Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supporting Information

Phase-tunable synthesis and upconversion photoluminescence of rare-earth-doped sodium scandium fluoride nanocrystals

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Experimental Section

Chemicals and materials

All chemicals were of analytical grade and were used without further purification. Ethanol and cyclohexane were purchased from Sino-pharm Chemical Reagent Co., China. $Na(CF_3COO)$, RE_2O_3, oleic acid (OA), 1-octadecene (ODE) and oleylamine (OM) were purchased from Alad din(China). $RE(CF_3COO)_3$ was prepared as reported.[1] Distilled water was used throughout.

Synthesis of RE doped Na_xScF_{3+x} NCs

In the case of the preparation of Na_xScF_{3+x}:20% Yb^{3+}/2% Er^{3+} NCs, 0.78 mmol $Sc(CF_3COO)_3$, 0.2 mmol $Yb(CF_3COO)_3$, 0.02 mmol $Er(CF_3COO)_3$ and stoichiometric amounts $Na(CF_3COO)$ were taken as the precursors and were added into 20 mL OA/OM/ODE in a three-necked flask at room temperature (RT). The obtained mixture was heated at 120 °C for 30 min under vigorous stirring in N_2 atmosphere to form a transparent solution. Thereafter, the solution was then heated to a a certain temperature in the range of 270-310 °C at a rate of 10 K min^{-1} and maintained at the given temperature for 30-60 min under N_2 atmosphere. After cooling this to RT, the resulting NCs were precipitated by addition of ethanol, collected via centrifugation, washed with ethanol several times and then dried at 60 °C overnight. The products can be easily redispersed in various nonpolar organic solvents, such as hexane, toluene, and cyclohexane.

Characterization

TEM and HRTEM measurements were carried out on an FEI transmission electron microscope at an operating voltage of 200 kV. The XRD measurement was performed on a Rigaku X-ray diffractometer with Cu-Ka radiation. The upconversion spectra were obtained by using a 980 nm laser diode. The emission attributed to the transitions between 400 and 900 nm was dispersed by a triple grating monochromator (Spectra Pro-2758, Acton Research Corporation, USA) equipped with a Photo-multiplier (Hamamatsu R928). The fluorescence images and photographs were obtained by a Panasonic FS25 camera. All of the measurements were performed at room temperature.

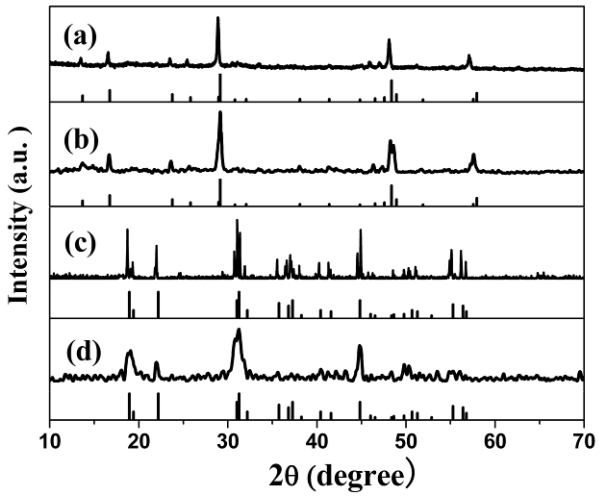

Fig. S1 XRD patterns of the Na_xScF_{3+x} :Yb^{3+}/Er^{3+} (20/2 mol %) NCs in the pure (a) (b) hexagonal, (c) (d) monoclinic phase and their corresponding standard peaks in the pure monoclinic and hexagonal phases, respectively. NCs obtained under (a) Na:Sc=1:1, OA/ODE (1:1) at 310 °C for 1h, (b) Na:Sc=1:1,OA/OM/ODE (1:2:2) at 310 °C for 1h, (c) Na:Sc=3:1, OA/ODE (1:1) at 310 °C for 1h and (d) Na:Sc=3:1,OA/OM/ODE (1:2:2) at 270 °C for 30 min.

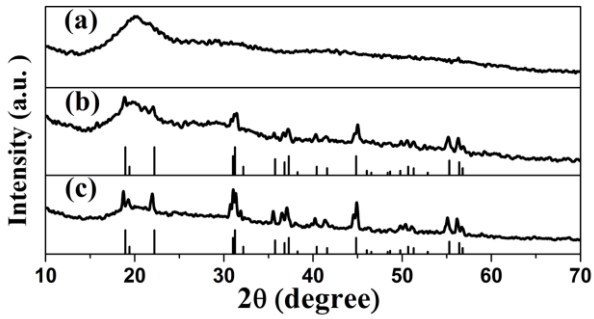

Fig. S2 XRD patterns of the Na_xScF_{3+x} :Yb^{3+}/Er^{3+} (20/2 mol %) NCs obtained under (a) Na:Sc=0.5:1, OA/ODE (1:1) at 300 °C for 1h, (b) Na:Sc=2:1,OA/ ODE (1:1) at 300 °C for 1h, (c) Na:Sc=4:1, OA/ODE (1:1) at 300 °C for 1h and their corresponding standard peaks in monoclinic phase.

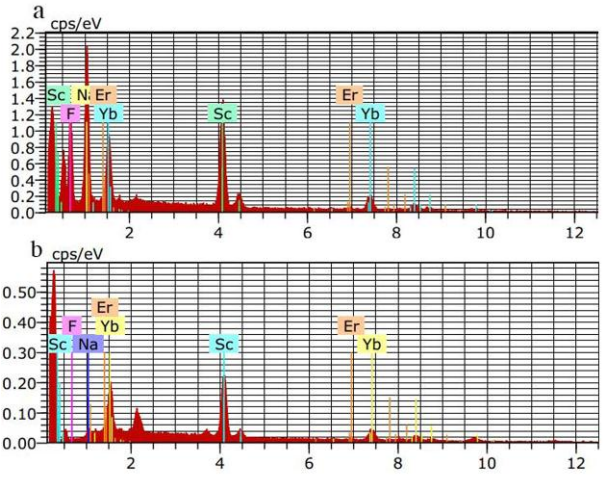

Fig. S3 EDX spectra of (a) Na_3ScF_6: Yb^{3+}/Er^{3+} and (b) $NaScF_4$:Yb^{3+}/Er^{3+} NCs.

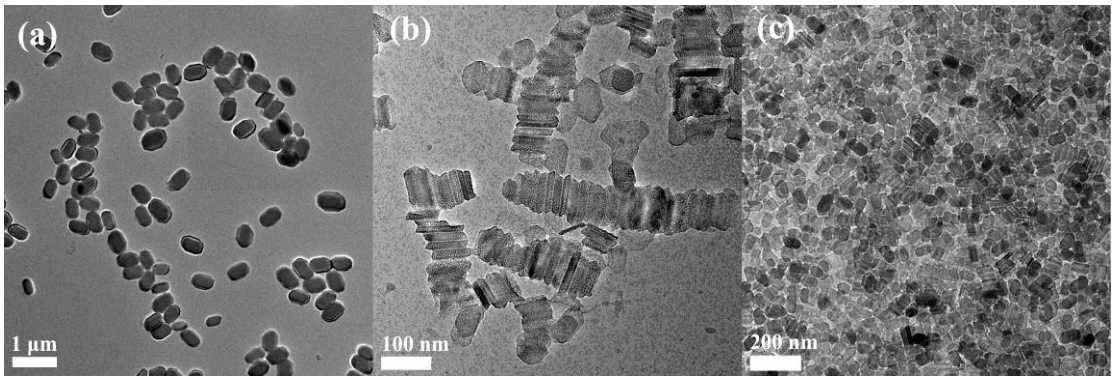

Fig. S4 TEM images of Na_3ScF_6 NCs obtained under (a) OA/ODE (1:1) at 310 °C for 1h, (b) OA/OM/ODE (1:2:2) at 300 °C for 1h and (c) OA/OM/ODE (1:2:2) at 310 °C for 1h.

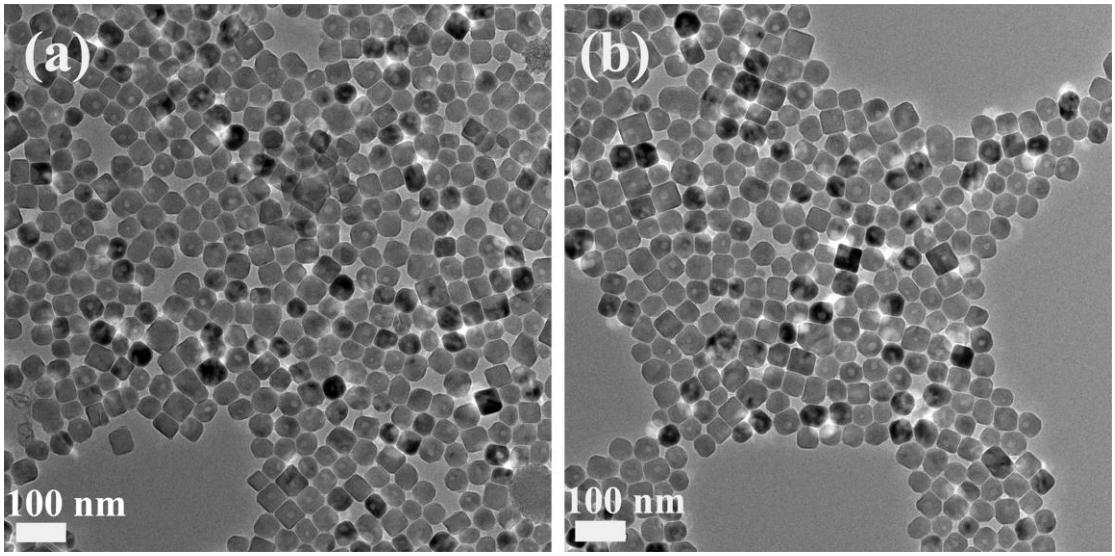

Fig. S5 TEM images of Yb^{3+}/Er^{3+}-doped $NaScF_4$ (a) and Na_3ScF_6 (b) NCs.

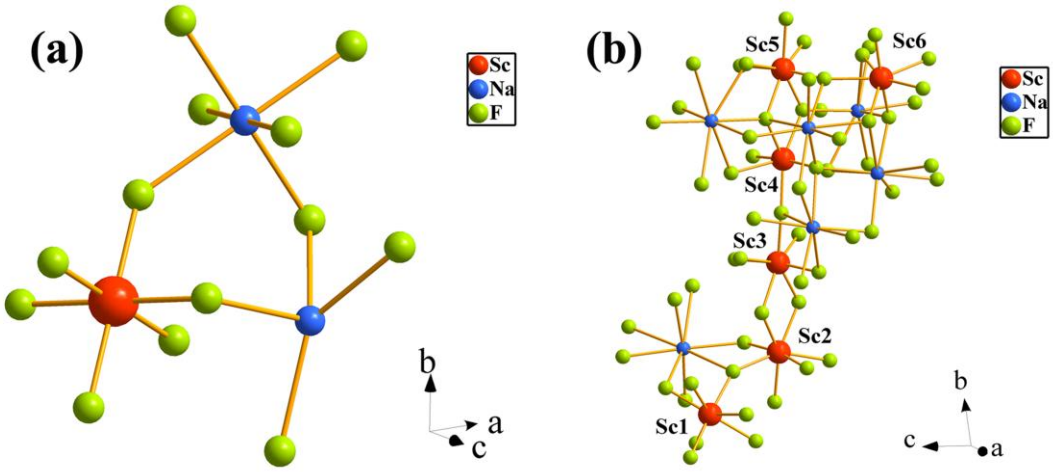

Fig. S6 The coordination environments of crystallographically unique Sc atoms in the asymmetric unit of monoclinic-phase Na_3ScF_6 (a) and hexagonal-phase $NaScF_4$ (b).

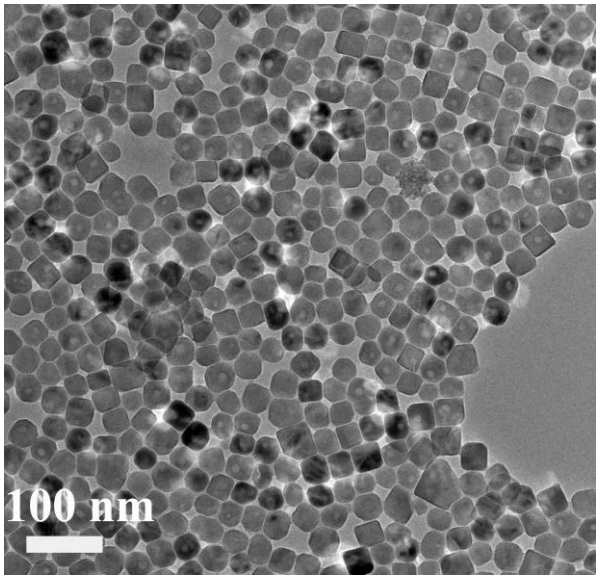

Fig. S7 TEM images of $NaScF_4$: Yb^{3+}/Er^{3+} (18/2 mol%) NCs.

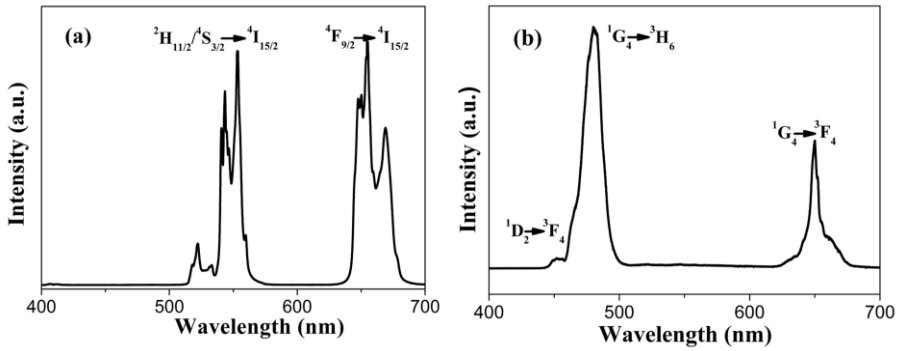

Fig. S8 UC luminescence spectra of hexagonal-phase (a) $NaScF_4$:Yb^{3+}/Er^{3+} (18/2 mol%) and (b) $NaScF_4$:Yb^{3+}/Tm^{3+} (18/0.2 mol%) NCs.

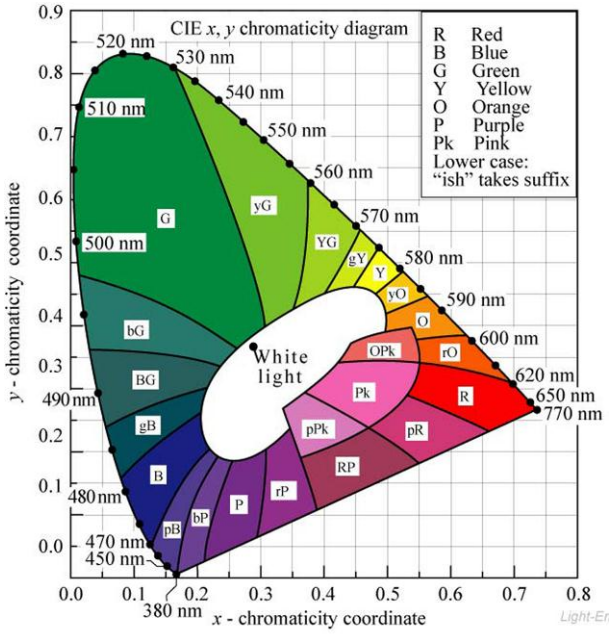

Fig. S9 The CIE color coordinate diagram for the white light luminescence when r = 10:5.

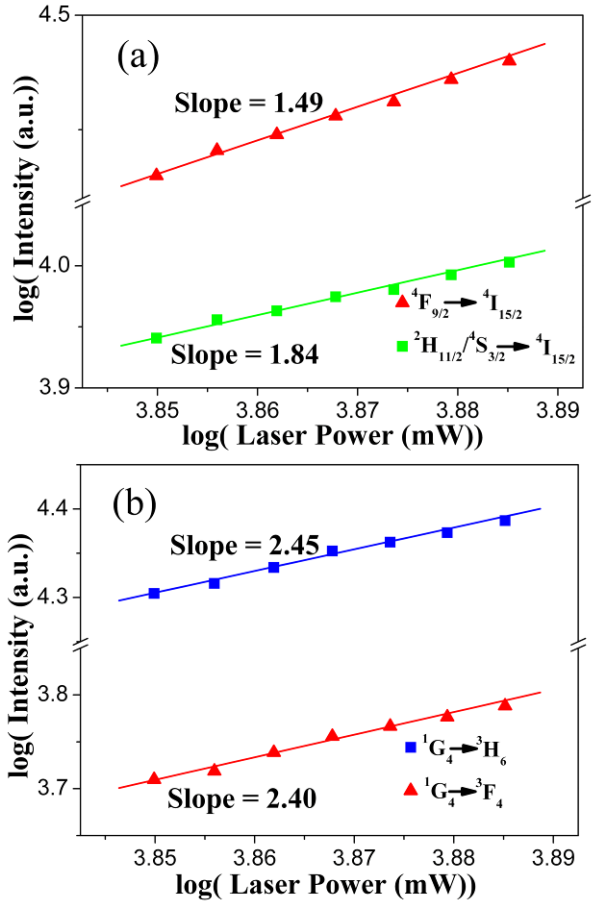

Fig. S10 Log–log plots of the UC emission intensity versus NIR excitation power density for (a) $NaScF_4$:Yb^{3+}/Er^{3+} and (b) $NaScF_4$:Yb^{3+}/Tm^{3+} NCs.

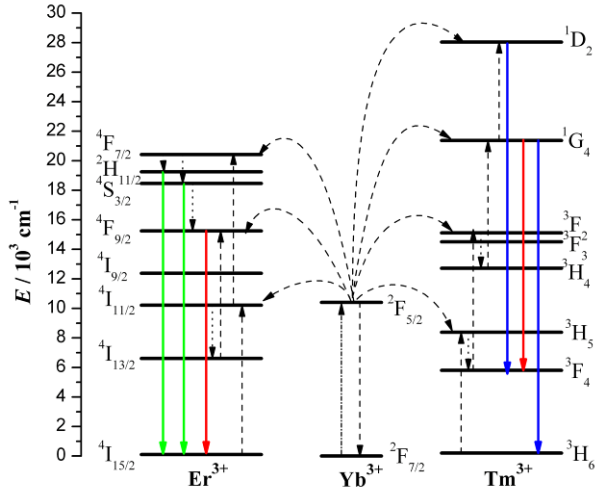

Fig. S11 UC energy transfer mechanisms of the as-prepared NCs.

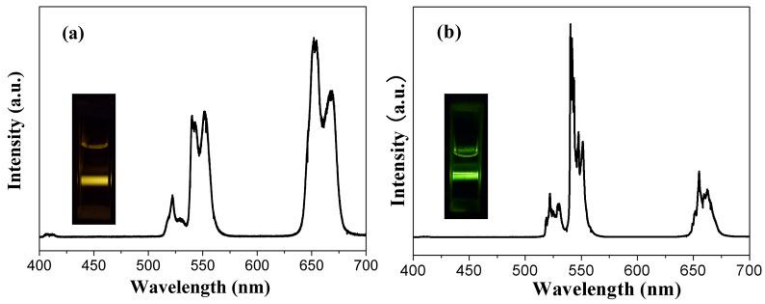

Fig. S12 UC luminescence spectra of hexagonal-phase (a) $NaScF_4:Yb^{3+}/Er^{3+}$ and (b) $NaYF_4:Yb^{3+}/Er^{3+}$ nanocrystals. The insets show corresponding PL photographs of nanoparticles dispersed in cyclohexane.

References

1 J. E. Roberts, *J. Am. Chem. Soc.*, 1961**, 83**, 1087