Molecular magnetic hysteresis at 60 K in dysprosocenium

1   **Molecular magnetic hysteresis at 60 K in dysprosocenium**

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4   **Lanthanides have been extensively investigated for potential applications in quantum**

5   **information processing and high-density data storage at the molecular and atomic scale;**

6   **remarkable experimental achievements include reading and manipulating single nuclear**

7   **spins[1,2], exploiting atomic clock transitions for robust qubits[3], and most recently**

8   **magnetic data storage in single atoms[4,5]. Single molecule magnets (SMMs) display**

9   **magnetic hysteresis of molecular origin[6] – a magnetic memory effect and a prerequisite**

10   **of data storage – and lanthanide examples have exhibited this phenomenon at the**

11   **highest temperatures to date. However, in nearly 25 years since the landmark discovery**

12   **of SMMs[7] hysteresis temperatures have only increased from 4 K to ~14 K[8-10] (using a**

13   **consistent magnetic field sweep rate of *ca.* 20 Oe s^{-1}, though higher temperatures have**

14   **been achieved by using very fast sweep rates,[11,12] e.g. 30 K with 200 Oe s^{-1})[12]. Here we**

15   **report a hexa-*tert*-butyldysprosocenium complex, $[Dy(Cp^{ttt})_2][B(C_6F_5)_4]$ [1; Cp^{ttt} =**

16   **$\{C_5H_2{}^tBu_3\text{-}1,2,4\}$; $^tBu = C(CH_3)_3$], which shows magnetic hysteresis up to 60 K at 22 Oe s^{-1}.**

17   **We observe a clear change in the relaxation dynamics at this temperature, which persists**

18   **in magnetically diluted samples, suggesting that the origin of the hysteresis is the**

19   **localised metal-ligand vibrational modes unique to dysprosocenium. *Ab initio* spin**

20   **dynamics demonstrate that magnetic relaxation at high temperatures is due to local**

21   **molecular vibrations, and thus indicate that with judicious molecular design, magnetic**

22   **data storage in single molecules at temperatures above liquid nitrogen may become**

23   **possible.**

24   Metallocenium cations are positively charged species that contain a metal ion

25   sandwiched between two aromatic π-ligands; the *bis*-cyclopentadienyl (Cp) family is the

26   classical example. The isolation of $[Ln(Cp^R)_2]^+$ (Ln = lanthanide; $Cp^R = C_5R_5$; R = H, alkyl or silyl)

27   has proved problematic because lanthanide bonding is predominantly ionic and Ln(III) cations

28   are relatively large, thus additional ligands tend to coordinate equatorially. Notably, the nearest

29   structurally characterised lanthanide and rare earth examples reported to date,

30     $[Sm\{C_5Me_4(SiMe_2CH_2CH=CH_2)\}_2][BPh_4]$ (Me = CH_3, Ph = C_6H_5)[13], $[Sc(Cp^*)_2\{\mu-(C_6F_5)_2B(C_6F_5)_2\}]$

31   ($Cp^* = C_5Me_5$)[14], $[\{Ln(Cp^*)_2\}_2\{\mu-(C_6F_5)_2B(C_6F_5)_2\}_2]$ (Ln = Pr, Nd)[15] and $[Dy(Cp^*)_2\{\mu-$

32     $(Ph)_2BPh_2\}]$[16,17] all feature weak equatorial ligand interactions. Recently, the elusive

33   dysprosocenium cation had become a significant synthetic target[18] because the near-cylindrical

34   symmetry and axial concentration of negative charge should give a very high energy barrier to

35   magnetic relaxation[19,20] and hence possibly allow magnetic hysteresis at relatively high

36   temperatures. However, some ligand fields are better suited to Ln(III) cations where the most

37   magnetic states are prolate in nature; e.g. $[Er(C_8H_8)(Cp^*)]$ exhibits hysteresis up to 5 K[21] but for

38     $[Dy(C_8H_8)(Cp^*)]$[22] and $[Dy\{C_8H_6(SiMe_3)_2-1,4\}_2Li(THF)(DME)]$[23] this behaviour is not observed

39   above 1.8 K (all *ca.* 20 Oe s^{-1}), and $[Er\{N(SiMe_3)_2\}_3]$ shows hysteresis while $[Dy\{N(SiMe_3)_2\}_3]$

40   does not[24].

41   Complex **1** was synthesised by the reaction of $[Dy(Cp^{ttt})_2(Cl)]$ with the silylium reagent

42     $[H(SiEt_3)_2][B(C_6F_5)_4]$ (Et = CH_2CH_3) in benzene at room temperature (Fig. 1)[25]. Guo *et al.* have

43   simultaneously reported the synthesis and magnetic data for **1**[26]. Bright yellow crystals of **1** were

44   obtained in 60% yield by layering a saturated DCM solution of crude material with hexane at 4

45   °C, followed by storage at –25 °C. Detailed synthetic information and full characterisation of all

46   compounds is given in the Supplementary Information. Crucially, single crystal X-ray diffraction

47   studies show no appreciable interactions of the $\{B(C_6F_5)_4\}$ anion with the cation in **1** [shortest

48   equatorial Dy⋯F distance: 5.996(3) Å], due to the steric demands of the six ^{t}Bu groups, though

49 two short intramolecular Dy···C_{methyl} distances [2.964(5) Å mean] produce an approximately

50 linear H···Dy···H motif [174.96°; Dy···H: 2.4989 Å mean]. The bent dysprosocenium cation

51 exhibits a $Cp_{centroid1}$···Dy···$Cp_{centroid2}$ angle of 152.56(7)° with the two C_5 rings approximately

52 eclipsed, in contrast with [Dy(Cp*)$_2${μ-(Ph)$_2$BPh$_2$}] [$Cp_{centroid1}$···Dy···$Cp_{centroid2}$ = 134.00(4)°], which

53 adopts a staggered conformation[16]. The mean Dy···$Cp_{centroid}$ distance in **1** is relatively short

54 [2.316(3) Å], as expected from electrostatic considerations for an isolated cation *cf.* [Dy(Cp*)$_2${μ-

55 (Ph)$_2$BPh$_2$}] [2.373(2) Å][16]. Complete active space self-consistent field spin-orbit (CASSCF-SO)

56 calculations on the X-ray structure of **1** show that it possesses large easy-axis magnetic

57 anisotropy (Fig. 4b, Table S13), and thus should exhibit SMM behaviour. Further calculations

58 show that the close equatorial H atoms, the bent geometry, and the eclipsed rings do not make

59 significant contributions to the electronic structure of **1** (Tables S14 – S16).

60 Magnetic measurements reveal that **1** shows open hysteresis at and below 60 K using a

61 sweep rate of 22 Oe s^{-1}, with 83% remanent magnetisation and a coercive field of 20 – 25 kOe

62 at 2 K (Fig. 2). The low temperature hysteresis data show a step at zero-field, likely due to

63 enhanced relaxation by quantum tunnelling of the magnetisation (QTM), a common feature in

64 SMMs[6]. To confirm that the magnetic hysteresis is of molecular origin and does not owe to long-

65 range ordering, we have measured a structurally analogous doped sample, 8%

66 Dy@[Y(Cp^{ttt})$_2$][B(C$_6$F$_5$)$_4$] **2**, and two frozen dichloromethane solutions of **1** with concentrations

67 *ca.* 21 mM, **3**, and 170 mM, **4**, (Figs. S32 – S35, Table S3); these samples also show hysteretic

68 behaviour, confirming these properties are intrinsic to the [Dy(Cp^{ttt})$_2$]$^+$ cation. Interestingly, while

69 the zero-field step is reduced for **2** (Figs. S32 and S35), suggesting that dipolar interactions are

70 partially responsible for this feature in **1**, the step is more significant for the DCM solution

71 samples **3** and **4** (Figs. S33 – S35), implying that the local environment of the molecule plays a

72 crucial role in the zero-field dynamics. Similar results are found for a solution sample with an

73 alternative solvent, 1,2-difluorobenzene (Fig. S35), indicating that this step is not due to

74   coordination of DCM. Despite the faster zero-field relaxation, hysteresis still persists up to at

75   least 54 K for **4** (Fig. S34). Field cooled (FC) and zero-field cooled (ZFC) magnetic

76   susceptibility, χ, for **1**-**4** coincide with the theoretical equilibrium trace until 61 K, below which

77   they bifurcate and are out of equilibrium (Figs. 3a and S36 – S39).

78   To probe the origin of the magnetic hysteresis, we measured the magnetic relaxation

79   rate by alternating current (AC) magnetic susceptibility and direct current (DC) magnetisation

80   decay. The out-of-phase component of the AC susceptibility, χ'', of **1** exhibits frequency

81   dependent peaks between 72 and 112 K (Fig. S40), and fitting these data with the Debye

82   model[6] shows that the relaxation rate follows an Arrhenius law $\tau^{-1} = \tau_0^{-1}\ exp[-U_{eff}/kT]$ with U_{eff} =

83   1223 cm^{-1} (1760 K) and τ_0 = 1.986×10^{-11} s (Figs. 3b and S56); this is consistent with an Orbach

84   relaxation mechanism over an effective energy barrier, U_{eff}. To extend investigation of the

85   relaxation dynamics to lower temperatures, we measured the DC magnetisation decay between

86   26 and 62 K; fitting these data with single exponentials[6] yields the magnetic relaxation rates

87   (Figs. S43 – S46, Table S8). Between 26 and 50 K the relaxation rate has a power-law

88   dependence on temperature and is well-modelled by $\tau^{-1} = CT^n$ with C = 1.664×10^{-6} s^{-1} K^{-n} and n

89   = 2.151 (Figs. 3b and S57). While the value of n is close to that expected for a phonon

90   bottleneck (n = 2)[27], the relaxation rates for the doped and solution samples **2**-**4** follow almost

91   exactly the same temperature dependence as **1** (Figs. S58 – S61), and thus these dynamics are

92   intrinsic to the [Dy(Cp^{ttt})$_2$]$^+$ cation and not the result of inefficient heat flow between the lattice

93   and the bath. Intriguingly, the intersection of the exponential and power-law dynamics occurs at

94   60.4 K for **1**, coincident with the temperature at which magnetic hysteresis appears and the

95   FC/ZFC susceptibilities bifurcate.

96   The computational and magnetic data for **1** are generally in excellent agreement with

97   those reported by Guo *et al.*[26]. Slight differences are observed in the FC/ZFC behaviour, likely

98   due to different temperature sweep rates having a profound effect on the relaxation dynamics

99   below 61 K. The origin of the discrepancy between the power-law relaxation exponents (n =

100   2.151 *vs.* 3.92[26]) is not obvious. However, we find consistent behaviour for samples of different

101   concentrations and phases, and at lower temperatures (Fig. S61), thus we suggest that the

102   results herein show the intrinsic properties of **1**.

103   To investigate the mechanism of magnetic relaxation, we have undertaken an *ab initio*

104   study of the spin dynamics; such approaches have only recently become viable[28,29]. Magnetic

105   relaxation in SMMs is effected by the coupling of the electronic states to the quantised

106   vibrational modes of the lattice (phonons). However, as the relaxation dynamics for $[Dy(Cp^{ttt})_2]^+$

107   are consistent between the crystalline phase and amorphous frozen solution, we hypothesise

108   that magnetic relaxation is moderated by localised molecular vibrations (optical phonons). Thus,

109   as a first approximation we consider only the gas-phase vibrational modes of the $[Dy(Cp^{ttt})_2]^+$

110   cation. Our approach consists of four stages: (i) calculation and (ii) calibration of vibrational

111   modes; (iii) calculation of spin-phonon coupling; and, (iv) simulation of dynamics. We calculate

112   the vibrational modes with density functional theory, and calibrate the vibrational energies and

113   atomic displacements by comparison to the vibrational spectra (Fig. S63, Table S19) and to the

114   thermal displacement parameters from X-ray diffraction, respectively. We determine the spin-

115   phonon coupling by performing a CASSCF-SO calculation for each vibrational mode on

116   molecular geometries distorted from equilibrium along the relevant normal mode vector,

117   followed by a crystal field decomposition of the electronic structure; thus, we define the

118   electronic part of the spin-phonon coupling from the change in the crystal field potential. We

119   then calculate the transition rates between each electronic state by allowing a finite Gaussian

120   linewidth, σ, for each vibrational mode and finally simulate the spin dynamics by solution to the

121   master equation[6].

122   Considering single-phonon transitions (Table S22), we find one slow relaxation rate

123   (Table S23) corresponding to the Orbach mechanism; this result echoes the archetypal case of

124   Mn_{12}[6]. As a function of temperature, the calculated relaxation rate reproduces the slope of the

125   AC data well (Figs. 4a and S65), demonstrating that the Orbach mechanism is moderated by

126   local molecular vibrations. Variation of σ slightly affects the effective pre-factor τ_0^{-1} of the

127   Orbach mechanism (Fig. S65), but we fix $\sigma = 10$ cm^{-1} to be consistent with the full-width-half-

128   maximum linewidth of the experimental vibrational spectra. Given our approximations, the

129   agreement between our *ab initio* spin-dynamics and experimental measurements is remarkable.

130   The calculated transition rates reveal a heterogeneous relaxation pathway that does not

131   proceed through all states sequentially; the most probable pathway for Orbach relaxation is

132     $|\pm 15/2\rangle \rightarrow |\pm 13/2\rangle \rightarrow |\pm 11/2\rangle \rightarrow |\pm 9/2\rangle \rightarrow |\pm 5/2\rangle \rightarrow |\mp 3/2\rangle \rightarrow |\mp 7/2\rangle \rightarrow |\mp 11/2\rangle \rightarrow$

133     $|\mp 13/2\rangle \rightarrow |\mp 15/2\rangle$ (Fig. 4b, Table S24). Decomposing the transition rates further, it is the

134   vibrational motion of the C–H groups on the Cp^{ttt} rings that facilitate the initial $|\pm 15/2\rangle \rightarrow$

135     $|\pm 13/2\rangle$ relaxation step (Fig. S66, Table S25). Therefore, we propose that substitution of these

136   groups would significantly affect the relaxation dynamics and possibly lead to magnetic

137   hysteresis at higher temperatures.

138   Considering the two-phonon second-order Raman process (Table S26), we find three

139   slow relaxation rates (Table S27), however only one contributes to the relaxation dynamics.

140   While we have shown that the low-temperature $\tau^{-1} \propto T^2$ region is not due to a phonon

141   bottleneck, the temperature dependence of the calculated Raman mechanism deviates

142   considerably from the experiment, a feature that is not improved by altering σ (Fig. 4a and S67).

143   This could be due to our gas-phase approximation which lacks the true dispersion of the optical

144   modes and their coupling to the acoustic modes[30], or to the neglect of explicit anharmonicity[28].

145   Whilst simple electrostatic models have predicted that the quintessential Ln SMM should

146   be a Dy(III) complex with negatively charged ligands along a single axis[19,20], and considerable

147   magnetic anisotropy has been achieved for such complexes[9-12,31], until now a thirty-fold increase

148   in the largest U_{eff} barrier (~42 cm^{-1} [7] to 1261 cm^{-1} [10]) had been accompanied by only a four-fold

149 increase in the highest temperature at which magnetic hysteresis was observed (4 K[7] to 14 K[8-10]

150 at *ca.* 20 Oe s^{-1}). The U_{eff} value for **1** is similar to that of 1261 cm^{-1} for

151 [Dy(^{t}BuO)$_2$(pyridine)$_5$][BPh$_4$][10], however the highest temperature at which magnetic hysteresis is

152 observed is substantially larger (60 K *vs.* 3 K) and there is significantly more remanent

153 magnetisation at 2 K (83% *vs. ca.* 11%). Furthermore, the zero-field step observed here is much

154 smaller than for other Dy(III) SMMs[9-12,31], suggesting that such steps which plague SMMs are

155 not solely due to hyperfine coupling or local dipolar fields as is routinely suggested. We theorise

156 that the lack of a severe zero-field step and the notably improved relaxation dynamics for **1** are

157 due to the unique spin-phonon coupling of the constrained metal-ligand vibrational modes

158 intrinsic to the bis-η^5-Cp^{ttt} coordination geometry. This is in contrast to other molecules with

159 large U_{eff} that do not show hysteresis at comparably high temperatures, for example

160 [Dy(^{t}BuO)$_2$(pyridine)$_5$][BPh$_4$][10], where the first coordination sphere is constructed from mono-

161 atomic donors which have greater metal-ligand flexibility.

162

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255

256 **Author contributions** C.A.P.G. and D.P.M. provided the original concept. C.A.P.G.
257 synthesised and characterised the compounds. F.O. carried out the single crystal X-ray
258 diffraction analysis and supporting synthetic/characterisation work. N.F.C. collected and
259 interpreted magnetic data. N.F.C. devised the relaxation dynamics model and wrote computer
260 programs to perform these calculations. D.R. and N.F.C. performed the calculations. D.P.M. and
261 N.F.C. wrote the manuscript with contributions from all authors. D.P.M. and N.F.C. supervised
262 the project.

263

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265 www.nature.com/reprints. The authors declare no competing financial interests.
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268

Figure 1 | **Synthesis and structure of [Dy(Cp^{ttt})$_2$][B(C$_6$F$_5$)$_4$] (1). a**, Synthesis of **1**. **b**, Molecular structure of **1** with selective atom labelling (B = yellow, C = grey, Dy = cyan, F = green). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Selected distances and angles: Dy1···Cp$_{centroid1}$, 2.318(2) Å; Dy1···Cp$_{centroid2}$, 2.314(2) Å; Dy1···C7, 2.971(5) Å; Dy1···C24, 2.956(5) Å; Cp$_{centroid1}$···Dy1···Cp$_{centroid2}$, 152.56(7)°.

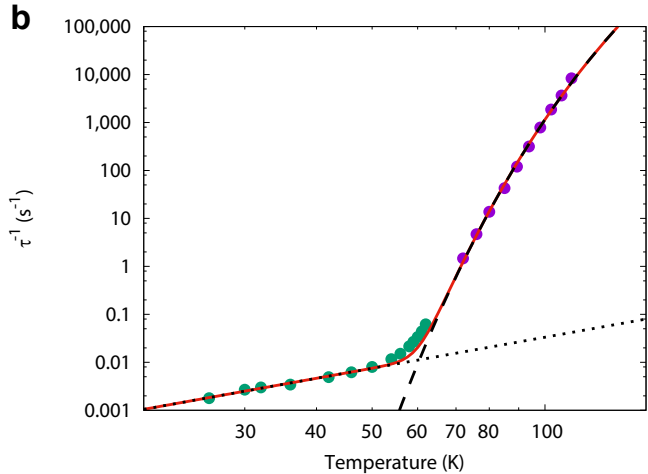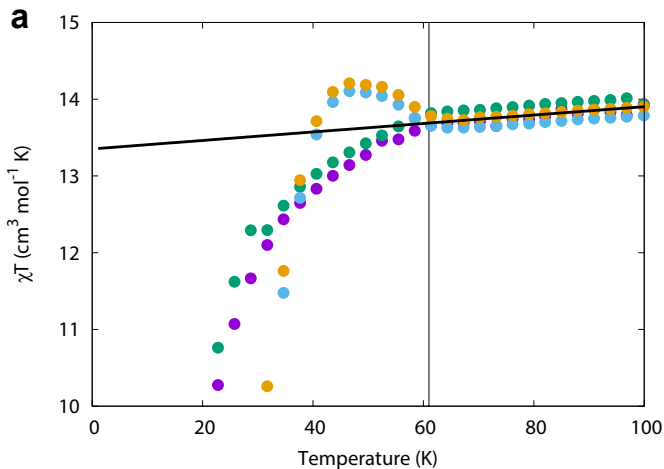**Figure 2** | **Magnetic hysteresis of 1**. Hysteresis was measured with a mean field sweep rate of 22(9) Oe s^{-1} for |H| < 10 kOe, 54(15) Oe s^{-1} for 10 < |H| < 20 kOe, and 91(17) Oe s^{-1} for 20 < |H| < 70 kOe, giving an overall mean sweep rate of 50(33) Oe s^{-1}. The sweep rate was slow (22 Oe s^{-1}) around zero-field where the relaxation dynamics of SMMs are crucially dependent on sweep rate. **a**, Hysteresis loops recorded at 2 (purple) – 30 K (black) in 4 K steps. **b**, Hysteresis loops recorded at 52 (blue) – 60 (red) and 62 K (black) in 2 K steps, with truncated *x*- and *y*-axes, showing open hysteresis at 60 K but closed at 62 K.
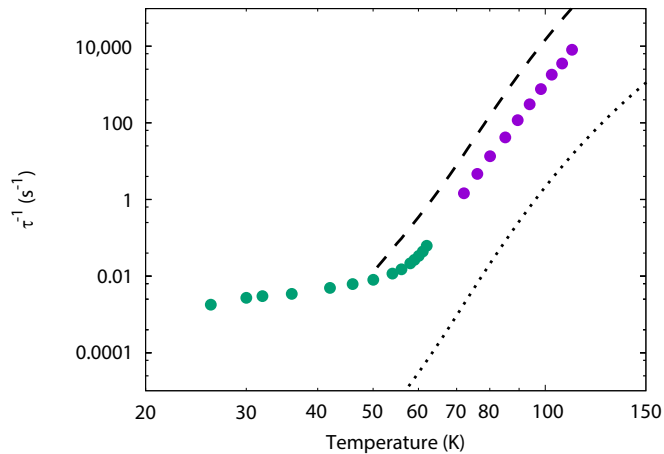
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Figure 3 | Relaxation dynamics of 1. a, FC and ZFC magnetic susceptibilities (as χT product) at 1 kOe FC (purple), 500 Oe FC (green), 1 kOe ZFC (light blue) and 500 Oe ZFC (orange), with the CASSCF-SO-calculated curve scaled by 1.08 (black line). Vertical line shows bifurcation point at 61 K. **b**, Temperature dependence of the magnetic relaxation rate. Solid purple points are the relaxation rates extracted from AC susceptibility data (Table S5) and solid green points from DC magnetisation decay data (Table S8). Solid red line is given by $\tau^{-1} = \tau_0^{-1}$ $exp[-U_{eff}/kT] + CT^n$, dashed black line is given by $\tau^{-1} = \tau_0^{-1}\, exp[-U_{eff}/kT]$ and dotted black line is given by $\tau^{-1} = CT^n$ with U_{eff} = 1223 cm^{-1} (1760 K), τ_0 = 1.986×10^{-11} s, C = 1.664×10^{-6} s^{-1} K^{-n} and n = 2.151.

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Figure 4 | *Ab initio* spin dynamics. a, Temperature dependence of the magnetic relaxation rate. Solid purple points are the relaxation rates extracted from AC susceptibility data (Table S5) and solid green points from DC magnetisation decay data (Table S8). Dashed black line gives the *ab initio* calculated Orbach relaxation rate and dotted black line gives the *ab initio* calculated Raman relaxation rate. **b**, Energy barrier to magnetic relaxation for **1**. Electronic states from CASSCF-SO calculations, labelled with their dominant m_J composition in the J = 15/2 basis (Table S20). Arrows represent the Orbach relaxation pathway at 150 K with σ = 10 cm^{-1}, where the opacity of the arrows is proportional to the single-phonon transition probability normalised from each departing state and commencing with unit population in |−15/2>; only relaxation pathways towards |+15/2> are shown (Table S24).

a

b

a

b

a

b