Ferrotoroidic ground state in a heterometallic \{\text{Cr}^{III}\text{Dy}^{III}_6\} complex displaying slow magnetic relaxation

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Toroidal quantum states are most promising for building quantum computing and information storage devices, as they are insensitive to homogeneous magnetic fields, but interact with charge and spin currents, allowing this moment to be manipulated purely by electrical means. Coupling molecular toroids into larger toroidal moments via ferrotoroidic interactions can be pivotal not only to enhance ground state toroidicity, but also to develop materials displaying ferrotoroidic ordered phases, which sustain linear magneto-electric coupling and multiferroic behavior. However, engineering ferrotoroidic coupling is known to be a challenging task. Here we have isolated a \{\text{Cr}^{III}\text{Dy}^{III}_6\} complex that exhibits the much sought-after ferrotoroidic ground state with an enhanced toroidal moment, solely arising from intramolecular dipolar interactions. Moreover, a theoretical analysis of the observed sub-Kelvin zero-field hysteretic spin dynamics of \{\text{Cr}^{III}\text{Dy}^{III}_6\} reveals the pivotal role played by ferrotoroidic states in slowing down the magnetic relaxation, in spite of large calculated single-ion quantum tunneling rates.
The magnetic behavior of molecular coordination complexes continues to intrigue scientists around the world, revealing many interesting physical properties and offering many potential applications such as new storage and information processing technologies. Fundamental research into, e.g., single-molecule magnets (SMMs), spin-crossover, and magnetic systems with toroidal moments, are recognized as important areas of molecular magnetism. SMMs exhibit slow relaxation of the magnetization, acting as nano-magnets below their blocking temperature. Molecular coordination complexes with a toroidal arrangement of local magnetic moments are rare, but are of great interest as they have several potential applications such as quantum computation, molecular spintronics devices, and the development of magneto-electric coupling for multiferroics. In order to isolate materials with the above mentioned properties, we target coordination complexes containing anisotropic 4f ions. In contrast to the great deal of work on the synthesis of 3d–4f coordination complexes using 3d ions such as Mn, Fe, and Co, there have been few reports of studies, both structurally and magnetically, on mixed Cr(III)–Ln(III) systems. We have recently shown, however, that the combination of the isotropic Cr(III) ion and the anisotropic Dy(III) ion resulted in a family of SMMs with long relaxation times, relative to other lanthanide-based SMMs. With this in mind, we have chosen to expand our studies, utilizing chromium(III) nitrate, with various lanthanide(III) ions, with carboxylic acid pro-ligands.

Herein, we describe the synthesis, structural characterization, and magnetic properties of a heterometallic complex of formula \([\text{Cr}^{III}\text{Dy}^{III}(\text{OH})_8(\text{ortho-tolu})]_2(\text{NO}_3)(\text{MeOH})_5\text{MeOH}\). Complex \(1\) displays slow magnetic relaxation and SMM behavior at temperatures below 2 K. Furthermore, in \([\text{Cr}^{III}\text{Dy}^{III}]_6\), we find, for the first time, a ferrotoroidically coupled ground state fully determined by dipolar coupling between the two con-rotating toroidal triangles. Our observations on \(1\) have been compared to earlier reported studies on coupled molecular \([\text{Dy}^{III}]_6\) foroids. The ferrotoroidically coupled ground state thus leads to an enhanced toroidal moment in the ground state for the \([\text{Cr}^{III}\text{Dy}^{III}]_6\) complex, which is shown to play a central role in the observed magnetization dynamics featuring zero-field hysteresis.

**Fig. 1** Molecular structure and exchange pathways. a The molecular structure of complex \(1\). The solvent and H atoms are omitted for clarity. Color scheme: Cr, pink; Dy, green; O, red; N, blue; C, light gray. b Top view of the molecular structure of \(1\). c Metal topology found in \(1\) with d magnetic exchange pathways \(J_1\) and \(J_2\) highlighted.
are observed with respect to the ideal triangular dodecahedron.

Each triangle. Six of the is likely a consequence of the limited solubility of Cr
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(Supplementary Methods). Suitable single crystals (pale purple

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heterometallic heptanuclear complex consisting of a single CrIII

a single DyIII ion. Terminal MeOH ligands coordinate to all six

2.7 for Dy1 and Dy1, 1.2 for Dy2 and Dy2', 1.5 for Dy3 and Dy3'

are observed with respect to the ideal triangular dodecahedron.

Selected bond lengths and DyIII–O–DyIII and CrIII–O–DyIII bond
angles are given in Supplementary Table 2. The DyIII–O bond
lengths are in the range, 2.391–2.492 Å. In the {DyIII} triangular
unit, the bond distance between Dy1–Dy2, Dy1–Dy3, and
Dy2–Dy3 is found to be 3.749, 3.767, and 3.780 Å, respectively
and the Dy3–Dy1–Dy2, Dy1–Dy2–Dy3, and Dy2–Dy3–Dy1 bond
angles are 55.99°, 60.52°, and 59.49°, respectively. The average
Dy–(μ3-OH)–Dy angle is 106.0°, while the average Dy–(μ3-OH)–
Dy angle also bridging to the CrIII ion is slightly smaller at 103.4°.
The centroid to centroid distance between the two triangular
units is found to be 5.38 Å. A shorter distance, compared to other
linked {DyIII} triangles11 (5.64 Å) is likely to yield stronger
dipolar coupling between the two {DyIII} units. Packing

Fig. 2 Susceptibility and magnetization plots. The measured (blue circles)
and simulated (via the ab initio-parameterized model, orange solid line)
plot of a $\chi_M T$ vs. T at 1 T and b M vs. H isotherms at 2 K for complex 1.
(inset) M vs. H isotherms for complex 1 at 2, 3, 4, 5, 5.5, 10, and 20 K (solid
lines just join the points here)

Results

Synthesis and magnetic properties. Compound 1 was synthe-
sized by the reaction of Cr(NO3)3·9H2O and Dy(NO3)3·6H2O,
with ortho-toluic acid in acetonitrile at ambient temperature.
The solvent was then removed and re-dissolved in MeOH/PrOH
(Supplementary Methods). Suitable single crystals (pale purple
color) for X-ray analysis were isolated after allowing the solvent
to slowly evaporate.

Single-crystal X-ray analysis reveals that compound 1 crystal-
lizes in the triclinic space group, P-1 (see Supplementary Table 1
for full crystallographic details). The asymmetric unit contains
half the complex, (three DyIII ions and one half of the CrIII ion)
which lies upon an inversion center. Compound 1 is a heterometallic heptanuclear complex consisting of a single CrII
ion and six DyIII ions (Fig. 1). The low CrIII to DyIII ratio of 1:6 in
1 is likely a consequence of the limited solubility of Cr
(NO3)3·9H2O in MeCN. The metallic core is based on two
diagonal DyIII units that lie above and below a single central
CrIII ion, revealing two vertex sharing trigonal pyramids or
tetrahedra. The metallic core is stabilized by 8 μ1-hydroxide, 12
ortho-toluic, with MeOH and [NO3]− ligands. Six of the μ3
hydroxide ligands bridge two DyIII ions to the central CrIII ion,
while the remaining two bridge the three DyIII ions that make up
each triangle. Six of the ortho-toluic ligands each bridge a
DyIII–DyIII triangular edge, while six are found to chelate, each to
a single DyIII ion. Terminal MeOH ligands coordinate to all six
DyIII ions. It is found, however, that, at two of the DyIII sites,
disordered MeOH and nitrate ions (50:50 occupancy) are present.
The CrIII ion is six coordinate with an octahedral geometry, while
the six DyIII ions are eight coordinate.

We have examined the structural distortions at individual
DyIII sites using SHAPE software37, 38. The geometry of each DyIII ion
is best described by a triangular dodecahedron. The deviation of
2.7 for Dy1 and Dy1', 1.2 for Dy2 and Dy2', 1.5 for Dy3 and Dy3'
are observed with respect to the ideal triangular dodecahedron.

The isothermal $\chi_M T$ plot at 2 K (3 K, 4 K, 4.5, 5, and 5.5 K)
for complex 1 at 2, 3, 4, 5.5, 10, and 20 K (solid
lines just join the points here)

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expected on the basis of the in-plane anisotropy predicted by our model (vide infra). Thus, when the field is parallel to two inversion-related tangential Dy magnetic axes, and perpendicular to none, this leads to an in-plane easy axis, while a magnetic field perpendicular to that direction, thus perpendicular to two Dy easy axes and parallel to none, leads to an in-plane hard axis. In particular, when the field is applied along any Dy–Dy bond vector as in Fig. 3a, i.e., along the y-axis in Fig. 6, hysteresis is observed below 0.8 K, with the coercive field as in Fig. 3a, i.e., along the y-axis in Fig. 6, hysteresis is increased the temperature we found that the intensity of this g = 5, 10, and 20 K (Fig. 4). The EPR spectrum recorded at 5 K reveals developed later in the paper. A theoretical model explaining this behavior is characteristic of an SMM, with slow zero-field relaxation. We then observe a large step in the magnetization behavior is that pro-

**Fig. 3** Single-crystal studies. Single-crystal magnetization (M) vs. applied field measurements (μ-SQUID) for complex 1 at a 0.03–0.8 K with the scan rate of 0.14 T s⁻¹; b with different field sweep rates at 0.03 K.

**Fig. 4** EPR spectroscopy. Powder EPR spectra of 1 at X-band frequency at 5, 10, and 20 K and the simulated curve.

Dy\textsuperscript{III} ion and a S = 3/2 state for the Cr\textsuperscript{III} ion. Ab initio computed g-anisotropies, directions, and J values are given as inputs (see below for details) along with the Dy–Dy and Dy–Cr distances from the X-ray structure. A small perturbation to the Euler angles without altering any other parameters yield reasonable fit to the experimental spectrum recorded at 5 K (Fig. 4). The further details of simulation are given in Supplementary Note 1), offering confidence on the estimated parameters. However, the lines appearing at g ~ 1.23 and g ~ 1.03 are much broader than they appear in the simulation and this may be attributed to a fact that only [Cr\textsuperscript{III}Dy\textsuperscript{III}]\textsubscript{1} has been employed in the simulation and not the full [Cr\textsuperscript{III}Dy\textsuperscript{III}]\textsubscript{3} Hamiltonian. Multi-frequency EPR including HF-EPR spectra are required, in future, to independently obtain the spin Hamiltonian parameters\textsuperscript{42}.

**Theoretical analysis and characterization of a ferrotoroidic ground state.** To explain the experimental observations, we performed ab initio calculations of electronic structure and magnetic properties, using MOLCAS 7.8\textsuperscript{43}, on individual Dy\textsuperscript{III} and Cr\textsuperscript{III} centers. The computed orientation of the anisotropy axes is shown in Fig. 5. In particular, we employed the ab initio MJ decomposition of the single-ion thermally isolated ground Kramers doublet (KD) wavefunctions along the ab initio g-tensor principal axis, to set up a model Hamiltonian for intramolecular magnetic coupling including dipolar coupling between all pairs of ions, which is parameters-free, intra-ring Dy\textsuperscript{III}–Dy\textsuperscript{III} superexchange interactions parameterized by a single coupling constant J\textsubscript{2} and Dy\textsuperscript{III}–Cr\textsuperscript{III} superexchange interactions parameterized by a single coupling constant J\textsubscript{1}. The coupling parameters J\textsubscript{1} and J\textsubscript{2} were evaluated via DFT calculations. The well-known dipolar Hamiltonian reads:

\[ H_{\text{dip}} = \frac{\mu_0}{4\pi} \sum_{p,q} M_p \cdot M_q \left( \frac{R_{pq}}{|R_{pq}|^3} - 3 \left( \frac{M_p \cdot R_{pq}}{|R_{pq}|^2} \right) \left( \frac{M_q \cdot R_{pq}}{|R_{pq}|^2} \right) \right) \]  

where \( M_p \) is the magnetic moment of the \( p \)th ion, and \( R_{pq} \) is the distance between ions \( p \) and \( q \). The superexchange contribution is modeled by an isotropic Heisenberg Hamiltonian\textsuperscript{44}:

\[ H_{\text{exch}} = -J_1 \sum_{p,q} (S_p \cdot S_q + S_p' \cdot S_q') - J_2 \sum_q (S_q + S_q') \cdot S_{\text{Cr}} \]  

where \( S_p (S_{\text{Cr}}) \) are the true spin moments of the Dy (Cr) ions, with the primed and unprimed subscripts labeling Dy ions belonging to different triangles. We note here that when the simple isotropic exchange Hamiltonian is projected on the thermally isolated ground KDs, it becomes a strongly anisotropic
non-collinear Ising Hamiltonian, a widely employed protocol for \{3d–4f\} systems.

To estimate the low-energy wavefunctions and magnetic anisotropy for each of the seven ions in 1, we have undertaken CASSCF+RASSI-SO calculations on the individual Dy\textsuperscript{III} centers\textsuperscript{43}. The calculations yielded the following g-tensor principal values: (Dy\textsubscript{1}; g\textsubscript{x} = 0.0523, g\textsubscript{y} = 0.0927, and g\textsubscript{z} = 19.5707); (Dy\textsubscript{2}; g\textsubscript{x} = 0.0737, g\textsubscript{y} = 0.0979, and g\textsubscript{z} = 19.4723); (Dy\textsubscript{3}; g\textsubscript{x} = 0.0233, g\textsubscript{y} = 0.0361, and g\textsubscript{z} = 19.6059) and (Cr; g\textsubscript{xy} = g\textsubscript{yz} = g\textsubscript{zz} = 2.002) (Supplementary Tables 4, 5).

The symmetry-related Dy\textsubscript{1} and nitrate in Dy\textsubscript{1} ions possess essentially the same toroidal magnetic moment and the yellow arrow is the S\textsubscript{6} symmetry axis.

The core structure of the molecule has a pseudo S\textsubscript{6} axis passing through the Cr\textsuperscript{III} ion and the center of both of the \{Dy\textsubscript{III}\}\textsuperscript{3} triangular units (Fig. 5). The local principal anisotropy axes are found from the calculations to lie in the \{Dy\textsubscript{III}\}\textsuperscript{3} plane with an out-of-plane angle of 0.29, 4.5, and 4.7\textdegree; for Dy\textsubscript{1}, Dy\textsubscript{2}, and Dy\textsubscript{3}, respectively. The Dy\textsubscript{III} magnetic axes are also found to be almost perfectly aligned with the tangents to an ideal circumference enclosing the triangles (the angle of the anisotropy axis with these tangential directions are in the range of 1.1–7.9\textdegree). The computed energies of the eight low-lying KDs reflect that there are two types of Dy\textsuperscript{III} ions in the complex (Supplementary Tables 4, 5), although the ground states of all Dy\textsuperscript{III} ions consist of almost pure atomic 1\textpm 15/2 > KDs. The energy gap between the ground and the first excited state KDs are found to be 142.8, 121.9, and 152.7 cm\textsuperscript{-1} for Dy\textsubscript{1}, Dy\textsubscript{2}, and Dy\textsubscript{3}, respectively. For the Cr\textsuperscript{III} ion calculations yield isotropic g-tensors (Supplementary Table 3) and an axial zero-field splitting of ~1.0 \times 10\textsuperscript{-4} cm\textsuperscript{-1}.

Thus the ab initio calculations suggest that magnetic coupling can be well described by projecting Hamiltonians Eqs. (1) and (2) on the basis of the ground KDs (Dy) and quartet (Cr) only, leading to a 256-dimensional product space with basis $|\mathbf{m}, M_{C_{6}}\rangle$.

The corresponding energies can be written as a sum of a superexchange contribution, an intra-ring dipolar contribution, an inter-ring dipolar contribution, and Dy\textsuperscript{III}–Cr\textsuperscript{III} dipolar contribution.

For the exchange energies we get (sum over $q$ is understood modulus 3, so that $m_{3} = m_{1}$):

$$E_{\text{exch.m}} = \frac{25}{8} J_{2} \sum_{q=1}^{3} \left( m_{q} m_{q+1} + m_{q} m_{q+1} \right) - J_{1} M_{C_{6}} M_{\mathbf{m}},$$

where $\mathbf{m} = [m_{1}, m_{2}, m_{3}, m_{1}, m_{2}, m_{3}, m_{1}]$ with $m_{q} = \pm 1$. We further assume that such KDs are pure $|\pm 15/2 >$ atomic states quantized along the local anisotropy axis, which is assumed to be exactly in the triangle’s plane and along the tangential direction, so that $S_{q}(m_{q}) = m_{q}(5/2)|m_{q}\rangle$, and $J_{1}(m_{q}) = m_{q}(15/2)|m_{q}\rangle$ ($S_{\text{tot}}$ and $J_{\text{tot}}$ are the spin and total angular momenta operators along the tangential direction for the qth Dy\textsuperscript{III} ion), and a seventh quantum number $M_{C_{6}} = \pm 3/2, \pm 1/2$ labeling the spin state for the Cr ion. Finally, given the quasi $S_{6}$ symmetry, in our model we assume two equilateral triangles with radius $r = 2.17 \text{ Å}$, their planes being at distance $h = 5.38 \text{ Å}$ (Fig. 6, r and h are average experimental values). Thus a ferrotoroidic (FT) state (con-rotating toroidal moments $\pm r_{1}, \pm r_{2}$ on the two triangles) correspond to $|\pm 1, \pm 1, \pm 1, \pm 1, \pm 1, M_{C_{6}}\rangle \equiv |\pm r_{1}, \pm r_{2}, M_{C_{6}}\rangle$.

Due to the large value of the ground KDs, angular momenta projections in $|\mathbf{m}, M_{C_{6}}\rangle$, Hamiltonians Eqs. (1) and (2) are both diagonal on such basis, and $|\mathbf{m}, M_{C_{6}}\rangle$ represent the low-energy exchange-coupled states of 1. The corresponding energies can be written as a sum over $q$ is understood modulus 3, so that $m_{3} = m_{1}$:

$$E_{\text{exch.m}} = \frac{25}{8} J_{2} \sum_{q=1}^{3} \left( m_{q} m_{q+1} + m_{q} m_{q+1} \right) - J_{1} M_{C_{6}} M_{\mathbf{m}},$$

where defining the angular coordinates of the six Dy\textsuperscript{III} ions as in Fig. 6 ($\alpha_{0} = 0$, $\alpha_{1} = 2\pi/3$, $\alpha_{2} = 4\pi/3$, $\alpha_{1} = \pi$, $\alpha_{2} = 3\pi/3$, $\alpha_{3} = 3\pi/3$), the total spin projection ($M_{m}$) of the six Dy\textsuperscript{III} ions in $|\mathbf{m}, M_{C_{6}}\rangle$ is given by Eq. (4) (sum over all Dy\textsuperscript{III} centers):

$$M_{m} = \pm \frac{5}{2} \sqrt{\left( \sum_{q} m_{q} \sin \alpha_{q} \right)^{2} + \left( \sum_{q} m_{q} \cos \alpha_{q} \right)^{2}}$$

along the direction given by the vector $\mathbf{u}_{m} = (-\sum_{q} m_{q} \sin \alpha_{q} / \sum_{q} m_{q} \cos \alpha_{q}, 0)$ (i.e., lying in the triangle’s planes).
Intra-ring (Eq. (5)) and inter-ring (Eq. (6)) dipolar coupling energies for the state \( |m, M_{Cr}\rangle \) are \( \mu_B \) is the Bohr magneton:

\[
E_{\text{dip},m}^{\text{intra}} = -\frac{\mu_B\mu_B^2}{4\pi} \frac{125\eta^2}{3\sqrt{3}r^3} \sum_{q=1}^{3} m_q m_{q+1} + m_q m_{q-1},
\]

\[
E_{\text{dip},m}^{\text{inter}} = \frac{\mu_B\mu_B^2}{4\pi} \frac{25\eta^2}{(r^2 + h^2)^2} \left[ 2 - \frac{9r^2}{r^2 + h^2} \right] \sum_{q=1}^{3} m_q (m_{q+1} + m_{q-1})
\]

\[
-\frac{\mu_B\mu_B^2}{4\pi} \frac{100\eta^2}{4(r^2 + h^2)^{3/2}} \sum_{q=1}^{3} m_q m_{q'},
\]

Finally, Dy\textsuperscript{III}–Cr\textsuperscript{III} dipolar coupling energy for \( |m, M_{Cr}\rangle \) reads:

\[
E_{\text{dip},m}^{\text{Dy–Cr}} = -\frac{\mu_B\mu_B^2}{4\pi} \frac{40\eta\eta}{(r^2 + h^2/4)^{7/2}} M_{Cr} M_m.
\]

The energy spectrum resulting from magnetic coupling can now be evaluated summing up Eqs. (3)–(7), and is reported in Fig. 7.

The dipolar coupling energies, Eqs. (5)–(7), contain no free parameter, as they only depend on the specific set of quantum numbers \( |m, M_{Cr}\rangle \), on the experimental geometrical parameters \( r \) and \( h \) (Fig. 6), and on the average ground state ab initio magnetic moment given by \( 10\mu_B \) with \( \eta = 0.975 \). Interestingly, from Eq. (5) it follows that intra-ring dipolar interactions always favor a toroidal texture on each triangle, penalizing the formation of a magnetic moment by an energy gap of \( ~0.28 \text{ cm}^{-1} \).

While inter-ring dipolar coupling is smaller than intra-ring coupling, due to larger separation between Dy\textsuperscript{III} ions, from Eq. (6) we learn that in fact this interaction splits FT and AFT states. In particular, the first term in Eq. (6) stabilizes a FT (AFT) ground state if \( h < \eta \sqrt{7}/2 \) \( (h > \eta \sqrt{7}/2) \), while the second term describing interactions between inversion-related centers always favors FT coupling and is stronger than the first term. In \( \{\text{Cr}^{III},\text{Dy}^{III}\}_r \), \( h > \eta \sqrt{7}/2 \), hence the two terms are in competition, the first (second) favoring AFT (FT) coupling. Since the second term is larger, we find here that dipolar interactions stabilize a FT ground state in \( \{\text{Cr}^{III},\text{Dy}^{III}\}_r \) (Fig. 5).

Moreover, from Eq. (6), we note that a structural design aimed at reducing the distance \( h \) between the two triangles will enhance FT coupling. We estimate the dipolar-induced FT/AFT splitting to be \( ~0.28 \text{ cm}^{-1} \). Note that, in our symmetric model, Dy–Cr dipolar interactions within FT and AFT states (Eq. (7)) are exactly zero (since \( M_m = 0 \) in FT and AFT states), leading to eight-fold degenerate FT and AFT manifolds. Thus in FT and
AFT states, the spin of Cr(III) is freely fluctuating, and FT/AFT toroidal spins, are fully determined by dipolar coupling. The energy gap of 3.3 cm\(^{-1}\) reported in Fig. 7 corresponds instead to the lowest magnetic excitation, obtained upon flipping a single Dy\(^{III}\) spin. In the excited states, the Cr(III) spin is blocked in the direction of the in-plane Dy\(_{6}\) magnetic moment.

Considering now superexchange interactions in Eq. (3), we note that the dipolar-induced FT ground state will survive provided that the intra-ring Dy–Dy coupling is antiferromagnetic (i.e., \(J_{2} < 0\)), or ferromagnetic but smaller than dipolar coupling. To estimate the two exchange coupling constants \(J_{1}\) and \(J_{2}\) appearing in Eq. (3), we have employed DFT calculations, replacing the Dy\(^{III}\) with Gd\(^{III}\) ions in the X-ray structure. The computed coupling constants for the Cr\(^{III}\)--Gd\(^{III}\) pairs were then rescaled by the ratio between the spin of Dy\(^{III}\) (\(S = 5/2\)) and that of Gd\(^{III}\) (\(S = 7/2\)), while Gd\(^{III}\)--Gd\(^{III}\) were rescaled by the ratio between the square of \(S = 5/2\) and the square of \(S = 7/2\). We obtained \(J_{1} = -0.08\) cm\(^{-1}\) (Cr\(^{III}\)--Dy\(^{III}\) coupling) and \(J_{2} = -0.043\) cm\(^{-1}\) (intra-ring Dy\(^{III}\)--Dy\(^{III}\) coupling), indicating antiferromagnetic coupling. The estimated antiferromagnetic interaction within the [Dy\(^{III}\)]\(_{3}\) triangles reinforces the effect of the intra-ring dipolar coupling, leading to a toroidal moment on each isolated triangle.

While a degenerate FT quantum ground state is compatible with the inversion symmetry of the molecule, such symmetry is not compatible with a ferrotoroidically ordered phase. Thus upon FT ordering, a concomitant structural phase transition should occur to rid the crystal of the inversion center, which, in turn, would allow the appearance of linear magnetoelectric coupling.

We now use the developed theoretical model to simulate the experimental molar susceptibility and magnetization. We report the results in Figs. 2 and 8. While the magnetization at 2 K and for fields up to 5 T is expected to be dominated by the low-energy states described by our model (Eqs. (1) and (2)), the molar susceptibility will be dominated by these states only at low temperatures, while at temperatures much higher than the reduced magnetic response, as is evident from the S-shape represented in Supplementary Fig. 8. Particularly relevant are the low-field ground state corresponding to saturation of the free fluctuating Cr spin (\(M_{Sat} \approx 3\mu_{B}\)) within the FT ground state. According to the Zeeman spectrum in Fig. 8b, the steep magnetization step observed in the theoretical magnetization at the level of magnetic field \(B_{LC} \approx 0.4\) T can be identified with the switching of the ground state from the low-field weakly magnetic FT Zeeman state \((\pm \tau, \pm \tau) \equiv \pm 1 \pm 1 \pm 1 \pm 1 \pm 1 \pm \tau, -3/2\) (Supplementary Fig. 8a), to the high-field onion magnetic state \(\pm \mu_{m} + m\), \(\pm \mu_{m} + m\) \(\equiv \pm 1 \pm 1 \pm 1 \pm 1 \pm 3/2\), in which half of the Dy spins circulate clockwise, the other half anticlockwise (Supplementary Fig. 8d), adding up to a magnetic moment \(M \approx 4\mu_{B}\) polarized along the field.

As expected, the calculated equilibrium magnetization cannot reproduce inherently dynamical features observed in the experiments, as in the calculations transitions between energy levels are instantaneous on the timescale of the experiment. There are, in particular, two important differences between theory and experiment displayed in Fig. 8a: in the experiment, a hysteresis loop opens up around the zero-field region between \(B_{LC}\) and \(B_{LC}\), and the experimental magnetization step separating low- and high-field plateaus is not abrupt, but occurs within \(0.5\) T field range starting at \(B_{LC}\).

Thus, to further analyze the measured magnetization dynamics, we explicitly consider finite-rate transitions between Zeeman states. We are not interested in the microscopic details of such transitions, other than those are driven by terms in the Hamiltonian that have so far been neglected (either because small, or because describing coupling with the surroundings), and other than broadly separating such processes in tunneling transitions characterized by coupling constants \(\gamma_{i}\) active between degenerate energy levels, and phonon-induced transitions characterized by coupling constants \(\gamma_{i}\) from higher to lower-energy states, with a probability that grows as the cube of the energy gap. The coupling constants \(\gamma_{i}\) and \(\gamma_{i}\) are related to the matrix elements of the relevant Hamiltonian between initial and final states.

Crucially, we propose that a hierarchy should exist in the magnitude of \(\gamma_{i}\) and \(\gamma_{i}\), based on the number of Dy\(^{III}\) spins that need to be flipped to change initial to final Zeeman states. We only consider in our model the 56 (out of 256) most relevant low-energy states involved in the relaxation dynamics, which are represented in Supplementary Fig. 8. Particularly relevant are the low-field ground FT states \((\pm \tau, \pm \tau)\), the high-field ground onion state \(\pm \mu_{m} + m\), and the excited intermediate magnetic states \((\pm \tau, \pm m)\) and \((\pm m, \pm \tau)\) (Supplementary Fig. 8c). Let us label the coupling constants \(\gamma_{i}(I_{2})\) as \(\gamma_{i}(I_{2})\) for transitions that only flip the Cr\(^{III}\) spin; \(\gamma_{i}(I_{1})\) for transitions flipping only one Dy\(^{III}\) spin; \(\gamma_{i}(I_{3})\) for transitions involving two simultaneous spin-flipping events; \(\gamma_{i}(I_{3})\) for transitions involving three or more spin-flipping events. Thus the hierarchy we invoke here reads: \(\gamma_{i} \geq \gamma_{i} \geq \gamma_{i} \geq \gamma_{i} \geq 0\), and \(\gamma_{i} \geq \gamma_{i} \geq \gamma_{i} \geq 0\).
Interpretation of single-crystal magnetization experiments. **a** Single-crystal magnetization experiment (blue curve) measured at $T = 0.03\,\text{K}$ and a sweep rate of $0.1\,\text{T s}^{-1}$ for a magnetic field oriented along the in-plane easy axis (γ-axis in Fig. 6), superimposed on the theoretical equilibrium magnetization (orange curve) computed for the same temperature and field direction. **b** Energy levels as function of magnetic field (Zeeman spectrum) computed using the model presented in the text. The magenta (green) arrows connecting **a** and **b** associate the steep (smooth) raise of the theoretical (experimental) magnetization with slow/quasi-forbidden (fast/allowed) transition mechanisms occurring at level crossing between the two ground states (involving excited states) encircled in magenta (green). **c** Magnification of the low-field region of the Zeeman spectrum, highlighting degeneracy points (level crossings) of states between which faster 1-flip and 2-flip tunneling transitions are allowed (green circles and hexagons), and also highlighting 3-flip or higher-flip processes that are essentially forbidden (magenta circles). Some of the allowed phonon emission processes are also indicated with dashed green arrows. **d** High-field region of the Zeeman spectrum, where the four onion states antiferromagnetically coupled to Cr spin states become isolated from excited states, leading the system’s magnetization to saturate.

Under such assumptions, we argue that both the zero-field hysteresis, and the smooth magnetization step observed in the experiment, can be explained by the fact that the direct $|\pm \tau, \pm \tau\rangle \rightarrow |+m, +m\rangle$ transition between the Zeeman ground states at level crossing $B_{\text{LC}} \sim 0.4\,\text{T}$ is essentially forbidden, as it involves at least the simultaneous flipping of three Dy$^{3+}$ spins ($\gamma_3$, $I_3 \sim 0$). Hence, on the timescale of field sweeping, exchange of population between $|\pm \tau, \pm \tau\rangle$ and $|+m, +m\rangle$ can only be indirect, occurring via multi-step processes involving the excited intermediate states $|+m, \pm \tau\rangle$ and $|\pm \tau, +m\rangle$, also via the excited AFT states $|\pm \tau, \mp \tau\rangle$ (Supplementary Fig. 8b). This microscopic scenario is visualized in Fig. 8c, where a multitude of level crossings of states between which faster 1-flip and 2-flip transitions can occur are highlighted with green circles (tunneling) or green dashed arrows (phonon-mediated) ($|\pm \tau, \pm \tau\rangle \rightarrow |\pm \tau, +m\rangle$ or $|\pm \tau, \pm \tau\rangle \rightarrow |+m, \pm \tau\rangle$), or highlighted with green hexagons (tunneling) and broad green arrows with a dashed contour (phonon-mediated) ($|\pm \tau, +m\rangle \rightarrow |+m, +m\rangle$ or $|+m, \pm \tau\rangle \rightarrow |+m, +m\rangle$). As illustrated in Fig. 8b, c, the existence of a broad range of magnetic fields around $B_{\text{LC}} \sim 0.4\,\text{T}$ for which fast transitions $|\pm \tau, \pm \tau\rangle \rightarrow |\pm \tau, +m\rangle$ can occur, followed, in higher fields, by fast phonon relaxation from higher-energy intermediate to lower-energy onion states (Fig. 8d), provides a rationalization for the gradual rise of the experimental dynamical magnetization.

Moreover, to quantitatively investigate the origin of the observed zero-field hysteresis loop, we implement these ideas in a dynamical model based on generalized Pauli master equations describing the dissipative dynamics of the non-equilibrium thermal populations of the CrDy$_6$ states, coupled to an equilibrium reservoir of acoustic phonons at $T = 0.03\,\text{K}$, and a source of random stray fields inducing incoherent tunneling between resonant energy levels. The states are obtained from our model Hamiltonians Eqs. (1) and (2), also including a time-dependent Zeeman term describing the interaction with the sweeping magnetic field-oriented along the easy axis, at sweeping rate $0.1\,\text{T s}^{-1}$, varying between $B = \pm 1.4\,\text{T}$ (a triangle wave signal is used). As outlined in the methods section, the relevant dissipative equations of motion for diagonal elements $\sigma_{ii}$ (populations) of the reduced density matrix $\sigma$, in the adiabatic approximation, are:

$$
\dot{\sigma}_{ii}(t) = \sum_k \left\{ W_{k-i}^{\text{ph}}(t) + \Omega_{k-i}^{\text{un}}(t) \right\} \sigma_{kk}(t) \\
- \sigma_{ii}(t) \sum_k \left\{ W_{i-k}^{\text{ph}}(t) + \Omega_{k-i}^{\text{un}}(t) \right\},
$$

where $\Omega_{k-i}^{\text{un}}(t)$ and $W_{i-k}^{\text{ph}}(t)$ are the time-dependent tunneling and phonon-induced transition rates given by Eqs. (12) and (10), respectively, proportional to the coupling constants $\gamma_i$ and $\Gamma_i$. 

**Fig. 8** Interpretation of single-crystal magnetization experiments. **a** Single-crystal magnetization experiment (blue curve) measured at $T = 0.03\,\text{K}$ and a sweep rate of $0.1\,\text{T s}^{-1}$ for a magnetic field oriented along the in-plane easy axis (γ-axis in Fig. 6), superimposed on the theoretical equilibrium magnetization (orange curve) computed for the same temperature and field direction. **b** Energy levels as function of magnetic field (Zeeman spectrum) computed using the model presented in the text. The magenta (green) arrows connecting **a** and **b** associate the steep (smooth) raise of the theoretical (experimental) magnetization with slow/quasi-forbidden (fast/allowed) transition mechanisms occurring at level crossing between the two ground states (involving excited states) encircled in magenta (green). **c** Magnification of the low-field region of the Zeeman spectrum, highlighting degeneracy points (level crossings) of states between which faster 1-flip and 2-flip tunneling transitions are allowed (green circles and hexagons), and also highlighting 3-flip or higher-flip processes that are essentially forbidden (magenta circles). Some of the allowed phonon emission processes are also indicated with dashed green arrows. **d** High-field region of the Zeeman spectrum, where the four onion states antiferromagnetically coupled to Cr spin states become isolated from excited states, leading the system’s magnetization to saturate.
fulfilling our proposed hierarchy $\chi_{C2} \gg \gamma_2 > \gamma_3 \sim 0$, and $\Gamma_{C2} \gg \Gamma_1 > \Gamma_2 > 0$. See methods section for a detailed discussion of the numerical choice of the parameters $\gamma_i$ and $\Gamma_i$. We numerically solved Eq. (8) for the time-dependent populations $\sigma(t)$ of the 56 CrDy$_6$ states considered here (Supplementary Figs. 8, 10). The magnetization curve $M(t) = \text{Tr}[\sigma(t)M]$ is then computed ($M$ is the magnetic moment operator along the field), parametrically plotted vs. the sweeping field, and reported in Fig. 9 with the experimental magnetization.

Quite remarkably, the opening of the hysteresis in the field region between $+B_{LC}$ and $-B_{LC}$ is captured by our model, together with the narrowing and closing of the hysteresis loop at fields $\sim B_{LC}$. Also, the simulated dynamical magnetization now displays a smooth increase between the low- and high-field “plateaus”, despite the low temperature, on account of the cascade of indirect transitions between the low-field (FT) and high-field (onion) ground states mediated by intermediate excited magnetic states.

There are, of course, shortcomings in our simulation. For instance, the zero-field hysteresis loop, after closing down as in the experiment, opens up again at larger fields, a feature that is only marginally present in the experiment. Also, the theoretical magnetization step covers a smaller field range than the experimental one. While we cannot exclude that a more thorough exploration of the parameter space might improve the fitting, we expect that these shortcomings will be partially overcome if all 256 states are included in the simulation, as the additional excited states will participate to the multi-step magnetization relaxation, further widening the field range covered by the magnetization step. Further discussion of our dynamical model, including a partitioning of the contributions to $M(t)$ from individual states, is reported in the Supplementary Note 5.

In summary, a heptanuclear [Cr$^{II}$Dy$^{III}$]$_6$ complex has been synthesized and structurally characterized. Experimental evidence in conjunction with theoretical calculations reveal and explain the presence of both SMM and single-molecule toroidal behavior. The toroidal states in the individual [Dy$^{III}$]$_3$ triangles are found to be ferrotoroidically coupled. We note here that the Cr$^{III}$ ion does not play any fundamental role in the predicted FT coupling, and the coupling between the two toroidal wheels can in fact be fully explained solely in terms of dipolar interactions, which depend solely on the structural parameters of the complex. The fundamental structural elements influencing the strength of dipolar FT coupling are the staggered arrangement of the two triangles with respect to each other, and the distance $h$ between the two wheels, which we found not to be optimal for maximizing FT coupling (i.e., $h>r\sqrt{7}/2$). The design and synthesis of similar [M$^{II}$Dy$^{III}$]$_n$ complexes, maintaining the staggered arrangement of the two triangular units, but featuring a smaller, even diamagnetic ion, is expected to lead to a smaller inter-ring distance $h$, or even to $h<r\sqrt{7}/2$, thus according to Eq. (6), to a stronger FT coupling. This route is currently being explored in our labs. Importantly, our findings indicate, for the first time, how coupling between toroidal magnetic moments can be manipulated by structural design. Finally, for the first time, the experimental single-crystal magnetization dynamics of a polynuclear Dy complex, displaying zero-field opening of a hysteresis loop, is simulated via a theoretical dynamical model, showing that the FT ground state plays a pivotal role in hindering the flipping of magnetic onion states in a sweeping field, thus slowing down the zero-field magnetic relaxation.

### Methods

#### Synthesis of [Dy$^{III}$Cr$^{III}$](OH)$_2$(ortho-tol)$_2$(MeOH)(NO$_3$)$_3$3MeOH (1)

The synthesis reaction was carried out under aerobic conditions. Chemicals and solvents were obtained from commercial sources and used without further purification.

#### X-ray crystallography

X-ray measurements for 1 were performed at 100(2) K at the Australian Synchrotron MX1 beam line 32. The data collection and integration were performed within Blu-Ice$^{46}$ and XDS$^{47}$ software programs. Compound 1 was solved by direct methods (SHELXS-97)$^{48}$, and refined (SHELXL-97)$^{49}$ by full least square matrix least squares on all $F^2$ data within X-Seed$^{50}$ and OLEX-2 GUIs$^{51}$. Crystallographic data and refinement parameters are summarized in Supplementary Table 1.

#### Magnetic measurements

The magnetic susceptibility measurements were carried out on a Quantum Design SQUID magnetometer MPMS-XL 7 operating between 1.8 and 300 K and fields ranging from 0 to 5 T. Microcrystalline samples were dispersed in vaseline in order to avoid torquing of the crystallites. The samples were mounted in a calibrated gelatine capsule held at the center of a drinking straw that was fixed at the end of the sample rod. Ac susceptibilities were carried out under an oscillating ac field of 3.5 Oe and frequencies ranging from 0.1 to 1500 Hz.

#### EPR instrumentation

The X-band measurements were made on Bruker spectrometers, at IIT Bombay, with a helium gas-flow cryostat. The X-band measurements were carried out at 5, 10, and 20 K.

#### Computational details

Even though there are only three crystallographically nonequivalent Dy$^{III}$ centers, we performed the calculations on all six Dy$^{III}$ ions to determine the direction of the local anisotropy axis. Using MOLCAS 7.8$^{52}$, we first calculated using the six Dy$^{III}$ ions using the crystal structure of 1. The structure of the modeled Dy fragment employed for calculation is shown in Supplementary Fig. 5, where the neighboring Dy$^{III}$ ions are replaced with diamagnetic Lu$^{III}$ ions and the Cr$^{III}$ ion replaced with Sc$^{III}$ ion. We have employed this methodology to study a number of Dy$^{III}$Er$^{III}$ SMs$^{53}$, the relativistic effects are taken into account based on the Douglas–Kroll Hamiltonian$^{54}$. The spin-free eigenstates are achieved by the Complete Active Space Self-Consistent Field (CASSCF) method$^{55}$. We have employed the [ANO-RCC...8s7p3d2g1h] basis set$^{56}$ for the Dy atoms, the [ANO-RCC...3s2p2d] basis set for the C atoms, the [ANO-RCC...2s1p] basis set for H atoms, the [ANO-RCC...3s2p1d] basis set for the N atoms, the [ANO-RCC...4s3p1d] basis set for the Sc atom, the [ANO-RCC...4s4p2d1f] basis set for the La atom, and the [ANO-RCC...3s2p1d] basis set for the O atoms. First we performed the CASSCF calculation including nine electrons across seven 4f orbitals of the Dy$^{III}$ ion. With this active space, we have computed 21 roots in the configuration interaction procedure. After computing these excited states, we have mixed all roots using RASSI$^{57}$ and spin–orbit coupling is considered within the space of calculated spin-free eigenstates. Moreover, we have considered these computed SO states into the SINGLE_ANISO$^{58}$.
program to compute the g-tensors. The Dy\textsuperscript{III} ion has eight low-lying K\textsubscript{q} levels for which the anisotropic g-tensors have been computed. The Cholesky decomposition for two electron integrals is employed throughout our calculations. We have extracted the crystal field parameters using the SINGLE_ANISO code as implemented in MOLCAS 7.8.

DFT calculations were performed using the B3LYP functional\textsuperscript{61} with the Gaussian 09 suite of programs\textsuperscript{62}. To estimate the exchange constant between Cr\textsuperscript{III}-Dy\textsuperscript{III} and Dy\textsuperscript{III}-Dy\textsuperscript{III} ions, the Cr\textsuperscript{III} ions were replaced with the spin-only Gd\textsuperscript{II} ions in order to investigate the exchange interaction between the Dy\textsuperscript{III} ions, which was then rescaled to the spin of dysprosium ions. We have used the LanL2DZ ECP basis set for Cr\textsuperscript{III},\textsuperscript{63} the double-zeta quality basis set employing Cundari-Stevans (CS) relativistic effective core potential on Gd atoms,\textsuperscript{64,65} and the 6-31G\textsuperscript{*} basis set for the rest of the atoms. The DFT calculations combined with the Broken Symmetry (BS) approach\textsuperscript{66} have been employed to compute the magnetic exchange interaction.

The actual energy spectrum and wavefunction and magnetic texture calculations, together with simulation of the magnetic measurements, was carried out by inserting the ab initio data into a model intramolecular magnetic coupling Hamiltonian, the development of which is described in the theoretical analysis section (see above).

Method of simulation of the magnetization dynamics. As is well known,\textsuperscript{57} in the derivation of the Pauli equations for the diagonal reduced density matrix \(\sigma\) from the Liouville–von Neumann equations for the total density matrix describing the coupled system–phonon reservoir, it is expedient to switch to the interaction picture, so that the unperturbed quantum system and reservoir Hamiltonians do not explicitly appear in the transformed equations of motion. The equations of motion in the interaction picture are thus propagated only by the spin–phonon coupling Hamiltonian, which in second order and in the Born–Markov limit generates the dissipative relaxation dynamics of the reduced density matrix. In our particular case, where time dependence arises both from the random dissipative relaxation fields, and from the periodic time dependence of the Zeeman Hamiltonian, a useful interaction picture can still be achieved by including the time-dependent Zeeman Hamiltonian in the zeroth order Hamiltonian, the development of which is described in the theoretical analysis section.

Finally, in order to account for the relaxation dynamics associated with tunneling processes induced by, e.g., random stray magnetic fields, we note in fact that in Eq. (9), the diagonal matrix elements of the commutator between the eigenstates of \(H_0\) are exactly zero in the adiabatic approximation, and thus the differential equations for the populations are then decoupled from those for the coherences. If on the other hand we now introduce the tunneling operator \(V\), so that in Eq. (8) \(H_0(t) \to H_0(t) + V\), since \(V\) by definition has non-zero off-diagonal matrix elements between the eigenstates of \(H_0\), this correction will re-introduce coupling between populations and coherences in Eq. (9). Assuming a steady-state approximation for the coherences, so that \(\sigma_\text{t}(t) \approx 0\) on the timescale over which the populations \(\sigma\text{a}_\text{t}(t)\) display appreciable changes, Eq. (9) can be transformed in a system of differential equations for the populations only, a set of generalized Pauli equations that reads (this is Eq. (8), reported here for convenience):  

\[
\sigma_\text{t}(t) = \sum_{i<j} \left( W_{ij}\exp(-E_{ij}/k_BT) \right) \Gamma_{ij} \sigma_{ij}(t) - \sigma_{ij}(t) \sum_{k,l} \left( W_{kl} + W_{lk} \right) \left( \sigma_{kl}(t) + \sigma_{lk}(t) \right),
\]

where the time-dependent incoherent tunneling transition rates \(W_{ij}\) are given by:

\[
W_{ij} = \frac{\Gamma_{ij} \exp(-E_{ij}/k_BT) \left( \sigma_{ij}(t) \right) \left( \sigma_{kl}(t) + \sigma_{lk}(t) \right)}{\sum_{j,k,l} \left( W_{ij} + W_{ji} \right) \left( \sigma_{kl}(t) + \sigma_{lk}(t) \right)}.
\]

Data availability. The X-ray crystallographic coordinates for structure reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 1430335. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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Author contributions
A.S., K.S.M., S.K.L., and G.R. visualized and designed the project. K.R.V. and S.K.L. carried out the syntheses and characterized the materials. S.K.L. and K.R.V. performed the synchrotron X-ray scattering measurements, analyzed the data, and solved the crystal structure. W.W. carried out micro-SQUID measurements. K.R.V. and A.S. carried out the ab initio calculations. A.S. developed the theoretical models for magnetic coupling, and for the hysteretic dynamics of the magnetization, and used them for the simulation and interpretation of the magnetic data. A.S., K.S.M., and G.R. wrote the manuscript. All the authors discussed the results and contributed to the manuscript.

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