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Solvent-Induced Single-Crystal-to-Single-Crystal Transformation in Multifunctional Chiral Dysprosium(III) Compounds

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Supporting Information

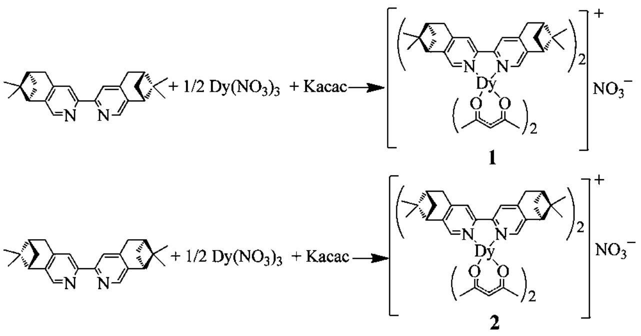
ABSTRACT: Two new enantiomeric ionic chiral dysprosium(III) compounds were designed and synthesized. These compounds show simultaneously the optical activity, ferroelectric effects, nonlinear-optical effects, and slow magnetic relaxation behavior. More interestingly, these compounds exhibit reversible single-crystal-to-single-crystal transformations associated with the release or absorption of solvent molecules. The structure transformations are accompanied by distinct changes in the physical properties.

Molecule-based multifunctional materials have been receiving intensive attention because they may involve an intrinsic coupling between coexisting properties.[1] With the rational design of building blocks and the use of self-assembly principles, it has become possible to produce molecular multifunctional materials with precisely defined structures and tunable physical properties. So far, it has been successfully demonstrated that the same compounds can show simultaneously various physical properties such as porosity, magnetism, conductivity, and ferroelectricity.[2]

Meanwhile, functional materials with properties that can be manipulated by external stimuli (such as light, heat, pressure, or guest molecules) are attracting increasing interest for their potential applications as switches and sensors.[3] In order to understand the origin of the changes in properties, structural information at different functional states is necessary. In this regard, single-crystal-to-single-crystal (SCSC) transformations of functional material are very helpful because retention of the single-crystalline phase can directly and accurately reveal the relationship between the structure and properties.[4]

In our previous work, we reported a series of neutral rare-earth complexes that show interesting optical, magnetic, and/or ferroelectric properties.[5] We have also demonstrated that ionic chiral metal coordination compounds with large net dipole moments might possess desirable ferroelectric properties when crystallized in polar space groups.[6] Here we report the design and synthesis of two new enantiomeric ionic chiral dysprosium(III) compounds, $[Dy(L_1)_2(acac)_2]NO_3$ and $[Dy(L_2)_2(acac)_2]NO_3$ [L_1 = (−)-4,5-bis(pinene)-2,2′-bipyridine; L_2 = (+)-4,5-bis(pinene)-2,2′-bipyridine; Scheme 1], which combine optical activity, ferroelectric effects, nonlinear-optical (NLO) effects, and slow magnetic relaxation behavior in the same compounds. More interestingly, these compounds show reversible SCSC transformations associated with the release or absorption of solvent molecules. The structure transformations are accompanied by distinct changes in the physical properties.

Scheme 1. Synthesis and Molecular Structures of 1 and 2



Compounds **1** and **2** were synthesized according to Scheme 1. The solid-state circular dichroism spectra of **1** and **2** are mirror images (Figure S1 in the Supporting Information, SI), in accordance with being enantiomeric structures. Recrystallization of **1** from methanol gave crystals of $[\mathbf{1}]\cdot CH_3OH\cdot H_2O$ (coded as structure **1a**), which has a polar space group $P2_1$ at room temperature (Table S1 in the SI). The molecule of **1a** consists of one cationic dysprosium(III) complex, one nitrate counterion, and two disordered solvate molecules (methanol and water; Figure 1). The coordination geometry of the dysprosium(III) ion in **1a** can best be described as a slightly distorted square antiprism (Tables S2 and S3 in the SI). Recrystallization of **2** from methanol gave crystals of $[\mathbf{2}]\cdot CH_3OH\cdot H_2O$ (coded as **2a**), which is a mirror structure of **1a**, except for the solvate methanol and water molecules (Figure S2 and Tables S1−S3 in the SI).

1a undergoes a SCSC transformation through the release of crystal solvent molecules at high temperature. Single-crystal X-ray analysis revealed that structure **1a** was transformed to nonpolar space group $C222_1$ at 373 K (coded as **1b**). The asymmetric unit of **1b** consists of one cationic dysprosium(III) complex, one disordered nitrate counterion, and one partially occupied noncoordinated water molecule (Figure 1). The thermogravimetric analysis curve of **1a** (Figure S3 in the SI) shows a continuous weight loss of ≈3.5% between room temperature and 373 K, corresponding to the release of one

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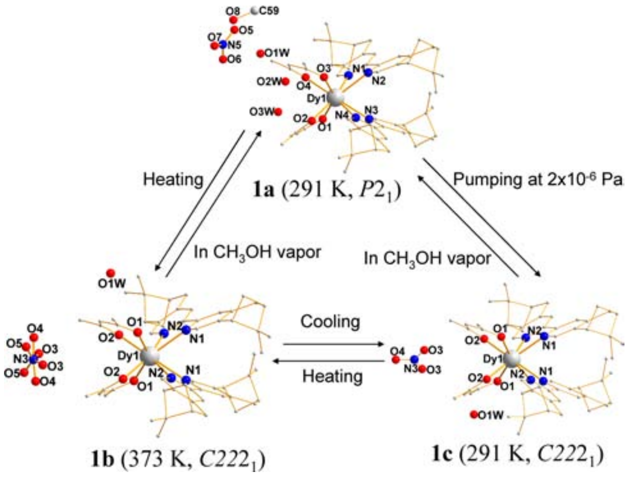

Figure 1. SCSC transformations of **1** under different conditions. Hydrogen atoms are omitted for clarity.

CH_3OH molecule and part of a H_2O molecules. The SCSC transformation of **1a** can also be triggered by removing the solvent molecule upon pumping (2×10^{-6} Pa) at 291 K for 1 h. The crystal structure of **1** upon pumping (coded as **1c**) is very similar to that of **1b** except that the NO_3^- anion is ordered (Figure 1). Interestingly, the SCSC transformation is reversible. As is evidenced by the crystal lattice parameter (Table S4 in the SI), **1b** and **1c** were changed back to **1a** after exposure to CH_3OH vapor. However, no SCSC transformation was observed when **1a** was heated to 373 K under CH_3OH vapor. Release of the residue water molecules in **1b** by heating to 423 K does not cause further SCSC transformation, indicating that the CH_3OH molecules play a key role in the SCSC transformation. Reversible transformation between **1c** and **1b** can be achieved by cooling or heating. The versatile structure transformation in **1** may be related to a solvent-induced internal "chemical pressure" effect, similar to the crystal transformations due to cation exchanges.[7]

1b and **1c** are indeed the same structures below room temperature. Therefore, we only investigated the physical properties of **1a** and **1b** here. The ferroelectric measurements (Figure 2) revealed that complex **1a** indeed displays an obvious ferroelectric behavior with a remnant polarization (P_r) of ca. 0.67 $\mu C \cdot cm^{-2}$ and E_c of ca. 0.18 $kV \cdot cm^{-1}$ by applying an electric field of 0.5 $kV \cdot cm^{-1}$ at 50 Hz. The saturation spontaneous polarization (P_s) is about 1.28 $\mu C \cdot cm^{-2}$, which is larger than that of the typical ferroelectrics $NaKC_4H_4O_6 \cdot 4H_2O$ (Rosal salt; P_s = 0.25 $\mu C \cdot cm^{-2}$). In contrast, **1b** shows no ferroelectric effect, in accordance with their nonpolar crystal structure. Because **1a** and **1b** can be regarded as pseudopolymorphs,[8] the structure transformation from **1a** to **1b** or from **1a** to **1c** can be viewed as pseudo phase transitions. Interestingly, the ferroelectric-to-paraelectric pseudo phase transition in **1a** follows the Curie symmetry principle because space group $P2_1$ of the low-temperature phase is a subgroup of space group $C222_1$ of the high-temperature phase.[9]

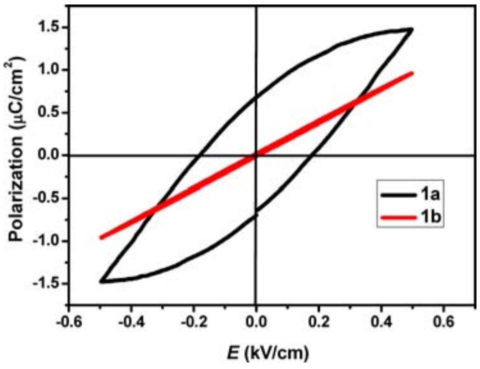

Figure 2. Electric hysteresis loops for compressed powder samples of **1a** and **1b** at 291 K, 0.5 $kV \cdot cm^{-1}$, and 50 Hz.

The dielectric constant of **1a** decreases rapidly between 10 and 10^3 Hz upon increasing frequency and remains effectively constant in range of 10^3–10^6 Hz (Figures S4 and S5 in the SI). A peak appearing at around 330 K in the temperature-dependent dielectric constant at 10 Hz (Figure 3) likely corresponds to the loss of a methanol molecule and the resulting SCSC transition because a similar peak is not observed for the analogous curve of **1b**. The rapid increase of the dielectric constant of both **1a** and **1b** upon heating in the range of 373–393 K is due to the thermal fluctuation accompanied by the elimination of crystallized H_2O molecules.[10] The dielectric constants of **1a** in the range of 335–355 K obey the Curie–Weiss law [$\varepsilon = \varepsilon_0 + C/(T - T_0)$].

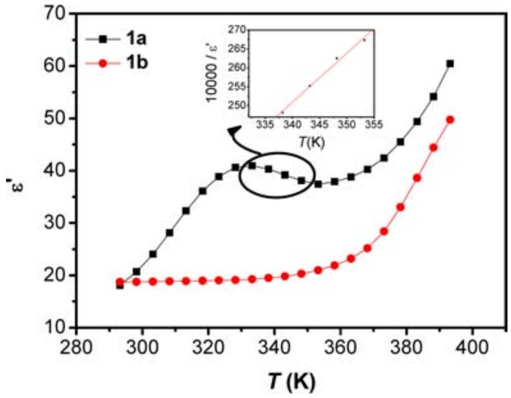

Figure 3. Temperature dependence of the real part of the dielectric constants (ε') of **1a** and **1b** at 10 Hz. The inset shows the reciprocal of ε' of **1a** versus the temperature at 335–355 K.

The magnetic properties of **1a** and **1b** were also investigated because mononuclear dysprosium(III) complexes often exhibit slow magnetic relaxation behavior due to their strong single-ion anisotropy and the presence of low-lying excited states.[11] Direct-current (dc) magnetic measurements revealed that the $\chi_M T$ value of **1a** is 14.13 $emu \cdot K \cdot mol^{-1}$ at room temperature, which slowly decreases to 8.54 $emu \cdot K \cdot mol^{-1}$ at 1.8 K (Figure S6 in the SI). The low-temperature M versus H/T data (Figure S7 in the SI) show nonsuperposition, suggesting the presence of significant magnetic anisotropy and/or low-lying excited states. The magnetization reaches a maximum value of 5.16 Nβ above 70 kOe at 1.8 K, lower than the theoretical value ($g_J J$ = $^4/_3 \times {}^{15}/_2$ = 10 Nβ), indicating a much smaller effective spin in **1a**.

Alternating-current (ac) magnetic measurements revealed that the χ' signals of dynamic magnetic susceptibility of **1a** are almost invariant upon changes in the frequency at zero field (Figure S8 in the SI). However, the χ'' signals show obvious frequency dependence at low temperature, but no peak was observed. By application of a 2 kOe dc field, both the χ' and χ'' signals are frequency-dependent (Figure 4). The χ'' peaks were

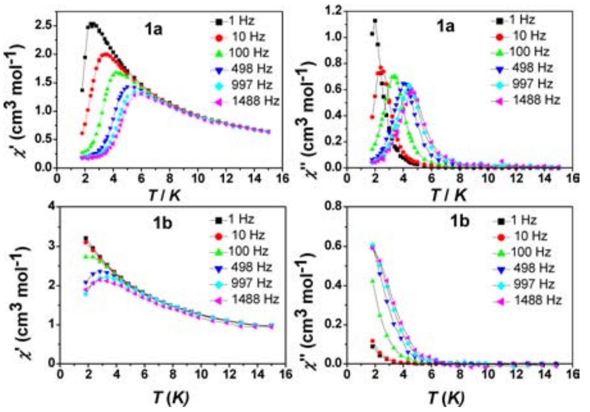

Figure 4. In-phase and out-of-phase dynamic magnetic susceptibilities measured in a 3 Oe ac magnetic field with a 2 kOe dc field for **1a** and **1b**.

determined by a Lorentz peak function fitting in 2000 Oe to estimate the magnetization−relaxation parameters with the Arrhenius law $\tau(T) = \tau_0 \exp(\Delta_{\mathrm{eff}}/k_{\mathrm{B}}T)$. The best-fitting parameters ($R = 0.995$) afford a barrier height ($\Delta_{\mathrm{eff}}/k_{\mathrm{B}}$) of 34.7 K with $\tau_0 = 2.1 \times 10^{-6}$ s (Figure S9 in the SI). The existence of slow magnetic relaxation in **1a** was also supported by the Cole−Cole plot with $\alpha = 0.2$−0.3 from 1 to 1500 Hz under a 2 kOe dc field (Figure S10 in the SI). **1b** also shows slow magnetic relaxation behavior under a 2 kOe dc field, but at significantly lower temperature than that of **1a** (Figures S11 and S12 in the SI and Figure 4). The distinct magnetic behavior of **1a** and **1b** represents more evidence that the single-ion magnetic behavior of dysprosium(III) ion is very sensitive to its local coordination environment.[12]

Both compounds **1a** and **1b** show second-order NLO properties. By using the Kurtz powder method,[13] the second-harmonic-generation responses of **1a** and **1b** are estimated to be 6 and 1 times that of KDP, respectively.

The multifunctional properties of **2a** are almost the same as those of **1a** (Figures S13−S21 in the SI), indicating that enantiomers are indistinguishable in the physical properties investigated in this work.

In summary, we designed and synthesized two new multifunctional enantiomeric ionic chiral dysprosium(III) compounds. These compounds show reversible SCSC transformations associated with the release or absorption of solvent molecules, resulting in significant changes in the ferroelectric, magnetic, and NLO properties. The tunable structures and properties reported here are very intriguing for multifunctional molecular materials. Moreover, the structure transformations in our compounds are the result of internal "chemical pressure" because of the release or absorption of solvent molecules, similar to the effect of external physical pressure.[14] Therefore, our compounds can be also regarded as elastic deformation crystalline materials, which were sparsely reported before.[15]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data (CIF format), further experimental details, and characterization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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