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Distinct magnetic dynamic behavior for two polymorphs of the same Dy(III) complex[†]

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Two polymorphs of the same Dy(III) complex show distinct slow magnetic relaxation behaviors due to the different local environments of Dy(III) in the crystal. This work represents the first example where the magnetic dynamic property of neutral rare earth complexes could be tuned by growing polymorphic crystals without changing the ligand.

Due to the potential applications in molecule-based information storage, quantum computing and molecular spintronics,¹ single-molecule magnets (SMMs), which exhibit magnetic hysteresis and slow magnetic relaxation at low temperature, have seen a rapid growth in research over the past two decades.^{2,3} The superparamagnetic behavior observed in these complexes stems from a negative axial magnetic anisotropy (*D*) acting on high-spin (*S*) ground states, which generates a thermal barrier ($U_{\text{eff}} = |D|S^2$) to spin inversion.

Recently, constructing SMMs using a single ion has been demonstrated to be possible in lanthanide complexes,⁴ actinide complexes⁵ and also in high spin iron complexes.⁶ In these single-ion magnets (SIM), the magnetic anisotropy required for observing slow relaxation of the magnetization arises from the interaction between a single metal ion and its ligand field (LF) which creates a strong preferential orientation of the magnetic moment.^{5a} Theoretical and experimental studies have demonstrated that the LF splitting of the (2J + 1)-fold ground state of the Ln^{III} ion can stabilize sublevels with a large $|M_I|$ value, thus achieving an easy axis of the magnetization.⁷

Interestingly, the spin dynamic can be modified by the careful adjustment of the ligand field around the metal center. Ishikawa *et al.*⁸ showed that longitudinal contraction of the coordination sphere of bis(phthalocyaninato)terbium anion $\{[Pc_2Tb]^-\}$ by a redox process can significantly increase the

energy barrier for magnetization reversal. Carretta *et al.*⁹ revealed that matrix arrangements around $[Pc_2Tb]^-$ can also appreciably alter the splitting of the crystal field levels, and hence, the spin dynamics. Recently, Long *et al.* demonstrated that the slow magnetic relaxation behavior of trigonal pyramidal Fe^{II} compounds can be finely adjusted by changing the substituent of the ligand.^{7d}

In this study, we obtained two polymorphic forms of Dy(III) complexes with diamine and β -diketone ligands. Although the polymorphic crystals contain the same molecule, they show quite different magnetic dynamic behaviors due to the different local environments of Dy(III). This work represents the first example where the magnetic dynamic behaviors of neutral rare earth complexes could be tuned by growing polymorphic crystals without changing the ligand.

The complex [Dy(NTA)₃L] (Scheme 1) was prepared by the reaction of the chiral diamine ligand with Dy(NTA)₃·2H₂O according to the literature method.¹⁰ The two polymorphic forms 1a and 1b of [Dy(NTA)₃L] were obtained by using different solvents during synthesis (see ESI⁺ for details).§ In both 1a and 1b, the molecule contains an eight-coordinated Dy(III) ion, bonded to six oxygen atoms from three β -diketonate anions and two nitrogen atoms from the diamine ligand. The Dv–O bond lengths of **1a** range from 2.288(3) to 2.433(3) Å, while the two Dy-N bond lengths are 2.496(4) and 2.502(4) Å, respectively (Table S1, ESI[†]). According to Continuous Shape Measure Analysis (Table S2, ESI[†]) the coordination geometry of the Dy(III) ion in 1a can be described as a distorted bicapped triangular prism (BTP-8) (Fig. 1, left). There are eight independent molecules in a unit cell of 1a (Fig. S1, ESI[†]). The shortest Dy–Dy distance in the crystal structure is 8.929 Å.



Scheme 1 Structure of complex 1.

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Fig. 1 The coordination environments of complex 1a (left) and 1b (right).

In **1b**, the average Dy–O bond distance (2.318 Å) is shorter while the average Dy–N bond distance (2.541 Å) is longer than those in **1a** (Table S2, ESI[†]), resulting in the coordination geometry of **1b** being more like a distorted dodecahedron (Fig. 1, right). In contrast to **1a**, there are only two independent molecules in the unit cell of **1b** (Fig. S2, ESI[†]). π – π interactions were observed in complex **1b** between different naphthyl groups of β -diketonate anions (3.569 Å), or the naphthyl groups and phenyl groups in diamine ligands (3.215 Å) (Fig. S3, ESI[†]). The shortest Dy–Dy distance in the crystal structure is 9.729 Å. No solvent molecules were found in the lattice of both polymorphs.

The (1R,2R)-1,2-diphenylethane-1,2-diamine ligands are racemated in **1a** and **1b**. Therefore, both *R*- and *S*-diamine ligands are observed in the unit cell (Fig. S1 and S2, ESI[†]). The powder X-ray diffraction patterns for **1a** and **1b** are displayed in Fig. S4–S6 (ESI[†]). The diffraction peaks of the experimental and simulated patterns match well in key positions, indicating the phase purities of compounds **1a** and **1b**. No ferroelectric and second harmonic generation (SHG) effect was observed for **1a** and **1b**, which is consistent with their nonpolar structures. The temperature dependence of the dielectric constant shows that there is no phase transition between 5–350 K. Sensitive calorimetric study indicates that **1a** has a higher melting point than **1b** (Fig. S7, ESI[†]).

Magnetic measurement (1.8–300 K under 100 Oe of external field) revealed that the $\chi_{\rm M}T$ value of **1a** is 13.36 emu K mol⁻¹ at room temperature, which slowly decreased to 11.75 emu K mol⁻¹ at 5 K upon cooling, and then slightly increased to 12.02 emu K mol⁻¹ at 1.8 K (Fig. 2). The decrease upon cooling at high temperature is associated with the thermal depopulation of Stark levels,¹¹ while the unusual small upturn observed at the low temperature may be due to the weak intermolecular dipolar interactions.¹² The experimental data above 50 K obey the Curie–Weiss law with a Curie constant C = 13.61 emu K mol⁻¹, which is close to the expected value of a paramagnetic Dy³⁺ ion (J = 15/2, g = 4/3, C = 14.17 emu K mol⁻¹), and a Weiss constant $\Theta = -3.26$ K.



Fig. 2 Variable-temperature magnetic susceptibility data for **1a** and **1b** (\Box for **1a**, \bigcirc for **1b**) (H = 100 Oe), $\chi_M T$: left; χ_M^{-1} : right). The red line represents the best fitting to Curie–Weiss law above 50 K.



Fig. 3 In-phase (χ'_m) and out-of-phase (χ''_m) dynamic magnetic susceptibilities measured in a 3 Oe ac magnetic field with a 2 kOe dc-field for **1a** (a and b) and **1b** (c and d).

The magnetization of **1a** reaches a maximum value of 5.26 N β above 65 kOe at 1.8 K (Fig. S8, ESI[†]), lower than the theoretical value ($g_J \times J = 4/3 \times 15/2 = 10 \text{ N}\beta$), indicating a much smaller effective spin in **1a**.^{4g,h}

The ac magnetic measurements reveal that 1a shows the typical features associated with the slow magnetic relaxation (Fig. S9, ESI†). The in-phase (χ_m') and out-of-phase (χ_m'') signals show obvious frequency dependence at low temperature, but no peak was observed. In order to further investigate the dynamic properties of the slow magnetic relaxation and obtain quantitative information of an effective energy barrier for 1a, a stronger field of 2 kOe was applied in ac measurements to quench the quantum tunneling.^{13,14} As shown in Fig. 3a and b, strong frequency dependence in both the in-phase and out-of-phase signals was observed. Upon cooling, $\chi'_{\rm m}$ shows a maximum and begins to decrease in the 2.5–8.0 K range at a frequency of 1–1500 Hz. The χ_m'' also shows a set of frequency dependent peaks at 2.5 K (10 Hz)-6.5 K (1500 Hz) and then decreases at lower temperatures. The χ''_m peaks were determined by Lorentz peak function fitting in 2000 Oe to estimate the magnetization-relaxation parameters with the Arrhenius law $[\tau(T) = \tau_0 \exp(\Delta_{\text{eff}}/k_{\text{B}}T)]$. The best fitting parameters (R = 0.999) afford a barrier height ($U_{\text{eff}}/K_{\text{B}}$) of 30.3 K with $\tau_0 = 4.5 \times 10^{-6}$ s (inset of Fig. 4). These values are in the range of those previously reported for SMMs and SCMs.4/,15

The existence of slow relaxation in **1a** was also supported by the dynamic studies of magnetic properties in the Cole–Cole plot. At a fixed temperature of 5 K in a 2 kOe dc field, a semicircle χ'_m vs. χ''_m diagram from 1 Hz to 1500 Hz was observed (Fig. 4). The fit of the data to a general Debye model gave $\alpha = 0.08$, indicating the distribution of a single relaxation process in **1a** ($\alpha = 0$ for an infinitely narrow distribution of relaxation time). The variable-frequency ac susceptibility data collected at multiple temperatures from 1 Hz to 1500 Hz provide $\alpha = 0.12$, 0.04, 0.06 at 1.8, 5 and 7 K with $H_{dc} = 0$ Oe; and $\alpha = 0.07$ at 7 K with $H_{dc} = 2$ kOe (Fig. S10, ESI†).

Owing to the encapsulation of the Dy(III) ion by the NTA and diamine ligands, complex **1a** is an isolated mononuclear complex without strong interaction between Dy(III) ions. Therefore, the slow magnetic relaxation showed by **1a** should be considered as a single-ion property.



Fig. 4 Cole–Cole diagram at 5 K in a 2 kOe dc field for **1a**. The solid line represents the best fitting with a Debye model. Inset: relaxation-time fitting to the Arrhenius law in the 10–1500 Hz interval for **1a**.

In contrast to **1a**, the $\chi_M T$ value of **1b** gradually decreases from 13.13 emu K mol⁻¹ at room temperature to 7.29 emu K mol⁻¹ at 1.8 K (Fig. 2). The Curie–Weiss law fit gave C = 13.47 emu K mol⁻¹ and $\Theta = -7.92$ K. Saturation of magnetization does not reach for **1b** above 65 kOe at 1.8 K. The χ'_m and χ''_m signals of dynamic magnetic susceptibility of **1b** are invariant upon changing the frequency at zero field (Fig. S11, ESI†). By applying a 2 kOe dc field, **1b** shows frequency dependent χ'_m and χ''_m signals (Fig. 3c and d), but no Cole–Cole plot can be obtained due to the poor discriminability of the signals. These data indicate that **1b** may also show singleion magnet behavior but at significantly lower temperature.

The distinct magnetic behavior of **1a** and **1b** can be attributed to the different local environments of the Dy(III) ion. According to the single crystal X-ray diffraction study and Continuous Shape Measure Analysis, the local ligand-field symmetry of the Dy(III) ion is close to C_{2v} in **1a** and close to D_{2d} in **1b**. The different local ligand-field symmetry of the Dy(III) ion results in different anisotropy and then different magnetic dynamic behaviors. Moreover, configuration interactions between ground state and low lying excited states in different symmetry may result in different spin ground states.

In conclusion, two polymorphic forms of Dy(III) complexes were prepared. The two polymorphs show quite different slow magnetic dynamic behaviors due to the different local environments of the Dy(III) ion. The difference may arise from the different crystal field effect and configuration interaction in different symmetry. However, more efforts are needed to understand the mechanism of polymorph formation and the relation between the structure and magnetic dynamic behaviors for rare earth complexes.

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Notes and references

§ Crystal data for **1a** ($C_{56}H_{40}F_9N_2O_6Dy$): M = 1170.40 g mol, monoclinic, space group C2/c, a = 35.754(5), b = 10.8207(15), c = 27.295(4) Å, $\beta = 105.515(3)^\circ$, V = 10175(2) Å³, Z = 8, $\mu = 1.554$ mm⁻¹, reflections collected/unique 26 280/9963, $R_{int} = 0.0316$, $R_1 = 0.0511$, $wR_2 = 0.1186$ for $[I > 2\sigma(I)]$, $R_1 = 0.0706$, $wR_2 = 0.1269$ for all data. CCDC 783990. Crystal data for **1b** ($C_{56}H_{40}F_9N_2O_6Dy$): M = 1170.40 g mol, triclinic, space group $P\overline{I}$, a = 9.7289(16), b = 13.557(3), c = 20.495(3) Å, $\alpha = 73.683$, $\beta = 77.666(3), \gamma = 87.015^{\circ}, V = 2534.3(7) \text{ Å}^3, Z = 2, \mu = 1.560 \text{ mm}^{-1}$, reflections collected/unique 13 573/9963, $R_{\text{int}} = 0.0214$, $R_1 = 0.0579, \text{ w}R_2 = 0.1248 \text{ for } [I > 2\sigma(I)], R_1 = 0.0786, \text{ w}R_2 = 0.1298 \text{ for all data. CCDC 783991.}$

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