Ferroelectric Materials

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Molecule-Based Ferroelectric Thin Films: Mononuclear Lanthanide Enantiomers Displaying Room-Temperature Ferroelectric and Dielectric Properties**

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Ferroelectricity is one of major subjects in the field of materials science owing to its wide applications in ferroelectric random-access memories (FeRAMs)[1] and tunable microwave devices.[2] In previous reports, considerable research on ferroelectric materials was devoted to inorganic compounds such as $NaKC_4H_4O_6{\cdot}4\,H_2O$[3] and perovskite-like oxides.[4,2b,5] Recently, molecule-based ferroelectric materials have received much attention owing to features distinctive from those of inorganic materials.[1a,b,6] For example, molecule-based complexes are easily polarized in an applied field because of polar groups in the organic ligands. Neutral mononuclear molecule-based ferroelectric materials can be more conveniently evaporated at low temperature than ionic inorganic compounds for the preparation of memory devices by chemical vapor deposition (CVD) methods. Consequently, the fabrication process is more controllable and the precursor molecule is not decomposed, which results in the retention of molecular structure in the resulting films.

As donor or acceptor dopants,[7b] lanthanide cations have typically been used to modify the properties of ferroelectrics such as lead zirconium titanate (PZT) for achieving high P_r (remnant polarization) values, square hysteresis loops, and enhanced fatigue resistance.[7] However, to the best of our knowledge, there are no reports on lanthanide-containing complexes in molecule-based ferroelectrics. In our work, two chiral 2,2′-bipyridine derivatives ($L_{R,R} = (-)$-4,5-pinene bipyridine and $L_{S,S} = (+)$-4,5-pinene bipyridine; see Scheme S1 in the Supporting Information) were prepared,[8] and their coordination to $[Eu(tta)_3]{\cdot}2\,H_2O$ was investigated (tta = 2-thenoyltrifluoroacetonate).[9] Subsequently, the neutral enantiomeric pair **1** and **2** with the formula $[Eu(tta)_3L]$ ($L = L_{R,R}$ for **1** and $L_{S,S}$ for **2**) and a C_2 polar point group were successfully synthesized, and they are among the simplest hybrid organic–inorganic ferroelectric materials. Furthermore, hybrid organic–inorganic ferroelectric thin films were prepared by CVD methods for the first time. Reported herein is a detailed description of the synthesis, crystal structures, and ferroelectric and dielectric properties of **1** and **2**.

Pale red crystals of **1** and **2** were obtained by slow evaporation over a period of three weeks of an acetone/ethanol solution containing $[Eu(tta)_3]{\cdot}2\,H_2O$ and the respective chiral 2,2′-bipyridine derivative. X-ray analysis revealed that the two complexes are enantiomers and their properties are similar, and hence only the results of **1** are given in the ensuing discussion (Figure 1). Complex **1** is a mononuclear neutral europium(III) complex. As shown in Figure 1, each molecule contains three β-diketonate anions, a chiral 2,2′-bipyridine derivative, and an eight-coordinate Eu^{III} cation.

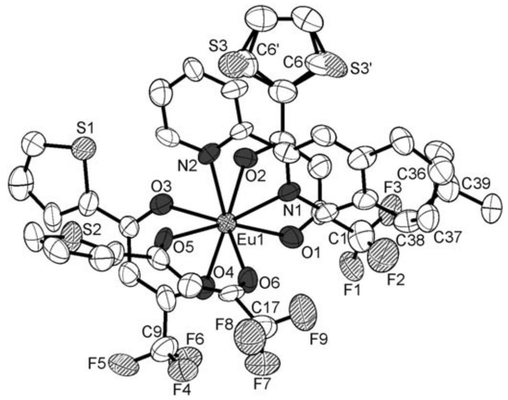

Figure 1. The structure of **1** showing 50% probability displacement ellipsoids; H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Eu1-O1 2.383(7), Eu1-O2 2.363(6), Eu1-O3 2.357(7), Eu1-O4 2.370(7), Eu1-O5 2.392(7), Eu1-O6 2.355(7), Eu1-N1 2.546(8), Eu1-N2 2.586(8); O1-Eu1-O3 116.1(3), O2-Eu1-O4 119.7(3), O5-Eu1-N1 109.7(3), O6-Eu1-N2 106.9(3).

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Each of the three diketonate anions provides two donor O atoms to coordinate to the Eu^{III} ion, and one thienyl ring is disordered at the S3 and C6 atoms. The other two coordination sites of the Eu^{III} ion are occupied by two N atoms of the chiral bipyridine derivative to complete the eight-coordinate configuration. The O−Eu bond lengths range from 2.355 to 2.392 Å, while the two N−Eu bond lengths are 2.546 and 2.586 Å. Eight bonds with different lengths give rise to a strongly distorted square-antiprism environment around the Eu^{III} ion. The O1-O2-O3-O4 (bottom plane) and O5-O6-N1-N2 atoms (top plane) comprise the two square-basic planes of the antiprism with mean deviations of 0.0315 and 0.0258 Å from each plane, and their dihedral angle is 2.8°. For a regular square antiprism, two square planes are parallel to each other and one square is rotated 45° from the other. However, in **1**, the top plane is rotated by only 22.6° from the bottom plane. The coordination geometry of the Eu^{III} ion is best described as an intermediate between square antiprism and dodecahedron. This type of coordination configuration around the Eu^{III} center leads to the very low structural symmetry of **1**. Complex **1** crystallizes in the chiral space group $P2_1$ owing to the presence of the chiral bipyridine derivative. Both pyridinyl groups in the bipyridine derivative coordinate to the Eu^{III} ion, making them completely coplanar. The chirality of **1** is dominated by the two chiral centers (C36 and C38) of the bipyridine derivative. The structural plot of **2** is presented in Figure S3 in the Supporting Information.

To confirm the enantiomeric nature of **1** and **2**, the circular dichroism (CD) spectra (Figure 2) were measured in THF. Compound **1** (*R*,*R* isomer) exhibits a positive Cotton effect at $\lambda_{max} = 220$ nm and negative effects at $\lambda_{max} = 255$ and 280 nm. Complex **2** (*S*,*S* isomer) exhibits Cotton effects with opposite signs at the corresponding wavelengths, and its CD spectrum is a mirror image of that of **1**. Additionally, the SHG (second harmonic generation) efficiency was measured for the optical activity of **1** and **2**. According to the principle proposed by Kurtz and Perry,[10] we estimated the second-order nonlinear optical effects of **1** and **2**, which display an SHG efficiency approximately five times that of urea.

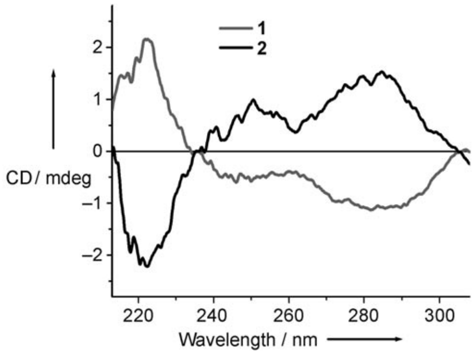

Figure 2. Circular dichroism spectra of **1** and **2**.

The ferroelectric data of **1** and **2** were recorded at room temperature by using powdered samples in pellets (Figure 3). The observed hysteresis loop and the extremely low leakage current (less than 10^{-11} A cm^{-2}; Figure S5 in the Supporting Information) indicate that **1** and **2** exhibit an apparent ferroelectric behavior. Because **1** and **2** are neutral mononuclear complexes, they are volatile in vacuum at low temperature, which enables the thin-film growth of **1** and **2** on Pt/Ti/SiO_2/Si substrates (see the Supporting Information). The ferroelectric measurements (Figure 4) revealed an enhanced *E*–*P* hysteresis loop with $P_r = 0.022$ µC cm^{-2}, which is higher than other molecule-based ferroelectric materials reported previously.[1a,6c] The coercive field (E_c) is 25 kV cm^{-1} and the leakage currents (ca. 10^{-8} A cm^{-2}) are lower than those of previously reported ferroelectric thin films,[11] which indicates that the observed *E*–*P* loops originate from the ferroelectricity. We suggest that highly distorted structures with a strongly local dipole in the CF_3 groups in **1** and **2** result in the ferroelectricity.[6a,12]

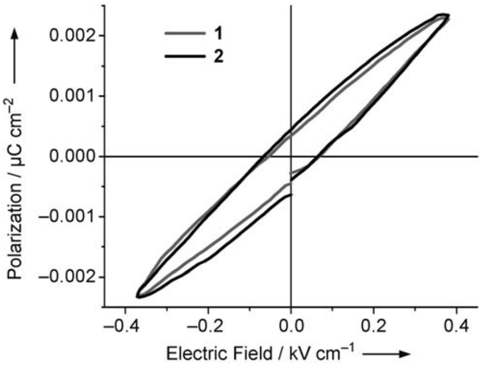

Figure 3. *E*–*P* hysteresis loops on powdered samples of **1** and **2**.

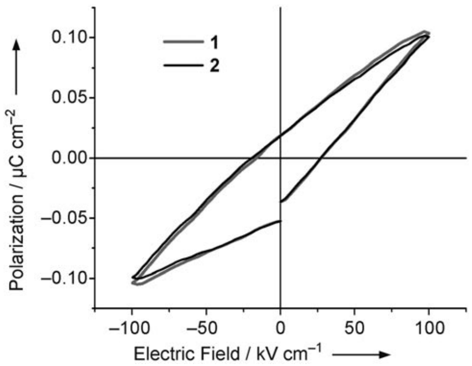

Figure 4. *E*–*P* hysteresis loops on thin films of **1** and **2**.

Since **1** and **2** constitute a pair of enantiomers, they exhibit the same physical properties, and only the dielectric properties of **1** are described in detail. The temperature dependence of the ac dielectric constant and dielectric loss of **1** were measured at various frequencies in the range 10^2–10^6 Hz. A dielectric constant peak of about 10^5 at 100 Hz appears at 28.0 °C (Figure 5 a), indicating the presence of a phase transition at $T_c = 28.0$ °C. The peak height decreases with increasing frequency, but does not show the temperature dependence. An additional superimposed shoulder component at 100 Hz is centered at the low-temperature side of the peak (less than 28.0 °C) and becomes indistinguishable at high

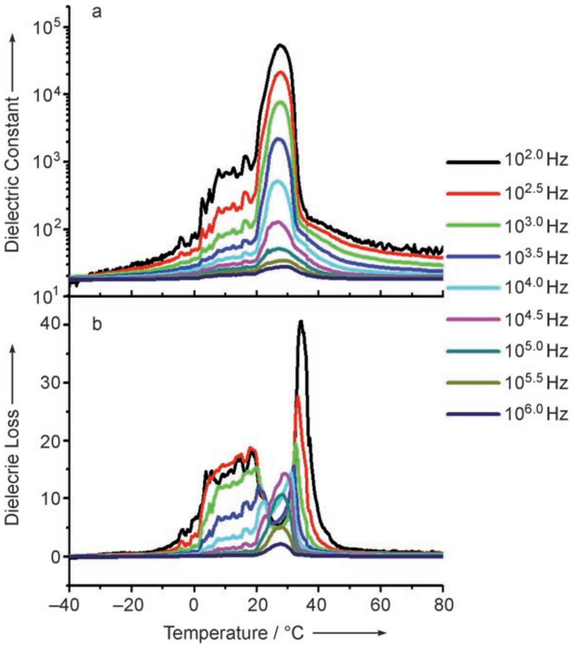

Figure 5. a) Temperature dependence of the dielectric constant ε' (real part) of complex **1** at various frequencies (10^2–10^6 Hz). b) Temperature dependence of the dielectric loss $\varepsilon''/\varepsilon'$, where ε'' and ε' are the imaginary and real parts of dielectric constant for complex **1**, at various frequencies (10^2–10^6 Hz).

frequencies. Correspondingly, a dissipation peak (Figure 5b) is observed at a similar temperature and moves towards high temperature with increasing frequency ($10^{2.0}$–$10^{4.5}$ Hz), which implies a relaxation process. Additional evidence can be found in the frequency dependence of the dielectric constant (see Figure S6 in the Supporting Information). The peak observed in the low-frequency region indicates that the orientation polarization of electric dipoles of the molecule is dominant because the separated centers of positive and negative charges, localized on the Eu^{III} ion and the CF_3 groups, respectively, result in a strong dipole in the molecule along the *b* axis (Figure S2 in the Supporting Information). The broad and dissymmetrical peak suggests that disorder exists at the sublattice level, which we ascribe to the disordered thienyl ring, and leads to the relaxation phenomenon. The characteristic relaxation frequency (peak in the dielectric loss spectra) obeys the Arrhenius Law, and the activation energy is approximately 6.06 eV. It is interesting that an additional dielectric loss peak is observed at low frequencies above 28.0°C and shifts to lower temperature with increasing frequency, while the dissipation peak is only in the range of $10^{4.5}$–$10^{6.0}$ Hz at 28.0°C. This anomaly may arise from the different response of the rotation of the strongly polar CF_3 groups and the disorder of the thienyl ring in the structure of **1** under an applied field.

In summary, two mononuclear chiral lanthanide complexes, a pair of enantiomers, were synthesized, and they display room-temperature ferroelectric properties and a high dielectric constant ($\varepsilon' \approx 10^5$). Thin films of these complexes were successfully prepared, and they exhibit superior ferroelectric properties to those of the powder samples. To the best of our knowledge, they are the simplest hybrid organic–inorganic ferroelectic materials reported so far. Ferroelectric thin films based on this type of neutral metal complexes represent a novel approach to molecule-based ferroelectric materials, which play a significant role in the manufacture of the organic memory devices by CVD methods.

Experimental Section

$[Eu(tta)_3]\cdot 2H_2O$ was prepared by the reaction of $EuCl_3\cdot 6H_2O$ and 2-thenoyltrifluoroacetone (Htta) according to a literature method.[9] The chiral 2,2′-bipyridine derivative shown in Scheme S1 of the Supporting Information was synthesized from 2-acetylpyridine and (1*R*)-(−)-myrtenal or (1*S*)-(+)-myrtenal according to literature procedures.[8]

1 (or **2**): A solution of $[Eu(tta)_3]\cdot 2H_2O$ (85.1 mg, 0.1 mmol) in ethanol (10 mL) was added to a solution of (−)-4,5-pinene bipyridine ($L_{R,R}$) [or (+)-4,5-pinene bipyridine ($L_{S,S}$)] (25 mg, 0.1 mmol) in acetone (10 mL) with gentle stirring. The mixture was left to stand for three weeks. Pale red crystals of **1** and **2** were obtained in 67% or 71% yield, respectively. Elemental analysis (%) calcd for **1** and **2** ($C_{41}H_{30}N_2O_6F_9S_3Eu$): C 46.20, H 2.84, N 2.63; found for **1**: C 46.26, H 2.89, N 2.61; found for **2**: C 46.27, H 2.84, N 2.58. IR (KBr) for **1**: $\tilde{\nu} = 1601$ (s, C=O), 1537 (s, C=N), 1141 cm^{-1} (s, C−F); IR (KBr) for **2**: $\tilde{\nu} = 1601$ (s, C=O), 1552 (s, C=N), 1141 cm^{-1} (s, C−F).

Crystal data for **1**: $C_{41}H_{30}N_2O_6F_9S_3Eu$, $M_r = 1065.81$, monoclinic, space group $P2_1$, $a = 10.184(2)$, $b = 19.003(4)$, $c = 12.052(3)$ Å, $\beta = 113.315(4)°$, $V = 2142.0(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.652\ g\,cm^{-3}$, $T = 298(2)$ K, $R_1\,(wR_2) = 0.0659\,(0.1485)$, $S = 1.050$. The data reduction was made with the Bruker SAINT package. An absorption correction was performed with the SADABS program. The structure was solved by direct methods and refined on F^2 by full-matrix least squares by using SHELXL-2000 with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in the calculations by using the riding model. All computations were carried out with the SHELXTL-2000 program package.[13] CCDC-644702 and CCDC-644703 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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