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### **ARTICLE TYPE**

# Field enhanced thermally activated mechanism in a square Dy<sub>4</sub> aggregate

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A rare  $\mu_4$ -OH centred square Dy<sub>4</sub> aggregate displays field enhanced thermally activated mechanism with 3-fold increase in the single-molecule magnetic relaxation barrier upon application of an optimal field.

<sup>10</sup> Since the discovery that slow relaxation of the magnetization above cryogenic temperature can occur in the celebrated molecule  $(Bu_4N)[Tb(Pc)_2]$   $(H_2Pc = phthalocyanine)$ ,<sup>1</sup> the elaboration of high performance single molecular magnets (SMMs) featuring heavier lanthanides has rejuvenated the 15 interest of physicists and chemists because of their envisioned technological applications.<sup>2</sup> Notably, the success of such application hinges upon the inherent molecular spin-inversion barrier and blocking temperature. There have been remarkable outcomes, such as  $(Bu_4N)[Tb(Pc)_2]$  with effective barrier <sup>20</sup> accessible to 330 K.<sup>1</sup> Equally remarkable has been attributable to slow relaxation observed in the notable Dy<sub>3</sub> molecule in spite of its non-magnetic ground state.<sup>3</sup> Interest in the polynuclear lanthanides complexes thus has pushed the slow relaxation to 40 K in a pyramidal Dy<sub>5</sub> molecule.<sup>4</sup> Moreover,  $_{25}$  the exceptionally strong magnetic exchange occurs in a  $N_2^{3-1}$ 

radical bridged  $Tb_2$  compound with a record magnetic blocking temperature of 14 K.<sup>5</sup>

To date, however, a crucial roadblock to the isolation of zero-field lanthanide-based SMMs with large barriers is fast <sup>30</sup> quantum tunneling of the magnetization (QTM) resulted from the mixing of  $\pm M_S$  levels via hyperfine coupling, dipolar spin-spin interactions, or transverse zero-field splitting (*E*).<sup>2a</sup> The latter two factors can be minimized by design a perfectly high-symmetrical coordination environment of a Kramers ion <sup>35</sup> as well as ensuring a large separation between molecules.

- Rationally optimizing the ligand field around metallic centre is therefore beholden to the study of magnetic relaxation. The effect of coordination sphere with a high-order single axis, such as  $S_8$  in the square antiprism (SAP),<sup>1, 6</sup>  $C_4$  in the 40 coordinated symmetry of  $C_{4v}^4$  and  $C_3$  in the trigonal prism
- environment,<sup>7</sup> is that of breaking the spherical symmetry, splitting the (2J+1) degenerate ground states into new sublevels, thus achieving an easy axis of magnetization and Ising-type anisotropy. Additionally, recent advances have
- <sup>45</sup> manifested that for many SMMs, the slow relaxation behaviour varies significantly with applied field, as it can predominantly reduce the efficiency of the underbarrier process<sup>8</sup> or bring about the occurrence of another relaxation

process.<sup>7a, 9</sup>



**Fig. 1** Tetranuclear unit of **1**. Hydrogen atoms, counter ions and solvents are omitted for clarity. In the left corner the coordination polyhedra of mono capped square-antiprismatic geometry for Dy1.

In the present work, we describe a rare  $\mu_4$ -OH centred Dy<sub>4</sub> <sup>55</sup> square molecule, [Dy<sub>4</sub>( $\mu_4$ -OH)(Hhpch<sup>-</sup>)<sub>8</sub>)]·(ClO<sub>4</sub>)<sub>3</sub>·2CH<sub>3</sub>CN·MeOH·4H<sub>2</sub>O (1) (where H<sub>2</sub>hpch = 2hydroxylbenzaldehyde (pyridine-4-carbonyl) hydrazone), with quasi mono capped square-antiprism coordination environment around the metallic centre. This compound <sup>60</sup> displays field enhanced thermally activated mechanism with 3-fold increase in the single-molecule magnetic relaxation barrier upon application of 1 kOe field.

The reaction between  $H_2$ **hpch** and  $Dy(ClO_4)_3 \cdot 6H_2O$  in 1:3 methanol/acetonitrile, in the presence of NaHCO<sub>3</sub> (see 65 Experimental Section), yielded yellow crystalline plates of  $[Dv_4(\mu_4-OH)(Hhpch^{-})_8] \cdot (ClO_4)_3 \cdot 2CH_3CN \cdot MeOH \cdot 4H_2O$ (1)over three days. Single-crystal X-ray studies revealed that 1 crystallized in the monoclinic space group  $P2_1/c$ . A perspective view of the square core-shaped molecule is 70 represented in Fig. 1. The central core of this aggregate consists of four dysprosium cations arranged in a corner fashion around the central  $\mu_4$ -OH group (O17) as well as eight Hhpch ligands like "petals" enclosing the core alternately. Each pair of Hhpch<sup>-</sup> ligands coordinates to two dysprosium 75 (III) centres in an antiparallel or "head-to-tail" fashion with deprotonated phenol oxygen atoms (O2 and O6), imine nitrogen atoms (N3 and N9) and the keto-form carbonyl oxygen atoms (O1 and O5) (Fig.S1). Furthermore, all the deprotonated phenol groups derived from ligands function as so  $\mu_2$ -bridge along one of the edges of the square plane and create a twelve-membered Dy<sub>4</sub>O<sub>8</sub> central core with the Dy–O– Dy angles falling in the range 97.13(18)–99.73(19)° and the average Dy–O distance of 2.356 Å. When attention is diverted to this  $\mu_4$ -OH centred tetranuclear skeleton, it is reminiscent s of those reported for 4f compounds with a rhombus arrangement Ln<sub>4</sub> unit linked by  $\mu_n$ -O group (n = 2, 4)<sup>10</sup> as well as for transition metal-based MOFs.<sup>11</sup>

All Dy sites are nine-coordinated with contributions from four phenol atoms, two carbonyl atoms and two imine atoms <sup>10</sup> but the distance between the metallic centre and  $\mu_4$ -OH atom is a little longer than that of the  $\mu_2$ -O groups, making them with the geometry of quasi mono capped square-antiprism (Fig. 1). The shortest Dy...Dy distance between adjacent molecules is 11.883 Å.

Direct current (dc) magnetic susceptibility studies of a polycrystalline sample (Fig. S2) reveal a room-temperature  $\chi_{\rm M}T$  value equals to 56.05 cm<sup>3</sup> K mol<sup>-1</sup>, approaching the expected value for four uncoupled  $Dy^{III}$  ions (C = 14.17 cm<sup>3</sup> K mol<sup>-1</sup>), which indicates the Stark sublevels of <sup>6</sup>H<sub>15/2</sub> ground 20 state split by the ligand field are statistically populated at room temperature, and the free-ion approximation applies.<sup>12</sup> With lowering the temperature, however, the components of higher energy are successively depopulated, thus the  $\chi_{\rm M}T$ value of 1 gradually decreases deviated from the Curie Law. <sup>25</sup> After reaching the minimum (50.58 cm<sup>3</sup> K mol<sup>-1</sup>) at 10 K, the  $\chi_{\rm M}T$  value slightly increases and reaches 51.1 cm<sup>3</sup> K mol<sup>-1</sup> at 2.0 K. Reduced magnetization data do not lie on a single master-curve below 7 K, suggesting the presence of significant magneto-anisotropy in the dysprosium (III) system 30 (Fig. S3, inset).



Fig. 2 Left: Temperature dependence of the out-of-phase ac susceptibility  $(\chi'')$  of 1 in zero static field. Right: Frequency dependence of the out-of-phase ac susceptibility  $(\chi'')$  of 1 collected at indicated temperature in zero <sup>35</sup> static field. Solid lines are guides for the eye.

Temperature dependences of the alternating current (ac) susceptibilities in zero static field reveal a slowly relaxing magnetic moment below ~20 K, that is hallmarks of typical SMM behaviour of the "freezing" of the spins by the <sup>40</sup> anisotropy barriers (Fig. 2, left). In comparison with another similar analogue Dy<sub>4</sub> reported by Bi,<sup>10d</sup> for which the slow magnetic relaxation was observed only at low temperatures (below 8 K), relatively high-temperature relaxation occurs in **1**. The difference in magnetic behaviour could be due to the <sup>45</sup> disparate local coordination geometry around the metallic

centre in light of the detail bond lengths and slightly acute bridging angles, which presumably influence the axial anisotropy.<sup>13</sup>

The out-of-phase component  $\chi$ " for higher frequencies 50 shows a series of frequency-dependent peaks around 13 K,

View Online with a second set around 3 K (Fig. 2, left). Evidence of possible multiple relaxation processes has been observed in several reported SMMs due to the different anisotropic centres<sup>13a, 14</sup> or the existence of the isomers or conformers in 55 the crystal.<sup>15</sup> For 1, the slight differences in the local coordination spheres at the Dy<sup>III</sup> centres are probably responsible for two processes. Therefore, Arrhenius analysis of the relaxation time was extracted from  $\chi''(v)$  plot (Fig. 2, right) by fitting the data to two relaxation processes using the 60 sum of two modified Debye functions.<sup>16</sup> The two limiting values for the energy barrier and relaxation times obtained by a linear fit of the high and low temperature data, respectively, are reported in Table 1. At high temperature (HT, T > 7 K), the similar values of preexponential factor indicate that the 65 relaxation times of two relaxation processes will get close to each other with increasing temperature; as we can see, the Cole-Cole plots go through a fusion of FR and SR at the frequency range of the test (Fig. S4).



<sup>70</sup> **Fig. 3** Magnetization relaxation time,  $\tau$ , versus  $T^1$  plot for **1** under 0 and 1 kOe. The solid line is fitted with the Arrhenius law. • The relaxation time was extracted from the  $\chi''(\nu)$  plot;  $\circ$  The relaxation time was extracted from the plot of  $\chi''/\chi$  against temperature T (Fig. S3).

**Table 1** Characteristic dynamic parameters extracted from the 75 Arrhenius law ( $\tau = \tau_0 \exp(\Delta/T)$  for **1** 

H <sub>dc</sub> / Oe	$\Delta_{\rm LT}$ / K	$\tau_{0\text{LT}}/10^{-6}\text{s}$	$\varDelta_{\rm HT}$ / K	$\tau_{0 \text{ HT}} / 10^{-6} \text{ s}$
(SF	R) 6.2	1960	30.3	30
0 (FF	R) 3.3	182	16	37
1000	6.7	5850	92	0.2

To better understand the nature of the dynamics, measurements at various applied dc fields at 3.5 K were carried out and the application of dc fields indeed <sup>80</sup> dramatically alter the profile of the  $\chi$ " frequency scan, as shown in Fig. 4, left. Here, the peak centred at high frequencies under zero field rapidly diminishes with a concomitant increase of a much lower-frequency peak. This change continues until 1 kOe, at which point the high-<sup>85</sup> frequency peak has completely disappeared. Strong frequency dependence of ac susceptibility with varying temperature was observed under this field (Fig. 4, right). The data plotted as Cole-Cole plots (Fig. S5) at fixed temperature below 17 K show a relatively symmetrical shape and can be fitted to the <sup>90</sup> generalized Debye model,<sup>17</sup> with  $\alpha$  parameters below 0.30 ( $\alpha$ = 0 for a Debye model).

At low temperature (LT, T < 4 K), the activation energies ( $\Delta_{LT}$ ) are comparable for the two fields ( $\Delta_{LT} = 6.2$  (SR), 3.3 (FR) and 6.7 K for 0 and 1 kOe, respectively). However, with

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- temperature increasing, the Arrhenius fitting between 12 K and 16 K (solid line, Fig. 3) gives a strongly enhanced barrier of  $U_{\text{eff}} = 92$  K, which is more than triple that of zero dc field. This suggests a thermally activated mechanism seems to be s strongly affected by dc-field. Usually in SMMs the application of a static field results in the suppression of the underbarrier process deduced from transverse anisotropy
- terms<sup>8a, 18</sup> rather than the enhancement of the effective barriers as occurred in **1**. All the above magnetic analysis in combination with Field-
- <sup>10</sup> All the above magnetic analysis in combination with Fieldcooled and Zero-field cooled measurements (Fig. S6) indicates that the magnetic relaxation phenomenon of **1** basically originates from an intrinsic molecular properties of the compound, rather than intermolecular interactions and
- <sup>15</sup> long-range magnetic order. One possible scenario of magnetic dynamics in **1** is that dc-field alters the thermally activated relaxation pathway, and plays a key role in the switch of low-lying excited states in **1**. After all, the energy  $\varDelta$  of about 30 K under zero dc field is not comparable to the one of above 90 K
- <sup>20</sup> under 1 kOe dc-field. It's noteworthy that simple magnetostructural relationships based on the coordination environment seem hardly to prognose not only the correct magnetic anisotropy, but also the dynamic behaviour of lanthanide complex with nonideal symmetry environment.<sup>19</sup> The ab initio <sup>25</sup> calculations are thus planned in order to provide more precise information on crystal field splitting of this complex as well
  - as on the role played by anisotropy.



**Fig. 4** Top: Out-of-phase ac susceptibility  $(\chi^{"})$  collected on 1 at 3.5 K <sup>30</sup> under indicated dc field. Bottom: Frequency dependence of  $\chi^{"}$  of 1 under an applied dc field of 1 kOe.

In conclusion, we report a peculiar  $\mu_4$ -OH centred square Dy<sub>4</sub> aggregate featuring SMM behaviour. The most striking property evidenced in this study is the optimal field has <sup>35</sup> unparalleled impact on the thermally activated regime with the remarkable enhancement of effective barrier up to triple of magnitude. It has proven to be a novel protype for further investigations of magneto-structural correlations to shed light on the complicated relaxation mechanism for pure 4f systems.

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#### Notes and references

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#### **Graphical Abstract**

A rare  $\mu_4$ -OH centred square Dy<sub>4</sub> aggregate displays field enhanced thermally activated mechanism with 3-fold increase in <sup>5</sup> the single-molecule magnetic relaxation barrier upon application of an optimal field.

