**Supporting information for** 

# Chainlike Assembly of Oleic Acid-capped NaYF<sub>4</sub>:Yb,Er Nanoparticles and Their Fixing by Silica Encapsulation

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### Chemicals

All chemicals were obtained from commercial suppliers and used as received without further purification. Rare earth chlorides hexahydrate (LnCl<sub>3</sub>· $6H_2O$ ; Ln=Y, Yb, and Er, 99.99%), Oleic acid (OA, 90%), 1-octadecene (ODE, 90%), Tetraethyl orthosilicate (TEOS, 99.999%), and IGEPAL® CO-520 were purchased from Sigma-Aldrich. Ammonium fluoride (NH<sub>4</sub>F, 98%), Sodium hydroxide (NaOH), Ammonium hydroxide solution (28.0-30.0% NH<sub>3</sub> basis), acetone, ethanol (EtOH), methanol, and cyclohexane (CHX) were purchased from Sinopharm chemical reagent Co., Ltd.

#### Synthesis of OA-capped NaYF4:Yb,Er Nanoparticles by thermal decomposition

The hexagonal NaYF<sub>4</sub>:Yb(20 mol%),Er(2 mol%) nanoparticles were synthesized following a protocol that was reported previously.<sup>1</sup> Briefly, YCl<sub>3</sub>· $6H_2O$  (0.78 mmol), YbCl<sub>3</sub>· $6H_2O$  (0.2 mmol), ErCl<sub>3</sub>· $6H_2O$  (0.02 mmol), OA (6 mL), and ODE (15 mL) were mixed together in a 50 mL three-necked flask, and then the solution mixture was heated to 170°C under a gentle flow of Argon gas, forming a homogeneous solution of lanthanide oleate complexes. Thereafter, the solution was allowed to cool down to room temperature. Then a methanol solution (10 ml) containing NaOH (2.5 mmol) and NH<sub>4</sub>F (4 mmol) was slowly injected into the reaction flask and stirred for 30 min. The reaction solution was slowly heated to remove the methanol and excess water, degassed at 100°C for 10 min, subsequently heated to 300°C at a rate of 20 Kmin<sup>-1</sup>, and then kept at 300°C for 60 min under Argon protection. When the reaction was completed, the solution was allowed to cool down to room temperature naturally. The yield of the NaYF<sub>4</sub>:Yb,Er nanoparticles is ca. 3–5 mg/ml. The sample was stored and ready for the following experiments.

#### Chainlike assembly of OA-capped NaYF4:Yb,Er nanoparticles

0.1 mL of the as-synthesized NaYF<sub>4</sub>:Yb,Er nanoparticles were precipitated from the solution with acetone and washed with a mixture of EtOH and CHX (1:1 v/v) three times at a centrifugal speed of 8000 rpm. The nanoparticles were then redispersed in 2 mL of CHX at a reduced concentration. To initializing the assembly, a calculated amount of EtOH was added to the suspension of the nanoparticles. The volume ratio of EtOH:CHX was controlled at 1:6, 1:3, 1:2, and 1:1, respectively. Chainlike assembly of the nanoparticles was obtained at 1:6 of the EtOH:CHX ratio.

#### Silica encapsulation of the assemblies

The silica encapsulation was performed following a protocol reported previously.<sup>2</sup> Briefly, the assemblies were washed two times with the CHX and then redispersed into the original volume of CHX (0.1 mL). To the assembly solution, CO-520 (0.02 mL) and CHX (1 mL) were added, and then the solution mixture were stirred for 10 min. Subsequently, CO-520 (0.03 mL) and ammonia (9  $\mu$ L, 30 wt%) were added. The container was sealed and sonicated for 20 min until a transparent emulsion was formed. TEOS (4  $\mu$ L) was then added into the reaction solution, and the solution was gentally shaken for two days at a speed of 600 rpm. The resultant products were precipitated by adding acetone, washed with the mixture of EtOH and water (1:1 v/v) twice, and stored in EtOH.

#### Characterizations

The morphology of the as-synthesized NaYF<sub>4</sub>:Yb,Er nanoparticles, their assemblies, and silica-encapsulated assemblies were characterized by an FEI Quanta 200 scanning electron microscope (SEM) operated at 5 kV, and an FEI Tecnai G2-F20 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded using a Brucker D8 Advance X-ray powder diffractometer with Cu-K $\alpha$  (40 kV, 40 mA) radiation ( $\lambda = 1.5418$  Å). The 20 XRD spectra were recorded at a scanning rate of 12° min<sup>-1</sup>. Dynamic light scattering (DLS) measurements were performed on a particle size and zeta potential analyzer from Malvern (Zetasizer Nano ZS90).



Figure S1. The upconversion luminescence spectrum and image of the as-synthesized NaYF<sub>4</sub>:Yb,Er Nanoparticles



Figure S2. Severely aggregated NaYF<sub>4</sub>:Yb,Er Nanoparticles in pure EtOH.



Figure S3. (a-f) TEM images showing irregular chainlike assemblies.



Figure S4. The SEM image showing the chainlike structures remain almost unchanged after redispersing in CHX.



Figure S5. The SEM image showing silica-encapsulated chainlike nanoparticle assemblies in a large area.

## References

- 1. Z. Q. Li and Y. Zhang, *Nanotechnology*, 2008, **19**, 345606.
- 2. H. S. Qian, H. C. Guo, P. C. Ho, R. Mahendran and Y. Zhang, *Small*, 2009, 5, 2285.