Attaining record-high magnetic exchange, magnetic anisotropy and blocking barriers in dilanthanofullerenes†

Sourav Dey‡ and Gopalan Rajaraman‡,*

While the blocking barrier ($U_{\text{eff}}$) and blocking temperature ($T_B$) for “Dysprocenium” SIMs have been increased beyond liquid N$_2$ temperature, device fabrication of these molecules remains a challenge as low-coordinate Ln$^{3+}$ complexes are very unstable. Encapsulating the lanthanide ion inside a cage such as a fullerene (called endohedral metallofullerene or EMF) opens up a new avenue leading to several Ln@EMF SIMs. The ab initio CASSCF calculations play a pivotal role in identifying target metal ions and suitable cages in this area. Encouraged by our earlier prediction on Ln$_2$@C$_{79}$N, which was verified by experiments, here we have undertaken a search to enhance the exchange coupling in this class of molecules beyond the highest reported value. Using DFT and ab initio calculations, we have studied a series of Gd$_2$@C$_{2n}$ ($30 \leq 2n \leq 80$), where an antiferromagnetic $J_{\text{Gd-Gd}}$ of $-43$ cm$^{-1}$ was found for a stable Gd$_2$@C$_{59}$–D$_{3h}$ cage. This extremely large and exceptionally rare 4f–4f interaction results from a direct overlap of 4f orbitals due to the confinement effect. In larger cages such as Gd$_2$@C$_{60}$ and Gd$_2$@C$_{80}$, the formation of two centre-one-electron (2c-1e) Gd–Gd bonds is perceived. This results in a radical formation in the fullerene cage leading to its instability. To avoid this, we have studied heterofullerenes where one of the carbon atoms is replaced by a nitrogen atom. Specifically, we have studied Ln$_2$@C$_{59}$N and Ln$_2$@C$_{79}$N, where strong delocalisation of the electron yields a mixed valence-like heterofullerenes where one of the carbon atoms is replaced by a nitrogen atom. Specifically, we have studied Ln$_2$@C$_{59}$N and Ln$_2$@C$_{79}$N, where strong delocalisation of the electron yields a mixed valence-like behaviour. This suggests a double-exchange ($B$) is operational, and CASSCF calculations yield a $B$ value of 434.8 cm$^{-1}$ and resultant $J_{\text{Gd-rad}}$ of 869.5 cm$^{-1}$ for the Gd$_2$@C$_{59}$N complex. These parameters are found to be two times larger than the world-record $J$ reported for Gd$_2$@C$_{79}$N. Further ab initio calculations reveal an unprecedented $U_{\text{cal}}$ of 1183 and 1501 cm$^{-1}$ for Dy$_2$@C$_{59}$N and Tb$_2$@C$_{59}$N, respectively. Thus, this study offers strong exchange coupling as criteria for new generation SMMs as the existing idea of enhancing the blocking barrier via crystal field modulation has reached its saturation point.

Introduction

Single molecule magnets (SMMs) are of prime interest in molecular magnetism due to their potential application in memory storage devices, qubits, etc. 1,2 The figure of merit of an SMM is determined by the blocking barrier for magnetisation reversal ($U_{\text{eff}}$) and blocking temperature ($T_B$), the temperature below which opening of magnetic hysteresis is observed. These $U_{\text{eff}}$ and $T_B$ values are generally very high for lanthanides, thanks to their strong spin–orbit coupling.3–10 The enhancement of $T_B$ as high as 80 K in “Dysprocenium” complexes was an important breakthrough, replenishing the hope for potential applications in information storage devices.11–15 Among others, important bottlenecks that are likely to hamper the futuristic application of these SMMs are (i) enhancing the blocking temperature beyond 80 K (ii) obtaining molecules that are stable under ambient conditions so that fabrication can be attempted (iii) retaining their intriguing magnetic properties upon fabrication – many of the best transition metal SMMs failed these criteria.16–21

To address the first challenge, among other strategies that could help enhance the barrier height/blocking temperature is the quenching of quantum tunnelling of magnetisation (QTM), which is prevalent at low temperatures. If a robust magnetic exchange between two Ln$^{3+}$ ions is induced, it can act as a perturbation to reduce the degeneracy of Kramers doublets (KDs). This quenches the QTM and gives rise to large $U_{\text{eff}}$ and $T_B$ values.22–24 However, obtaining a large exchange coupling between two Ln$^{3+}$ metal ions is a formidable task as 4f orbitals are deeply buried, leading to a weak/no interaction in dinuclear or polynuclear Ln$^{3+}$ complexes.25–30

In this regard, lanthanide encapsulated fullerenes (called endohedral metallofullerenes or EMFs) are gaining tremendous attention for various reasons: (a) they offer stability to guest molecules which are otherwise unstable;31 (b) thanks to their...
strong π cloud, fabrication of such molecules on graphene/ 
HOPG/CNTs and other surfaces is straightforward;31–39 (c) 
during this process guest molecules stay intact, and hence they 
are unlikely to lose their characteristics upon fabrication;31 (d) 
as fullerenes are made of pure carbon, and the source of nuclear 
spin of the guest molecules can be controlled, they offer 
a nuclear spin free system – a key criterion for some qubit 
applications.34,40 These key advantages mentioned here directly 
address the aforementioned goals (ii) and (iii), making them 
superior to traditional coordination chemistry/organometallic 
SMMs/SIMs.

One way to attain strong exchange coupling in lanthanide 
SMMs is to employ radical–Ln exchange which is substantially 
larger due to the direct exchange between 4f–2p orbitals.41–43 In 
the search for a stronger exchange in Ln–radical systems, using 
a combination of DFT and ab initio methods, we have predicted 
a record high magnetic exchange coupling for a Gd2@C79N 
radical fullerene complex and also suggested a very large 
blocking barrier for the Dy analogue.44,45 Both these predictions 
were proved in a span of few years independently by two 
groups,46–49 and Gd2@C79N is found to have a very large spin 
relaxation time opening up a new avenue in spin-based 
qubits.40,46 While a Ln–radical exchange could solve this 
problem,40 the majority of the conventional lanthanide–radical 
systems are highly reactive and could pose a challenge in 
accomplishing the aforementioned goals (ii) and (iii).41,42,43,50−55

In this connection, if a robust exchange is induced between 
two Ln3+ ions, this will be very rewarding. One strategy to 
enhance the exchange coupling is to induce a weak Ln–Ln 
bond, which is possible if two ions are brought very close to 
each other directly. The metal–metal bonds in transition metal 
complexes are common but are scarce for lanthanides.56–58 
Inspired from the report that even noble gas elements such as 
He form He⋯He bonds under confinement, we devise such 
models for lanthanides that can offer very large 4f–4f exchange 
interactions.59–61 In line with this idea, we have explored various 
Gd2@C2n (2n = 30–52, 60, 80) complexes in search of a stronger 
exchange and found Gd4⋯Gd8 exchange as high as ~43 cm−1. 
In the second approach, we have extended our study to air- 
stable azafullerene radical analogues such as Ln3@C59/79N (Ln = Gd, Tb, Dy). Using ab initio calculations, we have computed 
the double-exchange parameter B in these azafullerene cages. 
We have exploited the presence of double exchange to design 
SMMs based on Dy and Tb and unveil a new line of prediction 
with models exhibiting a Ueff value exceeding 1500 cm−1.

Results and discussion

Achieving large exchange coupling in lanthanides is chal- 
lenging as the 4f orbitals of lanthanides are deeply buried 
and interact weakly with ligand orbitals. The highest magnetic 
exchange between two Ln3+ ions is estimated in a {Gd2Cr3} 
complex where J_{fod-gd} is +1.4 cm−1 (H = −J_{fod-gd} S_{fod-gd}).62 As the Ln⋯ 
Ln distance plays a crucial role in controlling the 4f–4f exchange 
interaction, a large J is expected if two Ln3+ ions are confined in 
a fullerene cage. With this goal, we begin our study with Gd2 
endothedral fullerenes by varying the cage size from C30 to C80.

We have analysed the structure, binding energy, and magnetic 
properties within the DFT framework for two low energy 
conformers of the fullerene cages among various close-lying 
isomers.

**Structure and bonding in Gd2@C2n (2n = 30–48, 52, 60, 80)**

The C2n fullerene is the smallest cage where encapsulation leads 
to a stable geometry, as steric strain dominates over the metal- 
cage stabilisation in C28 and lower cages (Fig. 1, Table S1 and 
Appendix S1–S25†). For Gd2@C30, a C2v isomer is found to be 
stable by 52.3 kJ mol−1 compared to the D3h isomer due to 
stronger Gd–C interactions in the former as affirmed by the AIM 
analysis (see Table 1 for larger cages and Tables S1–S4 in the 
ESI†). In larger cages, the stability can be rationalised using (i) 
the number of APRs (Table S2†) and (ii) the nature of Gd–C 
interaction as obtained from the AIM analysis (see Fig. 1, S1–S26 
and Tables S3–S27 in the ESI†).

Considering the Gd3+ ionic radius,64 a Gd⋯Gd distance less 
than 2.5 Å (van der Walls radius) is likely to suggest a weak 
interaction or even a metal–metal bond. Such interactions are 
expected to reflect on J_{Gd-Gd} values with smaller values indicate 
weaker Gd⋯Gd interactions and not a metal–metal bond. 
Therefore, to compare the metal–metal interaction in Gd2@C2n 
with 30 ≤ 2n ≤ 52, the magnetic exchange J_{Gd-Gd} between two Gd3+ 
ions has been estimated using DFT calculations (B3LYP/ 
TZV, H = −J_{Gd-Gd} S_{Gd-Gd}, see computational details and Table 1). The J_{Gd-Gd} is found to be antiferromagnetic in all Gd2@C2n (2n 
≤ 52) EMFs with the exception of Gd2@C44 (2n = 52), Gd2@C60 (2n = 60), 
and Gd2@C72 (2n = 72) EMFs having a ferromagnetic coupling (Table 
1). The value in Table 1 suggests the decrease in antiferro-
magnetic interaction with the decrease in cage size. Within the 
same cage, the J_{Gd-Gd} value increases for a higher symmetry 
isomer. The largest antiferromagnetic J_{Gd-Gd} was estimated for 
Gd2@C30–D3h (−62.7 cm−1). This is several orders of magnitude 
larger than the experimentally known largest 4f–4f interaction. 
For the Gd2@C30–C2v isomer, the J_{Gd-Gd} decreases to ~49.6 cm−1 
despite a shorter Gd⋯Gd distance compared to the D3h isomer.

**Fig. 1** The optimized structures of (and Gd–C bond length range) (a) Gd2@C30–D3h (2.140–2.350 Å), (b) Gd2@C30–C2v (2.400–2.407 Å), and 
(c) Gd2@C59/C60 (2.400–2.407 Å). The corresponding spin density 
plots for the high spin state are given in figures (d–f) with an isosurface 
vale of 0.006 e− bohr−3. Colour code: Gd-pink, C-grey, N-blue.
Table 1 The estimated $J$ and the binding energy (kJ mol$^{-1}$) of chosen conformers in Gd$_2$@C$_{2n}$. Next to the symmetry label, the Gd···Gd distance is given in parentheses (Å). The value of spin density of each metal centre in the HS configuration of all Gd$_2$@C$_{2n}$ has been given below the exchange values in parentheses. All the $J$ and $B$ values are shown in cm$^{-1}$.

| Gd$_2$@C$_{2n}$ | $J_{\text{Gd-Gd}}$ (cm$^{-1}$) | $B_{\text{Gd-Gd}}$ (cm$^{-1}$) | $\Delta E$ (kJ mol$^{-1}$) |
|-----------------|------------------|-----------------|------------------|
| $2n = 30$       | C$_{2v}$ (2.185) | $D_{3h}$ (2.224) | C$_{2v}$ 1160.9 |
|                 |                  | D$_3$           | C$_{2v}$ 1149.8 |
|                 |                  | C$_3$           | C$_{2v}$ 0.0  |
|                 |                  | D$_3h$          | C$_{2v}$ 52.3 |
| $2n = 32$       | C$_{2v}$ (2.207) | $D_{3h}$ (2.272) | C$_{2v}$ 907.3 |
|                 |                  | D$_3$           | C$_{2v}$ 620.2 |
|                 |                  | C$_3$           | C$_{2v}$ 166.5 |
|                 |                  | D$_3h$          | C$_{2v}$ 0.0  |
| $2n = 34$       | C$_{2v}$ (2.283) | $D_{3h}$ (2.286) | C$_{2v}$ 279.1 |
|                 |                  | D$_3$           | C$_{2v}$ 392.1 |
|                 |                  | C$_3$           | C$_{2v}$ 73.0  |
|                 |                  | D$_3h$          | C$_{2v}$ 0.0  |
| $2n = 36$       | C$_{2v}$ (2.400) | $D_{3d}$ (2.269) | C$_{2v}$ 61.0  |
|                 |                  | D$_{2d}$        | C$_{2v}$ 330.0 |
|                 |                  | C$_{2}$         | C$_{2d}$ 37.2 |
| $2n = 38$       | C$_{2v}$ (2.443) | $D_{3h}$ (2.734) | C$_{2v}$ 1 |
|                 |                  | D$_{sh}$        | C$_{2}$  |
|                 |                  | C$_{sh}$        | C$_{2}$  |
|                 |                  | D$_{sh}$        | C$_{2}$  |

$^a$ The binding energy has been calculated with respect to electronic. In all other isomers, the binding energy has been calculated with respect to electronic and thermal free energies. $^b$ Here ‘n’ represents the total number of atoms, including the one nitrogen atom.

This is due to stronger 4f-4f overlaps (Tables S28–S29†). Although the Gd···Gd distances are very similar for C$_{30}$ and C$_{32}$, the $J_{\text{Gd-Gd}}$ value is significantly smaller in Gd$_2$@C$_{32}$ (see Table 1) due to symmetry constraints and the associated 4f-4f overlaps (see Tables S30–S49 in ESI†). Further increase in the cage size only nominally decreases the $J_{\text{Gd-Gd}}$ values with several exceptions, though lower symmetry models follow the trend (see Fig. S27†). A net ferromagnetic interaction is observed in Gd$_2$@C$_{4h}$, Gd$_2$@C$_{4h}$, and Gd$_2$@C$_{52}$ cages due to a meagre contribution to the antiferromagnetic part of $J$ (see Tables S42, S46 and S48†). Orbital orthogonality of 4f-orbitals and dipolar contributions due to shorter Gd···Gd distance leads to a net ferromagnetic coupling in these examples. A very large 4f-4f overlap suggests a possibility of direct 4f-4f interactions between two lanthanide ions, which are hard to observe in classical coordination chemistry. The binding energy becomes positive for Gd$_2$@C$_{2n}$ with $2n \leq 36$ and negative for Gd$_2$@C$_{2n}$ with $2n > 36$ (see Table 1) except for the Gd$_2$@C$_{40}$-C$_{38}$ isomer, where it is thermoneutral (0.7 kJ mol$^{-1}$). Thus, it suggests that the large antiferromagnetic interaction is feasible for the isomers of Gd$_2$@C$_{2n}$ with $2n > 36$.

The magnitude of the spin density of the two Gd$^{3+}$ ions increases with an increase in ring size, supported by the contour plots of the electron density map obtained from AIM analysis (Fig. S28–S54 and Tables S50, S51†). Particularly a sudden jump in the magnitude of spin density is noted for Gd$_2$@C$_{60}$ with nearly one electron found between the two Gd ions (see Fig. 1, S50–S52†). Our NBO analysis reveals that this electron is delocalised in the formally empty orbitals, which are hybridised among 6s, 6p, and 5d orbitals (6s$^0$6p$^0$5d$^0$, see Fig. S55†). Thus, it suggests a strong valence delocalisation where one unpaired electron is delocalised to vacant 5d/6s/6p orbitals of each Gd$^{3+}$ ion leading to a type-III class of mixed valence systems (Gd$_2$@C$_{3n}$, see later).

Mechanism of the formation of Gd$_2$@C$_{2n}$

To further investigate the unusual behaviour wherein the cage size decides the magnitude of the spin density present between the Gd$^{3+}$ ion, we have analysed the formation of Gd$_2$@C$_{2n}$ from the HOMO–LUMO gap perspective. In the formation of dmetallofullerene Gd$_2$@C$_{2n}$, we can presume that two Gd atoms donate three electrons each from their frontier orbitals (5d and
6s orbitals) to the three lowest unoccupied molecular orbitals (LUMOs) of the C2n cage resulting in Gd2@C2n6+. Thus, the formation of Gd2@C2n depends on the energy gap between the frontier orbitals of Gd2 and the LUMOs of the C2n cage. If the LUMOs of the C2n cage are found to be lower in energy than the frontier orbitals of the Gd2 fragment, a large stabilisation occurs after the electron transfer. Quite interestingly, this is the case for the C2n cage with 2n = 52, which favours the transfer of six electrons from Gd2 (with the Gd–Gd distance <3.0 Å, ignoring 4f orbitals, the valence electron configuration is $s^2g^6u^1$) to the C2n cage (Fig. 2a for Gd2@C30 and Fig. S56 and S57† for Gd2@C52$D_{2d}$ and Gd2@C48$C_{2v}$). As the ring size increases, the LUMOs of the C2n cage destabilised. In Gd2@C60 with the Gd–Gd distance of 3.056 Å, the bonding in the Gd2 fragment before encapsulation is found to be $s^2g^6u^1$ (ignoring the 4f orbitals, Fig. 2b). After encapsulation, the five electrons are fully transferred to the cage except one $s^1$ electron (here the β electron in Fig. 2b for Gd2@C60$I_h$) resulting in a 2c-1e bond between two Gd atoms. This is due to the comparable energy of the beta (6s/5d) $s^1$ orbital with the LUMO of the C2n cage.

**Estimation of magnetic exchange in Gd2@C59N–C5, Gd2@C79N–C5–1, and Gd2@C79N–C5–2**

The most sensitive parameter that yields insight into the spin density distribution discussed in the last section is the corresponding exchange coupling $J_{\text{Gd–Gd}}$. Here we intend to compute this parameter and analyse this with respect to the cage size. The mechanism of formation of Gd2@C2n suggests the presence of one unpaired electron between two Gd$^{3+}$ ions and another conjugate electron in the fullerene cage for Gd2@C60$I_h$, Gd2@C80$D_{5h}$, and Gd2@C80$C_{2v}$ isomers (see Table S50†). For these molecules, a complex set of magnetic coupling emerges: (i) the coupling between Gd$^{3+}$ and the radical that reside inside the cage ($J_1$), (ii) the second one describes the coupling between two Gd$^{3+}$ ions ($J_2$), (iii) the third one describes the coupling between two radicals ($J_3$) and (iv) in addition to these isotropic exchange coupling values, a strong electron delocalisation of the radical between two Gd$^{3+}$ ions suggests a double-exchange parameter ($B$) being operative between two Gd ions (in a fully delocalised case, Gd2$^{2.5+}$). All these exchanges have been illustrated in Scheme S2.† This is similar to a type-III mixed-valence

---

**Fig. 2** The MO diagrams corresponding to the formation of (a) Gd2@C30$C_{2v}$ and (b) Gd2@C60$I_h$ isomers. The three black and red horizontal lines correspond to the energy of the occupied and empty orbitals of the C2n fullerene ring, respectively. The blue and pink horizontal lines correspond to the energy of $\alpha$ and $\beta$ orbitals of the Gd2 fragment. We have shown the three lowest unoccupied $\alpha$ orbitals of the C2n fullerene cage with an isosurface value of 0.055 e\textsuperscript{-}Å\textsuperscript{3}. The three highest occupied $\alpha$ orbitals for Gd2 in the C30 and C60 fullerene cage are also shown (isosurface 0.06 e\textsuperscript{-}Å\textsuperscript{3}). Colour code: Gd–pink, C–grey.

**Fig. 3** The fifteen active orbitals of Gd2@C59N with CAS (15,15) active space for the $S = 15/2$ state. Colour code: Gd–pink, C–grey, N–blue.
system\(^{48,49}\) where the spin Hamiltonian parameters are estimated using the following Hamiltonian\(^{70}\)

\[
H = -J(S_A \cdot S_B \cdot \mathbf{O}_A + S_A \cdot S_B \cdot \mathbf{O}_B) + B \mathbf{T}_{AB},
\]

where \(J\) and \(B\) denote the exchange interaction and delocalisation parameter, respectively. \(S_A\) and \(S_B\) are the total spin multiplicity of centres \(A\) and \(B\), respectively, \(\mathbf{O}_A\) and \(\mathbf{O}_B\) are the localisation operator, and \(T_{AB}\) is the electron transfer operator (see computational details for more information).

The presence of one unpaired electron in the fullerene cage of \(\text{Gd}_2@\text{C}_{60}\), \(\text{Gd}_2@\text{C}_{50}\text{D}_{25}\), and \(\text{Gd}_2@\text{C}_{68}\text{C}_{25}\) leads to polymerisation or aggregation, and often, these complexes are not isolable.\(^{71-73}\) There are two strategies available to demonstrate their existence (i) by transforming them into a chemically stable form with one-electron reduction/substitution at the ring position. This has been adapted to stabilise the \(\text{Dy}_2@\text{C}_{90}\text{I}_n\) molecule by chemically transforming it to \(\text{Dy}_2@\text{C}_{90}(\text{CH}_2\text{Ph})_n\).\(^{72-75}\) (ii) By substituting one of the carbon with the nitrogen atom yielding azafullerenes such as \(\text{Ln}_2@\text{C}_{79}\text{N}\) and other similar to those hypothesised here.

While \(\text{Gd}_2@\text{C}_{79}\text{N}\) is a well-characterised and thoroughly studied molecule, \(\text{Gd}_2@\text{C}_{59}\text{N}\) is not known. However, the \(\text{X}\)-ray structure of \(\text{C}_{59}\text{N}\) and encapsulation of some metal ions are experimentally studied, and their existence has been proved beyond ambiguity.\(^{35,80-86}\) Particularly, \(K_2\text{C}_{59}\) has been isolated and characterised thoroughly. This suggests that the \(\text{C}_{59}\text{N}^+\) cage is a stable molecular fragment and can encapsulate \(\text{Ln}^{3+}\) cations similar to those hypothesised here.\(^{87-89}\)

This type-III mix valence moiety of \(\text{Gd}_2@\text{C}_{59}\text{N}\text{C}_3\), \(\text{Gd}_2@\text{C}_{59}\text{N}\text{C}_1\), and \(\text{Gd}_2@\text{C}_{59}\text{N}\text{C}_2\) isomer represents a multireference wave function as the unpaired electron is not localised on a particular centre. Therefore, a multireference method such as the state-average CAS\((15,15)\)SCF set up was employed to estimate the double exchange parameter (\(\beta\)) (Fig. 3, see computational details).\(^{90}\) As per the CASSCF calculations, the additional radical electron resides in a hybrid orbital containing coefficients from 6s, 5p\(_x\), 6p\(_x\), and 5d\(_{z^2}\) orbitals of \(\text{Gd}_1\) and \(\text{Gd}_2\) centres (see Table S55\(^\dagger\) for composition). The set of spin Hamiltonian parameters obtained from the CASSCF calculations are as follows, \(\text{Gd}_2@\text{C}_{59}\text{N}\text{C}_3\) (\(\text{Gd}_2@\text{C}_{59}\text{N}\text{C}_1\)) \([\text{Gd}_2@\text{C}_{79}\text{N}\text{C}_1]\) \(J_1 = +869.8 \pm (404.6) \pm [351.3] \text{cm}^{-1}, J_2 = 0.08 \pm (0.03) \pm [0.03] \text{cm}^{-1}\) \([0.03] \pm [0.03] \text{cm}^{-1}\) \([0.03] \pm [0.03] \text{cm}^{-1}\) \([0.03] \pm [0.03] \text{cm}^{-1}\) \([0.03] \pm [0.03] \text{cm}^{-1}\) and \(B = 434.8 \pm (202.2) \pm [175.6] \text{cm}^{-1}\) (Table 1).

For all three complexes, the \(J_1\) interaction is found to be extremely large, and this is due to the involvement of the diffuse virtual 6s and 6p\(_x\) and 5d\(_{z^2}\) orbitals of \(\text{Gd}\) ions, while the \(J_2\) coupling between two \(\text{Gd}^{3+}\) ions is found to be very small as the 4f orbitals are only weakly interacting here. It is worth mentioning that we have previously reported a very large \(J_1\) value of \(+400\) cm\(^{-1}\) (\(H = -J \mathbf{S}_1 \mathbf{S}_2\) in \(\text{Gd}_2@\text{C}_{79}\text{N}\) using the UB3LYP/TZV setup.\(^{44}\) The estimated \(J_1\) value by our \textit{ab initio} approach for \(\text{Gd}_3@\text{C}_{79}\text{N}\) lies in the range of \(350-405\) cm\(^{-1}\), and this is in line with the DFT calculations and experimental reports (\(-350 \pm 20\) cm\(^{-1}\) using \(H = J_1(\mathbf{S}_1 \cdot \mathbf{S}_2) + J_2(\mathbf{S}_1 \cdot \mathbf{S}_2)\) in ref. 40 and a \(J_1\) value of \(170 \pm 10\) cm\(^{-1}\) using the Hamiltonian \(H = -2J_1(\mathbf{S}_1 \cdot \mathbf{S}_2)\) in ref. 76; see ES\textsuperscript{†} for the discussion of \(J_3\)). These large exchange values have potential application in qubits as they enhance the quantum coherence required for qubit applications.\(^{40}\)

A case study of magnetic anisotropy in \(\text{Dy}_2@\text{C}_{59}\text{N}\) and \(\text{Tb}_2@\text{C}_{59}\text{N}\)

As heterofullerenes yield larger \(J_s\) and homofullerenes yields relatively smaller antiferromagnetic \(J_a\), the former is the best suited to design SMMs. The antiferromagnetic \(J_s\) in homofullerene yields diamagnetic ground states, and smaller ferromagnetic \(J_s\) observed in larger cage sizes such as \(\text{C}_{52}\) did not yield any appealing SMM characteristics. To harness SMMs in this class, heterodinuclear lanthanides with unequal m\(_j\) states were modelled. Models such as \(\text{Pr}_2@\text{C}_{38}\) yield a reasonable \(U_{\text{cal}}\) value with robust QTM quenching (\(ca. 109\) cm\(^{-1}\), see ES\textsuperscript{†}) but are not substantial to serve as a synthetic target.

Therefore, we aim to estimate the magnetic anisotropy in the \(\text{Dy}_2@\text{C}_{59}\text{N}\) and \(\text{Tb}_2@\text{C}_{59}\text{N}\). It is noteworthy to mention that the record-breaking magnetic anisotropy is previously achieved in \(\text{Dy}_2@\text{C}_{79}\text{N}\) and \(\text{Tb}_2@\text{C}_{79}\text{N}\) molecules.\(^{44,77}\) The metal centre in \(\text{Dy}_2@\text{C}_{59}\text{N}\) is found to interact in an \(\eta^6\) fashion with the \(\text{C}_{59}\text{N}\) cage, which creates a strong uniaxial anisotropy (see Fig. 1c) as a long Dy-Dy bond (3.056 Å) indicates a weak ligand field in the opposite site of cage binding. Thus, the coordination can be compared with \(\text{Dy}^{3+}-\text{O}\), which perfectly suits the oblate ground state.\(^{91,92}\) The easy axis of magnetisation is found to be nearly collinear with the Dy-Dy axis with a very small angle (2.0 (1.1°)) for \(\text{Dy}_1(\text{Dy}_2\), Fig. S72\textsuperscript{†}). The calculated \(g_z\) values of KD1 (\(-19.97\)) imply an Ising ground state for both the Dy centres (Tables S70, S71 and Fig. S71\textsuperscript{†}), with the relaxation predicted to

![Fig. 4 The POLY_ANISO computed relaxation mechanism of \(\text{Tb}_2@\text{C}_{59}\text{N}\). The anisotropy axis of the metal (represented by yellow) and radical (represented by red) centre are shown on the right. The thick black line represents the magnetic moment of KDs. The red arrows imply the QTMs for ground KD and TA-QTM for higher excited KDs. The blue dotted arrows indicate a possible Orbach process. The green arrows represent the mechanism of magnetic relaxation. Colour code: Tb-blue violet, C-grey, N-blue.](image-url)
Therefore, the relaxation process due to intermolecular interactions is expected to be minimal due to confinement, which is likely to yield large $T_B$ values. As our predictions on Gd$_2$@C$_{79}$N and Dy$_2$@C$_{79}$N are proved by experiments lately, with Dy$_2$@C$_{79}$N yielding an attractive blocking temperature ($24$ K), these smaller cages, if made, could enhance $T_B$ values even further.  

Conclusions

To this end, we have employed an array of theoretical tools in search of finding lanthanide encapsulated fullerenes with very large blocking barriers and blocking temperatures. Various ideas, such as enhancing the coupling between two lanthanide ions by bringing them close to each other in the confined space, have been tested, and the main conclusions drawn from this works are summarised below.

(i) Sourcing the large $J_{4f-4f}$ exchange via confinement: in search of increasing the magnetic exchange ($J_{4f-4f}$) between two lanthanide ions via confinement, we have varied the cage size from C$_{30}$ to C$_{80}$ where the Gd–Gd distance ranging from 2.185 Å to 4.107 Å is observed. Here smaller cages (C$_{2n}$, $2n$ ≤ 52) yield a weaker Gd–Gd interactions with a stable Gd$_2$@C$_{38}$-D$_{3h}$ complex having a record-high exchange for any 4f–4f interaction ($J_{Gd\cdots Gd} = -43.4$ cm$^{-1}$). A strong 4f–4f orbital overlap between two Gd$^{3+}$ ions suggests the Gd–Gd bond formation under confinement. As the exchange is antiferromagnetic, these are not ideal for SMMs, however among hetero dilanthanide EMFs, some promising SMMs are identified.

(ii) $Ab$ $initio$ estimation of double exchange in endohedral azafullerenes: the larger cages (Gd$_2$@C$_{56}$ and Gd$_2$@C$_{80}$) lead to the formation of a two-centre-one-electron Gd–Gd bond due to the comparable energy of the highest occupied orbitals of Gd$_2$ and lowest unoccupied orbitals of the fullerene cage. Here we have studied Gd$_2$@C$_{59}$F$_7$N complexes where the delocalisation of the electron between two Gd centres is treated via a double-exchange parameter. A protocol to compute the double-exchange using $ab$ $initio$ CASSCF calculations is proposed, and this methodology yields spin Hamiltonian parameters that are in excellent agreement with experiments for Gd$_2$@C$_{79}$N. The application of this method in Gd$_2$@C$_{59}$N unveils a massive $J_{\text{dd-rad}}$ exchange ($J_{\text{Gd-rad}} = +869$ cm$^{-1}$) which is two times larger than the record-high $J$ reported for Gd$_2$@C$_{79}$N.

(iii) Record-high blocking barrier for Dy$_2$@C$_{59}$N and Tb$_2$@C$_{59}$N: the huge ferromagnetic $J_{\text{dd-rad}}$ exchange found in the C$_{59}$N cage quenches the QTM significantly and yields a very high $U_{\text{cal}}$ value of 1502 cm$^{-1}$ for Tb$_2$@C$_{59}$N – the largest reported for any lanthanide EMF. This opens up the possibility of generating large magnetic anisotropy without relying on a stronger ligand field.

Computational details

All the DFT calculations have been performed using the Gaussian09 suite with the B3LYP functional. There are several isomers with different symmetries possible for a chosen...
fullerene cage. To estimate the effect of symmetry of the fullerene cage in the associated magnetic properties, we have chosen two low energy conformers of the C_{2n} (n = 15–24, 26, 30, 40) fullerene from http://www.nanotube.msu.edu/ and encapsulated two Gd atoms. The optimisation of the resulting Gd@C_{2n} has been performed using the UB3LYP/CSDZ(Gd), SVP (rest) methodology. Further single point energy calculations were performed with an Ahlrichs’ triple-ξ valence (TZV) basis set to obtain an excellent numerical estimate of energy/magnetic coupling. A quadratic convergence SCF method was used throughout all the calculations. One high spin (HS, the spin on both Gd³⁺ centres is “up”) and one broken symmetry (BS, the spin on one Gd³⁺ centre is “up” and another Gd³⁺ centre is “down”) configuration was used to estimate the magnetic exchange. The magnetic exchange has been calculated using the

Hamiltonian \( H = -J S_1 S_2 \), where \( J = \frac{E_{HS} - E_{102}}{2S_1S_2 + S_1^2} \).

Additionally, we have performed AIM (atoms in molecules) analysis with the AIM2000 programme package to determine the coordination number of the Gd³⁺ ion inside the fullerene cage along with the nature of Gd–C and Gd–Gd bonds. To estimate the double exchange in Gd₂@C₆₀ and Gd₂@C₇₉N molecules, ab initio CASSCF calculations have been performed using the MOLCAS 8.4 programme package. We have employed [Ln-ANO-RCC…8s7p5d3f2g1h], [C-ANO-RCC…3s2p1d] and [N-ANO-RCC…3s2p1d] contraction schemes in the basis set for Gd, C and N, respectively. The DKH Hamiltonian was used to take into account the scalar relativistic effect. The Cholesky decomposition technique was used to reduce the size of the disk space. The CASSCF calculations have been performed with the CAS (15,15) active space. The active space includes seven 4f orbitals from each Gd atom and one orbital for the unpaired electron. Within the active space, we have computed the energy of the S = 13/2, 11/2, 9/2, 7/2, 5/2 and 3/2 states with two roots while the energy of S = 15/2 and 1/2 states has been estimated using only one root. Further details on the computational methods are elaborated in the ESL.*

The magnetic anisotropy in the Gd₂@C₃₈–D₂₅ isomer has been estimated by replacing the isotropic Gd Gd bonds.

Author contributions
GR conceived the idea and SD performed all the calculations and interpret and analyse the data. Both wrote the manuscript together.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
SD would like to thank UGC for the SRF fellowship and Dr Hélène Bolvin, UPS, Toulouse for her helpful suggestions. GR would like to thank DST/SERB (CRG/2018/000430, DST/SJF/CSA03/2018-10; SB/SJF/2019-20/12; SPR/2019/001145) for funding.

Notes and references
1 R. Sessoli, D. Gatteschi, A. Caneschi and M. Novak, Nature, 1993, 365, 141–143.
2 E. Moreno-Pineda, C. Godfrin, F. Balestero, W. Wernsdorfer and M. Ruben, Chem. Soc. Rev., 2018, 47, 501–513.
3 N. Ishikawa, M. Sugita, T. Ishikawa, S.-y. Koshihara and Y. Kaizu, J. Am. Chem. Soc., 2003, 125, 8694–8695.
4 A. B. Canaj, S. Dey, E. R. Martí, C. Wilson, G. Rajaraman and M. Murrie, Angew. Chem., Int. Ed., 2019, 131, 14284–14289.
5 A. B. Canaj, S. Dey, C. Wilson, O. Céspedes, G. Rajaraman and M. Murrie, Chem. Commun., 2020, 56, 12037–12040.
6 S. Dey, G. Velmurugan and G. Rajaraman, Dalton Trans., 2019, 48, 8976–8988.
7 M. S. Norre, C. Gao, S. Dey, S. K. Gupta, A. Borah, R. Murugavel, G. Rajaraman and J. Overgaard, Inorg. Chem., 2019, 59, 717–729.
8 S. Dey and G. Rajaraman, Dalton Trans., 2020, 49, 14781–14785.
9 Y. S. Ding, N. F. Chilton, R. E. Winpenny and Y. Z. Zheng, Angew. Chem., Int. Ed., 2016, 55, 16071–16074.
10 S. K. Gupta, T. Rajeshkumar, G. Rajaraman and R. Murugavel, Chem. Sci., 2016, 7, 5181–5191.
11 C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, Nature, 2017, 548, 439–442.
12 F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikamäki and R. A. Layfield, Science, 2018, 362, 1400–1403.
13 D. Reta, J. G. Kragskow and N. F. Chilton, J. Am. Chem. Soc., 2021, 143(15), 5943–5950.
14 K. R. McClain, C. A. Gould, K. Chakarawet, S. J. Teat, T. J. Groshens, J. R. Long and B. G. Harvey, Chem. Sci., 2018, 9, 8492–8503.
15 P. Evans, D. Reta, G. F. Whitehead, N. F. Chilton and D. P. Mills, J. Am. Chem. Soc., 2019, 141, 19935–19940.

© 2021 The Author(s). Published by the Royal Society of Chemistry
D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
97 A. D. Beck, J. Chem. Phys., 1993, 98, 1372–1377.
98 D. Tománek, Guide through the nanocarbon jungle, 2014.
99 T. R. Cundari and W. J. Stevens, J. Chem. Phys., 1993, 98, 5555–5565.
100 F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297–3305.
101 A. Schäfer, H. Horn and R. Ahlrichs, J. Chem. Phys., 1992, 97, 2571–2577.
102 C. Ögretir and I. G. Csizmadia, Computational advances in organic chemistry: molecular structure and reactivity, Springer Science & Business Media, 2012.
103 E. Ruiz, J. Cano, S. Alvarez and P. Alemany, J. Comput. Chem., 1999, 20, 1391–1400.
104 L. Noodleman, J. Chem. Phys., 1981, 74, 5737–5743.
105 F. Biegler-König and J. Schönbohm, J. Comput. Chem., 2002, 23, 1489–1494.
106 F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. F. Galván, N. Ferré, L. M. Frutos and L. Gagliardi, J. Comput. Chem., 2016, 37, 506–541.
107 B. O. Roos, V. Veryazov and P.-O. Widmark, Theor. Chem. Acc., 2004, 111, 345–351.
108 M. Reiher, Theor. Chem. Acc., 2006, 116, 241–252.
109 F. Aquilante, P.-Å. Malmqvist, T. B. Pedersen, A. Ghosh and B. O. Roos, J. Chem. Theory Comput., 2008, 4, 694–702.
110 M. Lines, J. Chem. Phys., 1971, 55, 2977–2984.