Single-Molecule Magnet Behaviour in a Centrosymmetric Dinuclear Dysprosium(III) Complex: Sequential Distinguish of Triple Relaxation Pathways

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Physical Measurements

Elemental analyses of C, H and N were carried out with a PerkinElmer 240C elemental analyzer. The ratio of Dy/Y was determined with XRF (EDAX Orbis). The IR spectra were recorded with a Nicolet iS10 spectrometer using KBr pellets in the range 400-4000 cm$^{-1}$. Powder X-ray diffraction (PXRD) were measured on a Bruker AXS D8 Advance powder diffractometer (Cu-Kα, λ = 1.54056 Å), with a scan speed of 0.5 s/step and a step size of 0.01° in 2θ. Data of magnetic properties for crystalline sample were collected on a Quantum Design MPMP-XL 7 superconducting quantum interference device (SQUID) magnetometer and a Quantum Design MPMS SQUID-VSM.

Table S1 Crystallographic data and structural refinement parameters for Dy$_2$.

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<th>Dy$_2$</th>
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<tr>
<td>Formula</td>
<td>C$<em>{52}$H$</em>{56}$Cl$_2$Dy$_2$N$_6$O$_8$</td>
</tr>
<tr>
<td>f w</td>
<td>1288.93</td>
</tr>
<tr>
<td>$T$ / K</td>
<td>296(2)</td>
</tr>
<tr>
<td>$\lambda$ / Å</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>$a$ / Å</td>
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</tr>
<tr>
<td>$b$ / Å</td>
<td>10.371(3)</td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>19.538(6)</td>
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<tr>
<td>$\alpha$ / °</td>
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<tr>
<td>$\beta$ / °</td>
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<tr>
<td>$\gamma$ / °</td>
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<tr>
<td>$V$ / Å$^3$</td>
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<tr>
<td>$Z$</td>
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<tr>
<td>$D_c$ / g cm$^{-3}$</td>
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<tr>
<td>$\mu$ / mm$^{-1}$</td>
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<td>$F(000)$</td>
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<td>$\theta$ / °</td>
<td>2.144~27.594</td>
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<tr>
<td>Reflns collected, Reflns unique</td>
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<tr>
<td>$R_{\text{int}}$</td>
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<tr>
<td>GOF on F$^2$</td>
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<td>$R_1$ [I&gt; 2σ(I)]$^{[a]}$, $R_1$ (all data)$^{[a]}$</td>
<td>0.0437, 0.0499</td>
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<tr>
<td>$wR_2$ [I&gt;2σ(I)]$^{[b]}$, $wR_2$ (all data)$^{[b]}$</td>
<td>0.1288,0.1301</td>
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<tr>
<td>Largest diff. Peak, hole / (e Å$^{-3}$)</td>
<td>1.286, -1.801</td>
</tr>
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$^{[a]}$$R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|; \quad ^{[b]}wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$
**Table S2** Selected bond lengths (Å) and angles (°) for Dy₂.

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<thead>
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<th>Bond lengths around Dy1</th>
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<td>Dy1-O1</td>
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<td>Dy1-O3</td>
<td>2.398(3)</td>
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<td>Dy1-N1</td>
<td>2.492(4)</td>
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<td>Dy1-Cl1</td>
<td>2.681(11)</td>
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<td>Dy1-O2</td>
<td>2.239(3)</td>
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<tr>
<td>Dy1-O4</td>
<td>2.240(3)</td>
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<td>Dy1-N2</td>
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<table>
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<tr>
<th>Bond angles including Dy1</th>
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<td>O2-Dy1-O3</td>
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<td>O1-Dy1-N1</td>
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<td>O1-Dy1-N2</td>
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<td>O2-Dy1-N1</td>
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<td>145.56(12)</td>
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<td>O3-Dy1-N2</td>
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<td>O1-Dy1-Cl1</td>
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<td>O1-Dy1-Cl1</td>
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<td>N1-Dy1-Cl1</td>
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<td>N2-Dy1-Cl1</td>
<td>82.88(9)</td>
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**Table S3** Deviation parameters calculated by SHAPE for seven-coordinated Dy (III) center in Dy₂. The best match is displayed in bold with blue color.

<table>
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<th>Geometry</th>
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<td>D₇h</td>
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<td>HPY-7</td>
<td>C₆ᵥ</td>
<td>Hexagonal pyramid</td>
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<td>PBPY-7</td>
<td>D₅h</td>
<td>Pentagonal bipyramid</td>
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<tr>
<td>COC-7</td>
<td>C₃ᵥ</td>
<td>Capped octahedron</td>
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<td>CTPR-7</td>
<td>C₂v</td>
<td>Capped trigonal prism</td>
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<td>JPBPY-7</td>
<td>D₅h</td>
<td>Johnson pentagonal bipyramid (J13)</td>
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<td>JETPY-7</td>
<td>C₃ᵥ</td>
<td>Elongated triangular pyramid (J7)</td>
<td>17.210</td>
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Fig. S1 The theoretical X-ray powder diffraction patterns (black), the experimental ones of \( \text{Dy}_2 \) (red) and \( \text{Dy}_x\text{Y}_{2-x} \) (blue).

Fig. S2 The FT-IR spectra of \( \text{Dy}_2 \) (black) and \( \text{Dy}_x\text{Y}_{2-x} \) (red).

Fig. S3 Energy spectrum of \( \text{Dy}_x\text{Y}_{2-x} \).
**Fig. S4** (a) Perspective view of the asymmetric unit of Dy$_2$, (b) the coordination geometry of Dy(III) ion in Dy$_2$.

**Fig. S5** (a) The 2D network of Dy$_2$ in the $bc$ plane formed via hydrogen bonds, the shortest interdimer Dy···Dy separation is 6.898 Å, while the Dy···Dy distance within the dinuclear molecule is 10.464 Å. (b) View of the network along the b direction.
Fig. S6 Plots of $M$ vs $H/T$ for Dy$_2$ at 1.8, 2.5, 5.0 and 10 K.

Fig. S7 (a) $\chi''_M$ vs. $\nu$ plot at 1.8 K in the frequency range of 1-1000 Hz under various applied dc field for Dy$_2$. (b) Field-dependence of the relaxation time (blue circles) and the best fit curve (red line) for Dy$_2$.

Fig. S8 Frequency-dependent of in-put phase ($\chi_M'$) ac susceptibilities under zero field (a) and under 1.5 kOe dc field (b) for Dy$_2$. 
Fig. S9 Cole-Cole curves under zero dc-field (a) and under 1.5 kOe (b) for Dy$_2$. Solid lines represent the best fit with extended Debye model.

Table S4 The best-fitted parameters obtained from the analyses of the Cole-Cole plots using the extended Debye model for Dy$_2$ under zero field.

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$\chi^{(\text{total})}$ / cm$^3$ mol$^{-1}$</th>
<th>$\Delta \chi_1$ / cm$^3$ mol$^{-1}$</th>
<th>$\ln(\tau_1 / s)$</th>
<th>$\alpha_1$</th>
<th>$\Delta \chi_2$ / cm$^3$ mol$^{-1}$</th>
<th>$\ln(\tau_2 / s)$</th>
<th>$\alpha_2$</th>
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The best-fitted parameters obtained from the analyses of the Cole-Cole plots using the extended Debye model for Dy\textsubscript{2} under 1.5 kOe dc field.

<table>
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<tr>
<th>$T$ / K</th>
<th>$\chi_s$(Total)/ cm\textsuperscript{3} mol\textsuperscript{-1}</th>
<th>$\Delta \chi_1$ / cm\textsuperscript{3} mol\textsuperscript{-1}</th>
<th>ln($\tau$ / s)</th>
<th>$\alpha$</th>
<th>$\Delta \chi_2$ / cm\textsuperscript{3} mol\textsuperscript{-1}</th>
<th>ln($\tau$ / s)</th>
<th>$\alpha$</th>
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</table>

$\chi_{T1} = \chi_s$(Total) + $\Delta \chi_1$, $\chi_{T2} = \chi_s$(Total) + $\Delta \chi_1 + \Delta \chi_2$
$(\chi_{c})$ and the best fit curve (red line) for various applied $dc$ for $(a) = 2.85e-26$

<table>
<thead>
<tr>
<th>$\chi_{T1}$</th>
<th>$\chi_{T2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99673</td>
<td>1.0268</td>
</tr>
<tr>
<td>1.08131</td>
<td>1.09751</td>
</tr>
<tr>
<td>1.14065</td>
<td>1.1824</td>
</tr>
<tr>
<td>1.12051</td>
<td>1.1951</td>
</tr>
<tr>
<td>1.18051</td>
<td>1.2229</td>
</tr>
<tr>
<td>1.25051</td>
<td>1.2851</td>
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</table>

Fig. S10 (a) $\chi''_M$ vs. $\nu$ plot at 1.8 K in the frequency range of 1-1000 Hz under various applied dc for Dy$_x$Y$_{2-x}$. (b) Field-dependence of the relaxation time (blue circles) and the best fit curve (red line) for Dy$_x$Y$_{2-x}$.
**Fig. S11** Frequency-dependent of in-put phase ($\chi_M'$) ac susceptibilities under zero field (a) and under 1.5 kOe dc field (b) for Dy$_x$Y$_{2-x}$.

**Fig. S12** Frequency-dependent of out-put phase ($\chi_M''$) AC susceptibilities under zero field (a) and under 1.5 kOe dc field (b) for Dy$_x$Y$_{2-x}$.

**Fig. S13** Cole–Cole curves under zero DC-field (a) and under 1.5 kOe (b) for Dy$_x$Y$_2$. Solid lines represent the best fit with Debye model.
Fig. S14 Plot of ln(τ) versus $T^{-1}$ under zero field (a) and under 1.5 kOe dc field (b) for Dy$_x$Y$_{2-x}$.

Table S6 The best-fitted parameters obtained from the analyses of the Cole-Cole plots using the Debye model for Dy$_x$Y$_{2-x}$ under zero field.

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$\chi_s$(Total) / cm$^3$ mol$^{-1}$</th>
<th>$\Delta\chi$ / cm$^3$ mol$^{-1}$</th>
<th>ln(τ / s)</th>
<th>$\alpha$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.27E-08</td>
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<td>-2.23676</td>
<td>0.51406</td>
<td>0.03324</td>
</tr>
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<td>0.51973</td>
<td>0.02208</td>
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<tr>
<td>4</td>
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<td>-2.63711</td>
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<td>0.00996</td>
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<tr>
<td>5</td>
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<td>0.00468</td>
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<tr>
<td>6</td>
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<td>4.07911</td>
<td>-3.29513</td>
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<td>0.02933</td>
</tr>
<tr>
<td>7</td>
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<td>0.07014</td>
</tr>
<tr>
<td>8</td>
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<td>2.813</td>
<td>-4.33221</td>
<td>0.35771</td>
<td>0.11158</td>
</tr>
<tr>
<td>9</td>
<td>3.75E-07</td>
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<td>0.29969</td>
<td>0.10496</td>
</tr>
<tr>
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<td>0.25411</td>
<td>0.08521</td>
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<tr>
<td>11</td>
<td>1.52E-06</td>
<td>1.91187</td>
<td>-5.51532</td>
<td>0.21763</td>
<td>0.0622</td>
</tr>
<tr>
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<td>2.35E-06</td>
<td>1.72677</td>
<td>-5.86441</td>
<td>0.18242</td>
<td>0.04554</td>
</tr>
<tr>
<td>13</td>
<td>3.38E-06</td>
<td>1.58472</td>
<td>-6.17954</td>
<td>0.15863</td>
<td>0.03412</td>
</tr>
<tr>
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<tr>
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<tr>
<td>19</td>
<td>5.59E-02</td>
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<td>0.05237</td>
<td>2.15E-03</td>
</tr>
<tr>
<td>20</td>
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<tr>
<td>21</td>
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<td>0.03631</td>
<td>2.20E-03</td>
</tr>
<tr>
<td>22</td>
<td>6.48E-02</td>
<td>0.92116</td>
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<td>0.00154</td>
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<tr>
<td>23</td>
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<td>0.87835</td>
<td>-8.41837</td>
<td>0.00565</td>
<td>4.47E-03</td>
</tr>
</tbody>
</table>
\[ \chi_T = \chi_S^{\text{Total}} + \Delta \chi \]

Table S7 The best-fitted parameters obtained from the analyses of the Cole-Cole plots using the Debye model for Dy\( _x \)Y\( _{2-x} \) under 1.5 Oe dc field.

<table>
<thead>
<tr>
<th>( T / \text{K} )</th>
<th>( \chi_S^{\text{Total}} / \text{cm}^3 \text{ mol}^{-1} )</th>
<th>( \Delta \chi / \text{cm}^3 \text{ mol}^{-1} )</th>
<th>ln(( \tau / \text{s} ))</th>
<th>( \alpha )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.05</td>
<td>5.43002</td>
<td>-1.77093</td>
<td>0.06207</td>
<td>0.0038</td>
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<tr>
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<td>4.7983</td>
<td>-2.40222</td>
<td>0.06295</td>
<td>0.00282</td>
</tr>
<tr>
<td>8</td>
<td>0.04477</td>
<td>4.20578</td>
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<td>0.05445</td>
<td>0.00353</td>
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<tr>
<td>9</td>
<td>0.04292</td>
<td>3.72778</td>
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<td>0.04742</td>
<td>0.00645</td>
</tr>
<tr>
<td>10</td>
<td>3.23E-02</td>
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<td>11</td>
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<tr>
<td>16</td>
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<td>-8.72611</td>
<td>0.03362</td>
<td>8.19E-04</td>
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</tbody>
</table>

\[ \chi_T = \chi_S^{\text{Total}} + \Delta \chi \]

Details of \textit{ab initio} calculations
For centrosymmetric binuclear Dy$_2$, the type two individual of Dy (III) fragments were calculated. Complete-active-space self-consistent field (CASSCF) calculations on individual Dy(III) fragments (recorded as Dy1 and Dy1a, as show in Figure S11) on the basis of single-crystal X-ray determined geometry have been carried out with MOLCAS 8.4 program package.[S1-S5] Each individual Dy(III) fragment was calculated keeping the experimentally determined structure while the other Dy(III) ion was replaced by diamagnetic Lu(III). The Calculated results are the same for fragments Dy1 and Dy1a, as shown in Table S8 and S9.

The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANORCC library: ANO-RCC-VTZP for Dy(III); VDZP for close O; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. For individual Dy(III) fragment, active electrons in 7 active spaces include all f electrons (CAS(9 in 7)) in the CASSCF calculation. To exclude all the doubts, we calculated all the roots in the active space. We have mixed the maximum number of spin-free state which was possible with our hardware (all from 21 sextets, 128 from 224 quadruplets, 130 from 490 doublets). SINGLE_ANISO program was used to obtain the magnetic susceptibilities, energy levels, $g$ tensors, $m_J$ values, magnetic axes, et al., based on the above CASSCF/RASSI-SO calculations.[S2-S8]

![Fig. S15](image1.png)  
**Fig. S15** Calculated Dy(III) fragment of Dy$_2$.

![Fig. S16](image2.png)  
**Fig. S16** The orientations of the anisotropy axes of the individual Dy(III) centres in Dy$_2$. Symmetry codes: $a = 1 - x, -y, 1 - z$. 
Table S8 Calculated energy levels (cm$^{-1}$), g ($g_x$, $g_y$, $g_z$) tensors and $m_J$ values of the lowest eight Kramers doublets (KDs) of individual fragments in Dy$_2$.

<table>
<thead>
<tr>
<th>KDs</th>
<th>individual fragments Dy1 and Dy1a in Dy$_2$</th>
<th>$E$/cm$^{-1}$</th>
<th>$g$</th>
<th>$m_J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.0</td>
<td>0.004</td>
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<td></td>
<td></td>
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<td>674.7</td>
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<td>878.4</td>
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<tr>
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</table>

Table S9 Wave functions with definite projection of the total moment $|m_J>$ for the lowest two Kramers doublets (KDs) of individual fragments Dy1 and Dy1a in Dy$_2$.

<table>
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<tr>
<th>Dy1, Dy1a</th>
<th>$E$/cm$^{-1}$</th>
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</tr>
<tr>
<td></td>
<td>291.7</td>
<td>95.8%$</td>
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</table>

Table S10 Exchange energies $E$ (cm$^{-1}$), the energy differences between each exchange doublets $A_t$ (cm$^{-1}$) and the main values of the $g_z$ for the lowest two exchange doublets of Dy$_2$.

<table>
<thead>
<tr>
<th>$E$</th>
<th>$A_t$</th>
<th>$g_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>$1.0 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
To fit the exchange interaction of Dy₂, two steps were adopted to obtain parameters. Firstly, we calculated the individual Dy(III) fragment using CASSCF/RASSI-SO to obtain the corresponding magnetic properties. Then, the exchange interaction between the magnetic centres is considered within the Lines model, while the account of the dipole-dipole magnetic interaction is treated exactly. The Lines model is effective and has been widely used in the research field of d and f-elements single-molecule magnets. \(^{[S10,S11]}\)

The Ising exchange Hamiltonians for Dy₂ is as shown in equation (1). Total coupling constants \(J_{\text{total}}\) that include dipole–dipole interaction \(J_{\text{dip}}\) and exchange coupling parameters \(J_{\text{exch}}\), as shown in equation (2). The dipole–dipole interaction \(J_{\text{dip}}\) is calculated with equation (3).

\[
\hat{H}_{\text{exch}} = -J_{\text{total}} \hat{S}_{\text{Dy1}} \hat{S}_{\text{Dy1a}} \\
J_{\text{total}} = J_{\text{dip}} + J_{\text{exch}} \\
J_{\text{dip}} = -\frac{\mu_B^2 g_{1z} g_{2z}}{r^3} (\cos \theta - 3\cos \varphi_1 \cos \varphi_2)
\]

where \(\theta\) is the angle between the main anisotropy axes on both Dy sites; \(\varphi_1\) is the angle between the main magnetic axis on site 1 (Dy1) with the unit vector connecting the two Dy sites \(\hat{n}_{12}\); \(\varphi_2\) is the angle between the main magnetic axis on site 2 (Dy1a) with the unit vector connecting the two Dy sites \(\hat{n}_{12}\); \(g_{1z}\) is the Z component of the ground \(g\) tensor on site 1; \(g_{2z}\) is the Z component of the ground \(g\) tensor on site 2; \(\mu_B^2\) is a constant (\(= 0.4329701512063995\)) in units of \(\text{cm}^{-1}/\text{Tesla}\); \(r\) is the distance between the Dy1 and Dy1a, in Angstrom.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.449</td>
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</tbody>
</table>

Fig. S17 Scheme of the Dy\textsuperscript{III}…Dy\textsuperscript{III} magnetic couplings in Dy₂. Symmetry codes: a = 1 – x, – y, 1 – z.
The parameters of calculation results are $\theta = 0$, $\varphi_1 = \varphi_2 = 47.923^\circ$, $g_{1Z} = g_{2Z} = 19.75536463$, $r = 10.4636$ Å, $J_{\text{dip}} = -0.022$ cm$^{-1}$.

Fig S18 Schematic diagram of the spin-polarization mechanism between two Dy$^{\text{III}}$ centres of neighbouring molecules through hydrogen bonding.

References


