## Record High Magnetic Exchange and Magnetization Blockade in Ln<sub>2</sub>@C<sub>79</sub>N

## (Ln=Gd(III) and Dy(III)) Molecules: A Theoretical Perspective

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Additional notes:. The optimized structure of Gd@C<sub>82</sub> is found to be in excellent agreement with the reported X-Ray structure (see Table SX1 and Figure SX1) and this offer confidence on the methodology employed to compute good structures. Besides as  $C_{82}^{3-}$  cage is also a radical fullerene, we have computed the magnetic coupling constant for stable Gd@666-C<sub>82</sub> isomer and our calculations yield J=-0.25 cm<sup>-1</sup>. For other isomer Gd@665-C<sub>82</sub>, the same is found to be -10.5 cm<sup>-1</sup>(see Figure SX2). This weak anti-ferromagnetic coupling is in broad agreement with the experimental report (-0.9 cm<sup>-1</sup>),<sup>1</sup> and this offers additional confidence on the employed methodology for property evaluation.

**Table SX1.** DFT calculated structural parameters along with the X-Ray parameter for more stable  $Gd@666-C_{82}$  isomer and energy difference between both the optimized isomers of  $Gd@C_{82}$ .  $\Delta$  E (optimization) energy represents energy difference between optimized structures of both isomers and  $\Delta$  E (M=9, SP) represents single point energy difference between high spin (both paramagnetic centers, Gd(III) and radical, align parallel) for both isomers. Calculated structural parameters are found in good agreement to the experimental values, supporting the reliability of our methodology. Out of both possible structural isomers, 666 isomer is found to be more stable.

	Calculated (666)	X-Ray
Gd-C bond length	2.410-2.673 Å	2.469-2.474 Å
C – C	1.46 – 1.49 Å	1.46-1.48 Å
$\Delta E$ (optimization) => Gd@	-80.3 kJ/mol	
$\Delta E (M=9, SP) =>Gd@(0)$	-77.6 kJ/mol	

SP = Single Point Energy

**Figure SX1.** *DFT optimized structures of*  $Gd@C_{82}$  *isomers,*  $Gd@665-C_{82}$  *(left) and*  $Gd@666-C_{82}$  *(right).* 



**Figure SX2.** *Diagrammatic presentation of magnetic coupling constants for both isomers of*  $Gd@C_{82}$ .



**Table S1.** *DFT* calculated structural parameters along with energy difference between both the optimized isomers of  $Gd_2@C_{79}N$  hetero fullerene. Considering heterofullerene alone, 665 isomer is found to be more stable (because of less angle strain for hetero atom) and in case of encapsulated EMFs, again the same 665 isomer is found to be more stable than the other with a greater extent of stabilization (-17.3 vs -63.1 kJ/mol).

Isomer	665	666			
Gd-C bond length	2.410-2.673 Å	2.403-2.738 Å			
Gd-Gd bond length	3.77 Å	3.90 Å			
$\Delta E$ (optimization) => (	(665-666)	-17.3 kJ/mol			
$\Delta E \text{ (optimization)} \Rightarrow \mathrm{Gd}_2 @$	-63.1 kJ/mol				
$\Delta E (M=16, SP) =>Gd_2@(6)$	-63.1 kJ/mol				
SP = Single Point Energy					

**Table S2**. Radical localized natural bonding orbital composition in  $Gd_2@665-C_{79}N$ , indicating electron transfer to the empty 6s, 6p and 5d orbitals of metal ions from the ligand based molecular  $\pi^*$  orbital This dominant charge transfer is the cause for observed strong ferromagnetic interaction.

	Atomic Orbitals	Occupancy
Gd1 (50.20%)	Val(6s)	0.25
	Val(6p)	0.35
	Val(5d)-dx2-y2	0.25
	Val(5d)-dz2	0.18
	Val(5d)-dxy	0.21
	Val(5d)-dxz	0.22
	Val(5d)-dyz	0.14
Gd2 (49.80%)	Val(6s)	0.26
	Val(6p)	0.34
	Val(5d)-dx2-y2	0.25

Val(5d)-dz2	0.18
Val(5d)-dxy	0.20
Val(5d)-dxz	0.20
Val(5d)-dyz	0.16

**Table S3**. DFT computed spin densities on Gd(III)/La(III) ions of the some studied EMFs molecules. In all these studied diamagnetic fullerene EMFs, the spin density on the metal  $(Gd^{3+})$  atom/s are found to be in a range of 7.03 to 7.05. To further support the spin density transfer from radical based hetero-fullerene  $\{C_{79}N\}^{6-}$  to lanthanide metal ions, we have extended our studies to more simpler diamagnetic La(III) substituted La<sub>2</sub>@ $C_{79}N$ ,  $\{La_2@C_{79}N\}^+$  and La<sub>2</sub>@ $C_{80}$  EMFs. Spin density on both La(III) ions are found to be 0.46, 0.0 and 0.0, suggesting transfer only in case of heterofullerene radical cage.

Molecule	Spin density on Gd(III)/La(III) ions
Gd <sub>3</sub> N@C <sub>80</sub>	7.03, 7.03, 7.03
Gd <sub>3</sub> N@C <sub>82</sub>	7.02, 7.02, 7.00
$Gd_3N@C_{84}$	7.02, 7.02, 7.02
$Gd_2O@C_{79}N$	7.05
$La_2@C_{79}N$	0.46, 0.46
${La_2@C_{79}N}^+$	0.0, 0.0
La <sub>2</sub> @C <sub>80</sub>	0.0

**Table S4**. Ab initio computed principal values of the ground state g tensors and crystal field calculated electronic states resulting from single ion anisotropy calculations of Dy1(III) and Dy2(III) using SINGLE\_ANISO code for  $Dy_2@C_{79}N\_665$  isomer. For both ions, the ground state KD is found to be pure Ising in nature, whereas the first excited KD for both are either found to be transverse (as in Dy1) in nature or not collinear to the ground state KD (as in Dy2):

Kramers	Energy(cm <sup>-1</sup> ) Dy1	$g_{xx}$	$g_{yy}$	$g_{zz}$	angle(°)
doublets					
1	0.0	0.001	0.002	19.979	
2	244.5	0.083	0.120	17.119	7.7
3	357.2	0.603	0.663	14.152	173.1
4	456.7	0.935	2.114	11.530	171.8
5	571.2	1.826	4.862	8.906	13.8
6	686.8	6.932	6.014	0.045	104.5
7	782.4	0.342	3.543	7.478	93.2
8	837.6	1.174	6.540	14.607	90.6
Kramers	Energy(cm <sup>-1</sup> ) Dy2	a	σ	σ	angle(0)
ixiamers	Lifergy(effit) Dy2	8xx	8уу	822	angle()
doublets					
1	0.0	0.001	0.002	19.881	
2	134.3	0.011	0.014	17.453	16.1
3	314.9	0.104	0.129	14.536	6.6
4	474.2	0.204	0.451	12.470	160.1
5	577.6	1.194	1.960	10.544	141.8
6	662.7	3.058	5.126	7.961	118.5
7	738.9	1.609	3.714	11.281	78.8
8	785.7	0.816	3.737	16.947	90.3

**Table S5.** Energies (in  $cm^{-1}$ ) of the spin-free (RASSCF) and spin-orbit (RASSI) states of the Dy1(III) and Dy2(III) for spin multiplicity 6 of  $Dy_2@C_{79}N\_665$  isomer:

Dy1(III)		Dy2(III)	
Spin free states (RASSCF)	Spin free statesSpin-orbit states(RASSCF)(RASSI)		Spin-orbit states (RASSI)

0.0	0.0	0.0	0.0
9.0	244.5	9.8	134.3
327.4	357.2	210.4	314.9
381.6	456.7	213.3	474.3
416.1	571.2	499.7	577.6
498.9	686.8	543.5	662.7
621.0	782.4	624.7	738.9
701.1	837.6	728.5	785.7
835.4	3105.3	809.3	3045.6
861.2	3211.7	826.5	3236.2
927.0	3396.5	867.2	3363.9
7803.7	3532.3	7771.7	3471.0
7883.0	3602.9	7867.4	3560.3
7936.4	3653.9	7890.0	3634.9
7948.2	3719.2	7936.9	3698.2
7967.6	5747.7	7973.2	5685.4
8075.5	5836.4	8071.3	5868.2
8119.3	6033.0	8077.3	5986.5
34619.6	6132.9	34598.2	6058.4
35431.8		35413.8	
35588.9		35562.3	

**Table S6**. SINGLE\_ANISO computed crystal field parameters of the Dy1(III) and Dy2(III) for  $Dy_2@C_{79}N_{665}$  isomer. The major components in the Table are in the bold font. The crystal field Hamiltonian parameter:

$$\hat{H}_{CF} = \sum \sum_{k=-q}^{q} B_{q}^{k} \partial_{q}^{k}$$

Where  $B_q^{\ k}$  the crystal is field parameter and  $O_q^{\ k}$  is the extended Stevens operator. Quantization axis is chosen to be the main magnetic axes of the ground Kramer Doublet.

k	q	$B_q^k$	$B_q^k$
		Dy1	Dy2
2	-2	0.69749	-0.35884
	-1	-0.43059	-1.41278
	0	-4.54756	-4.53907
	1	-0.99574	1.09080
	2	1.03439	1.13549
4	-4	-0.00148	-0.00012
	-3	-0.00065	0.00643
	-2	0.00358	-0.00113
	-1	-0.00125	-0.00355
	0	0.00104	-0.00101
	1	0.00141	-0.00228
	2	0.00441	0.00564
	3	0.00212	0.01609
	4	0.00268	-0.00219
6	-6	0.00005	0.00002
	-5	0.00015	-0.00045
	-4	-0.00005	0.00019
	-3	0.00005	0.00023
	-2	-0.00006	0.00012
	-1	0.00008	0.00032
	0	-0.00004	0.00000
	1	0.00009	-0.00006
	2	-0.00014	-0.00002
	3	-0.00005	0.00026
	4	-0.00012	-0.00003
	5	0.00042	-0.00085
	6	0.00024	0.00001

Kramers	Energy(cm <sup>-1</sup> )	$g_{xx}$	$g_{yy}$	$g_{zz}$	angle(°)	$\Delta_{ ext{tun}}$
doublets	Dy1-radical					
	0.000	<b>a</b> 10.0	<b>2</b> 10 7	<b>0</b> 1 001		
1	0.000 713 4	$2x10^{-9}$ $3x10^{-8}$	2x10-7 2x10-9	21.981 17.976	0.00	0.15
-	/13.1	JAIO	2/110	17.970	0.00	0.10
Kramers	Energy(cm <sup>-1</sup> )	$g_{xx}$	$g_{yy}$	$g_{zz}$	angle(°)	$\Delta_{tun}$
doublets	Dy2-radical					
1	0.000	2 10 8	<b>2</b> 10 7	21.004		
1 2	0.000 710 8	$3x10^{-8}$ $3x10^{-8}$	$2x10^{-7}$ 1x10 <sup>-8</sup>	21.884 17.879	0.00	0.13
_	, 10.0	2		111017	0.00	0.110
Kramers	Energy(cm <sup>-1</sup> )	$g_{xx}$	$g_{yy}$	$g_{zz}$	angle(°)	$\Delta_{ ext{tun}}$
doublets	Dy1Dy2-radical					
1	0.000	3x10 <sup>-7</sup>	5x10-6	41.299		
2	582.2	4x10-6	$4x10^{-6}$	8.681	91	3x10 <sup>-8</sup>

**Table S7**. Energies (in  $cm^{-1}$ ) and  $g_{ZZ}$  values of the two low-lying exchange doublet states for Dy(III)1-Rad, Dy(III)2-Rad and complete molecule of  $Dy_2$ @ $C_{79}N_665$  isomer (at J = 285.7  $cm^{-1}$ ):

**Figure S1.** *DFT optimized structure of*  $Gd_2@666-(C_{79}N)$  *isomer.* 



**Figure S2**. Diagrammatic presentation of magnetic coupling constants for both isomers of  $Gd_2@C_{79}N$ .



**Figure S3.** DFT computed spin density plot of (a)  $\{C_{79}N\}^{6-}$ , (b)  $Gd@665-C_{82}$  (c)  $Gd@666-C_{82}$  (d)  $Gd_2@666-(C_{79}N)$  and (e)  $La_2@666-(C_{79}N)$  isomers. Red and blue regions indicate positive and negative spin populations, respectively. The isodensity surface shown corresponds to a value of  $0.001 \text{ e}^{-}/\text{bohr}^{3}$ . In heterofullerene  $\{C_{79}N\}^{6-}$  the spin is delocalized on the rings near to the hetero atom. In both the isomers of  $Gd@C_{82}$ , the unpaired electron density of fullerene radical is found to be delocalized on fullerene itself whereas in  $Gd2@C_{79}N$ , the hetero-fullerene radical spin density is localized between both Gd(III) ions.I diamagnetic La(III) substituted EMF, the radical spin density is again found to be localized between both metal ions, reconfirming the spin transfer from radical hetero-fullerene to metal centers.



**Figure S4.** Schematic presentation/reason of observed computed spin density values in diffrent spin configuration for  $Gd_2@C_{79}N$  along with tabulated values below. HS represent spin configuration with all three paramagnetic centers align parallel. In BS1 spin configuration both Gd(III) ions spins are anti-parallel and radical spin. BS2 and BS3 spin configurations represent one of the metal spin anti-parallel to the remaining two paramagnetic centers.



**Figure S5.** Possible mechanism of magnetic coupling for Lanthanide-radical interaction. Electron transfer from ligand based  $\pi^*$  orbital of hetero-fullerene radical to empty metal orbitals (such as in 5d, 6s and 6p) contribute to ferromagnetic interaction where as to filled 4f orbital will contribute to anti-ferromagnetic interaction.



**Figure S6.** Diagrammatic presentation of DFT computed overlap integral values for the interaction of Gd(III) 4f orbitals with radical orbital in Gd<sub>2</sub>@665-C<sub>79</sub>N. Smaller value of magnetic coupling suggest very small interaction between half filled metal 4f orbitals to ligand based  $\pi^*$  orbital of hetero-fullerene radical.



**Figure S7.** *DFT computed localized radical containing molecular orbital in*  $Gd_2@C_{79}N$ , *suggesting radical spin localization between both metal centers* 



**Figure S8.** DFT computed, selected NBO orbitals of  $Gd_2@C_{79}N$  showing five strongest interaction between Gd1 hybrid orbital with different C atoms of hereto-fullerene radical. Larger value of interaction suggest large fraction of charge transfer from these hetero-fulleren atoms to empty metal magnetic orbitals which is the reason for the observed large ferromagnetic interaction between Gd(III) and radical centers.



**Figure S9.** Ab initio SINGLE\_ANISO computed magnetization blocking barrier for both Dy(III) single ions of  $Dy_2@665-(C_{79}N)$ . The x- axis indicates the magnetic moment of each state along 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 contribution of magnetic relaxation. The solid black arrow lines show the most suitable relaxation pathway for magnetization reorientation. The dotted red lines correspond to the QTM/TA-QTM of relaxation contribution 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 KD and first excited state KD orientation for  $Dy2\_radical$  model system of  $LuDy@665-(C_{79}N)$  molecule along with the angle between both. This large angle is the outcome because of the large ferro-magnetic interaction between Dy-radical, which pushes up the first excited state KD more away from the ground state KD and decraeses the axiality of both KDs. This cause the relaxation of spin at first excited KD.



## **Computational Details:**

In case of  $Gd@C_{82}$  cage, the magnetic exchange interaction between  $Gd^{3+}$  and fullerene radical ions is described by the following spin Hamiltonian,

$$\hat{H} = -2JS_{Gd}S_{rad}$$

Here *J* is the isotropic exchange coupling constant and  $S_{Gd}$  and  $S_{rad}$  are spins on Gd<sup>III</sup> (S=7/2) and fullerene radical (S=1/2) atoms respectively. The DFT calculations combined with Broken Symmetry (BS) approach<sup>2</sup> has been employed to compute the *J* values. Here, we have performed most of our calculations using Gaussian 09 suite of programs.<sup>3</sup> All of the molecules were geometry optimized at the UB3LYP functional<sup>4</sup> with a 6-31G\* basis set<sup>5</sup> for carbon and nitrogen atoms and with a triple-zeta quality basis set employing Cundari-Stevens (CS) relativistic effective core potential for gadolinium atoms.<sup>6</sup> For single point calculations, we have employed spin-unrestricted B3LYP functional along with a triple-zeta quality basis set employing Cundari-Stevens (CS) relativistic effective core potential on Gd atom<sup>6</sup> and TZV basis set<sup>7</sup> for the rest of the atoms (C, N) for single point calculation. A very tight SCF convergence has been employed throughout to attain SCF convergence upto 1x10<sup>-8</sup> h.

For Gd<sub>2</sub>@C<sub>79</sub>N EHF, the following spin Hamiltonian has been adopted,

$$\hat{H} = -2J_{1A}S_{Gd_A}S_{rad} - 2J_{1B}S_{Gd_B}S_{rad} - 2J_2S_{Gd_A}S_{Gd_B}$$

The magnetic exchange interaction in trinuclear complexes were extracted using pair-wise interaction model where four spin configurations are computed to extract three different exchange interactions  $J_{1A-1B}$ - $J_2$ . The following four spin configurations has been computed (i) all spin up (S=15/2), (ii) spin down on only Gd<sub>A</sub> (S=1/2), (iii) spin down on only Gd<sub>B</sub> (S=1/2) and (iv) spin down only on fullerene radical (S=13/2). The energy differences between the spin configurations are equated to the corresponding exchange interactions from which all three *J* values have been extracted. Exchange coupling constant for Dy(III) has been calculated by dividing the corresponding *J* of Gd<sub>2</sub>@C<sub>79</sub>N by a factor of 5/7 (as the number of unpaired f electron in Dy(III) are five, 400\*5/7= 285.7 cm<sup>-1</sup>).

For incorporation of anisotropy in the molecule, we have replaced both Gd(III) ions with anisotropic Dy(III) ions one by one. Anisotropic studies suggest third large  $U_{cal}$  (computed

effective barrier for spin reversal and the average time for this magnetization reversal is known as relaxation time) value for this molecule because of very strong exchange interaction between metal-radical centers, which will be overestimating the blocking temperature,  $T_B$  (temperature between blocked magnetic and super paramagnetic state or the highest temperature at which hysteresis can be seen in magnetization versus magnetic field plots).

All the *ab initio* calculations have been performed using MOLCAS 7.8 code. Here we have employed the [ANO-RCC...8s7p5d3f2g1h.] basis set for Dy atoms, the [ANO-RCC...3s2p1d.] basis set for N and C and for Lu atom [ANO-RCC...7s6p4d2f.] atoms basis set. The ground state f-electron configuration for Dy(III) is  $4f^9$  with  ${}^{6}H_{15/2}$  multiplet as a ground state. First, we have generated the guess orbitals from there we have selected seven Dy(III) based starting orbitals to perform the CASSCF calculations. CASSCF calculations have been performed where eleven electrons are in the seven active orbitals with an active space of CAS(9,7). Using this active space first we have computed 21 sextets using the configuration interaction (CI) procedure. After this, we have performed RASSI-SO module to compute the spin-orbit coupled states. After computing these SO states, we have performed the SINGLE ANISO code to extract the corresponding g-tensors. Here we have computed the g-tensors for the eight low-lying Kramers Doublets. The cholesky decomposition for two electron integrals is employed throughout in the calculations to reduce the disk space. Using SINGLE ANISO code we have also extracted the crystal field parameters as implemented in MOLCAS 7.8 code. We have also used the POLY ANISO program to compute the anisotropic exchange interaction between the Dy(III)-radical centers.<sup>8</sup>

For POLY\_ANISO calculations we have used the Hamiltonian given below,

$$\hat{H} = -J_{1A}S_{Dy_{A}}S_{rad} - J_{1B}S_{Dy_{B}}S_{rad} - J_{2}S_{Dy_{A}}S_{Dy_{B}}$$

## **References.**

- 1 K. Furukawa, S. Okubo, H. Kato, H. Shinohara and T. Kato, *J. Phys. Chem. A*, 2003, **107**, 10933.
- 2(a)
   L. Noodleman, J. Chem. Phys., 1981, 74, 5737; (b)
   L. Noodleman and E. R. Davidson,

   Chem. Phys., 1986, 109, 131; (c)
   L. Noodleman and D. A. Case, Adv. Inorg.Chem.,

   1992, 38, 423; (d)
   L. Noodleman and J. G. Norman, J. Chem. Phys., 1979, 70, 4903.
- 3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota,

R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. Austin, J. R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, 2009.

- 4(a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; (d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *The J. Phys. Chem.*, 1994, **98**, 11623.
- 5 P. C. Hariharan and J. A. Pople, *Theor. chim. acta*, 1973, **28**, 213.
- 6 T. R. Cundari and W. J. Stevens, *J. Chem. Phys.*, 1993, **98**, 5555.
- 7(a) A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, 97, 2571; (b) A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, 100, 5829; (c) G. E. Scuseria and H. F. Schaefer, *III J. Chem. Phys.*, 1989, 90, 3700.
- 8 F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-å. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov and R. Lindh, *J. Comput. Chem.*, 2010, **31**, 224.