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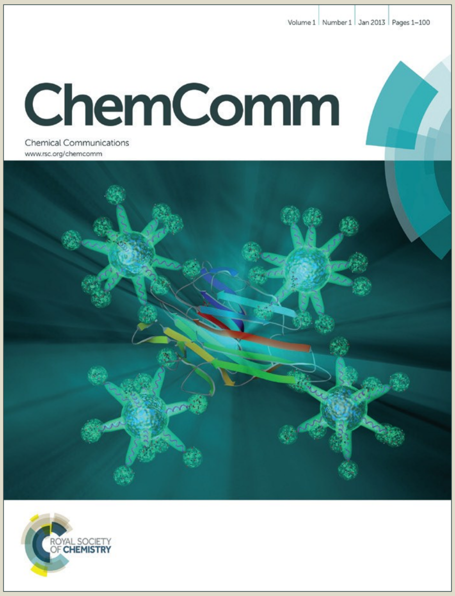

Journal Name

COMMUNICATION

Record High Magnetic Exchange and Magnetization Blockade in $Ln_2@C_{79}N$ (Ln=Gd(III) and 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 endohedral radical hetero-metallo-fullerene molecule $Gd_2@C_{79}N$. Calculations performed on the anisotropic $Dy_2@C_{79}N$ molecule reveals that very strong Dy-radical exchange not only quenches the QTM effects but also immensely enhances the barrier height for magnetization reversal.

Single Molecule Magnets are attractive area of research due to numerous potential applications proposed for this class of molecules.[1] There are several hurdles in realising these applications, particularly controlling the spin Hamiltonian parameters such as spin ground state, magnetic anisotropy, intra and intermolecular interactions are the top challenges to address in this area.[2] 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.[3] Large anisotropy due to very large spin-orbit coupling lead to extremely large barrier height for magnetization reversal and to-date several molecules are reported to possess barrier heights greater than the desired 300 K.[4] However large spin-orbit coupling under low symmetric conditions also aid 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 in this class of molecules.[5] 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 (ii) inducing splitting of the m*J* levels via exchange coupling with other lanthanide/transition metal/radical ions also serve the purpose.[5c, 6] Elegant examples to both categories are available, $[TbPc_2]$ and $\{Dy_4K_2\}$ molecules posses high symmetry around the lanthanide ions and thus reduces the tunnelling while inducing coupling with metal ions/radical lead to isolation of $\{Dy_2Cr_2\}$ and $\{TbN_2^{3-}\}$ complexes possessing very large blocking temperatures.[5d, 6b, 6c, 7] 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.[8]

In this regard, metal encapsulated fullerenes, .i.e. endohedral metallo-fullerenes (EMFs), where the metal ions are encapsulated inside the cage molecule are ideal candidate where symmetry, exchange interaction and dipolar interaction can be controlled easily.[9] Several lanthanide encapsulated EMFs been reported in the literature and some of them also found to exhibit SMM characteristics.[10] Among the EMFs, the most promising class of molecules are radical based fullerenes as this offers direct-exchange between the encapsulated lanthanide ions and the radical cage. In this regard, report of $(C_{79}N)^{6-}$ hetero-fullerene radical gain importance as it has been characterized thoroughly and crystal structure encapsulating different lanthanide ions are reported.[11] Of particular importance is the Gd(III) analogue $Gd_2@C_{79}N$, where the ground state is estimated to be S=15/2 arising from strong Gd(III)-radical exchange as revealed by several techniques including HF-EPR study. [12]

In this work, we aim to compute the magnetic exchange coupling present in $Gd_2@C_{79}N$ molecule and extend the work to anisotropic $Dy_2@C_{79}N$ cage using DFT and CASSCF+RASSI-SO/POLY_ANISO approach using MOLCAS code.[13] The mechanism of magnetic relaxation and how the radical-Dy(III) interaction quench the QTM effects are explored. The B3LYP/TZV (CSDZ for Gd(III)) combination has a proven track record to yield accurate structures and properties for this class of molecules.[14] To test the methodology further, we have studied the radical C_{82}^{3-} cage with Gd(III) .i.e $Gd@C_{82}$ molecule and the computed structures and magnetic coupling constants are in agreement with the experiments.[15] This offers confidence on the employed methodology (See ESI for details†). For the $Gd_2@C_{79}N$ molecule, based on the position of N atom there are two possible isomers, $Gd_2@666\text{-}(C_{79}N)$ and

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† Electronic supplementary information (ESI) available: Optimized structures, CASSCF+RASSI-SO energies, spin density plots, overlap integrals, NBO data mechanism of relaxation along with computational details.

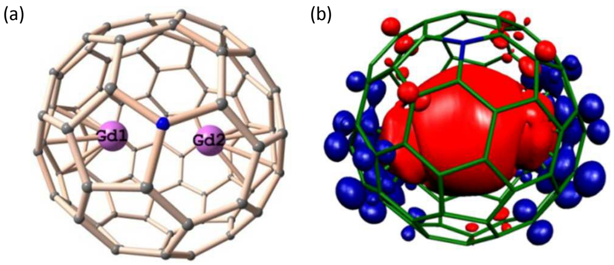

Figure 1. (a) DFT optimized structure of $Gd_2@665-(C_{79}N)$ isomer along with **(b)** its spin density plot for the S=15/2 state.

$Gd_2@665-(C_{79}N)$ (see Figure 1a).[12] The former one has the N atom at the junction of three hexagonal sites while the later one has the nitrogen atom at a junction of two hexagonal and one pentagonal site (see Figure 1a and Figure S1 of ESI).[10a, 16] The computed Gd-C bond lengths are found to be in the range of 2.410-2.673 Å for $Gd_2@665-(C_{79}N)$ isomer whereas for $Gd_2@666-(C_{79}N)$ isomer, it is found in the range of 2.403-2.738 Å. Here the $Gd_2@665-(C_{79}N)$ isomer is found to be stabilized by 61.6 kJ/mol compared to the $Gd_2@666-(C_{79}N)$ isomer (energy difference is merely 17.3 kJ/mol for the bare $C_{79}N$ cage; see Table S1 of ESI for selected structural parameters and the computed energies†).

As the two Gd(III) centres are symmetric, there are two exchange interactions present in this cluster: J_1 interaction describe coupling between the $C_{79}N$ radical and the Gd(III) ions while the J_2 interaction describe the coupling between two Gd(III) 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 $Gd_2@665-(C_{79}N)$ isomer. For the $Gd_2@666-(C_{79}N)$ 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} and Figure S2 of ESI†). Quite interestingly, the Gd(III)-radical exchange estimated here is the largest exchange interaction known. The second largest J value reported for this type of interaction is in $\{Gd_2N_2^{3-}\}$ complex where the radical-Gd(III) J is estimated to be -27 cm^{-1}.[5c, 17] The J values reported for all the other radical-Gd(III) complexes are an order of magnitude less compared to this estimate.[8] Although the exact value of J has not been uniquely determined, experimental data suggest strong ferromagnetic exchange between the Gd(III) and the radical leading 15 line EPR signal corresponding to S=15/2 ground state. The signals are visible even at room temperature suggesting isolated ground state at room temperature. Besides pulsed EPR measurement reveal a very long spin relaxation leading to detection of electron spin echo signal even at 20K. This also indicates strong Gd(III)-radical interaction.[18] Although the radical-Gd(III) interaction is very strong, the Gd(III)-Gd(III) interaction is estimated to be weak and is antiferromagnetic in nature. This is in accord with the long metal-metal distance (3.8 Å) offering small exchange interaction. To understand the origin of strong exchange interaction, we have analysed the molecular orbitals, NBOs and spin densities (see Figure 1b for spin density plot of S=15/2 state; see Figure S3 and S4 in ESI for plots of other spin states†). We have earlier established the mechanism (see Figure S5 of ESI†) of magnetic coupling in Gd(III)-radical and {3d-Gd} complexes[8, 14, 19] where ferromagnetic contribution to the J values are found to arise due to orbital orthogonality between the SOMOs (see Figure S6 for computed overlap integrals†) and charge-transfer contribution from the radical centre to the empty 5d/6s/6p orbitals of the Gd(III) (see Figure S7 and Table S2 of ESI†). The sole antiferromagnetic contribution to the J arise from overlap of π* orbital of the radical with the 4f orbitals of the Gd(III) which is found to be weak here. Here there is direct exchange between Gd(III) and the $C_{79}N$ radical molecule. As the HOMO of the $C_{79}N^{6-}$ is low-lying in energy, there is a substantial charge-transfer from the $C_{79}N$ unit to both the Gd(III) atoms leading to a significant gain in the spin density at the Gd(III) centres. The NBO analysis in fact reveal a $4f^7 5d^{0.6}$ electronic configuration revealing the extent of charge-transfer to the Gd(III) empty orbitals. The spin densities on Gd(III) centres are also found to be higher than the expected value (~7.45 on each Gd(III) centres). This leads to a very strong coupling between the radical and the Gd(III) centre. Spin density plot also reveal a significant polarization on the $C_{79}N$ unit. As the spin density on the hetero-fullerene $C_{79}N$ is localized on the nitrogen atom, this facilitates efficient charge transfer while such behaviour was not observed in the homo-fullerene such as C_{82}^{3-}. The charge-transfer is also clearly visible in the NBO second order donor-acceptor interactions (see Figure S8 in ESI†). EPR study undertaken earlier on $Y_2@C_{79}N$ complex yield anisotropic g-tensors and hyperfine tensors of Y(III) atoms are visible.[11b] This indicates that the unpaired electrons are certainly not localized on the radical centres but are largely delocalized also to the Y(III) atoms. This support our charge-transfer proposal to the Gd(III) centres in $Gd_2@C_{79}N$ cage. Besides our additional calculations performed on $La_2@C_{79}N$ clearly reveals that the delocalisation take place only when there is a radical centres (see Table S3 of ESI†).

Since the magnetic coupling is estimated to be very large, we have modelled the $Dy_2@665-(C_{79}N)$ molecule to explore the possibility of obtaining large blocking temperatures and quenching of QTM effects. We have performed *ab* initio CASSCF + RASSI-SO/SINGLE_ANISO/POLY_ANISO calculations using 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 $\eta_7(\eta_6)$ fashion with the hexagonal ring, offering strong interaction (Dy-C distances are estimated to be 2.4 to 2.6 Å) on one of the axial direction. On other axial direction, only a weak interaction due to the second Dy(III) ion is present. This along with a negligible equatorial interaction for both the Dy(III) centres is ideally suit to the oblate Dy(III) ion. The coordination environment could perhaps be compared to the mono-coordinated Dy(III)-O model studied earlier by Chibotaru and co-workers.[20] We have computed eight-low lying Kramer's Doublets (KDs) for both Dy(III) ions separately, corresponding to $^6H_{15/2}$ 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 the m_J = ±15/2 stabilized as the ground state. The computed ground state anisotropy for both Dy(III) ions are found to be purely Ising in nature (Dy1, g_{xx} = 0.001, g_{yy} = 0.002, g_{zz} = 19.979 and Dy2, g_{xx} = 0.001, g_{yy} = 0.002 and g_{zz} = 19.881,) suggesting very small QTM effects within the ground state KD (QTM = 0.0006 μ_B for both Dy1 and Dy2 ions; see Figure S9 and Table S4 of ESI†). The

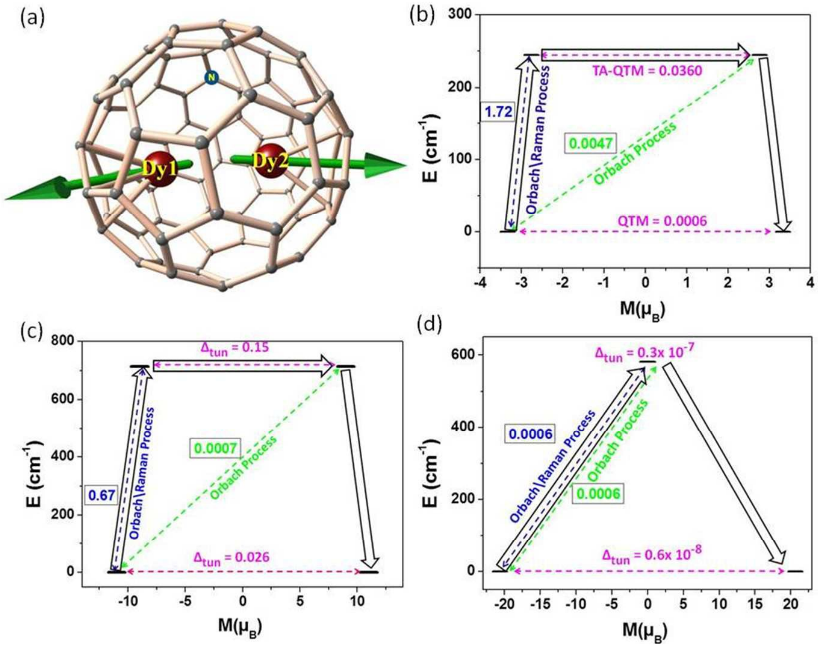

Figure 2. ***(a)*** *ground state KD orientation for both Dy(III) ions of $Dy_2@665$-($C_{79}N$);* ***(b)*** *ab initio SINGLE_ANISO computed magnetization blockade barrier for Dy1 ion;* ***(c)*** *ab initio POLY_ANISO computed magnetization blockade barrier for Dy1-radical exchange coupled systems for DyLu@665-($C_{79}N$) model and* ***(d)*** *ab initio POLY_ANISO computed magnetization blockade barrier for Dy1- Dy2@665-($C_{79}N$). In Figure 2b-d, the x- axis indicates the magnetic moment of each state along the main magnetic axis while y- axis denotes the energy of the respective states. The thick black lines imply the Kramer's doublet as a function of magnetic moment. The dotted green and blue lines indicate the possible pathway of the Orbach/Raman contribution of magnetic relaxation. The hollow black arrows indicate the most probable relaxation pathway for the magnetization reorientation. The dotted red lines corresponds to the QTM/TA-QTM/Δtunneling relaxation contributions between the connecting pairs. The numbers provided at each arrow are the mean value for the corresponding matrix element of the magnetic moment.*

ground state g_{zz} axis for both the Dy(III) ions are found to be oriented along the pseudo C_6 axis present in the hexagonal ring (see Figure 2a). The first excited state KD lies at 245 cm^{-1} and 134 cm^{-1} higher in energy for Dy1 and Dy2 ions respectively. These first excited KD for are also found to be Ising in nature with small transverse components (Dy1, g_{xx} = 0.083, g_{yy} = 0.120, g_{zz} = 17.119 and Dy2, g_{xx} = 0.011, g_{yy} = 0.014 and g_{zz} = 17.453). The computed transversal magnetic moments between the first excited KDs are found to be smaller in both Dy(III) ions (0.0360 μ_B and 0.0047 μ_B for Dy1 and Dy2 respectively), suggesting very small TA-QTM to be operative through the first excited KD. Orbach/Raman process, related to ground state and first excited state of opposite magnetization are also found to be very small (0.0047 μ_B and 0.0022 μ_B for Dy1 and Dy2 respectively) but relaxation within the same sign states (+1 to +2) are found large (1.7 μ_B for both Dy(III) ions). With respect to the ground state g_{zz} axis, the first excited g_{zz} axis is found to be tilted by 7.7° and 16.1° for Dy1 and Dy2 respectively (see Figure S9 and Table S4 of ESI†). Due to this deviation, the relaxation is expected to occur via the first excited state and this places the estimate of U_{cal} to be 244.5 cm^{-1} and 134.3 cm^{-1} for Dy1 and Dy2 ion respectively. As the coordination mode between Dy1 and Dy2 sites are different, with Dy1 interacting strongly with the $C_{79}N$ compared to the Dy2 ion, this difference is rather expected. Besides this analysis, the computed crystal field parameter B_q^k also offers insights into the relaxation mechanism. Smaller non-axial B_q^k (where q≠0,K=2,4,6) terms compared to their corresponding axial B_q^k (where q=0,K=2,4,6) terms are found to obstruct the QTM process. The ground state KD of both Dy(III) ions possess larger axial crystal field parameter while the first excited state found to posses both the axial and the non-axial terms leading to a relaxation via the first excited state KD (see Table S5 and S6 of ESI†).

To understand the mechanism of magnetic relaxation of the full molecule, we have modelled two structures, in the first model we have considered only one Dy(III) ion by replacing other with Lu(III) ion (DyLu/LuDy@$C_{79}N$ 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 POLY_ANISO program considering isotropic g-tensor for the radical centre. The ground state is estimated to be pure Ising type with the g_{zz} value of 21.981 (g_{xx} and g_{yy} are virtually zero) and the first excited state is estimated to lie at 713 cm^{-1} higher in energy. Besides, the tunnel splitting (Δ_{tun}) of the ground state is also computed to be small (2.6 x 10^{-2} cm^{-1}) and the relaxation is expected to occur via the first excited state possessing larger Δ_{tun}. This places the U_{cal} value to be 713 cm^{-1} for DyLu@$C_{79}N$ model which is *ca* three times higher than what is computed for the mononuclear Dy(III) ions without the radical counterpart. This U_{cal} estimated here one of the largest estimated and more importantly the strong exchange likely to quench the QTM significantly offering also a very large blocking temperatures. [1d, 6a, 7b-c] 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

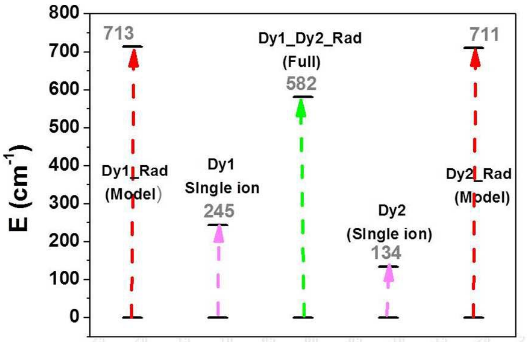

Figure 3. *Diagrammatic comparison of barrier heights (U_{cal} values) estimated for different models studied for $Dy_2@665\text{-}C_{79}N$ molecule.*

Dy(III) ions together in combination with the radical. Employing Dy-radical exchange of +285.7 cm^{-1} (using $\hat{H} = -JS_{Dy}S_{rad}$) along with a weak Dy(III)-Dy(III) exchange of -0.3 cm^{-1} yield the blockade barrier as shown in Figure 2d. The ground state is estimated to be pure Ising type and the Δ_{tun} is estimated to be very small. The stronger Dy-radical exchange and weaker Dy(III)-Dy(III) exchange places the first excited state at 582.2 cm^{-1} which is again higher than that computed for single-ion Dy(III) centres (see Figure 3). Although the Δ_{tun} of the first excited state is also small, the first excited state g_{zz} axis is tilted by 91.0° compared to the ground state KD (see Figure S10 of ESI†). This suggests relaxation to occur via the first excited state leading to an U_{cal} value of 582.2 cm^{-1}. Although the value is among the largest reported, higher value is essentially due to exchange interaction which additionally quenches the QTM. Other relaxation pathways such as through intermolecular interactions are also expected to be minimal here as the metal ion is encapsulated inside the cage brightening the chance of observing large T_B for this molecule. Although anisotropic $Ln_2@C_{79}N$ molecules are synthesized, magnetic studies in this direction has not yet been pursued.[11b]

To this end, our theoretical search for a very strong magnetic exchange in lanthanide-radical systems lead us to endohedral metallo hetero-fullerene molecules where extremely large magnetic exchange interactions are detected. Direct exchange and significant charge transfer offered by the radical hetero-fullerenes leads to very large *J* values that cannot possibly be achieved in a classical lanthanide coordination complexes. Besides, the $Dy_2@665\text{-}(C_{79}N)$ molecule studied here, found to yield larger barrier height compared to the corresponding single-ion Dy(III) anisotropy. This is the first of its kind observation where the magnetic exchange not only found to quench the QTM effects but also help to 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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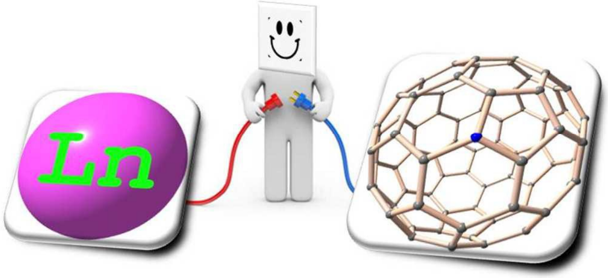

$Ln_2@C_{79}N$ EMFs are found to attain the largest magnetic coupling reported till date between Ln-radical paramagnetic centres. The offered U_{cal} values are very large and strong exchange likely to quench the QTM effects offering bright chance to obtain large blocking temperatures.