

A flexible approach for engineering macrocyclic high performance pentagonal bipyramidal Dy(III) single-ion magnets†

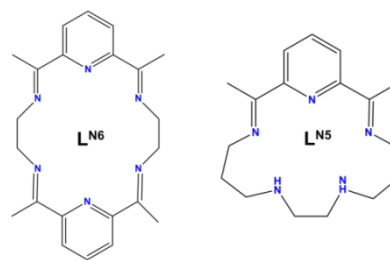
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A strong uniaxial ligand field generated by the Ph_3SiO^- ligand combined with the weak equatorial field of the macrocyclic ligand $\text{L}^{\text{N}5}$, generates $[\text{Dy}^{\text{III}}(\text{L}^{\text{N}5})(\text{Ph}_3\text{SiO})_2]^+$, a pentagonal bipyramidal Dy(III) Single-Molecule Magnet with a high anisotropy barrier of 1108 K, and hysteresis loops open up to 14 K. Based on our synthetic blueprint, we use *ab initio* calculations to predict changes to the macrocycle to increase the barrier to ~ 1800 K.

Molecular systems which display the ability to retain magnetisation, in the absence of an external magnetic field, resulting in the appearance of magnetic memory of molecular origin, are known as Single-Molecule Magnets (SMMs).¹ Lanthanide-based SMMs are often associated with large magnetic moments and large magnetic anisotropy. In 4f-SMMs, the energy barrier to reorientation of the magnetisation (U_{eff}) is strongly determined by the control of the coordination environment at the level of a single metal ion.² Specifically, the use of the Dy(III) ion in targeted coordination environments that promote strong uniaxial symmetry stabilizes the largest $m_j = \pm 15/2$ ground state and gives a large separation from the excited m_j states.² Monometallic complexes with axial symmetry such as square antiprismatic,³ trigonal bipyramidal,⁴ pentagonal bipyramidal,^{5,6} and hexagonal bipyramidal,^{7,8} are an effective way to favour slower relaxation of the magnetisation. Furthermore, sandwich type ligands (e.g. cyclopentadienyl (Cp) anionic ligands), have generated organometallic compounds with impressive blocking temperatures showing coercivity up to 30 K,⁹ 48 K,¹⁰ 55 K,¹¹ 60 K,¹² 66 K¹³ and 80 K.¹⁴ Additionally, of particular interest are the endohedral metallofullerenes (EMFS) with lanthanide ions.¹⁵

We have explored how the ligand electronics can tune SMM properties^{5,7,16,17} and recently first introduced a blueprint for engineering strong uniaxial magnetic anisotropy for Dy(III) ions in a hexagonal bipyramidal geometry,⁷ boosting the magnetisation reversal barrier from ~ 50 K¹⁸ to ~ 1100 K, by using the macrocyclic ligand $\text{L}^{\text{N}6}$ (Scheme 1 left). Implementing further the flexibility of our synthetic approach towards the engineering of new quasi- D_{nh} systems, we herein demonstrate the isolation of a new Single-Ion Magnet (SIM) with pentagonal bipyramidal geometry, $[\text{Dy}^{\text{III}}(\text{L}^{\text{N}5})(\text{Ph}_3\text{SiO})_2](\text{BPh}_4) \cdot \text{CH}_2\text{Cl}_2$ (**1**). Compound **1** shows out-of-phase peaks in the ac susceptibility up to 80 K under zero dc field, a high magnetization reversal barrier of 1108 K and hysteresis, $M(H)$, loops open up to 14 K, measured at an average sweep rate of 0.01 T/s (See Table S1). In our carefully designed step-by-step synthetic approach we first targeted the formation of a weak N5-pentagonal plane by employing the macrocyclic $\text{L}^{\text{N}5}$ ligand (Scheme 1, right), unused in 4f chemistry, formed from 2,6-

diacetylpyridine and N,N'-Bis-(3-aminopropyl)-ethylenediamine.¹⁹ We then used the anion of triphenylsilanol, Ph_3SiO^- , as stronger anionic donors at both axial positions to generate the pentagonal bipyramidal architecture (Fig. 1).



Scheme 1. The macrocyclic ligand $\text{L}^{\text{N}6}$ (left)⁷ and $\text{L}^{\text{N}5}$ (right, $\text{L}^{\text{N}5}$ = N5-pentagonal plane from the neutral Schiff base ligand formed from 2,6-diacetylpyridine and N,N'-Bis-(3-aminopropyl)-ethylenediamine).

Importantly, our synthetic strategy offers vast synthetic flexibility for carefully engineering the equatorial crystal field in order to further improve the relaxation dynamics and to target the isolation of new quasi- D_{nh} systems with enhanced magnetic anisotropy. In a quest to identify new promising directions towards high temperature SMMs we investigate the new *in-silico* model **1-O5** (*vide infra*), inspired by **1**. From our systematic study, we find that the proposed *in-silico* model is extremely promising as a new target system and has the potential to show improved SMM properties, with the magnetisation reversal barrier boosted up to *ca.* 1800 K (*vide infra*).

Compound **1** (Fig. 1) crystallises in the triclinic space group $P\bar{1}$ (Table S2) with the asymmetric unit containing two crystallographically independent molecules with a Dy...Dy distance of 11.667 Å. Both Dy(III) centres are found in an axially compressed pentagonal bipyramidal geometry, as confirmed via SHAPE analysis (see Table S4 and Fig S3).²⁰ Two Ph_3SiO^- ligands occupy the axial positions providing the shortest axial Dy-O bond lengths of 2.157(3) Å and 2.136(4) Å for Dy1A and 2.161(4) Å and 2.158(4) Å for Dy1B (See Table S3 and Fig S2). In addition, the axial O-Dy-O angle is 176.54(15)° and 173.13(15)° for Dy1A and Dy1B, respectively. In the equatorial plane of the $\text{L}^{\text{N}5}$ ligand (Fig. S2) the Dy-N bonds fall in the range of 2.400(5)-2.570(5) Å for Dy1A and 2.457(5)-2.564(5) Å for Dy1B (Table S3).

The static dc magnetic susceptibility and magnetization measurements for complex **1** are shown in the ESI (Fig. S4-S5). Upon cooling the $\chi_{\text{M}}T$ profile of **1** decreases steadily from the room temperature value of 14.1 $\text{cm}^3 \text{mol}^{-1} \text{K}$ to a value of 13.05 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 10 K followed by a sharp drop below 10 K (Fig.

S4). The field-cooled (FC) and zero-field cooled (ZFC) magnetic susceptibility (Fig. S6) diverge at 7 K for **1** with the maximum observed at ~ 5 K, indicative of a magnetic blocking temperature, T_B .²¹ The magnetic hysteresis measurements, $M(H)$ loops, performed on a microcrystalline powder sample of **1** remain open up to 14 K, measured at a sweep rate of 0.01 T/s (Fig. 2 and Fig. S7). The characteristic waist-restricted shape of the loops is strongly affected by the faster relaxation around zero field, due to the presence of unsuppressed Quantum Tunnelling of the Magnetisation (QTM).³

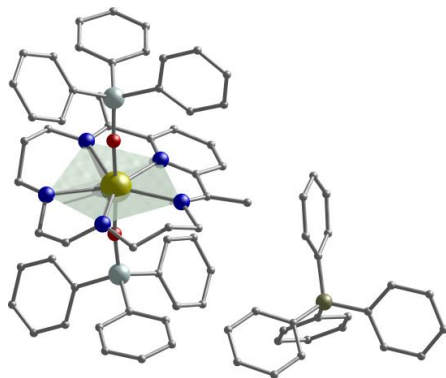


Figure 1. Molecular structure of **1** with two Ph_3SiO^- axial ligands and the polydentate ligand L^{NS} in the equatorial plane, highlighted in green. Dy, gold; O, red; N, blue; Si, light turquoise; C, gray; B, dark yellow. Hydrogen atoms, solvent molecules and disorder components are omitted for clarity.

around zero field, due to the presence of unsuppressed Quantum Tunnelling of the Magnetisation (QTM).³

Alternating current (ac) susceptibility measurements were performed in order to investigate the magnetic relaxation in **1** (Fig. 3 and Fig. S8-S11). Under zero dc field, the out-of-phase χ_M'' susceptibility data exhibit well-defined maxima, clearly observable at temperatures up to 80 K (Fig. 3), indicative of slow magnetic relaxation and a high magnetisation reversal barrier. The magnetisation relaxation times, τ , were extracted by fitting the Argand plots of χ_M'' vs. χ_M' using the generalized Debye model (Fig. S11).²² The α -parameters found are in the range of 0.17-0.43 (2-80 K) showing a relatively wide distribution of relaxation times. The τ^{-1} vs. T data were fitted using the equation $\tau^{-1} = \tau_{\text{QTM}}^{-1} + CT^n + \tau_0^{-1} \exp(-U_{\text{eff}}/T)$, in which C and n are the parameters of the Raman process and τ_{QTM} is the rate of QTM.^{3,21} The best fit gives an energy barrier of $U_{\text{eff}} = 1108$ K, $\tau_0 = 1.56 \times 10^{-11}$ s, $n = 2.05$, $C = 0.03 \text{ K}^{-n} \text{ s}^{-1}$, $\tau_{\text{QTM}} = 0.5$ s, under zero dc field (Fig. S12). The values of τ_0 , C and n are within the commonly observed range for Dy(III) SMMs.³ The exponent n of the Raman process has a smaller value than expected for a Kramers ions (*i.e.*, $n = 9$) suggesting the presence of Raman processes involving optical acoustic phonons.²²

Ab initio calculations on **1**, using the CASSCF/RASSI-SO/SINGLE_ANISO approach implemented in MOLCAS 8.227 (see ESI†),²³ reveal that the eight Kramers Doublets (KDs) span an energy range of ~ 1520 K. Inspection of the calculated g -tensors (Table S5) show a highly anisotropic ground state ($m_J = \pm 15/2$) with strong axiality ($g_{zz} = 19.979$, $g_{xx}, g_{yy} = 0.001$ for Dy1A and $g_{zz} = 19.984$, $g_{xx}, g_{yy} = 0.000$ for Dy1B). The main anisotropy axis in **1** is nearly collinear with the shortest O-Dy-O bonds, stabilised by the stronger donor

Ph_3SiO^- ligands located above and below the equatorial plane of the L^{NS} ligand (Fig. 1 and Fig. S13).

The first excited state ($m_J = \pm 13/2$, located at ~ 600 K (594 K for Dy1A and 602 for Dy1B) and the second excited state ($m_J = \pm 11/2$) located at ~ 1040 K (1033 for Dy1A and 1040 for Dy1B) are also axial in nature (Fig. 4 Upper, Fig. S14 and Table S5). The maximum calculated relaxation barrier, U_{cal} , for compound **1** is estimated at ~ 1040 K; in excellent agreement with the experimentally determined magnetisation reversal barrier (U_{eff}) of 1108 K found in zero dc field.

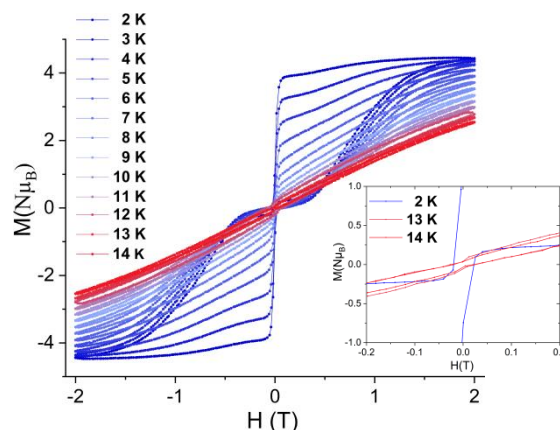


Figure 2. Powder magnetic hysteresis measurements for **1** with an average sweep rate of 0.01 T/s. Inset: $M(H)$ loops around zero field region open up to 14 K.

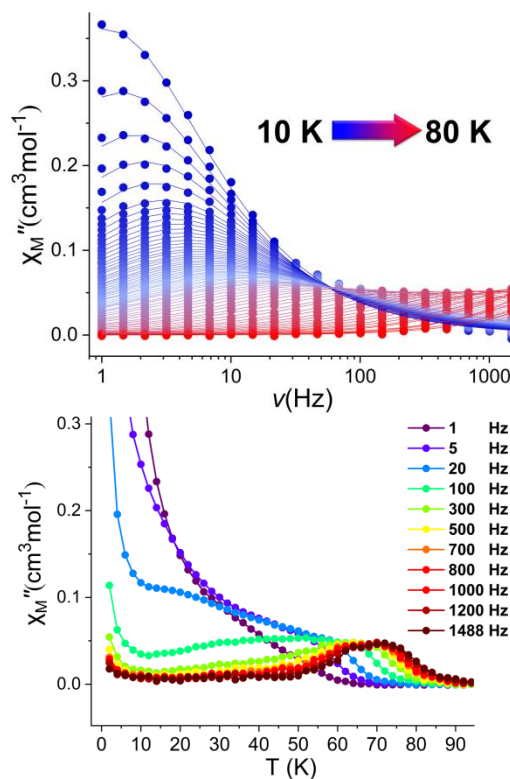


Figure 3. (Upper) Plots of $\chi_M''(\nu)$ in zero applied dc field in the temperature range of 10–80 K for **1**. (Lower) Plots of $\chi_M''(T)$ in zero applied dc field.

Significantly, the ability to find promising candidate systems that have the potential to show improved SMM properties and could be

targeted by experimental chemists is of key importance. Using **1** as a blueprint we have created the *in-silico* model system **1-O5**. In the new model system we examine how changes in the first coordination sphere of **1**, at the equatorial positions (Fig. S15), affect the magnetic anisotropy and have the potential to improve the performance of SMMs, boosting the magnetisation reversal barrier to new heights (*ca.* 1800 K). In the model system **1-O5** we have maintained the same coordination environment at the axial positions as in **1** (*i.e.*, the axial Ph_3SiO^- ligands), but the equatorial ligand L^{N5} has been modified *in-silico* to the 16-crown-5 ligand (*i.e.*, the closest candidate of the crown ether family to the L^{N5}) (Fig. S15). We have employed the crown ether ligand in the equatorial plane of our model system because of its neutral nature, long metal-ligand distances, the popularity of crown ether ligands in 4f chemistry²⁴ and to compare it with the nitrogen based macrocyclic ligand, L^{N5} , used in **1**. In the model system **1-O5** the strongly axial excited states are higher in energy than that of **1** (Table S6). In addition, the transverse components for model system **1-O5** are weaker giving lower g_x/g_y values (Table S6). Furthermore, using the CASSCF wavefunction, the computed Loprop²⁶ charges for **1** reveal larger negative charges at the secondary amine -NH- groups of the equatorial L^{N5} ligand (Fig. S16), compared to the lower charges generated by the oxygen atoms of the crown ether ligand of **1-O5** (Fig. S17). The QTM probabilities calculated for the first three KDs (0.45×10^{-4} , 0.49×10^{-2} , $0.68 \times 10^{-1} \mu_B$, respectively) are lower compared to **1** with the

magnetization relaxing *via* the fourth KD giving a calculated magnetization reversal barrier of 1788 K (Fig. 4, lower). The ratio between the axial B_2^0 parameter and the corresponding non-axial crystal field parameters also increases **1** < **1-O5** (Table S7) supporting the increase of U_{cal} from **1** (~ 1040 K) to **1-O5** (~ 1788 K). In conclusion, we report $[\text{Dy}^{\text{III}}(\text{L}^{\text{N5}})(\text{Ph}_3\text{SiO})_2](\text{BPh}_4)\text{CH}_2\text{Cl}_2$ (**1**) using the macrocyclic ligand L^{N5} , which is a strongly axial Dy(III) single-ion magnet in a pentagonal bipyramidal geometry showing out-of-phase peaks up to 80 K under zero field, a high anisotropy barrier of 1108 K, and hysteresis loops open up to 14 K (@ 0.01 T/s). This novel compound was engineered following our flexible synthetic approach where five long Dy-N bonds are formed by the macrocyclic ligand L^{N5} , while two strong donor Ph_3SiO^- ligands are used for the axial positions, creating the short O-Dy-O bonds, highlighting the vast synthetic scope for macrocyclic engineering of magnetic anisotropy. Furthermore, we show a promising direction towards a new pentagonal bipyramidal family by carefully tuning the equatorial ligand field of the macrocycle and synthetic efforts are underway with both O- and S-donors towards this goal.

We thank EPSRC UK (EP/N01331X/1, EP/M000923/1) for funding. S.D thanks UGC for an SRF fellowship. G.R thanks DST/SERB for funding (CRG/2018/000430; DST/SJF/CSA03/2018-10; SB/SJF/2019-20/12).

Conflicts of interest

There are no conflicts to declare.

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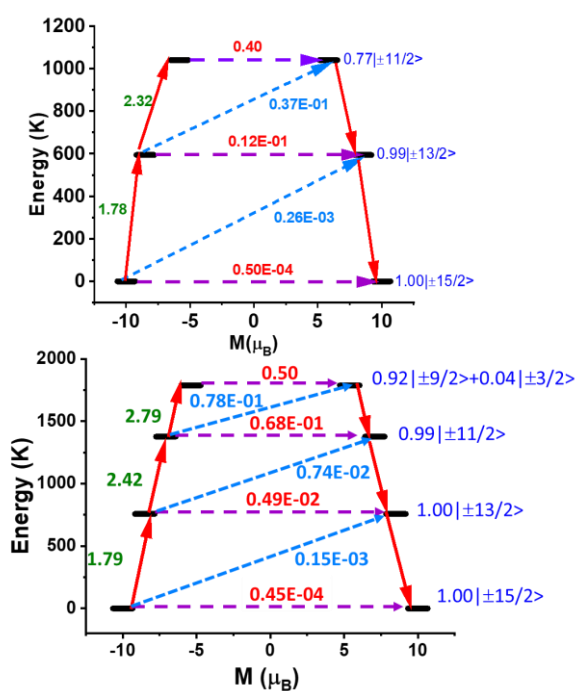


Figure 4. *Ab initio* calculated relaxation dynamics for **1** (Upper, shown for Dy1B) and **1-O5** (Lower). The black line indicates the KDs as a function of magnetic moments. The violet dashed arrow represents QTM (QTM = quantum tunnelling of the magnetisation) via the ground state and TA-QTM (TA-QTM = thermally assisted QTM) via excited states. The blue dashed arrow indicates possible Orbach processes. The red arrows indicate the mechanism of magnetic relaxation. The numbers above each arrow represent corresponding transverse matrix elements for the transition magnetic moments.²⁵

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