

Architecting Diabolo-Shaped Ln₉ (Ln = Tb, Dy, Ho, Er) Homonuclear Clusters: Structural Topology, Magnetic Relaxation, and Theoretical Elucidation

Vipanchi .

Indian Institute of Science Education and Research Mohali

Keiichi Katoh

Josai University

Nobuto Funakoshi

Tohoku University

Nabanita Deb

Indian Institute of Science Education and Research, Tirupati

Arun Kumar Bar

Indian Institute of Science Education and Research, Tirupati

Masahiro Yamashita

Tohoku University

Kuduva R. Vignesh

vigneshkudavar@iisermohali.ac.in

Indian Institute of Science Education and Research Mohali

Article

Keywords:

Posted Date: September 18th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10837324/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Architecting Diabolo-Shaped Ln₉ (Ln = Tb, Dy, Ho, Er) Homonuclear Clusters: Structural Topology, Magnetic Relaxation, and Theoretical Elucidation

Vipanchi,^a Keiichi Katoh,^b Nobuto Funakoshi,^c Nabanita Deb,^d Arun Kumar Bar,^{d*} Masahiro Yamashita,^{c,e*} Kuduva R. Vignesh^a

^a Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector-81, Knowledge City, S.A.S. Nagar, Mohali-140306, Punjab, India.

^b Department of Chemistry, Graduate School of Science, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, Japan

^c Institute of Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-Ku, Sendai 980-8577, Japan.

^d Department of Chemistry, Indian Institute of Science Education and Research Tirupati, Tirupati – 517619, Andhra Pradesh, India.

^e School of Chemical Science and Engineering, Tongji University, Siping Road 1239, Shanghai 200092, P. R. China

* Corresponding authors: Author One (vigneshkuduvar@iisermohali.ac.in); Arun Kumar Bar (a.bar@iisertirupati.ac.in); Masahiro Yamashita (masahiro.yamashita.c5@tohoku.ac.jp).

Abstract

Molecular nanomagnetism has witnessed a paradigm shift toward lanthanide-based polynuclear complexes for the realization of Single-Molecule Magnet (SMM) behavior, driven by the exceptional unquenched orbital angular momentum and large single-ion anisotropy of trivalent lanthanide ions. Unlike mononuclear and dinuclear air-stable complexes, which suffer from zero-field quantum tunnelling of the magnetisation (QTM) caused by transverse anisotropy components and limited exchange coupling, air-stable polynuclear assemblies establish robust cooperative magnetic networks. Intermetallic magnetic exchange interactions within multicenter architectures facilitate pathways to suppress QTM, thereby elevating energy barriers and enhancing spin-lattice dynamics. Furthermore, exploring neglected structures may enhance the comprehension of hydroxide-bridged polynuclear Ln(III) compounds, particularly in terms of optimizing their magnetic characteristics. Instances of two {Ln₄} squares coupled with a Ln(III) ion featuring hydroxide/oxide bridges are, nonetheless, quite restricted, despite the intriguing magnetic phenomena noted in certain of these materials. The initial implementation of 1-Phenyl-1,3-butanedione (HBzAc) as a ligand in 4f-metal chemistry has led to the isolation of a novel family of Ln(III) clusters exhibiting a distinctive diabolo-like topology series of nonanuclear lanthanide oxo-hydroxo complexes with the general composition of [Tb₉(μ₄-OH)₂(μ₃-OH)₈(μ-BzAc)₈(BzAc)₈].NO₃ (**1-Tb**), [Dy₉(μ₄-OH)₂(μ₃-OH)₈(μ-BzAc)₈(BzAc)₈].NO₃.2MeOH.MeCN (**2-Dy**), [Ln₉(μ₄-O)(μ₄-OH)(μ₃-OH)₈(μ-BzAc)₈(BzAc)₈], (Ln = Ho (**3-Ho**) and Er (**4-Er**)); where two {Ln₄} squares are coupled with a Ln(III) ion via hydroxide bridges. Direct current magnetic measurements revealed antiferromagnetic interactions for all studied complexes. Advanced *ab initio* CASSCF/RASSI-SO/SINGLE_ANISO/POLY_ANISO calculations were employed to evaluate the anisotropic magnetic parameters and exchange coupling constants, which support the experimental predictions. Our approach varies from the previous methods where it is difficult to regulate the parameters such as magnetic coupling and anisotropy at the same time, and is expected to have consequences beyond the nonanuclear {Ln^{III}₉} SMMs explored here.

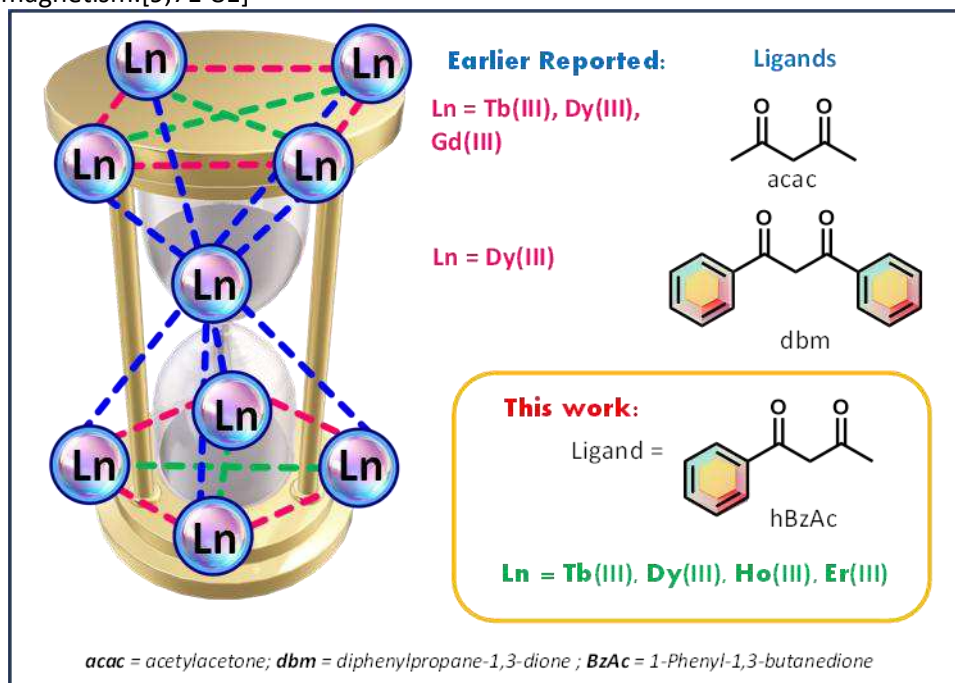
Introduction

Lanthanide-based Single-Molecule Magnets (SMMs) have evolved from mononuclear[1-6] and dinuclear[7,8] complexes toward polynuclear complexes, driven by the exceptional unquenched orbital angular momentum and large single-ion anisotropy of lanthanide(III) ions. Beyond their structural diversity, the lanthanide(III) complexes, with a broad spectrum of nuclearities, hold a remarkable promise in fields ranging from optical technologies,[9-12] catalysis,[13] spintronics,[14-17] quantum computing,[15,16,18] and molecular magnetism research.[19-22] Mononuclear and dinuclear air-sensitive complexes show fascinating SMM behaviour with larger energy barrier (U_{eff}) and blocking temperatures (T_B) [1-8]; however, most of the air-stable mononuclear and dinuclear complexes frequently suffer from rapid zero-field QTM caused by transverse anisotropy components and limited exchange coupling.[23-26] Whereas the polynuclear assemblies establish robust cooperative magnetic networks along with intermetallic magnetic exchange interactions within multi-center architectures, which facilitate pathways to suppress QTM, thereby elevating energy barriers and enhancing spin-lattice dynamics. Consequently, the rational design of polynuclear 4f clusters via tailored organic ligand coordination has emerged as a premier strategy for realising advanced SMMs.[27-30] Several higher nuclearity lanthanide(III) clusters have been reported; a few notable nuclearity systems are $\{\text{Ln}_6\}$ [31,32], $\{\text{Ln}_8\}$ [33,34], $\{\text{Ln}_{10}\}$ [35,36], $\{\text{Ln}_{11}\}$ [37,38], $\{\text{Ln}_{12}\}$ [39-42], $\{\text{Ln}_{15}\}$ [43,44], $\{\text{Ln}_{16}\}$ [45,46], $\{\text{Ln}_{18}\}$ [47], $\{\text{Ln}_{19}\}$ [42,48], $\{\text{Ln}_{20}\}$ [49], $\{\text{Dy}_{30}\}$ [50], and $\{\text{Ln}_{60}\}$ [50,51].

Investigations into wheel- or ring-shaped molecular nanomagnetic substances have accelerated recently due to their prospective utility as functional materials in nanotechnology, particularly emphasizing SMMs, one-dimensional chain models, and the exploration of quantum-size phenomena.[52] Several polynuclear dysprosium-based complexes with wheel or ring shapes exhibiting single-molecule toroidal (SMT) behavior and slow magnetic relaxation have been reported in the literature.[34,53-56] For instance, trinuclear $\{\text{Dy}_3\}$ SMMs, such as $[\text{Dy}_3\text{L}_{\text{RRRRRR}}/\text{SSSSS}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2(\text{SCN})_4]\cdot 6\text{CH}_3\text{OH}$ with an U_{eff} of 37 K,[57] while the complex $(\text{C}_5\text{Pr}_5)_3\text{Ln}_3\text{H}_3\text{I}_2$ has a U_{eff} of 39 K.[58] Powell and colleagues have prepared the foundational triangular $\{\text{Dy}_3\}$ SMT with the formula of $[\text{Dy}_3\text{L}_3(\mu_3\text{-OH})_2\text{Cl}(\text{H}_2\text{O})]\cdot \text{Cl}$ possesses remarkable toroidal moments and an effective barrier of 61.7 K.[59,60] Among various nuclearities, tetranuclear $\{\text{Dy}_4\}$ cores-particularly those adopting tetrahedral and square planar topologies represent a critical structural juncture. Similarly tetranuclear $\{\text{Dy}_4\}$ systems including $[\text{Dy}_4(\text{Bppd})_4(\mu_3\text{-OH})_4(\text{Pa})_4(\text{H}_2\text{O})_4]\cdot 0.333 \text{ H}_2\text{O}$ (where $\text{BppdH}=1,3\text{-Bis}(\text{pyridin-4-yl})\text{propane-1,3-dione}$ and $\text{PaH} = 2\text{-Picolinic acid}$),[61] and $[\text{Dy}_4(\mu_3\text{-OH})_2(\mu\text{-OH})_2(2,2\text{-bpt})_4(\text{NO}_3)_4(\text{EtOH})_2]$ [2,2-bptH = 3,5-bis(pyridin-2-yl)-1,2,4-triazole] have been reported to exhibit U_{eff} up to 80 K, and at the same time they show SMT behavior.[53,62] Apart from these, various complexes with more dysprosium nuclearity, such as square-pyramidal $\{\text{Dy}_5\}$ assemblies, have also shown remarkable magnetic anisotropy and large relaxation barriers.[63,64] In particular, $[\text{Dy}_5\text{O}(\text{O}i\text{Pr})_{13}]$ showed a high U_{eff} value of 530 K, but no SMT studies have been conducted on it.

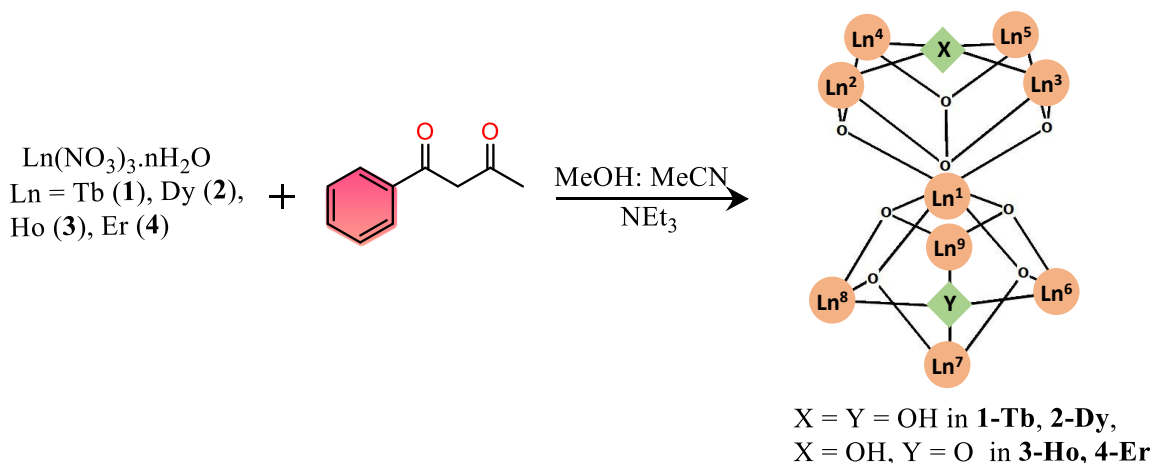
Among various nuclearities, the tetranuclear cyclic arrangement of four lanthanide ions in a wheel topology enforces high spatial symmetry and promotes a cooperative alignment or toroidal arrangement of local magnetic moments. These cyclic exchange interactions and local crystal field orientations can generate orthogonal or alternating magnetic axes that disrupt transverse tunneling paths. In addition, the study of new structures can improve the understanding of hydroxide-bridged polynuclear Ln(III) compounds, especially in terms of the enhancement of their magnetic properties. The linkage of two $\{\text{Ln}_3\}$ triangles through organic ligands and 3d ions is widely recognized.[65,66] [67] Interestingly, a set of heterometallic $\{\text{Cr}^{\text{III}}\text{Ln}^{\text{III}}_6\}$ complexes ($\text{Ln} = \text{Dy}, \text{Tb}$ and Ho), comprising two triangular $\{\text{Ln}_3\}$ wheels bridged through a central $\text{Cr}(\text{III})$ ion and/or other 3d ions, has been reported to stabilize the structure and showed a ferrotoroidic ground state.[67-69] However, the rare reports of two $\{\text{Ln}_4\}$ squares associated with a Ln(III) ion with hydroxide/oxide bridges are somewhat limited, yet interesting magnetic phenomena have

been seen in some of these materials.[57-67] Connecting two square-planar wheels via a shared central Ln(III) ion produces a three-dimensional nonanuclear sandglass/ hourglass topology (Scheme 1). Inspired by these findings, we sought to investigate hourglass structural motifs; such an arrangement was anticipated to favor cooperative toroidal coupling and several distinct magnetic exchange pathways to quench QTM. Earlier findings with hourglass topology include $[\text{Ln}_9(\text{OH})_{10}(\text{hmp})_8(\text{NO}_3)_8(\text{DMF})_8](\text{OH})$, ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Dy}$, and $\text{hmpH} = 2\text{-(hydroxymethyl)pyridine}$),[9] and $[\text{Dy}_9(\text{acac})_{16}(\mu_3\text{-OH})_8(\mu_4\text{-OH})_2]\text{OH}\cdot 6\text{H}_2\text{O}$ where $\text{acac} = \text{acetylacetonate}$,[70] $[\text{Y}_9\text{L}_{16}(\text{OH})_{10}](\text{OH})$ ($\text{L} = \text{Acac} = \text{acetylacetonate}$).[71] These examples have attracted considerable attention due to their fascinating hourglass topologies and their potential applications in areas such as luminescence and cooperative magnetic phenomena. Consequently, among the diverse families of lanthanide clusters, nonanuclear $\{\text{Ln}_9\}$ systems featuring an “hourglass”-type architecture have emerged as an important platform for exploring structure-property correlations in molecular magnetism.[9,71-81]



Scheme 1. Schematic representation of hourglass-shaped known and new $\{\text{Ln}_9\}$ complexes reported here.

Motivated by the diverse functional potential of polynuclear hourglass topologies, we report herein a series of isostructural nonanuclear lanthanide cationic clusters having the formula $[\text{Tb}_9(\mu_4\text{-OH})_2(\mu_3\text{-OH})_8(\mu\text{-BzAc})_8(\text{BzAc})_8]$ (**1-Tb**), $[\text{Dy}_9(\mu_4\text{-OH})_2(\mu_3\text{-OH})_8(\mu\text{-BzAc})_8(\text{BzAc})_8]\cdot\text{NO}_3\cdot 2\text{MeOH}\cdot\text{MeCN}$ (**2-Dy**), $[\text{Ho}_9(\mu_4\text{-O})(\mu_4\text{-OH})(\mu_3\text{-OH})_8(\mu\text{-BzAc})_8(\text{BzAc})_8]$, (**3-Ho**) and $[\text{Er}_9(\mu_4\text{-O})(\mu_4\text{-OH})(\mu_3\text{-OH})_8(\mu\text{-BzAc})_8(\text{BzAc})_8]$ (**4-Er**), where HBzAc is 1-Phenyl-1,3-butanedione, a diketone ligand widely used in 3d metal cluster chemistry for producing high-spin molecules and SMMs. However, it has been minimally explored with homometallic 4f clusters.[82] In this work, we describe the synthesis, structural characterization, molecular magnetic behavior, and high-level *ab initio* computational studies of the above four representatives from a family of nonanuclear Ln(III) clusters.



Scheme 2: Synthetic protocol for the preparation of the complexes **1-Tb** – **4-Er**.

Result and Discussion

Preparation of compounds: Nonanuclear lanthanide clusters, $[\text{Tb}_9(\mu_4\text{-OH})_2(\mu_3\text{-OH})_8(\mu\text{-BzAc})_8(\text{BzAc})_8]$ (**1-Tb**), $[\text{Dy}_9(\mu_4\text{-OH})_2(\mu_3\text{-OH})_8(\mu\text{-BzAc})_8(\text{BzAc})_8] \cdot \text{NO}_3 \cdot 2\text{MeOH} \cdot \text{MeCN}$ (**2-Dy**), $[\text{Ho}_9(\mu_4\text{-O})(\mu_4\text{-OH})(\mu_3\text{-OH})_8(\mu\text{-BzAc})_8(\text{BzAc})_8]$ (**3-Ho**) and $[\text{Er}_9(\mu_4\text{-O})(\mu_4\text{-OH})(\mu_3\text{-OH})_8(\mu\text{-BzAc})_8(\text{BzAc})_8]$ (**4-Er**) have been prepared from the stirring of correct stoichiometric amounts of respective hydrated Ln(III) nitrate salts with HbzAc and triethylamine (NEt_3), in a solvent mixture of MeOH and MeCN (1:1, v/v), under ambient conditions (Scheme 2) for 24h.[72] The mixture was then filtered, and the filtrate was allowed to stand at room temperature. Cubic-shaped colorless (for Tb_9 (**1-Tb**), Dy_9 (**2-Dy**), and Ho_9 (**3-Ho**)) and pink (for Er_9 (**4-Er**)) crystals suitable for X-ray structural analysis were collected after 12 days by filtration and via slow evaporation in 58–70% yield (See ESI for the detailed synthesis procedure).

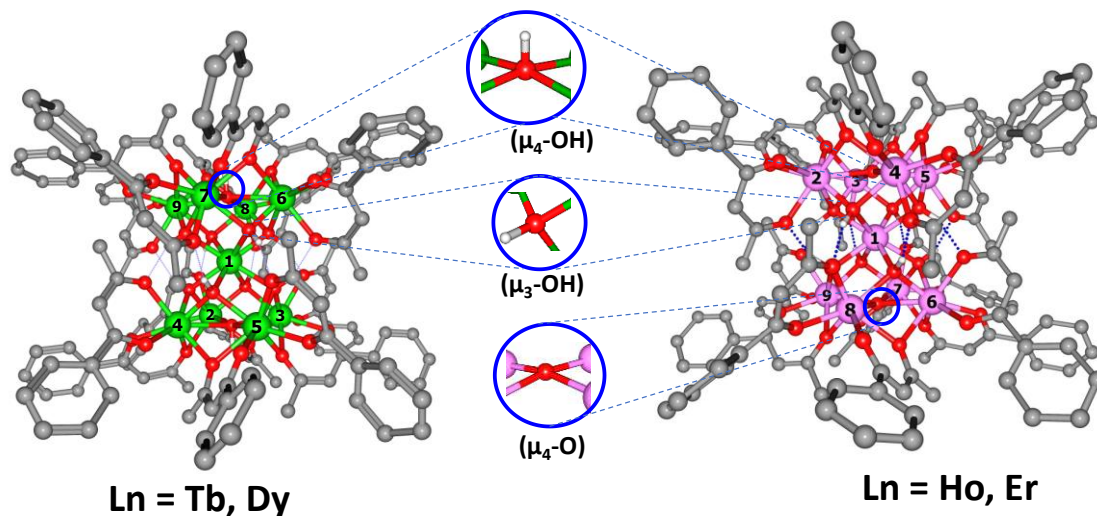


Figure 1. SC-XRD refined molecular structures: Molecular structure of compounds **1-Tb**, **2-Dy**, **3-Ho** and **4-Er**. Solvent molecules in the crystals and hydrogen atoms attached to carbon have been omitted for clarity.

Crystallographic studies: The molecular structures of the complexes **1-Tb** – **4-Er** consist of a nonanuclear Ln(III) supported by a dense network of oxygen-donor ligands, including μ_4 -oxo/ μ_4 -hydroxo/ μ_3 -hydroxo groups and bridging ketone moieties, with bulky organic substituents occupying the periphery of the molecule (Figure 1). Overall, all complexes **1-Tb** – **4-Er** follow the “diabolo” or “hourglass” architecture and exhibit a fourfold rotational axis that runs through the center of the Ln1 ions (Figure 2). Single-crystal X-ray diffraction (SCXRD) analysis demonstrates that cluster **1-Tb** crystallizes in the cubic $P_n/3_n$ space group, whereas **2-Dy**, **3-Ho**, and **4-Er** crystallize in the triclinic $P\bar{1}$ space group. Complete crystal data and structure refinement parameters of **1-Tb** – **4-Er** are given in Table S1. Representative bond distances and angles for these complexes are compiled in Tables S2-S9. Owing to the structural equivalence among **2-Dy**, **3-Ho** and **4-Er**, the structural description of **2-Dy** is discussed. As the central μ_4 -hydroxo ligand is present in the center of the metallacyclic rim, **2-Dy** serves as a representative example for the crystallographic description and discussion. In contrast, complexes **3-Ho** and **4-Er** differ slightly in their core composition, containing a μ_4 -oxo ligand in place of the μ_4 -hydroxo group in one of the metallacyclic Ln₄ rims, while retaining the same overall metal-ligand connectivity and coordination framework, and thus are briefly discussed here. In **2-Dy**, Dy(III) ions are arranged in a three-layered topology, comprising nine Ln(III) ions organized in a three-layered topology in a 4:1:4 ratio. The metal framework is composed of 16 BzAc[−] ligands, eight μ_3 -OH bridges, and two μ_4 -OH groups. An extra NO₃[−] anion located outside the primary coordination sphere maintains overall charge neutrality. The lattice of homometallic **2-Dy** contains five MeOH molecules and five MeCN molecules. The complex exhibits a well-defined nonanuclear structure composed of two distinct tetrameric Dy₄ rims and a central Dy(III) ion. The upper rim 1 consists of Dy2, Dy3, Dy4, and Dy5 centers, while the lower rim 2 has Dy6, Dy7, Dy8, and Dy9 centers (Figure 1). Within each rim, the Dy(III) ions are further interconnected by a μ_4 -OH unit that bridges the four basal metal ions. The Dy-O bond lengths obtained from the crystallographic data fall within the typical range for Dy(III)-oxygen interactions. Distances associated with μ_3 -oxo and μ_2 -oxo/ μ_3 -hydroxo bridges lie between 2.25 and 2.35 Å, while those involving bridging carboxylate oxygen atoms range from 2.30 to 2.45 Å. Slightly longer Dy-O distances (up to ~2.50 Å) are observed for terminal or weakly coordinated oxygen donors. The relatively short Dy-O separations involving μ_3 -oxo bridges indicate strong metal-oxygen interactions that stabilize the nonanuclear Dy₉ core. The diagonal Dy···Dy distances in the upper rim are 5.086 Å in Dy2···Dy5 and 5.100 Å in Dy3···Dy4, and similarly in the lower rim2. The two basal planes symmetrically encapsulate the central Dy1 (Figure 2). Thus, **2-Dy** can be regarded as two {Dy₄} basal planes, each forming a pentanuclear square pyramid with the apical Dy1 ion. The triangular faces of these square pyramids are capped by μ_3 -OH ligands, reinforcing the framework. The Dy1···Dy separations to the basal Dy atoms are 3.706 Å (Dy1···Dy2) and 3.694 Å (Dy1···Dy3), with comparable distances observed for the remaining Dy centers. The vertical distance between the two basal planes is 5.852 Å. The rim Dy(III) ions are coordinated by BzAc[−] ligands, which are organized so that eight ligands bind individual Dy centers and the remaining eight chelate one lanthanide ion while also bridging to a nearby ion via one oxygen atom. In the solid state, the shortest intermolecular Dy···Dy separation between adjacent core Dy atoms of rim1 and rim2 is 12.347 Å, as seen in the packing diagram (Figures S1-S8). Two core Dy1 ions are coupled to all eight peripheral Dy(III) centers through eight μ_3 -OH bridges. The hydroxide groups also form intramolecular hydrogen bonds, which help to enhance the cluster structure. Each Dy(III) center is coordinated exclusively by oxygen atoms, reflecting the strong oxophilicity of lanthanide ions. The coordination varies between eight and nine, which is typical for Dy(III) complexes. **3-Ho** and **4-Er** possess a similar structural environment and comparable structural parameters, and a slight difference was found in the Ln₄ rim, where the μ_4 -O^{2−} group in one rim and μ_4 -OH[−] bridging the other rim. SHAPE analysis was performed using SHAPE 2.1 to accurately analyze the geometry surrounding non-equivalent Dy(III) centers (Table S10). The central Ln1 center in all four

complexes has a square-antiprismatic geometry having CShM values of 0.058 (**1-Tb**), 0.028 (**2-Dy**), 0.033 (**3-Ho**), and 0.028 (**4-Er**). The remaining Ln(III) ions of both the basal planes have biaugmented trigonal-prismatic geometries. These assignments are corroborated by CShM values of 1.610 (**1-Tb**), 1.623 (**2-Dy**), 1.889 (**3-Ho**), and 1.497 (**4-Er**) (Figure 2b,c for visual representations of coordination polyhedra). The powder X-ray diffraction (PXRD) was used to test the bulk purity of the synthesized **1-Tb–4-Er** multiple times (Figure S9-S12).

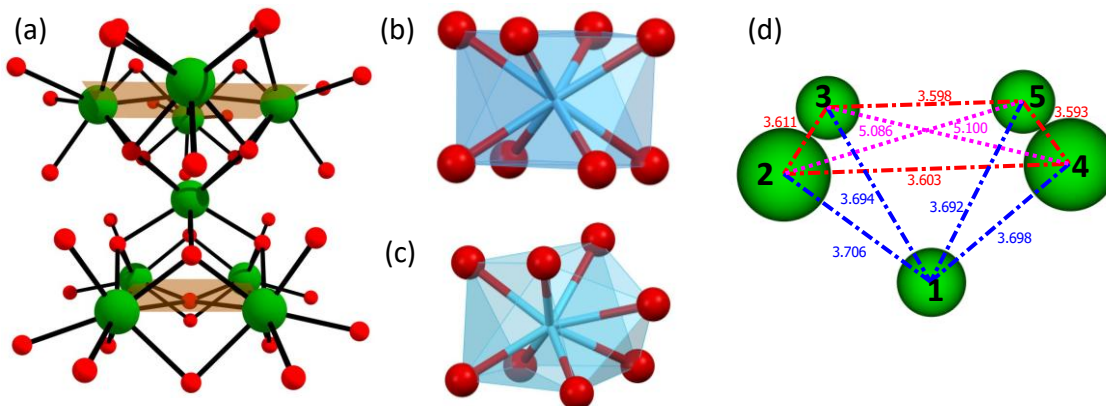


Figure 2. Structural cores, planes, and their descriptions. (a) Representation of the basal plane connecting four Dy(III) centers at the top and four Dy(III) centers at the bottom in compound **2-Dy**. Polyhedra of (b) center lanthanide and (c) the peripheral lanthanides. (d) Bond lengths (Å) of the respective lanthanide centers in the core.

Magnetic Measurements

Variable-temperature magnetic susceptibility measurements for complexes **1-Tb – 4-Er** were carried out on the polycrystalline samples under an applied direct current (dc) field of 0.1 T in the temperature range of 2–300 K (Figure 3). At 300 K, the $\chi_M T$ (χ_M = molar magnetic susceptibility) values are 104.89, 127.59, 125.99, and 104.25 cm³ K mol⁻¹ for complexes **1-Tb**, **2-Dy**, **3-Ho**, and **4-Er**, respectively with the expected theoretical values of 106 cm³ K mol⁻¹ for nine isolated /noninteracting Tb(III) ions (⁷F₆, S = 3, L = 3, g = 3/2) in **1-Tb**, 127.53 cm³ K mol⁻¹ for nine isolated Dy(III) ions (⁶H_{15/2}, S = 5/2, L = 5, g = 4/3) in **2-Dy**, 126.4 cm³ K mol⁻¹ for nine isolated Ho(III) ions (⁵I₈, S = 2, L = 6, g = 5/4) in **3-Ho**, 103.3 cm³ K mol⁻¹ for nine isolated Er(III) ions (⁴I_{15/2}, S = 4, L = 6, g = 6/5) in **4-Er**. The $\chi_M T$ values for all four complexes gradually decrease upon cooling from 300 K until around 120 K, revealing the antiferromagnetic exchange interactions within these complexes. After 120 K, a significant decrease in the magnetic susceptibility values is observed, which is further, i.e., from 104.89 to 71.16 cm³ K mol⁻¹ in **1-Tb**, 127.59 to 68.17 cm³ K mol⁻¹ in **2-Dy**, 125.99 to 51.31 cm³ K mol⁻¹ in **3-Ho**, and 104.25 to 49.0 cm³ K mol⁻¹ in **4-Er**, which may be due to the intermolecular magnetic exchange/depopulation of the Stark sublevels. The nonzero $\chi_M T$ value at 5.0 K is consistent with a S ≠ 0 spin ground state; however, in all complexes, where contributions from the orbital angular momentum and anisotropic effects do need to be taken into account, the decrease of the $\chi_M T$ values at T < 100 K could be attributed to the presence of weak antiferromagnetic interactions between the nine Ln(III) centers.

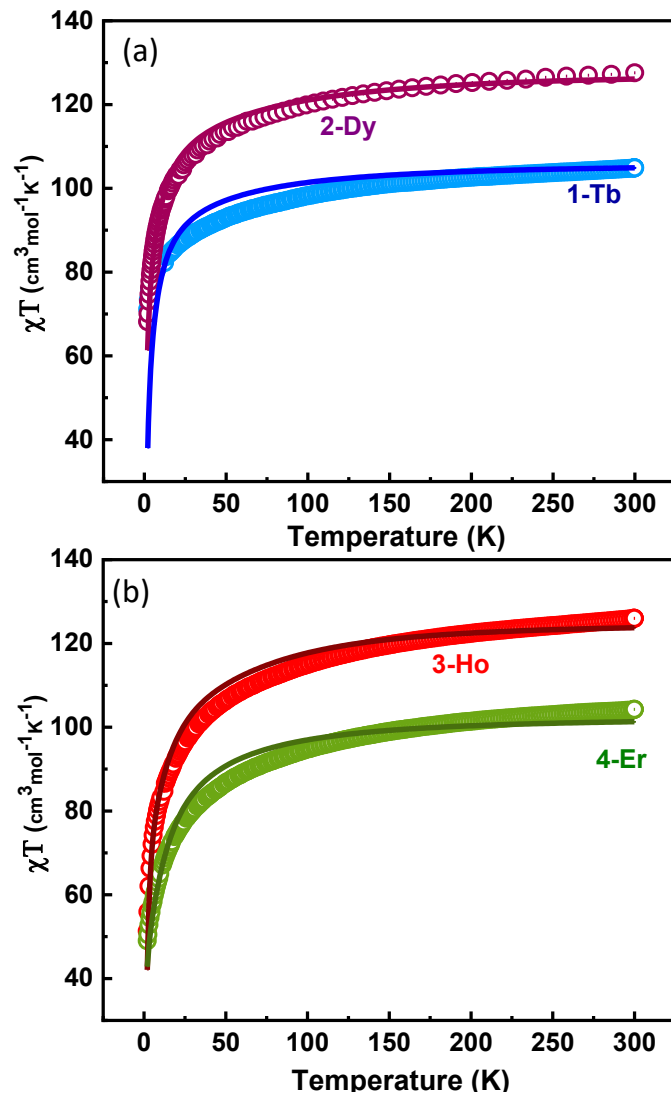


Figure 3. Magnetic Susceptibility plots. Temperature dependence of $\chi_M T$ for **1-Tb** – **4-Er** clusters at 0.1 T. The simulation of the susceptibility was performed using computed J values from POLY_ANISO simulations.

Field-dependent magnetization measurements for complexes **1-Tb** – **4-Er**, recorded in the 0-5 T field range over 2 - 10 K, reveal characteristic features for anisotropic, exchange-coupled lanthanide clusters (Figure S13). Complexes **1-Tb**, **2-Dy**, and **4-Er** show similar profiles with the rapid increase of M values at 2 T without saturating at 37.1 (**1-Tb**), 45.7 (**2-Dy**), 37.1 (**3-Ho**), and 36.4 (**4-Er**) $N\beta$ till 5T; indicating the presence of several low-lying thermally populated states which in turn lead to strong magnetic anisotropy and possibility of observing SMM characteristics. In all cases, the magnetization increases steeply at low applied fields, reflecting the presence of large magnetic moments and efficient alignment of the ground-state m_J levels under an external field. However, none of the complexes reach complete saturation even at 5 T, indicating the presence of significant crystal-field-induced magnetic anisotropy that hinders full spin alignment. The progressive decrease in magnetization with increasing temperatures further supports the thermal depopulation of the ground Kramers or quasi-doublet states, consistent with well-isolated but

thermally accessible excited states. Fitting the magnetization versus field data, presuming that the ground state is the only one populated in the lowest T and field ranges, all failed, and we consequently conducted investigations on ac susceptibility, which is a potent supplement to the DC investigations to ascertain the ground state of a system since they prevent any issues due to the existence of a DC field. The simulated magnetic susceptibility ($\chi_M T$ vs. T) and field-dependent magnetization (M vs. H) data from *ab initio* calculations (see later) show excellent agreement with the experimental results, confirming the reliability of the extracted exchange parameters.

Alternating current (ac) susceptibility measurements with a 5 Oe oscillating ac field were also performed for complexes **1-Tb** – **4-Er**, both in the absence and presence of the applied dc field. However, no out-of-phase component of ac susceptibility (χ_M'') was observed at zero dc field, signifying the absence of slow relaxation of magnetizations in all these clusters. For **1-Tb** and **3-Ho**, no SMM behavior was seen above 1.8 K since there were no frequency- or temperature-dependent out-of-phase (χ_M'') signals with various applied dc fields (Figures S14 and S15). For **2-Dy** and **4-Er**, a non-zero out-of-phase susceptibility component is seen; nevertheless, the peak maxima fall below the magnetometer's working temperature (Figure 4), indicating SMM behavior with fast magnetic relaxation times. It is interesting to note that applying a 2000 Oe static dc field produced the same susceptibility profile for both **2-Dy** and **4-Er** (Figure S17). With these experimental findings, it is critical to clarify the causes of the faster relaxation times seen in nearly all these complexes. In order to ascertain these parameters, we have conducted *ab initio* CASSCF calculations on all the complexes.

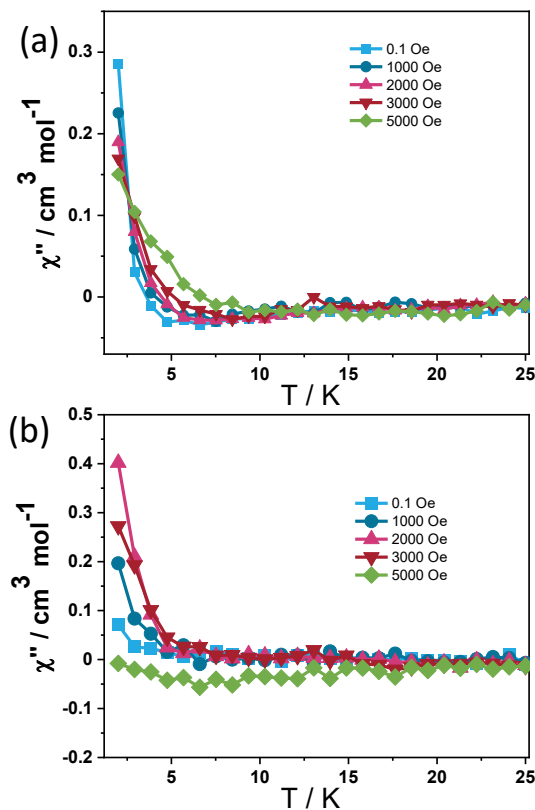


Figure 4. AC susceptibility Plots. Plots of χ_M'' versus T at various dc fields for a) **2-Dy** and (b) **4-Er**, to predict the optimum dc field.

Computational Studies

Ab initio Complete Active Space Self-Consistent Field (CASSCF) computational calculations using MOLCAS 8.2[83] were performed to comprehend the observed magnetic characteristics of the nonanuclear clusters (See computational details in the ESI), a successful method for interpreting the magnetism of lanthanide complexes.[26,70,84-86] First, a relaxation process associated with the single-ion anisotropy of lanthanide ions is examined, followed by an evaluation of the exchange-coupled state mechanism of the full nonanuclear structure, which includes all the magnetic exchange interactions between the Ln(III) centers. Single-ion calculations of each Ln(III) ion in complexes **1-Tb–4-Er** were carried out using their X-ray structures by substituting the neighbouring Ln(III) center with the diamagnetic Lu(III) ions at the RASSI-SO/SINGLE_ANISO routine to isolate and evaluate their magnetic anisotropy and the crystal-field splitting.

Non-Kramers ion complexes (1-Tb and 3-Ho): For complex **1-Tb**, the low-lying RASSI states associated with all nine Tb(III) are well separated; among these, eight peripheral Tb(III) exhibit similar crystal-field splitting in the range of 419.7 – 421.1 cm⁻¹, whereas the central Tb(III) ion shows a significantly larger splitting up to 700.2 cm⁻¹, which can be attributed to the higher local symmetry around this metal center (Table 1). The ground-first excited state gaps of these non-Kramers Tb(III) ions; Tb1, Tb2, Tb3, Tb4, Tb5, Tb6, Tb7, Tb8, and Tb9 centers are 53.9 cm⁻¹, 30.4 cm⁻¹, 34.2 cm⁻¹, 30.4 cm⁻¹, 34.2 cm⁻¹, 34.1 cm⁻¹, 34.2 cm⁻¹, 30.3 cm⁻¹, and 30.4 cm⁻¹, respectively (Table 1 and Figure S18). The computed ground-state *g*-tensors for all nine Tb(III) centers, with pronounced Ising anisotropy *g_z* values are 15.6753, 15.3900, 16.0329, 15.3720, 16.0425, 15.9399, 15.9526, 15.2836, and 15.2848, respectively (Table S11) which are lower than the expected *g_z* value of 18.0 for pure *m_J* = ± 6 states and indicate weak axial anisotropy for all centers. The weak anisotropic nature of each of these Tb(III) ions led large tunnelling (Δ_{tun}) gap in the ground-state Ising doublets (IDs), i.e., 22.38, 5.38, 4.27, 5.38, 4.28, 4.29, 4.29, 5.39, and 5.38 cm⁻¹ for Tb1, Tb2, Tb3, Tb4, Tb5, Tb6, Tb7, Tb8, and Tb9, respectively, and allow for the blockade of the magnetisation in the ground states itself. A similar crystal-field splitting was observed for all nine Ho(III) centers in complex **3-Ho**, where the eight peripheral Ho(III) ions' IDs split, ranging from 301.9 to 381.3 cm⁻¹ (Tables S13-14). Notably, the central Ho(III) ion also shows similar splitting as the peripheral Ho(III) ions, which can be attributed to the higher local symmetry (*C₄*) around this metal center.[70] The ground-first excited state gaps of the non-Kramers Ho(III) ions of Ho1, Ho2, Ho3, Ho4, Ho5, Ho6, Ho7, Ho8, and Ho9 are 8.15 cm⁻¹, 40.6 cm⁻¹, 39.3 cm⁻¹, 42.0 cm⁻¹, 39.8 cm⁻¹, 43.6 cm⁻¹, 39.9 cm⁻¹, 42.8 cm⁻¹, and 41.5 cm⁻¹, respectively (Figure S20) which are in the similar range observed for the Tb(III) ions in **1-Tb**. The computed ground state *g*-tensors for all nine Ho(III) centers (Ho1 to Ho9), with pronounced Ising anisotropy *g_z* values of 10.7393, 16.1864, 16.1030, 16.6563, 16.3220, 17.0168, 16.8930, 16.8930, and 16.5417, respectively, are lower than the expected *g_z* value of 20.0 for pure *m_J* = ± 8 states and indicate weak axial anisotropy for all centers. The weak anisotropic nature of Ho(III) ions led large tunnelling (Δ_{tun}) gap between the ground-state IDs, ranging from 0.8 – 1.8 cm⁻¹; allow for the blockade of the magnetisation in the ground states itself for all Ho(III) ions.

Table 1. *Ab initio* computed energies of low-lying Ising doublets (in cm^{-1}) of all Tb(III) centers in **1-Tb** and their ground state g -tensor values.

IDs	Energy (cm^{-1})								
	Tb1	Tb2	Tb3	Tb4	Tb5	Tb6	Tb7	Tb8	Tb9
1	11.2	2.1	2.1	2.6	2.1	2.1	2.1	2.7	2.7
2	53.9	30.4	34.2	30.4	34.2	34.1	34.2	30.3	30.4
3	103.5	89.2	87.9	89.2	87.9	87.8	87.9	89.1	89.2
4	223.5	116.9	115.1	116.9	115.1	115.0	115.1	116.8	116.9
5	223.7	149.7	151.1	149.7	151.1	151.0	151.1	149.6	149.7
6	417.5	222.8	223.4	222.8	223.4	223.6	223.4	222.9	222.8
7	532.6	253.2	251.1	253.2	251.1	251.2	251.1	253.3	253.2
8	646.9	275.7	273.9	275.7	273.9	274.0	273.9	275.8	275.7
9	700.2	420.9	419.7	420.9	419.8	419.9	419.7	421.1	420.9
	g -tensors								
g_x	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
g_y	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
g_z	15.6753	15.3900	16.0329	15.3720	16.0425	15.9399	15.9526	15.2836	15.2848

Kramers ion complexes (2-Dy and 4-Er): For the nine Dy centers in complex **2-Dy**, the calculated ground state g -anisotropies possess high transverse components (g_x and g_y) with weak axial anisotropies of $g_z = 17.1996, 18.3318, 17.9583, 15.2152, 15.6753, 18.1442, 15.0608, 18.7465,$ and 16.5888 in centers Dy1, Dy2, Dy3, Dy4, Dy5, Dy6, Dy7, Dy8, and Dy9, respectively, which are far from the g_z value of 20.0 expected for the pure $m_j = \pm 15/2$ states, and indicate that the ground Kramers Doublets (KDs) of each Dy(III) ion is highly mixed with other m_j states. Though each Dy(III) ion possesses weak anisotropy at the ground KDs, the eight low-lying KDs of all nine Dy(III) centers are well isolated. The eight low-lying KDs of eight peripheral Dy(III) ions display comparable total crystal-field splittings, falling within the range of $410.1 - 448.3 \text{ cm}^{-1}$. The ground-first excited KDs gaps of the nine Kramers Dy(III) ions were $26.1 \text{ cm}^{-1}, 32.6 \text{ cm}^{-1}, 27.6 \text{ cm}^{-1}, 17.0 \text{ cm}^{-1}, 21.8 \text{ cm}^{-1}, 30.5 \text{ cm}^{-1}, 20.7 \text{ cm}^{-1}, 37.2 \text{ cm}^{-1},$ and 24.4 cm^{-1} , for Dy1, Dy2, Dy3, Dy4, Dy5, Dy6, Dy7, Dy8, and Dy9 centers, respectively (Tables 2 and S12). It is observed that due to the presence of significant QTM between the ground KDs, ranging from $0.16 - 0.72 \mu_B$ in each of the Dy(III) ions, the magnetisation of all the Dy(III) centers is relaxing in the ground state itself. The computed energy barrier diagrams of each Dy(III) ion were plotted and are shown in Figures 6 and S19. Similarly, in complex **4-Er**, all nine Er(III) centers' KDs were well-separated, where the energies of the low-lying eight KDs span the range of $410.1 - 448.3 \text{ cm}^{-1}$ (see Tables S15-16 for the g_z -tensor values for the higher excited states). Interestingly, the central Er(III) ion shows similar splitting as the peripheral Er(III) ion values, which can be attributed to the minimum perturbation of its inherently prolate electron density distribution.[87] Consequently, the energy gap of ground to first excited states of Er(III) ions in **4-Er** remain similar across all metal centers, i.e., for Er1, Er2, Er3, Er4, Er5, Er6, Er7, Er8, and Er9 are $103.7 \text{ cm}^{-1}, 31.2 \text{ cm}^{-1}, 34.8 \text{ cm}^{-1}, 29.2 \text{ cm}^{-1}, 30.0 \text{ cm}^{-1}, 28.9 \text{ cm}^{-1}, 34.0 \text{ cm}^{-1}, 35.1 \text{ cm}^{-1},$ and 34.6 cm^{-1} , respectively (see Figure S21). Though the gaps are sufficient to yield, reasonable barrier, the presence of weak axial anisotropy g_z of 15.3900, 16.0329, 15.3720, 16.0425,

15.6753, 15.9399, 15.9526, 15.2836, and 15.2848, (the g_z value of 20.0 expected for the pure $m_J = \pm 15/2$ states of Er(III) ions), led to mixing of $m_J = \pm 15/2$ states with other smaller m_J states and large QTM in the ground state itself for the magnetisation blockade. The SINGLE_ANISO computed anisotropy barrier diagrams for each Er(III) ion in the **4-Er** are shown in Figure S21.

Table 2. *Ab initio* computed energies of low-lying Kramers doublets (in cm^{-1}) of all Dy(III) centers in **2-Dy** complexes and their ground state g -tensor values.

KDs		Energy (cm^{-1})							
	Dy1	Dy2	Dy3	Dy4	Dy5	Dy6	Dy7	Dy8	Dy9
1	0	0	0	0	0	0	0	0	0
2	26.1	32.6	27.6	17.0	21.8	30.5	20.7	37.2	24.4
3	106.9	99.2	97.8	100.0	108.2	111.2	103.2	127.4	112.8
4	191.6	176.5	173.3	172.5	189.3	189.0	188.7	203.2	194.9
5	264.5	234.5	228.6	234.1	264.5	262.1	259.5	278.2	267.2
6	306.7	265.8	264.0	261.7	311.2	319.2	314.1	329.8	312.7
7	400.5	387.9	374.5	376.9	391.5	389.8	395.0	416.2	403.7
8	433.2	420.3	419.7	410.1	423.1	437.6	440.9	448.3	434.7
g-tensors									
g_x	0.3909	0.2580	0.4088	0.6279	0.5245	0.3130	0.6337	0.2291	0.5072
g_y	1.6733	0.9447	1.5064	3.6955	2.6147	1.1394	3.5794	0.7457	2.2873
g_z	17.1996	18.3318	17.9583	15.2152	15.6753	18.1442	15.0608	18.7465	16.5888

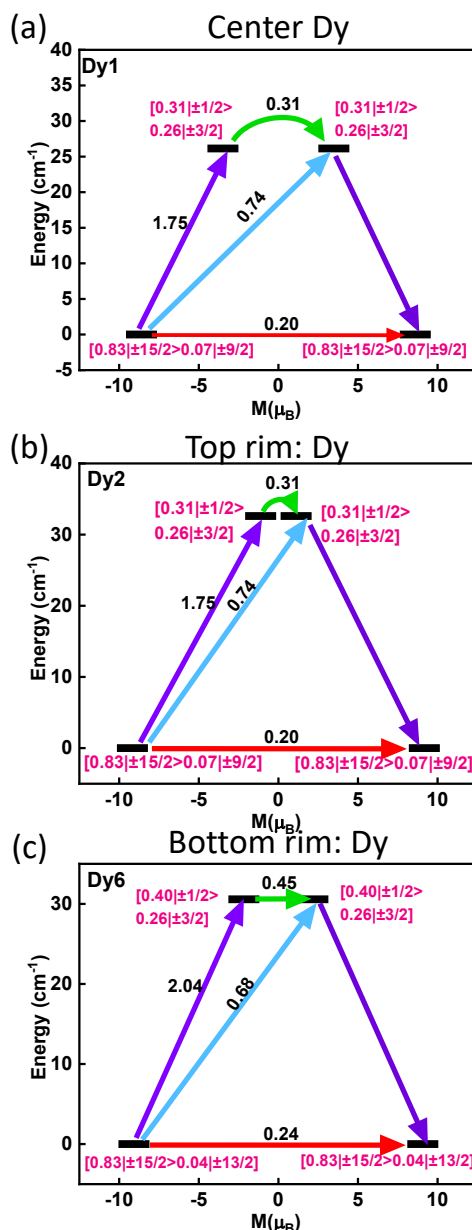


Figure 5. *Ab initio* computed energy barrier. (a) Dy1, (b) Dy2, and (c) Dy6 centers in **2-Dy**. The black bolded lines represent the m_j states. The red arrows show the QTM, green arrows represent the TA-QTM, and the purple and blue arrows show the possible spin-phonon transitions.

The g_{zz} axes of Ln(III) ions in both $\{\text{Ln}_4\}$ square units were seen to align in the plane of the square in **1-Tb**, **2-Dy**, and **3-Ho**, and aligned between the μ_4 -bridging $\text{OH}^-/\text{O}^{2-}$ ligands and the terminal oxygen atom of the diketone ligand, and this can be attributed to the oblate electron density nature of Tb, Dy, and Ho ions.[68,88] Though the g_{zz} axes are in the plane of the square, they do not form any circular pattern; therefore, lacking any anticipated torodicity.[34,53-56] Whereas the g_{zz} axes of Er(III) ions in both $\{\text{Er}_4\}$ square units are perpendicular to the plane of the square in **4-Er**, and this can be attributed to the prolate nature of Er(III) ions' electron density. The axial magnetic anisotropy axes (g_{zz}) of the

central Ln(III) ions in the complexes are found to deviate from the principal symmetry axis (C_4) passing through $\mu_4\text{-O}^{2-}/\text{OH}^-$ and the central Ln in a systematic manner. Such deviation angles are observed to be maximum for **1-Tb** (90°), followed by **2-Dy** (65.5°), and **3-Ho** (25.3°). While **4-Er** is nearly collinear with the principal axis, showing only a minimal deviation of 0.4° . This trend can be rationalized based on the variation in electron density distribution across the lanthanide series. The highly oblate Tb (III) ion exhibits the maximum deviation due to its strong sensitivity to the equatorial ligand field imposed by the surrounding oxygen donors. Dy(III), also oblate in nature, shows significant but comparatively lower deviation. Ho(III), being less oblate, experiences reduced equatorial repulsion and thus displays a smaller inclination toward the principal axis. In contrast, Er(III), characterized by a prolate electron density distribution, is less influenced by the negatively charged oxygen environment, resulting in an anisotropy axis that remains nearly aligned with the principal symmetry axis.

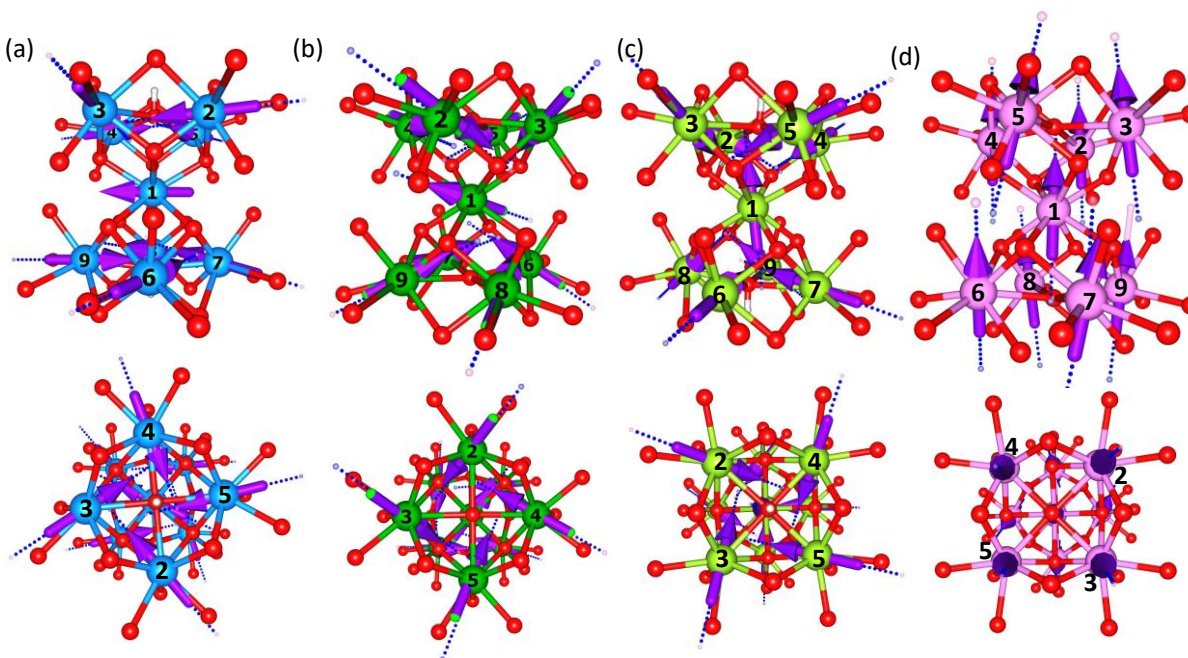


Figure 6. Orientation of the magnetic anisotropy axes. SINGLE_ANISO computed orientations of the magnetic anisotropy axes of each Ln(III) ion in complexes (a) **1-Tb**, (b) **2-Dy**, (c) **3-Ho**, and (d) **4-Er**.

The LoProp charge distribution shown in Figure S22 provides direct insight into how the nature of the central μ_4 -bridging $\text{OH}^-/\text{O}^{2-}$ ligands modulates the electrostatic environment within the $\{\text{Ln}_4\}$ core and, consequently, the magnetic behavior. In **2-Dy**, the oxygen atoms of the central $\mu_4\text{-OH}^-$ unit exhibit LoProp charges around -0.90 to -0.92 , while the peripheral oxygen donors of HBzAc ligands display a broader distribution (-0.66 to -1.01). This comparatively less negative charge on the $\mu_4\text{-OH}^-$ oxygen atoms reflects partial protonation and a reduced ability to concentrate electron density at the cluster centre. The large negative LoProp charges of the $\mu\text{-O}(\text{HBzAc})$ bridged cause the Dy(III) ion's β -electron to deviate from them, reducing the electrostatic repulsion and allowing all four g_z axes to align between the $\mu_4\text{-OH}^-$ ligand and the $\mu\text{-O}(\text{HBzAc})$ ligands. It is found that the electrostatic field generated by the $\mu_4\text{-OH}^-$ ligand along the pseudo-axial directions of the Dy(III) ions is weakened; for Dy(III), which possesses an oblate 4f electron density, optimal stabilization of the highest m_j states requires a strong

and highly localized axial negative charge density. Thus, the anisotropic directions do not follow each other, and this arrangement does not form any circular pattern to enable toroidal behavior in **2-Dy**. In complexes **1-Tb** and **3-Ho**, similar LoProp charges are observed around the coordinated atoms; therefore, orientations of g -anisotropic directions are also similarly aligned for the oblate Tb and Ho ions, thus no possibility to observe toroidal moments. In contrast, **4-Er** incorporates a μ_4 -oxide ligand, which carries a significantly more negative LoProp charge (-0.90), and the surrounding oxygen donors show a more symmetric charge distribution (-0.84 to -0.90) like in other complexes, indicating a more balanced redistribution of electron density throughout the coordination environment. Since the Er(III) ion has a prolate 4f electron density, magnetic anisotropy is intrinsically less sensitive to strong axial negative charge concentration and is instead more tolerant of equatorial electrostatic contributions, and the g_{zz} axes are perpendicular to the plane of the $\{\text{Er}_4\}$ squares.

To elucidate the role of magnetic exchange interactions (J s) between the 4f ions in governing the relaxation dynamics, the magnetic coupling constants in complexes **1-Tb** – **4-Er** were investigated using the POLY_ANISO module.[89,90] The possible magnetic exchange pathways in **1-Tb** – **4-Er** are shown in Figure 7. There are three types of magnetic exchange interactions for each complex: (i) eight J_1 exchange interactions (Dy2-Dy3, Dy3-Dy5, Dy4-Dy5, Dy2-Dy4, Dy6-Dy7, Dy7-Dy8, Dy8-Dy9, Dy6-Dy9), (ii) eight J_2 exchange interactions (Dy1-Dy2, Dy1-Dy3, Dy1-Dy4, Dy1-Dy5, Dy1-Dy6, Dy1-Dy7, Dy1-Dy8, Dy1-Dy9). (iii) four J_3 exchange interactions (Dy3-Dy4, Dy2-Dy5, Dy6-Dy8, Dy7-Dy9). All four complexes exhibit moderate antiferromagnetic J_1 , J_2 , and J_3 interactions and weak intermolecular interactions (zJ), as indicated by the decrease in $\chi_M T$ at the lowest temperatures. **1-Tb**, the fitted exchange constants ($J_1 = -0.002$, $J_2 = -0.001$, $J_3 = -0.001$, $zJ = -0.005 \text{ cm}^{-1}$) indicate very weak antiferromagnetic coupling between the Tb(III) centres.

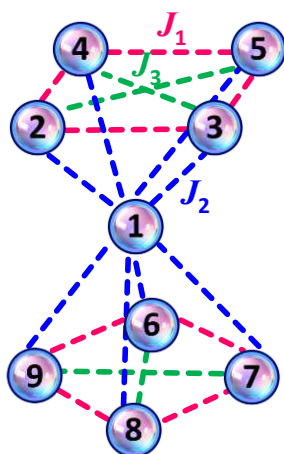


Figure 7. Exchange pathways. Magnetic exchange pathways (J_1 – J_3) for **1-Tb** – **4-Er**.

In **2-Dy**, the exchange interactions are comparatively stronger ($J_1 = -0.12$, $J_2 = -0.07$, $J_3 = -0.13$, $zJ = -0.005 \text{ cm}^{-1}$), yet remain within the weak coupling regime typical of Dy-based clusters. The extracted exchange constants for complex **3-Ho** ($J_1 = -0.18$, $J_2 = -0.17$, $J_3 = -0.16$, $zJ = -0.005 \text{ cm}^{-1}$), the extracted exchange constants indicate comparatively strong exchange. For **4-Er**, the extracted exchange constants ($J_1 = -0.12$, $J_2 = -0.12$, $J_3 = -0.12$, $zJ = -0.001 \text{ cm}^{-1}$) again indicate weak magnetic coupling between the Er(III) centres. The fitted exchange parameters obtained from the POLY_ANISO analysis

indicate that the Ln(III)-Ln(III) interactions in complexes **1-Tb** – **4-Er** are uniformly weak, with J values well below 0.2 cm^{-1} . Such small exchange constants are characteristic of 4f-4f coupling, where the strongly shielded 4f orbitals limit direct overlap and restrict magnetic communication to inefficient superexchange pathways mediated by bridging oxygen atoms.[68,88] All the J values are found to be antiferromagnetic despite the difference in oblate electron density of $m_J = \pm 6$ for Tb(III) and $\pm 15/2$ for Dy(III) ions, ± 8 for Ho(III) ions, and $\pm 15/2$ for Er(III) ions, respectively. As a result, these weak exchange interactions cannot effectively suppress QTM in all four complexes. The weak exchange interactions, therefore, act only as a secondary perturbation, unable to compensate for the transverse crystal-field components introduced by the μ_4 -OH-centred core.

POLY_ANISO-derived exchange-coupled state diagrams were derived based on the above calculated J values (Figures 9 and S23). In complex **1-Tb** and **3-Ho**, none of the metal centres exhibit strong magnetic anisotropy; as a consequence, significant mixing of the $\pm m_J$ states occurs, leading to enhanced tunneling. Furthermore, the weak J s between these Tb-Tb and Ho-Ho ions are not sufficient to quench the QTM, and this is reflected in the large tunneling gaps with $\Delta_{\text{tun}} = 3.94 \text{ cm}^{-1}$ in **1-Tb** and $\Delta_{\text{tun}} = 0.23 \text{ cm}^{-1}$ in **3-Ho** (Tables S18-19) in their ground exchange-coupled states, which facilitate rapid magnetic relaxation and ultimately preclude SMM behaviour as observed in experimental characterisation. In contrast, complexes **2-Dy** and **4-Er** are composed of Kramers ions, for which time-reversal symmetry ensures degeneracy between $\pm m_J$ states, theoretically suppressing QTM and favouring slow magnetic relaxation. In **2-Dy**, although individual Dy(III) centres do not favour slow magnetic relaxation due to significant QTM, the weak AF exchange slightly quenches the QTM in the ground state ($4.2 \times 10^{-6} \mu_B$), and the thermally assisted QTM (TA-QTM) at low-lying excited states persists up to the 19th excited exchange state. Beyond this, at the 20th excited state, the TA-QTM becomes operative, and these low-lying states are in very close proximity, providing an effective relaxation pathway with the relatively small energy barrier ($\sim 2.3 \text{ cm}^{-1}$). A similar trend is observed in **4-Er**, where efficient suppression of quantum tunneling is achieved in the ground state (4.5×10^{-3}) due to these weak J s and is maintained up to the 9th excited exchange-coupled states, and the relaxation occurs between the 10th excited states despite this partial quenching of QTM, yielding a negligible barrier; therefore, the system does not exhibit SMM behavior. These results highlight that while exchange interactions can partially quench QTM, their magnitude is too small to dominate the relaxation dynamics. The primary role is governed predominantly by single-ion anisotropy and the local electrostatic environment, with weak Ln-Ln exchange interactions providing only limited stabilization of the magnetic ground state across the series. These findings indicate that, despite the Kramers nature of the Dy and Er ions and the presence of weak axial anisotropy, significant transverse anisotropy and low-energy relaxation pathways remain sufficiently strong to override the expected suppression of QTM, ultimately resulting in the absence of magnetically blocked states at zero applied dc field or weak tail plots at 2000 Oe for both **2-Dy** and **4-Er** complexes.

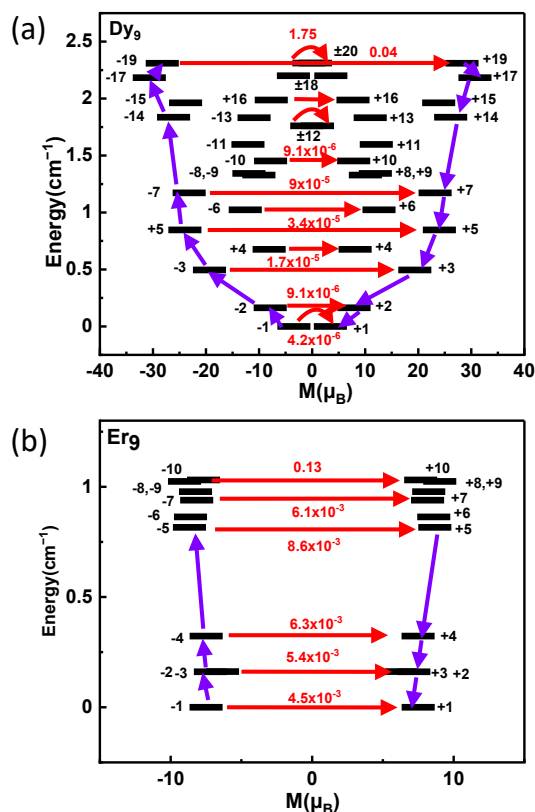


Figure 8. Exchange-coupled states spectra. In (a) **2-Dy** and (b) **4-Er**. The exchange states are placed on the diagram according to their magnetic moments (bold block lines). The red arrows show the tunnelling gaps (Δ_{tun}) between each doublet state, while the purple arrows show the possible pathway through spin-phonon transitions.

Finally, it could be informative to attempt direct comparisons between {Ln₉} systems and those with magnetic characterisation. These {Ln₉} complexes have advanced in architectural platform by having the bulky ligand, which offers rigidity and thereby enhances the cooperative exchange coupling J between the central apex and the peripheral square-pyramidal rims, leading to better isolated ground states.[9,70-81] In particular, for the {Dy₉} analogs, the reported magnetic relaxations are quite comparable and only make tiny contributions to the energy barriers. It is observed that the studied {Dy₉} analog, as well as earlier reported {Dy₉} complexes, lack the zero-field SMM behavior; however, our {Dy₉} complex showed tail plots in the applied dc field of 2000 Oe, which is a consequence of moderate exchange ($> -0.1 \text{ cm}^{-1}$) combined with better crystal-field effects. It was observed in the complex [Dy₉(acac)₁₆(μ₃-OH)₈(μ₄-OH)₂OH·6H₂O, where acac = acetylacetonate,[70] which is similar to our peripheral coordination sphere, where the bulkiness of the organic ligand is increased. However, no impact on the SMM behavior has been observed. In contrast, the hmpH-based [Dy₉(OH)₁₀(hmp)₈(NO₃)₈(DMF)₈](OH) (hmpH = 2-(hydroxymethyl)pyridine),[9] does show tail plots, suggesting the hmpH/NO₃⁻/DMF coordination environment creates a better ligand field for slow relaxation similar to the studied {Dy₉}. The heterodonor character likely contributes to the distinct coordination geometry around the Ln ions in hmpH-based {Dy₉} clusters. Our {Dy₉} analog also possesses asymmetry due to the organic HBzAc⁻ ligand. The bulky phenyl substitution in HBzAc⁻ successfully constructs the high-symmetry nonanuclear framework, but its steric

and electronic profile inadvertently weakens intermetallic exchange. The J values ($>0.1\text{ cm}^{-1}$) were sufficient to partially lift the crystal fields of individual Dy(III) ions, demonstrating that even weak magnetic exchange can enhance the barrier from a zero value at the single-ion level to ($\sim 2.3\text{ cm}^{-1}$) at the POLY_ANISO calculations. The local easy g_z axes of the nine Dy(III) ions lack the requisite cooperative alignment or orthogonal restraint to prevent zero-field tunneling, causing the relaxation to bypass the thermal barrier. We suggest that to transition from weak SMM toward robust zero-field SMM performance in $\{\text{Dy}_9\}$ systems, future synthetic efforts can focus on replacing β -diketonate co-ligands with heterodonor chelates or redox-active bridging ligands that mediate stronger exchange coupling to effectively quench QTM.

Conclusion

In this paper, we report four hourglass-shaped nonanuclear complexes, $\{\text{Ln}_9\}$ ($\text{Ln} = \text{Tb}$ (**1-Tb**), Dy (**2-Dy**), Ho (**3-Ho**), and Er (**4-Er**)), which are synthesised using the 1-Phenyl-1,3-butanedione ligand. These complexes were characterised using single-crystal X-ray diffraction (SC-XRD), Powder X-ray diffraction (PXRD), IR spectroscopy, and SQUID magnetometry. DC magnetic studies reveal that all complexes are antiferromagnetic in nature. The ac susceptibility measurements indicated the absence of magnetic relaxation for all complexes, which is an indication of fast QTM. For the **2-Dy** and **4-Er** analogs, the characteristic SMM behavior is observed with a dc field of 2000 Oe. The *ab initio*-based CASSCF/RASSI/SINGLE_ANISO calculations revealed that although the nonanuclear $\{\text{Ln}_9\}$ complex was expected to show net magnetic behavior, it unfortunately does not show due to weak Ln–Ln coupling and unfavourable Ln(III) anisotropy, which explain the quick magnetic relaxation. This can be attributed to the oblate electron density of the Dy (III) being incompetent to the easy g_z axes, canceling the overall SMM behavior and the possibility to observe toroidal behaviour. Though notable hourglass $\{\text{Dy}_9\}$ clusters have been reported, it was uncovered that the symmetry in the first coordination sphere influences the anisotropy axes of the metal centers more highly compared to the bulk asymmetry in the HBzAc[−] ligand, which was explained in detail in this work.

References

- 1 Emerson-King, J. *et al.* Soft magnetic hysteresis in a dysprosium amide–alkene complex up to 100 kelvin. *Nature*, 2025, **643**, pp. 125, 10.1038/s41586-025-09138-0.
- 2 Guo, F.-S. *et al.* Magnetic hysteresis up to 80 kelvin in a dysprosium metallocene single-molecule magnet. *Science*, 2018, **362**, pp. 1400, 10.1126/science.aav0652.
- 3 Goodwin, C. A. P., Ortu, F., Reta, D., Chilton, N. F. & Mills, D. P. Molecular magnetic hysteresis at 60 kelvin in dysprosocenium. *Nature*, 2017, **548**, pp. 439, 10.1038/nature23447.
- 4 Randall McClain, K. *et al.* High-temperature magnetic blocking and magneto-structural correlations in a series of dysprosium(III) metallocenium single-molecule magnets. *Chem. Sci.*, 2018, **9**, pp. 8492, 10.1039/C8SC03907K.
- 5 Vincent, A. H., Whyatt, Y. L., Chilton, N. F. & Long, J. R. Strong Axiality in a Dysprosium(III) Bis(borolide) Complex Leads to Magnetic Blocking at 65 K. *J. Am. Chem. Soc.*, 2023, **145**, pp. 1572, 10.1021/jacs.2c08568.
- 6 Vanjak, J. C. *et al.* A High-Performance Single-Molecule Magnet Utilizing Dianionic Aminoborolide Ligands. *J. Am. Chem. Soc.*, 2022, **144**, pp. 17743, 10.1021/jacs.2c06698.

- 7 Gould, C. A. *et al.* Ultrahard magnetism from mixed-valence dilanthanide complexes with metal-metal bonding. *Science*, 2022, **375**, pp. 198, 10.1126/science.abl5470.
- 8 Vipanchi & Vignesh, K. R. In Silico Investigation to Rationalize the Effect of Weak Donor versus Strong Donor Halides as Bridges in Dinuclear Dysprosium(III) Single-Molecule Magnets. *Inorg. Chem.*, 2025, **64**, pp. 21551, 10.1021/acs.inorgchem.5c03532.
- 9 Alexandropoulos, D. I. *et al.* A New Family of Nonanuclear Lanthanide Clusters Displaying Magnetic and Optical Properties. *Inorg. Chem.*, 2011, **50**, pp. 11276, 10.1021/ic2013683.
- 10 Collison, D. *et al.* Magnetic and optical studies on an S=6 ground-state cluster [Cr₁₂O₉(OH)₃(O₂CCMe₃)₁₅]: Determination of, and the relationship between, single-ion and cluster spin Hamiltonian parameters. *Inorg. Chem.*, 2003, **42**, pp. 5293, Doi 10.1021/IC034541b.
- 11 Kaur, G., Dwivedi, Y. & Rai, S. B. Synthesis, structural, thermal and optical studies of rare earth coordinated complex: Tb(Sal)₃Phen. *Mater. Chem. Phys.*, 2011, **130**, pp. 1351, <https://doi.org/10.1016/j.matchemphys.2011.09.028>.
- 12 Neese, F., Petrenko, T., Ganyushin, D. & Olbrich, G. Advanced aspects of ab initio theoretical optical spectroscopy of transition metal complexes: Multiplets, spin-orbit coupling and resonance Raman intensities. *Coord. Chem. Rev.*, 2007, **251**, pp. 288, DOI 10.1016/j.ccr.2006.05.019.
- 13 Lin, P. H. *et al.* Importance of Out-of-State Spin-Orbit Coupling for Slow Magnetic Relaxation in Mononuclear Fe-II Complexes. *J. Am. Chem. Soc.*, 2011, **133**, pp. 15806, Doi 10.1021/Ja203845x.
- 14 Bogani, L. & Wernsdorfer, W. Molecular spintronics using single-molecule magnets. *Nat. Mater.*, 2008, **7**, pp. 179.
- 15 Clemente-Juan, J. M., Coronado, E. & Gaita-Arino, A. Magnetic polyoxometalates: from molecular magnetism to molecular spintronics and quantum computing. *Chem. Soc. Rev.*, 2012, **41**, pp. 7464, Doi 10.1039/C2cs35205b.
- 16 E. Coronado, A. J. E. Molecular spintronics and quantum computing. *J. Mater. Chem.*, 2009, **19**, pp. 1670, 10.1039/B901955N.
- 17 Soncini, A. & Chibotaru, L. F. Molecular spintronics using noncollinear magnetic molecules. *Phys. Rev. B.*, 2010, **81**, pp. 132403.
- 18 Aromi, G., Aguila, D., Gamez, P., Luis, F. & Roubeau, O. Design of magnetic coordination complexes for quantum computing. *Chem. Soc. Rev.*, 2012, **41**, pp. 537, Doi 10.1039/C1cs15115k.
- 19 Sessoli, R. *et al.* High-spin molecules: [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄]. *J. Am. Chem. Soc.*, 1993, **115**, pp. 1804, 10.1021/ja00058a027.
- 20 Ishikawa, N., Sugita, M., Ishikawa, T., Koshihara, S. & Kaizu, Y. Lanthanide double-decker complexes functioning as magnets at the single-molecular level. *J. Am. Chem. Soc.*, 2003, **125**, pp. 8694, Doi 10.1021/Ja029629n.
- 21 Chibotaru, L. F. *et al.* Structure, Magnetism, and Theoretical Study of a Mixed-Valence Co₃^{II}Co₄^{III} Heptanuclear Wheel: Lack of SMM Behavior despite Negative Magnetic Anisotropy. *J. Am. Chem. Soc.*, 2008, **130**, pp. 12445.
- 22 Ding, Y.-S. *et al.* Field- and temperature-dependent quantum tunnelling of the magnetisation in a large barrier single-molecule magnet. *Nat. Commun.*, 2018, **9**, pp. 3134, 10.1038/s41467-018-05587-6.
- 23 Gavey, E. L., Beldjoudi, Y., Rawson, J. M., Stamatatos, T. C. & Pilkington, M. Slow relaxation in the first penta-aza Dy(III) macrocyclic complex. *Chem. Commun.*, 2014, **50**, pp. 3741, 10.1039/c4cc00930d.
- 24 Antal, P., Drahoš, B., Herchel, R. & Trávníček, Z. Muffin-like lanthanide complexes with an N₅O₂-donor macrocyclic ligand showing field-induced single-molecule magnet behaviour. *Dalton Trans.*, 2016, **45**, pp. 15114, 10.1039/c6dt02537d.
- 25 Qin, Y. *et al.* Supermolecular Aggregates of Mononuclear and Asymmetric Dinuclear Dysprosium Single-Molecule Magnets Assembled by Intermolecular Hydrogen Bonds. *Cryst. Growth Des.*, 2024, **24**, pp. 6148, 10.1021/acs.cgd.4c00246.
- 26 Vipanchi *et al.* Exploration of the role of carboxylate bridges on the magnetisation dynamics of {Ln^{III}₂} (Ln = Tb, Dy, Ho, and Er) paddle-wheel single-molecule magnets: structure–property correlations. *Dalton Trans.*, 2026, **55**, pp. 10602, 10.1039/d6dt01456a.
- 27 Zhu, Z. & Tang, J. Lanthanide single-molecule magnets with high anisotropy barrier: where to from here?
- 28 Gebrezgiabher, M. *et al.* Lanthanide-Based Single-Molecule Magnets Derived from Schiff Base Ligands of Salicylaldehyde Derivatives. *Inorganics* **8**, 66 (2020).
- 29 Wang, Y., Luo, Q. C. & Zheng, Y. A.-O. X. Organolanthanide Single-Molecule Magnets with Heterocyclic Ligands.
- 30 Woodruff, D. N., Winpenny, R. E. P. & Layfield, R. A. Lanthanide Single-Molecule Magnets. *Chem. Rev.*, 2013, **113**, pp. 5110, 10.1021/cr400018q.

- 31 Guo, Y.-N., Chen, X.-H., Xue, S. & Tang, J. Molecular Assembly and Magnetic Dynamics of Two Novel Dy₆ and Dy₈ Aggregates. *Inorg. Chem.*, 2012, **51**, pp. 4035, 10.1021/ic202170z.
- 32 Tian, H., Bao, S.-S. & Zheng, L.-M. Enlarging the ring by incorporating a phosphonate coligand: from the cyclic hexanuclear to octanuclear dysprosium clusters. *Dalton Trans.*, 2015, **44**, pp. 14208, 10.1039/c5dt02468d.
- 33 Li, Y.-L. *et al.* Double butterfly-shaped octanuclear dysprosium clusters: structure, magnetism and assembly mechanism. *CrystEngComm*, 2023, **25**, pp. 225, 10.1039/d2ce01506d.
- 34 Zhang, H.-L. *et al.* Single-Molecule Toric Design through Magnetic Exchange Coupling. *Matter*, 2020, **2**, pp. 1481, <https://doi.org/10.1016/j.matt.2020.02.021>.
- 35 Lu, J., Li, X.-L., Jin, C., Yu, Y. & Tang, J. Dysprosium-based linear helicate clusters: syntheses, structures, and magnetism. *New J. Chem.*, 2020, **44**, pp. 994, 10.1039/c9nj05192a.
- 36 Wang, H.-L. *et al.* Tracking the Stepwise Formation of the Dysprosium Cluster (Dy₁₀) with Multiple Relaxation Behavior. *Inorg. Chem.*, 2019, **58**, pp. 9169, 10.1021/acs.inorgchem.9b00760.
- 37 Miao, Y.-L. *et al.* Two novel Dy₈ and Dy₁₁ clusters with cubane [Dy₄(μ³-OH)₄]₈⁺ units exhibiting slow magnetic relaxation behaviour. *Dalton Trans.*, 2011, **40**, pp. 10229, 10.1039/c1dt10613a.
- 38 Wang, K. *et al.* Diacylhydrazone-assembled {Ln₁₁} nanoclusters featuring a “double-boats conformation” topology: synthesis, structures and magnetism. *Dalton Trans.*, 2018, **47**, pp. 2337, 10.1039/c7dt03179c.
- 39 Dinca, A. S. *et al.* Aggregation of [Ln₁₂^{III}] clusters by the dianion of 3-formylsalicylic acid. Synthesis, crystal structures, magnetic and luminescence properties. *Dalton Trans.*, 2019, **48**, pp. 1700, 10.1039/c8dt04602f.
- 40 Miao, Y.-L., Liu, J.-L., Leng, J.-D., Lin, Z.-J. & Tong, M.-L. Chloride templated formation of {Dy₁₂(OH)₁₆}₂₀⁺ cluster core incorporating 1,10-phenanthroline-2,9-dicarboxylate. *Cryst. Eng. Comm.*, 2011, **13**, pp. 3345, 10.1039/c1ce05211j.
- 41 Hao, J. *et al.* Ligand Induced Double-Chair Conformation Ln₁₂ Nanoclusters Showing Multifunctional Magnetic and Proton Conductive Properties. *Inorg. Chem.*, 2022, **61**, pp. 3690, 10.1021/acs.inorgchem.1c03866.
- 42 Peng, J.-M. *et al.* Series of the Largest Dish-Shaped Dysprosium Nanoclusters Formed by In Situ Reactions. *Inorg. Chem.*, 2022, **61**, pp. 6094, 10.1021/acs.inorgchem.2c00221.
- 43 Zou, Y. *et al.* Pentagon-type Ln₁₅ (Ln = Dy, Tb, Eu, Sm, Ho) clusters with different anion templates: magnetic and luminescence properties. *Dalton Trans.*, 2022, **51**, pp. 16383, 10.1039/d2dt02712g.
- 44 Thielemann, D. T. *et al.* Peptoid-Ligated Pentadecanuclear Yttrium and Dysprosium Hydroxy Clusters. *Chem. Eur. J.*, 2015, **21**, pp. 2813, <https://doi.org/10.1002/chem.201405569>.
- 45 Li, Y.-L. *et al.* Truncation reaction regulates the out-to-in growth mechanism to decrypt the formation of brucite-like dysprosium clusters. *Dalton Trans.*, 2022, **51**, pp. 197, 10.1039/d1dt03137f.
- 46 Tian, H. *et al.* Ring-forming transformation associated with hydrazone changes of hexadecanuclear dysprosium phosphonates. *Dalton Trans.*, 2021, **50**, pp. 1119, 10.1039/d0dt03536j.
- 47 Peng, S. *et al.* In situ synthesized homochiral dysprosium-oxo clusters with threonine Schiff bases. *Chin. Chem. Lett.*, 2023, **34**, pp. 108044, <https://doi.org/10.1016/j.ccllet.2022.108044>.
- 48 D'Alessio, D. *et al.* Lanthanoid “Bottlebrush” Clusters: Remarkably Elongated Metal–Oxo Core Structures with Controllable Lengths. *J. Am. Chem. Soc.*, 2014, **136**, pp. 15122, 10.1021/ja506677h.
- 49 Lin, W.-Q. *et al.* Lanthanide Oxide Clusters: From Tetrahedral [Dy₄(μ₄-O)]₁₀⁺ to Supertetrahedral [Ln₂₀(μ₄-O)₁₁]₃⁸⁺ (Ln=Tb, Dy, Ho, Er). *Chem. Eur. J.*, 2013, **19**, pp. 12254, <https://doi.org/10.1002/chem.201301397>.
- 50 Luo, Z.-R. *et al.* Assembly of Dy₆₀ and Dy₃₀ cage-shaped nanoclusters. *Commun. Chem.*, 2020, **3**, pp. 30, 10.1038/s42004-020-0276-3.
- 51 Kong, X.-J., Wu, Y., Long, L.-S., Zheng, L.-S. & Zheng, Z. A Chiral 60-Metal Sodalite Cage Featuring 24 Vertex-Sharing [Er₄(μ₃-OH)₄] Cubanes. *J. Am. Chem. Soc.*, 2009, **131**, pp. 6918, 10.1021/ja901214d.
- 52 Gatteschi, D., Sessoli, R. & Villain, J. *Molecular Nanomagnets*, (Oxford University Press, 2006).
- 53 Ungur, L., Lin, S.-Y., Tang, J. & Chibotaru, L. F. Single-molecule toroids in Ising-type lanthanide molecular clusters. *Chem. Soc. Rev.*, 2014, **43**, pp. 6894, 10.1039/C4CS00095A.
- 54 Murray, K. S., Vignesh, K. R., Hymas, K. & Soncini, A. in *Single Molecule Toroids: Synthetic Strategies, Theory and Applications* (ed Keith Murray) 1 (Springer International Publishing, 2022).
- 55 Li, X.-L. & Tang, J. Recent developments in single-molecule toroids. *Dalton Trans.*, 2019, **48**, pp. 15358, 10.1039/c9dt02113b.
- 56 Vignesh, K. R. & Rajaraman, G. Strategies to Design Single-Molecule Toroids Using Triangular {Ln₃} (n) Motifs, *ACS Omega*, 2021, **6**, pp. 32349, 10.1021/acsomega.1c05310.

- 57 Lin, S.-Y., Wang, C., Zhao, L. & Tang, J. Enantioselective Self-Assembly of Triangular Dy₃ Clusters with Single-Molecule Magnet Behavior. *Chem. Asian J.*, 2014, **9**, pp. 3558, <https://doi.org/10.1002/asia.201402670>.
- 58 Kwon, H. *et al.* Triangular ^{(C^{Si}Pr⁵)₃}Ln₃H₃l₂ (Ln = Tb, Dy, Ho, Er, Tm) Clusters with Lanthanide-Dependent Bonding, Valence Delocalization, and Magnetic Anisotropy.
- 59 Tang, J. *et al.* Dysprosium Triangles Showing Single-Molecule Magnet Behavior of Thermally Excited Spin States. *Angew. Chem. Int. Ed.*, 2006, **45**, pp. 1729, 10.1002/anie.200503564.
- 60 Chibotaru, L. F., Ungur, L. & Soncini, A. The Origin of Nonmagnetic Kramers Doublets in the Ground State of Dysprosium Triangles: Evidence for a Toroidal Magnetic Moment. *Angew. Chem. Int. Ed.*, 2008, **47**, pp. 4126, <https://doi.org/10.1002/anie.200800283>.
- 61 Fernandez Garcia, G. *et al.* A Dy₄ Cubane: A New Member in the Single-Molecule Toroids Family. *Angew. Chem. Int. Ed.*, 2018, **57**, pp. 17089, <https://doi.org/10.1002/anie.201810156>.
- 62 Guo, P.-H. *et al.* The First {Dy₄} Single-Molecule Magnet with a Toroidal Magnetic Moment in the Ground State. *Inorg. Chem.*, 2012, **51**, pp. 1233, 10.1021/ic202650f.
- 63 Blagg, R. J., Muryn, C. A., McInnes, E. J. L., Tuna, F. & Winpenny, R. E. P. Single Pyramid Magnets: Dys Pyramids with Slow Magnetic Relaxation to 40 K. *Angew. Chem. Int. Ed.*, 2011, **50**, pp. 6530, 10.1002/ange.201101932.
- 64 Peng, J.-B. *et al.* Trigonal Bipyramidal Dy₅ Cluster Exhibiting Slow Magnetic Relaxation. *Inorg. Chem.*, 2012, **51**, pp. 2186, 10.1021/ic202147h.
- 65 Lin, S.-Y. *et al.* Coupling Dy₃ Triangles to Maximize the Toroidal Moment. *Angew. Chem. Int. Ed.*, 2012, **51**, pp. 12767, 10.1002/anie.201206602.
- 66 Novitchi, G. *et al.* Heterometallic Cu^{II}/Dy^{III} 1D chiral polymers: chirogenesis and exchange coupling of toroidal moments in trinuclear Dy₃ single molecule magnets. *Chem. Sci.*, 2012, **3**, pp. 1169, 10.1039/C2SC00728B.
- 67 Vignesh, K. R. *et al.* Ferrotoroidic ground state in a heterometallic {Cr^{III}Dy₆^{III}} complex displaying slow magnetic relaxation. *Nat. Commun.*, 2017, **8**, pp. 1023, 10.1038/s41467-017-01102-5.
- 68 Vignesh, K. R. *et al.* Slow Magnetic Relaxation and Single-Molecule Toroidal Behaviour in a Family of Heptanuclear {Cr^{III}Ln^{III}₆} (Ln=Tb, Ho, Er) Complexes. *Angew. Chem. Int. Ed.*, 2018, **57**, pp. 779, <https://doi.org/10.1002/anie.201711844>.
- 69 Ashtree, J. M. *et al.* Tuning the Ferrotoroidic Coupling and Magnetic Hysteresis in Double-Triangle Complexes {Dy₃M^{III}Dy₃} via the M^{III}-linker. *Eur. J. Inorg. Chem.*, 2021, **2021**, pp. 435, <https://doi.org/10.1002/ejic.202001082>.
- 70 Pandey, P. *et al.* Hourglass-Shaped Homo- and Heteronuclear Nonanuclear Lanthanide Clusters: Structures, Magnetism, Photoluminescence, and Theoretical Analysis. *Inorg. Chem.*, 2024, **63**, pp. 11963, 10.1021/acs.inorgchem.4c00332.
- 71 Knighton, R. C. *et al.* Upconversion in molecular hetero-nonanuclear lanthanide complexes in solution. *Chem. Commun.*, 2021, **57**, pp. 53, 10.1039/D0CC07337G.
- 72 Xu, G. *et al.* Synthesis and Structural Characterization of Nonanuclear Lanthanide Complexes. *Inorg. Chem.*, 2002, **41**, pp. 6802, 10.1021/ic025929u.
- 73 G. Hubert-Pfalzgraf, L., Miele-Pajot, N., Papiernik, R. & Vaissermann, J. A novel example of self-assembly in lanthanide chemistry: synthesis and molecular structure of [Na(EtOH)₆][Y₉(μ₄-O)₂(μ₃-OH)₈]{μ-η²-MeC(O)CHC(O)OEt}₈{η²-MeC(O)CHC(O)OEt}₈}⁺. *J. Chem. Soc., Dalton Trans.*, 1999, pp. 4127, 10.1039/A907755C.
- 74 Addamo, M., Bombieri G Fau - Foresti, E., Foresti E Fau - Grillone, M. D., Grillone Md Fau - Volpe, M. & Volpe, M. Assembling process of charged nonanuclear cationic lanthanide(III) clusters assisted by dichromium decacarbonyl hydride.
- 75 Volpe, M., Bombieri, G., Clemente, D. A., Foresti, E. & Grillone, M. D. Synthesis and physico-chemical characterization of a new series of hydroxide ion acetylacetonate lanthanide(III)—ditungsten decacarbonyl hydride complexes. *J. Alloys Compd.*, 2004, **374**, pp. 382, <https://doi.org/10.1016/j.jallcom.2003.11.153>.
- 76 Petit, S., Baril-Robert, F., Pilet, G., Reber, C. & Luneau, D. Luminescence spectroscopy of europium(III) and terbium(III) penta-, octa- and nonanuclear clusters with β-diketonate ligands. *Dalton Trans.*, 2009, pp. 6809, 10.1039/B822883C.
- 77 Baril-Robert, F. *et al.* Site-Selective Lanthanide Doping in a Nonanuclear Yttrium(III) Cluster Revealed by Crystal Structures and Luminescence Spectra. *Inorg. Chem.*, 2010, **49**, pp. 10970, 10.1021/ic1011082.
- 78 Xu, X. *et al.* A diaboloid-shaped Dy₉ cluster: synthesis, crystal structure and magnetic properties. *Dalton Trans.*, 2011, **40**, pp. 6440, 10.1039/C1DT10450K.

- 79 Singh-Wilmot, M. A. *et al.* Nonanuclear lanthanide(III) nanoclusters: Structure, luminescence and magnetic properties. *Polyhedron*, 2013, **53**, pp. 187, <https://doi.org/10.1016/j.poly.2013.01.028>.
- 80 Zou, H.-H., Sheng, L.-B., Chen, Z.-L. & Liang, F.-P. Lanthanide nonanuclear clusters with sandglass-like topology and the SMM behavior of dysprosium analogue. *Polyhedron*, 2015, **88**, pp. 110, <https://doi.org/10.1016/j.poly.2014.12.024>.
- 81 Huang, Y. *et al.* Rationally assembled nonanuclear lanthanide clusters: Dy₉ displays slow relaxation of magnetization and Tb₉ serves as luminescent sensor for Fe³⁺, CrO₄²⁻ and Cr₂O₇²⁻. *New J. Chem.*, 2019, **43**, pp. 19344, 10.1039/C9NJ04893F.
- 82 Ekennia, A. C., Onwudiwe, D. C., Olasunkanmi, L. O., Osowole, A. A. & Ebenso, E. E. Synthesis, DFT Calculation, and Antimicrobial Studies of Novel Zn(II), Co(II), Cu(II), and Mn(II) Heteroleptic Complexes Containing Benzoylacetone and Dithiocarbamate.
- 83 Aquilante, F. *et al.* Molcas 8: New capabilities for multiconfigurational quantum chemical calculations across the periodic table. *J. Comput. Chem.*, 2016, **37**, pp. 506, <https://doi.org/10.1002/jcc.24221>.
- 84 Dey, S. & Rajaraman, G. An approach to estimate the barrier height for magnetisation reversal in {Dy₂} SMMs using ab initio calculations. *Dalton Trans.*, 2020, **49**, pp. 14781, 10.1039/D0DT03129A.
- 85 Sharma, N., Vipanchi & Vignesh, K. R. Impact of Bulky Counteranions on the Magnetization Dynamics of Cationic D_{5h}-Symmetrized Dy(III) Single-Ion Magnets. *Cryst. Growth Des.*, 2026, 10.1021/acs.cgd.6c00562.
- 86 Kumar, P. *et al.* Peroxide Ligands Support Tetranuclear Lanthanide Ensembles: Synthesis, Structure, Magnetism, and Theoretical Studies. *Inorg. Chem.*, 2025, **64**, pp. 22802, 10.1021/acs.inorgchem.5c03943.
- 87 Rinehart, J. D. & Long, J. R. Exploiting single-ion anisotropy in the design of f-element single-molecule magnets. *Chem. Sci.*, 2011, **2**, pp. 2078, 10.1039/C1SC00513H.
- 88 Langley, S. K., Vignesh, K. R., Moubarak, B., Rajaraman, G. & Murray, K. S. Oblate versus Prolate Electron Density of Lanthanide Ions: A Design Criterion for Engineering Toroidal Moments? A Case Study on {Ln^{III}} (Ln=Tb, Dy, Ho and Er) Wheels. *Chem. Eur. J.*, 2019, **25**, pp. 4156, <https://doi.org/10.1002/chem.201805765>.
- 89 Lines, M. E. Orbital Angular Momentum in the Theory of Paramagnetic Clusters. *J. Chem. Phys.*, 1971, **55**, pp. 2977, doi:<http://dx.doi.org/10.1063/1.1676524>.
- 90 Chibotaru, L. F. & Ungur, L. *Program POLY_ANISO*, 2006, **University of Leuven**.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data supporting the findings of this study are included in the supplementary information (SI).

Supplementary information: crystallographic data, PXRD, magnetic plots and tables, and computational analysis plots and tables. See DOI:

CCDC: 2583384-2583387 contains the supplementary crystallographic data for this paper.

Funding

Anusandhan National Research Foundation (ANRF)/SERB: Research grant No. SRG/2023/000286.

Acknowledgements

Vipanchi thanks IISER Mohali for providing a PhD fellowship. K. R. V. thanks IISER Mohali for High Performing Computing Facility for providing computing resources, other laboratory and infrastructural facilities, library facilities, and ANRF (SERB) for providing a start-up research grant (SRG/2023/000286).

KRV thanks the Department of Chemical Sciences, IISER Mohali, for the central X-ray facility of IISER Mohali for the PXRD facility.

Author contributions

Vipanchi: Synthesis, Computational Methodology, Data analysis, and Writing - original draft.

Keiichi Katoh and Nobuto Funakoshi: Performance of magnetic measurements and analysis;

Nabanita Deb: Collection of structural data and Refinement.

Arun Kumar Bar: Validation - Crystal data, Resources, Funding acquisition and Supervision

Masahiro Yamashita: Validation - Magnetic data, Resources, Funding acquisition and Supervision

Kuduva R. Vignesh: Conceptualization, Supervision, Resources, Software, Project administration, Funding acquisition, Writing - original draft, review & editing.

All the authors reviewed and approved the manuscript.

Competing interests

“The authors declare no competing interests.”

Supplementary information

Experimental Details, Structural parameters; Figures S1-S8, Table S1-S10, PXRD; Figures S9-S12, Magnetic measurements; Figures S13-S17, Theoretical Studies; Tables S11-S29, SINGLE_ANISO Computed Energy Barrier Diagram; Figures S18-S21, Lowest Exchange Tunneling Gap; Tables S18-S19; LoProp Charges; Figure S22, Low-Lying Exchange Coupled States Relaxation Diagram; Figure S23.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [ESILn9Hourglassfinal.docx](#)