

Experimental details

Materials. $\text{LaCl}_3 \cdot x\text{H}_2\text{O}$ (99.99 %), $\text{PrCl}_3 \cdot x\text{H}_2\text{O}$ (99.99 %), $\text{NdCl}_3 \cdot x\text{H}_2\text{O}$ (99. 9 %), $\text{SmCl}_3 \cdot x\text{H}_2\text{O}$ (99.9 %), $\text{EuCl}_3 \cdot x\text{H}_2\text{O}$ (99. 9 %), $\text{GdCl}_3 \cdot x\text{H}_2\text{O}$ (99.99 %), $\text{TbCl}_3 \cdot x\text{H}_2\text{O}$ (99.9 %), $\text{DyCl}_3 \cdot x\text{H}_2\text{O}$ (99.9 %), $\text{YCl}_3 \cdot x\text{H}_2\text{O}$ (99.99 %), $\text{ErCl}_3 \cdot x\text{H}_2\text{O}$ (99.9 %), $\text{TmCl}_3 \cdot x\text{H}_2\text{O}$ (99.9 %), $\text{YbCl}_3 \cdot x\text{H}_2\text{O}$ (99.9 %) and $\text{LuCl}_3 \cdot x\text{H}_2\text{O}$ (99 %) are synthesized by dissolving corresponding rare earth oxides in hydrochloride solution and dried up by evaporation of water. $\text{Ce}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, (99.9 %) (Aladdin), $\text{LiOH} \cdot \text{H}_2\text{O}$ (99 %), ethylenediamine (98 %), 1,4-butanediamine (98 %), hydrofluoride solution (40 % w/w in water), NaOH (98+ %), NH_4F (98+ %), linoleic acid (LA)(80 %, Xuchang Yuanhua Biotechnology Co., Ltd, China), and oleic acid (OA) (90 %, Alfa Aesar) are used as starting materials without further purification. Ethylenediamine dihydrofluoride (EDADF) is synthesized by the neutralization reaction between ethylenediamine (EDA) and hydrofluoride with *CAUTION*.

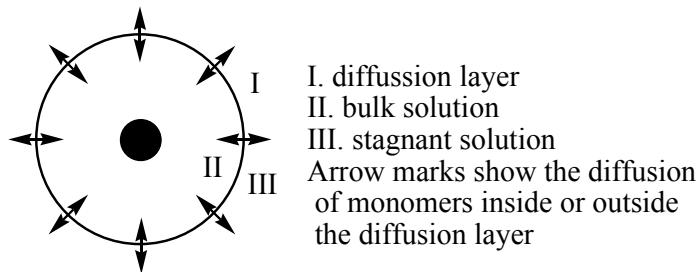
Synthesis of $\beta\text{-NaYF}_4$: Yb,Er and $\beta\text{-NaGdF}_4$:Yb,Er nanocrystals. In a typical hydrothermal synthesis, 2.5 mmol ethylenediamine (EDA) is mixed with 2 mL deionized water, 7.5 mL ethanol, and 2.25 mL linoleic acid (LA) by magnetic stirring for ten minutes. The water solution of 1.25 mmol NaNO_3 , 0.625 mmol (Y, Yb, Er) Cl_3 (20, 2 mol %) or (Gd, Yb, Er) Cl_3 dissolved in 1.5 mL deionized water is dropped in. After ten minutes, the water solution of 4mmol ethylenediamine dihydrofluoride (EDADF) dissolved in 4mL deionized water is also dropped in. After five minutes, the mixture is transferred into a 30 mL Teflon-lined autoclave. The autoclave is sealed and kept in oven for 2 hours at 120 °C. The molar ratio of EDA: LA: Na^+ : RE^{3+} : F^- is 2.5: 7.23: 1.25: 0.625: 8. $\beta\text{-NaYF}_4$: Yb,Tm (20, 0.5 mol %) and $\beta\text{-NaGdF}_4$: Yb,Tm (20, 0.5 mol %) nanocrystals are synthesized under the same conditions.

Synthesis of $\gamma\text{-REF}_3$ (RE = Eu-Tm, Y) and $(\text{C}_2\text{H}_{10}\text{N}_2)_{0.5}\text{RE}_3\text{F}_{10} \cdot x\text{H}_2\text{O}$ (RE = Ho-Lu, Y) nanocrystals. In a typical hydrothermal synthesis of $\gamma\text{-YF}_3$ nanocrystals, 5 mmol ethylenediamine (EDA) is mixed with 2 mL deionized water, 7.5 mL ethanol, and 4.5 mL linoleic acid (LA) by magnetic stirring for ten minutes. The water solution of 0.5 mmol YCl_3 dissolved in 1.5 mL deionized water is dropped in. After ten minutes, the water solution of 0.75 mmol ethylenediamine dihydrofluoride (EDADF) dissolved in 4 mL deionized water is also dropped in. After five minutes, the mixture is transferred into a 30 mL Teflon-lined autoclave. The autoclave is sealed and kept in oven for 10 hours at 120 °C. The molar ratio of EDA: LA: Y^{3+} : F^- is 5: 14.46: 0.5: 1.5. For Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , the molar ratio of EDA: LA: RE^{3+} : F^- is 2.5: 7.23: 0.625: 2. $(\text{C}_2\text{H}_{10}\text{N}_2)_{0.5}\text{Y}_3\text{F}_{10} \cdot x\text{H}_2\text{O}$ nanocrystals can be obtained, when the molar ratio of EDA: LA: Y^{3+} : F^- is selected as 2.5: 7.23: 0.625: 8. For Ho^{3+} , Yb^{3+} and Lu^{3+} , the molar ratio of EDA: LA: RE^{3+} : F^- is selected as 1.5: 7.23: 0.625: 2. For Er^{3+} and Tm^{3+} , the molar ratio of EDA: LA: Y^{3+} : F^- is selected as 2.5: 7.23: 0.625: 8.

Synthesis of hexagonal LiREF_4 nanocrystals. In a typical hydrothermal synthesis, 5.8 mmol $\text{LiOH} \cdot \text{H}_2\text{O}$ is mixed with 2 mL deionized water, 7.5 mL ethanol, and 4.5 mL linoleic acid (LA) by magnetic stirring for ten minutes. The water solution of 0.625 mmol YCl_3 and 0.05 g tetrabutylammonium bromide (TBAB) dissolved in 1.5 mL deionized water is dropped in. After ten minutes, the water solution of 2.5 mmol NH_4F dissolved in 1.25 mL deionized water is also dropped in. After five minutes, the mixture is transferred into a 30 mL Teflon-lined autoclave. The autoclave is sealed and kept in oven for 4 hours at 200 °C. The temperature for La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , and Tb^{3+} is 240 °C, while the temperature for Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , and Lu^{3+} is 200 °C.

Physical Characterization

XRD patterns are recorded with a Bruker D8 diffractometer using Cu K α radiation with 40 mA and 40 kV. Transmission electron microscope (TEM) and High resolution transmission electron microscope (HRTEM) is carried out on a JEOL JEM-2010F electron microscope operated at 200 kV. Field emission scanning electron microscopy (FESEM) is carried out on a Hitachi S4800 electron microscope. XPS experiment is carried out on a Perkin Elmer PHI-5000C ESCA system with Mg K α radiation ($\hbar\nu = 1253.6$ eV) under a base pressure of 10^{-9} Torr. ^1H NMR measurements are performed on a Bruker 400 MHz NMR spectrometer. Luminescence spectra including upconversion luminescent spectra measurements are carried out on an Edinburgh Instruments FLS920 phosphorimeter using a 450 W xenon lamp as excitation source.



Scheme S1 The presentation of the dynamic process of the nucleation and growth of colloidal nanocrystals

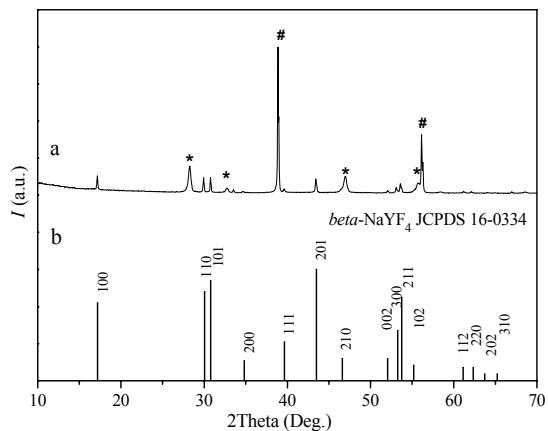


Figure S1 XRD patterns of NaYF_4 nanocrystals with EDA replaced by NaOH. a, XRD patterns of NaYF_4 nanocrystals obtained at $200\text{ }^\circ\text{C}$ for 3 hours. **b,** Standard pattern of $\beta\text{-NaYF}_4$ (JCPDS 16-0334). Diffraction peaks of $\alpha\text{-NaYF}_4$ (JCPDS 06-0342) are marked with asterisk, while those of NaF (JCPDS 36-1455) are marked with pound.

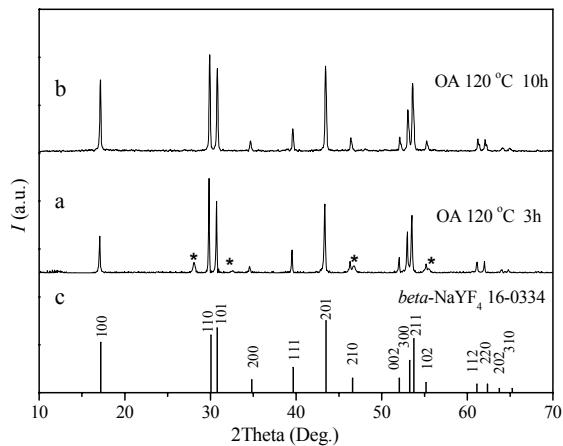


Figure S2 XRD patterns of NaYF_4 nanocrystals with LA replaced by OA. a, $120\text{ }^\circ\text{C}$ for 3 hours. **b,** $120\text{ }^\circ\text{C}$ for 10 hours. **c,** $\beta\text{-NaYF}_4$ (JCPDS 16-0334). Diffraction peaks of $\alpha\text{-NaYF}_4$ (JCPDS 06-0342) are marked with asterisk.

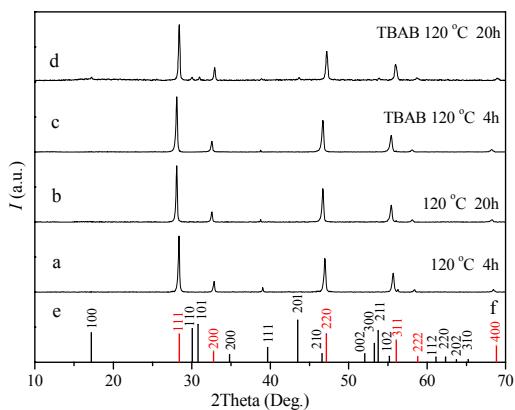


Figure S3 XRD patterns of NaYF₄ nanocrystals with or without TBAB in lower concentration of fluoride. **a**, 120 °C for 4 hours. **b**, 120 °C for 20 hours. **c**, 120 °C for 4 hours with 0.3 g TBAB. **d**, 120 °C for 20 hours with 0.3 g TBAB. **e**, β -NaYF₄ (JCPDS 16-0334). **f**, α -NaYF₄ (JCPDS 06-0342) in red lines. Molar ratio of EDA: LA: Na^+ : Y^{3+} : F⁻ is 2.5: 7.25: 1.25: 0.625: 3.

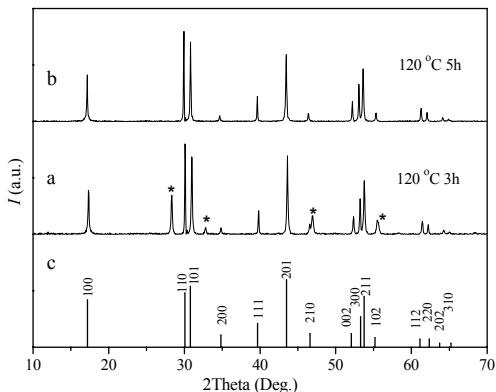


Figure S4 XRD patterns of NaYF₄ nanocrystals with lower concentration of sodium ion. **a**, 120 °C for 3 hours. **b**, 120 °C for 5 hours. **c**, β -NaYF₄ (JCPDS 16-0334). Molar ratio of EDA: LA: Na^+ : Y^{3+} : F⁻ is 2.5: 7.25: 0.625: 0.625: 8. Diffraction peaks of α -NaYF₄ (JCPDS 06-0342) are marked with asterisk.

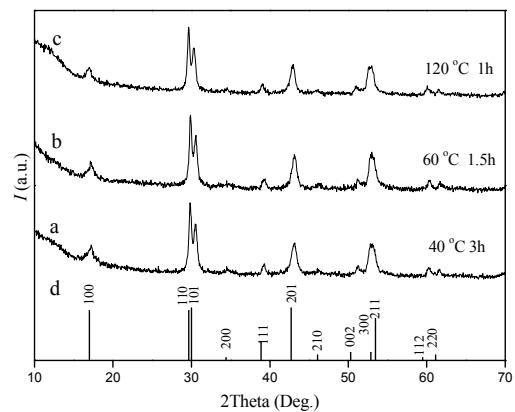
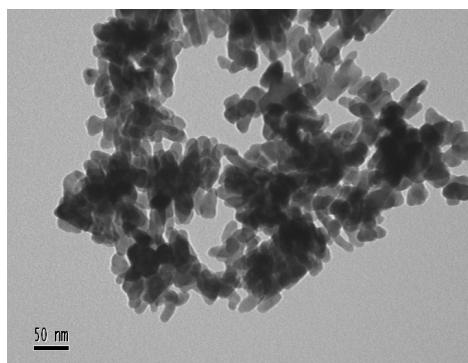
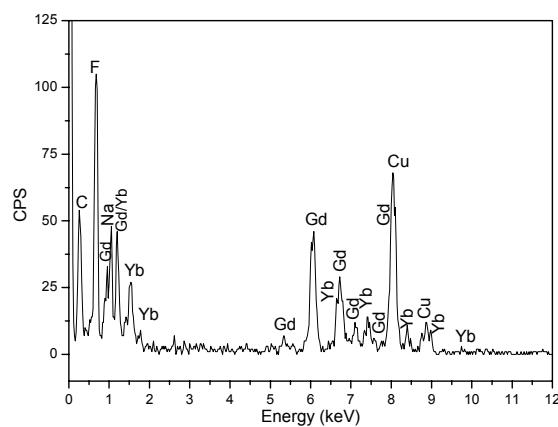


Figure S5 XRD patterns of β -NaGdYF₄: Yb,Tm (20, 0.5 mol %) nanocrystals obtained at different conditions. **a**, 40 °C for 3 hours. **b**, 60 °C for 1.5 hours. **c**, 120 °C for 1 hours. **d**, β -NaGdF₄ (JCPDS 27-0699).

a



b



c

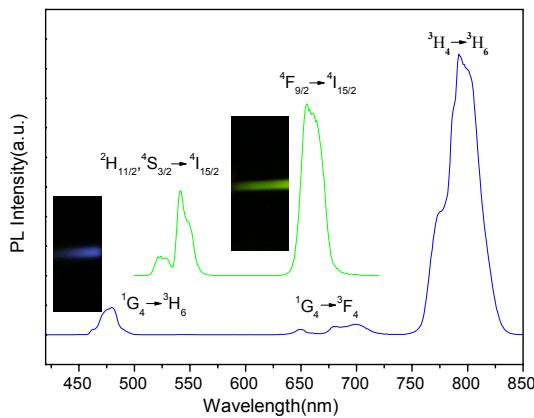
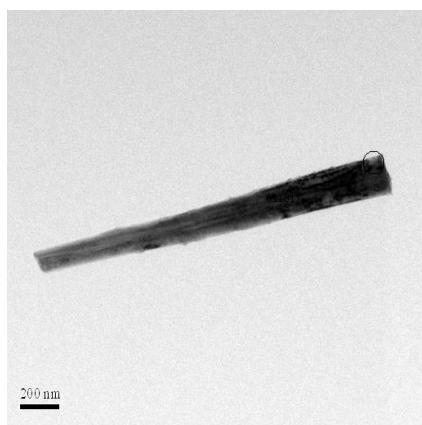


Figure S6 TEM characterization and upconversion luminescence of hexagonal NaGdF_4 : Yb, Er (20, 2 mol %) and NaGdF_4 :Yb,Tm (20, 0.5 mol %) nanocrystals. a, TEM image of $\beta\text{-NaGdF}_4$: Yb,Tm (20, 0.5 mol %) nanocrystal obtained at 120 °C for 1 hour. b, EDS of $\beta\text{-NaGdYF}_4$: Yb,Tm (20, 0.5 mol %) nanocrystals. Due to the low content of Tm element, there are no signals of it. Cu and carbon elements are coming from the holey carbon film coated Cu grid supporting sample during EDS measurements. c, Upconversion luminescence spectra of $\beta\text{-NaGdF}_4$: Yb, Er (20, 2 mol %) (green curve) and $\beta\text{-NaGdF}_4$:Yb,Tm (20, 0.5 mol %) (blue curve) nanocrystals excited with a 980-nm laser diode; power density of 500 $\text{W}\cdot\text{cm}^{-2}$). Insets are the photographs of the upconversion luminescence of 1 wt % solution of $\beta\text{-NaGdF}_4$: Yb, Er (20, 2 mol %) and $\beta\text{-NaGdF}_4$:Yb,Tm (20, 0.5 mol %) in cyclohexane (excited with a 980-nm laser diode; laser power of 1.5 W).

a



b

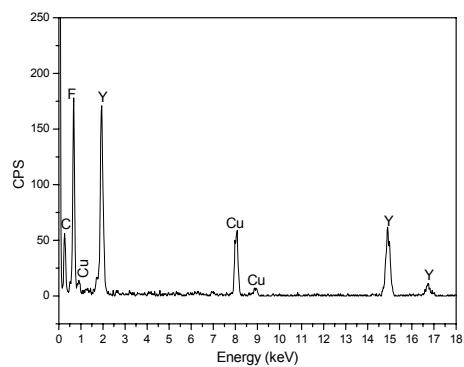


Figure S7 TEM characterization of γ -YF₃ nanocrystals. a, TEM image of γ -YF₃ nanocrystal. **b,** EDS of γ -YF₃ nanocrystal. Cu and carbon elements are coming from the holey carbon film coated Cu grid supporting sample during EDS measurements.

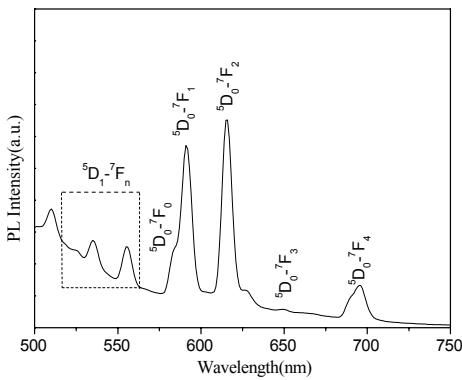


Figure S8 Fluorescence spectra of γ -YF₄: Eu (2 mol %) nanocrystals excited at 395 nm.

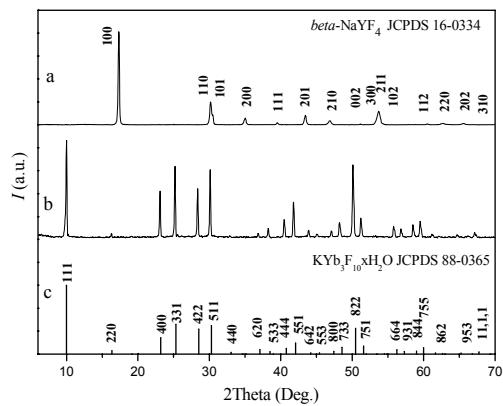


Figure S9 XRD characterization of γ - YF_3 nanocrystals and zeolitic new rare earth fluoride. a, XRD pattern of γ - YF_3 nanocrystals. Molar ratio of EDA: LA: Y^{3+} : F^- is 5: 14.5: 0.5: 1.5. **b,** XRD pattern of $(\text{C}_2\text{H}_{10}\text{N}_2)_{0.5}\text{Y}_3\text{F}_{10} \cdot \text{Yb},\text{Er} \cdot x\text{H}_2\text{O}$ (20, 2 mol %) nanocrystal. Molar ratio of EDA:LA:(Y^{3+} , Yb^{3+} , Er^{3+}): F^- is 5: 14.5: 0.5: 1.5.

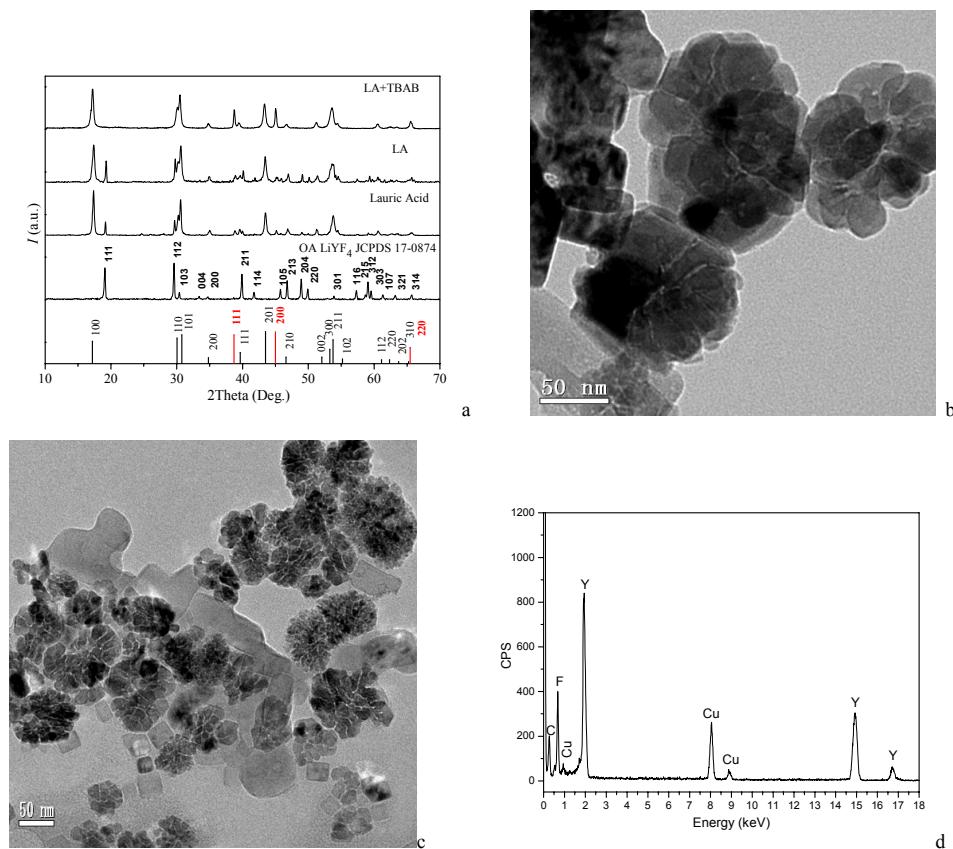


Figure S10 XRD and TEM characterization of hexagonal LiREF_4 nanocrystals. a, XRD patterns of hexagonal LiREF_4 nanocrystals at different conditions. Curves from upside to bottom, LA and TBAB, LA only, Lauric acid only, and OA only, respectively. Molar ratio of LiOH : Acid: Y^{3+} : F^- is maintained the same-5.8: 14.46: 0.625: 2.5. **b-c,** TEM images of hexagonal LiREF_4 nanocrystals obtained different amount of TBAB: 0.1g for **b** and 0.4 g for **c**. **d,** EDS of hexagonal LiREF_4 nanocrystal shown in **b**.

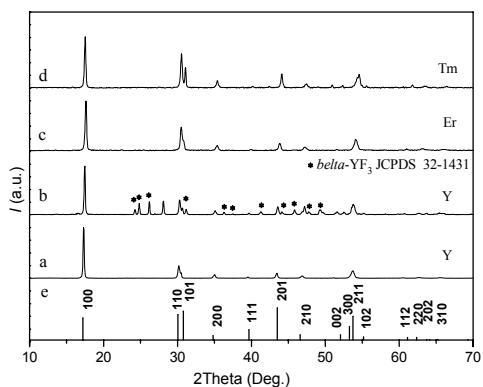


Figure S11 XRD characterization of γ -REF₃ nanocrystals. **a**, XRD pattern of γ -YF₃ nanocrystals obtained at 120 °C for 10 hours. Molar ratio of EDA: LA: Y³⁺: F⁻ is 5: 14.5: 0.5: 1.5. **b**, XRD pattern of γ -YF₃ nanocrystals obtained at 230 °C for 10 hours. Molar ratio of EDA: LA: Y³⁺: F⁻ is 5: 14.5: 0.5: 1.5.

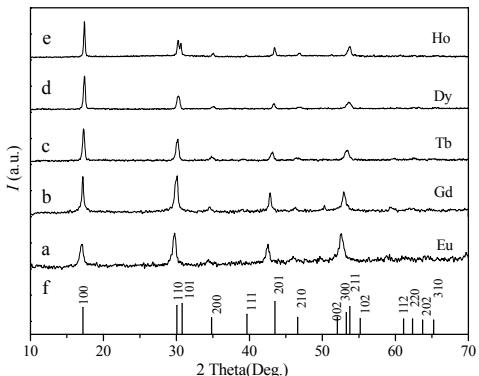


Figure S12 XRD patterns of γ -REF₃ nanocrystals. **a**, Eu³⁺. **b**, Gd³⁺. **c**, Tb³⁺. **d**, Dy³⁺. **e**, Ho³⁺. **f**, β -NaYF₄ (JCPDS 16-0334). Molar ratio of EDA: LA: RE³⁺: F⁻ is 2.5: 7.25: 0.625: 2.

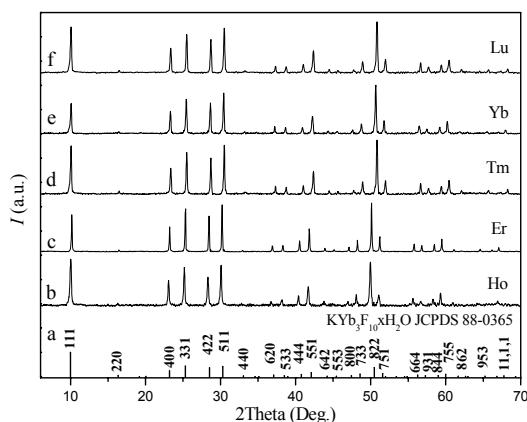


Figure S13 XRD characterization of (C₂H₁₀N₂)_{0.5}RE₃F₁₀·xH₂O nanocrystals.
a, δ -KYb₃F₁₀·xH₂O (JCPDS 88-0365). **b**, Ho³⁺. **c**, Er³⁺. **d**, Tm³⁺. **e**, Yb³⁺. **f**, Lu³⁺.

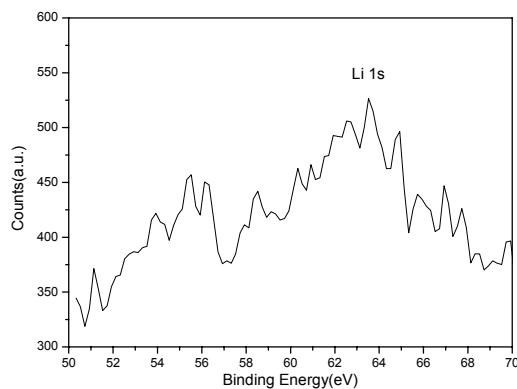


Figure S14 XPS spectra of hexagonal LiGdF₄ nanocrystals. XPS spectra of hexagonal LiGdF₄ nanocrystals.

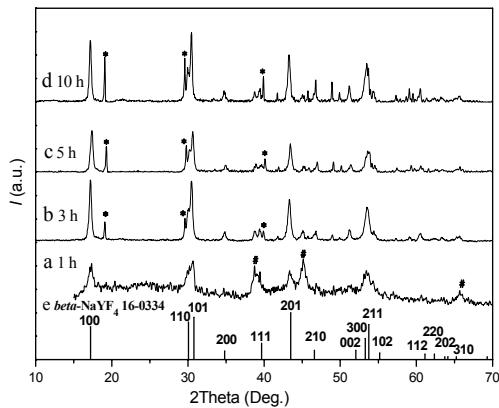


Figure S15 XRD patterns hexagonal LiYF₄ nanocrystals obtained at 200 °C for different time. **a**, 1 hour. **b**, 3 hours. **c**, 5 hours. **d**, 10 hours. **e**, β-NaYF₄ (JCPDS 16-0334). Diffraction peaks of tetragonal LiYF₄ (JCPDS 17-0874) are marked out with asterisk, while those of LiF (JCPDS 45-1460) are marked with pond.

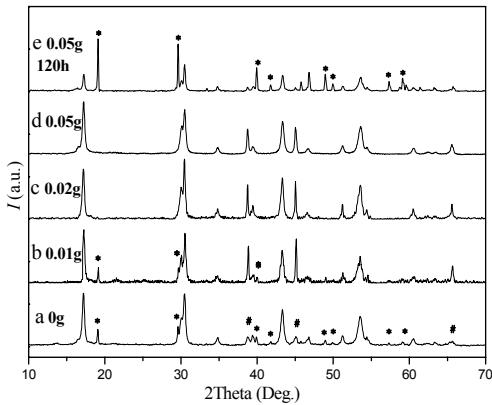


Figure S16 XRD patterns of hexagonal LiYF₄ nanocrystals obtained at 200 °C with different amount of TBAB. **a-d**, XRD patterns of hexagonal LiYF₄ nanocrystals at 200 °C for 4 hours without or with 0.01, 0.02, and 0.05 g TBAB, respectively. **e**, XRD patterns of hexagonal LiYF₄ nanocrystals at 200 °C for 120 hours with 0.05 g TBAB. Diffraction peaks of tetragonal LiYF₄ (JCPDS 17-0874) are marked out with asterisk, while those of LiF (JCPDS 45-1460) are marked with pond.

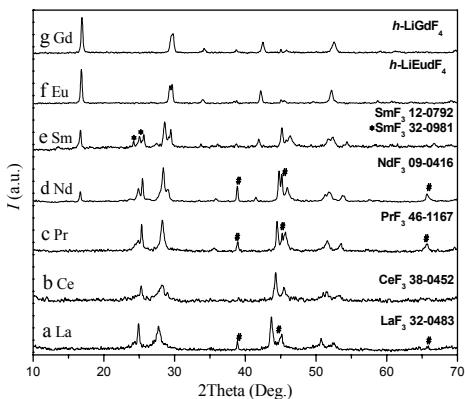


Figure S17 XRD patterns of hexagonal LiREF₄ nanocrystals. **a**, La³⁺. **b**, Ce³⁺. **c**, Pr³⁺. **d**, Nd³⁺. **e**, Sm³⁺. **f**, Eu³⁺. **g**, Gd³⁺. XRD patterns of hexagonal LiYF₄ nanocrystals at 200 °C for 120 hours with 0.05 g TBAB. Diffraction peaks of LiF (JCPDS 45-1460) are marked with pond.

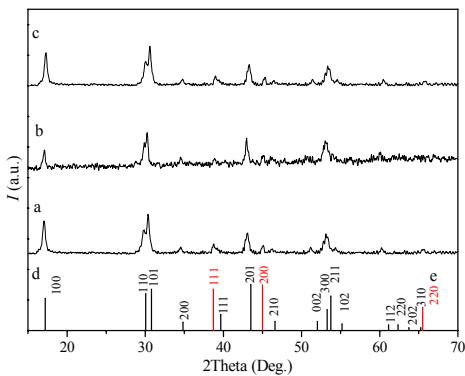


Figure S18 XRD patterns of hexagonal LiREF₄ nanocrystals. **a**, Tb³⁺. **b**, Dy³⁺. **c**, Ho³⁺. **d**, β-NaYF₄ (JCPDS 16-0334). **e**, LiF JCPDS 45-1460 red line.

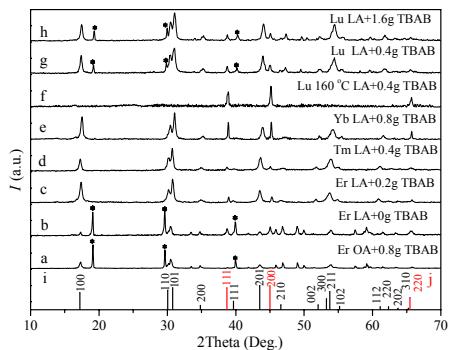


Figure S19 XRD patterns of hexagonal LiREF₄ nanocrystals obtained at 200 °C for 4 hours. **a**, Er³⁺ OA with 0.8 g TBAB. **b**, Er³⁺ LA without TBAB. **c**, Er³⁺ LA with 0.2 g TBAB. **d**, Tm³⁺. **e**, Yb³⁺. **f**, Lu³⁺ 160 °C LA with 0.4 g. **g**, Lu³⁺ LA with 0.4 g TBAB. **h**, Lu³⁺ LA with 1.6 g TBAB. **i**, β-NaYF₄ (JCPDS 16-0334). **j**, LiF JCPDS 45-1460 red line. Diffraction peaks of tetragonal LiREF₄ are marked with asterisk.

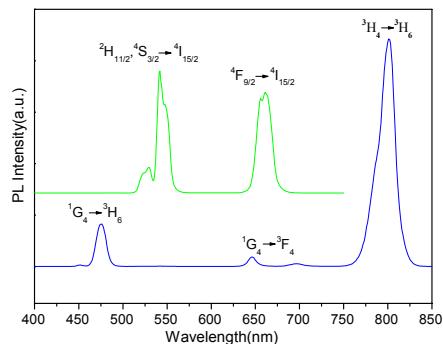


Figure S20 Upconversion luminescence spectra of hexagonal LiYF₄: Yb, Er (20, 2 mol %) (green curve) and hexagonal LiYF₄: Yb, Tm (20, 0.5 mol %) (blue curve) nanocrystals excited with a 980-nm laser diode. 2 wt % solution of hexagonal LiYF₄: Yb, Er (20, 2 mol %) and hexagonal LiYF₄: Yb, Tm (20, 0.5 mol %) nanocrystals dispersed in cyclohexane is excited by power density of 600 W·cm⁻².