

Two mono- and dinuclear Eu(III) enantiomeric pairs based on chiral bis-bidentate bridging ligands: synthesis, structures, luminescent and ferroelectric properties†

Xi-Li Li,^{*a} Yu-Liang Gao,^a Xiang-Li Feng,^a You-Xuan Zheng,^b Chun-Lai Chen,^a Jing-Lin Zuo^{*b} and Shao-Ming Fang^{*a}

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Using the enantiomeric bis-bidentate bridging ligands (+)/(−)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_S/L_R) and depending on the ratio control of reactants, two mono- and dinuclear Eu(III)-based enantiomeric pairs with the formulae $\text{Eu}(\text{dbm})_3\text{L}_{R/S}\cdot 2\text{H}_2\text{O}$ (L_R in **R-1**, L_S in **S-1** and dbm = dibenzoylmethanato) and $\text{Eu}_2(\text{dbm})_6\text{L}_{R/S}\cdot \text{H}_2\text{O}$ (L_R in **R-2** and L_S in **S-2**) have been stereoselectively synthesized and structurally characterized. The circular dichroic (CD) spectra confirmed their chiroptical activities and enantiomeric natures. The homochiral dinuclear species represents the first example of a polynuclear lanthanide β -diketonate complexes with circular dichroic and crystallographic evidences. The photoluminescent properties studies revealed that both mono- and dinuclear Eu(III) complexes exhibited the characteristic red emissions of Eu(III) ions in the solid state (at 77 K and 300 K) and CH_2Cl_2 solution. Notably, the photophysical properties of the mononuclear enantiomers were superior to the dinuclear species. Interestingly, **R-2** displayed a ferroelectric property at room temperature, which was not observed for **R-1** due to the lack of crystalline polarity. **R/S-2** are the first examples of homochiral polynuclear lanthanide complexes with luminescence and ferroelectric properties, being potential multifunctional materials.

Introduction

The construction of homochiral metal–organic complexes has been a subject of great interest owing to their potential applications including enantioselective synthesis and separation, asymmetric catalysis and chiroptical probes.¹ Besides, they may show other intriguing physical properties such as nonlinear optics, ferroelectricity and piezoelectricity, which are based on the non-centrosymmetric molecular arrangements.² Among these, the ferroelectricity is most appealing because of its wide applications in non-volatile memory storage and optical communication.³ However, searching for new ferroelectric compounds, especially metal–organic ferroelectrics, is still a challenging task owing to the fact that ferroelectric materials must crystallize in acentric space groups belonging to one of the 10 polar point groups (1, 2, 3, 4, 6, *m*, *mm*2, 3*m*, 4*mm* and

6*mm*).^{2b} To satisfy such a prerequisite, introducing chirality into metal complexes is the optimal method, which can be reliably achieved by using *R* and *S* configurations of organic ligands and transferring the chiral information to the resulting molecular structures.^{2c,d}

On the other hand, luminescent lanthanide β -diketonate complexes, especially Eu(III) and Tb(III)-based species, have attracted researchers for decades due to their unique photophysical properties such as long emission lifetimes and sharp emission bands.⁴ These features make them promising for use as luminescent materials for electroluminescent devices, lasers, luminescent probes in biology and photo-conversion molecular devices.⁵ So far, the great majority of reported lanthanide β -diketonate complexes are mononuclear species and only a limited number of dinuclear lanthanide β -diketonate complexes with crystallographic evidence were reported, which were mostly constructed by employing 2,2'-bipyrimidine (bpm) as a bridging ligand to accommodate two metal centers.⁶ In addition to their excellent luminescence features, lanthanide β -diketonate complexes bearing chiral moieties may display other interesting properties such as circularly polarized luminescence (CPL), second harmonic generation (SHG), triboluminescence, chirality sensing and/or ferroelectricity.^{2d,7} However, the known examples are limited to mononuclear species, and there is no report on homochiral dinuclear lanthanide β -diketonate complexes with circular dichroic (CD) nature and crystallographic evidence.

^aHenan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, China. E-mail: lixl@zzuli.edu.cn

^bState Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China. E-mail: zuojl@nju.edu.cn

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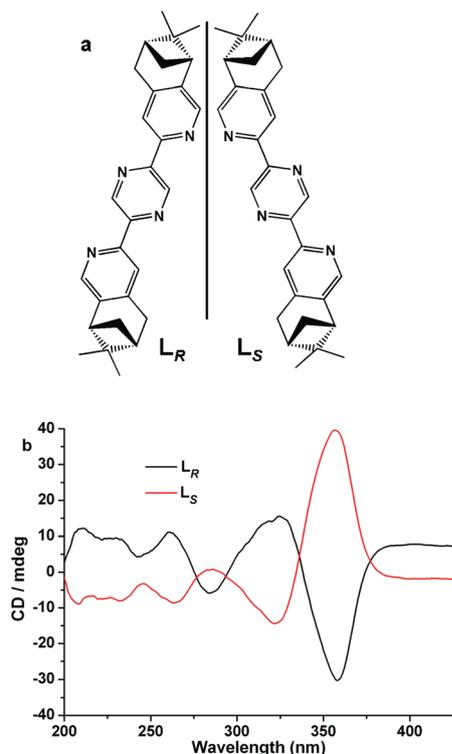


Fig. 1 (a) Enantiomeric bridging ligands L_R and L_S ; (b) the solid-state CD spectra of L_R and L_S .

Ligands play a key role in the preparation of homochiral polynuclear lanthanide β -diketonate complexes, especially for the aim of controlling the nuclearity of the central metal ions. An effective ligand should be homochiral and possess at least two sets of coordinating sites, which must be separated by a rigid spacer so that each set of coordinating sites is able to coordinate to targeted metal ions independently. Recently, we synthesized such a bis-bidentate enantiomeric pair, (+)/(–)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_S/L_R , Fig. 1a) as bridging ligands to treat with $\text{Eu}(\text{dbm})_3\text{H}_2\text{O}$. By ratio control of ligand-to-metal, two pairs of mono- and dinuclear $\text{Eu}(\text{III})$ enantiomers with the formulae $\text{Eu}(\text{dbm})_3L_{R/S} \cdot 2\text{H}_2\text{O}$ (L_R in **R-1**, L_S in **S-1** and dbm = dibenzoylmethanato) and $\text{Eu}_2(\text{dbm})_6L_{R/S} \cdot \text{H}_2\text{O}$ (L_R in **R-2** and L_S in **S-2**) were stereoselectively synthesized. They all exhibited intense red emissions. Notably, **R-2** showed room-temperature ferroelectric property, representing the first example of homochiral polynuclear lanthanide complexes with luminescent and ferroelectric properties. Herein, we report the synthesis, crystal structures and physical properties of two mono- and dinuclear $\text{Eu}(\text{III})$ enantiomeric pairs.

Experimental

Materials and general methods

All of the chemicals are commercial available and used without further purification. $\text{Eu}(\text{dbm})_3\text{H}_2\text{O}$ (Fig. S1, ESI†) was prepared according to a literature method.⁸ Elementary analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on a TENSOR27 Bruker

spectrophotometer from KBr pellets in the region of 4000–400 cm^{-1} . UV-vis absorption spectra were obtained on a UV-4802 spectrometer. The solid-state CD spectra were performed on a JASCO J-810 spectropolarimeter from KBr pellets (1% wt.) at room temperature. The P – E hysteresis loop of **R-2** was obtained with a Ferroelectric Tester Precision Premier II made by Radiant Technologies Inc. at room temperature. A single crystal of **R-2** with an approximate size of $1.2 \times 0.7 \times 0.5 \text{ mm}^3$ was carefully connected to the instrument with electrodes made of Cu wire of 120 μm diameter covered by Ag-conducting glue on two opposite surfaces of the crystal. The photoluminescent spectra and lifetimes were measured with an Edinburgh Instruments FLS920P fluorescence spectrometer. The quantum yields of **R-1** and **R-2** in CH_2Cl_2 solution were calculated by comparison of the fluorescence intensities (integrated areas) of a standard sample (air-equilibrated $\text{Ru}(\text{bpy})_3\text{Cl}_2$ aqueous solution, $\Phi_{\text{std}} = 0.028$) and the unknown samples according to the following equation:⁹

$$\Phi_{\text{unk}} = \Phi_{\text{std}} \left(\frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left(\frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left(\frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \quad (1)$$

where Φ_{unk} is the luminescence quantum yield of the sample, Φ_{std} is the luminescence quantum yield of air-equilibrated $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ aqueous solution ($\Phi_{\text{std}} = 0.028$), I_{unk} and I_{std} are the integrated fluorescence intensities of the sample and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ aqueous solution at the excitation wavelengths, respectively, and A_{unk} and A_{std} are the absorbances of the sample and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ aqueous solution at the excitation wavelengths. The η_{unk} and η_{std} represent the refractive indices of the corresponding solvents. The measurements of the quantum yields were performed thrice at excitation wavelengths at which the Beer–Lambert law is obeyed.

Synthesis of $\text{Eu}(\text{dbm})_3L_{R/S} \cdot 2\text{H}_2\text{O}$ (R/S-1**).** A solution of $\text{Eu}(\text{dbm})_3\text{H}_2\text{O}$ (85 mg, 0.1 mmol) in ethanol (15 mL) was added to a solution of (–)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_R) (42 mg, 0.1 mmol) in acetone (10 mL) with gentle stirring for 20 minutes at room temperature. Subsequently, the mixture was placed undisturbed for two weeks. Pale red block crystals of **R-1** were obtained in 63% yield (based on Eu). Elementary analysis (%) calcd. for **R-1** ($\text{C}_{73}\text{H}_{67}\text{N}_4\text{O}_8\text{Eu}$): C, 68.48; H, 5.27; N, 4.38. Found: C, 68.56; H, 5.12; N, 4.47. IR (KBr pellet, cm^{-1}): 3458 (b, w), 3058 (w), 2924 (w), 1600 (s), 1551 (s), 1516 (s), 1478 (m), 1458 (m), 1403 (s), 1296 (m), 1216 (m), 1163 (w), 1056 (w), 1012 (w), 940 (w), 786 (w), 750 (m), 726 (m), 686 (w), 620 (w), 504 (w). **S-1** was obtained as pale red crystals by a method similar to that of **R-1**, except that (+)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_S) was employed instead of (–)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_R). Yield: 67%. Elementary analysis (%) calcd for **S-1** ($\text{C}_{73}\text{H}_{67}\text{N}_4\text{O}_8\text{Eu}$): C, 68.48; H, 5.27; N, 4.38. Found: C, 68.42; H, 5.21; N, 4.32. IR (KBr pellet, cm^{-1}): 3455 (b, w), 3063 (w), 2925 (w), 1602 (s), 1549 (s), 1516 (s), 1478 (m), 1453 (m), 1408 (s), 1306 (m), 1216 (m), 1170 (w), 1065 (w), 1017 (w), 940 (w), 784 (w), 756 (m), 726 (m), 689 (w), 618 (w), 505 (w).

Synthesis of $\text{Eu}_2(\text{dbm})_6L_{R/S} \cdot \text{H}_2\text{O}$ (R/S-2**).** A solution of $\text{Eu}(\text{dbm})_3\text{H}_2\text{O}$ (180 mg, 0.2 mmol) in ethanol (10 mL) was added to a solution of (–)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine

Table 1 X-ray crystallographic data for complexes **R/S-1** and **R/S-2**

	R-1	S-1	R-2	S-2
Chemical formula	C ₇₃ H ₆₇ N ₄ O ₈ Eu	C ₇₃ H ₆₇ N ₄ O ₈ Eu	C ₁₁₈ H ₉₈ N ₄ O ₁₃ Eu ₂	C ₁₁₈ H ₉₈ N ₄ O ₁₃ Eu ₂
Formula weight	1028.27	1028.27	2083.92	2083.92
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁
<i>a</i> /Å	17.207(3)	17.264(5)	13.951(8)	14.102(9)
<i>b</i> /Å	18.244(8)	18.193(6)	20.082(8)	20.326(9)
<i>c</i> /Å	21.772(5)	21.766(6)	18.742(11)	19.103(5)
β /°	90	90	104.474(6)	105.540(3)
<i>V</i> /Å ³	6825(4)	6836.1(4)	5084.3(5)	5275.6(4)
<i>Z</i>	4	4	2	2
<i>D</i> /g cm ⁻³	1.244	1.244	1.361	1.312
μ /mm ⁻¹	0.973	0.972	1.287	1.240
GOF	1.041	1.062	1.038	1.066
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b	0.0463/0.0970	0.0501/0.1092	0.0550/0.1252	0.0466/0.1205
Flack parameter	0.095(11)	0.003(9)	0.053(11)	0.034(9)

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

(**L_R**) (42 mg, 0.1 mmol) in acetone (10 mL) with gentle stirring for 30 minutes at room temperature. Subsequently, the mixture was placed undisturbed for one week. Deep red block crystals of **R-2** were obtained in 71% yield (based on Eu). Elementary analysis (%) calcd for **R-2** (C₁₁₈H₉₈N₄O₁₃Eu₂): C, 68.01; H, 4.74; N, 2.69. Found: C, 67.95; H, 4.81; N, 2.62. IR (KBr pellet, cm⁻¹): 3432 (b, w), 3058 (w), 2925 (w), 1599 (s), 1554 (s), 1516 (s), 1478 (m), 1458 (m), 1410 (s), 1296 (m), 1216 (m), 1163 (w), 1056 (w), 1012 (w), 940 (w), 786 (w), 750 (m), 726 (m), 686 (w), 610 (w), 513 (w). **S-2** was obtained as deep red crystals by a method similar to that of **R-2**, except that (+)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (**L_S**) was used instead of (-)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (**L_R**). Yield: 69% (based on Eu). Elementary analysis (%) calcd for **S-2** (C₁₁₈H₉₈N₄O₁₃Eu₂): C, 68.01; H, 4.74; N, 2.69. Found: C, 68.16; H, 4.84; N, 2.65. IR (KBr pellet, cm⁻¹): 3436 (b, w), 3052 (w), 2924 (w), 1599 (s), 1551 (s), 1520 (s), 1473 (m), 1458 (m), 1413 (s), 1292 (m), 1213 (m), 1163 (w), 1056 (w), 1012 (w), 940 (w), 786 (w), 753 (m), 725 (m), 683 (w), 610 (w), 510 (w).

X-ray crystallography

The crystal structures of seven complexes were determined on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature. Data reductions were made with the Bruker SAINT package. Absorption corrections were performed using the SADABS program. The structures were solved by direct methods and refined on *F*² by full-matrix least-squares using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model. All computations were carried out using the SHELXTL-2000 program package. Detailed crystallographic data and structures refinement parameters for enantiomeric pairs **R/S-1** and **R/S-2** are summarized in Table 1.

Results and discussion

As shown in the experimental section, two enantiomeric pairs **R/S-1** and **R/S-2** were synthesized by the reaction of

Eu(dbm)₃H₂O and homochiral bis-bidentate ligand (**L_R**/**L_S**) depending on the control of ligand-to-metal ratio. The bis-bidentate ligands **L_R** and **L_S** were synthesized according to similar procedures.¹⁰ Their crystal structures show a linear appearance (Fig. S2, ESI†). Their crystallographic data and structures refinement parameters are summarized in Table S1 (ESI†). The mirror-imaged solid-state CD spectra verified their enantiomeric nature (Fig. 1b). X-ray crystallographic analysis revealed that **R/S-1** and **R/S-2** are enantiomers with respective chiral space groups *P*2₁2₁2₁ and *P*2₁, suggesting that chirality deriving from chiral bis-bidentate organic ligands has been transferred successfully into the resulting solid structures. As each of the enantiomeric pairs show similar physical properties, only the results of **R-1** and **R-2** are described.

Crystal structure of **R-1**

R-1 is a mononuclear Eu(III)-based complex. As shown in Fig. 2, the asymmetric unit contains three β -diketonate anions, a chiral bis-bidentate ligand (**L_R**), an eight-coordinated Eu(III) ion and two lattice water molecules. The central Eu(III) ion is bound by six O atoms of three β -diketonate ligands and two N atoms from one of the bis-bidentate **L_R** to form a EuN₂O₆ polyhedra. The Eu–O distances range from 2.280(3) to 2.391(3) Å, while the two Eu–N bonds are 2.591(4) and 2.633(4) Å. A detailed analysis of coordination geometry reveals that the two faces defined by O3–O4–O5–O6 and O1–N1–O2–N2 are twisted about the respective diagonals O4–O5 and N1–O2 with angles of 21.35° and 6.42°. The corresponding angles are 0° and 0° for a square-antiprism, 29.5° and 29.5° for a dodecahedron, 21.8° and 0° for a bicapped trigonal prism.¹¹ Hence, the coordination polyhedron around Eu(III) ion can be best described as a bicapped trigonal prism (Fig. S3, ESI†). The O6 and O3 atoms cap the two quadrilateral faces O2–O4–O5–N2 and O1–O4–O5–N1 of the trigonal prism.

Crystal structure of **R-2**

The molecular structures of **R-** and **S-2** are depicted in Fig. 3. **R-2** has two eight-coordinated Eu(III) sites bridged by **L_R**, and

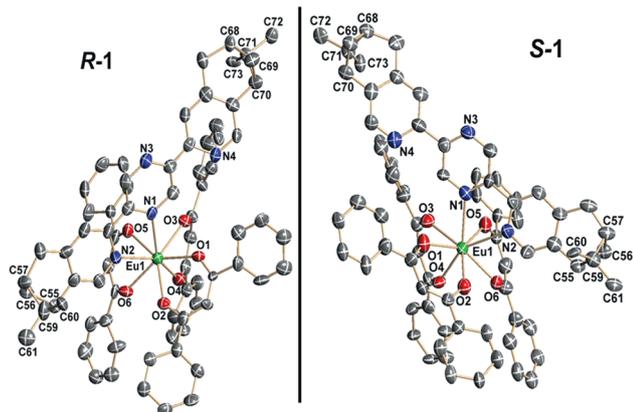


Fig. 2 The structures (ORTEP at 50% probability) of *R/S*-1. H atoms and lattice water molecules are omitted for clarity.

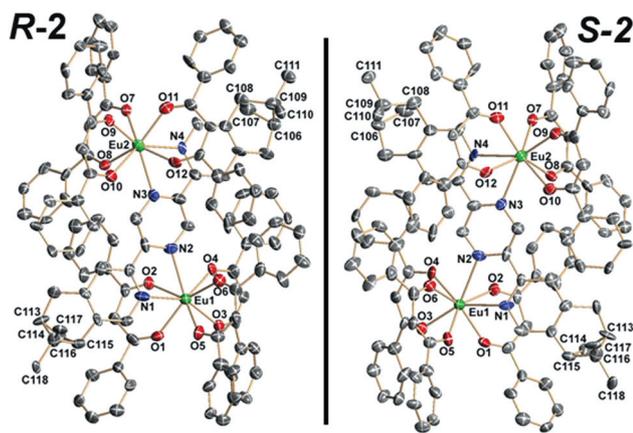


Fig. 3 The structures (ORTEP at 50% probability) of *R/S*-2. H atoms and lattice water molecules are omitted for clarity.

separated by 8.043 Å, which is apparently longer than that of analogues (7.011 Å) bridged by 2,2'-bipyrimidine (bpm).^{6a} The longer Eu...Eu distances favor the high luminescence since energy migration between metal ions will be decreased.¹² Each Eu(III) ion has the same coordination atoms as those of *R*-1. For Eu1, the average Eu–O distance is 2.331 Å, while the average Eu–N distance is 2.635 Å. The corresponding averages for Eu2 are 2.311 and 2.636 Å. Each Eu(III) center is in a distorted square antiprismatic environment with the approximate square planes defined as N1–N2–O5–O6 (top plane) and O1–O2–O3–O4 (bottom plane) for Eu1, N3–N4–O7–O8 (top plane) and O9–O10–O11–O12 (bottom plane) for Eu2 (Fig. S4, ESI†). The twisted angles of two approximate square planes for Eu1 are 16.95° and 16.23° and the corresponding angles for Eu2 are 17.00° and 17.09°. Therefore, the coordination geometry of each Eu(III) ion is best described as an intermediate between square antiprism and dodecahedron.¹¹

Circular dichroism (CD) spectra

To prove the chiroptical activities and enantiomeric natures of *R/S*-1 and *R/S*-2, their solid-state CD spectra were recorded.

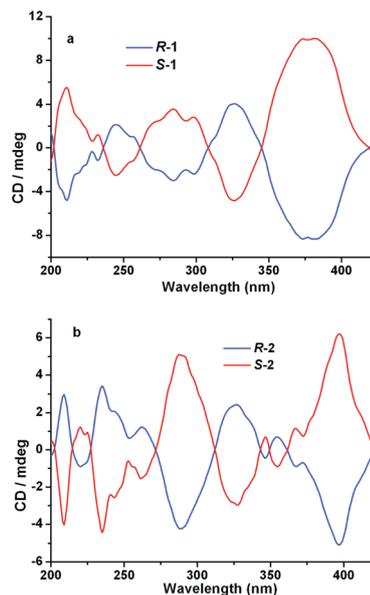


Fig. 4 (a) Solid-state CD spectra of *R*- and *S*-1; (b) *R*- and *S*-2 based on pressed KBr disks including 1% (wt.) of enantiopure crystal grains at room temperature.

As shown in Fig. 4, each pair of enantiomers exhibit mirror-symmetrical CD spectra of one another. *R*-1 exhibits positive Cotton effects at $\lambda_{\text{max}} = 210, 285$ and 380 nm with negative Cotton effects at $\lambda_{\text{max}} = 245$ and 325 nm, while *S*-1 shows Cotton effects with opposite signs at the same wavelengths. *R*-2 exhibits positive Cotton effects at $\lambda_{\text{max}} = 288$ and 397 nm with negative signs at $\lambda_{\text{max}} = 208, 235$ and 328 nm, while *S*-2 shows Cotton effects with opposite signs at the same wavelengths. The bands between 200–300 nm are assigned to $\pi \rightarrow \pi^*$ transitions of the dbm, chiral L_R or L_S chromophores, while the bands above 300 nm can be ascribed to their $n \rightarrow \pi^*$ transitions.¹³

Photophysical properties

The emission spectra of *R*-1 and *R*-2 in the solid state (at 77 K and 300 K) and CH_2Cl_2 solution were investigated. In the solid state, upon excitation at 410 nm (Fig. S6, ESI†), *R*-1 and *R*-2 displayed the characteristic line-like emission of Eu(III) ion at 580, 590, 612, 650 and 705 nm (Fig. 5a and 5b) at 77 and 300 K, which can be attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions of Eu(III) ion. The strength of the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is known to be very sensitive to the ligand environment about the Eu(III) ion.¹⁴ For *R*-1 and *R*-2, the dominant $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions are very intense compared to the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, implying a highly distorted chemical environment around the Eu(III) ions, which favors the intense red emissions of *R*-1 and *R*-2.^{5d,15} The profiles of the emission spectra of *R*-1 and *R*-2 are similar because the ligands coordinated to Eu(III) ion are identical and the coordination surroundings of Eu(III) ion in *R*-1 and *R*-2 are also analogous. Additionally, the outlines of emission spectra at 77 and 300 K for *R*-1 and *R*-2 are the same. Further, only one sharp band of symmetry-forbidden emission of $^5\text{D}_0 \rightarrow ^7\text{F}_0$ at 580 nm and three

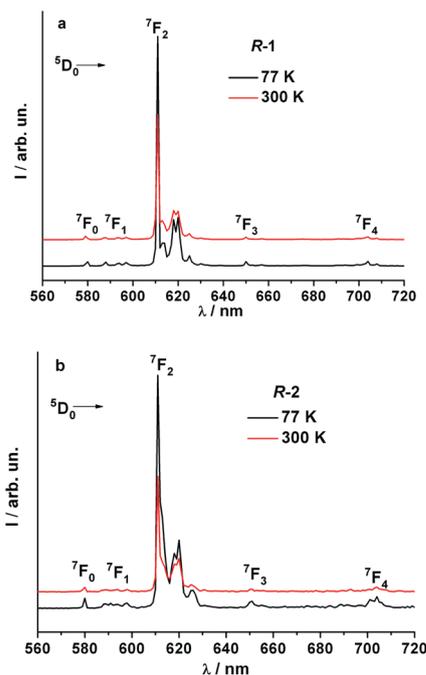


Fig. 5 Emission spectra of **R-1** (a) and **R-2** (b) in the solid state at 77 and 300 K.

Stark components ($2J + 1$) for the $^5D_0 \rightarrow ^7F_1$ transition are observed, which indicate that there is only one symmetry site of the Eu(III) ion in **R-1** and **R-2**.¹⁶ Although there are two Eu(III) ions in **R-2**, both Eu(III) ions indeed have the same coordination environments and geometries. Additionally, the intensity ratios $I_2(^5D_0 \rightarrow ^7F_2)/I_1(^5D_0 \rightarrow ^7F_1)$ are equal to 9.6 for **R-1** and 7.9 for **R-2** based on the respective emission spectra at 300 K, which are higher than those of Eu(III) luminescent complexes reported previously.¹⁷ The results further verified that the Eu(III) ions in **R-1** and **R-2** occupy sites with low symmetry and have no inversion center,¹⁸ which is consistent with the crystal structure analyses of **R-1** and **R-2**.

In the solid state, the lifetime values were determined from the luminescence decay profiles for **R-1** and **R-2** at 77 and 300 K by fitting with a monoexponential curve. The decay profiles of **R-1** and **R-2** are shown in Fig. S7 and S8, respectively (ESI†). For **R-1**, the lifetime values are 0.670 and 0.533 ms at 77 and 300 K, respectively. The corresponding lifetime values for **R-2** are 0.607 and 0.447, which are shorter than those of **R-1**. The relatively shorter lifetimes result from the energy migration between Eu(III)—Eu(III), which results in the non-radiative decay pathway.¹² Finally, the absolute quantum yields were measured at 300 K to be 39% for **R-1** and 21% for **R-2** in the solid state by means of an integrating sphere method.¹⁹

The emission spectra of **R-1** and **R-2** in CH_2Cl_2 solution also displayed the typical emission of Eu(III) ions (Fig. 6). Noticeably, the luminescence signal of **R-1** is more intense than that of **R-2** under same conditions, which was also observed in the solid state at 77 and 300 K. For further comparison of photophysical properties, their emission quantum yields and lifetimes were investigated in CH_2Cl_2 solution. The quantum yields were calculated to be 9.1% for **R-1** and 3.7% for **R-2** by using $\text{Ru}(\text{bpy})_3\text{Cl}_2$

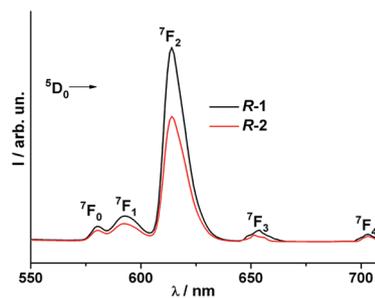


Fig. 6 Emission spectra of **R-1** and **R-2** in CH_2Cl_2 solution ($1.5 \times 10^{-5} \text{ mol L}^{-1}$) at room temperature.

($\Phi_{\text{std}} = 2.8\%$ in water) as a standard reference. The quantum yield of **R-1** is nearly 3 times that of **R-2**, and is also larger than those of reported mononuclear analogues with centrosymmetric structures.²⁰ Meanwhile, the quantum yield of **R-2** is comparable with triple-stranded dinuclear β -diketonate Eu(III) complexes in solution (5%).²¹ The decay curves for **R-1** and **R-2** were monitored within the $^5D_0 \rightarrow ^7F_2$ emission (Fig. S9, ESI†) and could be described by a single exponential behavior, implying the presence of a single type of local environment for Eu(III) ions in **R-1** and **R-2**. The lifetime values for **R-1** and **R-2** were found to be 0.379 and 0.322 ms, respectively. Our results showed that the photophysical properties (intensity, quantum yield and lifetime value) of **R-1** are superior to **R-2** in both the solid state and solution. Such a phenomenon is similar to those of reported dinuclear β -diketonate Eu(III) complexes.^{6a}

Ferroelectric properties

Although **R-1** crystallizes in chiral space group $P2_12_12_1$, having a non-centrosymmetric molecular arrangement, it does not belong to a polar point group. However, **R-2** crystallizes in polar point group 2 with a highly distorted coordination environment, which satisfies the prerequisite for occurrence of ferroelectricity.² In addition, the keto–enol (in β -diketonate molecules) transformation usually results in switching molecular polarity (ferroelectricity).^{2a} Fig. 7 clearly showed the P – E hysteresis loop of **R-2** based on a single crystal sample at room temperature, obviously indicating its ferroelectricity. The remnant polarization (P_r) value

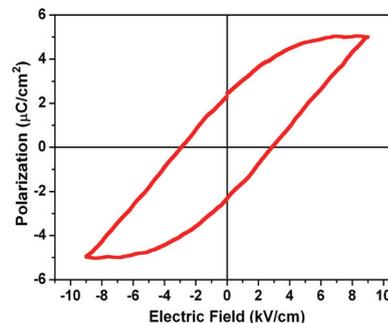


Fig. 7 P – E hysteresis loop of **R-2** based on a single crystal sample at room temperature.

is about $2.4 \mu\text{C cm}^{-2}$ at an applied field of 3.1 kV cm^{-1} . The saturation value of spontaneous polarization (P_s) is about $4.7 \mu\text{C cm}^{-2}$ for **R-2**, which is much larger than that of inorganic ferroelectrics $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ($P_s = 0.25 \mu\text{C cm}^{-2}$) and is smaller than those of chiral metal–organic hybrids [*m*-RBz-1-APy][PbI_3] (*m*-RBz-1-APy = 3-*R*-benzylidene-1-amino-pyridinium, R = NO_2 , Cl, Br or F, $P_s = 12.8\text{--}48 \mu\text{C cm}^{-2}$).²² In particular, the temperature dependence of dielectric constant for **R-2** was measured at 0.1, 1, 10, 100 kHz and 1 MHz (Fig. S10, ESI†). The results showed that the dielectric constant is strongly temperature dependent (dielectric anomaly) with a magnitude of 2.1×10^3 at 325 K and 0.1 kHz, which is slightly smaller than that of mononuclear $\text{Eu}(\text{tta})_3\text{L}_{RR}$ ($\sim 10^5$ at 0.1 kHz, tta = 2-thenoyltrifluoroacetate, $\text{L}_{RR} = (-)$ -4,5-pinenepiperidine) previously reported by us.^{2d} The large dielectric constant with dielectric anomaly further confirmed that the well-shaped *P*–*E* hysteresis loop of **R-2** originates from its ferroelectricity.^{2c,23} Complex **R-2** exhibits a ferroelectric property but **R-1** does not, indicating that the modulation of the Eu nuclearity based on the bis-bidentate bridging ligand may change the crystalline polarity and the corresponding ferroelectric properties. To the best of our knowledge, **R/S-2** represent the first example of homochiral polynuclear lanthanide complexes with luminescent and ferroelectric property, being potential multifunctional materials.

Conclusions

In conclusion, with the use of enantiomeric bis-bidentate bridging ligands and depending on the ratio control of reactants, two mono- and dinuclear Eu(III) enantiomeric pairs have been synthesized and structurally characterized. Chiroptical activities and enantiomeric natures of each enantiomeric pair were confirmed by circular dichroism spectra measurements. Among them, the homochiral dinuclear Eu(III) complexes represent the first example of chiral polynuclear lanthanide β-diketonate complexes with crystallographic evidence. The solid-state photoluminescent investigations at 77 and 300 K revealed that both mono- and dinuclear Eu(III) complexes exhibit the characteristic red emissions of Eu(III) ions with a shorter lifetime for **R-2** compared to that of **R-1**. Further studies on the photophysical properties were performed in CH_2Cl_2 solution. The results also showed that the intensity, lifetime and quantum yield of mononuclear enantiomer were superior to dinuclear species. Ferroelectric studies demonstrated that **R-2** displays a ferroelectric property at room temperature, which is not observed for **R-1**. **R-2** and **S-2** are the first example of homochiral polynuclear lanthanide complexes with photoluminescent and ferroelectric properties, being potential multifunctional materials.

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Notes and references

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