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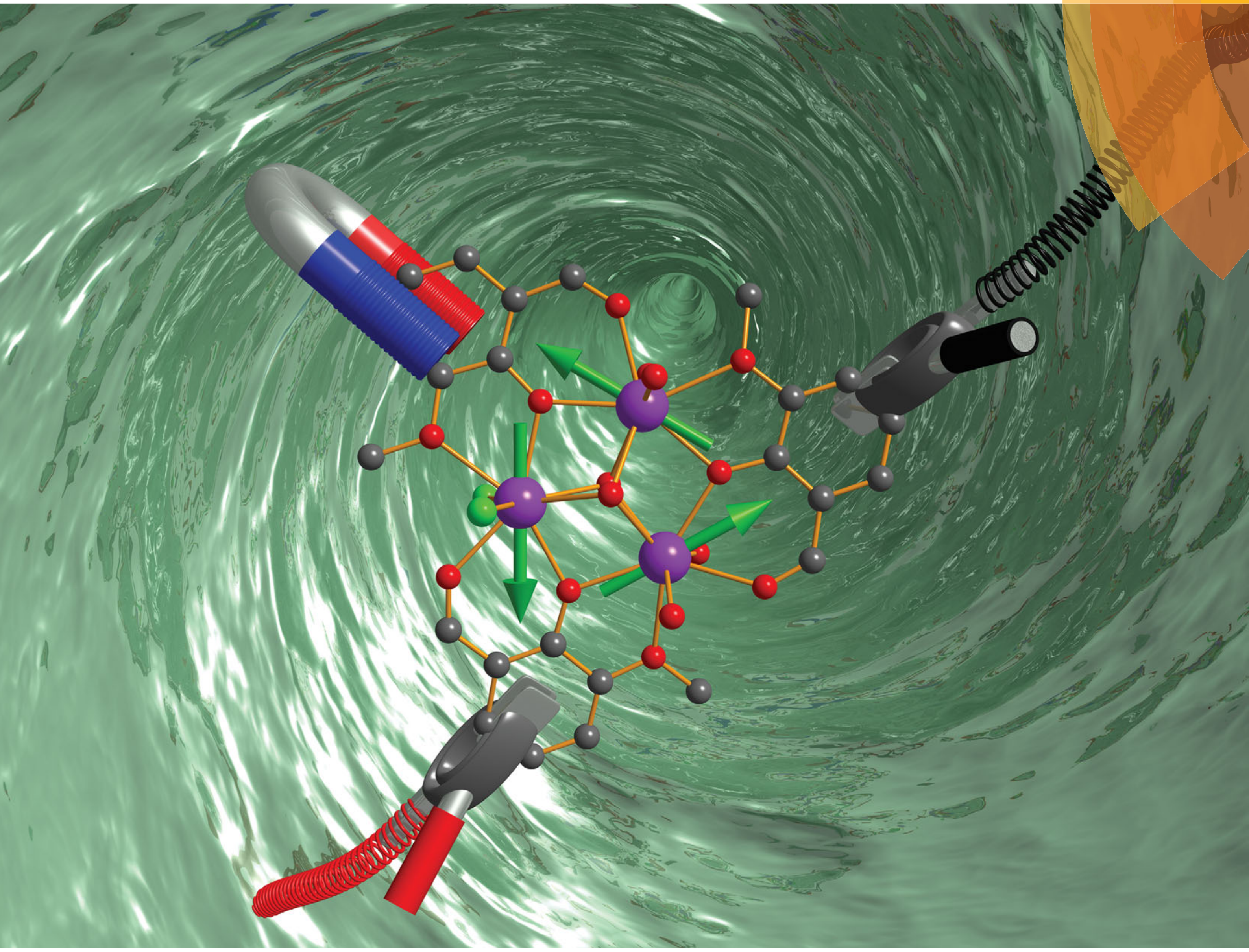

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TUTORIAL REVIEW

Jinkui Tang *et al.*

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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Single-molecule toroics (SMTs) are defined, by analogy with single-molecule magnets, as bistable molecules with a toroidal magnetic state, and seem to be most promising for future applications in quantum computing and information storage and use 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 *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 the magnetic moment in these systems. Herein, nine 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 a 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

[1] This paper is about single-molecule toroics (SMTs) which are defined as molecules with a toroidal magnetic state.
[2] The molecular symmetry, local magnetic moment and magnetic interaction are essential parameters for the 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 which allow the detection of the toroidal moment.
[5] Progress in the emerging field of SMTs still faces many challenges.

1. Introduction

The toroidal magnetic moment characterized by vortex distributions of magnetic dipoles is regarded as the third kind of electromagnetic moment after the traditional polarization and magnetization.[1–3] A classical example is a ring-shaped torus with 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, the toroidal moment (t) is defined as the outer product of the 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]

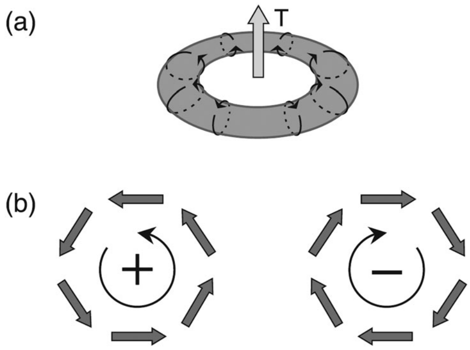

Fig. 1 (a) Ring-shaped solenoid with electric-current loops as classical example for a toroidal moment. (b) Quantum-mechanical example of a toroidal moment with two opposite toroidal moments. Reproduced from ref. 4 by permission of IOP Publishing.

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In reality, the toroidal moment has long been discussed in the context of particle physics in 1958 by Zel'dovich who called them anapoles.[8] However, the existence of a macroscopic moment asymmetric under both time reversal and space inversion has long been remained elusive because of the weaker response, compared with electric or magnetic dipole moment, and is usually neglected.[9,10] An important step occurred when finally toroidal domains were observed by optical second harmonic generation in LiCoPO$_4$,[3,11] which suggests that ferrotoroidicity (something which is 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 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 space-asymmetric electric polarization is induced by a time-asymmetric and space-asymmetric magnetic order.[13]

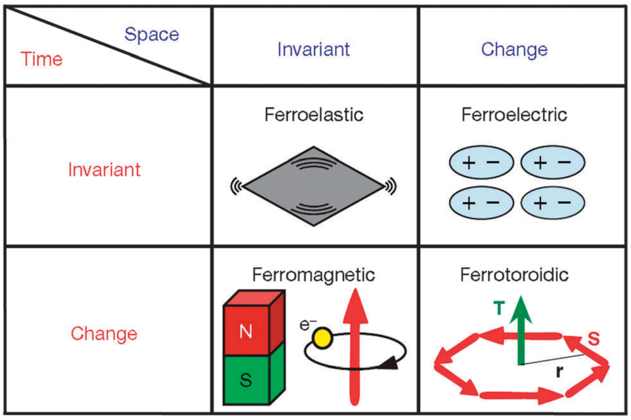

Fig. 2 Possible forms of ferroic order under the parity operations of space and time. Reprinted with the permission from ref. 3. Copyright 2007 Nature Publishing Group.

In particular, the unique property of toroidal response is a non-radiating configuration which results from destructive

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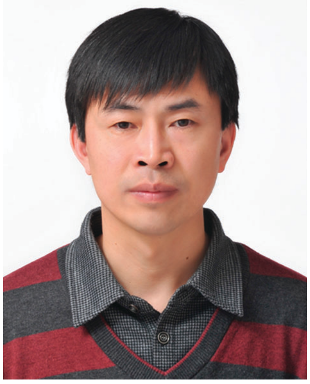

Jinkui Tang

Jinkui Tang received his PhD degree in 2001 from Nankai University under the supervision of Prof. Dai-Zheng Liao and then worked as a post-doctoral fellow at Universität Karlsruhe (TH) in the research group of Prof. Annie K. Powell and Universiteit Leiden with Prof. Jan Reedijk, before initiating his independent career at Changchun Institute of Applied Chemistry, Chinese Academy of Sciences in 2007. The Tang group research interests centre around the design and characterization of coordination compounds with interesting magnetic properties.

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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 was 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 the 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 moments 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 and attributed to the toroidal susceptibility.[24]

As mentioned above, the search for the toroidal moment is mainly on atom-based materials in solid-state chemistry and physics, particularly in multiferroics.[4,12] In contrast 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 Dy_3 triangular cluster has been recently synthesized (Fig. 3a) displaying a non-magnetic ground state,[25] as evidenced by low-temperature magnetism of this complex (Fig. 3c and d). The *ab initio* calculations of CASSCF/RASSI level, performed with the MOLCAS suite of programs,[26] have shown that the reason for a non-magnetic ground state in this compound is an almost toroidal arrangement of magnetic moments on Dy sites (arrows in Fig. 3a and 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 Dy_3 triangle.[29–32] In particular, investigations of the magnetoelectric properties of this compound revealed 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 Dy_3 clusters could be called single-molecule toroics (SMTs).[30]

For molecule-based materials, SMTs belong to a new class of magnetic materials in which the toroidal moment arises from a vortex arrangement of local magnetic moments due to wheel-shaped topology (or local wheel-shape) and specific magnetic interaction between metal sites. Toroidal moments can be influenced by the molecular symmetry and local magnetic moment, as well as magnetic interactions including dipole interactions and exchange interactions 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

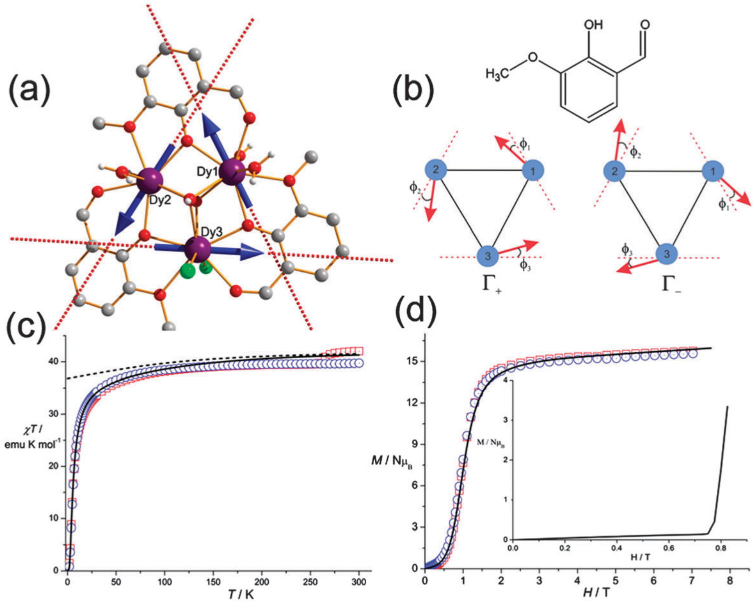

Fig. 3 (a) The structure of **Dy_3-1** with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state. (b) The two components of the ground Kramer's doublet. (c and d) The static magnetic properties of **Dy_3-1** and their *ab initio* simulations (lines). Adapted from ref. 28. Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

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.

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 a bottom up molecular approach. Single dispersed SMTs represent the simplest molecular units which allow the study of magnetic interactions between spin carriers and molecular symmetry as well as local magnetic moment, thus one could potentially build larger molecules with enhanced toroidal magnetization. However, systematic research on the SMTs is still lacking. We believe that it is timely to review the development and 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 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.

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 arrangement, which defines their macroscopic magnetic behaviour. Such compounds are currently only known with dysprosium complexes and all show SMM behaviour. The advantages of lanthanides (in particular Dy) over transition metals for obtaining SMTs is due to the strong uniaxial magnetic 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. Since the discovery of the toroidal magnetic state in Dy_3 triangle,[25,27–29] the fascinating magnetic properties have ignited new interest in the exploitation of coupling several such Dy_3 building blocks to obtain larger dysprosium compounds.[37–44] Indeed, recent efforts have produced fascinating results with the successful assembly of two typical Dy_6 complexes[42,43] and a heterometallic 1D **$CuDy_3$** coordination polymer,[44] which not only shows similar structural features to Dy_3 triangles in each building block but also retains the functionality of Dy_3 triangles and the toroidal arrangement of single-ion magnetic anisotropy axes. Meanwhile, three other Dy_3 triangle compounds[45,46] and a coplanar **Dy_4** compound[47] as well as a **Dy_6 wheel** compound[36] have been reported with toroidal magnetic structure. As in the case of Dy_3 triangle, the existence of toroidal moment in all these compounds has been detected exclusively by *ab initio* calculations. Despite 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.

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

	Net toroidal moment		Mixed moment			Zero toroidal moment	Enhanced toroidal moment
Compounds	**Dy_4**	**Dy_6 wheel**	**Dy_3-1**	**Dy_3-2**	**Dy_6-1**	**$CuDy_3$**	**Dy_6-2**
T_z	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$	$=0$	$T_{z1} + T_{z2}$
M/μ_B	$=0$	$=0$	$=0.56$	$=11.5$	$\neq 0$	$=0.8$	$=13.1$

2.1 Net toroidal moment SMTs

Net toroidal moment SMTs refer to the compounds with a toroidal magnetic state in the 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), $[Dy_4(\mu_3\text{-}OH)_2(\mu\text{-}OH)_2(2,2\text{-}bpt)_4(NO_3)_4(EtOH)_2]$ [**Dy_4**; 2,2-bptH = 3,5-bis(pyridin-2-yl)-1,2,4-triazole], reported by Tong *et al.*[47] The compound is a centrosymmetric complex with four precisely coplanar Dy ions with Dy···Dy distances of 3.73–4.28 Å. All Dy ions are the vertices of the parallelogram bridged by two μ_3-OH, two μ-OH, and four μ-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 ($U_{eff}/k_B = 80(3)$ K). Moreover, the $\chi'T$ value (χ', in-phase of the AC susceptibilities) drops to nearly 0 which indicates the nonmagnetic ground state.

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 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 Kramer's 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. 4a). 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

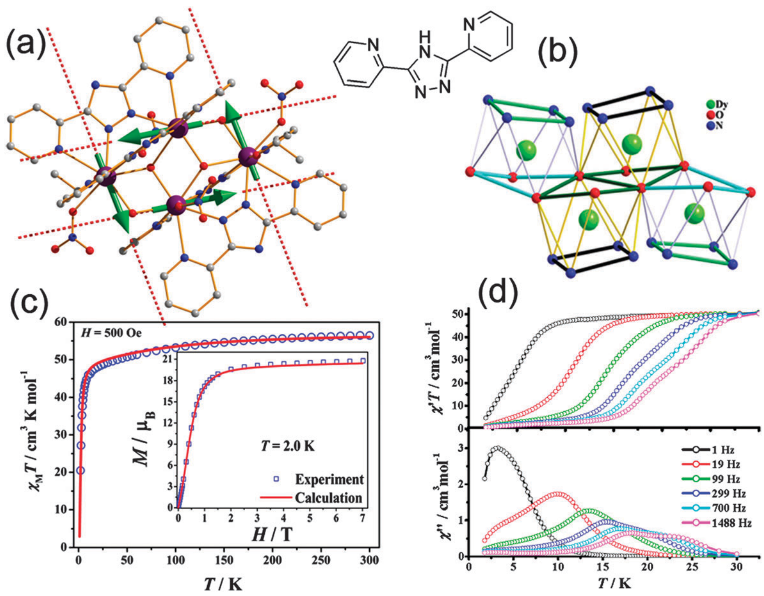

Fig. 4 The structure and magnetic properties of compound **Dy4**. Reprinted with the permission from ref. 47. Copyright 2012 American Chemical Society.

state (2.967 cm^{-1}), its large magnetic moment of the first excited exchange doublet (g_z = 59.8) explains why the low-field M(H) do not show a pronounced S shape (Fig. 4c). The exclusive presence of a 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).

Ungur *et al.* discovered another net toroidal moment compound (Fig. 5),[36] $[Dy(Htea)(NO_3)]_6 \cdot 8MeOH$ (**Dy_6 wheel**, H_3tea = triethanolamine), synthesized and characterized by Murray's group.[48] The S_6 symmetric **Dy_6 wheel** is stabilized by six $\mu_3:\eta^2:\eta^2:\eta^1:\eta^1$ doubly deprotonated $teaH^{2-}$ 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 **Dy_6 wheel.** The gap (56 cm^{-1}) of the first excited Kramer's 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 Kramer's doublets on the Dy ions were relevant. The g tensor of the ground Kramer's doublet of individual Dy centres, being axial (g_z = 19.26), contain 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 the anisotropy axes with the main symmetry axis of the complex (S_6) 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 S_6 symmetry of the complex force the **Dy_6 wheel** to have no magnetic moment.

Furthermore, since the tunnelling gap of the **Dy_6 wheel** (a non-Kramer's system) is negligible (tunnelling splitting is exactly zero for a Dy_3 triangle due to Kramer's theorem), the net toroidal magnetic moment of the complex will be completely blocked when temperatures are significantly lower than the energy gap

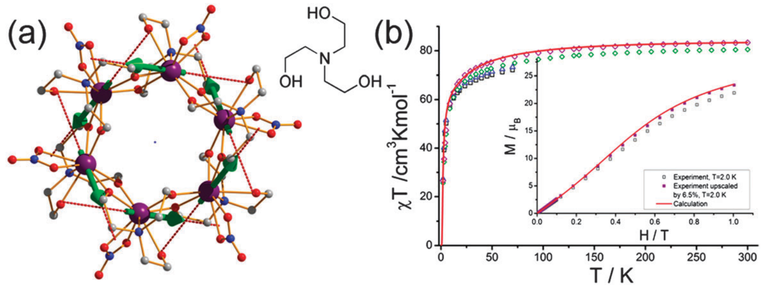

Fig. 5 (a) The structure with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state, (b) and static magnetic properties of **Dy_6 wheel**. Reprinted with the permission from ref. 36. Copyright 2012 American Chemical Society.

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 **Dy_6 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 a much stronger dipolar coupling between neighbouring centres, increasing significantly the stabilization energy of the toroidal state.[36] In contrast to the present **Dy_6 wheel**, the stabilization energy of the toroidal moment in the **Dy_4** compound[47] 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. Examples of such molecules are the following four Dy_3 complexes and a **Dy_6-1** formed by linking two Dy_3 in a vertex-to-vertex arrangement.

As mentioned in the introduction, the unprecedented magnetic properties of the triangular $[Dy_3(\mu_3\text{-OH})_2L_3Cl(H_2O)_5]Cl_3$ (**Dy_3-1**, 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 **Dy_3-1** consists of triangles of dysprosium centres capped by two μ_3-OH groups, each side of the triangle bridged by phenoxo groups of the ligand. Each dysprosium centre is eight-coordinate and displays a pentagonal bipyramid but where one site in the pentagonal plane is vacant and instead of two μ_3-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 Dy_3 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 Dy_3 plane with an out-of-plane angle in the range 2.4 to 8.8° and close to the 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 to be predominantly of non-collinear Ising type.[28] In order to describe the magnetism of the complex (Fig. 3c and 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 and 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 Dy_3 triangles do not compensate completely but sum up into a small total momentum of *ca.* 0.56 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 Kramer's 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 Kramer's doublets correspond to a reversal of the direction of magnetization on one of the three dysprosium sites. After each such a reversal, the complex acquires a huge magnetic moment of *ca.* 20 μ_B in the Dy_3 plane, which is manifested in a large magnetization step (Fig. 3d).

The revealed magnetic ground state of Dy_3 is corroborated by 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 Dy_3 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 $\varphi = 13° + n{\cdot}60°$, $n = 0, 1,\ldots, 5$.[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 the 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 Dy_3 is *ca.* 7.5 cm^{-1},[26,29] which is relatively large. Hence, as in the case of **Dy_6 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]

As part of their continuing studies on this type of trinuclear system, Powell and co-workers reported a Dy_6 molecule,[42] $[Dy_6(\mu_3\text{-OH})_4L_4L'_2(H_2O)_9Cl]Cl_5{\cdot}15H_2O$ (**Dy_6-1**, HL = *o*-vanillin and H_2L' = 2-hydroxymethyl-6-methoxyphenol) (Fig. 6), which can be considered as a linkage of two Dy_3 units related by an inversion centre in a vertex-to-vertex fashion. The two triangles in the Dy_6 unit are strictly co-parallel, each triangular Dy_3 unit is less equilateral than found for **Dy_3-1**, 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 an effective energy of U_{eff} = 200 K.

The static magnetic behaviours are different from the **Dy_3-1** due to breaking the almost C_{3h} symmetry of local Dy_3 triangles (Fig. 6c): low-temperature susceptibility exhibits a maximum

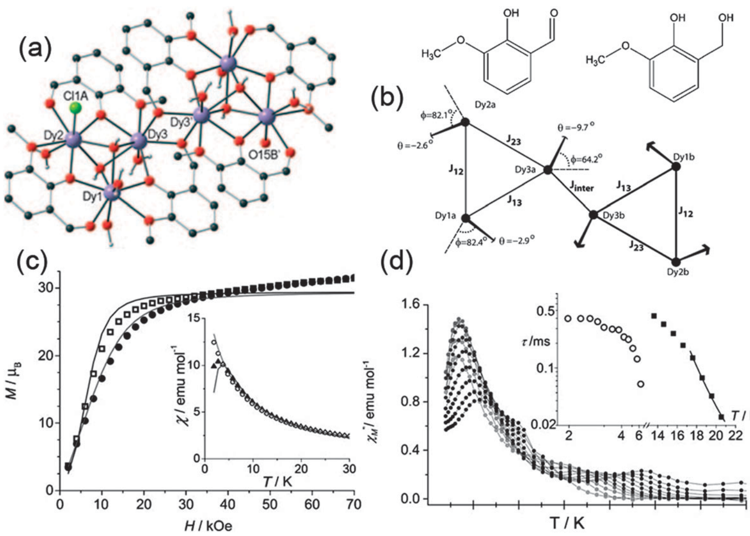

Fig. 6 The structure and the calculated six easy axes, and magnetic properties of **Dy$_6$-1**. Reprinted with the permission from ref. 42. Copyright 2010 Wiley-VCH.

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 Dy$_3$ triangle.

To explore this further, the angle-resolved single-crystal magnetic data were fitted with an Ising spin Hamiltonian, which gives $J^{zz}{}_{12}$ = 7.6 K, $J^{zz}{}_{13}$ = 6.0 K, $J^{zz}{}_{23}$ = 5.0 K, and $J^{z}{}_{\text{int}}$ = 1.2 K, corresponding to the Ising magnetic interactions within and between the two Dy$_3$ units, respectively. Therefore, the ground state of **Dy$_6$-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 **Dy$_3$-1** (0.6 K compared with about 10 K in **Dy$_3$-1**), due to the breaking of the trigonal symmetry and a larger deviation of the easy axis of the 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.

Recently, a novel triangular Dy$_3$ compound,[45] [Dy$_3$(HL)(H$_2$L)(NO$_3$)$_4$] (**Dy$_3$-2**, H$_4$L = *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)-ethylene-diamine), different from the classical **Dy$_3$-1** triangle, has been reported by Shi and co-workers (Fig. 7). **Dy$_3$-2** exhibits not only SMM behaviour with characteristic hysteresis loops (Fig. 7d), but also dielectric hysteresis loops and a phase transition with the dielectric anomalies at 470 K (Fig. 7c). Structural analysis shows three Dy ions are doubly capped by two μ_3-O atoms from the ligands, and only two pairs of Dy ions are bridged by a μ_2-O atom, thus leading to a pseudo-isosceles triangle with the Dy···Dy distances of 3.488(1), 3.509(1) and 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 non-vanishing magnetic moment in the Kramer's doublet of **Dy$_3$-2**. *Ab initio* calculations were carried out to study the nature of the magnetic interactions. The 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 of the main anisotropy axes lie almost in the plane of the triangles with θ in range of 0.568–10.398° (Fig. 7a) and the angles between the main anisotropy are 25.10–77.97°. The calculations show that the anisotropy axes (red dashed lines in Fig. 7a) form an isosceles triangle, while the non-collinear Ising exchange interactions between localized moments arrange them along corresponding anisotropy axes. As a result the local magnetic moments in the ground Kramer's doublet (M = 11.5 μ_B) do no compensate each other anymore, which is the reason why **Dy$_3$-2** remains magnetic to very low temperatures.

Another two Dy$_3$ compounds[46] 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, [Dy$_3$(μ_3-OH)$_2$(Hpovh)$_3$(NO$_3$)$_3$(CH$_3$OH)$_2$H$_2$O]·NO$_3$·3CH$_3$OH·2H$_2$O and [Dy$_3$(μ_3-OH)$_2$(H$_2$vovh)$_3$Cl$_2$(CH$_3$OH)(H$_2$O)$_3$][Dy$_3$(μ_3-OH)$_2$(H$_2$vovh)$_3$Cl$_2$(H$_2$O)$_4$]·Cl$_4$·2CH$_3$OH·2CH$_3$CN·7H$_2$O (**Dy$_3$-3**, H$_2$povh = *N*-(pyridylmethylene)-*o*-vanilloylhydrazone; **Dy$_3$-4**,

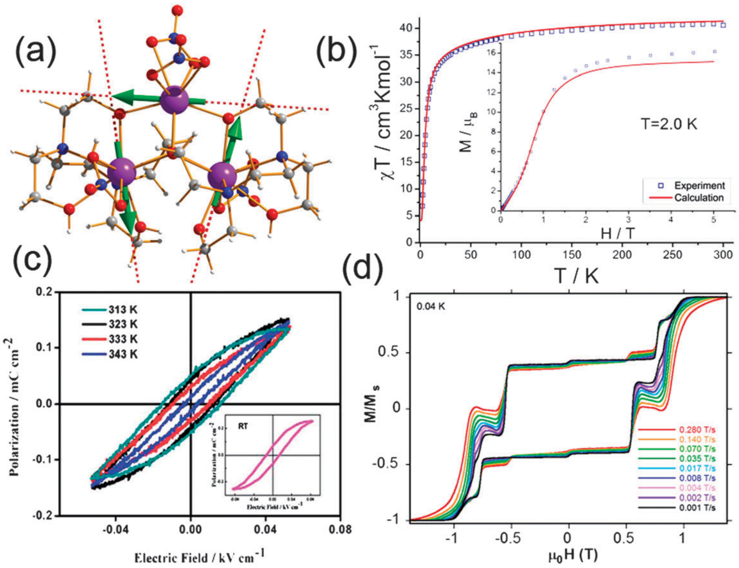

Fig. 7 (a) The structure with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state; (b) the static magnetic properties; (c) dielectric hysteresis loops; (d) hysteresis loops at different field sweep rates for **Dy$_3$-2**. Adapted from ref. 45. Reproduced by permission of The Royal Society of Chemistry.

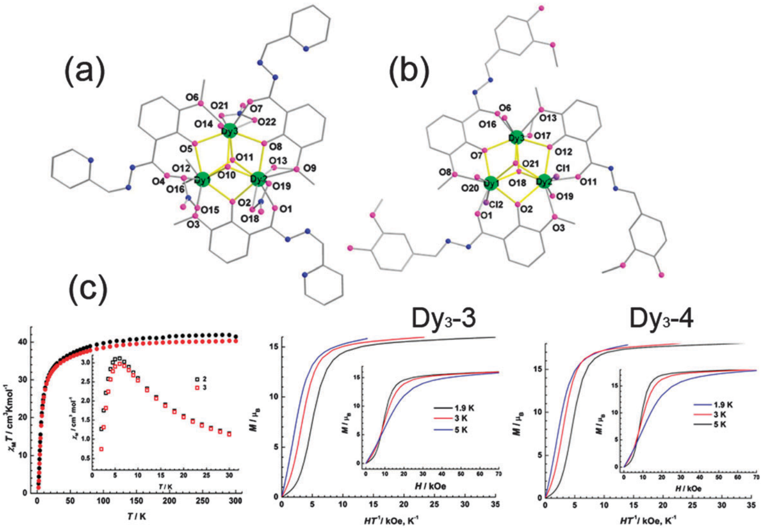

Fig. 8 The structure, and static magnetic properties for **Dy$_3$-3** and **Dy$_3$-4**. Reprinted with the permission from ref. 46. Copyright 2012 American Chemical Society.

H$_3$vovh = *N*-vanillidene-*o*-vanilloylhydrazone), have a similar two-μ$_3$-OH-capped triangular skeleton. Each nine-coordinate Dy ion in **Dy$_3$-3** possesses a slightly distorted monocapped square-antiprismatic geometry, while all eight-coordinate Dy centres in **Dy$_3$-4** still possess the original pentagonal bipyramid as the parent complex **Dy$_3$-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 their AC susceptibility. Although lacking theoretical calculations, both the vanishing susceptibility at low temperature and the obvious inflection at low field in *M vs.* H plots indicate a 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 for each other. In this case, the compound is called a zero toroidal moment SMT.

One typical example is the enantiopure heterometallic 1D **CuDy$_3$** coordination polymers (Fig. 9), ([Cu(Val)$_2$CH$_3$OH]-[L$_3$Dy$_3$(μ$_3$-OH)$_2$(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

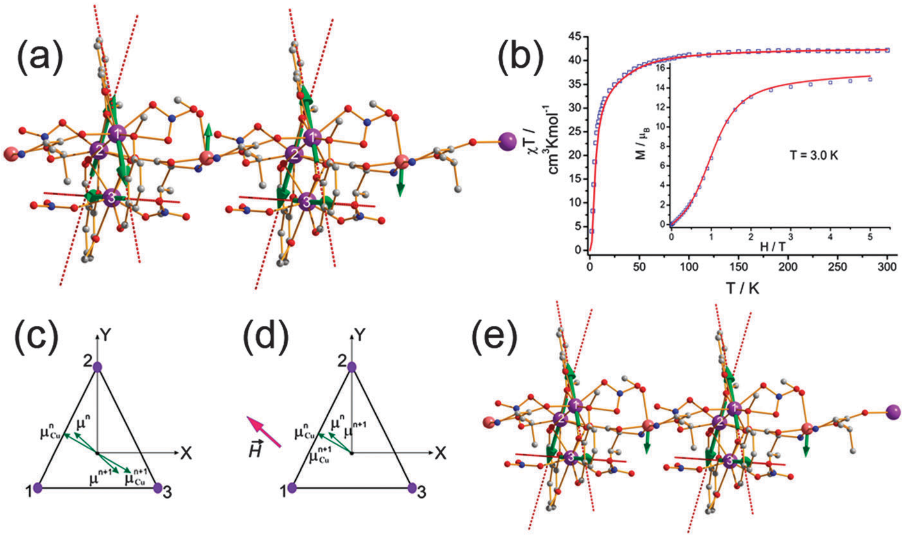

Fig. 9 (a) The structure with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state; (b) the static magnetic properties; (c and d) view along the Z axis of μ and μ_{Cu} in the ground state of the chain with $H = 0$ and $H > H_c$; (e) arrangement of toroidal moments along the chain at $H > H_c$. Adapted from ref. 44. Reproduced by permission of The Royal Society of Chemistry.

are capped by two μ_3-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 $[Dy_3(\mu_3\text{-}OH)_2]$ triangle units, the Dy···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 the 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 the 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 **Dy_3-1** triangle showing that this motif is preserved despite the polymerization of the Dy_3 units. Indeed, the Dy_3 units have uncompensated moments ($\mu^n \approx 0.8\ \mu_B$, Fig. 9c).

As shown in Fig. 9, the magnetic structure shows no bulk toroidal magnetization, because the toroidal moments in the 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 and e). With the possibility of induced ferrotoroidicity, the **$CuDy_3$** polymers described here represent the first molecular-based materials among the inorganic multiferroic crystals known to date.

2.4 Enhanced toroidal moment compounds

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

In continuation of our interest in toroidal spin topologies, we synthesized another Dy_6 compound (Fig. 10),[43] $[Dy_6L_4(\mu_4\text{-}O)(NO_3)_4(CH_3OH)]\cdot CH_3OH$ (**Dy_6-2**, H_3L = 2,6-bis((2-hydroxyethylimino)methyl)-4-methylphenol), the hexanuclear Dy_6 core can be regarded as the linkage of two $[Dy_3(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2]$ triangular units placed in a robust edge-to-edge arrangement, which are linked by one $\mu_4\text{-}O^{2-}$ ion in the centre and consolidated by four deprotonated phenol oxygen atoms from ligands in the periphery. Each triangular unit is capped by two μ_3-O alcohol oxygen atoms from one arm of the ligands, and the other μ_2-O alcohol oxygen atoms from the same ligands bridge edges of the triangles. The coordination spheres of the eight-coordinate Dy1/Dy2/Dy3/Dy4/Dy5 centres have distorted square antiprismatic geometries and the nine-coordinate Dy6 ion a distorted monocapped square antiprismatic geometry. The triangular Dy_3 units in **Dy_6-2** are less equilateral than the prototype **Dy_3-1** with Dy···Dy distances in range 3.3934(3)–3.5412(4) Å. AC susceptibilities and the magnetization hysteresis ensure the SMM behaviour of this **Dy_6-2**.

The static magnetic behaviour resembles the case of the prototype **Dy_3-1**. 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

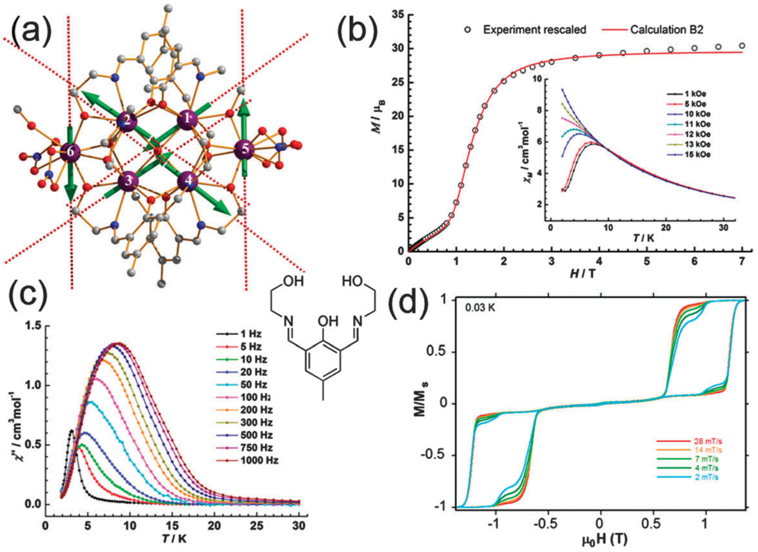

Fig. 10 The structure with main anisotropy axes (dashed lines) and local magnetizations (arrows) in the ground state, and magnetic properties of **Dy_6-2**. Reprinted with the permission from ref. 43. Copyright 2012 Wiley-VCH.

shows that the ground state of **Dy_6-2** cannot be qualified as a nonmagnetic doublet, in contrast to the case of prototype **Dy_3-1**.

Ab initio calculations on the individual Dy magnetic sites in **Dy_6-2** were performed. The results show the ground Kramer's 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. 10a) are nearly tangential and lie almost in the plane of the corresponding Dy_3 triangles with θ of 5.368–9.754°, and toroidal moments of both triangle units in **Dy_6-2** have 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 prototypes **Dy_3-1**, **$CuDy_3$**, **Dy_6-1**, and **Dy_6-2**, we can conclude that for both triangles of the edge-to-edge Dy_3 + Dy_3 arrangement, the toroidal spin structure of the prototype **Dy_3-1** triangle has been basically preserved. Most importantly, similar orientations of toroidal moments in **Dy_6-2** are stabilized by strong couplings through the μ_4-O^{2-} ion between two triangles. Therefore, **Dy_6-2** 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

Whilst being 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 moments, and classified them with the aim to draw some lessons in synthesizing SMTs with enhanced toroidal magnetization. As shown above, toroidal moments can be influenced by the molecular symmetry, the coordination environment and/or the bridging ligands which act as super-exchange pathways, which should be considered when designing new SMTs in the future.

Three major conclusions emerge from the undertaken research.

First, the chances of synthesizing 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 **Dy_3-1**. There is also a third requirement of suitable exchange/dipolar interaction between lanthanide ions in order to stabilize a toroidal type of arrangement of the 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 Dy_3N molecule embedded into C_{80} fullerene cage, which shows three quasidegenerate magnetic exchange doublets in the ground state, while the first excited exchange Kramer's doublet appears as a non-magnetic radial state.[49]

Second, the toroidal states in the synthesized SMTs are quite robust. This is clearly seen in the example of **$CuDy_3$** chains,[46] containing polymerized Dy_3 triangles, and of **Dy_6-2** complex,[45] containing two strongly interacting Dy_3 units. In both cases the toroidal moment in the ground state survives and is not much different from the one detected in the **Dy_3-1** complex.[27] This robustness of toroidal magnetization is a highly important property in view of the possible applications of such molecules in various electronic devices, which require the survival of electronic properties of the molecule after drafting on a surface functionalization and attachment of the leads.

Third, the approach based on the application of high-level *ab initio* methods has proved to be a reliable tool for detecting and predicting the noncollinear magnetism in polynuclear lanthanide complexes.[26] This is this research methodology which allowed the toroidal ground state to be discovered in the **Dy$_3$-1** triangle[27] and then in all other polynuclear complexes reviewed here. In contrast 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 an 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 will always 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 the unambiguous detection of the toroidal magnetic moment in complexes. The direct visualization of toroidal moments in such compounds is in principle possible *via* neutron diffraction, but requires the application of this technique at a much higher level that it is presently done. Another prospective 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 Mn$_{12}$acac, Fe$_4$, [TbPc$_2$]$^-$, *etc.*

Another appealing aim of SMTs is to create multifunctional molecular materials. In this aspect the possibilities offered by the molecular approach are unparalleled in the word 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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