Record high magnetic exchange and magnetization blockade in $\text{Ln}_2@\text{C}_{79}\text{N}$ ($\text{Ln}=\text{Gd(III)}$ and $\text{Dy(III)}$) molecules: a theoretical perspective†

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Ab initio and DFT calculations reveal a very strong ferromagnetic exchange of the order of 200 cm$^{-1}$ in an endohedral radical hetero-metallo-fullerene molecule $\text{Gd}_2@\text{C}_{79}\text{N}$. Calculations performed on the anisotropic $\text{Dy}_2@\text{C}_{79}\text{N}$ molecule reveal that very strong Dy–radical exchange not only quenches the QTM effects but also immensely enhances the blocking height for magnetization reversal.

Single molecule magnets are an attractive area of research due to numerous potential applications proposed for this class of molecules. There are several hurdles in realising these applications, particularly controlling the spin Hamiltonian parameters such as the spin ground state, magnetic anisotropy, intra- and intermolecular interactions are the top challenges to address in this area. As controlling the zero-field splitting parameter in transition metal clusters is challenging, research groups have moved to lanthanide based SMMs as they inherit very large anisotropy. Large anisotropy due to very large spin-orbit coupling leads to an extremely large barrier height for magnetization reversal and to date several molecules have been reported to possess barrier heights greater than the desired 300 K. However large spin-orbit coupling under low symmetry conditions also aids in the mixing of wave functions, leading to the undesired faster quantum tunnelling of magnetization (QTM) between the ground/excited states. This drastically reduces the blocking temperature of this class of molecules. There are two approaches proposed to quench the QTM effects: (i) preserving a very high-symmetry around the lanthanide ion reduces the mixing of states and (ii) inducing splitting of $m_f$ levels via exchange coupling with other lanthanide/transitional metal/radical ions also serves the purpose. Elegant examples for both categories are available; $\{\text{Tb}\text{Pc}_2\}$ and $\{\text{Dy}_2\text{K}_2\}$ molecules possess high symmetry around the lanthanide ions and thus reduce tunnelling while inducing coupling with metal ions/radicals leading to the isolation of $\{\text{Dy}_2\text{K}_2\}$ and $\{\text{Tb}\text{N}_2\}$ complexes possessing very high blocking temperatures. Despite these breakthrough achievements, a rational approach to achieve very large magnetic coupling as required to reach large $T_b$ is not available. These parameters are often difficult to control in classical coordination complexes.

In this regard, metal encapsulated fullerenes, i.e. endohedral metallo-fullerenes (EMFs), in which the metal ions are encapsulated inside the cage molecule, are ideal candidates in which symmetry, exchange interaction and dipolar interaction can be controlled easily. Several lanthanide encapsulated EMFs have been reported in the literature and some of them have also been found to exhibit SMM characteristics. Among the EMFs, the most promising class of molecules are radical based fullerenes as these offer direct-exchange between the encapsulated lanthanide ions and the radical cage. In this regard, the report of $\{\text{C}_{79}\text{N}\}$ hetero-fullerene radicals has gained importance as they have been characterized thoroughly and the crystal structure encapsulating different lanthanide ions has been reported. Of particular importance is the Gd(m) analogue $\text{Gd}_2@\text{C}_{79}\text{N}$, in which the ground state is estimated to be $S = 15/2$ arising from strong Gd(m)-radical exchange as revealed by several techniques including HF-EPR study.

In this work, we aim to compute the magnetic exchange coupling present in the $\text{Gd}_2@\text{C}_{79}\text{N}$ molecule and extend the work to the anisotropic $\text{Dy}_2@\text{C}_{79}\text{N}$ cage using DFT and the CASSCF + RASSI-SO/POLY_ANISO approach using the MOLCAS code. The mechanism of magnetic relaxation and how the radical–Dy(m) interaction quench the QTM effects are explored. The B3LYP/TZV (CSDZ for Gd(m)) combination has a proven track record to yield accurate structures and properties for this class of molecules. To test the methodology further, we have studied the radical $\text{C}_{62}$ cage with Gd(m), i.e. the Gd@C$_{62}$ molecule and the computed structures and magnetic coupling constants are in agreement with experiments. This offers confidence in the employed methodology (see ESI† for details). For the $\text{Gd}_2@\text{C}_{79}\text{N}$ molecule, based on the position of the N atom there are two possible isomers, $\text{Gd}_2@666$ ($\text{C}_{79}\text{N}$) and $\text{Gd}_2@665$ ($\text{C}_{79}\text{N}$) (see Fig. 1a). The former one has the N atom at the junction of three hexagonal sites while the latter one has the nitrogen atom at a junction of two hexagonal and one pentagonal sites (see Fig. 1a and...
is very strong, the Gd(III)–Gd(III) interaction is estimated to be weak comparatively, for the lowest lying Gd2@665-(C79N) isomer. For the Gd2@666-(C79N) isomer, they are found in the range of 2.403–2.738 Å. Here the Gd2@665-(C79N) isomer is found to be stabilized by 61.6 kJ mol\(^{-1}\) compared to the Gd2@666-(C79N) isomer (energy difference is merely 17.3 kJ mol\(^{-1}\) for the bare C79N cage; see Table S1 of ESI† for selected structural parameters and the computed energies).

As the two Gd(\textit{m}) centres are symmetric, there are two exchange interactions present in this cluster: \(J_1\) interaction describes coupling between the C79N radical and the Gd(\textit{m}) ions while \(J_2\) interaction describes the coupling between two Gd(\textit{m}) ions. The \(J_1\) and \(J_2\) interactions are estimated to be \(+200\) cm\(^{-1}\) and \(-0.4\) cm\(^{-1}\) respectively, for the lowest lying Gd2@665-(C79N) isomer. For the Gd2@666-(C79N) isomer on the other hand, calculations yield a similar set of \(J\) constants \((J_1 = +189\) cm\(^{-1}\) and \(J_2 = -0.4\) cm\(^{-1}\) using \(\hat{H} = -2\Sigma_{\text{C}0\text{rad}}\) Hamiltonian Fig. S2 of ESI†). Quite interestingly, the Gd(\textit{m})–radical exchange estimated here is the largest exchange interaction known. The second largest \(J\) value reported for this type of interaction is in the \{3d-Gd\} complexes where the radical-Gd(\textit{m}) \(J\) is estimated to be \(-27\) cm\(^{-1}\).\(^{16,17}\) The \(J\) values reported for all the other radical-Gd(\textit{m}) complexes are an order of magnitude less compared to this estimate.\(^{8,14,19}\) Although the exact value of \(J\) has not been uniquely determined, the experimental data suggest strong ferromagnetic exchange between the Gd(\textit{m}) and the radical leading to the 15 line EPR signal corresponding to the \(S = 15/2\) ground state. The signals are visible even at higher temperatures suggesting the isolated ground state at these temperatures. Besides, pulsed EPR measurements reveal a very long spin relaxation leading to the detection of an electron spin echo signal even at 20 K. This also indicates strong Gd(\textit{m})–radical interaction.\(^{18}\) Although the radical-Gd(\textit{m}) interaction is very strong, the Gd(\textit{m})–Gd(\textit{m}) interaction is estimated to be weak and antiferromagnetic in nature. This is in accordance with the long metal–metal distance (3.8 Å) offering small exchange interaction. To understand the origin of the strong exchange interaction, we have analysed the molecular orbitals, NBOs and spin densities (see Fig. 1b for spin density plot of \(S = 15/2\) state; see Fig. S3 and S4 in ESI† for plots of other spin states). We have earlier established the mechanism (see Fig. S5 of ESI†) of magnetic coupling in Gd(\textit{m})–radical and \{3d-Gd\} complexes\(^{8,14,19}\) where the ferromagnetic contribution to \(J\) values is found to arise due to orbital orthogonality between the SOMOs (see Fig. S6, ESI† for computed overlap integrals) and the charge-transfer contribution from the radical centre to the empty 5d/6s/6p orbitals of the Gd(\textit{m}) (see Fig. S7 and Table S2 of ESI†). The sole antiferromagnetic contribution to \(J\) arises from the overlap of the \(\pi^*\) orbital of the radical with the 4f orbitals of the Gd(\textit{m}) which is found to be weak here. Here there is direct exchange between Gd(\textit{m}) and the C79N radical molecule. As the HOMO of C79N\(^{6+}\) is low-lying in energy, there is a substantial charge-transfer from the C79N unit to both the Gd(\textit{m}) ions, leading to a significant gain in the spin density at the Gd(\textit{m}) centres. The NBO analysis in fact reveals a \(4\pi^*\) configuration revealing the extent of charge-transfer to the Gd(\textit{m}) empty orbitals. The spin densities on the Gd(\textit{m}) centres are also found to be higher than the expected value (~7.45 on each Gd(\textit{m}) centres). This leads to a very strong coupling between the radical and the Gd(\textit{m}) centre. The spin density plot also reveals a significant polarization on the C79N unit.

As the spin density on the hetero-fullerene C79N is localized on the nitrogen atom, this facilitates efficient charge transfer while such behaviour was not observed in the homo-fullerene such as C83\(^{3+}\). The charge-transfer is also clearly visible in the NBO second order donor–acceptor interactions (see Fig. S8 in ESI†). The EPR study undertaken earlier on the Y3@C79N complex yields anisotropic g-tensors, and hyperfine tensors of Y(\textit{m}) atoms are visible.\(^{11}\) This indicates that the unpaired electrons are certainly not localized on the C79N cage but are largely delocalized also on the Y(\textit{m}) atoms. This supports our charge-transfer proposal to the Gd(\textit{m}) centres in the Gd2@C79N cage. Besides, our additional calculations performed on La2@C79N clearly reveal that delocalisation takes place only when there is a radical centre (see Table S3 of ESI†).

Since the magnetic coupling is estimated to be very large, we have modelled the Dy2@665-(C79N) molecule to explore the possibility of obtaining high blocking temperatures and quenching of QTM effects. We have performed \(ab\) \textit{initio} CASSCF + RASSI-SO/SINGLE_ANISO/POLY_ANISO calculations using the MOLCAS 7.8 code (see ESI† for computational details†). Analysis of both the single-ion anisotropy and the exchange anisotropy has been performed to predict the magnetisation relaxation process. The Dy1 (Dy2) ions are found to coordinate in an \(\eta_5\) fashion with the hexagonal ring, offering strong interaction (Dy–C distances are estimated to be 2.4 to 2.6 Å) in one of the axial directions. In the other axial direction, only a weak interaction due to the second Dy(\textit{m}) ion is present. This along with a negligible equatorial interaction for both the Dy(\textit{m}) centres ideally suits the oblate Dy(\textit{m}) ion. The coordination environment could perhaps be compared to the mono-coordinated Dy(\textit{m})–O model studied earlier by Chibotaru and co-workers.\(^{20}\) We have computed eight low-lying Kramer’s Doublets (KDs) for both Dy(\textit{m}) ions separately, corresponding to the \(^{1}H_{15/2}\) state. These states are found to lie within an energy span of 837.6 cm\(^{-1}\) and 785.7 cm\(^{-1}\) for Dy1 and Dy2 sites, respectively, with \(m_J = \pm 15/2\) stabilized as the ground state. The computed ground state anisotropy for both Dy(\textit{m}) ions are found to be purely Ising in nature (Dy1, \(g_{zz} = 0.001, g_{xy} = 0.002, g_{zz} = 19.979\) and Dy2, \(g_{zz} = 0.001, g_{xy} = 0.002, g_{zz} = 19.881\)) suggesting very small QTM effects within the ground state KD (QTM = 0.0006 \(\mu_B\) for both Dy1 and Dy2 ions; see Fig. S9 and Table S4 of ESI†). The ground state \(g_{zz}\) axes for both the Dy(\textit{m}) ions are found to be oriented along the pseudo \(C_6\) axis present in the hexagonal ring (see Fig. 2a). The first excited state KDS lie at 245 cm\(^{-1}\) and 134 cm\(^{-1}\) higher in energy for Dy1 and Dy2 ions, respectively. These first excited KDS for Dy1 and Dy2 ions are
Dy(III) ions possesses a larger axial crystal field parameter while found to obstruct the QTM process. The ground state KD of both 0.0022 m deviation, relaxation is expected to occur via Dy2 respectively (see Fig. S9 and Table S4 of ESI† and this results in the gyy non-axial terms leading to relaxation the first excited state is found to possess both the axial and the gzz magnetization is also found to be very small (0.0047 m to the ground state and the first excited state of opposite through the first excited KD. The Orbach/Raman process related to the ground state and the first excited state of opposite magnetization is also found to be very small (0.0047 μB and 0.0022 μB for Dy1 and Dy2 respectively) but relaxation within the same sign states (+1 to +2) is found to be large (1.7 μB for both Dy(III) ions). With respect to the ground state gzz axis, the first excited gzz axis is found to be tilted by 7.7° and 16.1° for Dy1 and Dy2 respectively (see Fig. S9 and Table S4 of ESI†). Due to this deviation, relaxation is expected to occur via the first excited state and this results in the Ucal values of 244.5 cm⁻¹ and 134.3 cm⁻¹ for Dy1 and Dy2 ions, respectively. As the coordination mode between Dy1 and Dy2 sites is different, with Dy1 interacting strongly with the C79N compared to the Dy2 ion, this difference is rather expected. Besides this analysis, the computed crystal field parameter Beq also offers insights into the relaxation mechanism. Smaller non-axial Beq (where q ≠ 0, k = 2, 4, 6) terms compared to their corresponding axial Beq (where q = 0, k = 2, 4, 6) terms are found to obstruct the QTM process. The ground state KD of both Dy(III) ions possesses a larger axial crystal field parameter while the first excited state is found to possess both the axial and the non-axial terms leading to relaxation via the first excited state KD (see Tables S5 and S6 of ESI†).

To understand the mechanism of magnetic relaxation of the full molecule, we modelled two structures; in the first model we have considered only one Dy(III) ion by replacing the other with the Lu(III) ion (DyLu/LuDy@C79N models). The Dy(III)–radical exchange is estimated to be +285.7 cm⁻¹ (see ESI† for details), with this exchange coupling, we have simulated the exchange coupled states using the POLY_ANISO program considering an isotropic g-tensor for the radical centre. The ground state is estimated to be a pure Ising type with the gzz value of 21.981 (gxx and gyy are virtually zero) and the first excited state is estimated to lie at 713 cm⁻¹ higher in energy. Besides, the tunnel splitting (Δtun) of the ground state is also computed to be small (2.6 × 10⁻² cm⁻¹) and relaxation is expected to occur via the first excited state possessing larger Δtun. This results in the Ucal value of 713 cm⁻¹ for the DyLu@C79N model which is ca. three times higher than what is computed for the mononuclear Dy(III) ions without the radical counterpart. This Ucal estimated here is one of the largest estimated and more importantly the strong exchange likely to quench the QTM significantly offers also very high blocking temperatures. For the second Dy2–radical combination, the same is estimated to be 711 cm⁻¹ (see Table S7 of ESI†). In the second step, we have considered both the Dy(III) ions together in combination with the radical. Employing Dy–radical exchange of +285.7 cm⁻¹ (using $\hat{H} = -J_D y S_{rad}$) along with a weak Dy(III)–Dy(III) exchange of ~0.3 cm⁻¹ leads to the blockade barrier as shown in Fig. 2d. The ground state is estimated to be pure Ising type and the Δtun is estimated to be very small. The stronger Dy–radical exchange and weaker Dy(III)–Dy(III) exchange
place the first excited state at 582.2 cm\(^{-1}\) which is again higher than that computed for single-ion Dy(III) centres (see Fig. 3).

Although the \(\Delta_{\text{act}}\) of the first excited state is also small, the first excited state \(g_{\text{zz}}\) axis is tilted by 91.0° compared to the ground state KD (see Fig. S10 of ESI†). This suggests relaxation to occur via the first excited state leading to an \(U_{\text{cal}}\) value of 582.2 cm\(^{-1}\). Although the value is among the largest reported, the higher value is essentially due to exchange interaction, which additionally quenches the QTM. Other relaxation pathways such as inter-molecular interactions are also expected to be minimal here as the metal ion is encapsulated inside the cage increasing the chance of observing a larger \(T_{\text{q}}\) for this molecule. Although anisotropic Ln@C\(_{79}\)N molecules are synthesized, magnetic studies in this direction have not been pursued yet.\(^{1,1b}\)

To this end, our theoretical search for a very strong magnetic exchange in lanthanide–radical systems lead us to endohedral metallo-hetero-fullerene molecules in which extremely large magnetic exchange interactions are detected. Direct exchange and significant charge transfer offered by the radical hetero-fullerenes lead to very large \(J\) values that cannot possibly be achieved in classical lanthanide coordination complexes. Besides, the Dy\(_2@665\)-C\(_{79}\)N molecule studied here was found to yield a larger barrier height compared to the corresponding single-ion Dy(III) anisotropy. This observation is the first of its kind where the magnetic exchange was not only found to quench the QTM effects but was also found to help enhance the barrier height significantly. Our predictions warrant magnetic studies on these molecules and theoretical studies on other EMFs possessing interesting magnetic properties are underway in our laboratory.

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References