Polarized upconversion luminescence from a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal for orientation tracking

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ABSTRACT Polarized upconversion luminescence (UCL) of lanthanide-doped micro/nano-crystals has shown great promise in single-particle tracking and super-resolution bioimaging. However, because of the spectral line broadening and multiple sites of lanthanide in upconversion particles (UCPs), the crystal-field (CF) polarization components of UCL are usually undistinguishable. Herein, we report the linearly polarized UCL in $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ single microcrystals with resolvable CF transition lines and a polarization degree up to 0.82. The CF levels and CF transition lines of Er^{3+} , as well as their emission polarization anisotropy, are unraveled for the first time through low-temperature and high-resolution photoluminescence (PL) and UCL spectroscopies. By taking advantage of the well-resolved and highly-polarized CF transition lines of Er^{3+} , we demonstrate the application of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ single microcrystals as anisotropic UCL probes for orientation tracking. These findings provide fundamental insights into the polarization anisotropy of UCL in lanthanide-doped single particles, thus laying a foundation for the future design of anisotropic luminescent probes towards versatile applications.

Keywords: LiLuF_4 , upconversion luminescence, single particle, polarization anisotropy, crystal-field level

INTRODUCTION

Micropolarized spectroscopy that focuses on the luminescence of single lanthanide (Ln^{3+})-doped upconversion particles (UCPs) or their assemblies has recently attracted great attention, not only for its fundamental scientific importance but also because of its potential applications in diverse areas such as microscopic information transportation, microfluidics, single-particle tracking, and super-resolution bioimaging [1–10]. In contrast to anisotropic emitters such as semiconductor nanowires, quantum rods, and nanoplates that exhibit size- and shape-dependent polarized luminescence [11–14], Ln^{3+} -doped UCPs show distinguished nature of emission polarization which is independent of the particle size and morphology [15–19]. The upconversion

luminescence (UCL) of Ln^{3+} in a crystalline host matrix consists of many sharp emission peaks due to the multiple transition levels within the $4f^N$ configuration and their crystal-field (CF) splitting into degenerate sublevels [20–30]. Each CF sublevel emission is polarized along a particular direction allowed by the crystallographic symmetry [31–34]. However, the CF transition lines of Ln^{3+} in UCPs are usually elusive and undistinguishable at room temperature because of the line broadening and multiple sites of Ln^{3+} in micro/nano-crystals [35–38]. As a consequence, it is difficult to make full use of the polarization of UCL of Ln^{3+} and its functionality has been largely unexplored. In this regard, it is urgent to assign the CF transition lines of Ln^{3+} in UCPs and unravel their polarization directions, which is of fundamental significance for designing Ln^{3+} -based anisotropic UCL probes toward many innovative applications.

LiLuF_4 is a uniaxial crystal with a tetragonal structure (space group $I4_1/a$) isomorphic to LiYF_4 and a single site symmetry of S_4 for all Lu^{3+} ions [39–42]. It is an efficient host material for UCL of Ln^{3+} dopants owing to its low phonon energy and high chemical stability [43,44]. The UCL of Ln^{3+} in LiLuF_4 lattice is characterized by sharp emission peaks even at room temperature due to the strong CF level splitting [45], which facilitates the discrimination of the CF transition lines of Ln^{3+} and thereby enables the determination of their polarization directions in micro/nano-scale LiLuF_4 .

Herein, we report the unique linearly polarized UCL of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ single microcrystals. The dependence of the UCL intensities for the CF transitions of Er^{3+} in a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal on the polarization of both excitation and emission light is unveiled upon 980-nm linearly polarized laser excitation. The CF levels and CF transition lines of Er^{3+} , as well as the intrinsic relationship between the polarization anisotropy of UCL and the local site symmetry of Er^{3+} , are systematically investigated through high-resolution photoluminescence (PL) and UCL spectroscopies at 8 K. By taking advantage of the well-resolved and highly-polarized CF transition lines of Er^{3+} , we show in a proof-of-concept experiment the application of the polarized UCL for tracking the microcrystal orientation, thus revealing the great potential of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ UCPs as sen-

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sitive anisotropic luminescent probes.

EXPERIMENTAL SECTION

Chemicals and materials

$\text{Lu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%), and $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%) were purchased from Aladdin (Shanghai, China). Ethanol, ethylenediaminetetraacetic acid (EDTA, 99.5%), LiF (98.0%), and NH_4F (96.0%) were purchased from Sinopharm Chemical Reagent Co (Shanghai, China). All the chemical reagents were used as received without further purification.

Synthesis of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals

$\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals were synthesized through a modified hydrothermal method. In a typical synthesis, EDTA (0.1461 g, 0.5 mmol) was dissolved in 25 mL of distilled water followed by addition of 1.2 mL of $\text{Ln}(\text{NO}_3)_3$ solution (0.5 mol L^{-1} , $\text{Ln} = \text{Lu}$, Yb , and Er). The mixed solution was stirred for 40 min and then 0.0741 g of NH_4F and 0.052 g of LiF were added under vigorous stirring. After aging for 20 min, the mixture was transferred to a 50-mL Teflon-lined autoclave and allowed for reaction at 200°C for 48 h. After being cooled to room temperature, the precipitates were collected by centrifugation, washed with ethanol and distilled water several times, and finally re-dispersed in ethanol.

Characterization

The powder X-ray diffraction (XRD) pattern of the microcrystals was collected on an X-ray diffractometer (MiniFlex 600, Rigaku) with Cu $\text{K}\alpha_1$ radiation ($\lambda = 0.154187 \text{ nm}$). The morphology of the microcrystals was characterized by using a JSM6700F scanning electron microscope (SEM). Polarized UCL spectra and microscopic UCL images of the microcrystals were recorded by an inverted confocal laser microscope (CLM, Nikon Ti-E) equipped with a spectrometer (Acton SpectraPro SP-2300), a Si charge-coupled device (CCD) camera (Nikon DIGITAL SIGHT DS-Ri1), and a fiber-coupled 980-nm linearly polarized diode laser (MDL-III-980). PL excitation and emission spectra were recorded on an FLS980 spectrometer (Edinburgh) equipped with both continuous xenon (450 W) and pulsed flash lamps. UCL spectra were collected under excitation with the 980-nm diode laser. For low-temperature measurements, samples were mounted on a closed cycle cryostat (8–350 K, DE202, Advanced Research Systems). The emission or excitation monochromator's slits were set as small as possible to maximize the instrumental resolution, and the highest wavelength resolution was 0.05 nm. The line intensities and positions of the measured spectra were calibrated according to the correction curve of the instrument and standard mercury lamp.

RESULTS AND DISCUSSION

$\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ (20:2 mol/mol) microcrystals were synthesized through a modified hydrothermal method [46]. SEM image of the as-synthesized $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals shows that they are rhombohedral with a mean size of $\sim 20 \mu\text{m} \times 12 \mu\text{m}$ (Fig. S1). The XRD pattern of the microcrystals displays intense diffraction peaks that can be well indexed to tetragonal LiLuF_4 (JCPDS No. 027-1251), indicating pure phase and high crystallinity of the microcrystals (Fig. S2). Elemental mappings by energy dispersive X-ray spectrum (EDS) revealed the homo-

geneous distribution of Lu, Yb, Er, and F in the microcrystals (Fig. S3). The absence of Li is because of its small atomic number that cannot be detected by EDS.

An inverted CLM (Nikon Ti-E) system was employed for microscopic studies of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals. The schematic diagram of the CLM system is shown in Fig. 1a. A 980-nm linearly polarized diode laser was used as the excitation source, which passed through a half-wave plate and a high reflective dichroic mirror at 980 nm, and then was focused with a microscope objective lens ($\text{NA} = 0.50$, $20\times$) to a spot diameter of $\sim 5 \mu\text{m}$. The UCL emission spectra were collected by the same microscope objective, sent to the detection part after spectral filtering, and then detected by a spectrometer equipped with a Si CCD camera (Nikon DIGITAL SIGHT DS-Ri1). To investigate the polarization-dependent UCL, we located a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal on a glass slide with its c -axis (optical axis) parallel to the horizontal plane. In this scheme, both the excitation and emission light propagates perpendicularly to the c -axis, yielding two polarization configurations, π - and σ -configurations, with polarizations parallel and perpendicular to the c -axis, respectively (Fig. 1b). The α -configuration, with light propagation along the c -axis, is non-polarized due to the axial symmetry of LiLuF_4 [39]. Based on the customized CLM system, single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals with certain orientations can be readily distinguished, and their bright green UCL can be visualized under 980-nm laser excitation (Fig. 1c–e).

We began with the spectral scanning of a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal upon 980-nm linearly polarized diode laser excitation with a power of 74 mW. The UCL spectrum shows a set of sharp emission peaks with full-width at half maximum (FWHM) smaller than 0.70 nm, which are well-resolved and can be assigned to the CF transitions of Er^{3+} from the $^2\text{H}_{11/2}$ (515–530 nm), $^4\text{S}_{3/2}$ (538–554 nm), and $^4\text{F}_{9/2}$ (645–675 nm) multiplets to the $^4\text{I}_{15/2}$ ground state (Fig. 2a and b). Specifically, the emissions from $^2\text{H}_{9/2}$ to $^4\text{I}_{13/2}$ ($\sim 559.75 \text{ nm}$) and $^4\text{I}_{11/2}$ ($\sim 692.60 \text{ nm}$), which are normally assumed to be weak and undetectable for microcrystal powder in ordinary detection system (Fig. S4) [47,48], were explicitly observed at room temperature based on the CLM system with a high excitation power density (377 kW cm^{-2}), affirming the high sensitivity of the CLM system for research of micropolarized UCL of lanthanides. Power dependence investigation revealed that the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ multiplets of Er^{3+} were populated *via* a two-photon energy transfer upconversion process (Fig. S5). No noticeable change in the UCL intensity of the microcrystal was observed after several hours of continuous irradiation, manifesting absolute photostability of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals.

To probe the excitation polarization, we added a half-wave plate coupled with a polarizer in front of the laser source, whereby the polarization angle (φ) of excitation light was controlled by rotating the half-wave plate. The excitation polarized UCL spectra of a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal were collected with the starting excitation polarization parallel ($\varphi = 0^\circ$) to the crystal c -axis and with no polarizer in the detection part. When φ was tuned from 0° to 360° , the UCL intensity of the microcrystal remained essentially unchanged (Fig. 2c), in parallel with concentric circles in the polar plots of the integrated UCL intensities for the CF transitions of Er^{3+} as a function of φ (Fig. 2d), unraveling that the UCL of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals was independent of the polarization of excitation light.

Figure 1 (a) Schematic diagram of the customized CLM system for polarized UCL measurement. (b) Illustration of the two main excitation/emission configurations for a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal. In π -configuration, light propagates perpendicularly to the crystal c -axis with a polarization parallel ($\theta = 0^\circ$) to the c -axis. In σ -configuration, light propagates perpendicularly to the c -axis with a polarization perpendicular ($\theta = 90^\circ$) to the c -axis. (c) Macroscopic UCL image, (d) microscopic bright-field image, and (e) microscopic UCL image of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ single microcrystals cast on a microscope slide under excitation with a 980-nm diode laser.

Figure 2 (a) UCL spectrum of a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal upon 980-nm linearly polarized laser excitation with a power of 74 mW; (b) energy level diagram showing the energy transfer upconversion processes in $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals, accompanied with the CF splitting levels of $2\text{H}_{11/2}$, $4\text{S}_{3/2}$, and $4\text{F}_{9/2}$ of Er^{3+} ; (c) excitation polarized UCL spectra of a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal under 980-nm excitation with the excitation polarization angle (ϕ) varying from 0° to 360° ; (d) polar plots of integrated UCL intensities (normalized at their maxima) for the CF transitions of Er^{3+} as a function of ϕ .

For probing the emission polarization, we removed the polarizer from the excitation part and placed it in front of the detector. The emission polarized UCL spectra of a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal were recorded by rotating the half-wave plate in the detection part under 980-nm excitation. As shown in Fig. 3a and b, the UCL intensity of the microcrystal exhibits a periodic variation with the emission polarization angle (θ) tuning from 0° to 360° , indicative of an emission polarization anisotropy. Specifically, different CF transition lines originating from two identical multiplets of Er^{3+} display drastically distinct polarization dependence (Fig. 3c–e). The integrated UCL intensities for the CF transitions from $^4\text{S}_{3/2}$ to $^4\text{I}_{15/2}$ at 541.35, 548.00, and 548.70 nm increase gradually with increasing θ from 0° to 90° , indicating σ -polarization for these transitions. By contrast, the integrated UCL intensities for the CF transitions from the same $^4\text{S}_{3/2}$ multiplet at 539.70, 540.65, 541.95, 543.05, 550.50, 550.65, and 551.30 nm decrease with increasing θ , indicative of π -polarization for these transitions; and the intensities for the CF transitions at 540.35 and 542.30 nm remain constant and thus they are non-polarized (Fig. 3f and g). Different emission polarizations were also observed for the CF transitions from $^2\text{H}_{11/2}$ and $^4\text{F}_{9/2}$ to $^4\text{I}_{15/2}$ (Fig. 3h and i, Fig. S6, and Table S1). The polarization degrees (ρ), defined as $\rho = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$, where $I_{\max}$ and $I_{\min}$ are the maximum and

minimum integrated UCL intensities, respectively, were determined, with the largest values of 0.62, 0.65, and 0.82 for the CF transitions from $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ to $^4\text{I}_{15/2}$ at 521.40, 543.05, and 668.20 nm, respectively. Such emission polarization diversity and countercyclical polarization dependence of different CF transitions between identical multiplets of Er^{3+} in $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ single microcrystals reveal that the CF transitions instead of the overall multiplet emission are the fundamental element that should be considered for exploring the applications of polarized UCL of lanthanides.

To gain deep insights into the emission polarization anisotropy of UCL and assign the CF transition lines in detail, we measured the high-resolution PL and UCL spectra of Er^{3+} in $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals. The excitation and emission spectra were recorded at 8 K to avoid thermal broadening of spectral lines at room temperature (Fig. S7) [49,50]. Fig. 4 shows the high-resolution PL spectra of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystals at 8 K. By monitoring the Er^{3+} emission at 668.20 nm, a series of CF transition lines of Er^{3+} from the $^4\text{I}_{15/2}$ ground state to the excited multiplets ($^2\text{P}_1$, $^2\text{G}_7$, $^2\text{K}_7$, $^4\text{G}_7$, $^2\text{H}_9$, $^4\text{F}_7$, and $^4\text{S}_3$) with FWHM smaller than 0.5 nm were detected (Fig. 4a). Particularly, eight excitation lines at 539.60, 540.25, 540.55, 541.25, 541.40, 541.85, 542.25, and 543.05 nm were observed for the $^4\text{S}_{3/2}$ multiplet (inset of Fig. 4a), which can be ascribed to the CF tran-

Figure 3 (a) Schematic illustration of the microcrystal orientation for emission polarized UCL measurement. (b) Emission polarized UCL spectra of a single $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ microcrystal upon 980-nm linearly polarized laser excitation with the emission polarization angle (θ) varying from 0° to 360° . The enlarged polarized UCL spectra for the CF transitions of Er^{3+} from (c) the $^2\text{H}_{11/2}$, (d) $^4\text{S}_{3/2}$, and (e) $^4\text{F}_{9/2}$ multiplets to the $^4\text{I}_{15/2}$ ground state, showing drastically different polarization states for different CF transition lines. Polar plots of integrated UCL intensities (normalized at their maxima) for the CF transitions of Er^{3+} from (f, g) the $^4\text{S}_{3/2}$ and (h, i) $^4\text{F}_{9/2}$ multiplets to the $^4\text{I}_{15/2}$ ground state as a function of θ .

Figure 4 (a) PL excitation spectrum (recorded at 8 K) of $\text{LiLuF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystals by monitoring the Er^{3+} emission at 668.20 nm. The inset enlarges the CF transition lines for the $^4\text{S}_{3/2}$ multiplet. (b) UCL spectrum (recorded at 8 K) of $\text{LiLuF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystals upon 980-nm excitation at a power density of 10 W cm^{-2} . The insets show the CF transition lines of Er^{3+} from the upper (black dash-dot line) and lower (red dash-dot line) Stark sublevels of $^4\text{S}_{3/2}$ to (left) four low-lying and (right) four high-lying Stark sublevels of $^4\text{I}_{15/2}$. (c) CF energy levels of the $^4\text{S}_{3/2}$ and $^4\text{I}_{15/2}$ multiplets of Er^{3+} in LiLuF_4 microcrystals, showing all CF transitions from $^4\text{S}_{3/2}$ to $^4\text{I}_{15/2}$.

sitions from the four low-lying Stark sublevels of $^4\text{I}_{15/2}$ to the two Stark sublevels of $^4\text{S}_{3/2}$. As expected for a Kramers ion, the $^4\text{I}_{15/2}$ and $^4\text{S}_{3/2}$ levels of Er^{3+} in LiLuF_4 microcrystals with a single S_4 site symmetry are doubly degenerate and split into eight ($4\Gamma_{5,6} + 4\Gamma_{7,8}$) and two ($\Gamma_{5,6} + \Gamma_{7,8}$) CF levels, respectively (Table S2) [51,52]. As a result, the two CF levels of $^4\text{S}_{3/2}$ and the four low-lying CF levels of $^4\text{I}_{15/2}$ as well as their CF transition lines were unequivocally assigned, as listed in Table 1. With the definite CF levels of $^4\text{S}_{3/2}$, the other four high-lying CF levels of $^4\text{I}_{15/2}$ and the total 16 CF transition lines from $^4\text{S}_{3/2}$ to $^4\text{I}_{15/2}$ were specified based on the high-resolution PL ($\lambda_{\text{ex}} = 378.80 \text{ nm}$) and UCL ($\lambda_{\text{ex}} = 980 \text{ nm}$) spectra at 8 K (Fig. 4b and c, and Fig. S8). Similarly, CF transition lines from the Stark sublevels of $^2\text{H}_{11/2}$ and $^4\text{F}_{9/2}$ to those of $^4\text{I}_{15/2}$ can be distinguished by virtue of the high-resolution PL excitation and UCL emission spectra, from which six

CF levels of $^2\text{H}_{11/2}$ and five CF levels of $^4\text{F}_{9/2}$ were identified (Figs S9 and S10). The numbers of CF levels for $^2\text{H}_{11/2}$ (6), $^4\text{S}_{3/2}$ (2), $^4\text{F}_{9/2}$ (5), and $^4\text{I}_{15/2}$ (8) of Er^{3+} determined by the high-resolution PL spectroscopy agree well with the theoretically predicted ones ($J + 1/2$) for a Kramers ion, thus confirming a single spectroscopic site of Er^{3+} in LiLuF_4 microcrystals, as we previously reported in Eu^{3+} - and Nd^{3+} -doped LiLuF_4 nanocrystals [45].

With the known site symmetry of S_4 , we are able to specify the irreducible representation (irreps) for each CF level of Er^{3+} in LiLuF_4 microcrystals based on the group theory and the reference of $\text{LiYF}_4\text{:Er}^{3+}$ isomorphism (Table 1 and Table S2) [51,52]. Utilizing the irreps labels, the polarization directions for each CF transition of Er^{3+} in LiLuF_4 microcrystals can be theoretically predicted according to the selection rules for S_4 point group

(Table S3) [32]. As outlined in Table S1 in the Supplementary information, the polarization directions of the UCL for all CF transitions of Er^{3+} in $\text{LiLuF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ single microcrystals experimentally observed on the CLM system are consistent with those predicted in theory, demonstrating unambiguously that the polarized UCL of lanthanides is dictated by the crystal symmetry and the selection rules for their local site symmetry.

The polarized CF emissions of UCL from a single $\text{LiLuF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystal, along with the sharp and well-resolved

spectral lines at room temperature, enables the precise monitoring of the spatial orientation of the microcrystal. To this regard, we fixed the polarizer in the detection part and rotated the microscope slide, whereby the microcrystal orientation varied along the horizontal plane. It was found that the UCL intensity of the microcrystal under 980-nm excitation changed remarkably with increasing orientation angle (β) between the crystal c -axis and the polarization direction. As shown in Fig. 5a, the UCL intensity for the CF transition from $^4\text{S}_{3/2}$ to $^4\text{I}_{15/2}$ in σ -

Table 1 Experimental energy levels for the $^4\text{I}_{15/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$, and $^2\text{H}_{11/2}$ multiplets of Er^{3+} in LiLuF_4 microcrystals

Multiplet	Energy (cm^{-1})	Irreps	Multiplet	Energy (cm^{-1})	Irreps
$^4\text{I}_{15/2}$	0	$\Gamma_{5,6}$	$^4\text{S}_{3/2}$	18,471	$\Gamma_{5,6}$
-	23	$\Gamma_{7,8}$	-	18,532	$\Gamma_{7,8}$
-	34	$\Gamma_{5,6}$	$^2\text{H}_{11/2}$	19,199	$\Gamma_{5,6}$
-	63	$\Gamma_{7,8}$	-	19,218	$\Gamma_{7,8}$
-	284	$\Gamma_{7,8}$	-	19,270	$\Gamma_{7,8}$
-	307	$\Gamma_{7,8}$	-	19,355	$\Gamma_{5,6}$
-	331	$\Gamma_{5,6}$	-	19,374	$\Gamma_{7,8}$
-	369	$\Gamma_{5,6}$	-	19,393	$\Gamma_{5,6}$
$^4\text{F}_{9/2}$	15,334	$\Gamma_{7,8}$	-	-	-
-	15,353	$\Gamma_{5,6}$	-	-	-
-	15,372	$\Gamma_{7,8}$	-	-	-
-	15,448	$\Gamma_{7,8}$	-	-	-
-	15,481	$\Gamma_{5,6}$	-	-	-

Figure 5 (a) Polarized UCL spectra for the CF transitions of Er^{3+} from $^4\text{S}_{3/2}$ to $^4\text{I}_{15/2}$ in a single $\text{LiLuF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystal at different spatial orientations upon 980-nm linearly polarized laser excitation. The insets show the corresponding microscopic UCL images of the microcrystal at different orientations. The red and black arrows denote the directions of the polarizer and the crystal c -axis, respectively. Polar plots of (b) the integrated UCL intensity at 540.65 nm and (c) the UCL intensity ratio between the CF transitions at 540.65 and 541.35 nm for the six orientations of the microcrystal in (a) as a function of emission polarization angle.

polarization at 541.35 nm increases significantly with increasing β from 0° to 90° , in marked contrast to those in π -polarization at 539.70, 540.65, 543.05, and 550.50 nm. Because of the sinusoidal or cosinusoidal dependence of the UCL intensities on the emission polarization angle, the polarized UCL spectrum of the microcrystal at an orientation angle β is identical to that at $(180^\circ - \beta)$. Therefore, the UCL intensity alone is not a good parameter for microcrystal orientation analysis. Instead, the polar plot of UCL intensities for the CF transitions can be exploited for indicating the microcrystal orientations. By rotating the emission polarizer, the polarized UCL spectra of microcrystal at different orientations were recorded (Fig. S11). Fig. 5b shows the polar plots of the integrated UCL intensity at 540.65 nm (π -polarization) for microcrystals of different orientations as a function of emission polarization angle, wherein the angles of maximum intensities are in good agreement with $(180^\circ - \beta)$ ($\beta = 0^\circ, 33^\circ, 47^\circ, 77^\circ, 88^\circ$, and 106°). Particularly, the UCL intensity ratio between the CF transitions of distinct polarization directions at 540.65 and 541.35 nm can be utilized as a ratiometric signal readout in a polar plot for monitoring the microcrystal orientation with improved accuracy and reliability (Fig. 5c). These results reveal the great potential of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ UCPs as anisotropic UCL probes for orientation tracking, which is highly desirable for flow shear tomography and intracellular microrheometry [2,16]. It is worth mentioning that, since the polarization properties of Ln^{3+} ions are governed by their local site symmetry, the polarized UCL properties of Er^{3+} in $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ are independent of the particle size and morphology and also applicable to their nanoscale counterparts, in view of the single site symmetry of S_4 for Ln^{3+} in LiLuF_4 lattice.

CONCLUSIONS

In summary, we have systematically investigated the linearly polarized UCL properties of $\text{LiLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ single microcrystals based on the customized CLM system. We unraveled that the UCL of the microcrystals was independent of the excitation polarization but exhibited an emission polarization anisotropy with drastically different polarizations for the CF transitions of Er^{3+} from identical multiplets. By means of low-temperature (8 K) and high-resolution PL and UCL spectroscopies, 21 CF energy levels and 52 CF transition lines of Er^{3+} in UCL of interest were unequivocally identified, which enabled the accurate assignment of their polarization directions according to the selection rules for S_4 symmetry in LiLuF_4 . Furthermore, by utilizing the well-resolved and highly-polarized CF transition lines of Er^{3+} , we achieved the precise monitoring of the spatial orientation of the microcrystals. The unambiguous revelation of the CF levels and CF transition lines of Er^{3+} and their polarization directions in single UCPs is of vital importance for the future design of lanthanide-based anisotropic UCL probes towards many innovative applications such as single-particle tracking and super-resolution bioimaging.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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LiLuF₄:Yb³⁺/Er³⁺单颗粒微米晶的偏振上转换发光和取向示踪应用

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摘要 稀土掺杂微/纳晶体的偏振上转换发光在单颗粒示踪和高分辨成像等领域具有广泛的应用前景. 然而, 由于稀土上转换颗粒的多位置发光和谱线展宽, 其上转换发光的晶体场偏振组分往往难以区分. 本文报道了LiLuF₄:Yb³⁺/Er³⁺单颗粒微米晶的线偏振上转换发光, 其晶体场跃迁谱线容易分辨, 偏振度达到0.82. 通过低温高分辨荧光光谱和上转换光谱测试, 我们揭示了LiLuF₄:Yb³⁺/Er³⁺微米晶Er³⁺的晶体场能级、晶体场跃迁谱线及其上转换发光的偏振各向异性. 利用Er³⁺易分辨且高度偏振的晶体场跃迁谱线, 我们还证明了LiLuF₄:Yb³⁺/Er³⁺单颗粒微米晶作为各向异性上转换荧光探针在取向示踪方面的潜在应用. 这些发现为稀土掺杂单颗粒的上转换偏振各向异性研究提供了理论基础, 也为各向异性荧光探针的设计和多功能用途的开发提供了新思路.