Electronic Supplementary Information for Nanoscale

## Rational morphology control of β-NaYF<sub>4</sub>:Yb,Er/Tm upconversion nanophosphors using ligand, additive, and lanthanide doping

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**Figure S1.** Large area TEM image of  $\beta$ -NaYF<sub>4</sub>:Yb,Er UCNRs (Scale bar = 200 nm).



**Figure S2.** (a, b) TEM images and (c) scanning electron microscopy (SEM) image of  $\beta$ -NaYF<sub>4</sub>:Yb,Er UCNPs synthesized with LnCl<sub>3</sub> instead of Ln(oleate)<sub>3</sub> as Ln precursors (Ln = Y, Yb, and Er). (d) HR-TEM image of the  $\beta$ -NaYF<sub>4</sub>:Yb,Er UCNPs (Inset shows FFT diffractogram for red frame). Scale bars represent 100 nm for panels (a) and (c), 20 nm for panel (b), and 5 nm for panel (d), respectively.



**Figure S3.** XRD patterns of  $\beta$ -NaYF<sub>4</sub>:Yb,Er UCNPs synthesized in (a) an ODE solvent (OA:ODE = 0:21) and (b) an OA solvent (OA:ODE = 21:0), respectively. Insets show corresponding TEM images. Scale bars indicate 20 nm. (\*: NaF)



**Figure S4.** XRD patterns of NaYF<sub>4</sub>:Yb,Tm UCNPs synthesized at various ratios of OA to ODE of (a) 2:19, (b) 6:15, (c) 15:6, and (d) 19:2, respectively.



**Figure S5.** HR-TEM image of a  $\beta$ -NaYF<sub>4</sub>:Yb,Tm UCNRs synthesized at various ratios of OA to ODE of (a) 15:6 and (b) 19:2.



**Figure S6.** HR-TEM image of a NaYF<sub>4</sub>:Yb,Er polyhedron synthesized with 3.0 mmol of Cl<sup>-</sup> ions.



**Figure S7.** PL spectra of  $\beta$ -NaYF<sub>4</sub>:Yb,Tm nanospheres and nanorods under the excitation of 980 nm. Insets show photographs showing upconversion blue luminescence from the  $\beta$ -NaYF<sub>4</sub>:Yb,Tm nanospheres and nanorods.



**Figure S8.** TEM images of  $\beta$ -NaYF<sub>4</sub>:Yb,Er,Gd UCNPs with varying Gd amount of (a) 0.4 mmol, (b) 0.6 mmol, and (c) 0.8 mmol (that is  $\beta$ -NaGdF<sub>4</sub>:Yb,Er), respectively. Scale bars represent 20 nm.



**Figure S9.** Transmittance spectrum of  $\beta$ -NaYF<sub>4</sub>:Yb,Er upconversion hexagonal prism (UCHP)-PDMS composite. Inset shows prepared UCHP-PDMS disk and bar under room light (left) and under NIR laser (right).



**Figure S10.** (a) Scanning electron microscopy image of micrometer-sized upconversion phosphor (mUCP) and (b) transmittance spectrum of mUCP-PDMS composite. Inset shows prepared mUCP-PDMS bar (left) and disk (right) under NIR laser. Scale bar represents 10  $\mu$ m.

| OA:ODE | shape  | size   | AR            |
|--------|--------|--|---------------|
| 2:19   | sphere | $22.4\pm0.9~\text{nm}$   | -             |
| 6:15   | sphere | $19.6\pm0.7~\text{nm}$   | -             |
| 15:6   | rod    | $L = 47.1 \pm 1.0 \text{ nm}$<br>$W = 22.4 \pm 0.9 \text{ nm}$ | 2.11 ± 0.09   |
| 19:2   | rod    | $L = 58.7 \pm 1.7 \text{ nm}$<br>$W = 23.8 \pm 1.1 \text{ nm}$ | $2.47\pm0.12$ |

Table S1. Shape, size, and aspect ratio (AR) of  $\beta$ -NaYF<sub>4</sub>:Yb,Tm UCNPs synthesized at various ratios of OA to ODE. (L: length and W: width)

Table S2. Shape, size, and aspect ratio (AR) of  $\beta$ -NaYF<sub>4</sub>:Yb,Er UCNPs with varying Cl<sup>-</sup> amount. (L: length and W: width)

| Cl <sup>-</sup> amount<br>(mmol) | shape             | size   | AR              |
|----------------------------------|-------------------|--|-----------------|
| 0                                | rod               | $L = 60.1 \pm 1.6 \text{ nm}$<br>$W = 21.5 \pm 0.9 \text{ nm}$ | $2.80\pm0.10$   |
| 2.5                              | hexagonal prism   | $L = 52.9 \pm 1.5 \text{ nm}$<br>$W = 35.1 \pm 2.3 \text{ nm}$ | $1.51\pm0.11$   |
| 2.7                              | hexagonal prism   | $L = 48.8 \pm 1.6 \text{ nm}$<br>$W = 44.0 \pm 2.8 \text{ nm}$ | $1.11 \pm 0.08$ |
| 3.0                              | sphere/polyhedron | $12.0 \pm 4.9 \text{ nm}$                                      | -               |

Table S3. Shape, size, and aspect ratio (AR) of  $\beta$ -NaYF<sub>4</sub>:Yb,Er,Ce UCNRs with varying Ce amount. (L: length and W: width)

| Ce amount<br>(mmol) | shape | size   | AR            |
|---------------------|-------|--|---------------|
| 0                   | rod   | $L = 60.1 \pm 1.6 \text{ nm} \\ W = 21.5 \pm 0.9 \text{ nm}$   | $2.80\pm0.10$ |
| 0.05                | rod   | $L = 49.0 \pm 1.7 \text{ nm}$<br>$W = 27.6 \pm 1.4 \text{ nm}$ | $1.78\pm0.09$ |
| 0.1                 | rod   | $L = 42.3 \pm 1.1 \text{ nm}$<br>$W = 29.8 \pm 1.3 \text{ nm}$ | $1.42\pm0.08$ |
| 0.15                | rod   | $L = 48.9 \pm 1.7 \text{ nm}$<br>$W = 38.6 \pm 1.8 \text{ nm}$ | $1.27\pm0.07$ |