

**Multifunctional BiF₃:Ln³⁺(Ln = Ho, Er, Tm)/Yb³⁺ nanoparticles:
investigation on the emission colour tuning, thermosensitivity and bio
imaging**

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1. Experimental

1.1 Materials

Analytical grade bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ AR grade), ammonium fluoride (NH_4F , 98%), Yttrium oxide (Yb_2O_3 , 99.99%), Erbium oxide (Er_2O_3 , 99.99%), Thulium oxide (Tm_2O_3 , 99.99%), Holmium oxide (Ho_2O_3 , 99.99%), and Ethylene glycol (EG) were purchased from Aladdin Chemical Reagent Factory (China). The corresponding rare earth oxides are dissolved in dilute HNO_3 under stirring and then the solvent is evaporated to obtain all the rare earth nitrates.

1.2 Preparation of cubic $\text{BiF}_3:\text{Ln}^{3+}$ ($\text{Ln} = \text{Ho}, \text{Er}, \text{Tm}$)/ Yb^{3+} UCNPs

0.78 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.02 mmol $\text{Er}(\text{NO}_3)_3$ and 0.20 mmol $\text{Yb}(\text{NO}_3)_3$ were added to 10 mL EG in a beaker under vigorously stirring. Then 25 ml EG with 5 mmol NH_4F was added into the above solution and stirred for 1 min. Subsequently, the resulting suspension was separated and washed with deionized water and ethanol several times by centrifugation, after that dried at room temperature. In addition, 20% Yb^{3+} , 2% Ho^{3+} /0.5% Tm^{3+} co-doped BiF_3 UCNPs were obtained by the same method. The similar procedure was used for comparative experiments at different temperatures and reaction time.

1.3 Characterization

XRD experiments were carried out with a Bruker D8 VENTURE diffractometer (Bruker, German) using Cu-K α radiation. SEM images were examined using a Hitachi S-4800 system. TEM images were obtained using FEI TECNAIG2F20-S-TWIN transmission electron microscope. TG-DSC measurements were measured with an SDT

Q600 instrument (heating rate ($5^{\circ}\text{C min}^{-1}$), 200-1200 $^{\circ}\text{C}$, under an air flow of 200 mL/min). XPS was carried out with a VG Scientific Model ESCALab220i-XL electron spectrometer using 300 W Al K α radiation. Using a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer system to collect two continuous 980 nm and 1550 nm laser diode. In order to analyze chemical components, FT-IR was used (Nicolet NEXUS 670).

1.4 In vitro cytotoxicity evaluation

To evaluate the cytotoxicity of $\text{BiF}_3:20\%\text{Yb}^{3+}/2\%\text{Er}^{3+}$ UCNPs, CCK-8 assays were used on B16-F10 cells incubated with UCNPs. B16-F10 cells were seeded in a 96-well plate at a density of 8000 cells per well and cultured in 5% CO_2 at 37 $^{\circ}\text{C}$ for 24 h. The $\text{BiF}_3:20\%\text{Yb}^{3+}/2\%\text{Er}^{3+}$ UCNPs (1 mg/mL) were dispersed in phospholipid aqueous solution (2 mg/mL) by ultrasound for 6 h (1:1).

1.5 In vivo imaging

100 μL of $\text{BiF}_3:20\%\text{Yb}^{3+}/2\%\text{Er}^{3+}$ NPs phospholipid aqueous solution with concentration of 100 $\mu\text{g/mL}$ was injected intraperitoneally and subcutaneously into a Kunming mouse. In order to eliminate the interference of 980 nm excitation laser, a short-pass filter (700 nm) was used.

1.6 In vivo X-Ray imaging

200 μL of $\text{BiF}_3:20\%\text{Yb}^{3+}/2\%\text{Er}^{3+}$ NPs phospholipid aqueous solution with concentration of 100 $\mu\text{g/mL}$ was subcutaneously injected into the mouse. Then, in vivo X-ray imaging was tested by a BRUKER In Vivo FXPRO imaging system. All animal procedures comply with the care and use regulations of animal institutions.

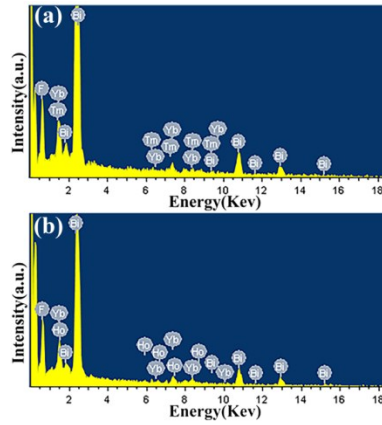


Figure S1 Energy-dispersive X-ray (EDX) spectroscopy: (a) $\text{BiF}_3:20\%\text{Yb}^{3+}/0.5\%\text{Tm}^{3+}$, (b) $\text{BiF}_3:20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}$.

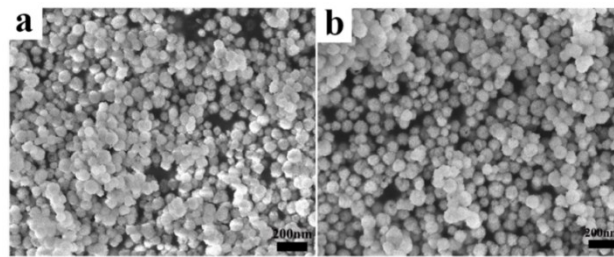


Figure S2 SEM images: (a) $\text{BiF}_3:20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}$, (b) $\text{BiF}_3:20\%\text{Yb}^{3+}/0.5\%\text{Tm}^{3+}$. (obtained in 1 min at room temperature)

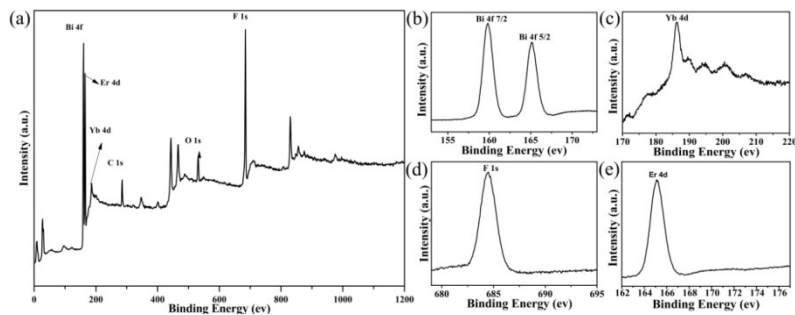


Figure S3 XPS survey spectra of $\text{BiF}_3:20\%\text{Yb}^{3+}/2\%\text{Er}^{3+}$ NPs. (a) survey, (b) Bi 4f, (c) Yb 4d, (d) F 1s and (e) Er 4d.

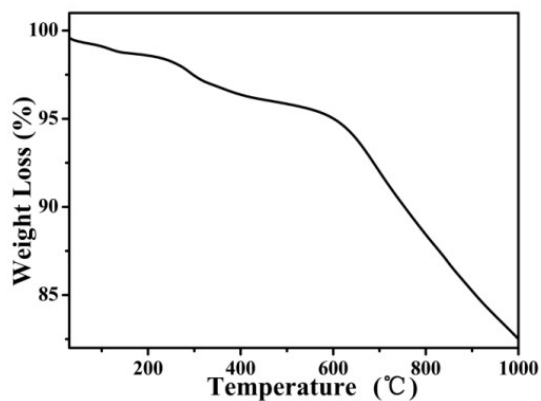


Figure S4 TG-DSC curve of the sample $\text{BiF}_3:2\%\text{Er}^{3+}/20\%\text{Yb}^{3+}$.

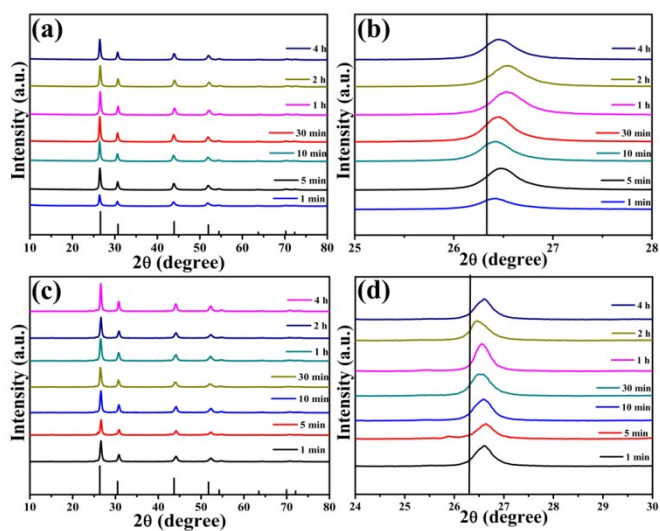


Figure S5 XRD patterns: (a-b) $\text{BiF}_3: 20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}$, (c-d) $\text{BiF}_3: 20\%\text{Yb}^{3+}/0.5\%\text{Tm}^{3+}$ NPs obtained at different reaction time.

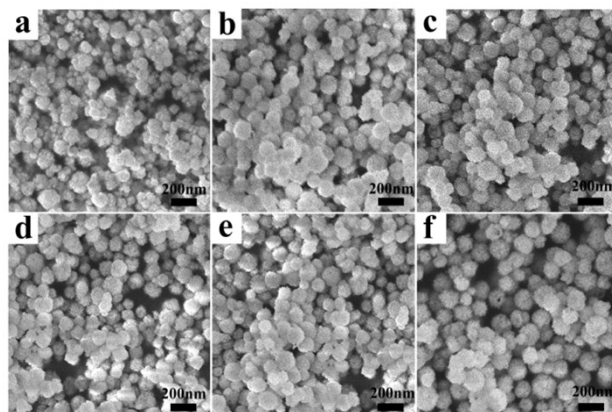


Figure S6 SEM images of $\text{BiF}_3:20\% \text{Yb}^{3+}/2\% \text{Ho}^{3+}$ NPs obtained at different reaction time. (a) 5 min, (b) 10 min, (c) 30 min, (d) 1 h, (e) 2 h, and (f) 4 h.

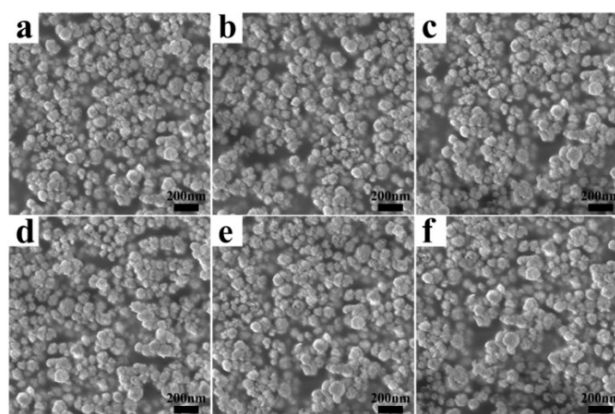


Figure S7 SEM images of $\text{BiF}_3:20\% \text{Yb}^{3+}/0.5\% \text{Tm}^{3+}$ NPs obtained at different reaction time. (a) 5 min, (b) 10 min, (c) 30 min, (d) 1 h, (e) 2 h, and (f) 4 h.

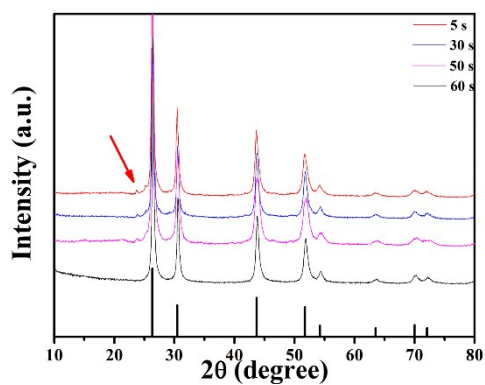


Figure S8 XRD patterns of the products obtained at different reaction time of $\text{BiF}_3:20\% \text{Yb}^{3+}/2\% \text{Er}^{3+}$ nanoparticles.

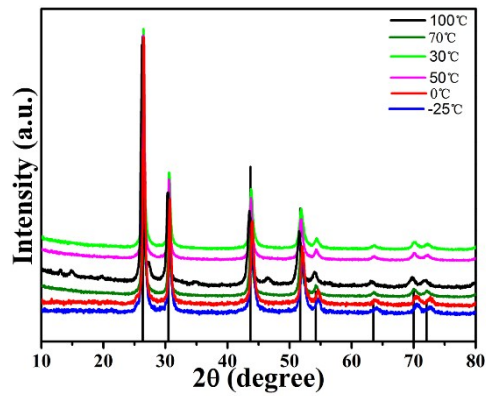


Figure S9 XRD patterns of BiF₃: 20%Yb³⁺/2%Er³⁺ NPs obtained at different temperatures (T = -25, 0, 30, 50, 70 and 100°C).

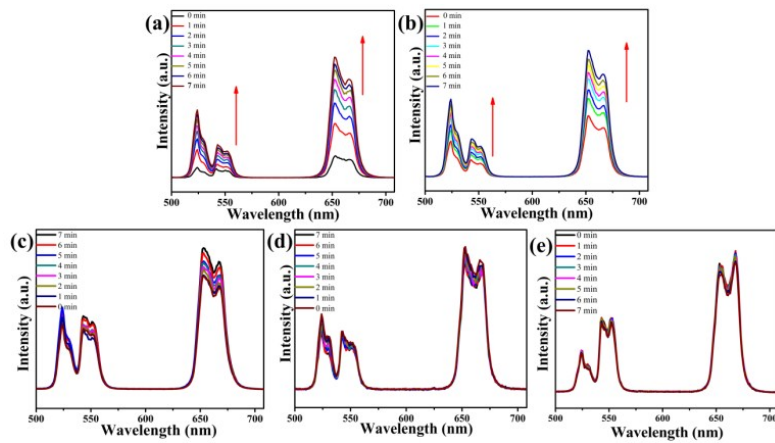


Figure S10 UCL spectra of BiF₃: 20%Yb³⁺/2%Er³⁺ nanoparticles under excitation of 980 nm with (a) uncalcined; (b) calcined at 50 °C; (c) calcined at 100 °C; (d) calcined at 200 °C and (e) calcined at 400 °C.

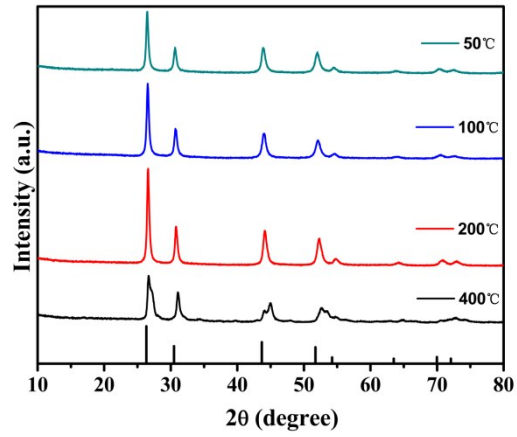


Figure S11 XRD patterns of BiF₃: 20%Yb³⁺/2%Er³⁺ with different calcination temperatures.

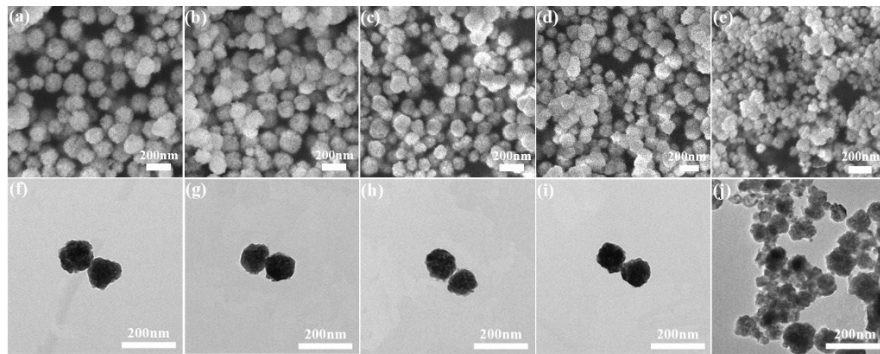


Figure S12 SEM and TEM images of BiF₃:2%Er³⁺/20%Yb³⁺ NPs obtained at different calcination temperatures. (a,f) uncalcined, (b,h) calcined at 50 °C, (c,i) calcined at 100 °C, (d,j) calcined at 200 °C, and (e,k) calcined at 400 °C.

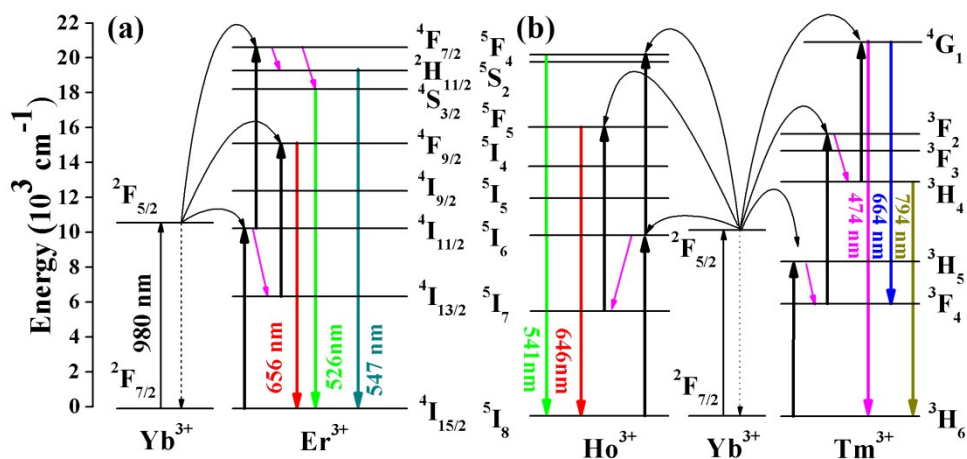


Figure S13 Energy level diagrams of Yb^{3+} , Er^{3+} , Tm^{3+} and Ho^{3+} ions and proposed UC mechanisms in $\text{BiF}_3:\text{Ln}^{3+}$ NPs.

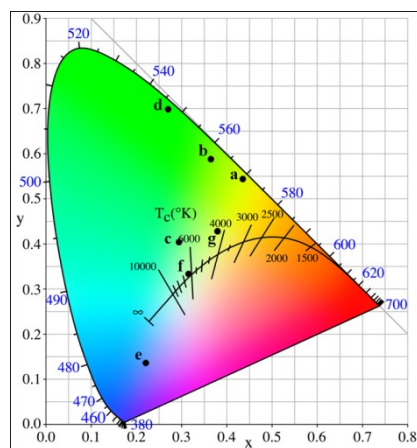


Figure S14 The CIE 1931 chromaticity diagram of $\text{BiF}_3:\text{Ln}^{3+}$ NPs excited with a 980 nm laser.

Table S1 The summary of chemical composition, chromaticity coordinates (x, y) and emission color of the $\text{BiF}_3:\text{Ln}^{3+}$ NPs.

Sample	Chromaticity Coordinates (x, y)	Emission color
(a) BiF ₃ :20%Yb ³⁺ /2%Er ³⁺	(0.4355,0.5438)	Yellow
(b) BiF ₃ : 20%Yb ³⁺ /1%Er ³⁺ /0.15%Ho ³⁺	(0.3667,0.5897)	Yellow green
(c)BiF ₃ : 20%Yb ³⁺ /1%Er ³⁺ /0.5%Tm ³⁺	(0.2947,0.4059)	Bluish white
(d) BiF ₃ : 20%Yb ³⁺ /2%Ho ³⁺	(0.269,0.6978)	Green
(e) BiF ₃ : 20%Yb ³⁺ /0.5%Tm ³⁺	(0.2225,0.1364)	Purplish blue
(f) BiF ₃ : 20%Yb ³⁺ /0.5%Tm ³⁺ /0.15%Ho ³⁺	(0.3166,0.3327)	White
(g) BiF ₃ : 20%Yb ³⁺ /1%Er ³⁺ /0.5%Tm ³⁺ /0.15%Ho ³⁺	(0.3783,0.4264)	pinkish