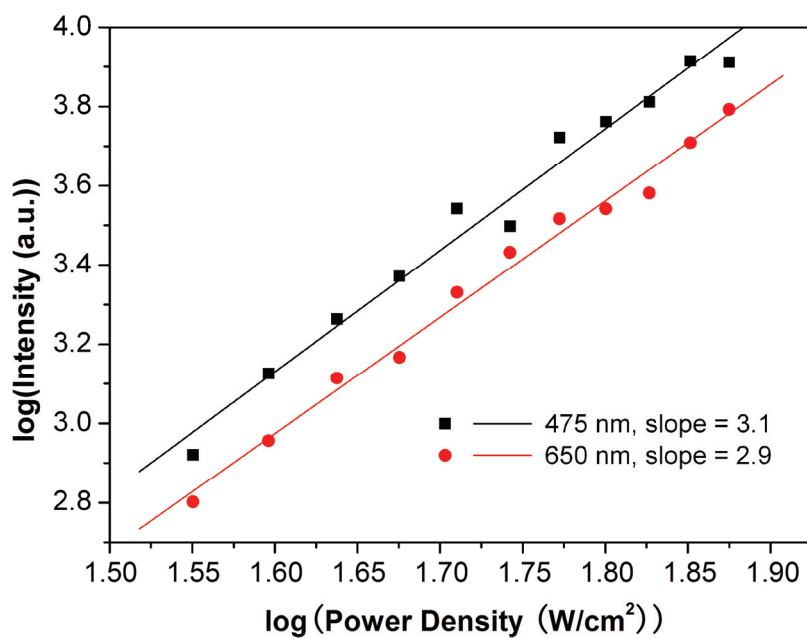


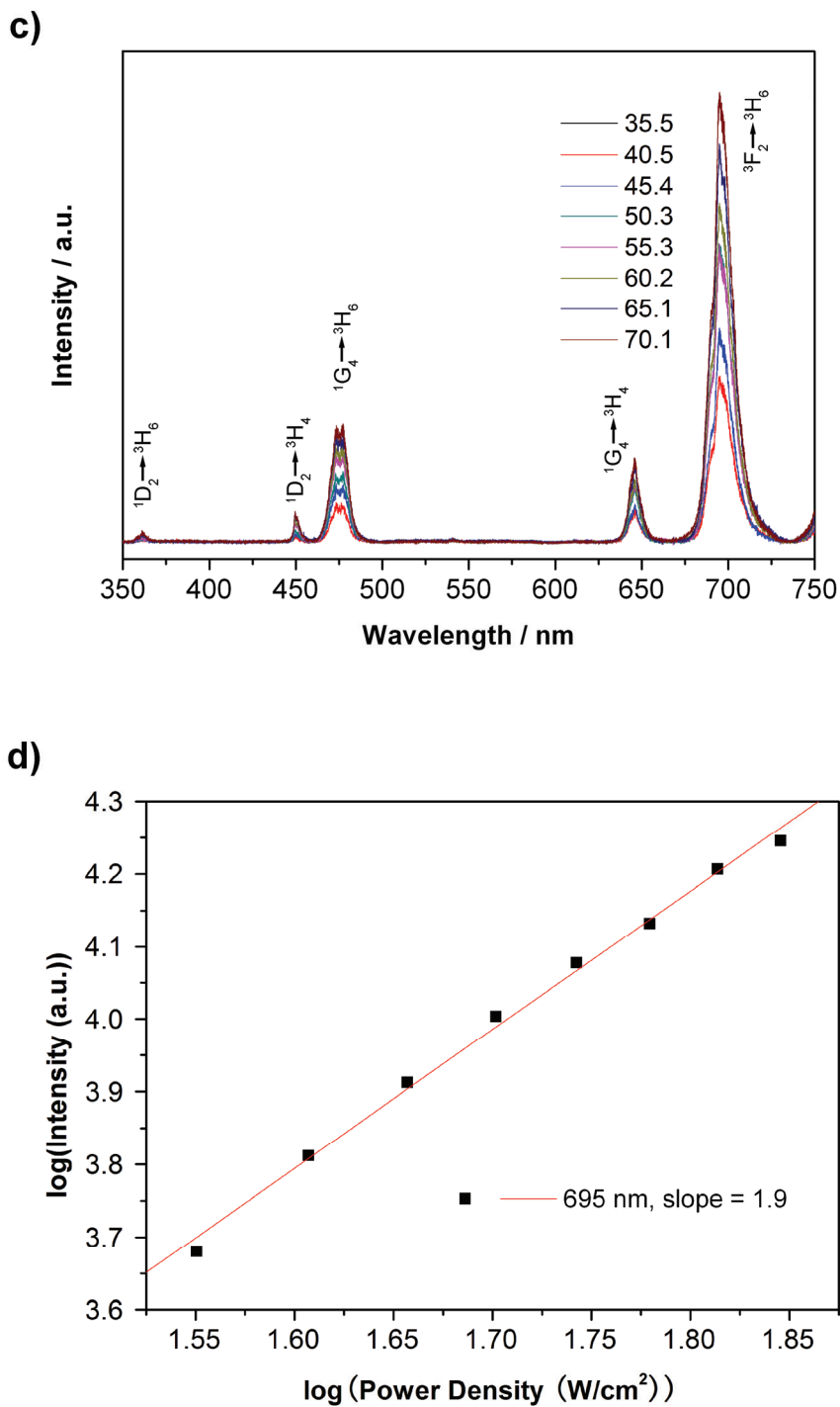
**Figure S2.** UC spectra of  $\beta$ -NaYF<sub>4</sub>:30%Yb,0.5%Tm nanoplates ( $\sim 150$  nm  $\times$   $\sim 70$  nm, Figure 1c) measured (a) from 350 to 750 nm, and (b) from 350 to 900 nm pumped by a 980 nm laser. The numbers in the figures are different power density values of the 980 nm CW diode laser.

a)

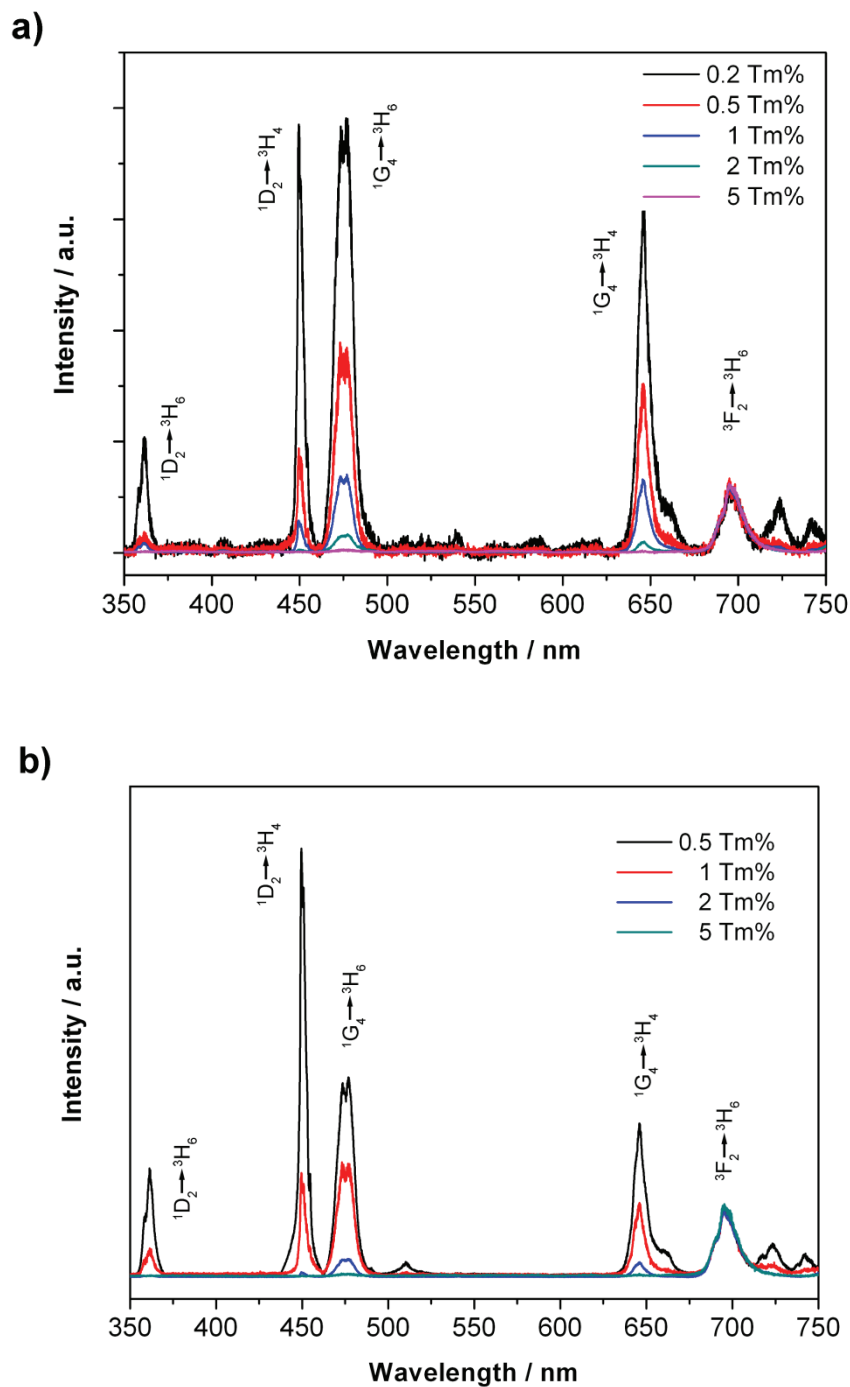


b)

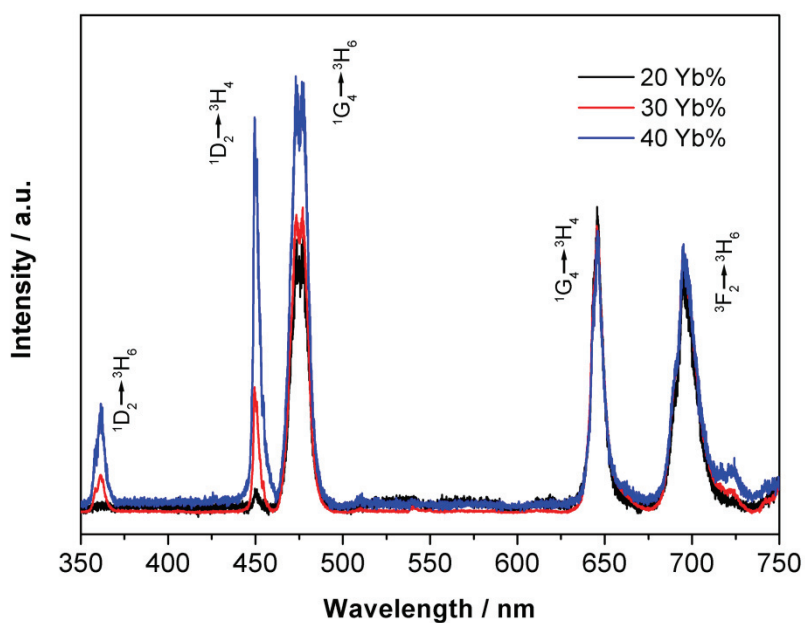




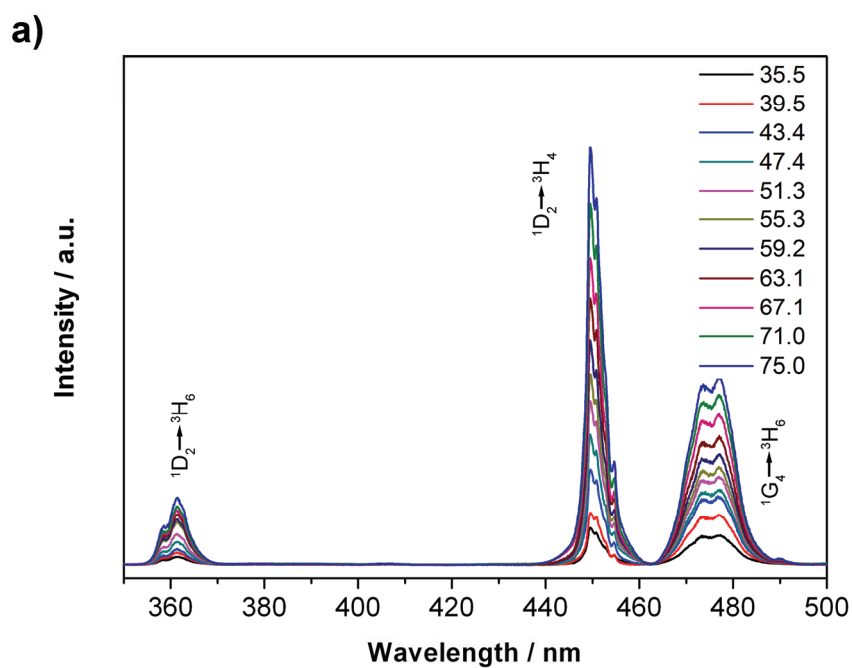
**Figure S3.** (a) UC spectra and (b) Intensity-Power curves (emissions at 475 and 650 nm) of  $\beta$ -NaYF<sub>4</sub>:20%Yb,0.5%Tm nanocrystal dispersion in cyclohexane (1 wt%;  $25.4 \pm 1.0$  nm). (c) UC spectra and (d) Intensity-Power curve (emission at 695 nm) of  $\beta$ -NaYF<sub>4</sub>:40%Yb,2%Tm nanocrystal dispersion in cyclohexane (1 wt%;  $25.2 \pm 0.9$  nm). The numbers in (a) and (c) are different power density values of the 980 nm CW diode laser.

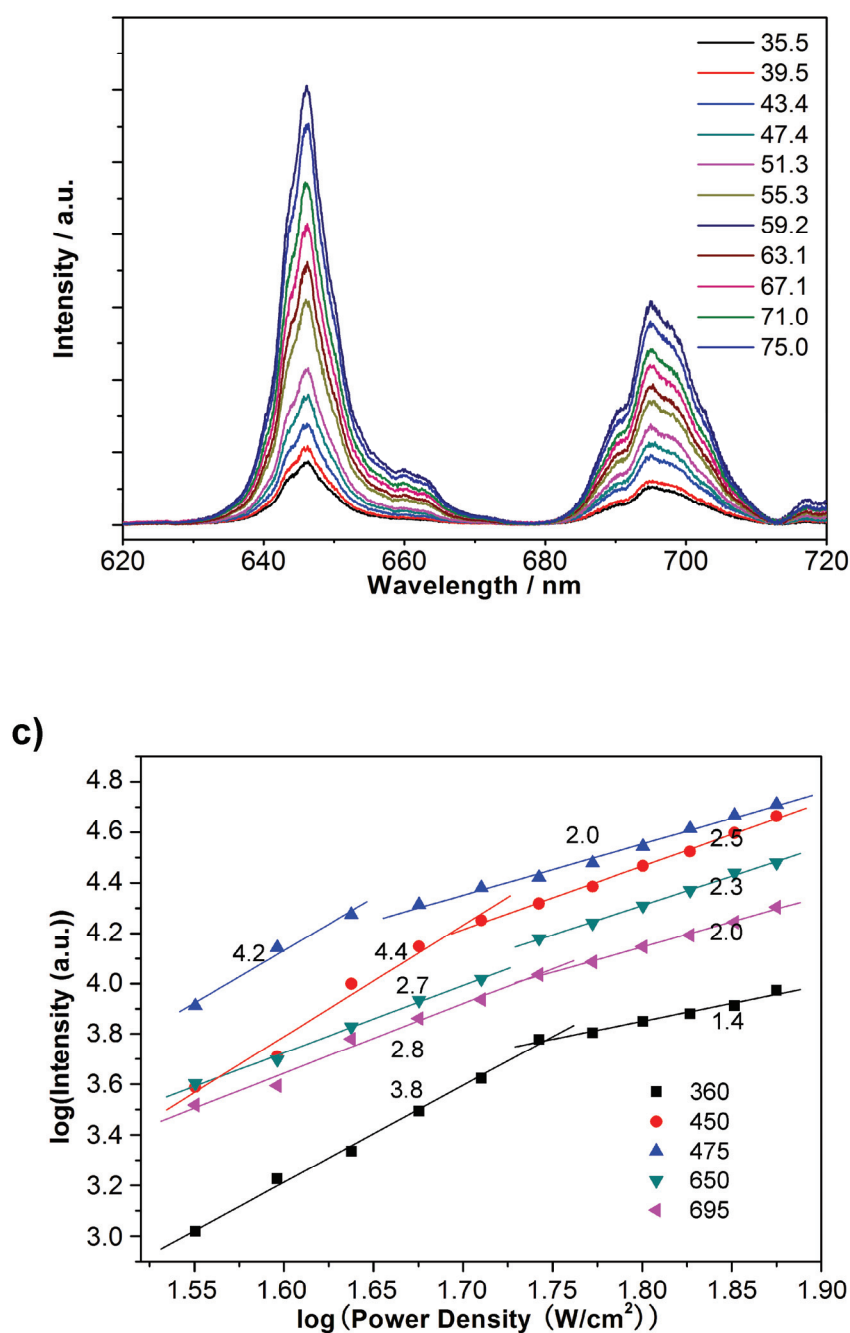


**Figure S4.** UC spectra of (a)  $\beta$ -NaYF<sub>4</sub>:30%Yb,0.2-5%Tm (~25 nm) and (b)  $\beta$ -NaYF<sub>4</sub>:40%Yb,0.5-5%Tm nanocrystal dispersions in cyclohexane (1 wt%; ~25 nm) pumped by a 980 nm laser. All spectra are normalized at the emission peak of ~695 nm.



**Figure S5.** UC spectra of  $\beta$ -NaYF<sub>4</sub>:20-40%Yb,1%Tm nanocrystal dispersion in cyclohexane (1 wt%; ~25 nm) normalized at the emission peak of ~650 nm pumped by a 980 nm laser.





**Figure S6.** UC spectra of  $\beta$ -NaYF<sub>4</sub>:20%Yb,0.5%Tm nanocrystal dispersions in cyclohexane (1 wt%;  $23.9 \pm 0.8$  nm) pumped by a 980 nm laser: (a) from 350 to 500 nm, and (b) from 620 to 720 nm, and (c) the calculated Intensity-Power curves of different UV-visible UC emissions. The numbers in (a) and (b) are different power density values of the 980 nm CW diode laser.