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# Acquiring a record barrier height for magnetization reversal in lanthanide encapsulated fullerene molecules using DFT and *ab initio* calculations†

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***Ab initio* calculations performed on a series of lanthanide encapsulated fullerenes reveal {DyOSc}@C<sub>82</sub> to be one of the best host–guest pairs to offer a barrier height exceeding 1400 cm<sup>−1</sup>. The high-symmetry environment preserved inside the cage quenches the QTM effects up to third-excited states leading to very larger barrier heights and this opens up a new possibility of obtaining attractive SMMs based on lanthanide based endohedral metallo-fullerenes (EMFs).**

Endohedral fullerenes are molecular carbon cages with atom(s) confined within the cages.<sup>1</sup> Paramagnetic endohedral fullerenes have been found to show relatively long electron spin relaxation times which make them ideal candidates for the construction of molecular quantum computer and memory storage devices.<sup>2</sup> Since the birth of the first single-ion magnet based on the terbium phthalocyanine complex by Ishikawa *et al.*, there has been growing interest in the synthesis of lanthanide based molecular magnets.<sup>3</sup> Despite tremendous progress, lanthanide based single molecular magnets (SMMs) still face stiff hurdles in the realization of practical applications, as quantum tunneling of magnetization (QTM) is very efficient in lanthanides. The QTM can be quenched by (i) preserving high-symmetry around lanthanide ions,<sup>4</sup> (ii) weakening the intermolecular interactions, (iii) promoting strong exchange coupling,<sup>1e,5</sup> (iv) suppressing the hyperfine interactions of lanthanides and the coordinated ligands and (v) besides these points, stability of the SMM under ambient conditions is also necessary to meet the potential applications proposed. Addressing all these points simultaneously in classical coordination chemistry is extremely challenging<sup>6</sup> and therefore other avenues to achieve the same have been explored. In this regard, lanthanide encapsulated metallo-fullerenes are attractive and some examples in this direction have already been reported.<sup>2a,7</sup> In particular, Greber *et al.*<sup>2a</sup> reported the DySc<sub>2</sub>N@C<sub>80</sub> EMF which exhibits a hysteresis

loop up to 4 K even after adsorption on the Rh(111) surface.<sup>8</sup> It is only the second molecule to do so after the Fe<sub>4</sub> SMM.<sup>9</sup> Chibotaru *et al.*<sup>7b,c</sup> have undertaken theoretical studies to explore the magnetic relaxation of such molecules.

Quite interestingly, points (i)–(v) mentioned above can be simultaneously achieved in {DyOM}@EMF (where M = Lu and Sc) complexes, where a high-symmetry around Dy(III) can be preserved. Besides coordination of oxygen atoms to the lanthanide yields a large magnetic anisotropy and also avoids possible relaxation *via* super-hyperfine interaction as natural isotopes of oxygen do not have nuclear spins. The metal atom M being a diamagnetic element helps to avoid weak exchange coupling which generally leads to close lying excited states and faster relaxation.<sup>10</sup> The intermolecular and dipolar interactions can be reduced significantly as the Ln(III)··Ln(III) distances are expected to be very large in the EMFs.<sup>2a</sup>

With this background, here we have performed detailed density functional and CASSCF calculations on a {DyOM}<sup>4+</sup> unit encapsulated in three different EMFs such as DyOM@C<sub>72</sub>, DyOM@C<sub>76</sub> and DyOM@C<sub>82</sub> to find a suitable pair which exhibits superior SMM characteristics. The chosen models also draw inspiration from the report of the DySc<sub>2</sub>N@C<sub>80</sub> complex exhibiting hysteresis up to 6 K.<sup>2a</sup>

To start with, we have optimized Gd(III) analogues of all the selected EMFs (see Fig. 1 and Fig. S1 and Table S1 of the ESI† for selected structural parameters). To ascertain the effect of various energetically close lying isomers on magnetic anisotropy, we have studied four different possible isomers in the case of a DyOLu@C<sub>76</sub> molecule. Structure optimizations have been performed using G09

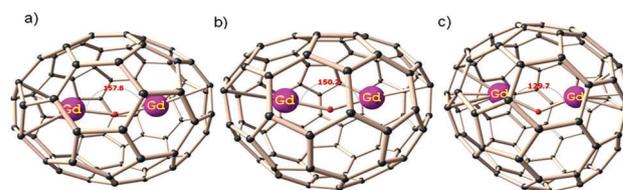


Fig. 1 DFT optimized structures for Gd analogues of (a) DyOLu@C<sub>72</sub>; (b) DyOLu@C<sub>76</sub>(1) and (c) DyOLu@C<sub>82</sub>.

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suite of programme<sup>11</sup> using an unrestricted B3LYP functional<sup>12</sup> employing a CSDZ basis set<sup>13</sup> for Gd(III) and a 6-31G\* basis set for all other (C and O) atoms.<sup>14</sup> To explore the bonding, we have also performed the Atoms in Molecules (AIM) analysis.<sup>15</sup>

In these studied EMFs (DyOLu@C<sub>72</sub>, DyOLu@C<sub>76</sub> (isomers 1–4) and DyOLu@C<sub>82</sub>), a Dy(III) ion is coordinated to the hexagonal/pentagonal aromatic ring inside the fullerene where the Dy–C distances are estimated to be in the range of 2.4 to 2.6 Å. The Dy–O distances are estimated to be in the range of 2.0 to 2.1 Å in the studied structures, suggesting a stronger axial interaction with oxygen atoms.<sup>7b</sup> For the DyOLu@C<sub>76</sub> molecule, four possible isomers are optimized (see Fig. 1, and Fig. S1 in the ESI†) with the isomer possessing the C<sub>s</sub> symmetry found to be the ground state (DyOLu@C<sub>76</sub>-1). Other isomers (2–4) are found to lie 6.2, 41.1 and 55.2 kJ mol<sup>-1</sup> higher in energy, respectively, as compared to the DyOLu@C<sub>76</sub>-1 species. AIM analysis reveals that the interaction between the lanthanide and C<sub>72</sub> cage is a η<sub>6</sub> interaction with a six-membered ring while in C<sub>76</sub> and C<sub>82</sub>, it is a η<sub>2</sub> interaction with a six-membered ring (see Fig. S2 and Table S2 of the ESI†). The AIM analysis also suggests a stronger Ln–fullerene interaction for the C<sub>82</sub> species compared to the C<sub>76</sub> species and this is correlated with the difference in the Ln–O–C angles and the Ln–C distances.

To understand the nature of magnetic anisotropy, we have performed CASSCF+RASSI-SO/SINGLE\_ANISO calculations using the MOLCAS 8.0 code (see computational details). This chosen methodology has been very successful in predicting the energy and the g-tensors of low-lying states of anisotropic lanthanides.<sup>16</sup> We have computed eight low lying Kramer's Doublets (KDs), corresponding to the <sup>6</sup>H<sub>15/2</sub> state. These states are found to lie within an energy span of 1475–1625 cm<sup>-1</sup> for all the studied EMFs (see Table 1 for DyOLu@C<sub>72</sub>, DyOLu@C<sub>76</sub>-1, DyOLu@C<sub>82</sub> and Table S3 of the ESI† for other isomers of DyOLu@C<sub>76</sub>). In all these studied cases, the m<sub>J</sub> = ±15/2 is found to be the ground state and suggests that the chosen ligand field best suited for the oblate Dy(III) ion.<sup>4</sup> We would like to note here that for DySc<sub>2</sub>N@C<sub>80</sub> molecule reported by Greber *et al.*,<sup>2a</sup> the ground state was determined to be pure ±15/2.<sup>7d</sup> The computed ground state anisotropy for all the studied EMFs are found to be purely Ising in nature, suggesting very small QTM effects within the ground state KD (in the range of 10<sup>-5</sup> to 10<sup>-6</sup> μ<sub>B</sub>, see Fig. 2 for DyOLu@C<sub>72</sub>, DyOLu@C<sub>76</sub>-1, DyOLu@C<sub>82</sub> and Fig. S3 of the ESI†). All the four isomers of DyOLu@C<sub>76</sub> are found to have similar anisotropic properties and the ground state g<sub>zz</sub> axis

of all the isomers are found to be oriented along the hexagonal/pentagonal ring (Fig. S4 of the ESI†). In all these molecules, the first and second-excited KDs are also Ising in nature, whereas the third-excited KD has significant transverse anisotropy. The computed transversal magnetic moments between the first-excited KDs are found to be smaller, suggesting a very small operative TA-QTM through the first-excited KD (see Fig. 2 and Fig. S3 of the ESI†). The Orbach/Raman process related to the ground state and the first-excited state of opposite magnetization is found to be large in DyOLu@C<sub>76</sub>-4, suggesting relaxation *via* the first-excited state. With respect to the ground state g<sub>zz</sub> axis, the first-excited g<sub>zz</sub> axis is found to be non-collinear for DyOLu@C<sub>72</sub> and for all four isomers of DyOLu@C<sub>76</sub>(1–4), with the ground state to first-excited state energy separation (U<sub>cal</sub> values) of 451.6 cm<sup>-1</sup>, 396.7 cm<sup>-1</sup>, 425.7 cm<sup>-1</sup>, 487.0 cm<sup>-1</sup> and 476.6 cm<sup>-1</sup> respectively. This suggests relaxation *via* the first-excited state for DyOLu@C<sub>72</sub> and DyOLu@C<sub>76</sub>(1–4) EMFs (–1 → –2 → +2 → +1 for DyOLu@C<sub>72</sub> and DyOLu@C<sub>76</sub>(1–3)), while –1 → +2 → +1 for DyOLu@C<sub>76</sub>-4. For the DyOLu@C<sub>82</sub> complex, on the other hand, the g<sub>zz</sub> axes of the first three states are collinear whereas that of the third-excited state is tilted by 4.5° (Table 1) and this suggests relaxation *via* the third-excited state for DyOLu@C<sub>82</sub> EMFs (–1 → –2 → –3 → –4 → +4 → +3 → +2 → +1). This places the estimate of U<sub>cal</sub> to be 1220.3 cm<sup>-1</sup> for DyOLu@C<sub>82</sub> EMFs. As the size of the fullerene cage increases, the equatorial interaction of the aromatic ring with Dy(III) is minimized leading to a smaller transverse anisotropy and a larger barrier height for this molecule. This is clearly witnessed in the AIM analysis where electron density ρ(r) and Laplacian of the electron density {∇<sup>2</sup>ρ(r)} at the bond critical points (BCPs) reveal an increasing transverse ligand field interaction of the aromatic ring with Dy(III) ions in the following order DyOLu@C<sub>82</sub> < DyOLu@C<sub>76</sub>(4) < DyOLu@C<sub>72</sub>.

To further support this point, calculations are performed on three different models (models a–c with ethylene, η<sub>2</sub>-benzene and η<sub>6</sub>-benzene interacting with Dy(III) respectively. See Fig. 3) with varying Dy(III)–π interactions. These models a–c closely resemble the lanthanide–fullerene interactions present in C<sub>82</sub>, C<sub>76</sub> and C<sub>72</sub> species respectively. The number of carbon atoms that are interacting with Dy(III) increases (as we move from a to c), which leads to a reduction in the effective barrier height. This is due to relaxation *via* lower-excited states and stabilization of lower m<sub>J</sub> levels such as ±1/2 or ±3/2 due to enhanced

**Table 1** CASSCF+RASSI-SO computed relative energies of eight low lying KDs and g tensors of eight low lying KDs for DyOLu@C<sub>72</sub>, DyOLu@C<sub>76</sub>-1 and DyOLu@C<sub>82</sub> molecules, along with deviations from the principal magnetization axes of the first KD

M	DyOLu@C <sub>72</sub>				DyOLu@C <sub>76</sub> -1				DyOLu@C <sub>82</sub>			
	E (cm <sup>-1</sup> )	g <sub>x</sub> , g <sub>y</sub> , g <sub>z</sub>	(°)		E (cm <sup>-1</sup> )	g <sub>x</sub> , g <sub>y</sub> , g <sub>z</sub>	(°)		E (cm <sup>-1</sup> )	g <sub>x</sub> , g <sub>y</sub> , g <sub>z</sub>	(°)	
1	0.0	0.000, 0.000, 19.970			0.0	0.000, 0.000, 19.980			0.0	0.000, 0.000, 19.982		
2	451.6	0.006, 0.006, 17.089	4.6		396.7	0.001, 0.001, 17.139	5.1		475.2	0.001, 0.001, 17.028	2.0	
3	868.6	0.037, 0.042, 14.280	7.4		790.2	0.006, 0.007, 14.293	4.7		896.1	0.029, 0.036, 14.126	1.9	
4	1194.5	0.339, 0.398, 11.410	4.2		1112.2	0.080, 0.093, 11.595	1.5		1220.3	0.158, 0.194, 11.326	4.5	
5	1375.5	3.852, 4.746, 7.632	16.9		1312.4	1.680, 1.869, 9.041	11.6		1430.3	0.436, 0.605, 8.486	6.2	
6	1444.3	1.333, 2.344, 9.237	96.6		1385.3	2.434, 3.624, 15.367	102.3		1533.1	6.130, 6.022, 4.113	166.4	
7	1470.2	0.830, 4.592, 11.085	79.5		1421.5	0.735, 3.572, 12.438	84.3		1578.8	0.012, 1.308, 14.940	84.6	
8	1516.0	0.627, 1.245, 16.452	88.6		1475.4	0.663, 2.687, 17.573	87.9		1615.7	0.266, 2.198, 17.348	90.1	

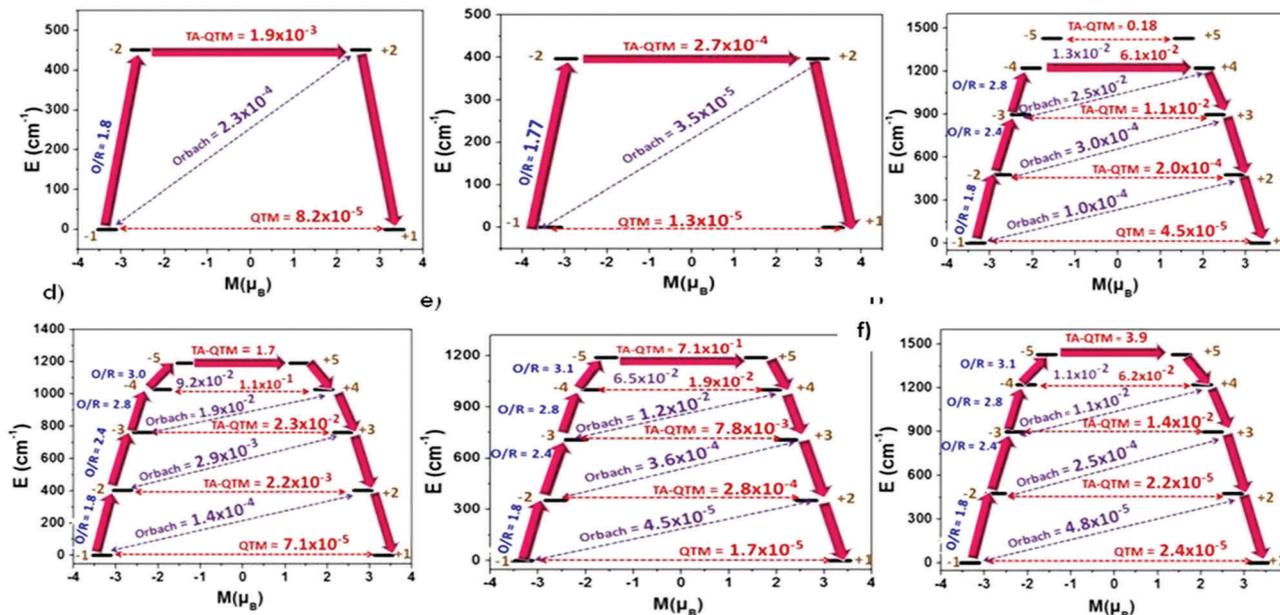


Fig. 2 Qualitative mechanism developed based on SINGLE\_ANISO calculations for (a) DyOLu@C<sub>72</sub>; (b) DyOLu@C<sub>76-1</sub>; (c) DyOLu@C<sub>82</sub>; (d) DyOSc@C<sub>72</sub>; (e) DyOSc@C<sub>76-1</sub> and (f) DyOSc@C<sub>82</sub>. The arrows show the connected energy states, and the numbers represent the matrix element of the transversal magnetic moment (see the text for details).

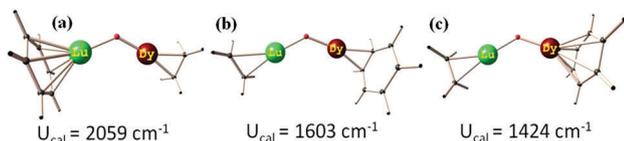


Fig. 3 Models (a)–(c) with their respective calculated  $U_{\text{cal}}$  values.

equatorial interaction as we move from a to c (see Fig. S5 and Table S4 of the ESI†).

To explore further the role of the diamagnetic ion in enhancing the barrier height,<sup>17</sup> we have replaced Lu(III) with a Sc(III) ion in our models and the corresponding structures are further optimized (see Table S5 of the ESI† for selected structural parameters for DyOSc@C<sub>72</sub>, DyOSc@C<sub>76(1-4)</sub> and DyOSc@C<sub>82</sub>). The report of Dy<sub>2</sub>ScN@C<sub>80</sub> SMM containing Sc(III) suggest that the predicted models are viable.<sup>2a</sup> In Sc(III) structures, the Ln–O–Sc angles are wider compared to the corresponding Ln–O–Lu angles. This is due

to stronger Sc(III)–O interaction and the smaller size of Sc(III) ions compared to Lu(III) ions.

We have performed CASSCF+RASSI-SO/SINGLE\_ANISO calculations on these molecules to probe the nature of magnetic anisotropy. The ground state is estimated to be  $m_j = \pm 15/2$  for all the computed species (see Table 2). The computed ground state anisotropies for DyOSc@C<sub>72</sub>, DyOSc@C<sub>76(1-4)</sub> and DyOSc@C<sub>82</sub> are found to be purely Ising in nature ( $g_{zz} \approx 19.98$  with  $g_{xx} = g_{yy} = 0$ ) suggesting very a small QTM within the ground state KD (in the range of  $1 \times 10^{-5} \mu_B$  to  $7 \times 10^{-5} \mu_B$ , see Fig. 2 and Table 2 for DyOSc@C<sub>72</sub>, DyOSc@C<sub>76-1</sub>, DyOSc@C<sub>82</sub> and, Fig. S3 and Table S6 of the ESI† for other isomers (2–4) of DyOSc@C<sub>76</sub>). Here, in all these molecules, both the first and second-excited KDs are also found to be purely axial whereas the third-excited state is found to have a very small transverse magnetic component. In all these molecules, first to third-excited state KDs are collinear with respect to the ground state KD, suggesting relaxation *via* the fourth-excited state which is having substantial transverse magnetic moment.

Table 2 CASSCF+RASSI-SO computed relative energies of eight low lying KDs and  $g$  tensors of eight low lying KDs for DyOSc@C<sub>72</sub>, DyOSc@C<sub>76-1</sub> and DyOSc@C<sub>82</sub> molecules, along with deviations from the principal magnetization axes of the first KD

M	DyOSc@C <sub>72</sub>			DyOSc@C <sub>76-1</sub>			DyOSc@C <sub>82</sub>		
	$E \text{ (cm}^{-1}\text{)}$	$g_x, g_y, g_z$	(°)	$E \text{ (cm}^{-1}\text{)}$	$g_x, g_y, g_z$	(°)	$E \text{ (cm}^{-1}\text{)}$	$g_x, g_y, g_z$	(°)
1	0.0	0.00, 0.000, 19.976		0.0	0.000, 0.000, 19.980		0.0	0.000, 0.000, 19.988	
2	403.9	0.007, 0.007, 17.097	0.3	354.1	0.001, 0.001, 17.144	2.9	453.1	0.000, 0.000, 17.043	0.2
3	761.7	0.066, 0.070, 14.323	0.5	709.4	0.022, 0.024, 14.332	3.0	867.8	0.038, 0.043, 14.122	0.5
4	1027.2	0.295, 0.401, 11.559	0.2	999.8	0.036, 0.073, 11.634	1.6	1192.2	0.163, 0.201, 11.290	2.3
5	1191.1	4.711, 5.476, 7.870	0.9	1188.9	2.030, 2.127, 8.887	3.0	1406.0	0.950, 1.309, 8.436	5.6
6	1284.6	3.288, 4.734, 11.979	89.6	1276.1	4.298, 5.022, 9.259	99.5	1508.2	2.075, 2.330, 4.773	18.4
7	1309.4	0.036, 0.222, 18.373	90.4	1303.6	0.458, 2.080, 13.335	86.8	1537.5	13.349, 7.310, 0.990	178.7
8	1343.8	0.588, 1.066, 18.154	90.1	1358.8	0.376, 1.081, 18.575	89.4	1600.1	0.133, 0.520, 19.145	90.4

The computed mechanism of relaxation reveals the absence of TA-QTM up to third-excited states. The Orbach/Raman process related to the ground state and the first-excited state of opposite magnetization ( $-1$  to  $+2$ ) is also found to be very small, but within the same sign states ( $-1 \rightarrow -2$ ) are found to be large (*ca.*  $1.8 \mu_B$ ) suggesting spin excitation *via*  $-1 \rightarrow -2$  as a feasible pathway. The computed mechanism suggests relaxation *via* the fourth-excited KD ( $-1 \rightarrow -2 \rightarrow -3 \rightarrow -4 \rightarrow -5 \rightarrow +5 \rightarrow +4 \rightarrow +3 \rightarrow +2 \rightarrow +1$ ) with the estimated  $U_{\text{cal}}$  to be  $1191 \text{ cm}^{-1}$ ,  $1189 \text{ cm}^{-1}$ ,  $1231 \text{ cm}^{-1}$ ,  $1341 \text{ cm}^{-1}$ ,  $1346 \text{ cm}^{-1}$  and  $1406 \text{ cm}^{-1}$  for DyOsc@C<sub>72</sub>, DyOsc@C<sub>76</sub>(1-4) and DyOsc@C<sub>82</sub> EMFs respectively. The  $U_{\text{cal}}$  value of  $1406 \text{ cm}^{-1}$  predicted for the DyOsc@C<sub>82</sub> molecule is one of the largest computed for single-ion magnets. Larger Dy–O–Sc angles and stronger Dy–O interaction compared to DyOLu structures lead to collinearity of anisotropic axis up to the fourth-excited state in these species leading to a very large barrier height for magnetization reversal (Table 2). This is further supported by our calculations on model-a where the Dy–O–Lu angles varied from 100 to 180 degrees where an increase in the barrier height with an increase in the angle is witnessed. This is due to the fact that at larger angles, complexes achieve higher symmetry and therefore the  $g_{zz}$  axis of the excited-states becomes collinear pushing the relaxation to higher and higher states (see Table S7 in the ESI†).

Our calculations suggest that C<sub>82</sub> is the best host molecule and the {DyOsc} unit is the best guest molecule to yield superior SMMs. Barrier heights as large as  $700 \text{ cm}^{-1}$  are found to exhibit hysteresis up to 30 K,<sup>16a</sup> and the very large  $U_{\text{cal}}$  value of  $1406 \text{ cm}^{-1}$  predicted for this molecule may translate into a larger blocking temperature. Other factors which generally reduce the barrier heights in classical coordination compounds such as stronger intermolecular interactions, and a low-symmetry environment are absent here, thus brightening the chances of achieving greater barrier heights. Besides, these molecules are very stable under ambient conditions and can be fabricated easily by placing them on surfaces such as graphene.<sup>18</sup> Recent studies<sup>1c</sup> on {Sc<sub>2</sub>C<sub>2</sub>}@C<sub>86</sub> suggest a viable way to fine-tune the structural parameters of the host molecule encapsulated inside the fullerene cage and if such an approach is employed to achieve linear Dy–O–Sc angles, one can obtain even larger barrier heights.

To this end, we have performed detailed DFT and *ab initio* calculations on lanthanide encapsulated fullerene molecules to understand the mechanism of magnetic relaxation. Our calculations unveil the ideal host–guest pair that yields a very large barrier height for magnetization relaxation and opens up new avenues in the search for new generation SMMs.

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