SUPPORTING INFORMATION

Highly Polarized Upconversion Emissions from Lanthanide-Doped $LiYF_4$ Crystal as Spatial Orientation Indicators

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METHODS

Materials and Instrumentation. Rare earth chloride hydrate (YCl_3, $ErCl_3$, $TmCl_3$, $YbCl_3$, $HoCl_3$, >99.9%) were purchased from Energy Chemical. HCl (GR) was purchased from XiLong Chemical Co. Ltd., Ethylenediaminetetraacetic acid (EDTA-6H, AR) was purchased from Sinopharm Chemical Reagent Co. Ltd., $NH_3 \cdot H_2O$ (AR) was purchased from Beijing Tong Guang Fine Chemicals Company, LiCl (AR) was purchased from Beijing Chemical Works. All reagents were used as received without further purification. SEM images were obtained from a Hitachi S-4800 field emission scanning electron microscope. The X-ray diffraction patterns were recorded on a PANalytical X'Pert[3] powder diffractometer, using Cu Kα radiation (λ=1.5406 Å).

Synthesis of $LiYF_4$ Crystal. $LiYF_4$ crystal was synthesized through a hydrothermal method. Firstly, 0.25 mol/L EDTA-2NH_4 aqueous solution with pH being about 3~4 was produced through the reaction of EDTA-6H with $NH_3 \cdot H_2O$. Taking $LiYF_4$:Yb/Er for example, 1 mL 0.25 mol/L EDTA-2NH_4 was stirred with 780 µL 0.5 mol/L YCl_3, 200 µl 0.5 mol/L $YbCl_3$, 20 µL 0.5 mol/L $ErCl_3$ and 250 µL 2 mol/L LiCl aqueous solution for 30 min. Then, 3 mL 2 mol/L NH_4F and 1 mL 1mol/L HCl aqueous solution was added dropwise to stir for another 30 min. Finally, the solution was transferred to a 25 mL Teflon-lined autoclave and heated at 200 °C for 24 h. The produced crystals were washed by DI water and ethanol severally and then dispersed in ethanol for further characterizations.

Measurement of Three-Dimensional Orientation. The theoretical method is based on the researches of Fourkas[1] and Yanagida[2]. When a linearly polarized light is collected by a high-numerical aperture (NA) objective, the detected intensity at polarized angles of 0°, 45° and 90° at certain α and β angles can be given as following equations:

$$I_0 = I_{tot}(A + Bsin^2\beta + Csin^2\beta cos2\alpha)$$

$$I_{45} = I_{tot}(A + Bsin^2\beta + Csin^2\beta sin2\alpha)$$

$$I_{90} = I_{tot}(A + Bsin^2\beta - Csin^2\beta sin2\alpha)$$

Where I_0、I_{45} and I_{90} are the intensities at corresponding polarized angles, I_{tot}

is the total intensity emitted during the period of measurement. A, B and C are parameters which are related to the NA of objective and the refractive index of environmental medium. In our case, an air objective with NA of 0.9 is used, so A, B and C equal 0.11、0.025 and 0.13, respectively. Three unknowns, α、β and I_{tot}, can be solved through the above three equations:

$$I_{tot} = \frac{G - B}{2AC}\sqrt{2(I_0 - I_{45})^2 + 2(I_{90} - I_{45})^2}$$

In which

$$G = \frac{C(I_0 + I_{90})}{\sqrt{2(I_0 - I_{45})^2 + 2(I_{90} - I_{45})^2}}$$

Finally, the information of orientation can be solved:

$$\beta = sin^{-1}\sqrt{\frac{A}{(G - B)}}$$

$$\alpha = \frac{1}{2}tan^{-1}(\frac{2I_{45} - I_0 - I_{90}}{I_0 - I_{90}})$$

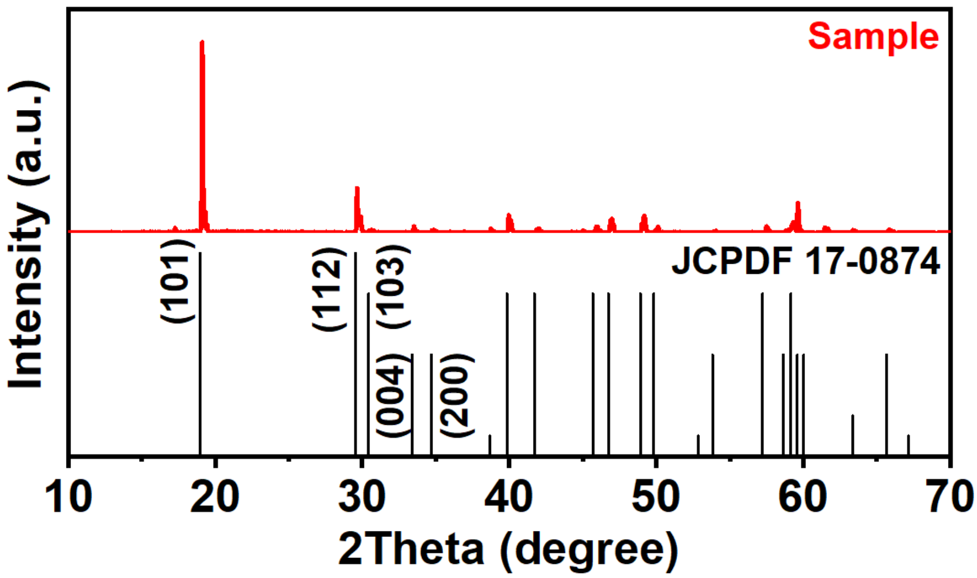

Figure S1. The X-ray diffraction patterns of the obtained $LiYF_4$:Yb/Er crystals.

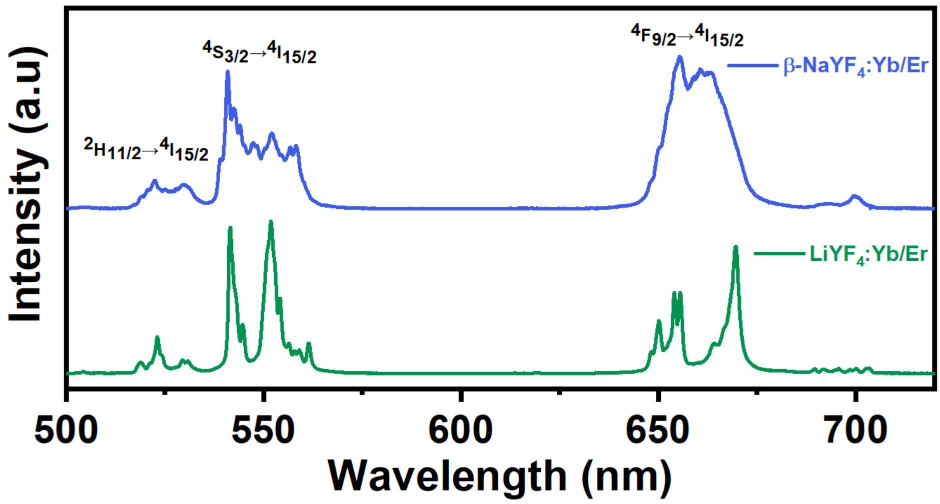

Figure S2. The upconversion emission spectra of β-$NaYF_4$:Yb/Er and $LiYF_4$:Yb/Er.

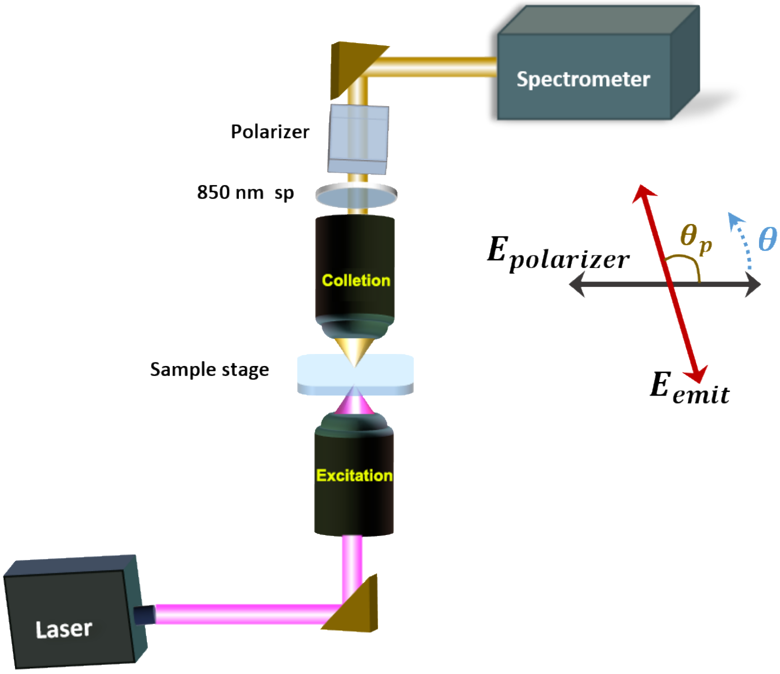

Figure S3. Schematic diagram of the microscopy setup for the polarization studies. The emission is detected by a fiber optic spectrometer, so there is no response difference to the light with various polarization because of the depolarization by numerous reflections. Owing to the morphology of elongated octahedron, $LiYF_4$ crystal lies on the sample stage with one of the octahedron facets, and its *c*-axis is not in the sample stage plane. For the polarized emission studies, an objective with small NA (0.25) is used to collect the emitted light, in order to reduce the impact of the tilted *c*-axis[1]. In the studies of 3D orientation sensing, an objective with high NA (0.9) is used.

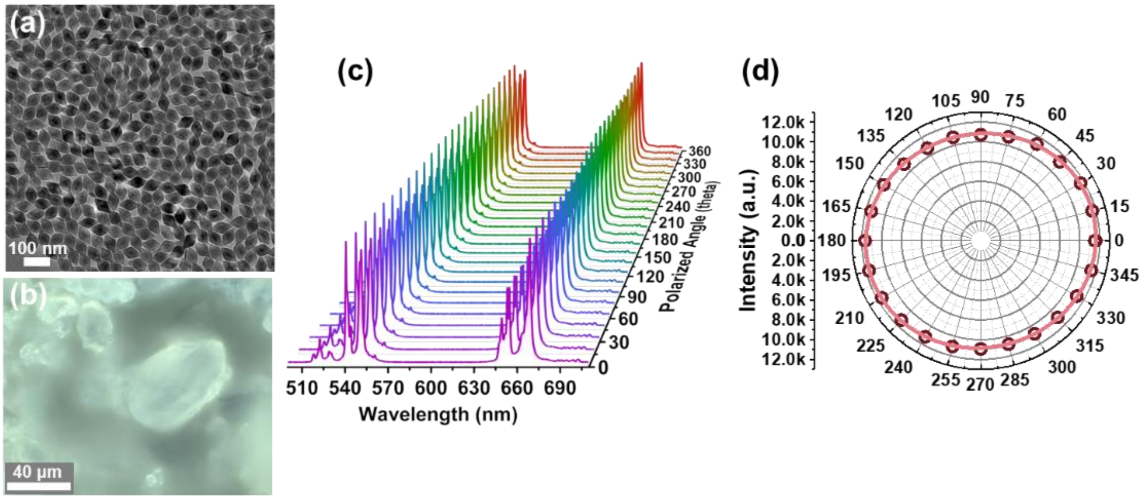

Figure S4. The polarization behavior of disorderly aggregates of $LiYF_4$:Yb/Er nanocrystals was studied. (a) TEM image of the tested $LiYF_4$:Yb/Er nanocrystals, (b) the optical image of the powder, (c) upconversion emission spectra recorded at various polarized angles, (d) the *I–θ* polar diagrams of the emission at 668.0 nm. The spectrum and emission intensity remain the same at various polarized angles, no artificial polarized emission was detected.

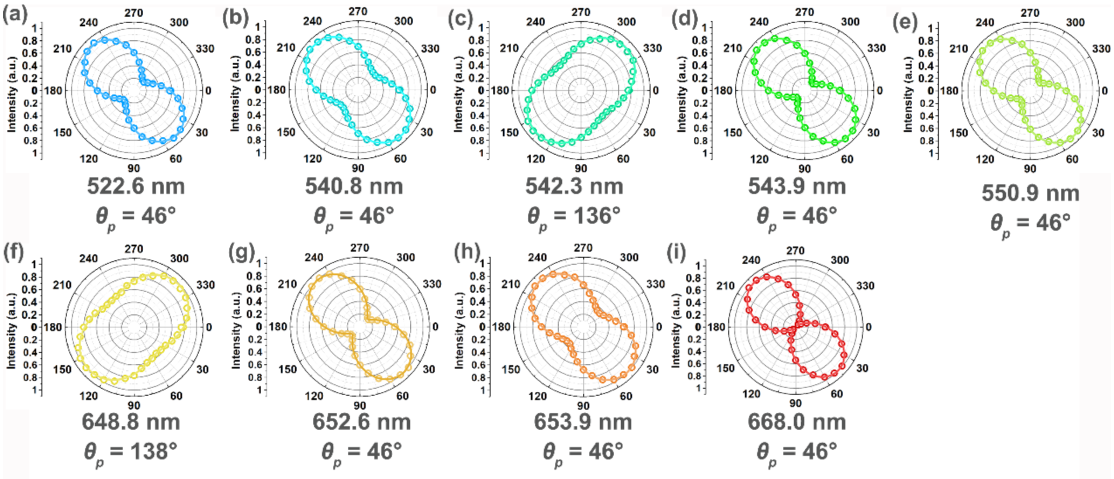

Figure S5. The *I*–*θ* polar diagrams of typical emissions from a single $LiYF_4$:Yb/Er crystal.

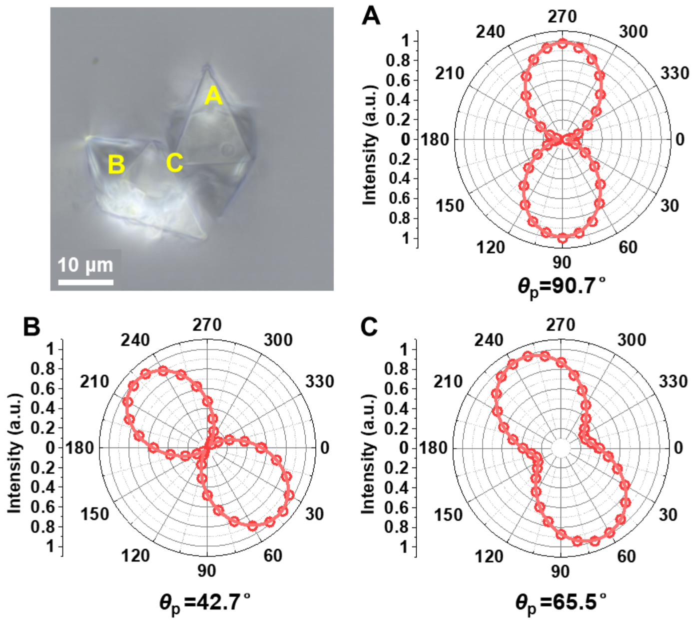

Figure S6. The optical image of two neighboring $LiYF_4$ crystals and the I–θ polar diagrams of emission at 668.0 nm taken at spots A, B and C.

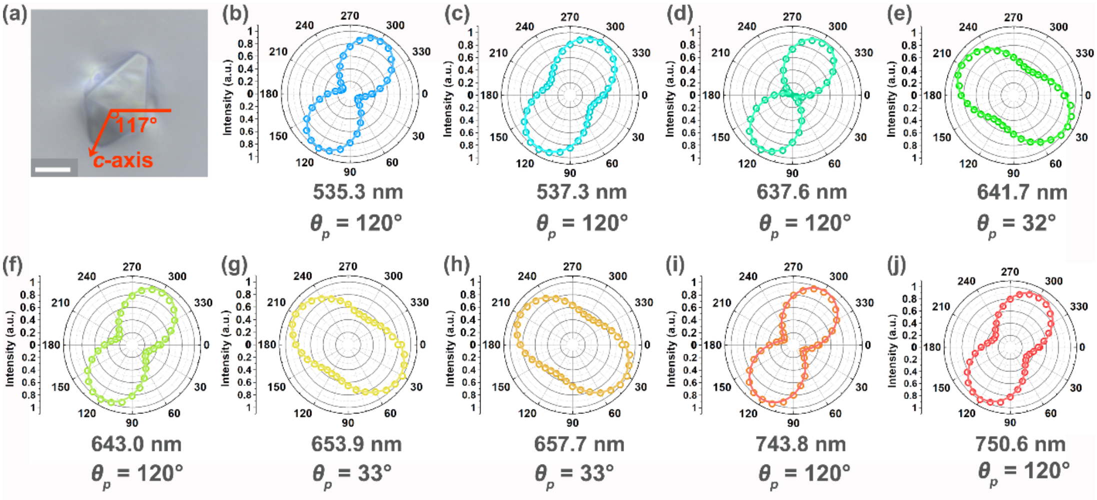

Figure S7. (a) The optical image of the tested $LiYF_4$:Yb/Ho crystal, scale bar: 5 μm. (b–j) The *I*–*θ* polar diagrams of typical emissions.

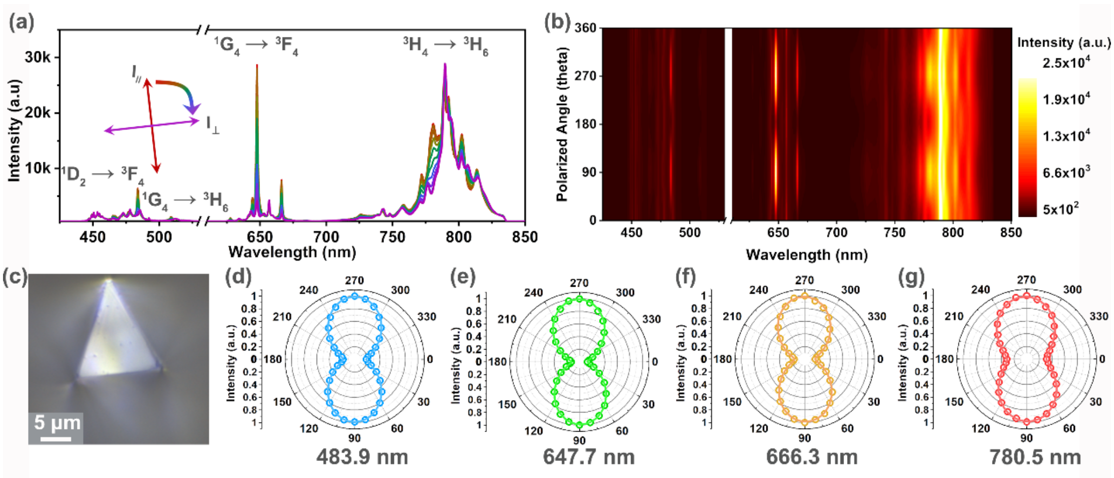

Figure S8. The polarization behavior of the upconversion emission from a single $LiYF_4$:Yb/Tm crystal. (a) The upconversion spectra at polarized angles from being parallel to perpendicular to the *c*-axis of crystal, (b) the matrix diagram of upconversion intensity *versus* polarized angle, (c) the optical image of the tested crystal, and (d–g) the I–θ polar diagrams of typical emissions.

Table S1. Polarization of the upconversion emissions from $LiYF_4$:Yb/Ho and $LiYF_4$:Yb/Tm crystals

Activator	Wavelength (nm)	DOP	Polarization
Ho^{3+}	535.3	0.75	π
	537.3	0.44	π
	637.6	0.91	π
	641.7	0.34	σ
	643.0	0.59	π
	653.9	0.31	σ
	657.7	0.31	σ
	743.8	0.70	π
	750.6	0.52	π
Tm^{3+}	483.9	0.68	π
	647.7	0.77	π
	666.3	0.71	π
	780.5	0.52	π

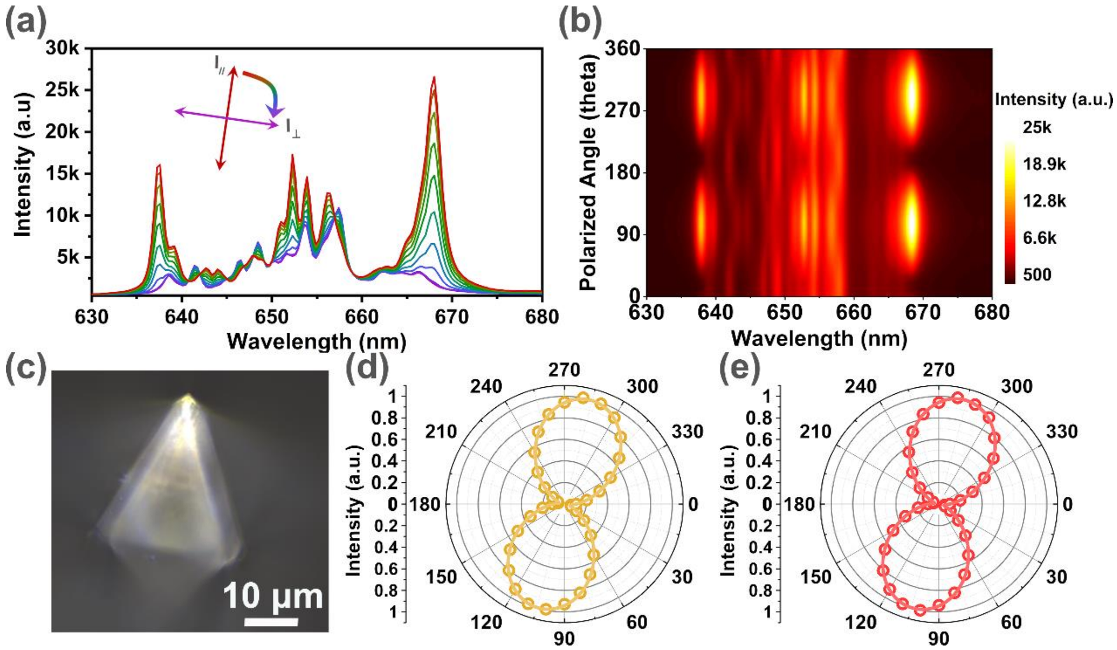

Figure S9. The polarization behavior of the upconversion emission from a single $LiYF_4$:Yb/Er/Ho crystal. (a) The upconversion emission spectra at polarized angles from being parallel to perpendicular to *c*-axis of the crystal, (b) the matrix diagram of upconversion intensity *versus* polarized angle, (c) the optical image of the tested crystal, (d, e) the I–θ polar diagrams of emissions at 637.6 nm (d) and 668.0 nm (e). Noted that two linearly polarized emissions are obtained in one crystal, and the DOP are 0.90 (637.6 nm) and 0.92 (668.0 nm).

REFERENCE

(1) Fourkas, J. T. Rapid Determination of the Three-Dimensional Orientation of Single Molecules. *Opt. Lett.* **2001,** *26,* 211-213.

(2) Ohmachi, M.; Komori, Y.; Iwane, A. H.; Fujii, F.; Jin, T.; Yanagida, T. Fluorescence Microscopy for Simultaneous Observation of 3D Orientation and Movement and its Application to Quantum Rod-Tagged Myosin V. *Proc. Natl. Acad. Sci. U. S. A.* **2012,** *109,* 5294-5298.