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Angle-Resolved Magnetic Chirality Control in a Dy_3 Single Molecule Toroid

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ABSTRACT:

Toroidal moments—distinct components in the multipole expansion of electromagnetic fields—possess unique symmetry properties that enable exotic quantum phenomena, magnetoelectric coupling, and non-trivial quantum tunneling, making them attractive for spintronic and memory applications. Single-molecule toroids (SMTs), typically incorporating strongly anisotropic Dy^{3+} ions, exhibit degenerate toroidal ground states of opposite chirality with toroidal moments $\pm\tau$. Although magnetically silent due to zero net magnetization, these states remain theoretically addressable through magnetoelectric coupling, while the relevant excitations involve large spin flips or forbidden transitions. Here, we propose and demonstrate an alternative route to chirality selection in a nearly perfect Dy_3 toroidal complex, based on angle-resolved quantum-tunnelling history. Using μSQUID magnetometry on oriented microcrystals at 30 mK, we observe angular-history-dependent remanence from uncompensated out-of-plane components, directly evidencing chirality selection across the crystal. Angle-dependent switching maps confirm the toroidal ground state and allow estimation of Dy–Dy interactions. We further identify a persistent chiral bias associated with specific angular histories, maintained over extremely long relaxation times ($>10^6$ s), placing this system among the slowest-relaxing single-molecule magnets. This mechanism could, in principle, operate at the single-molecule level, providing a route to initialize magnetic chirality without electric fields, microwaves, or optical excitation, and advancing prospects for chirality-based memory.

Introduction

The toroidal (or anapole) moment, recognized as the third family of electromagnetic multipoles, represents a missing link in the multipole expansion of electromagnetic fields and currents^{1,2}. Since its discovery, it has captivated both theorists and experimentalists due to its unique symmetry properties—being odd under both time reversal and parity inversion^{2,3}. These characteristics endow the toroidal moment (τ) with exotic quantum behavior^{4–7}, and make it a promising candidate for spintronic applications^{2,7,8}, while its non-radiating anapole character also echoes the coupling structure invoked in anapole dark-matter models^{9,10}.

At the molecular scale, this phenomenon manifests in single-molecule toroids (SMTs), a subclass of single-molecule magnets (SMMs) that has attracted significant attention over the past two decades^{4,11,12}. In SMTs, the toroidal moment arises from a magnetic vortex arrangement of local spins (or total angular momenta) at each magnetic center. This configuration is feasible when the centers exhibit strong axial anisotropy (Ising-like), typically found in 4f-based systems with large anisotropies and weak intramolecular interactions.

Common examples include tri- or multi (n)-dysprosium complexes, where the anisotropy axes lie nearly in one plane¹³⁻²⁰, yielding a general expression of toroidal moment $\tau = \sum_{i=1}^n \mathbf{r}_i \times \boldsymbol{\mu}_i$, with $\mathbf{r}_i$ as the position vectors of the i -th Dy³⁺ ion relative to the cluster center, and $\boldsymbol{\mu}_i = g_i \mu_B \mathbf{S}_i$ as the magnetic moment of the i -th Dy³⁺ ion. Here g_i is the effective Landé g -factor, μ_B is the Bohr magneton and $\mathbf{S}_i$ is the effective spin operator for the i -th site. More complex multi-Dy systems, which exhibit coupling between distinct toroidal moments²¹⁻²⁵, have revealed exceptionally striking static and dynamic magnetic signatures^{21,25}.

SMTs are particularly appealing because of their (ideally) magnetically silent ground state—despite large local magnetic moments—combined with ultraslow quantum tunnelling of magnetization (QTM) between the two chiral states (clockwise and anticlockwise with toroidal moment $\pm\tau$)²¹. Furthermore, their potential coupling to electric fields²⁶⁻²⁸ offers a route to coherent chirality manipulation, a highly sought-after effect for quantum technologies. Current efforts focus on achieving homochiral ground states²⁵ or selective manipulation of chirality, including optical manipulation and readout, aiming toward single-molecule and single-crystal chiral selectivity and ultimately spin-chirality-based qubits. However, the toroidal moments $\pm\tau$ of the usually degenerate ground doublet cannot be coupled to homogeneous magnetic fields due to symmetry constraints^{1,29,30}. Instead, chirality selection requires a molecular-scale magnetic-field gradient²⁹, or electric field pulses, invoking a magnetoelectric effect akin to proposed EPR schemes³¹. While the first approach is beyond present experimental capabilities, the second approach is challenging because the relevant transitions involve large spin flips (e.g., $\Delta m_J = 15$ for Dy³⁺ ions), resulting in strongly quenched EPR signals.

Here, we introduce a fundamentally different route to chirality selection—one governed by angle-resolved quantum-tunnelling history rather than molecular-scale magnetic-field gradients. This mechanism emerges from a finely balanced, angle-dependent interplay between thermal relaxation and resonant one-body and many-body QTM processes, primarily occurring at sub-kelvin temperature, producing a measurable macroscopic outcome without requiring microscopic field asymmetry. To test this concept, we synthesize single microcrystals of a Dy³⁺ trimer exhibiting near-perfect toroidal alignment. Using μ SQUID magnetometry, which is sensitive to the net magnetization vector—including its small out-of-plane component in non-perfect SMTs—we identify the fraction of molecules in each chiral state within a single crystal. Our results show that specific field-sweep orientations can impose a chosen homochirality at the single-crystal level which is stabilized by the ultraslow relaxation of the toroidal states. These results pave the way for the chiral selection and manipulation of the chiral states in SMMs as quantum registers in novel quantum technologies.

Results and Discussion

Electronic states switching in triangular toroics: The triangular toroic (TT)—with three Ising-like moments arranged at the vertices of an equilateral triangle with easy axes separated by $\approx 120^\circ$ in a common plane—represents the most elementary realization and first reported example of an SMT^{13,32,33}. In this geometry, the ground-state manifold is doubly degenerate, corresponding to clockwise (CW) and counterclockwise (CCW) toroidal chirality ($'c_1'$ and $'c_2'$ in **Figure 1**). Remarkably, these states, despite having near zero magnetization, can exhibit open loops at sub-kelvin temperatures, with very long-lived relaxation arising from quenched many-body tunnelling^{21,22,34}. These features make the system simple yet appealing for information encoding. However, realizing a deterministic, homochiral configuration (selectively stabilizing either $'c_1'$ or $'c_2'$) in TTs or in any SMT using external stimuli such as microwaves, light, or electric fields remains an outstanding experimental challenge, limited by intrinsically forbidden transitions.

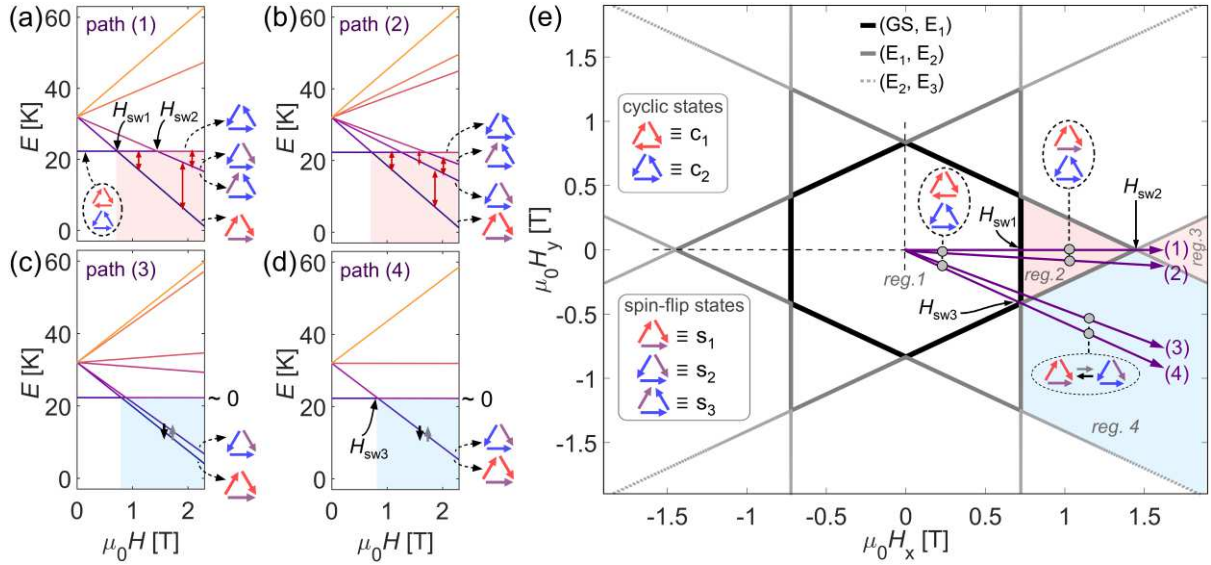


Figure 1. Simulated angular map of (anti-) level crossings: (a–d) Zeeman diagrams for a hypothetical Dy_3 toric system, simulated using Eq. 1 for four in-plane field directions—paths (1)–(4) with $\phi = 0^\circ, 5^\circ, 25^\circ$, and 30° —relative to a Dy^{3+} easy axis. Representative dominant spin configurations are annotated next to their corresponding eigenstates. Such angle-dependent Zeeman diagrams are used to track the (anti-) level crossing positions such as $H_{\text{sw}1,2,3}$. (e) Simulated angle-dependent map of (anti-) level crossings between the ground state (GS) and first three excited states (E_1 – E_3), extracted from the angle-dependent Zeeman diagrams. Cyclic and spin-flip states relevant for polarity of magnetic-field are labelled. Four field-cycling trajectories of interest—paths (1)–(4) with $\phi = 0^\circ, 5^\circ, 25^\circ$, and 30° , respectively—are highlighted by magenta arrows, with the dominant spin states indicated at selected points along each path.

An alternative, non-spectroscopic method by which the chiral states in TTs can be manipulated relies on their underlying spin Hamiltonian and the field-orientation-dependent tunneling at avoided level crossings. The method is based on the application of the magnetic field along an appropriate direction and driving the system through specific avoided crossings within the spin manifold, hence, allowing the initialization of a homochiral state.

We can exemplify this by considering an ideal TT case consisting of three Dy^{3+} ions with single-ion axial anisotropies (D_i), exceeding interionic interactions (J_{eff}) by several orders of magnitude, and with three local easy axes lying in the Dy_3 plane and oriented at $\approx 120^\circ$. The simulation of the exact spin Hamiltonian for three Dy^{3+} ions ($J = 15/2$) is computationally expensive; however, the dominant axial anisotropy, and sole Boltzmann population of the ground and low-lying excited state at very low temperatures, permits an effective description using a smaller spin. Therefore, three effective $S_i = 3/2$, for which only the ground doublets arising from individual ions are concerned, are enough to account for the Dy_3 properties. Such an effective scenario can be simulated assuming the following Hamiltonian:

$$\hat{H}_{S\text{-trimer}} = \sum_{i=1}^3 \{ \mu_B g \mathbf{B}^T \hat{\mathbf{S}}_i + h D_i (\hat{S}_{zi}^2 - S(S+1)/3) \} - 2J_{\text{eff}} \hbar \sum_{\langle i,j \rangle} \hat{\mathbf{S}}_i^T \hat{\mathbf{S}}_j \quad (1)$$

where $\hat{\mathbf{S}}_i$ are spin operators for each effective $S_i = 3/2$; $g = (4/3) \times (15/3)$ (Dy^{3+} g value in pseudo-spin 3/2 formalism), $J_{\text{eff}} = J_{\text{Dy-Dy}}(15/3)^2$ and $\mathbf{B}^T = (\mu_0 H_x, \mu_0 H_y, \mu_0 H_z)^T$. Individual spin frames are related by $\approx 120^\circ$ forming an equilateral triangle. Employing this Hamiltonian with a set of hypothetical parameters for the system [$D_i = -144$ K (-100 cm^{-1}), $J_{\text{eff}} = 1$ K (-0.75 cm^{-1})], the Zeeman diagrams are simulated for different field-directions in the Dy_3 plane. By solving the spin Hamiltonian and identifying the eigenstate anti-crossings in the Zeeman diagrams across field orientations, we obtain the switching-field landscape. Owing to the dominance of the single-ion anisotropy, the switching mechanism is visually intuitive: each moment reverses only along its local easy axis under an external bias. This enables visualizing field sequences that may selectively initialize homochirality.

We assess four field-directions that are sufficient to interpret angle-dependent tunneling mechanisms. These directions are marked by ‘path (1)–(4)’ where the paths are

related to $\varphi = 0^\circ, 5^\circ, 25^\circ$, and 30° respectively. Here, φ denotes the angle between applied field and the easy axis of one of the three Dy^{3+} ions. We employ the path nomenclature, given that depending to the path taken different magnetic outcome might arise, as detailed below. The Zeeman diagrams for these four field-directions are shown in **Figure 1a-d** with the spin configurations indicated to their corresponding eigenstates. Several (anti-) level crossings (H_{swi}) between the eigen states of the ground state and the low-lying excited states are observed (**Figure 1a-d**). For path (1) ($\varphi = 0^\circ$), two non-degenerate levels characterize the energy landscape at zero field. Upon field application, the excited state splits leading to two levels crossings occurring at H_{sw1} and H_{sw2} . These crossing corresponds to the c_1+c_2 degenerate ground state with s_1 and $s_{2,3}$, respectively (**Figure 1a**). An angle between the Dy^{3+} spin and the applied field of $0^\circ > \varphi > 30^\circ$ (path (2) to path (3)), splits the degeneracy of the s_2 and s_3 states, leading to an additional level crossing with c_1 and c_2 (**Figure 1b,c**). For $\varphi = 30^\circ$ (path (4)), the ground and excited states split in field leading to a single level crossing H_{sw3} occurring between c_1 and c_2 with s_1 and s_3 (**Figure 1d**). The crossings $H_{\text{sw1,2,3}}$ in **Figure 1a-d**, mark the field magnitudes at which QTM leads to flipping one (or multiple) Dy^{3+} spins. In general, such (anti-) level crossings dictate the magnetization dynamics of the system at very low temperatures.

Mapping the field-magnitudes at (anti-) level crossings as a function of φ yields the simulated switching-field map (**Figure 1e**). The positions of crossings between cyclic ground states (GS) and the angle-dependent first excited state (E_1) yields a hexagon pattern indicated in thick black, while grey lines denote subsequent crossings such as (E_1, E_2) and (E_2, E_3). Since the field-direction is defined by the angle of the applied field φ with respect to one Dy^{3+} easy axis, $\varphi = 0^\circ, 60^\circ, 120^\circ$ denote the three orientations where $\mathbf{H}$ is parallel to each Dy^{3+} easy axis, with $\varphi = 0^\circ$ taken as the H_x direction. Clearly, the three dominant anisotropy axes permit individual Dy^{3+} spin flips only along their respective easy directions, producing three sets of parallel lines that together form the hexagonal switching-field map.

Experimentally, a fit of the switching-field maps of the hexagonal pattern can provide a fine estimation of $J_{\text{Dy-Dy}}$ in a triangular torus, i.e., an angle-resolved study allows the precise determination of the underlying interactions. Notably, the hexagonal behavior of switching fields has been experimentally shown in recent studies²¹; however, so far, there has been no report on the experimental observations or theoretical predictions of the hexagon-arms extending to infinity (gray lines in **Figure 1e**). Observing these extended arms is the prerequisite for further investigation into the possibility of chirality selection in such systems (*vide infra*), given that these arms signal a prefer Dy_3 motif, i.e., excellent crystal quality, high symmetry, and pure wave-functions.

Initialization of magnetic homochirality: Two general features of SMM behavior at sub-kelvin temperatures are particularly relevant for discussing the angle-dependent state history. First, many-body resonant QTM—i.e., the simultaneous co-tunnelling of multiple spins—occurs with significantly lower probability than one-body resonant tunnelling^{21,22,34}. Second, at sufficiently large magnetic fields, any residual population in excited states relaxes thermally through phonon-mediated processes^{35,36}; these phonons are efficiently reabsorbed by neighboring molecules due to the scarcity of bath phonon modes at 30 mK. Such a process, thus, causes local heating of the crystal and raises the effective spin temperature. Consequently, repopulation of excited states occurs during subsequent resonant QTM events.

To emphasize the angular-history-driven chiral selectivity, we assign the dominant states in **Figure 1e** using the Zeeman simulations of **Figure 1a-d** and the preceding physical considerations. Here, the evolution of the toroidal and spin-flip states is traced for the field-directions of interest (path (1)-(4)') (see magenta arrows in **Figure 1e**). These directions are subsequently extended into full field-cycling trajectories along fixed φ , to illustrate the state history including both ramp-up and ramp-down sweeps ($0 \rightarrow H_{\text{max}} \rightarrow 0$). The detailed state evolution for selected field directions, covering the complete field-cycling process, is shown in **Figure 2a, b**. At zero magnetic field, after a long waiting time and/or in the absence of any prior angular-dependent manipulation, the system is usually equilibrated: the clockwise (c_1) and anticlockwise (c_2) chiral states are equally populated (see the states with weights $w_1 = w_2$

in **Figure 2**). In a single-crystal experiment, this corresponds to a spatially random distribution of molecular chirality across equivalent sites (and minimized demagnetization energy if any small out-of-plane net magnetization persists). For a single-molecule case, it would imply that the molecule can be found in either c_1 or c_2 with equal probability, reflecting thermal equilibrium between the two degenerate states.

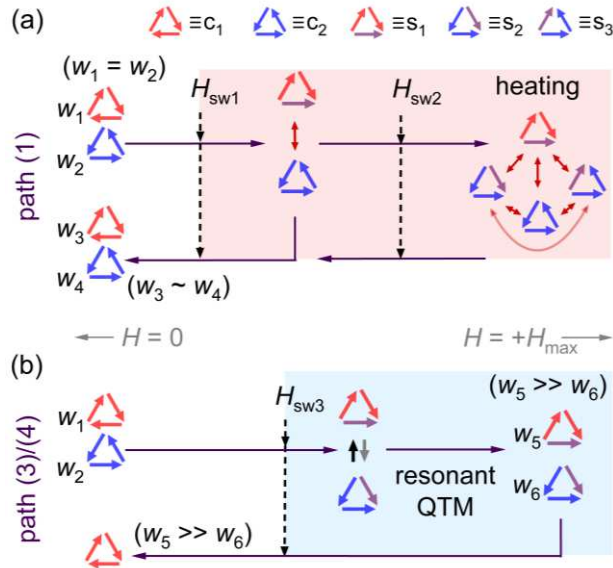


Figure 2. Angle-resolved route to magnetic homochirality: The complete schematic evolution of dominant states, including both field ramp-up and ramp-down cycles, are indicated for fields (a) along a Dy³⁺ easy axis (path (1), $\varphi = 0^\circ$), and (b) along $\varphi \sim 30^\circ$ (path (3)/(4)) with respect to a Dy³⁺ easy axis. The double-sided arrows in (a) indicate thermal relaxation processes and the black, gray arrows in (b) indicate resonant QTM. The relative weights of dominant states are denoted by w_i .

For field directions along paths (1) and (2) (magenta arrows nearly along H_x in **Figure 1e**), as the field is increased from 'reg. 1' to 'reg. 2', the first resonant one-body QTM at H_{sw1} switches one chirality (c_1 , red cyclic state) to the magnetic state (s_1) with the largest moment along H_x (**Figure 2a**). The other chirality (c_2 , blue cyclic state) probabilistically retains the cyclic state since it requires two-body resonant QTM at H_{sw1} . As the external field is increased further, this leftover population in c_2 is bound to thermally relax to the spin-flip states ($s_{2,3}$ and s_1) since the effective barrier (cyclic $\rightarrow$ spin-flip) monotonically reduces with increasing field. This leads to an avalanche of heat and thermally driven mixing between populations as indicated in **Figure 2a**. The same has been marked by red-double sided arrows in **Figure 1a,b**, and red-shaded reg. 2,3 in **Figure 1e**. Unless driven to much larger fields and equilibrated, reversing the field back to zero would lead to mixed cyclic populations ($w_3 \sim w_4$ in **Figure 2a**), assuming the dominance of 1-body tunneling processes in the reverse cycle. The desired experimental signature for such behavior would be the signs of heating or a sudden increase of spin temperature for fields about H_{sw1} , only for such field-directions and zero net-chirality upon return to zero-field. Any experimental route allowing the detection of the chirality in this system would yield a mixed chirality state.

In contrast, for field directions along paths (3) and (4), the situation drastically differs as the field is increased and the system is driven from 'reg. 1' to 'reg. 4' (**Figure 1e**). This is due to: (i) efficient QTM for both chirality at same/nearly same fields (about H_{sw3}), leaving negligible cyclic populations and hence avoiding thermal relaxation and heating; (ii) states s_1 and s_2 approach degeneracy, enabling resonant one-body QTM between them (equilibrium black and grey arrows in **Figure 2b** and **Figure 1e**). Above H_{sw3} , the population in s_1 gradually increases as tunneling from s_2 to s_1 becomes favorable due to the broken degeneracy. Even at the hexagon corners (path 4), slight out-of-plane tilts of the Dy³⁺ easy axis (not considered in simulations) usually lift the degeneracy, favoring the QTM to one state. Nonetheless, throughout paths 3 and 4 the spin-flip processes are dominated by resonant one-body QTMs and therefore circumvent thermal processes that leave residual heat at low temperatures. As

a result, the system passes through a comparatively cold region (reg. 4' indicated by blue shade in **Figure 1e** and **Figure 2b**) with favored tunneling to s_1 . Upon reducing the field (reversed arrows in **Figure 2b**), the more-populated s_1 state re-traps to its chiral counterpart (c_1) via one-body tunneling, resulting in a strong preference for state c_1 over c_2 . The desired signature of such a behavior would be no sign of heating near H_{sw3} and large net-magnetic chirality upon return to zero-field if experimentally measured.

At this point, depending on the path taken, that is, upon cycling between zero field, finite field, and back to zero field at the correct φ angle, the system can be initialized in either a mixed or chiral selected state. To experimentally verify such a mechanism that is acutely sensitive to both quantum-tunnelling and thermal-relaxation rates, the system must be as close to ideal as possible. This requires exceptionally high-quality single crystals in which the toroidal moments are aligned with minimal deviation from the configuration predicted by the ideal TT Hamiltonian. Measurements must be conducted at millikelvin temperatures—well below the typical blocking temperatures reported for this class of systems—to ensure that the relevant tunnelling pathways dominate. Most critically, the experiment must incorporate a direct probe of chirality: an observable whose magnitude or evolution is modulated by the handedness of the spin circulation, or equivalently by the relative population of the clockwise and counterclockwise chiral states. Moreover, it is worth noting that we exemplify this with Dy^{3+} ions, given the number of reported toroidal Dy-based systems. However, extension of an analogue procedure can be done to non- Dy^{3+} systems.

Molecular and magnetic characteristics of an ideal Dy_3 toroic: In the quest for a near-ideal TT, a new Dy-based SMM was synthesized. The complex was obtained by reacting $Dy(ClO_4)_3 \cdot 6H_2O$ in methanol with HL (where HL = *N*'-benzylidene-2-hydroxy-3-methoxybenzohydrazide) in acetonitrile in the presence of triethylamine. Hexagonal crystals belonging to the *R*-3 space group were obtained, with one-third of the molecule in the asymmetric unit, while two differently oriented molecules (related by inversion), reside within the unit cell. Single crystal analysis reveals the formula of the complex to be $[Dy_3(\mu_3-OH)_2L_3(MeOH)_6] \cdot (ClO_4)_4$ (hereon denoted **Dy₃-Ph**) (**Figure 3**). The molecule is highly symmetric, featuring a three-fold axis through two μ_3-OH groups above and below the Dy_3 plane. The Dy···Dy distances are 3.522(1) Å, forming an equilateral triangle. Each Dy^{3+} ion is eight-coordinate, adopting a distorted triangular dodecahedron geometry confirmed by CShM analysis (**Table S1**). The coordination sphere includes four oxygen atoms from HL (two phenoxides, one methoxy, one carbonyl), two from methanol, and two μ_3-O^{2-} atoms. Dy–O distances range from 2.311(8)–2.385(11) Å, with O–Dy–O angles of 61.1(3)–141.0(3)° (**Table S2**). The short Dy–Ophenolate bonds and large Ophenolate–Dy–Ophenolate angles suggest the magnetic anisotropy axis aligns along this direction. The crystal packing forms double layers along the *c*-axis, reminiscent of trimethylsumanene, with opposite bowl chirality of the ligand and Dy_3 planes parallel to the *ab* plane. Such characteristics are optimal for single crystal angle-dependent SMT studies.

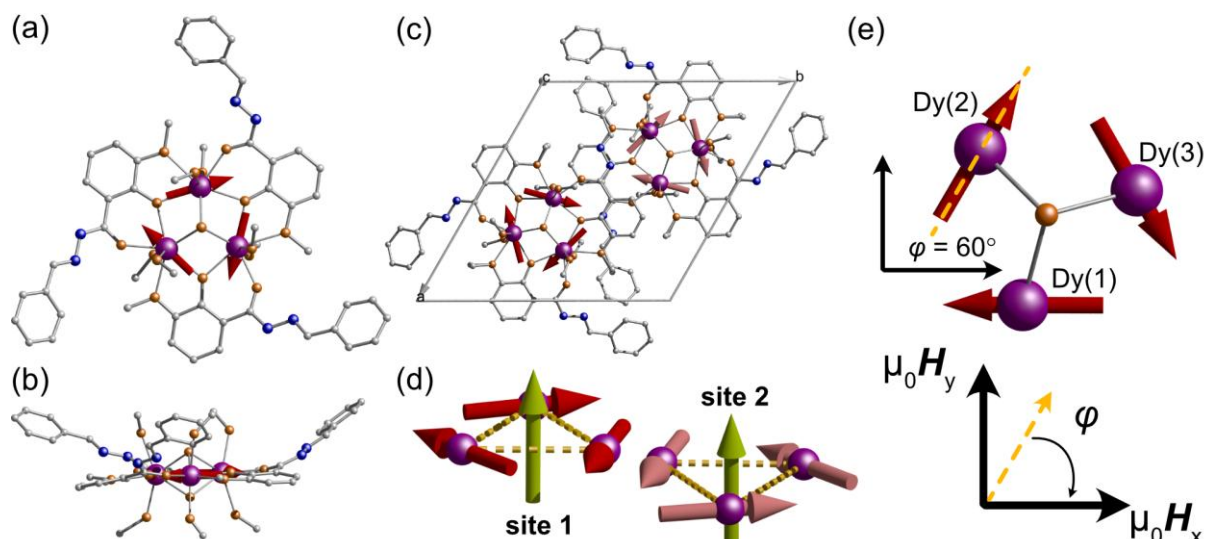


Figure 3. Crystal structure of $[\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3(\text{MeOH})_6]$ viewed along the C_3 axis (a) and perpendicular to the C_3 axis (b). Color code: Dy, purple; O, orange; N, blue; C, grey. Hydrogens and the ClO_4^- groups were omitted for clarity. The red arrows are the anisotropy axes for the Dy^{3+} ions in the complex, as obtained from CASSCF calculations. (c) Shows the unit cell with the two inversion-related molecules contained within the unit cell. (d) Depicts one of the two chiral magnetic structures for the $\text{Dy}_3\text{-Ph}$ system (left), while the second molecule shows the inversion related molecule (right). The light red arrows in (c) and (d) showcase the inversion related easy axis orientation within the trimer. (e) angle orientation between the easy axis of the Dy^{3+} ions in the triangle and the applied magnetic field.

The DC susceptibility (2–300 K, 1 kOe) shows $\chi_M T = 39.9 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 300 K, close to the theoretically expected $42.5 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for three Dy^{3+} ions. $\chi_M T$ decreases at low temperatures, reaching $2.5 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K, indicating antiferromagnetic coupling and/or depopulation of the Stark levels. Evidence for a non-magnetic ground state includes a $\chi_M T(T)$ maximum at ~ 6 K, a sigmoidal $M(H)$ at 1.9 K, and a zero-field step in hysteresis (**Figures S9–10**), consistent with Dy_3 SMTs. Moreover, AC susceptibility reveals slow relaxation with an out-of-phase component (χ'') ranging from 1.9–13 K, and two processes below 3 K, with a barrier of $U_{\text{eff}} = 35.1(3)$ K and $\tau_0 = 4.1(1) \times 10^{-6}$ s.

To investigate the spin arrangement of the Dy_3 system, complete active Space Self-consistent field (CASSCF) calculations were conducted^{37–39}. The results show the system to indeed possess a toroidal spin arrangement. The ground state is found to be highly anisotropic ($g_{xx}, g_{yy} \sim 0$ and $g_{zz} \sim 20$), with a separation of ~ 180 K between the ground and first excited state (**Tables S6,7**). In terms of wavefunction, the centers are found to be highly pure with a $96\%|\pm 15/2\rangle$ composition and a very small contribution ($\sim 3\%$) from the $|\pm 11/2\rangle$ state. The anisotropy axes of the Dy^{3+} ions are found to lie in the Dy_3 plane nearly along the phenolate moiety (**Figure 1**). This indicates a near-perfect TT system; however, the actual system parameters—such as the precise orientation of the easy axis—can exhibit slight deviations from the CASSCF simulations, particularly at low temperatures.

Confirmation of toroidal alignment: To examine the history-dependent selection of magnetic homochirality in this system, it is essential to first experimentally confirm the toroidal ground states and study their angle-dependent switching at low temperatures, where solely the ground state is populated. For this purpose, we performed angle-resolved magnetic switching measurements on oriented single micro-crystals using μSQUIDS arrays operated between 30 mK and 4.5 K. The temperature-dependent $M(H)$ measurements in **Figure S15** show the necessity to study the system at sub-kelvin temperatures, i.e., well below the blocking temperature of such toroidal systems.

Detailed angle dependence studies, at 30 mK, were carried out by varying the field direction within the μSQUID plane ($H_{x,y}$). Due to the limitations of vector-field magnitude (± 0.5 for H_y and ± 1.4 T for H_x fields), various crystal orientations were examined for reproducibility and completeness of the results. The single micro-crystals exhibit a well-defined, planar

triangular morphology with the ‘in-plane’ arm length far exceeding the ‘out-of-plane’ (z-axis) thickness. This pronounced shape, in correlation with the crystal packing, allows the measurement plane ($H_{x,y}$) to be aligned unambiguously with the Dy_3 molecular plane (see SI: experimental details on μSQUID measurements). As all three Dy^{3+} easy axes are expected to lie nearly *in-plane* at 120° to each other, two field-directions are of particular interest: (i) parallel to one Dy^{3+} easy axis, and (ii) at 30° from a Dy^{3+} easy axis. **Figure 4a,c** shows sweep-rate-dependent $M(H)$ curves for these two directions respectively, obtained by rotating the same crystal by $\sim 30^\circ$ in two different cool-downs. The $M(H)$ curves for an intermediate direction are captured in **Figure 4b**, measured in another crystal. These in-plane $M(H)$ curves generally show the characteristic two-step hysteresis of SMTs. At 30 mK, the steps—marking switching between toroidal and spin-flip states—are dominated by resonant QTM. The nearly flat region between $\sim \pm 0.5$ T, with a small zero-field step, confirms the expected nearly non-magnetic ground state. The corresponding Zeeman diagrams in **Figure 4d-f**, simulated using **Equation 1**, indicate the position of (anti-) level crossings between the eigenstates.

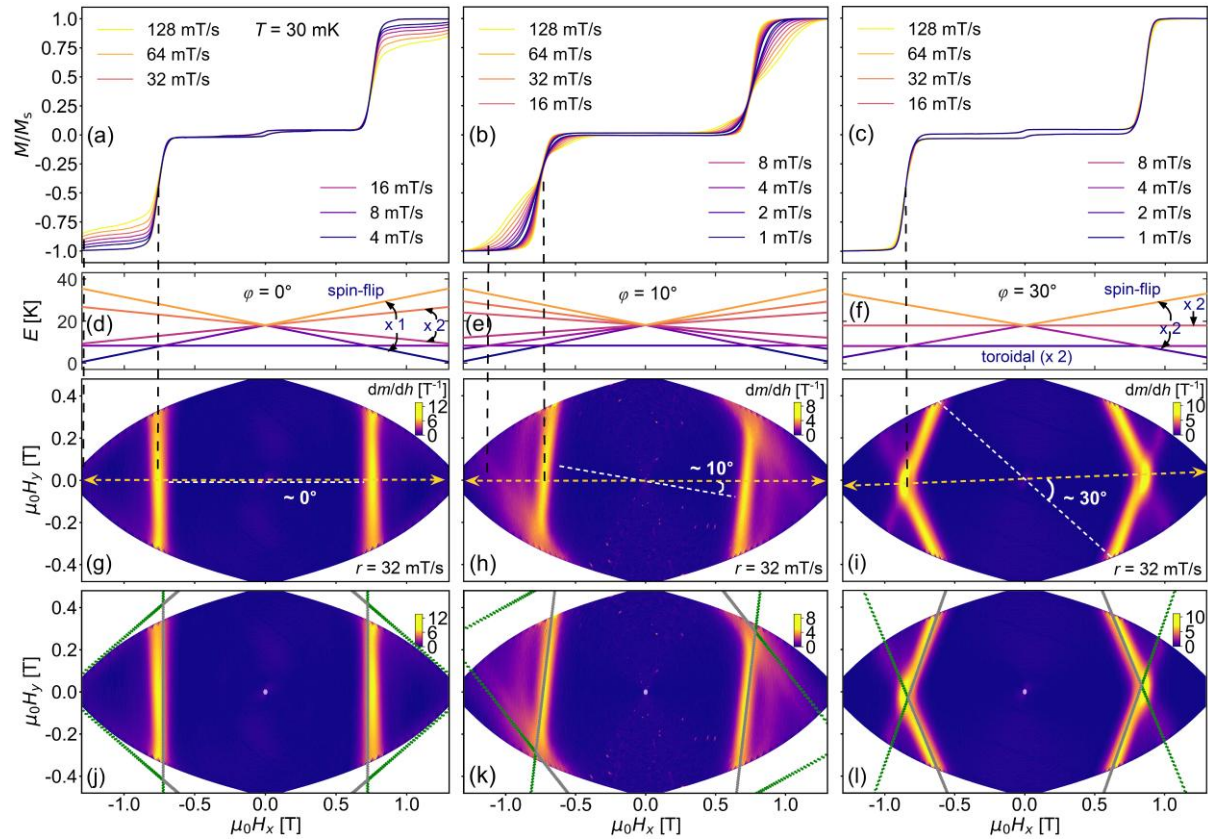


Figure 4. μSQUID measurements at 30 mK: (a)–(c) $M(H_x)$ loops for single crystal of $\text{Dy}_3\text{-ph}$ at different sweep rates for three different crystal-orientations with respect to the applied field (H_x). (d)–(f) show the Zeeman diagrams (with only ground multiplet simulated using **Equation 1**) for the corresponding field-directions, i.e. $\varphi = 0^\circ$, 10° , and 30° with respect to a Dy easy-axis. For each of these three crystal-orientations, the vector-field directions were varied in the measurement plane ($H_{x,y}$ plane, ideally aligned to the Dy_3 plane) to obtain angle-dependent $M(H)$ curves. These yield the field-angle dependent derivative maps ($dm/dh = \frac{1}{\mu_0 M_s} dM/dH$), as shown in (g–i) for positive field-cycle ($0 \rightarrow H_{\text{sat}}$). Panels (j–l) display the corresponding simulations—overlaid on the experimental data.

Further validation of the toroidal ground state (particularly confirmation of an ideal TT) is provided by the angle-dependent crossings. For a clear visualization, the derivatives $dm/dH = |1/(\mu_0 M_s) dM/dH|$ were obtained from the angle-dependent $M(H)$ curves and plotted as a function of field direction (**Figure 4g–i**). At such low temperatures, the large dm/dH magnitudes mark the resonant QTMs, or switching fields, H_{swi} . An ideal TT would require the three Dy^{3+} easy axes at $\sim 120^\circ$ apart, each with strong Ising anisotropy allowing spin-flips only along its respective easy axis. This would yield three sets of parallel lines (60° apart) in the angular maps, forming a hexagonal pattern as observed reproducibly throughout all *in-plane*

angle-dependent derivative maps (**Figure 4g-i** and SI **Figure S16**). A quantitative analysis based on entire angle-dependent data is possible by fitting the angle-dependent hexagonal map (see **Equation 1** and **Figure 1e**). One set of parameters suffices to fit the angle-dependent switching fields in all orientations or different crystal measurements (see fittings in **Figure 4j-l**). The magnitude of interaction is found to be $J_{\text{Dy-Dy}} = -0.03040(8) \text{ cm}^{-1}$, i.e. the interaction between two neighboring spin 15/2 (see below **Equation 1**). It is worth noting that this magnitude is comparable to that reported for other Dy-based triangular systems of the same class (compare J_{ising} in ³³ as $J_{\text{ising}} \sim 15^2 J_{\text{Dy-Dy}}$). However, the method employed here to determine $J_{\text{Dy-Dy}}$ incorporates the full two-dimensional angle-dependent dataset and therefore, in principle, yields more reliable values than those obtained from the mean-exchange-field (H_{ex}) approach based solely on the $M(H)$ curve along easy-axis^{21,40}. The near-perfect planar alignment of Dy³⁺ easy axes was further supported by probing in-plane to out-of-plane angular dependence using vertically mounted micro-crystals (see **Fig S17**).

Intiguing angle-dependent features are observed consistently in **Figure 4**, such as different remanence near zero-field among **Figure 4a-c**, indicating net out-of-plane magnetization (M_z , see later) of the toroidal states, and signatures of angle-dependent thermal processes near the switching-fields. Another consistent feature—the lines extending beyond the hexagon towards infinity (see fitted green dots in **Figure 4g-i**)—is observed for the first time in the forward field cycles ($0 \rightarrow H_{\text{sat}}$). The extended lines crucially represent early-indicators of homochirality-selection and are observed only owing to the near-ideal character of the present system (*vide supra*). Collectively, these observations suggest the history-dependent chirality selection in this near-ideal TT architecture.

Homochirality Selection: At this point, it is important to recall the experimental signature that would in principle signal the magnetic chirality selection. At sub-Kelvin temperatures, The experimental signatures for the mechanisms described above would therefore be: (i) the appearance of heating or a sudden rise in the spin temperature when the field is swept through H_{sw1} for $\varphi = 0$ and 5° (path (1), (2)), reflecting the thermally assisted relaxation and avalanche-like mixing triggered by the asymmetric QTM rates of the two chiral states; (ii) a return to zero field that yields no net magnetic chirality for these same field directions, since the heating-driven population redistribution restores a mixed occupation of the two cyclic states. In contrast, we expect to observe (iii) the absence of detectable heating when the field is swept through H_{sw3} at $\varphi = 25$ and 30° (path (3), (4)). This behavior is consistent with efficient tunnelling of both chiralities and the resulting negligible population of the cyclic state above H_{sw3} . Moreover, (iv) for these favorable orientations, a large (and long-lived) net magnetic homochirality is expected upon returning to zero field. This arises from the population imbalance generated in the spin-flip manifold above H_{sw3} , followed by its selective re-trapping into a single chiral state via one-body tunnelling.

Experimentally, although the ground state of the **Dy₃-ph** is expected to be ideally silent, a residual M/M_s near zero-field is observed in **Figure 4a-c**. Such a moment can arise due to a small out-of-plane (Z) component due to slight misalignment of Dy³⁺ easy axes, as the wavefunction mixing between m_J states ($\sim 96\% |\pm 15/2\rangle$, $3\% |\pm 11/2\rangle$) does not lead to any additional Z-component (see **Table S6**). Note that the theoretical easy axis calculated via CASSCF is usually within $\pm 10^\circ$ accuracy with respect to the experimental easy axis. The μ SQUID magnetometry technique provides high sensitivity to both in-plane (XY) and out-of-plane (Z) magnetic moments. The measured signal reflects a weighted sum of M_x , M_y , and M_z . For crystals aligned in-plane near the μ SQUIDS, small M_z components in toroidal states (arising from slight misalignment of the easy axis relative to the Dy₃ plane) can be clearly isolated as the net X/Y magnetization cancels. These Z components encode chirality: clockwise and anticlockwise states yield opposite net Z magnetization. Assuming the system occupies cyclic ground states at zero field, enhanced M_z requires most molecules at equivalent sites to adopt the same chirality, aligning their Z components. Crucially, the second orientation in the crystal packing ('second site', see **Figure 3d**), related by inversion and 60° rotation, selects the opposite chirality for a field-history along path (3)/(4). Owing to the same underlying

tunnelling dynamics that enforce chiral selection at the first site, the second site inevitably adopts a configuration in which one Dy^{3+} easy axis aligns with that of the first. Eventually the resulting net Z moment combines contributions from both orientations (see **Figure 3d**), akin to AFT states in 6-Dy complexes²¹. This yields a measurable signal whenever homochirality, at least among symmetry-equivalent molecular sites in the unit cell, is selected across the crystal. Thus, angle-dependent remanence indicates crystal-level chiral selectivity, where all triangles at first site adopt clockwise and those at second site anticlockwise arrangements.

We quantify this remanence by M_r/M_s , defined slightly away from zero field (~ 0.1 T) to avoid the zero-field QTM effects. The magnitude of M_r/M_s , i.e. assumed as the experimental measure of net-homochirality, is apparently largest for fields along hexagon-corner and approaches zero along hexagon-arm (see **Figure 4a-c**). To examine this further, we attempt an ideal alignment of the crystal (Dy_3 plane perfectly to $H_{x,y}$) verified by several experimental signs, such as a small step at zero-field and maximized angle-dependent modulation of M_r/M_s (see **Figure 5**). Upon achieving such successful alignments, we confirmed maximum hysteresis (or largest M_r/M_s) for fields along the hexagon-corner (see **Figure 5a,b** and marked directions in **Figure 5c**) and minimum hysteresis along hexagon-arm (see **Figure 5e,f**). The insets in **Figure 5a,e** show the measured derivative (dm/dh)-maps as a function of field-angle to indicate the orientation of the corresponding crystal. The detailed angle-dependent variation of M_r/M_s for the crystal corresponding to **Figure 5a** is displayed in **Figure 5d**. Note that, due to the limited vector field-magnitudes, the two angular extremes (hexagon-corner to hexagon-arm) could not be accessed in a single set of measurements, hence repeated measurements at different crystal-orientations were required. **Figure 5f** shows the overlapping magnetizations for forward and backward field-cycles, representing an ideal scenario, i.e. the perfect alignment of external-field in the Dy_3 -plane and along a Dy^{3+} easy axis. Even when such a perfect condition is not fulfilled (see **Figure 4a**), such directions (along a hexagon-arm) consistently yield the smallest hysteresis compared to other angles in the measured $H_{x,y}$ plane.

Further signs of angle-selective heating or raise of spin-temperature near switching fields strengthen the chirality selection argument. The region indicated by blue circle in **Figure 5a** (also see sweep-rate dependence in **Figure 4c**) shows no sign of heating or slow thermal processes. This indicates that only resonant QTMs dominate for a field applied along hexagon-corners, eventually leading to homochirality, as predicted in **Figure 1, 2**. While for fields-along the hexagon-arm, see red circles in **Figure 5e,f** (also see sweep-rate dependence in **Figure 4a,b**), a raise of spin temperature is indicated about $H_{\text{sw}1}$ by thermal broadening, slow thermal processes or the artificially enlarged hysteresis in these regions. These eventually lead to a mixture of chiral states upon return to zero-field and hence the diminished hysteresis (or small M_r/M_s).

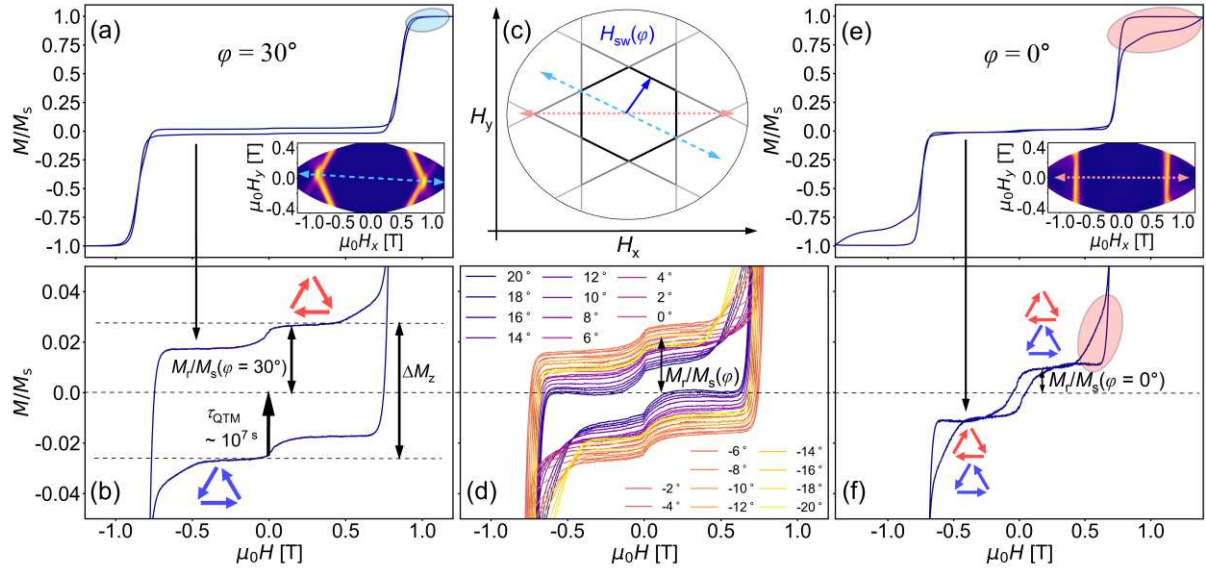


Figure 5. Experimental signature of imposed homochirality: (a) $M(H)$ curves at 30 mK with H applied along the hexagon-corner direction ($\varphi = 30^\circ$) for a $\text{Dy}_3\text{-ph}$ crystal whose Dy_3 plane is perfectly aligned with the measurement plane ($H_{x,y}$). The inset shows the angular map of dm/dH indicating the field direction used in (a). (b) Enlarged region of (a), highlighting the maximum remanence M_r/M_s , reflecting the net M_z component of the homochiral states and the resulting enlarged hysteresis. (c) Applied field directions for (a) and (e) shown on the simulated switching-field map. (d) Enlarged angle-dependent $M(H)$ curves corresponding to the angular dm/dH map shown in the inset of (a). It shows the angle-dependent variation in M_r/M_s , approaching a minimum toward the hexagon-arm direction, even though the states there should be dominated solely by cyclic configurations. (e) $M(H)$ curves at 30 mK with H applied along the hexagon-arm direction ($\varphi = 0^\circ$), again with the Dy_3 plane perfectly aligned with the measurement plane ($H_{x,y}$). The inset shows the dm/dH angular map indicating the direction used in (e). (f) Enlarged region of (e), highlighting the minimum remanence M_r/M_s , where the nearly overlapping forward and backward field cycles indicate the compensated net M_z component of the heterochiral states.

Robust homochiral states: Besides the chirality selection characteristics, a nearly sweep-rate independent remanence further indicates ultraslow relaxation of toroidal states. To support that the chirality-selected toroidal states are robust and potentially suitable for encrypted (ideally magnetically silent) memory applications, we investigate the ultraslow relaxation characteristics of the system. Magnetic relaxation ($M(t)$) curves were acquired at various bath temperatures (0.03–0.7 K) in zero field, following saturation and subsequent sweep through a field-cycle along the hexagon-corner. This field direction, i.e. corresponding to **Figure 5a,b**, yields the maximum hysteresis, and in-principle the imposed homochiral state. **Figure 6a** shows ($M(t)$) normalized to the initial magnetization (M_0) for each temperature. Strikingly, in the range 0.03–0.3 K, magnetization barely relaxes within 2 h, indicating that the system lies among those with the longest relaxation times at low temperature, i.e. comparable to the observed slow relaxation in the ‘giant spin’ SMMs⁴¹. Such large relaxation times ($>10^6$ s) can be assessed by scaling $M(t)$ curves to a $M(t/\tau)$ master curve^{21,25} (**Figure 6b**). The master curve generally resembles a stretched exponential, but it can become more convoluted due to multiple serial and parallel relaxation pathways^{21,42}, requiring a scaling method that avoids stretched-exponential fitting. Extracted temperature-dependent mean relaxation times τ are plotted against $1/T$ (**Figure 6b** inset) and fitted using an Orbach, Raman, and QTM processes, i.e. $\ln(\tau) = -\ln[\tau_0^{-1} \exp(-U_{\text{eff}}/k_B T) + CT^n + 1/\tau_{\text{QTM}}]$. The fitting yields an effective barrier of $U_{\text{eff}} = 8.6(6)$ K, (with the Raman coefficient $C = 5(5) \times 10^{-5}$ and Raman exponent $n = 2.9(8)$) and a QTM time $\tau_{\text{QTM}} \approx \tau_{01} = 8(1) \times 10^6$ s. Notably, the extracted τ_{QTM} is the largest reported value for triangular TTs (three-spin SMTs) approaching the record-slow QTM rates of the six-spin ferro-toroidal system²¹ and lies among the largest τ_{QTM} observed in any SMM^{40,41,43-}

⁴⁵. Such an exceptionally long QTM time signals a strongly suppressed many-body (three-body) co-tunnelling process—consistent with our previous observations in multinuclear transition-metal SMMs^{21,46} yet further enhanced here by the near-ideal symmetry of the present system. These prolonged relaxation times—linked to imposed homochirality—underscore the technological promise of such SMMs, which can host robust and magnetically silent toroidal states with tunable chirality.

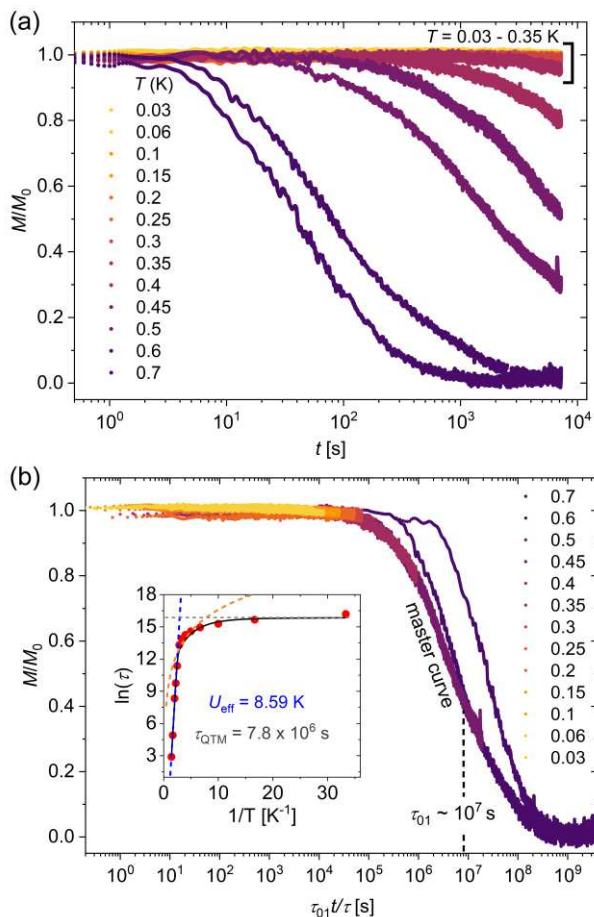


Figure 6. Magnetic Relaxation of homochiral states: (a) Zero-field magnetic relaxation curves $M(t)$ measured by μ SQUIDS, for fields along the hexagon-corner and at different bath temperatures and (b) corresponding $M(t/\tau)$ curves scaled to achieve a relaxation-master curve. The scaling yields temperature-dependent relaxation times τ as plotted in the inset of (b).

Conclusion

This work reveals an angular-history-dependent mechanism for selecting magnetic chirality in a near-perfect **Dy₃-ph** toroidal molecule at sub-Kelvin temperatures, a phenomenon not previously reported for single-molecule magnets. At low sweep rates, the zero-field population at 30 mK consists exclusively of toroidal states, making path-dependent quantum-tunneling-mediated chiral selection the only viable explanation for the observed angle-dependent remanence. The effect persists across sweep rates and relaxes on extremely long timescales, underscoring its stability. Comparative studies on Dy₃ systems with larger out-of-plane easy-axis components will confirm a correlation between remanence and the Z component, to be detailed in a forthcoming work.

Attempts to detect crystal-level homochirality in this family of molecular crystals are typically hindered by packing constraints that impose at least two molecular orientations per unit cell, which adopt opposite chirality under identical field-angle histories. Proving homochirality through existing experimental methods—such as techniques involving

polarized-light—remains highly challenging, as it would require either isolating a single Dy₃ orientation within the unit cell (currently chemically unfeasible) and imposing a homochiral state on it, or achieving homochirality through advanced supramolecular design strategies²⁵. Nonetheless, we show that direction-sensitive local magnetic measurements can reveal chirality selection because the out-of-plane moments from inversion-related sites add when their toroidal chiralities oppose each other.

The mechanism demonstrated here can, in principle, be extended even to an isolated single molecule. In addition, it offers a reliable protocol for initializing the system in a chosen chirality, thereby enabling future experiments that employ microwave- or optics-driven excitation between pre-selected chiral states. Deterministic control of molecular spin chirality is a key requirement for chirality-based memory concepts in nanoscopic devices. Although ideal toroidal ground states are magnetically silent, our findings show that their chirality can be tuned and preserved over month-long timescales, pointing toward encrypted-memory architectures based on toroidal degrees of freedom. Only detectors that are exclusively sensitive to chirality or to toroidal moments could probe these exceptionally stable, magnetically encrypted states in further optimized single-molecule magnets with perfect in-plane anisotropy.

Author Contributions

S.P. and Z.Z. contributed equally to this work. W.W., S.P., Z.Z. and J.T. conceived the research idea. Z.Z. designed the structure, and S.L. carried out the preparation, structural and basic magnetic characterization. S.P. and A.S. performed the μ -SQUID measurements, and S.P. conducted the corresponding analysis of the angle-dependent magnetic properties. E.M.-P. performed the *ab initio* calculations. S.P., S.L., Z.Z., E.M.-P., and J.T. wrote the manuscript, with input from all co-authors.

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