Electronic Supplementary Information

Intrinsic Single-band Upconversion Emission in Colloidal Yb/Er(Tm): $Na_3Zr(Hf)F_7$ Nanocrystals

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EXPERIMENTAL PROCEDURES

Materials: All chemicals were of analytical grade and were used as received without further purification. Deionized water was used throughout. $ZrOCl_2 \cdot 8H_2O$, $Ln(NO_3)_3 \cdot 6H_2O$ (Ln=La-Lu), $LnCl_3 \cdot 6H_2O$, sodium oleate (NaOA), cyclohexane, ethanol, NaOH and NH_4F were all supplied by Sinopharm Chemical Reagent Company. $HfOCl_2 \cdot 8H_2O$, oleic acid (OA) 1-octadecence (ODE), and oleylamine (OM) were purchased from Aladdin Chemical Reagent Company.

Synthesis of lanthanide-doped Na_3MF_7 (M=Zr, Hf) NCs: In a typical procedure, 40 mL ethanol solution (0.0125 mol/L) containing $MOCl_2 \cdot 8H_2O$ (M=Zr, Hf) and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln=La-Lu) was mixed with oleic acid (25 mL), oleylamine (5 mL) and NaOA (2.5 g) under thorough stirring. Then, 1mL NH_4F (3.0 mol/L) aqueous solution was dropwise added to the mixture. After vigorous stirring at room temperature for about 30 min, the colloidal solution were transferred into a 100 mL Teflon-lined autoclave, sealed and heated at 130 ^oC for 12 h. The final products were collected, washed several times with ethanol/cyclohexane, and purified by centrifugation. The as-prepared lanthanide-doped Na_3ZrF_7 nanocrystals can be easily dispersed in various nonpolar organic solvents such as cyclohexane.

Synthesis of lanthanide-doped $NaYF_4$ NCs: In a typical synthesis, 4 mL methanol solution of $LnCl_3 \cdot 6H_2O$ (0.4 mol/L, Ln=Y, Yb, Er and Tm) was added to a 100-mL flask containing 6 mL of oleic acid and 14 mL of 1-octadecence. The resultant solution was heated to 150 ^0C for 30 min and then cooled down to room temperature. Afterwards, 10 mL methanol solution containing NH_4F (1.6 mmol) and NaOH (1 mmol) was introduced and the mixed solution was stirred for 30 min. After

removal of methanol, the solution was heated to 280~300 ^{0}C under N_2 atmosphere for 1.5 h and then cooled down to room temperature. The resulting NCs were precipitated by the addition of excess ethanol, collected by centrifugation, washed with methanol and ethanol several times. The as-prepared lanthanide-doped $NaYF_4$ NCs can be easily dispersed in various nonpolar organic solvents such as cyclohexane.

Characterizations: XRD analysis was carried out with a powder diffractometer (DMAX2500 RIGAKU) using CuK_α radiation (λ=0.154 nm). The size and shape of the samples were observed by a transmission electron microscope (TEM, JEM-2010) equipped with an energy dispersive x-ray spectroscope (EDS). TEM specimens were prepared by directly drying a drop of a dilute cyclohexane dispersion solution of the products on the surface of a carbon-coated copper grid. The valence states and the actual composition of the products were detected by X-ray photoelectron spectroscopy (XPS) using a VG Scientific ESCA Lab Mark II spectrometer equipped with two ultra-high vacuum 6 (UHV) chambers. All the binding energies were referenced to the C_{1s} peak of the surface adventitious carbon at 284.8 eV. Upconversion emission spectra were carried out on an Edinburgh Instruments FLS920 spectrofluorimeter upon 980 nm excitation by a power-controllable 980 nm diode laser (DPL-II, Module-HTL98M10) with a maximum power output of 3 W. To enable comparison of the upconversion emission intensities among different samples, the emission spectra were measured with the same instrumental parameters (for example: same excitation wavelength and power, same excitation and emission slits, same quantity of UC powders dispersed in the cyclohexane solution). All photoluminescence studies were carried out at room temperature.

Figure S1-S15

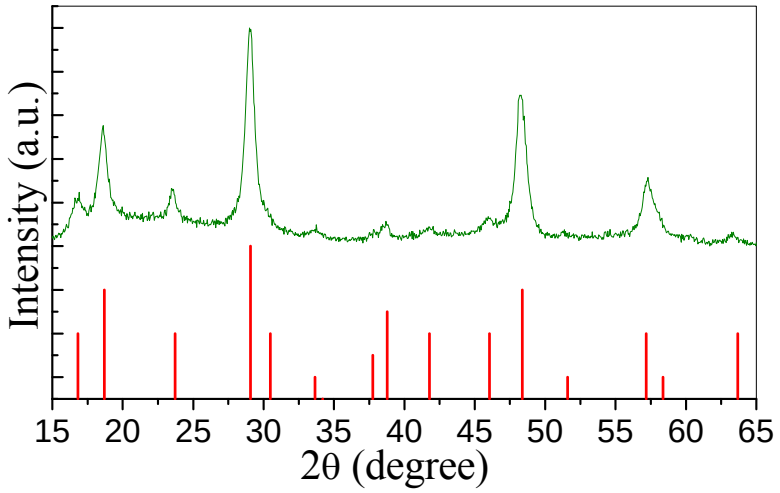

Figure S1. XRD pattern of Yb/Er (20/0.5 mol%): Na_3ZrF_7 NCs, bars represent standard tetragonal Na_3ZrF_7 crystal data (JCPDS No. 12-0562), showing the as-prepared product is pure tetragonal Na_3ZrF_7 phase.

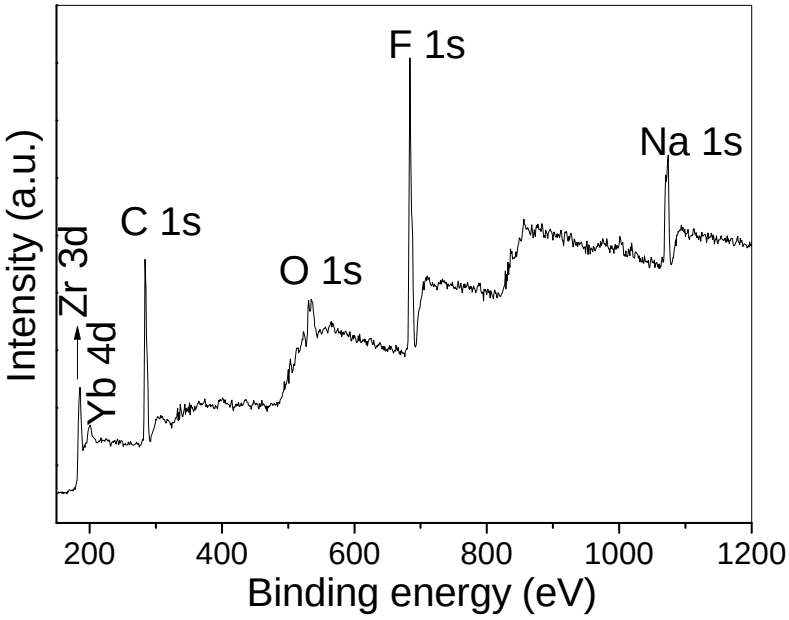

Figure S2. XPS spectrum of Yb/Er (20/0.5 mol%): Na_3ZrF_7 NCs, showing the existence of Na, F, Zr and Yb signals (Er signal is not detected owing to the low doping content).

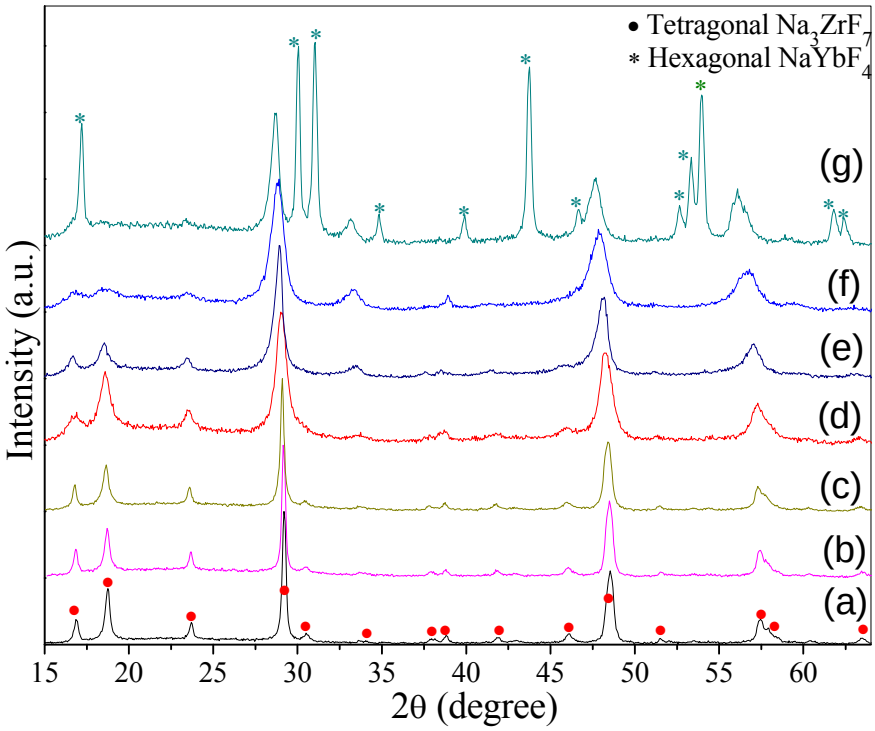

Figure S3. XRD patterns of Yb/Er (x/0.5 mol%): Na_3ZrF_7 NCs: (a) x=0, (b) x=5, (c) x=10, (d) x=20, (e) x=40, (f) x=60 and (g) x=80, showing that the tetragonal Na_3ZrF_7 structure is retained as the Yb^{3+} content reaches as high as 60 mol%.

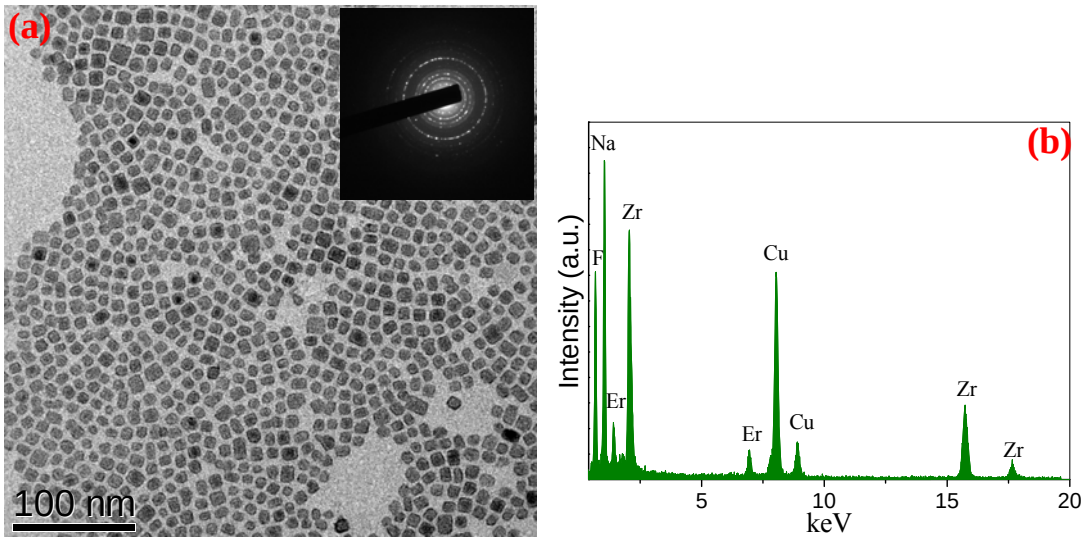

Figure S4. (a) TEM micrograph and (b) EDS spectrum of the tetragonal Er (20 mol%): Na_3ZrF_7 NCs, inset of (a) is the corresponding SAED pattern.

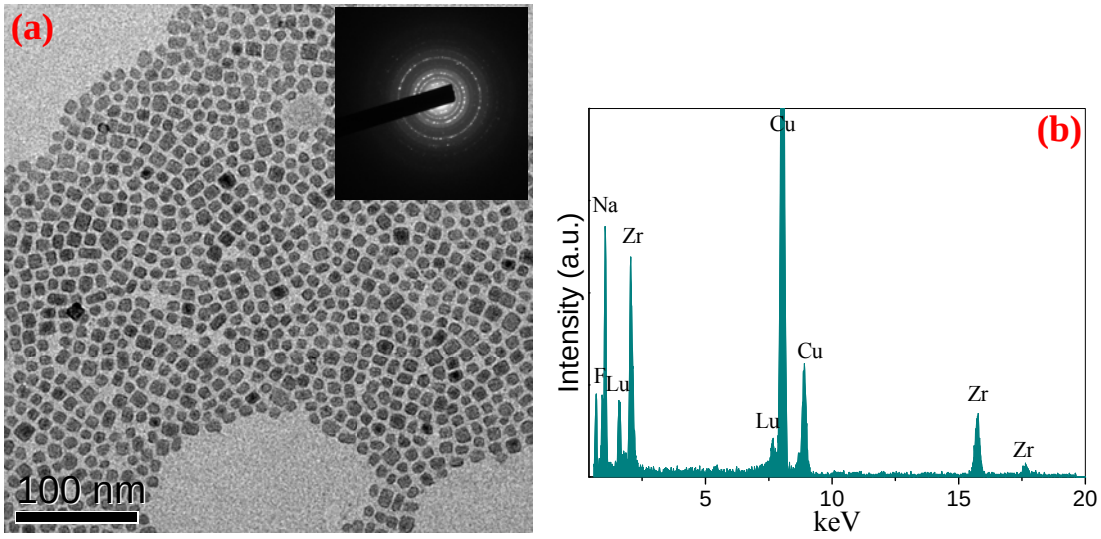

Figure S5. (a) TEM micrograph and (b) EDS spectrum of the tetragonal Lu (20 mol%): Na_3ZrF_7 NCs, inset of (a) is the corresponding SAED pattern.

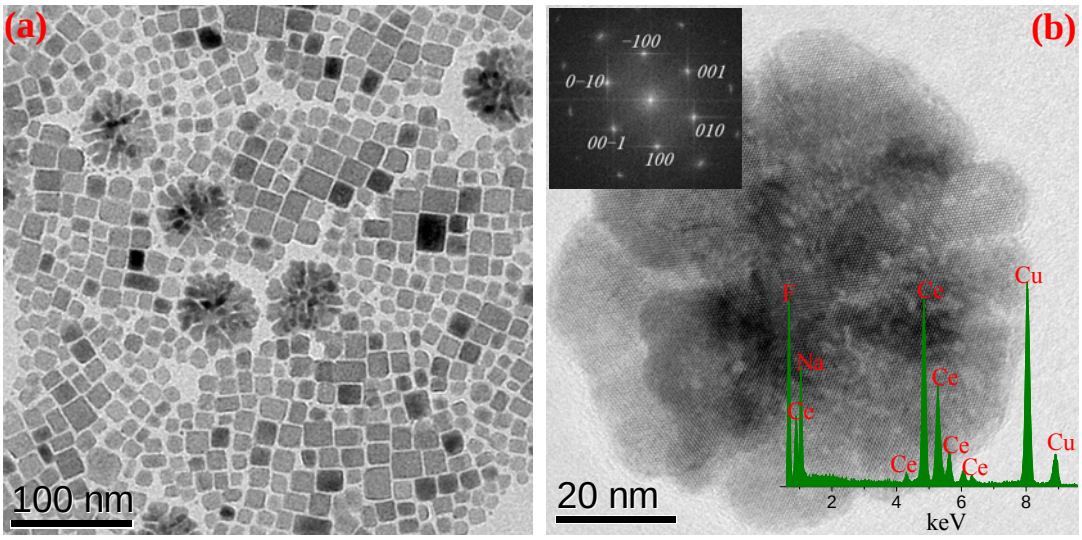

Figure S6. (a) TEM micrograph of the 20 mol% Ce^{3+} doped product; (b) HRTEM image of an individual flower-shaped hexagonal $NaCeF_4$ NC, insets are the corresponding FFT pattern and EDS spectrum.

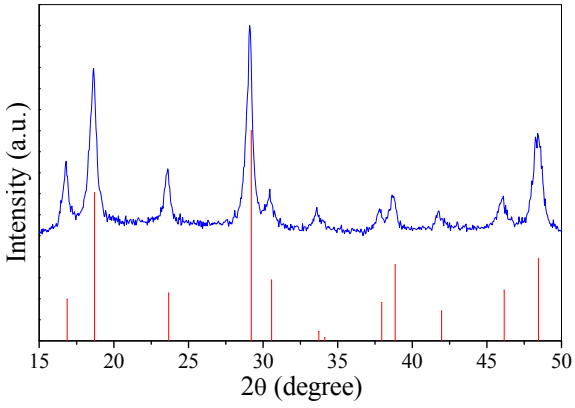

Figure S7. XRD pattern of Yb/Er (20/0.5 mol%): Na_3HfF_7 NCs, bars represent standard tetragonal Na_3HfF_7 crystal data (JCPDS No. 74-0809), showing the as-prepared product is pure tetragonal Na_3HfF_7 phase.

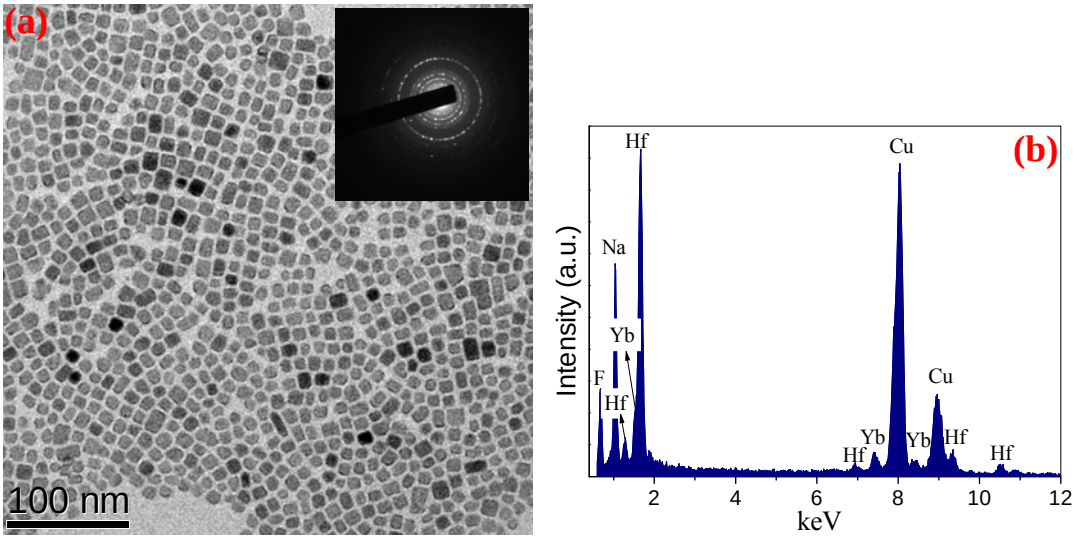

Figure S8. (a) TEM micrograph and (b) EDS spectrum of the tetragonal Yb/Er (20/0.5 mol%): Na_3HfF_7 NCs, inset of (a) is the corresponding SAED pattern.

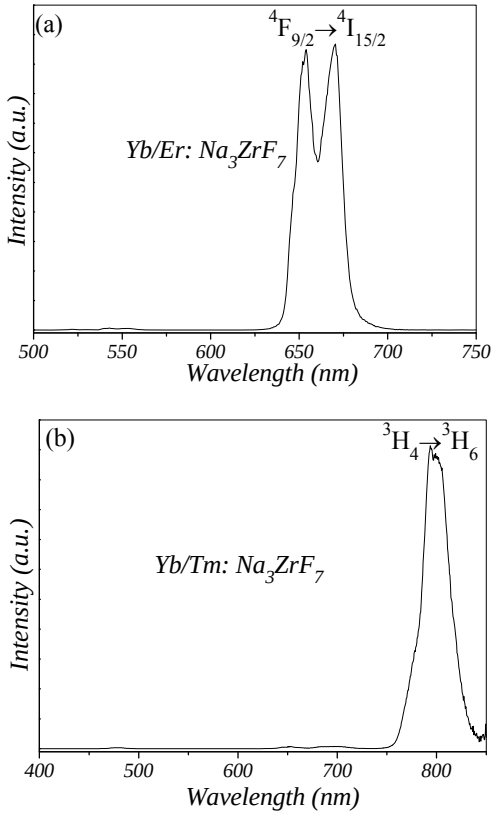

Figure S9. Room temperature UC spectra of (a) Yb/Er (20/0.5 mol%): Na_3ZrF_7 and (b) Yb/Tm (20/0.5 mol%): Na_3ZrF_7 NCs under 980 nm laser excitation. Both samples exhibit single-band emission feature.

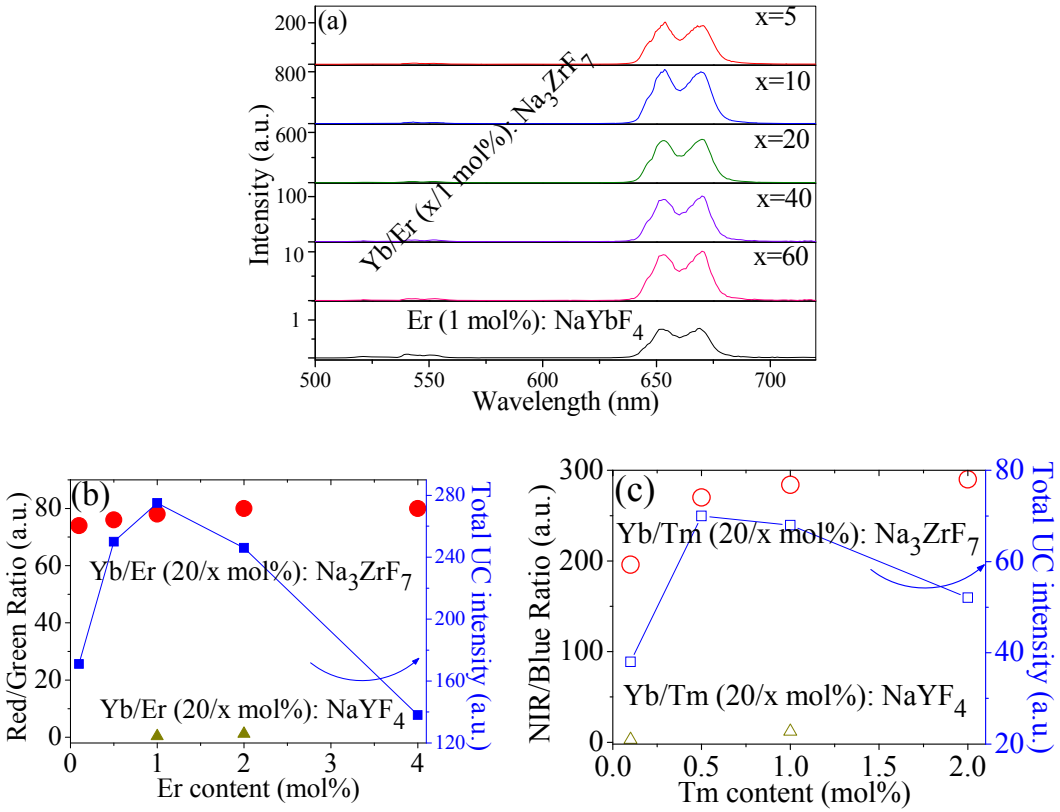

Figure S10. UC emission spectra of (a) Yb/Er (x/1 mol%, x=5, 10, 20, 40, 60): Na_3ZrF_7 and Er (1 mol%): $NaYbF_4$ NCs. (b) Dependence of red/green ratio (●) and the total UC intensity (■) on the Er^{3+} content in Yb/Er (20/x mol%, x=0.1, 0.5, 1, 2, 4): Na_3ZrF_7 NCs. (c) Dependence of NIR/blue ratio (○) and the total UC intensity (□) on Tm^{3+} content in Yb/Tm (20/x mol%, x=0.1, 0.5, 1, 2): Na_3ZrF_7 NCs. As a comparison, the red/green (▲) and NIR/blue (△) ratios of hexagonal Yb/Er(Tm): $NaYF_4$ samples are also provided in (b) and (c) respectively.

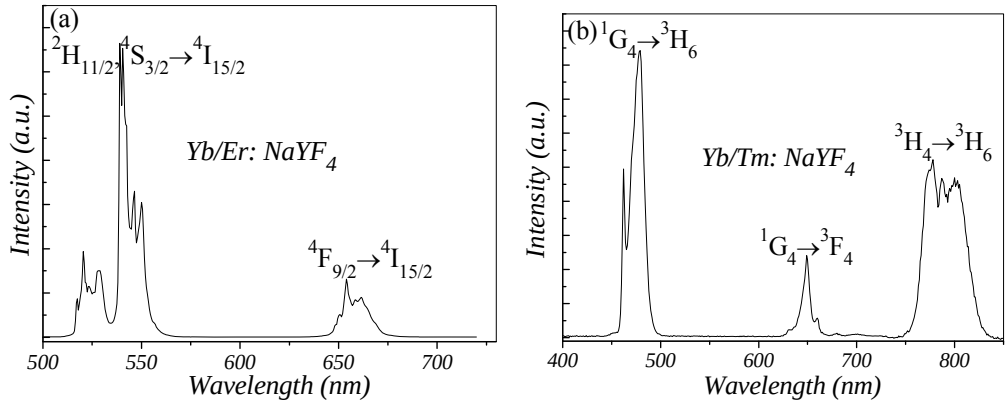

Figure S11. Room temperature UC spectra of (a) Yb/Er (20/0.5 mol%): $NaYF_4$ and (b) Yb/Tm (20/0.5 mol%): $NaYF_4$ NCs under 980 nm laser excitation. Both samples exhibit multiple-band emission feature.

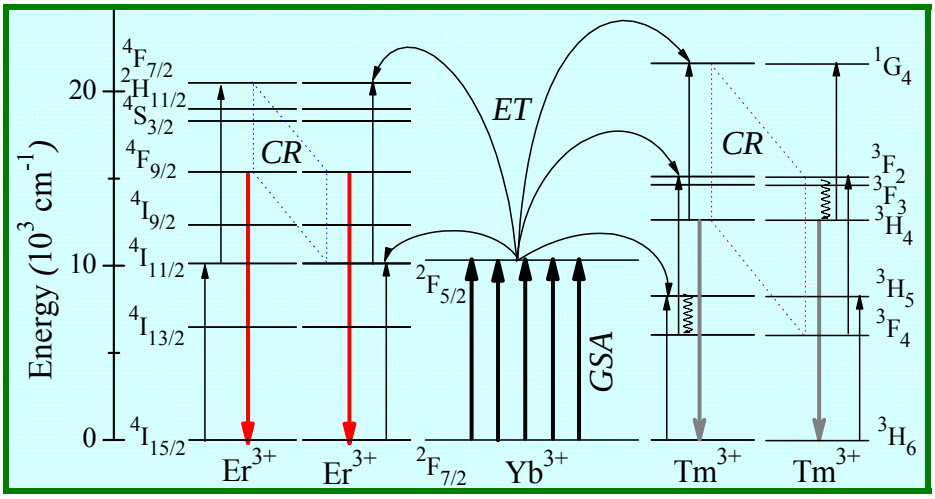

Figure S12. Energy level diagrams of Er^{3+}, Yb^{3+} and Tm^{3+} ions, showing the possible energy transfer mechanisms for the single-band red (NIR) UC emission of Er^{3+}(Tm^{3+}) activators in Na_3ZrF_7 host, under 980 nm laser excitation.

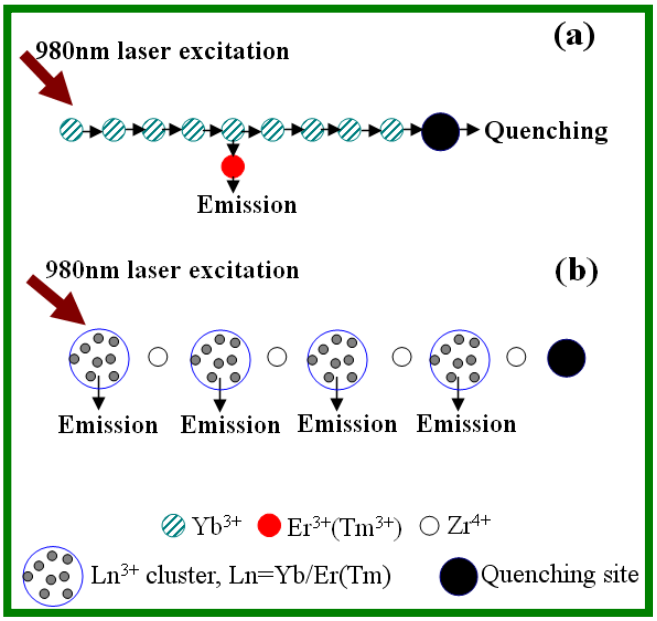

Figure S13. Schematic illustration of the possible UC emission processes in (a) the Er(Tm): $NaYbF_4$ NCs, and (b) Yb/Er(Tm): Na_3ZrF_7 NCs. In the Er(Tm): $NaYbF_4$ NCs, NIR excitation energy migrates among Yb^{3+} ions and finally transfers to the emitting ion Er^{3+}(Tm^{3+}) or the quenching site. In contrast, in the Yb/Er(Tm): Na_3ZrF_7 NCs, individual Ln^{3+} cluster can produce single-band UC emission under NIR laser excitation, and energy transfer from Yb^{3+} to the quenching site is broken due to the separation of Ln^{3+} clusters by Zr^{4+} ions.

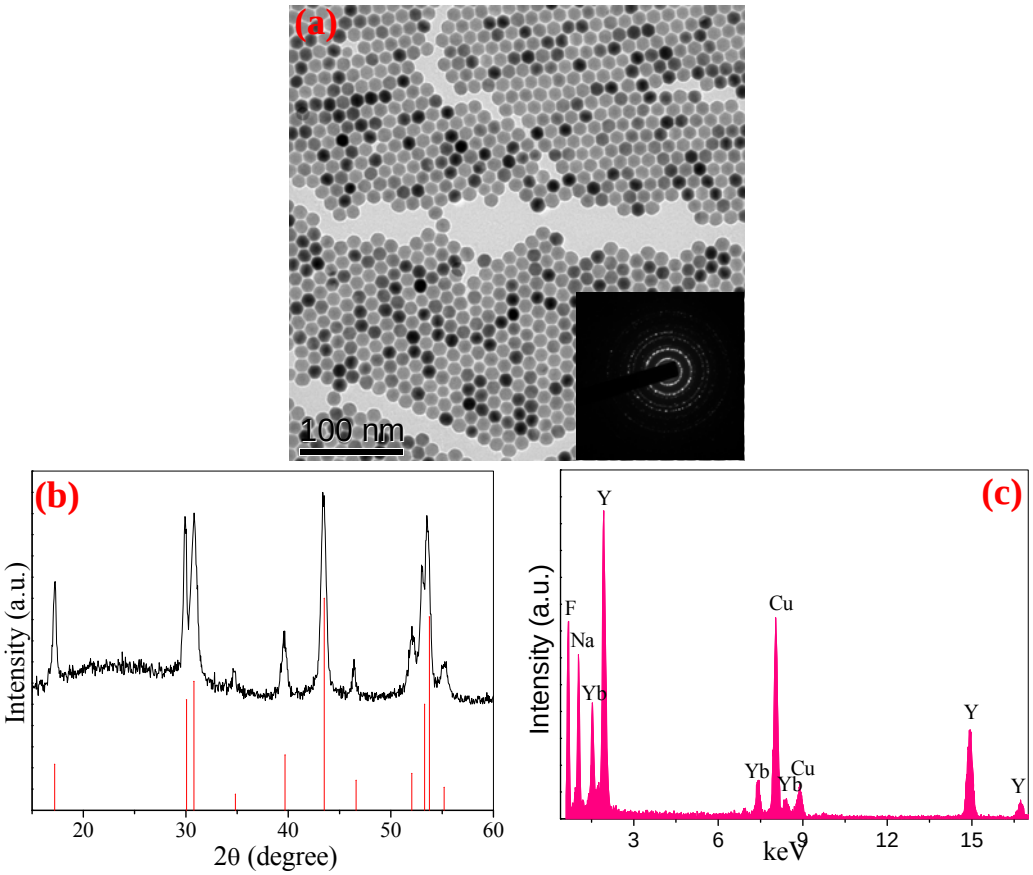

Figure S14. (a) TEM micrograph, (b) XRD pattern, and (c) EDS spectrum of the as-prepared hexagonal Yb/Er (20/1 mol%): $NaYF_4$ NCs; inset of (a) is the corresponding SAED pattern and bars in (b) are standard hexagonal $NaYF_4$ crystal data (JCPDS No. 16-0334). These characterization techniques indicate that the product is pure hexagonal $NaYF_4$ NCs with size of ~15 nm, and the lanthanide activators are incorporated into the host lattice.

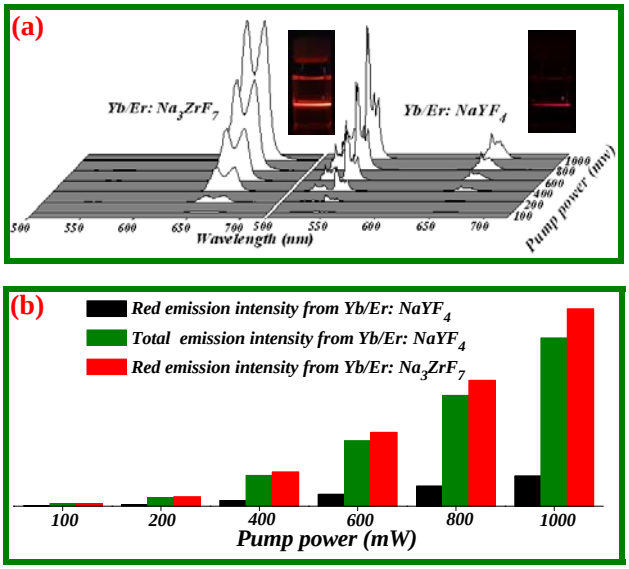

Figure S15. (a) Pump-power-dependent UC emission of hexane solutions containing same amounts of Yb/Er (20/1 mol%): Na_3ZrF_7 and Yb/Er (20/1 mol%): $NaYF_4$ NCs; insets are the respective red UC emission photos recorded under the identical

condition with a power density of 40 W/cm^2, an appropriate green filter is used to isolate red emission from the total yellow luminescence in Yb/Er: $NaYF_4$ NCs. (b) Comparison of red emission intensity in Yb/Er: Na_3ZrF_7 with the total emission intensity and the red one in Yb/Er: $NaYF_4$ NCs.