# SUPPORTING INFORMATION

# Comprehensive Studies of Li<sup>+</sup> Effect on NaYF<sub>4</sub>:Yb/Er

### Nanocrystals: Morphology, Structure, and Upconversion

# Luminescence<sup>†</sup>

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#### Experimentation

**Preparation of lithium oleate (LiOA: 0.5 mol/L).** In a typical synthesis, LiOH (12.5 mmol) and oleic acid (25 mL) were added to a 100 mL flask, then the solution was heated to 150 °C for 1 h under argon atmosphere with vigorous stirring.

**Preparation of Li**<sub>x</sub>**Na**<sub>1-x</sub>**YF**<sub>4</sub>**:Yb/Er nanocrystals (LiOA as Li<sup>+</sup> source).** In a typical synthesis, RECl<sub>3</sub> (RE = Y, Yb, Er) were added by a molar ratio of 80:18:2 (in total 1 mmol) to a 100 mL flask containing oleic acid (7.5 mL) and 1-octadecence (17.5 mL). The solution was then heated to 150 °C for 30 min under argon atmosphere with vigorous stirring. After cooling to 40 °C, the methanol solution (10 mL) containing NH<sub>4</sub>F (4 mmol) and NaOH (2.5(1-x) mmol), and LiOA (2.5x mmol) were added into the mixture quickly and maintained for 30 min, after which the temperature was raised to 80 °C to remove the methanol. The reaction mixture was then heated to 300 °C for 1.5 h. Finally, the as-prepared nanoparticles were separated by centrifugation, washed by ethanol and deionized water, and stored in cyclohexane for testing.



**Fig. S1** HRTEM images of NaYF<sub>4</sub>:Yb/Er nanocrystals doped with different concentrations of Li<sup>+</sup>: (a) 0 mol%, (b) 10 mol%, (c) 40 mol%, (d) 100 mol%.



**Fig. S2** XRD signals of as-synthesized  $Li_xNa_{1-x}YF_4$ :Yb/Er nanocrystals using (a) LiOA and (b) LiOH as Li<sup>+</sup> sources, respectively. The standard diffraction patterns are: hexagonal NaYF<sub>4</sub> (red): JCPDS no. 16-0334, cubic NaYF<sub>4</sub> (yellow): JCPDS no. 06-0342, and tetragonal LiYF<sub>4</sub> (green): JCPDS no. 17-0874, respectively.



**Fig. S3** Intensity variation of the upconversion luminescence of  $Li_xNa_{1-x}YF_4$ :Yb/Er (x = 0-100 mol%) nanocrystals, after excluding the large size contribution The green line and red line represent the intensity in green region and red region, respectively.



Fig. S4 TEM images of  $Li_xNa_{1-x}YF_4$ : Yb/Er (x = 0-1 mol%) nanocrystals synthesized at extremely low  $Li^+$  doping concentrations.



**Fig. S5** Intensity variation of the upconversion luminescence of  $Li_xNa_{1-x}YF_4$ :Yb/Er (x = 0-1 mol%) nanocrystals, after excluding the large size contribution. The green and red lines represent the luminescence intensities in green and red regions, respectively.



**Fig. S6** (a) Surface area to volume ratio at different Li<sup>+</sup> doping concentrations. (b) Intensity variation of the upconversion luminescence of  $Li_xNa_{1-x}YF_4$ :Yb/Er (x = 0-1 mol%) nanocrystals before and after excluding the size contribution.



Fig. S7 Upconversion luminescence spectra of  $Li_xGd_{1-x}YF_4$ :Yb/Er (x = 0, 0.5 mol%) nanocrystals using continuous wave 980 nm diode laser as the excitation source.



**Fig. S8** Log-Log plots of the upconversion intensities of  $Li_xNa_{1-x}YF_4$ :Yb/Er ((18/2 mol%) nanocrystals at (a) x = 0.5, (b) 1, (c) 20, (d) 40, (e) 50, and (f) 100 mol%, respectively.



Fig. S9 Upconversion luminescence decay curves of  $Er^{3+}$  at (a) 540 nm, and (b) 654 nm.



**Fig. S10** Lifetime variation of  $Li_xNa_{1-x}YF_4$ :Yb/Er (x = 0-100 mol%) nanocrystals at different Li<sup>+</sup> doping concentrations.