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Single-Molecule Magnets

A Polynuclear Lanthanide Single-Molecule Magnet with a Record Anisotropic Barrier**

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Dedicated to Professor Annie K. Powell on the occasion of her 50th birthday

Single-molecule magnets (SMMs) continue to be an attractive research field because of their unique and intriguing properties and potential applications in high-density data storage technologies and molecular spintronics.[1] The anisotropic barrier (U) of an SMM is derived from a combination of an appreciable spin ground state (S) and uniaxial Ising-like magneto-anisotropy (D).[2] The magnet-like behavior can be observed by slow relaxation of the magnetization below the blocking temperature. Since the discovery of SMMs in the early 1990s, this assumption has formed the basis for the understanding of the origin of the anisotropic barrier. However, in recent years the development of novel lanthanide-only SMMs that challenge and defy this theory pose a number of questions:[3] How can slow relaxation of the magnetization be observed in a nonmagnetic state complex? Why are large energy barriers seen for mononuclear lanthanide(III) complexes? To answer such important questions, it is vital to investigate novel SMMs with high magneto-anisotropy for which the influence of the large negative D value could result in higher anisotropic barriers.[4]

Clearly lanthanide-based polynuclear systems are an important avenue to explore in the pursuit of SMMs with higher anisotropic barriers, because of the strong spin–orbit coupling commonly observed in 4f systems.[3–5] However, lanthanide-only SMMs are rare.[3,5] The majority of reported SMMs have been prepared with transition-metal ions,[2] although the recent application of a mixed transition-metal/lanthanide strategy also yielded many structurally and magnetically interesting systems.[6] The scarcity of lanthanide-only SMMs results from the difficulty in promoting magnetic interactions between the lanthanide ions. The interactions can, however, be enhanced by overlapping bridging ligand orbitals. In addition, fast quantum tunneling of the magnetization (QTM), which is common for lanthanide systems, generally prevents the isolation of SMMs with high anisotropic energy barriers.

Our recent work suggests[5a–c] that dysprosium(III) ions may hold the key to obtaining high-blocking-temperature lanthanide-only SMMs. When an appropriate ligand system is employed, it is possible to exploit the large intrinsic magneto-anisotropy, high spin, and reduced QTM that dysprosium(III) ions offer. Recently, we have focused our attention towards the synthesis of dysprosium(III) cluster complexes with 1,2-bis(2-hydroxy-3-methoxybenzylidene) hydrazone (H_2bmh) and 3-methoxysalicylaldehyde hydrazone (Hmsh) as chelating agents (see Figure S1 in the Supporting Information). This strategy has proven to be successful and has led to a polynuclear lanthanide SMM with a record anisotropic barrier. Herein, we report the synthesis, structure, and magnetism of a tetranuclear dysprosium(III) SMM that exhibits the largest relaxation barrier seen for any polynuclear SMM to date.

A suspension of $DyCl_3{\cdot}6H_2O$ and *o*-vanillin (2:1 ratio) in DMF/CH_2Cl_2 (1:5 ratio) was treated with 4 equivalents of Et_3N. The solution was stirred for 1 minute, and then 4 equivalents of $N_2H_4{\cdot}H_2O$ was added. The resulting yellow solution yielded rectangular, orange-yellow crystals of the tetranuclear complex $[Dy_4(\mu_3\text{-}OH)_2(bmh)_2(msh)_4Cl_2]$ (**1**) in 19.1 % yield after 2 days. The msh and bmh ligands were formed in situ by the reaction of *o*-vanillin and hydrazine. The slight excess of hydrazine is essential for the formation of both ligands; when an excess of *o*-vanillin was used instead, no product was isolated. The basic conditions promote the deprotonation of the ligands and the formation of bridging hydroxide anions.

Single-crystal X-ray analysis revealed the centrosymmetric complex **1** (Figure 1), which has a defect-dicubane central core. The four coplanar Dy^{III} ions are bridged by two μ_3-OH ligands displaced above and below (0.922 Å) the Dy_4 plane with Dy–O bond lengths of 2.362(6), 2.302(6), and 2.447(6) Å and Dy–O–Dy angles of 106.5(2), 107.7(2), and 105.7(2)°, and also by a combination of four phenoxide oxygen atoms [Dy–O 2.312(2), 2.298(6), 2.448(6), 2.345(6) Å] and two diaza bridging groups [Dy–N 2.508(8), 2.564(8) Å]. Close inspection of the packing arrangement reveals stacking of the

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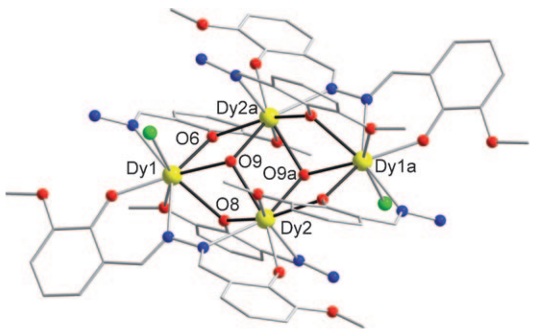

Figure 1. Partially labeled crystal structure of the centrosymmetric complex $[Dy_4(\mu_3\text{-}OH)_2(bmh)_2(msh)_4Cl_2]$ (**1**) with hydrogen atoms omitted for clarity. Symmetry-equivalent positions are denoted by an "a". Yellow Dy, red O, blue N, green Cl.

molecules along the a axis with intermolecular Dy⋯Dy distances of 11.86 Å and a zigzag arrangement of molecules along the b axis (Figure S2 in the Supporting Information). A Dy_4 complex with a similar planar central core recently reported by Zheng et al. was obtained using a 2-[(2-hydroxyethylimino)methyl]-6-methoxyphenol ligand.[5e]

Both dc and ac magnetic susceptibilities of **1** were carried out on a freshly prepared and filtered sample. The dc magnetic susceptibility of **1** at 0.1 T between 2 and 300 K reveals a room-temperature χT value of 55.6 $cm^3\,K\,mol^{-1}$ per molecule, which is close to the expected value of 56.6 $cm^3\,K\,mol^{-1}$ (Dy^{III}: $S=5/2$, $L=5$, $^6H_{15/2}$, $g=4/3$; Figure 2). The χT product remains roughly constant with decreasing temperature down to 10 K, and then drops to a minimum value of 49.4 $cm^3\,K\,mol^{-1}$ at 2 K. Furthermore, the field dependence of the magnetization below 8 K is not saturated even at 7 T (inset of Figure 2). These features are presumably due to the presence of large magneto-anisotropy in the dysprosium(III) system as well as weak intramolecular interactions between metal ions making the low lying exited states accessible even at 1.8 K. The crystal-field (CF) effect seen in molecular Dy^{III} based systems is also a major contributor to the final decrease of the χT product at low temperature.[6m]

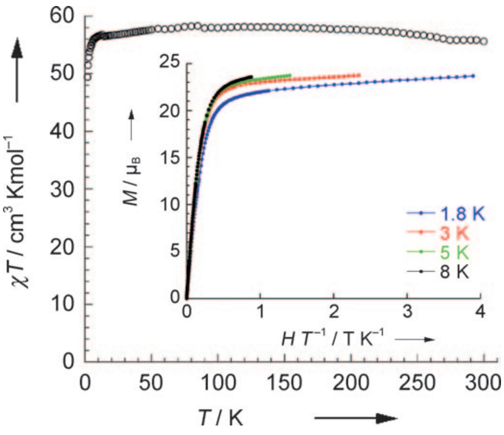

Figure 2. Temperature dependence of χT at 0.1 T for **1** (with $\chi = M/H$ normalized per mol). Inset: M vs. H/T plot at various temperatures between 1.8 and 8 K.

The temperature- (Figure 3) and frequency-dependent (Figures S6 and S7 in the Supporting Information) ac susceptibility of **1** was measured under zero dc field. Out-of-phase (χ'') ac signals, indicating slow relaxation of magnetization, are observed with maxima at 30 and 9 K for 1500 Hz, indicating the presence of two modes of relaxation. These frequency-dependant signals are indicative of SMM behavior. The observation of slow relaxation of the magnetization at high temperatures is unique, as most reported SMMs exhibit relaxation below 10 K. Such unusual behavior in a weakly coupled molecular system is presumably due to the large intrinsic magnetic anisotropy of the Ln^{III} ions.[3] To further investigate this property, ab initio calculations were carried out to determine the local anisotropy on each metal site.[7a,c] The calculated directions of the anisotropy axes at the four Dy^{III} sites are shown in the inset of Figure 3. Anisotropy axes in **1** are parallel to each other for the opposite ions and point almost radially to each Dy site. The axis passing though the Dy1 and Dy2 ions makes an angle of 28.7° and 3.1° with the Dy_4 plane. The corresponding g factors for the lowest Kramers doublets on the dysprosium sites were calculated to be very anisotropic ($g_{\parallel}=19.5$ for Dy1, $g_{\parallel}=19.2$ for Dy2, and $g_{\perp}$ is negligible for both types of ions). From these large values of local axial g factors, we may conclude that the exchange interaction between the lowest Kramers doublets on the dysprosium sites will be close to Ising type, which is similar to what was found in other dysprosium-only SMMs.[7] Since the anisotropy axes on Dy1 and Dy2 are almost orthogonal, the exchange interaction between the lowest Kramers doublets of these ions is expected to be very small. Ab initio calculations also predict the first excited Kramers doublet on Dy1 and Dy2 lying 83 K and 199 K over the ground one, respectively. Since the exchange interaction

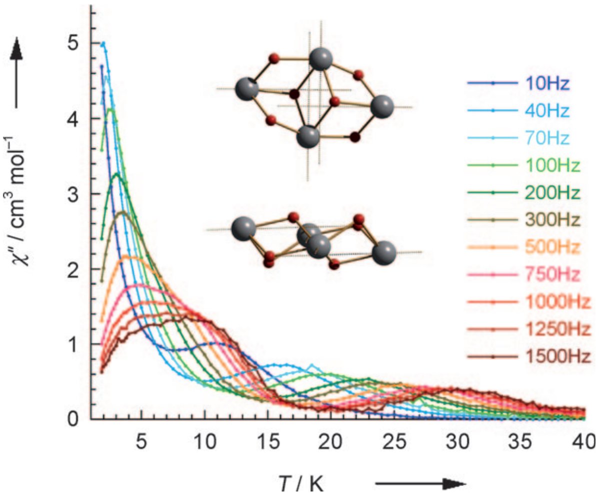

Figure 3. Temperature dependence of out-of-phase (χ'') ac susceptibility of **1** under zero dc field at indicated frequencies. Inset: Anisotropy axis direction on each Dy^{III} site.

between the dysprosium sites is much smaller than the obtained local excitation energies, the main contribution to the barrier of blockage of magnetization in **1** comes from the blockage of magnetizations of individual dysprosium ions. The two maxima of the out-of-phase (χ'') ac signals can then be naturally associated with two relaxation times (and two barriers of blocking of magnetization) corresponding to two types of dysprosium ions in **1**. The large difference of local excitation energies on Dy1 and Dy2 support this scenario. In comparison with the Dy_4 complexes obtained by Zheng et al.[5e] for which the out of phase ac signals were observed only at low temperatures (below 12 K), high-temperature relaxation was clearly observed for complex **1** (Figure 3). The difference in magnetic behavior between the previously reported complexes[5e] and complex **1** could be due to differences in bond lengths and slightly acute bridging angles in the central core of **1** as well as different orientations of the anisotropy axes. Further comparative calculations are required to elucidate this hypothesis.

Low-temperature, single-crystal dc magnetization measurements of **1** were carried out on a micro-SQUID[8] magnetometer between 0.04 and 7 K (Figure 4). Below 7 K, multistep hysteresis loops were observed with an opening at a temperature of 7 K (inset Figure 4; Figures S8–S11 in the Supporting Information). The coercivities of the hysteresis loops increase with decreasing temperature and increasing field sweep rate, as expected for an SMM. To our knowledge, this hysteresis loop opening temperature is the largest reported to date for an SMM. The multisteps seen in the loops are generally due to the resonant QTM.[1,2] Owing to the Ising exchange interaction between the lowest Kramers doublets of the dysprosium centers, each step in the magnetization curve corresponds to a reversal of magnetic moment on an individual dysprosium site. For such polynuclear Ln systems, the shape and positioning of the steps usually originate from the weak exchange interactions and also depend on the orientation of the applied field in relation to the anisotropic plane of the molecule.[3a,e,7] However, the zigzag packing arrangement of the molecules in the crystal lattice precludes the in-depth analysis of the steps. Further modeling studies using ab initio calculations are currently underway. Arrhenius plots were obtained from ac (χ'') and dc magnetization decay versus time data (Figure S12 in the Supporting Information). The relaxation times deduced from this data (Figure S13) are consistent with an activated behavior with effective energy barriers of $U_{\mathrm{eff}} = 9.7$ K (pre-exponential factor of $\tau_0 = 3.2 \times 10^{-5}$ s) and $U_{\mathrm{eff}} = 170$ K ($\tau_0 = 4 \times 10^{-7}$ s) for low- and high-temperature dynamics, respectively. The latter barrier of 170 K is considerably higher than any reported U_{eff} value for polynuclear SMMs.[5a,9] Although the height of this barrier matches well the calculated local excitation energy (199 K) on Dy2 sites, we note that these two quantities are not directly related.

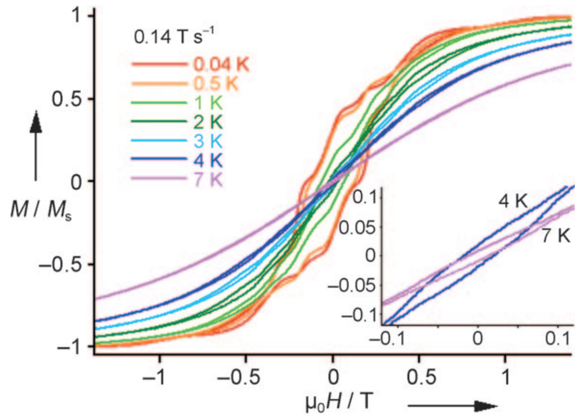

Figure 4. Magnetization (*M*) vs. applied dc field sweeps at the indicated sweep rate and temperatures. Inset: Zoomed-in section of the hysteresis loops showing an opening at 7 K.

The presented result confirms the merit of a solely lanthanide approach to higher anisotropic barrier SMMs. The large anisotropy provided by the Dy^{III} ions together with the careful choice of ligand, in this case, combine to generate the record barrier seen, which surpasses that previously achieved by transition-metal systems. We are confident that the use of lanthanide metals in SMM chemistry will continue to pave the way towards even higher anisotropic barriers in the future.

Experimental Section

1: A suspension of $DyCl_3{\cdot}6H_2O$ (0.125 mmol) and *o*-vanillin (0.25 mmol) in DMF/CH_2Cl_2 (5 mL/25 mL) was treated with Et_3N (0.5 mmol). The solution was stirred for 1 min, and then $N_2H_4{\cdot}H_2O$ (0.5 mmol) was added. The resulting pale-yellow solution was stirred for a further 15 min and then filtered, and the filtrate was left undisturbed. After 2 days, rectangular, X-ray-quality orange-yellow crystals of the tetranuclear $[Dy_4(\mu_3\text{-}OH)_2(bmh)_2(msh)_4Cl_2]$ (**1**) were formed in 19.1 % yield. The sample was maintained in contact with the mother liquor to prevent deterioration of the crystals, which were identified crystallographically as **1**. Selected IR data for **1** (KBr): $\nu =$ 3441(br), 1647(m), 1603(2), 1576(w), 1537(m), 1465(s), 1381(w), 1332(w), 1298(w), 1238(s), 1217(m), 1170(m), 993(w), 965(w), 851(w), 778(w), 731 cm^{-1} (m).

Crystal structure data for **1**: $C_{64}H_{66}Cl_2Dy_4N_{12}O_{18}$, crystal size: $0.20 \times 0.15 \times 0.10$ mm^3, monoclinic, $P21/c$, $a = 11.8651(9)$, $b = 20.3761(16)$, $c = 14.5767(11)$ Å, $\beta = 102.3160(10)°$, $V = 3443.0(5)$ Å^3, $T = 200(2)$ K, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.941$ Mg m^3, $\mu(\lambda{=}0.71073$ Å$) = 4.447$ mm^{-1}, 36039 reflections collected, 7062 [R(int) = 0.0994], $R1 = 0.0491$ and $wR2 = 0.1063$ using 4356 reflections with $I > 4\sigma(I)$. CCDC 735900 (**1**) contains 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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