



Single-molecule toroics in Ising-type lanthanide molecular clusters

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Single-molecule toroics in Ising-type lanthanide molecular clusters

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5 Single-molecule toroics (SMTs) are defined, by analogy with single-molecule magnets, as bistable molecules with toroidal magnetic state, which seem to be most promising for future applications in quantum computing and information storage and used as multiferroic materials with magnetoelectric effect. As an interdisciplinary research area that spans chemistry, physics and material sciences, synthetic chemists have produced systems suitable for detailed study by physicists and materials scientists, while
 10 *ab initio* calculations have been playing a major role in the detection of toroidal magnetization and the advancement of this field. In this tutorial review, we demonstrate the research developed in the fascinating and challenging field of molecular-based SMTs with particular focus on how recent studies tend to address the issue of toroidal arrangement of magnetic moment in these systems. Herein, nine
 15 typical SMTs are summarized, showing that the assembly of wheel-shaped complexes with the high symmetry of the molecule unit and strong intra-molecular dipolar interactions using strong anisotropy metal ions represents the most promising route toward the design of toroidal moment. Furthermore, the linkage of such robust toroidal moment units with ferromagnetic type through appropriate bridging ligands enhances the toroidal magnetic moment per unit cell.

Key Learning Points:

- 20 [1]. This paper is about single-molecule toroics (SMTs) which are defined as molecules with toroidal magnetic state.
 [2]. The molecular symmetry, local magnetic moment and magnetic interaction are essential parameters for toroidal moment.
 [3]. The field of SMTs will provide an even more fundamental knowledge and potential for future applications as multiferroic materials.
 [4]. *Ab initio* calculations and single-crystal magnetic studies are the tools allowing to detect the toroidal moment.
 [5]. Progress of the emerging field of SMTs still faces many challenges.

25 Introduction

Toroidal magnetic moment characterized by vortex distributions of magnetic dipoles is regarded as the third kind of electromagnetic moments after traditionally polarization and magnetization.¹⁻³ A classical example is a ring-shaped torus with
 30 current windings, as shown in Fig. 1a.³⁻⁵ It is known as a multi-spin object breaking both space inversion and time reversal symmetries (Fig. 1b), and can be generated either by persistent orbital currents or certain spin orderings.^{4, 6} In the latter case, toroidal moment (t) is defined as the outer product of the
 35 displacement of magnetic ions from the centre position r_i and their spins S_i , i.e. $t \propto \sum_i r_i \times S_i$.^{4, 7}

In reality, the toroidal moment has long been discussed in the context of particle physics in 1958 by Zel'dovich who called them as anapoles.⁸ However, the existence of a macroscopic
 40 moment asymmetric under both time reversal and space inversion has long been remained elusive because the weaker response, compared with electric or magnetic dipole moment, and is usually neglected.^{9, 10} An important step followed when finally toroidal domains were observed by optical second harmonic generation in
 45 LiCoPO_4 ,^{3, 11} which suggests that ferrotoroidicity (ferrotoroidic is

defined to have a spontaneous alignment of toroidal moments^{1, 12, 13}) is a fundamental form of ferroic order, along with ferromagnetism, ferroelectricity, and ferroelasticity. As is evident from Fig. 2,³ moments have the basic symmetry requirements of a
 50 multiferroic material, for the ferrotoroidic state, toroidal moments change sign not only upon time reversal, which inverts electric currents and spins, but also upon spatial inversion.¹⁴ This result provides a motivation for investigating toroidal effects in the ferroelectric phases of multiferroic materials, in which the
 55 space-asymmetric electric polarization is induced by a time-asymmetric and space-asymmetric magnetic order.¹³

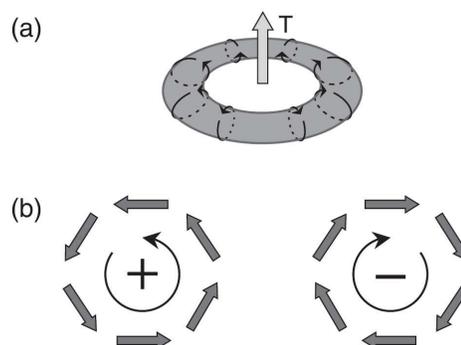


Fig. 1 (a) Ring-shaped solenoid with electric-current loops as classical example for a toroidal moment. (b) Quantum-mechanical example of a toroidal moment with two opposite toroidal moments. Adapted from Ref. [4].

In particular, the unique property of toroidal response is a non-radiating configuration which results from destructive interference between electromagnetic fields.^{5, 15} To be able ultimately to observe the weak toroidal dipole moment, metamaterials were designed to suppress the component of electric or magnetic dipole moments.^{9, 16-19} The toroidal dipole response in metamaterials can be explained intuitively by a magnetoelectric effect. In 2010, toroidal response in microwave region was first experimentally demonstrated and separated from other multipoles by an artificial metamaterial;¹⁷ in 2012, the toroidal metamaterial was theoretically studied in far-infrared wavelengths by scaling down the split-ring structure;¹⁹ in the same year, toroidal response is demonstrated in the optical regime by designing a toroid-like metamaterial comprising six asymmetric double bars.⁹ The resonance-enhanced optical toroidal response can provide an experimental avenue for various interesting optical phenomena associated with the elusive toroidal moment.

Due to potential applications based on the antisymmetric linear magnetoelectric effect, the elusive electromagnetic response of toroidal moment has attracted great attentions in molecular and ferroelectric physics.^{4, 6, 7, 17, 20, 21} In recent years, a lot of intriguing properties based on toroidal moment have been observed and other potential applications for the toroidal response in nanostructured artificial materials have been reported, such as circular dichroism and polarization controllability due to the optical activity,²² and negative refraction and backward waves due to the toroidal nature.^{20, 23} Furthermore, optical nonlinearity enhancement was experimentally confirmed attributed to the toroidal susceptibility.²⁴

As above mentioned, the search for the toroidal moment is mainly on atom-based materials in solid-state chemistry and physics, particularly in multiferroics.^{4, 12} Contrary to them, molecular materials offer much richer possibilities for the design of multicentre systems with desired non-collinear arrangement of magnetic moments, including the one corresponding to toroidal magnetization, Fig. 1b. Thus, a Dy₃ triangular cluster has been recently synthesized (Fig. 3a) displaying non-magnetic ground state,²⁵ as evidenced by low-temperature magnetism of this complex (Fig. 3c,d). The *ab initio* calculations of CASSCF/RASSI level, performed with MOLCAS suite of programs,²⁶ have shown that the reason for non-magnetic ground state in this compound is an almost toroidal arrangement of magnetic moments on Dy sites (arrows in Fig. 3 a, b),^{27, 28} which explains their almost complete mutual cancellation in the ground

state. This was the first detection of a toroidal moment in a molecular system, which caused its intensive study, first of all, in the original Dy₃ triangle.²⁹⁻³² In particular, investigations of magnetoelectric properties in this compound revealed toroidal moment specific magnetoelectric and magneto-current effects related to its toroidal moment.^{33, 34} It was shown that this molecule is rather rich and versatile for manipulation by external electric and magnetic fields or just by current. By analogy with single-molecule magnets (SMMs), the Dy₃ clusters could be called as single-molecule toroics (SMTs).³⁰

For molecule-based material, SMTs belong to a new class of magnetic materials in which toroidal moment arises from vortex arrangement of local magnetic moments due to wheel-shaped topology (or local wheel-shape) and specific magnetic interaction between metal sites. Toroidal moment can be influenced by the molecular symmetry, local magnetic moment, as well as magnetic interaction including dipole interaction and exchange interaction between metal ions.^{35, 36} A key feature of toroidal magnetic moments is their insensitivity to homogeneous magnetic fields.⁴ Moreover, qubits or memory storage elements designed on the basis of toroidal moments could be packed much more densely than spin qubits or SMM correspondingly, because the magnetic field produced by a net toroidal moment decays much faster than the field of a normal magnetic dipole,³⁵ allowing, in principle, for further miniaturization of the designed nanodevices. Finally, the toroidal magnetic moment interacts with a dc current passing through magneto-electric coupling,^{30, 34} depending on symmetry, which allows the moment to be controlled and manipulated purely by electrical means, a property much sought-after for molecular devices.

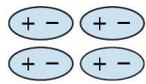
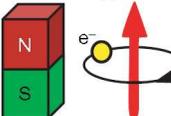
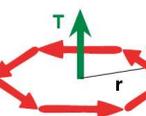
Time \ Space	Invariant	Change
Invariant	Ferroelastic 	Ferroelectric 
Change	Ferromagnetic 	Ferrotoroidal 

Fig. 2 Possible forms of ferroic order under the parity operations of space and time. Adapted from Ref. [3].

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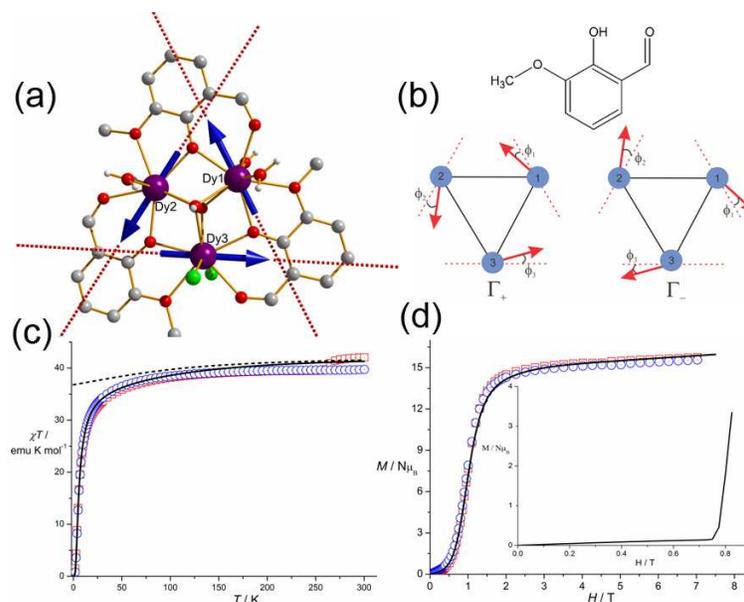


Fig. 3 (a) The structure of Dy₃-1 with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state. Adapted from Ref. [29]. (b) The two components of the ground Kramer's doublet. Adapted from Ref. [29]. (c-d) The static magnetic properties of Dy₃-1 and their *ab initio* simulations (lines). Adapted from Ref. [28].

5 Molecular materials can offer an appealing alternative route towards SMTs and ultimately multiferroic compounds, because SMTs can be designed and isolated in a controllable manner using bottom up molecular approach. Single dispersed SMTs represent the simplest molecular units which allow the study of
 10 magnetic interactions between spin carriers, molecular symmetry as well as local magnetic moment, thus one could potentially build larger molecules with enhanced toroidal magnetization. However, a systematic research on the SMTs is still lacking. We believe that it is timely to review the researches developed and
 15 problems in this emerging field for a better understanding of the quantum mechanism of intramolecular interactions involving toroidal spin structures. Therefore, in this tutorial review we will focus on the structure and magnetic properties as well as *ab initio* calculations of SMTs with the hopes of shedding some light on
 20 the design of SMTs. By investigating such systems one could expect to understand the nature of toroidal response interactions between lanthanide ions as well as the factors governing the toroidal arrangement of anisotropy axes and magnetic moments on the corresponding metal ions.

25 Table 1. Classification of SMTs based on toroidal magnetization and traditional magnetization.

	Net toroidal moment					Zero toroidal moment CuDy ₃	Mixed moment Dy ₆ -2
	Dy ₄	Dy ₆ wheel	Dy ₃ -1	Dy ₃ -2	Dy ₆ -1		
T_z	≠ 0	≠ 0	≠ 0	≠ 0	≠ 0	= 0	$T_{z1} + T_{z2}$
M/μ_B	= 0	= 0	= 0.56	= 11.5	≠ 0	= 0.8	= 13.1

2. Survey of SMTs

At present, SMTs form a relatively small group of complexes whose local easy axes on the metal sites have a toroidal
 30 arrangement, which defines their macroscopic magnetic behaviour. Such compounds are currently only known with dysprosium complexes and as all show SMM behaviour. The advantages of lanthanides (in particular Dy) over transition metals for obtaining SMTs is due to the strong uniaxial magnetic
 35 anisotropy of the Dy ions in common low-symmetry ligand environments ($g_z \gg g_{x,y}$). Large values of the local magnetic moments on the magnetic sites afford strong intramolecular dipolar coupling, which was found to be responsible for the toroidal moment of the ground states of all investigated SMTs.
 40 Since the discovery of toroidal magnetic state in Dy₃ triangle,^{25, 27-29} the fascinating magnetic properties have ignited new interest in the exploitation of coupling several such Dy₃ building blocks to obtain larger dysprosium compounds.³⁷⁻⁴⁴ Indeed, recent efforts have produced fascinating results with the successful
 45 assembly of two typical Dy₆ complexes^{42, 43} and a heterometallic 1D CuDy₃ coordination polymers,⁴⁴ which not only show the similar structural features to Dy₃ triangles in each building block but also retain the functionality of Dy₃ triangles, the toroidal arrangement of single-ion magnetic anisotropy axes. Meanwhile,
 50 other three Dy₃ triangle compounds^{45, 46} and a coplanar Dy₄ compound⁴⁷ as well as a Dy₆ wheel compound³⁶ have been reported with toroidal magnetic structure. As in the case of Dy₃ triangle, the existence of toroidal moment in all these compounds has been detected exclusively by *ab initio* calculations. Despite
 55 the limited number of examples, SMTs can be subdivided into four types based on magnetic moment (Table 1), that is, net

toroidal moment compounds, mixed-moment compounds, zero toroidal moment compounds and enhanced toroidal moment compounds. In the following we will review each of these groups

of complexes in the order they have been mentioned, without paying attention to the chronological order of their investigation.

2.1 Net toroidal moment SMTs

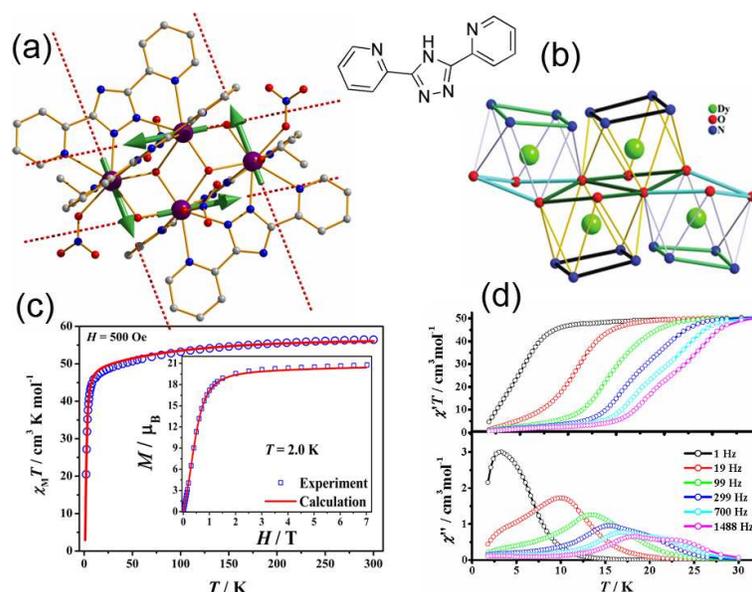


Fig. 4 The structure and magnetic properties of compound Dy_4 . Adapted from Ref. [47].

Net toroidal moment SMTs refer to the compounds with a toroidal magnetic state in absence of a conventional total magnetic moment. This situation is achieved with special symmetry requirements, depending on the number of Ln ions and the topology of their arrangement.

The first net toroidal moment SMT was observed in a novel planar Dy_4 cluster (Fig. 4), $[\text{Dy}_4(\mu_3\text{-OH})_2(\mu\text{-OH})_2(2,2\text{-bpt})_4(\text{NO}_3)_4(\text{EtOH})_2]$ [Dy_4 ; 2,2-bptH = 3,5-bis(pyridin-2-yl)-1,2,4-triazole], reported by M-L. Tong et al.⁴⁷ The compound is a centrosymmetric complex with four precisely coplanar Dy ions with the Dy...Dy distances of 3.73–4.28 Å. All Dy ions are the vertices of the parallelogram bridged by two $\mu_3\text{-OH}$, two $\mu\text{-OH}$, and four $\mu\text{-bpt}$ ligands. Each eight-coordinate Dy ion possesses a distorted square-antiprismatic geometry. Ac (alternating current) susceptibilities (Fig. 4d) are indicative of slow relaxation of the magnetization associated with SMM behaviour ($U_{\text{eff}}/k_{\text{B}} = 80(3)$ K). Moreover, the $\chi''T$ value (χ'' , in-phase of the ac susceptibilities) drops to nearly 0 indicates the nonmagnetic ground state.

The *ab initio* calculations were performed in order to gain insight into the local electronic and magnetic properties on

individual Dy centres. It was found that the main values of the g_z tensors of the lowest doublets on Dy sites are very axial with g_z values of 19.90 and 19.88 for Dy1 and Dy2, respectively, while the main anisotropy axes of the ground Kramers doublets on Dy sites form an almost perfect parallelogram and lie practically in the Dy_4 plane with θ of 4.52 and 10.77°, respectively (θ : the angles between the axes and the plane, the same meaning as below). The spectrum of the lowest exchange levels shows the ground exchange state is nonmagnetic and corresponds to a toroidal arrangement of local magnetic moments on Dy sites (Fig. 3a). Moreover, the toroidal ground state is quite robust and can be stabilized already by dipolar interactions alone. Given the relatively small energy separation from the ground doublet state (2.967 cm^{-1}), its large magnetic moment of the first excited exchange doublet ($g_z = 59.8$) explains why the low temperature $\chi_{\text{M}}T$ and low-field $M(H)$ do not show a pronounced S shape (Fig. 4c). The exclusive presence of net toroidal moment in this compound is entirely due to its inversion symmetry. Under this symmetry, opposite Dy ions pass into each other, while the corresponding main magnetic axes are parallel, causing the complete cancellation of the total magnetic moment (Fig. 4a).

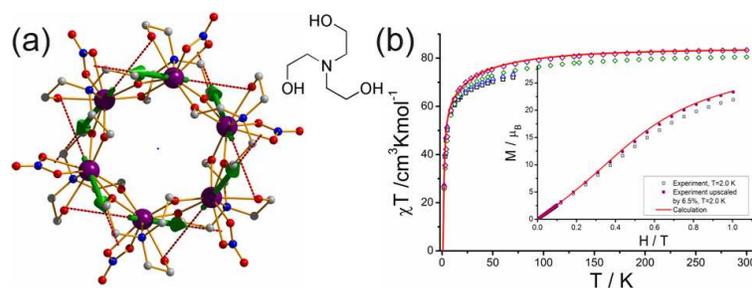


Fig. 5 (a) The structure with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state, (b) and static magnetic properties of Dy_6 wheel. Adapted from Ref. [36].

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L. Ungur et. al. discovered another net toroidal moment compound (Fig. 5),³⁶ [Dy(Htea)(NO₃)₆·8MeOH (**Dy₆ wheel**, H₃tea = triethanolamine), synthesized and characterized by K. S. Murray's group.⁴⁸ The S₆ symmetric **Dy₆ wheel** is stabilized by six μ₃:η²:η²:η¹:η¹ doubly deprotonated teaH²⁻ ligands and six capping nitrate ions with Dy...Dy distance of 3.72975(17) Å, in which each Dy ion is eight-coordinate with a distorted square antiprismatic geometry. Ac susceptibilities data gives evidence for slow relaxation of the magnetization, albeit without reaching the characteristic maxima above 2 K.

Ab initio calculations were performed for the mononuclear Dy fragments of the **Dy₆ wheel**. The gap (56 cm⁻¹) of the first excited Kramers doublet on Dy sites separated from the ground one is much larger than the expected exchange splitting, which means that only the magnetic interactions between the ground Kramers doublets on the Dy ions were relevant. The *g* tensor of the ground Kramers doublet of individual Dy centres, being axial (*g_z* = 19.26), although contains relatively large transverse components (*g_x* = 0.18; *g_y* = 0.53). The magnetic moments of the Dy ions have a toroidal component (Fig. 5a), projected onto the plane of the wheel, where the angle of anisotropy axes with the main symmetry axis of the complex (S₆) is 43°. The dipolar interaction between nearest neighbour Dy sites is antiferromagnetic, which is the reason for the arrangement of magnetic moments shown in Fig. 5a. As a result, local magnetic moments on Dy centres completely compensate each other in the ground exchange state. We stress once again that this (predominantly) antiferromagnetic dipolar coupling between Dy sites and the S₆ symmetry of the complex force **Dy₆ wheel** to have no magnetic moment.

Furthermore, since the tunnelling gap of the **Dy₆ wheel** (a non-Kramers system) is negligible (tunnelling splitting is exactly zero for Dy₃ triangle due to Kramers theorem), the net toroidal magnetic moment of the complex will be completely blocked when temperatures are significantly lower than the energy gap separating the excited doublets from the ground state (ca. 4.4 cm⁻¹). Therefore, it could be possible to store the information in the toroidal moment of the **Dy₆ wheel**.

The obtained toroidal magnetic moment could be, in principle, increased by forcing the local anisotropy axes of the Dy ions to lie in the plane of the molecule through modifying the ligand environment on the Dy sites. Furthermore, such an arrangement of the local anisotropy axes would lead to much stronger dipolar coupling between neighbouring centres, increasing significantly the stabilization energy of the toroidal state.³⁶ In contrast to the present **Dy₆ wheel**, the stabilization energy of the toroidal moment in the Dy₄ compound⁴⁷ mentioned above is already at its highest limit, because the magnetic moments of the four Dy ions lie almost in the plane of the molecule.

2.2 Mixed moment SMTs

In general, compounds having toroidal moments also possess conventional magnetic moments, which do not cancel completely due to their low symmetry. These compounds form the group of

mixed-moment SMTs. As examples of such molecules are the following four Dy₃ complexes and a Dy₆-1 one formed by linking two Dy₃ in vertex-to-vertex arrangement.

As mentioned in the introduction, the unprecedented magnetic properties of the triangular [Dy₃(μ₃-OH)₂L₃Cl(H₂O)₅]Cl₃ (**Dy₃-1**, HL = o-vanillin) complex (Fig. 3) were reported firstly by Tang and co-workers,²⁵ which show the unusual coexistence of the slow magnetic relaxation and an almost diamagnetic ground state. The crystal structure of **Dy₃-1** consists of triangles of dysprosium centres capped by two μ₃-OH groups, each side of the triangle bridged by phenoxo groups of the ligand. Each dysprosium centre is eight-coordinate and displays pentagonal bipyramid but where one site in the pentagonal plane is vacant and instead of two μ₃-OH groups sites above and below it. Ac magnetic susceptibility shows typical features of SMM behaviour with an effective barrier of 61.7 K. Dc (direct current) magnetic susceptibility shows a maximum around 6.5 K and the vanishing susceptibility at low T indicating the presence of a nonmagnetic ground state. The unexpected behaviour was confirmed by the magnetization curve *M*(*H*) with well-defined step around 8 kOe.

The nature of the nonmagnetic ground state in the Dy₃ triangle was elucidated by *ab initio* calculations.^{25, 27, 28} As revealed by fragment *ab initio* calculations,²⁷ the *g* tensor for the three Dy ions is Ising-like and strongly anisotropic with *g_z* > 19.7 and *g_{x,y}* < 0.06. The local anisotropy axes are found to lie almost in the Dy₃ plane with out-of-plane angle in range 2.4 to 8.8° and close to tangential direction (the angles of anisotropy axis with tangential direction are 8.72-9.49°).^{27, 28} The magnetic interaction (exchange and dipolar) between Dy sites was found predominantly of non-collinear Ising type.²⁸ In order to describe the magnetism of the complex (Fig. 3c, d), the sign of this interaction should be chosen such as to stabilize the toroidal arrangement of local magnetic moments along corresponding anisotropy axes (Fig. 3a, b). If these axes would have formed an ideal equilateral triangle and all Dy sites would have been magnetically equivalent, the vector sum of three magnetic moments would be exactly zero. Actually, magnetic moments of the Dy ions in the Dy₃ triangles do not compensate completely but sum up into a small total momentum of ca 0.28 μ_B pointing perpendicularly to the plane. Compared to the magnetic moment on each Dy site in the ground state (Fig. 3a), ca 10 μ_B, this value appears to be negligible. The obtained value of the total magnetic moment is confirmed by the fact that the ground Kramers doublet splits almost linearly with field applied perpendicular to the plane and shows no splitting for the in-plane direction of the field. The case is therefore, different from the net toroidal compounds, which is explained by deviations from an exact trigonal symmetry. The lowest excited Kramers doublets correspond to reversal of the direction of magnetization on one of the three dysprosium sites. After each such reversal, the complex acquires a huge magnetic moment of ca 20 μ_B in the Dy₃ plane, which is manifested in a large magnetization step (Fig. 3d).

The revealed magnetic ground state of Dy₃ is corroborated by

the single-crystal magnetic studies.²⁹ These magnetic data have been fitted with an idealized model of trigonal symmetry, with equivalent magnetic moments on Dy sites lying in the Dy₃ plane and making an angle of 120° with each other. However, the directions of these moments with respect to the tangential directions at the corresponding centres could only be extracted in the form $\varphi = 13^\circ + n \cdot 60^\circ$, $n = 0, 1, \dots, 5$.³⁰ One of these six predicted directions, corresponding to $n=0$, matches closely the *ab initio* prediction (Fig. 3b), with a deviation of only a few degrees. This comparison shows that *ab initio* calculations are indispensable for the determination of the local anisotropy axes in polynuclear compounds, even if the latter possess a high

symmetry. Another conclusion is that the *ab initio* calculations are quite reliable for an accurate description of magnetic structure of lanthanide compounds. This is of paramount importance, since *ab initio* calculations are, for the moment, the only tool to detect toroidal magnetic moments.

Finally, the energy of the first excited state in Dy₃ is ca 7.5 cm⁻¹,^{26,29} which is relatively large. Hence, as in the case of Dy₆ wheel, it could be possible to store the information in the bistable toroidal state of each such molecule, with a clear advantage over conventional SMMs of much weaker dipolar intermolecular interactions and a strongly reduced sensitivity to external fields.³⁵

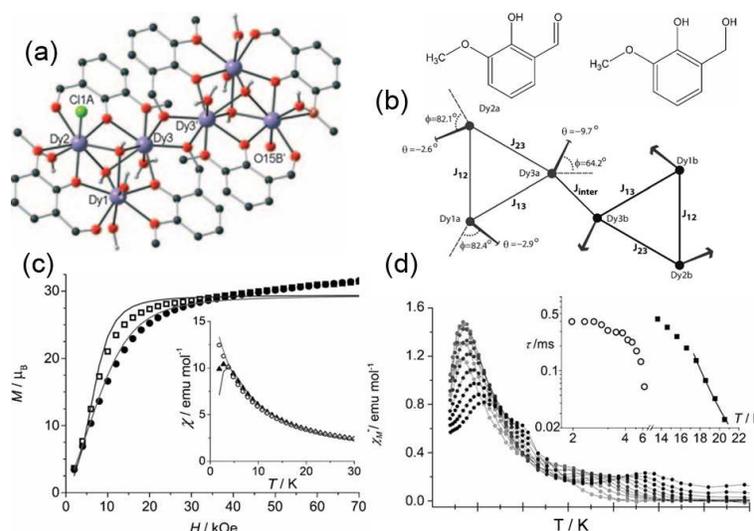


Fig. 6 The structure and the calculated six easy axes, and magnetic properties of Dy₆-1. Adapted from Ref. [42].

As part of their continuing studies on this type of trinuclear system, A. K. Powell and co-workers reported a Dy₆ molecule, [Dy₆(μ₃-OH)₄L₄L'₂(H₂O)₉Cl]Cl₅·15H₂O (**Dy₆-1**, HL = o-vanillin and H₂L' = 2-hydroxymethyl-6-methoxyphenol) (Fig. 6), which can be considered as linkage of two Dy₃ units related by an inversion centre in a vertex-to-vertex fashion. The two triangles in the Dy₆ unit are strictly co-parallel, each triangular Dy₃ unit is less equilateral than found for Dy₃-1, with Dy⋯Dy distances of 3.5127(3), 3.5371(3), and 3.5797(3) Å. The dynamics of the magnetization show the typical SMM behaviour with multiple relaxation processes, and the higher temperature data gives effective energy U_{eff} = 200 K.

Static magnetic behaviours are different from the Dy₃-1 due to breaking the almost C_{3h} symmetry of local Dy₃ triangles (Fig. 6c): low-temperature susceptibility exhibits a maximum around lower temperature (T = 3 K); the magnetization M(H) curve at 1.8 K shows a less obvious inflection around 0.5 kOe. The absence of the S shape feature on the low-temperature molar magnetization curve is indicative of a less pronounced nonmagnetic ground state (i.e. holding a larger magnetic moment).

Ab initio calculations were performed for the three different Dy ions. The g_z factors are 19.8, 19.7 and 19.3 for Dy1, Dy2 and Dy3, respectively. As shown in Fig. 6b, the directions of the local

easy axes for Dy1 and Dy2 lie almost in the plane of the triangle with $\theta < 3^\circ$ and are tangential to the triangle with φ ranging between 82.1 and 82.4° (φ : the angles of their projections on to the triangular plane with the bisector of the triangle). However, the local easy axis for Dy3 ion deviates by about 10° out of the plane of the triangle and makes a smaller angle (64.2°) to the bisector, leading to a lower symmetry of local Dy₃ triangle.

To explore this further, the angle-resolved single-crystal magnetic data were fitted with an Ising spin Hamiltonian, which gives $J_{12}^z = 7.6$ K, $J_{13}^z = 6.0$ K, $J_{23}^z = 5.0$ K, and $J_{\text{int}}^z = 1.2$ K, corresponding to the Ising magnetic interactions within and between the two Dy₃ units, respectively. Therefore, the ground state of Dy₆-1 is a nonmagnetic doublet, which results from the weak antiferromagnetic interaction between the triangles. However, this compound has a lower magnetic excited state compared with that in prototype Dy₃-1 (0.6 K compared with about 10 K in Dy₃-1), due to the breaking of the trigonal symmetry and a larger deviation of the easy axis of Dy3 ion from the plane of the triangle, which contributes to the disappearance of a well-step in the M versus H curve. Furthermore, interaction between the two triangles is too weak to stabilize the clockwise or anticlockwise arrangement of the magnetic moments in each triangle.

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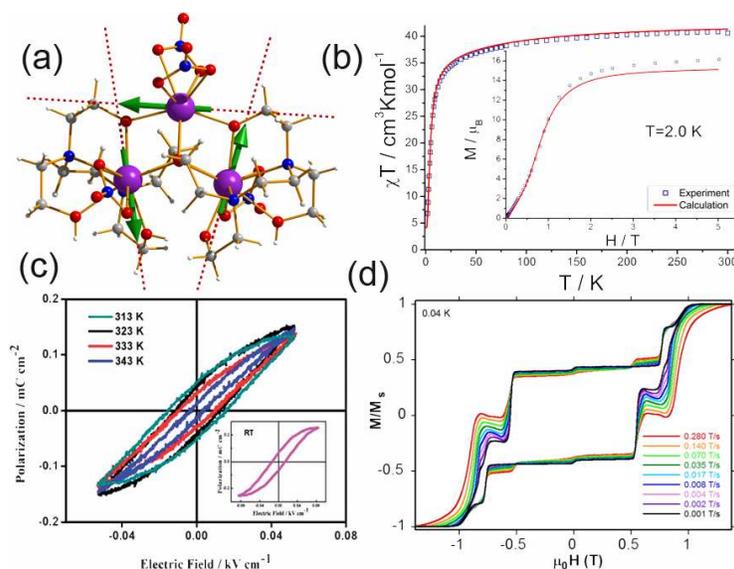


Fig. 7 (a) The structure with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state; (b) The static magnetic properties; (c) Dielectric hysteresis loops; (d) Hysteresis loops at different field sweep rates for $\text{Dy}_3\text{-2}$. Adapted from Ref. [45].

Recently, a novel triangular Dy_3 compound,⁴⁵
 5 $[\text{Dy}_3(\text{HL})(\text{H}_2\text{L})(\text{NO}_3)_4]$ ($\text{Dy}_3\text{-2}$, $\text{H}_4\text{L} = \text{N,N,N',N'}$ -tetrakis(2-hydroxyethyl)-ethylene-diamine), different from the classical $\text{Dy}_3\text{-1}$ triangle has been reported by W. Shi and co-workers (Fig. 7). $\text{Dy}_3\text{-2}$ exhibits not only SMM behaviour with characteristic hysteresis loops (Fig. 7d), but also dielectric hysteresis loops and
 10 a phase transition with the dielectric anomalies at 470 K (Fig. 7c). Structural analysis shows three Dy ions are doubly bridged by two $\mu_3\text{-O}$ atoms from the ligands, and only one pair of Dy ions is not bridged by $\mu_2\text{-O}$ atom, thus leading to a pseudo-isosceles triangle with the Dy...Dy distances of 3.488(1), 3.509(1) and
 15 3.898(1) Å. The coordination geometry of Dy2 is a distorted square antiprism, while Dy1 and Dy3 are in distorted capped square antiprismatic coordination spheres.

Both low-temperature χT and low-field $M(H)$ show non-negligible positive slopes, which points to a nonvanishing

20 magnetic moment in the Kramers doublet of $\text{Dy}_3\text{-2}$. *Ab initio* calculations were carried out to study the nature of the magnetic interactions. Main values of the g tensor for the lowest doublets are strongly axial with $g_z > 19.7$ and $g_{x,y} < 0.08$. Both the dipolar magnetic interaction and exchange interaction favour the toroidal alignment of local magnetic moments. The relative orientations
 25 of the main anisotropy axes lie almost in the plane of the triangles with θ in range of $0.568\text{--}10.398^\circ$ (Fig. 7a) and the angles between the main anisotropy are $25.10\text{--}77.97^\circ$. The calculations show that the anisotropy axes (red dashed lines in Fig. 7a) form an isosceles triangle, while the non-collinear Ising exchange interaction between localized moments arrange them along corresponding anisotropy axes. As a result the local magnetic moments in the ground Kramers doublet ($M = 11.5 \mu_B$) do not compensate each other anymore, which is the reason why $\text{Dy}_3\text{-2}$ remains magnetic
 35 till very low temperatures.

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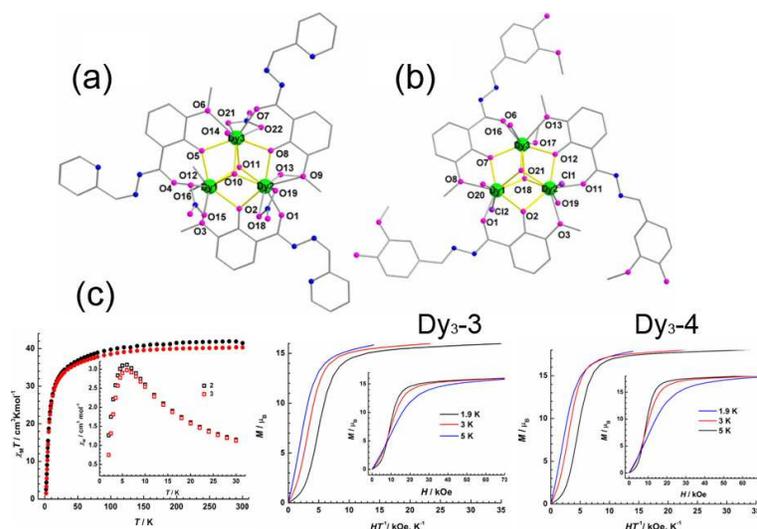


Fig. 8 The structure, and static magnetic properties for $\text{Dy}_3\text{-3}$ and $\text{Dy}_3\text{-4}$. Adapted from Ref. [46].

Another two Dy_3 compounds⁴⁶ maintaining vortex-spin structure have been assembled by some of us through grafting bulky hydrazine onto the vanillin group. The two compounds (Fig. 8), namely, $[\text{Dy}_3(\mu_3\text{-OH})_2(\text{Hpvoh})_3(\text{NO}_3)_3(\text{CH}_3\text{OH})_2\text{H}_2\text{O}]\cdot\text{NO}_3\cdot 3\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O}$ and $[\text{Dy}_3(\mu_3\text{-OH})_2(\text{H}_2\text{vovh})_3\text{Cl}_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})_3][\text{Dy}_3(\mu_3\text{-OH})_2(\text{H}_2\text{vovh})_3\text{Cl}_2(\text{H}_2\text{O})_4]\cdot\text{Cl}_4\cdot 2\text{CH}_3\text{OH}\cdot 2\text{CH}_3\text{CN}\cdot 7\text{H}_2\text{O}$ ($\text{Dy}_3\text{-3}$, H_2pvoh = N-(pyridylmethylene)-o-vanilloylhydrazone; $\text{Dy}_3\text{-4}$, H_3vovh = N-vanillidene-o-vanilloylhydrazone), have a similar two- $\mu_3\text{-OH}$ -capped triangular skeleton. Each nine-coordinate Dy ion in $\text{Dy}_3\text{-3}$ possesses a slightly distorted monocapped square-antiprismatic geometry, while all eight-coordinate Dy centres in $\text{Dy}_3\text{-4}$ still possess the original pentagonal bipyramid as

the parent complex $\text{Dy}_3\text{-1}$ with one missing site in the pentagonal plane. The subtle but crucial structural differences between their respective structures give birth to their distinct dynamic magnetic behaviour revealed by ac susceptibility. Although without theoretical calculations, both the vanishing susceptibility at low temperature and the obvious inflection at low field in M vs. H plots indicate nonmagnetic ground state. This might again be of vortex-spin state, i.e. possessing a toroidal magnetic moment.

2.3 Zero toroidal moment compounds

The whole magnetic structure may show zero toroidal moment because the toroidal moments in the neighbouring units are opposite in sign and compensate each other. In this case, the compound is called zero toroidal moment SMT.

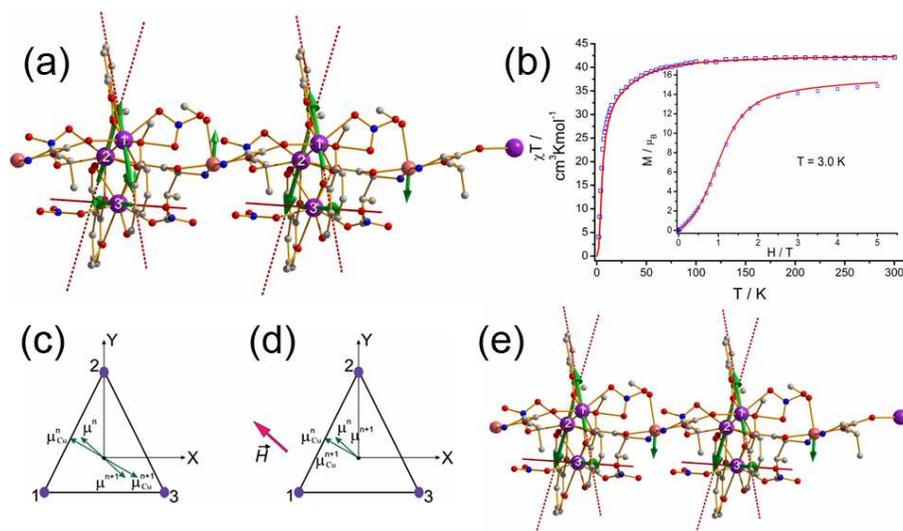


Fig. 9 (a) The structure with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state; (b) The static magnetic properties; (c-d) View along the Z axis of μ and μ_{Cu} in the ground state of the chain with $H = 0$ and $H > H_c$; (e) Arrangement of toroidal moments along the chain at

$H > H_c$. Adapted from Ref. [44].

One typical example is the enantiopure heterometallic 1D CuDy_3 coordination polymers (Fig. 9), $([\text{Cu}(\text{Val})_2\text{CH}_3\text{OH}][\text{L}_3\text{Dy}_3(\mu_3\text{-OH})_2(\text{NO}_3)_4])_n$ (CuDy_3 , HL = o-vanillin, Val = valine) investigated by Novitchi et al.⁴⁴ CuDy_3 contains two independent chiral chains, A(Δ) and B(Λ), in which alternating Dy_3 triangular building blocks and chiral mononuclear Cu^{II} bis-valinate complexes can be observed. The trinuclear Dy_3 units are capped by two $\mu_3\text{-OH}$ and three phenoxide groups of o-vanillin ligands link pairs of Dy ions. For both chains, the coordination environments of two Dy sites are the same, being completed by one bidentate nitrate group and one carboxylate oxygen. However, coordination environments of the remaining Dy sites are different: for the chain A(Δ), the environment is completed by one monodentate NO_3^- and one H_2O ; in chain B(Λ), the coordination sphere of the third Dy site is completed by two NO_3^- groups in both mono- and bi-dentate coordination modes. Each Dy ion is eight-coordinated with a distorted geometry. Within the $[\text{Dy}_3(\mu_3\text{-OH})_2]$ triangle units, the $\text{Dy}\cdots\text{Dy}$ distances are in the range 3.505(2)–3.543(2) Å. Ac magnetic susceptibility shows strong frequency dependence but without observable maxima.

Ab initio calculations on the individual Dy and Cu magnetic sites were performed. The results show the strong axiality of Dy sites with main values of the g tensors $g_z > 19.5$, $g_{x,y} < 0.11$. The

main magnetic axes on Dy sites are close to tangential directions with angles between anisotropy axis and the tangential direction of 10.3–15.6°, and lie almost in the plane of the Dy_3 triangle with θ of 0.1–10.2°, which are very similar to the case found in the ground state of the $\text{Dy}_3\text{-1}$ triangle showing that this motif is preserved despite the polymerization of Dy_3 units. Indeed, Dy_3 units have uncompensated moments ($\mu^{\text{Dy}} \approx 0.8 \mu_{\text{B}}$, Fig. 9c).

As shown in Fig. 9, the magnetic structure shows no bulk toroidal magnetization, because the toroidal moments in neighbouring Dy_3 units are opposite in sign and compensate each other due to the involvement of different types of Dy ion in the exchange pathway. However, according to the calculations, a very strong toroidal magnetization can be induced in single-crystals of these compounds by applying a magnetic field perpendicular to the chain at low temperature (Fig. 9d,e). With the possibility of induced ferrotoroidicity, the CuDy_3 polymers described here represent the first molecular-based material among the inorganic multiferroic crystals known to date.

2.4 Enhanced toroidal moment compounds

When toroidal moment units are linked in ferromagnetic way, the whole toroidal moment is enhanced compared with the ingredient unit. In this case, we call the compound as enhanced toroidal moment SMT.

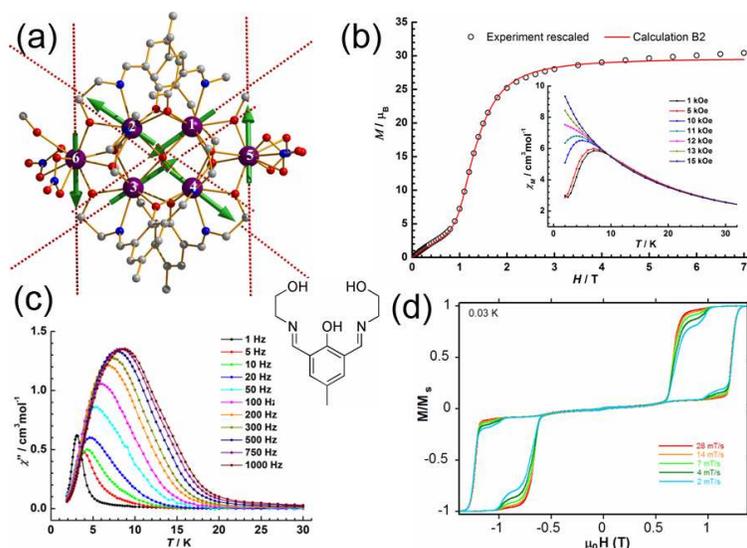


Fig. 10 The structure with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state, and magnetic properties of $\text{Dy}_6\text{-2}$. Adapted from Ref. [43].

In continuation of our interest in toroidal spin topologies, we synthesized another Dy_6 compound (Fig. 10),⁴³ $[\text{Dy}_6\text{L}_4(\mu_4\text{-O})(\text{NO}_3)_4(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}$ ($\text{Dy}_6\text{-2}$, H_3L = 2,6-bis((2-hydroxyethylimino)methyl)-4-methylphenol), the hexanuclear Dy_6 core can be regarded as the linkage of two $[\text{Dy}_3(\mu_3\text{-O})_2(\mu_2\text{-O})_2]$ triangular units placed in a robust edge-to-edge arrangement, which linked by one $\mu_4\text{-O}^{2-}$ in the centre and consolidated by four deprotonated phenol oxygen atoms from ligands in the periphery. Each triangular unit is capped by two $\mu_3\text{-O}$ alcohol oxygen atoms from one arm of ligands, and the other $\mu_2\text{-O}$ alcohol oxygen atoms from the same ligands bridge edges of the triangles. The coordination spheres of

eight-coordinate $\text{Dy}_1/\text{Dy}_2/\text{Dy}_3/\text{Dy}_4/\text{Dy}_5$ centres are distorted square antiprismatic geometries and nine-coordinate Dy_6 ion a distorted monocapped square antiprismatic geometry. The triangular Dy_3 units in $\text{Dy}_6\text{-2}$ are less equilateral than the prototype $\text{Dy}_3\text{-1}$ with $\text{Dy}\cdots\text{Dy}$ distances in range 3.3934(3)–3.5412(4) Å. Ac susceptibilities and the magnetization hysteresis ensure the SMM behaviour of this $\text{Dy}_6\text{-2}$.

The static magnetic behaviour resembles the case of the prototype $\text{Dy}_3\text{-1}$. The low-temperature susceptibility shows a maximum around $T = 7$ K under 1 kOe dc field, but a constant increase with an applied field of 13 kOe. This constant increase suggests the presence of weak antiferromagnetic interactions,

which are overcome by the application of a moderate field. The $M(H)$ curve at 1.9 K shows an obvious inflection around 9 kOe. However, the non-vanishing slope of $M(H)$ at low temperature shows that the ground state of **Dy₆-2** cannot be qualified as a nonmagnetic doublet, contrary to the case of prototype **Dy₃-1**.

Ab initio calculations on the individual Dy magnetic sites in **Dy₆-2** were performed. The results show the ground Kramers doublet on each dysprosium site is well separated from the first excited state, whilst the g tensors are strongly axial with $g_z > 19.6$ and $g_{x,y} < 0.02$. The corresponding directions of anisotropy axes in both triangles (Fig. 9a) are nearly tangential directions and lie almost in the plane of the corresponding **Dy₃** triangles with θ of 5.368–9.754°, and toroidal moments of both triangle units in **Dy₆-2** are similar vortex-like arrangements. The calculated energies show a magnetic state at 7.6 cm⁻¹ above the ground state, and a non-negligible magnetic moment in the ground exchange doublet. The slope and the pronounced step in the $M(H)$ curve are well reproduced.

From comparisons between prototype **Dy₃-1**, **CuDy₃**, **Dy₆-1**, and **Dy₆-2**, we can conclude that for both triangles of the edge-to-edge **Dy₃+Dy₃** arrangement, the toroidal spin structure of the prototype **Dy₃-1** triangle has been basically preserved. Most importantly, similar orientations of toroidal moments in **Dy₆-2** are stabilized by strong couplings through the $\mu_4\text{-O}^{2-}$ ion between two triangles. Therefore, **Dy₆-2** is characterized by enhanced toroidal magnetization, which may lead to new possibilities in multiferroic systems and magnetic data storage technology. The present results provide a promising strategy for enhancing the toroidal magnetisms of polynuclear lanthanide-based compounds via fine-tuning of the arrangements of the lanthanide ions and strengthening couplings between lanthanide ions.

3. Challenges and prospects

Yet a few in number, the potential of SMTs is self-evident. Indeed, the rapid development of this emerging field will provide an even more fundamental knowledge and potential for future applications as multiferroic materials.^{30, 31, 33, 34} Above we have examined nine typical dysprosium complexes showing toroidal moment, and classified them with the aim to draw some lessons in synthesizing SMTs with enhanced toroidal magnetization. As shown above, toroidal moment can be influenced by the molecular symmetry, the coordination environment and/or the bridging ligands which act as superexchange pathways, which should be considered when designing new SMTs in the future.

Three major conclusions emerge from the undertaken research.

First, the chances to synthesize a polynuclear Ln complex with an almost net toroidal momentum are not low. The two necessary conditions for that are: i) the planar arrangement of local anisotropy axes and ii) the cyclic symmetry of the polynuclear lanthanide complex. Both these requirements are not expected to be fulfilled exactly, as is evident from the geometry of the first SMT **Dy₃-1**. There is also a third requirement of suitable exchange / dipolar interaction between lanthanide ions in order to stabilize a toroidal type of arrangement of magnetic moments. However, this condition is fulfilled for almost all cases when the first two requirements are satisfied, as the reviewed examples show. There is only one exception known to date, the **Dy₃N** molecule embedded into **C₈₀** fullerene cage, which shows three

quasidegenerate magnetic exchange doublets in the ground state, while the first excited exchange Kramers doublet appears as a non-magnetic radial state.⁴⁹

Second, the toroidal states in the synthesized SMTs are quite robust objects against linking, sometimes strong, and polymerization of molecular units containing toroidal moments. This is clearly seen in the example of **Dy₃Cu** chains,^[46] containing polymerized **Dy₃** triangles, and of **Dy₆-2** complex,^[45] containing two strongly interacting **Dy₃** units. In both cases the toroidal moment in the ground state survives and is not much different from the one detected in the **Dy₃-1** complex.²⁷ This robustness of toroidal magnetization is a highly important property in view of possible application of such molecules in various electronic devices, which require survival of electronic properties of the molecule after is drafted on a surface functionalization and attachment of the leads.

Third, there is a reliable tool to strongly in detail the non-collinear magnetism in polynuclear lanthanide complexes based on the applications of high-level *ab initio* methods.²⁶ This is this research methodology which allowed the toroidal ground state to be discovered in the **Dy₃-1** triangle²⁷ and then in all other polynuclear complexes reviewed here. Contrary to this theoretical tool, the magnetic measurements themselves are not sufficient to draw the conclusion about the toroidal nature in the ground state. Even if a non-magnetic ground state is detected in complexes with odd number of electrons, implying its non-collinear magnetic structure with vanishing total magnetic moment,^{25, 29} there is no reason to suppose an *a priori* toroidal arrangement of magnetic moments. This situation is not clarified significantly by measuring single-crystal angular-dependent magnetization, which always will offer several possibilities for such an arrangement.³⁰ The situation is even more complicated in the case of complexes with even number of electrons (i.e. containing an even number of Dy ions). This allows us to conclude that *ab initio* calculations appear nowadays to be an indispensable tool for unambiguous detection of toroidal magnetic moment in complexes. The direct visualization of toroidal moments in such compounds is in principle possible via neutron diffraction, but requires application of this technique at a much higher level than it is presently done. Another perspective way to detect molecular toroidal moments is via a magnetic STM and AFM measurements.⁵⁰

The studies so far have provided some very valuable indicators for the structural features required to optimize the contribution of an Ising type spin to SMTs, but this task is far from straightforward, thus requiring an interdisciplinary vision of scientific research by bringing together synthetic chemists and physicists to achieve the final goal. Progress in many different fields is needed for the advancement of knowledge in this subject.

The important next step in the SMT studies is preparing electronic molecular devices based on them for the investigation of their spintronic properties. Such investigations are routinely done nowadays on many SMMs, like **Mn₁₂acac**, **Fe₄**, **[TbPc₂]**, etc.

Another appealing aim of SMTs is to create multifunctional molecular materials. In this aspect the possibilities offered by the molecular approach is unparalleled in the world of solid state chemistry. Thus, from a wise choice of molecular building blocks one can combine in the same crystal lattice two properties of

molecular magnetic properties such as SMMs behaviours as well as multiferroic properties that are difficult or impossible to achieve in a conventional inorganic solid.

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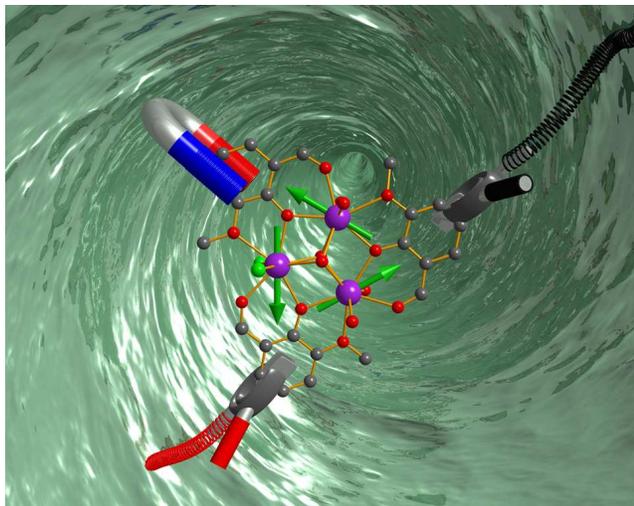
[‡] Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

[‡] Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Graphical Abstract

Bistable molecules with toroidal magnetic state (Single-molecule toroids) are promising for applications in quantum computing and information storage.



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Liviu Ungur graduated Chemistry at the State University of Moldova (Chisinau) in 2005, and received his Ph. D. from the University of Leuven, Belgium, in 2010, under the supervision of Prof. Liviu F. Chibotaru. He is presently working at KU Leuven after receiving a post-doctoral mandate from the Flemish Science Foundation. His current research is oriented towards development and application of novel approaches for theoretical description of magnetism and magnetic interactions in mono- and polynuclear compounds containing strongly anisotropic metal sites.

Shuang-Yan Lin



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Jinkui Tang



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Liviu F. Chibotaru



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