

# Observation of Magnetodielectric Effect in a Dysprosium-Based Single-Molecule Magnet

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## S Supporting Information

**ABSTRACT:** Materials that possess coupled magnetic and electric properties are of significant interest because of their potential use in next-generation magnetoelectric devices such as digital information storage. To date, the magnetoelectric materials that have been studied in-depth have been limited mainly to inorganic oxides such as perovskite oxides. Molecular materials are a promising alternative because their magnetic and electric elements can be combined together at the molecular level via relatively simple molecular designs. Here, we report the coupling of magnetic and electric properties through a magnetodielectric (MD) effect in a single-crystal sample, which is constructed from dysprosium(III) single-molecule magnets (SMMs). The MD effect originates from intrinsic spin–lattice coupling of the dysprosium(III) ion within the sample. This is the first observation of the MD effect in a SMM-based material, which could pave the way toward the synthesis of advanced materials that combine distinct magnetic and electric properties using molecular chemistry for use in molecular devices with nanoscale size.

Single-molecule magnets (SMMs) are discrete molecular species with unique, quantum magnetic properties that originate from their molecular anisotropy. Their potential uses range from next-generation, high-density data storage to spintronics to quantum computing devices.<sup>1–3</sup> SMMs based on *f*-block elements perform very well in terms of both the energy barriers and blocking temperatures because the molecular anisotropy arises from strong intrinsic spin–orbital coupling of *f*-electrons and the crystal-field effect.<sup>2</sup> SMMs with a single metal center, namely single-ion magnets (SIMs), have attracted particular attention because the magnetic anisotropy of the molecule can be precisely controlled by the coordination geometry of the metal center.<sup>1–3</sup> As a result, SMMs may prove valuable for storing information at temperatures around that of liquid nitrogen (about 77 K) or even higher, with the rational designs from the coordination environment of the metal center and magnetic interactions between them.<sup>4,5</sup>

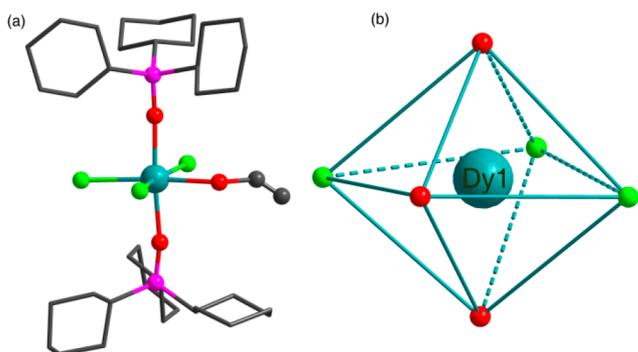
Although the magnetic properties of SMMs have been extensively studied, their electric properties have not been fully explored.<sup>6–8</sup> Their dielectric behavior in response to external magnetic fields, namely the MD effect or the magneto-

capacitance (MC) effect, is usually the precursor of the magnetoelectric (ME) effects, which could potentially be harnessed in next-generation electric devices that permit data to be written electrically and read magnetically.<sup>9</sup> MD and ME effects have been well studied in exotic magnetic insulators or semiconductors based on multiferroic or magnetoelectric materials<sup>10,11</sup> and have also been observed in metal–organic frameworks<sup>12–16</sup> and organic ferroelectrics,<sup>17,18</sup> but they remain unexplored in SMMs due to synthesis challenges of growing large diameter and high quality single crystals. A recent theoretical study suggested that an intrinsic molecular MD effect could exist in SMMs<sup>19</sup> through the Coulomb blockade effect with a bias voltage and applied external magnetic field in single-molecule junctions.<sup>19,20</sup>

Here, we report the observation of the MD effect in an SMM,  $[\text{Dy}(\text{L})_2(\text{C}_2\text{H}_5\text{OH})\text{Cl}_3] \cdot \text{C}_2\text{H}_5\text{OH}$  (**1**, L = tricyclohexylphosphine oxide), which can grow millimeter-sized single crystals prepared by a well-controlled synthetic process that satisfy the requirement of crystal electrode preparation for the MD measurement. Millimeter-sized single-crystals of **1** were obtained via slow evaporation of the solution of the SMM (see **Methods** for details), and crystallized in the orthorhombic space group  $P2_12_12_1$  (**Figure S1** and **Table S1**). The high stability and purity of the sample were confirmed by thermogravimetric analysis and powder X-ray diffractions (**Figures S2** and **S3**). Single-crystal X-ray diffraction studies revealed that a crystallographically independent Dy(III) center is hexa-coordinated by three oxygen atoms and three chloride ions. The top and bottom two oxygen atoms come from the two tricyclohexylphosphine oxide ligands, and the in-plane oxygen atom comes from ethanol (**Figure 1**). To accurately analyze the local coordination symmetry of the Dy<sup>III</sup> center, which is key for the SMM property, continuous shape measures (CSM) calculations were performed on the  $\text{DyO}_3\text{Cl}_3$  site (**Table S2**).<sup>21</sup> The minimum derivation from an ideal model for the  $O_h$ -octahedron geometry is 1.1, which is much smaller than that for the  $D_{3h}$ -trigonal prism value of 14.6. The result of the CSM analysis indicates that the Dy<sup>III</sup> ion is situated within a slightly distorted octahedral coordination environment and hence could exhibit SMM behavior.<sup>2,22</sup>

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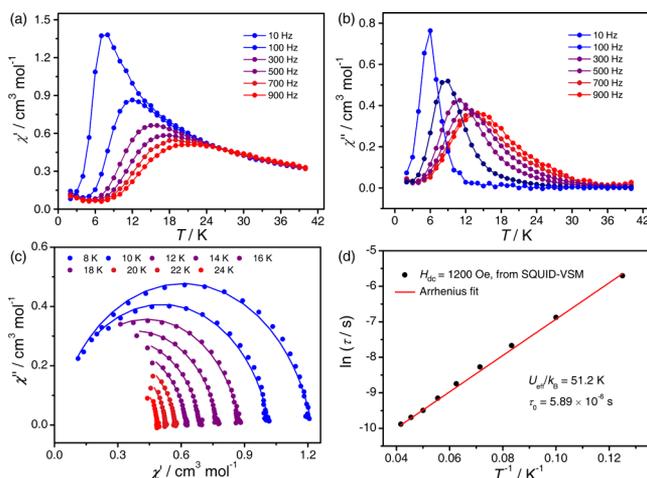


**Figure 1.** (a) Molecular structure of **1** determined by single-crystal X-ray diffraction. Solvent molecules and hydrogen atoms are omitted for clarity. (b) Coordination environment of the Dy<sup>III</sup> center.

To study the magnetic properties of **1**, direct-current (d.c.)-magnetic susceptibilities were first measured at temperatures ranging from 2 to 300 K under a d.c. field of 1 kOe (Figure S4). At a temperature ( $T$ ) of 300 K,  $\chi_M T$ , where  $\chi_M$  is the molar magnetic susceptibility, is  $14.03 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  and is in good agreement with the expected value of  $14.17 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  for a free Dy<sup>III</sup> ion ( ${}^6H_{15/2}$ ,  $S = 5/2$ ,  $L = 5$ ,  $J = 15/2$ ,  $g = 4/3$ ), indicating that the material is highly pure.  $\chi_M T$  gradually decreases as the temperature drops, reaching a minimum of  $11.04 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 2 K, due to the depopulation of the  $M_J$  states of the Dy<sup>III</sup> ions and/or antiferromagnetic intermolecular interactions.<sup>23</sup> At temperatures of 2, 4, 6, 8, and 10 K, the  $M$  vs  $H$  plots do not superimpose in a master curve, and at high magnetic fields the magnetization saturation cannot be achieved, indicating the presence of significant magnetic anisotropy and/or low-lying excited states (Figure S5).

Because of the magnetic anisotropy of the molecule, magnetization dynamics are expected for **1**, which is one of the most important characteristics of SMMs measured under alternating-current (a.c.)-magnetic field with varied frequencies and temperatures.<sup>1</sup> The a.c.-magnetic susceptibilities were collected under a zero d.c. field as a way to study the magnetization dynamics of **1**. Both in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) a.c. signals show a strong frequency dependence, indicating magnetization dynamics in **1** (Figures S6 and S7).  $\chi'$  and  $\chi''$  were observed to increase as the temperature was cooled down to 2 K, which is mainly due to the fast quantum tunneling of the magnetization (QTM) (Figure S6).<sup>24</sup>

To slow QTM and induce magnetization relaxation between the  $\pm M_J$  states of the lanthanide ion, an external d.c. field was applied, given that QTM can be mediated by transverse anisotropy, dipole–dipole interactions and hyperfine coupling.<sup>25</sup> External d.c. fields ranging in value from 200 to 2000 Oe were tested in order to identify the magnetic field value that optimally suppresses QTM (Figure S8). This optimized value, a 1200 Oe d.c. field, was applied to measure the a.c.-magnetic susceptibilities (Figures 2a,b and S9). The relaxation times ( $\tau$ ) were extracted from the fit of the Cole–Cole plots using a generalized Debye model (Figure 2c and Table S3).<sup>26</sup> As can be seen in Figure 2d,  $\ln(\tau)$  is inversely proportional to  $T$ ; this is the result of a thermally activated Orbach pathway.<sup>27</sup> The effective energy barrier ( $U_{\text{eff}}$ ) is obtained by Arrhenius fitting to give a  $U_{\text{eff}}$  of  $51.2 \pm 1.6 \text{ K}$  with a pre-exponential factor  $\tau_0$  of  $5.89(3) \times 10^{-6} \text{ s}$ . These values are well in the range for SMMs.<sup>2–8,22,24</sup> Owing to the fast relaxation process, no



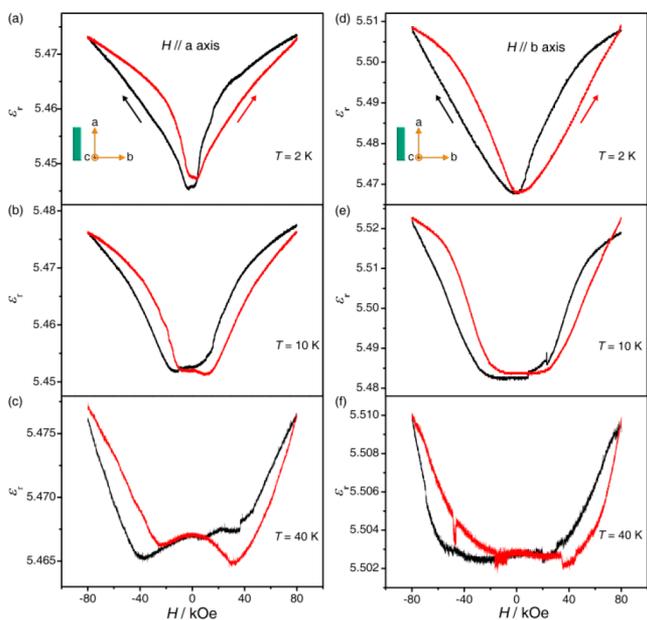
**Figure 2.** (a,b) In-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) a.c.-magnetic susceptibilities under a 1200 Oe d.c. field. Lines provide guides for the eyes. (c) Cole–Cole plots under a 1200 Oe d.c. field. The solid lines represent a best fit to the generalized Debye model. (d) Temperature dependence of the relaxation time ( $\tau$ ) under a 1200 Oe d.c. field. The solid red line is the best fit to the Arrhenius law.

obvious hysteresis loops were detected on a single-crystal sample along different directions (Figure 4c,d).

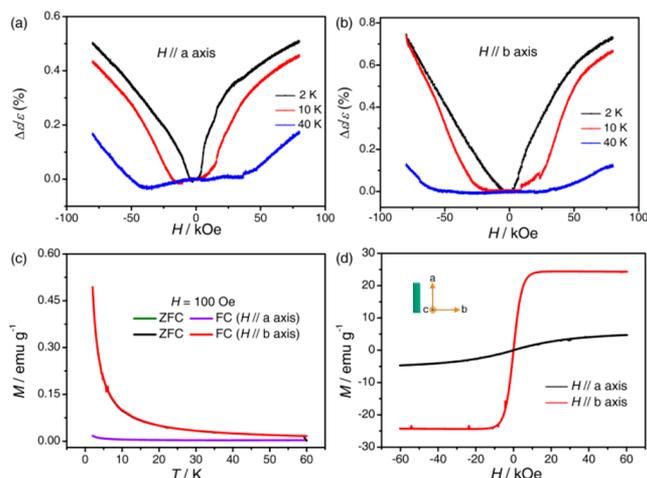
To investigate the dielectric properties of **1**, one may use a thin pellet made from pressed powders. However, the dielectric response of polycrystalline samples usually contains extrinsic contributions from grain boundaries and space trapped charges. Fortunately, the growth of a millimeter-sized single crystal of **1** allows us to study the intrinsic effect of the magnetic field on the dielectric permittivity in the SMM. We measured the  $\epsilon_r$  value along the  $a$ -axis of the single-crystal as a function of magnetic field up to 8 T at 2, 10, and 40 K, along different crystalline axes and using a single-crystal sample (with dimensions  $2.0 \text{ mm} \times 2.0 \text{ mm} \times 1.0 \text{ mm}$ ). These three temperatures were selected because the slow magnetic relaxation can only be observed below 40 K. As shown in Figure 3, for all  $H$ -directions and temperatures, the value of  $\epsilon_r$  increases with increasing magnetic field in the high-field region, mainly showing a positive MD effect.

To directly compare the MD effect at different temperatures and along different crystalline axes, we calculated the relative change in dielectric permittivity ( $\Delta\epsilon/\epsilon(0 \text{ kOe})$ ), where  $\Delta\epsilon = \epsilon(H) - \epsilon(0 \text{ kOe})$  (Figures 4 and S10). Below 40 K, the magnitude of  $\Delta\epsilon/\epsilon(0 \text{ kOe})$  of  $H$  along the  $b$ -axis is larger than that along the  $a$ -axis, exhibiting anisotropic behavior. This MD anisotropy is consistent with the magnetic anisotropy (Figure 4c,d). At 40 K, the MD effect for both  $H$ -directions is very similar, which implies weak magnetic anisotropy in the paramagnetic phase. Moreover, for a given  $H$ -direction,  $\Delta\epsilon/\epsilon(0 \text{ kOe})$  increases as temperature decreases, and at 2 K, the value of  $\Delta\epsilon/\epsilon(0 \text{ kOe})$  for  $H$  along the  $b$ -axis is approximately 0.75%. It can be seen that  $\Delta\epsilon/\epsilon(0 \text{ kOe})$  does not saturate up to 80 kOe, which suggests that if a larger magnetic field was applied, a larger  $\Delta\epsilon/\epsilon(0 \text{ kOe})$  value would be possible. It is worthy to note that this MD effect is comparable to some prototype inorganic multiferroic compounds such as BiMnO<sub>3</sub>, where the maximum MD effect is about 0.7% for 90 kOe.<sup>28</sup>

This is the first time that the MD effect has been observed in SMM materials. Though the MD effect is still a little bit far from practical applications, our observation is promising because it strongly suggests that electric control of magnetism



**Figure 3.** Relative dielectric permittivity at 10 kHz of **1** as a function of applied magnetic field at temperatures of 2, 10, and 40 K. (a–c) Field applied along the *a*-axis of a single crystal; (d–f) field applied along the *b*-axis. The red and black arrows in panels a and d indicate the ascending magnetic field and descending magnetic field.



**Figure 4.** Relative change in the dielectric permittivity of **1** as a function of applied magnetic field at temperatures of 2, 10, and 40 K. (a) Field applied along the *a*-axis of a single crystal; (b) field applied along the *b*-axis. under the applied magnetic field along *a*-axis and *b*-axis (c) zero-field cooling (ZFC) and field-cooling (FC) magnetization under 100 Oe as a function of temperature. (d) Magnetic hysteresis loops for a single crystal sample of **1** at 2 K.

and magnetic control of polarization (ME) would be possible when the SMMs become electrically polarized. In other words, SMMs with diverse structures could be good candidates for molecular multiferroics showing strong ME coupling.

To gain further insight into why MD arises in our SMM system, we now consider its possible microscopic origin. First, for the SMM under study, the crystal-space group of the material under ambient conditions is  $P2_12_12_1$ , which is nonpolar, thus in theory the material cannot exhibit any ferroelectricity. Since no dielectric anomaly was observed over the temperature range 2–300 K, the same symmetry persisted

down to 2 K. Meanwhile, the above magnetic characterization tells us there is no long-range magnetic order down to 2 K, which implies a nonmagnetoelectric 222 point group for this system at 2 K. According to the expansion of the Landau free energy,<sup>10,29</sup> it is impossible to account for MD behavior in an SMM in terms of any linear ME effect. Second, the dielectric loss of the SMM below 40 K is very small ( $\approx 0.0017$ ), which indicates that the sample is highly insulating. Thus, we can rule out the MD effect due to the Maxwell–Wagner effect proposed by G. Catalan from the existence of the magnetoresistance effect.<sup>30</sup> Instead, we propose that the crystal lattice can be modified by the strong spin–lattice coupling provided by the high-spin state of the Dy<sup>III</sup> ion, which is common in inorganic materials with rare-earth elements.<sup>31,32</sup> For example, such a large spin–lattice interaction or magnetoelastic effect can change the measured capacitance by changing the local structure of the sample, giving rise to an MD effect.<sup>33</sup>

In summary, we explore the magnetoelectric properties of a nanoscale molecular magnet experimentally for the first time. Our hexa-coordinated dysprosium-based SMM displays an MD effect below the magnetization dynamics temperature of 40 K. This SMM is nonpolar, thus ferroelectricity is strictly forbidden in theory, and, however, in practice the MD effect arises as a result of the spin–lattice coupling of the rare-earth element ions (in this case provided by the Dy<sup>III</sup>). A significantly enhanced ME coupling would be expected in polar SMMs. This could pave the way for the design of molecular multiferroics and magnetoelectric materials using ferroelectric SMMs in the near future.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b04818.

Materials and methods, experimental details, X-ray diffraction patterns, SHAPE software calculations and additional magnetic/magnetodielectric data (DOCX) Crystallographic information files for **1** (CIF)

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### Notes

The authors declare no competing financial interest.

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