Supporting Information

Achieving Circularly Polarized Luminescence and Large Piezoelectric Response

in Hybrid Rare-Earth Double Perovskite by a Chirality Induction Strategy

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1. Synthesis methods

The single crystals of all of compounds were obtained by evaporation of aqueous solutions containing the stoichiometric amounts of organic ammine nitrates, Eu(NO₃)₃·6H₂O, and RbNO₃.

1.1 (Q)₂RbEu(NO₃)₆

Quinuclidinium (Q) nitrates (4 mmol, 0.7 g), $Eu(NO_3)_3 \cdot 6H_2O$ (2 mmol, 0.892 g), and RbNO₃ (2 mmol, 0.295 g) were dissolved in a water solution (20 ml). The solution was stirred at room temperature until completely dissolved, and then evaporated at room temperature. After 2-3 days, the colorless bulk single-crystal of (Q)₂RbEu(NO₃)₆ precipitated at the bottom of the beaker.

1.2 (MeQ)₂RbEu(NO₃)₆, Rac, R1, and S1

The synthesis method and large-sized crystal preparation were the same as that for $(Q)_2RbEu(NO_3)_6$. Powder X-ray diffraction measurements for R1 and S1 were performed to confirm the purity of the phase. As shown in Figure S16, Supporting Information, PXRD patterns (green curve) match well with the calculated one, confirming the purity of the phase. Thermogravimetric (TG) measurements disclose that the decomposition temperature for R1 and S1 was 561 and 560 K, respectively, indicating that they possess superior thermostability in hybrid compounds (Figure S17, Supporting Information).

2. Measurement methods

2.1 Crystal structure determination

The X-ray single-crystal diffraction data were collected using a Rigaku XtaLAB Synergy R, HyPix diffractometer. Data were measured using *w* scans and using Mo K_a (λ = 0.71073 Å) radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation of the program CrysAlisPro. The unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.39a, 2019). Data reduction, scaling and absorption corrections were performed using CrysAlisPro. The structure was solved with the ShelXS or ShelXT solution program using direct methods and by using Olex2 as the graphical interface. The model was refined with ShelXL 2018/1 using full matrix least squares minimisation on *F*². R1 and S1 are suggested to belong to space group of *P*2₁3 at HTP and LTP. However, by physical properties, the structure in LTP is assumed to be the space group *R*3.

The X-ray crystallographic structures have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers 2096217-2096223), and can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/ get structures.

2.2 Circular dichroism spectrum measurement

The CD and absorbance spectra were collected at room temperature using a CD spectrometer (JASCO, J-1700) with a scan rate of 500 nm min⁻¹, and the data pitch being 1 nm. The single crystal slice of R1 and S1 with thickness of about 0.1 mm were prepared for CD spectrum measurement.

2.3 Thermomechanical analysis

DSC measurements were performed using a netzsch differential scanning calorimeter under nitrogen atmosphere at atmospheric pressure. The heating/cooling rate is 10 K/min.

2.4 Polarized light microscopy measurements

Polarized light microscopy measurements were performed using an Eclipse E600 POL polarizing microscope (Nikon) equipped with a Linkam THMSE 600 cooling/heating stage. The temperature was stabilized with an accuracy of 0.1 K.

2.5 SHG measurements

For second harmonic generation (SHG) experiments, an unexpanded laser beam with low divergence (pulsed Nd: YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate) was used. The instrument model is FLS 920, Edinburgh Instruments, and the control temperature system is DE 202, while the laser is Vibrant 355 II, OPOTEK. The numerical values of the nonlinear optical coefficients for SHG have been determined by comparison with a KH_2PO_4 (KDP) reference. The test samples were polycrystalline powder.

2.6 Variable-temperature dielectric permittivity, pyroelectric property and P-E hysteresis loops measurements

For variable-temperature dielectric permittivity measurements, a Tonghui TH2828A impedance analyzer was used. The single-crystal plates of R1 with well-defined directions along the [111]direction of HTP were used (thickness, 0.5 mm; area, 6.5 mm²). The Rigaku Synergy diffractometer was used to determine the direction of the crystals. Silver conducting paste deposited on the plate surfaces was used as electrodes. The crystal plate used in the dielectric testing process was used for the Pyroelectric property, and P-E hysteresis loops measurement. Pyroelectric property was measured with an electrometer/high resistance meter (keithley 6517B) with the heating rate of 10 K/min. The P-E loops were calculated from current density–electric field (J-V) curves using the double wave method (*Nat. Commun.* 2014, 5, 3279; *J. Phys. Soc. Jpn.* 2008, 77, 064706).

2.7 Piezoresponse force microscopy measurements

The measurements of nanoscale polarization imaging and local switching spectroscopy were carried out using a resonant-enhanced piezoresponse force microscopy (MFP–3D, Asylum Research). Conductive Pt/Ir-coated silicon probes (EFM–50, Nanoworld) were used for domain imaging and polarization switching studies. To verify the piezoresponse, we applied a 1 V AC driving voltage on the sample to measure the normal and shear responses, with the AC frequency set at the second resonant peak of cantilever-sample system to enhance the sensitivity. The measurement was carried out on the thin crystals, which were prepared as follows. Firstly, commercial ITO-coated glass substrate was ultrasonic cleaned in ethanol for 20 minutes. A drop of aqueous solution of R1 (20 mg/ml) was carefully spread on a freshly cleaned ITO-coated glass. The slow evaporation gave the thin film consisting of small thin crystals, whose shape is similar to the large crystals.

2.8 Piezoelectric measurements

For macroscopic piezoelectric coefficient (d_{33}) , we adopted the quasi-static method by a commercial

piezometer (Piezotest, model: PM200). The single crystal plates for R1 and S1 were clamped between two flat metal plates, then a dynamic force of about 0.25 N along [111]-direction of HTP was applied.

2.9 Photoluminescence measurements

The measurements of emission, excitation, and emissive lifetimes for R1 and S1 in solid states were carried out using an Edinburgh FLS-920 fluorescence spectrometer. The luminescent quantum yields of powder samples for R1 and S1 in sealed quartz cuvettes were determined by the integrating sphere (142 mm in diameter) using Edinburgh FLS-920 Spectro fluorophotometer.

2.10 Circularly polarized luminescence (CPL) spectra measurements

Circularly polarized luminescence (CPL) spectra were measured on JASCO CPL-300 spectrophotometers using Xe lamp excited by 397 nm at room temperature. Crystals have been measured CPL spectra by sticking on the quartz plate perpendicular to the test direction. The crystals were rotated 90°, 180° , 270° after one measurement. Powder samples have been measured by filling in quartz clip with 1 mm thick groove. Measurement conditions were as follows: scanning speed 100 nm/min, D.I.T. 1sec, data pitch 0.5 nm, and excitation slit width 3000 μ m, emission bandwidth 15 nm.

2.11 DFT calculations

The projector-augmented wave method^[1] with the generalized gradient approximation of the Perdew–Burke–Ernzerh of exchange-correlation functional^[2] in the Vienna Ab initio Simulation Package^[3] was used. Van der Waals interaction was considered by applying the Grimme's DFT-D3 method. The cut-off energy was set to be 400 eV. The threshold of force and energy convergence was set to be 0.01 eV Å⁻¹ and 10⁻⁵ eV, respectively. The transition electric dipole moment and transition magnetic dipole moment of MA, R-M3HQ⁺, S-M3HQ⁺, and Eu(NO₃H)₆³⁺ were calculated in the framework of time-dependent density functional theory by using the Gaussian code.^[4] The B3LYP exchange-correlation functional and def2-TZVP Gaussian basis set were employed.^[5] The influence of lone pair on Eu(NO₃H)₆³⁺ is investigated by comparing the intraoctahedron distortion of between Eu(NO₃H)₆³⁺ in R1 and relaxed Eu(NO₃H)₆³⁺ in R1. The (NO₃)⁻ anions are fixed during the structural optimization. The orbitals of Eu(NO₃H)₆³⁺ are plotted by utilizing the Multiwfn software.^[6]

2.12 PXRD measurements

The Rigaku D/MAX 2000 x-ray diffractometer adopting Cu-K α radiation ($\lambda = 0.15406$ nm, 40 kV and 40 mA) and a secondary beam graphite monochromator was used to perform PXRD measurement. Measurement angle ranges from 5° to 50° with step size of 0.02° and scanning speed 2°/min.

2.13 Thermogravimetric measurements

Thermogravimetric (TG) measurements were recorded on a NETZSCH TG 209F3 apparatus under an N_2 atmosphere with a heating rate of 10 K min⁻¹.

3. Supporting Figures



Figure S1. CD (A) and UV-visible absorption spectra (B) of S1 (blue) and R1 (red).

We carried out the circular dichroism (CD) spectra measurements in the ultraviolet–visible (UV– vis) absorption range to demonstrate the chirality of R1 and S1. As depicted in Figure S1, R1 and S1 exhibit obvious CD signals at the same wavelength, located at around 305 nm, corresponding to those in the UV-visible absorption spectra. The CD signal responses of the R1 and S1 are opposite, revealing the enantiomorphic structure feature.



Figure S2. DSC curves of R1 (A) and S1 (B) in heating and cooling run.



Figure S3. Structural unit of K₂NaAlF₆, R1 and S1.



Figure S4. Distribution of the equivalent spontaneous polarizations in R1 and S1.



Figure S5. Multiaxial ferroelastic and ferroelectric properties for R1. (A-C) Evolution of ferroelastic domains of R1 from HTP to LTP to HTP. (D) SHG signal response of the power sample as a function of temperature. (E) Pyroelectric current curve for R1 in a heating run. (F) Temperature dependence of polarization.



Figure S6. *J*-*E* loop for R1 at 250 K.



Figure S7. The schematic diagram of (A) N–M–N bond angle and (B) M–N bond length. (C) The distortion originated from Eu 6s² lone pair.



Figure S8. The orbital plot of (A) HOMO, (B) HOMO-1, (C) HOMO-2, (D) HOMO-11, (E) HOMO-12, and (F) HOMO-13 of $Eu(NO_3H)_6^{3+}$ in R1.



Figure S9. The orbital plot of (A) HOMO, (B) HOMO-1, (C) HOMO-2, (D) HOMO-11, (E) HOMO-12, and (F) HOMO-13 of relaxed $Eu(NO_3H)_6^{3+}$ in R1.



Figure S10. Piezoelectric constant (d_{33}) measurement for R1 (left) and S1 (right), using quasi-static

(Berlincourt) method.



Figure S11. Photoluminescence properties for R1. (A) Excitation (blue line) and emission spectra (red line) for R1 at room temperature. Photographs of R1 under ambient light and UV light (365 nm) (inset). (B-C) Quantum yield and fluorescence lifetime for R1 and S1 compared with those of other Mn-based molecular ferroelectrics. Including TMCM-MnCl₃ (trimethylchloromethyl ammonium trichloromanganese), (Pyrrolidinium)MnCl₃, (3-pyrrolinium)MnCl₃, [(CH₃)₃NH]₃(MnBr₃)(MnBr₄) and (Pyrrolidinium)MnBr₃.



Figure S12. Excitation (blue line) and emission spectra (red line) for S1 at room temperature.



Figure S13. Photoluminescence properties measurements. The lifetime measurement results for R1 (A) and S1 (B). The quantum yield measurement results for R1 (C) and S1 (D).



Figure S14. CPL spectra. (A) Simplified CPL test configuration. (B) Circularly polarized luminescence spectra of S1 and R1 crystal samples after rotating crystal at different angles (90°, 180°, 270°). (C) $g_{lum} vs$ wavelength curves.



Figure S15. The DFT-calculated band structure of (A) R1 without R-M3HQ and (B) S1 without S-M3HQ.



Figure S16. Experimental (green) and calculated (red) PXRD patterns of R1 (a) and S1 (b) in

HTP.



Figure S17. TG curves of R1 (a) and S1 (b).

4. Determination of [1 1 1]-direction of the crystal for R1

To determine [1 1 1]-direction of the crystal of R1 follow these steps. First, the morphology of single-crystal for R1 was calculated by the software (Mercury) based on the cif structure. Then, according to results, the single-crystal was cut along the (1 1 1)-plane perpendicular to the [1 1 1]-direction, Figure R3. Finally, the flat-single-crystal was tested by XRD. As shown in Figure R4, the major Bragg diffractions are (1 1 1), (2 2 2), (3 3 3) and (4 4 4), suggesting that the direction of the vertical biggest plane is [1 1 1]-direction.



Figure S18. Calculated morphology of single-crystal for R1 is obtained *via* the software (Mercury) based on the cif structure.



Figure S19. XRD patterns (red curve) of cut single-crystal of the R1. The calculated pattern (blue curve) for comparison is obtained *via* the software (Mercury) based on the cif structure.

5. Supplementary Tables

Crystal	Aizu notation ^{<i>a</i>} for multiaxial ferroelectr	Aizu notation ^a for			
system	Ferroelectrics/ferroelastics	Ferroelectrics	uniaxial		
			ferroelectrics		
Monoclinic	2F1 (2/2)				
Orthorhombic	222F1 (4/2)		222F2 (1)		
Tetragonal	4F1 (4/2); 422F1 (8/2); 422F2(s) (2)		422F4 (1)		
Trigonal	3F1 (3/2); 32F1 (6/2); 32F2 (3/2)		32F3 (1)		
Hexagonal	6F1 (6/2); 622F1 (12/2); 622F2(s) (3)		622F6 (1)		
Cubic	23F1 (12/2); 23F2 (3); 23F3 (4/2);	432F4 (3);			
	432F1 (24/1); 432F2(s) (6)	432F3 (4)			

Table S1. 22 species of chiral-to-chiral ferroelectric phase transitions.

a"F" represents ferroelectric phase transition. The parentheses contain the number of polarization directions, and those ones with "/2" indicate reorientable ferroelectrics.

Compound	$(Q)_2 RbEu(NO_3)_6$	(MeQ) ₂ RbEu(NO ₃) ₆	Rac		
Formula	(C ₇ H ₁₄ N) ₂ RbEu(NO ₃) ₆	(CH ₃ C ₇ H ₁₃ N) ₂ RbEu(NO ₃) ₆	(CH ₃ C ₇ H ₁₂ NOH) ₂ RbEu(NO ₃) ₆		
<i>T</i> /K	293	293	293		
Crystal	1.		trigonal		
System	cubic	trigonal			
Space	F	ה	רַק		
Group	Fm3m	K3	кзт		
a/Å	14.10910(10)	9.7309(2)	9.7075(7)		
<i>b</i> /Å	14.10910(10)	9.7309(2)	9.7075(7)		
c/Å	14.10910(10)	26.8130(7)	27.5091(17)		
$a/^{\circ}$	90	90	90		
b/°	90	90	90		
$g/^{\circ}$	90	120	120		
V/Å ³	2808.65(6)	2198.78(11)	2245.0(4)		
<i>R</i> _{int}	0.0174	0.0344	0.0521		
GooF	1.149	1.109	1.055		

Table S3. The selected crystallographic data for R1 and S1 at LTP and HTP.

Compound R1		R1	S1	S1			
Formula $(CH_3C_7H_{12}NOH)_2R$ $(CH_3C_7H_{12}NOH)_2RbE(CH_3C_7H_{12}NOH)_2RbE(CH_3C_7H_{12}NOH)_2RbE$							
	bEu(NO ₃) ₆	u(NO ₃) ₆	u(NO ₃) ₆	u(NO ₃) ₆			
T/K	253	303	253	303			
Crystal		1.	2 · · · · 1	1.			
System	trigonal	cubic	trigonal	cubic			
Flack	0.150(10)	0.011/10)	0.125(12)	0.000(17)			
Parameter	0.150(10)	0.011(10)	0.135(12)	0.009(17)			
Space	22		22				
Group	K3	<i>P2</i> ₁ 3	<i>K</i> 3	<i>P2</i> ₁ 3			
a/Å	20.3362(5)	14.43640(10)	20.3555(3)	14.42890(10)			
b/Å	20.3362(5)	14.43640(10)	20.3555(3)	14.42890(10)			
c/Å	24.9333(6)	14.43640(10)	24.9006(6)	14.42890(10)			
$a/^{\circ}$	90	90	90	90			
$b/^{\circ}$	90	90	90	90			
$g^{/^\circ}$	120	90	120	90			
$V/Å^3$	8930.0(5)	3008.68(6)	8935.2(3)	3004.00(6)			
R _{int}	0.0559	0.0445	0.0581	0.0644			
GooF	1.118	1.038	1.073	1.067			

Table S4. The bond length distortion and the bond angle variance of R1, S1, and Rac.

System	$\Delta d_{\rm Eu}(10^{-5})$	$\Delta d_{\rm Rb}(10^{-5})$	$\Delta d(10^{-5})$	$\sigma^{2}_{\mathrm{Eu}}(^{\mathrm{o2}})$	$\sigma^2_{\rm Rb}$ (°2)	$\sigma^2(^{o2})$
R1	1.23	2.52	1.88	1.16	89.83	45.50
S 1	2.8×10^{-3}	7.75	3.88	3.43	90.31	46.87
Rac	0	0	0	0.08	105.95	53.01

Table S5. The bond length distortion and the bond angle variance of $Eu(NO_3H)_6^{3+}$ in R1 and relaxed

 $Eu(NO_{3}H)_{6}^{3+}$ in R1.

System	$\Delta d(10^{-5})$	σ^{2} (° ²)
$Eu(NO_3H)_6^{3+}$	1.23	1.16
Relaxed Eu(NO ₃ H) ₆ ³⁺	37.2	4.71

Table S6. Luminescence dissymmetry factor (g_{lum}) for R1 and S1 crystals and powder under 397 nm Xe lamp excitation.

	$g_{\text{lum}} \times 10^3 \ (\lambda_{\text{em}} = 588 \text{ nm})$)	$g_{lum} \times 10^3 (\lambda_{em} = 613 \text{ nm})$)	
Sample	Crystal			Powder	Crystal			Powder		
	0°	90°	180°	270°		0°	90°	180°	270°	
S1	3.6	3.7	3.4	3.0	0.59	-3.3	-3.8	-4.0	-3.3	-0.77
R1	-2.9	-2.9	-2.6	-3.5	-0.39	4.4	3.7	3.8	3.4	0.49

Table S7. The g factor of methylamine (MA), (R)-M3HQ, (S)-M3HQ, and $Eu(NO_3)_6^{3+}$.

System	g factor
MA	1.78 × 10 ⁻⁵
(<i>R</i>)-M3HQ	-0.3045
(<i>S</i>)-M3HQ	-0.4385
$\operatorname{Eu(NO_3)_6^{3+}}$	1.592

5. Supporting References

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