Mixed-Valent $Ln_2@C_{79}N$ Endohedral Metallofullerenes: Magnetic Exchange, Magnetic Anisotropy, and Electric−Field Control of SMM Characteristics

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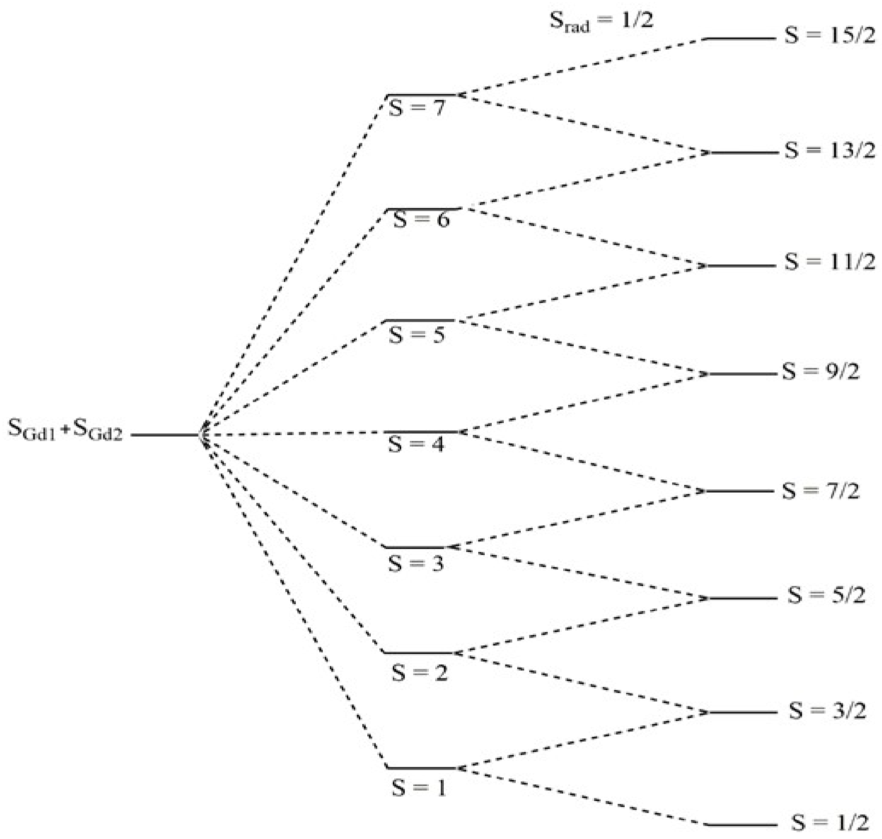
Computational Details



Scheme S1: The qualitative MO scheme of the formation of various spin states from the spin of two Gd centres and one unpaired electron between them.

The energy of a spin state of $Gd_2@C_{79}N$ is represented by Equation (2) with the Hamiltonian Equation (1);[1, 2]

$$H = -J(S_A S_B O_A + S_A S_B O_B) + BT_{AB} \ldots\ldots (1),$$

$$E\,(S, \pm) = -\frac{J}{2}S(S+1) \pm B\left(S+\frac{1}{2}\right) \ldots\ldots (2),$$

Here, J and B is the interaction and delocalisation parameter respectively. A and B corresponds to the Gd1 and Gd2 centre respectively. S is the total spin multiplicity (see scheme S1), where the additive combination is represented by E(S,+) and the subtractive combination is represented by E (S, −). Consider a spin state S = 13/2, which can be formed by two combinations; $[\left(S_{Gd1}=\frac{7}{2}\right)+\left(S_{Gd2}=\frac{5}{2}\right)+\left(S_{rad}=\frac{1}{2}\right)]$ or $[\left(S_{Gd1}=\frac{7}{2}\right)+\left(S_{Gd2}=\frac{7}{2}\right)-\left(S_{rad}=\frac{1}{2}\right)]$. The former one is reprented as E(S,+) while the latter one is denoted as E (S, −).

Table S1: Term symbols and the number of roots computed in CASSCF calculations for different Ln ions.		
Metal	**Term Symbol**	**Number of roots**
Ce^{III}	$^2F_{5/2}$	7 doublets
Pr^{III}	$^3H_4$	21 triplets, 28 singlets
Nd^{III}	$^4I_{9/2}$	35 quartets, 112 doublets
Pm^{III}	$^5I_4$	35 quintets, 210 triplets

Here T_{AB} is the electron transfer operator

$$T_{AB}\left|S_A S_B S >^A = \left(S+\frac{1}{2}\right)\right|S_A S_B S >^B \quad \text{....... (3)}$$

and $$T_{AB}|S_A S_B S >^B = (S+\frac{1}{2})|S_A S_B S >^A \quad \text{.........(4)}$$

O_A and O_B electron localisation operator

$$O_B|B,S,M_s> \; = |B,S,M_s> \quad \text{.......... (5)}$$

$$O_B|A,S,M_s> \; = 0 \quad \text{............ (6)}$$

The delocalisation parameter B is determined with Equation (7), where the energies of E(S,+) and E(S,–) states has been computed by ab initio CASSCF calculation.

$$B = \frac{E(S,+) - E(S,-)}{2S+1} \quad \text{.......... (7)}$$

On the other hand, using Heisenberg Hamilton $\hat{H}^H = -J_1(S_{Gd1}S_{rad} + S_{Gd2}S_{rad}) - J_2 S_{Gd1}S_{Gd2}$, the energy of a spin state (S) is computed with Equation (8); [3]

$$E^H(S,\pm) = \pm\left(\frac{J_1 - J_2}{2}\right)\left(S+\frac{1}{2}\right) - \frac{J_2}{2}\left[S(S+1) - S^{DE}_{max}\left(S^{DE}_{max}+1\right)\right] \text{.....(8)}$$

where J_1 is the metal–radical exchange, and J_2 is the metal–metal exchange interaction. The DE represents double exchange, S_{max} represents maximum spin multiplicity. Comparing the Equation (2) and (8), one can derive

$$J_1 = 2B + J_2 \quad \text{.......... (9)}$$

$$J_2 = \frac{1}{S}\left[\{(E(S-1,-) - E(S,-)\} - B\right] \quad \text{................ (10)}$$

Sm^{III}	$^6H_{5/2}$	21 sextets, 224 quartets
Eu^{III}	$^7F_0$	7 heptets, 140 quintets
Gd^{III}	$^8S_{7/2}$	–
Tb^{III}	$^7F_6$	7 heptets, 140 quintets
Dy^{III}	$^6H_{15/2}$	21 sextets, 224 quartets
Ho^{III}	$^5I_8$	35 quintets, 210 triplets
Er^{III}	$^4I_{15/2}$	35 quartets, 112 doublets
Tm^{III}	$^3H_6$	21 triplets, 28 singlets
Yb^{III}	$^2F_{7/2}$	7 doublets

Table S2: Complexes and their corresponding Ln−Ln bond distances.

Metal	Ln−Ln bond distance (Å)	Metal	Ln−Ln bond distance(Å)
$\mathbf{1}_{Ce}$	3.588	$\mathbf{1}_{Tb}$	3.751
$\mathbf{1}_{Pr}$	3.382	$\mathbf{1}_{Dy}$	3.417
$\mathbf{1}_{Nd}$	3.398	$\mathbf{1}_{Ho}$	3.425
$\mathbf{1}_{Pm}$	3.666	$\mathbf{1}_{Er}$	3.761
$\mathbf{1}_{Sm}$	3.452	$\mathbf{1}_{Tm}$	3.444
$\mathbf{1}_{Gd}$	3.737	$\mathbf{1}_{Yb}$	3.438

Table S3: Mulliken Spin populations in (Ln1, Ln2, cage) in all $Ln_2@C_{79}N$ complexes, where Ln varies from Ce to Yb.

Metal	Spin density	Metal	Spin density
$\mathbf{1}_{Ce}$	1.852, 1.259, -0.111	$\mathbf{1}_{Tb}$	6.551, 6.545, -0.097
$\mathbf{1}_{Pr}$	3.018, 3.019, -1.103	$\mathbf{1}_{Dy}$	4.527, 4.517, 1.955
$\mathbf{1}_{Nd}$	4.029, 4.034, -1.064	$\mathbf{1}_{Ho}$	3.502, 3.500, 1.997
$\mathbf{1}_{Pm}$	4.023, 5.029, -0.268	$\mathbf{1}_{Er}$	3.412, 3.402, 0.184
$\mathbf{1}_{Sm}$	6.061, 6.063, -1.125	$\mathbf{1}_{Tm}$	1.492, 1.487, 2.020
$\mathbf{1}_{Gd}$	7.586, 7.560, -0.167	$\mathbf{1}_{Yb}$	0.484, 0.481, 2.034

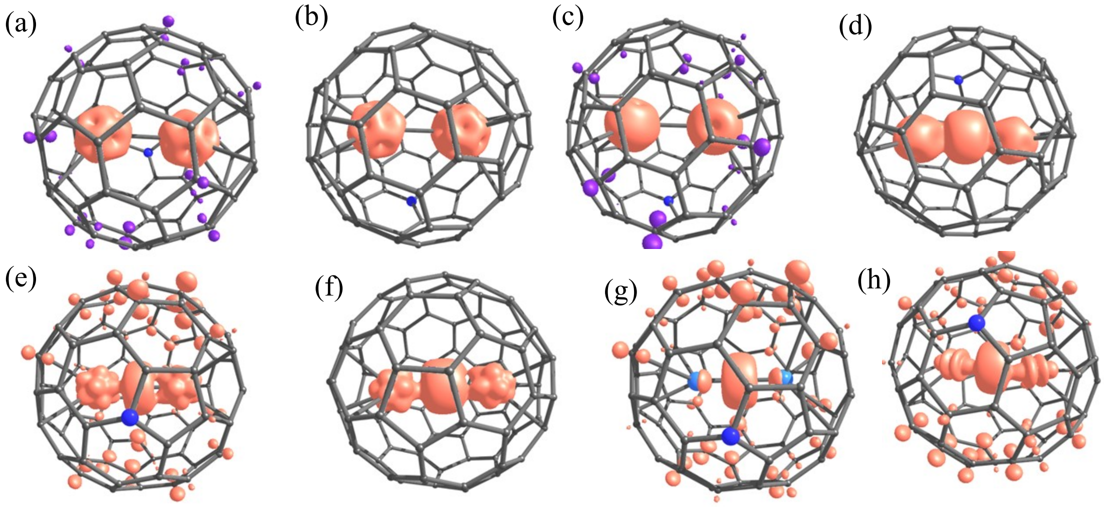


Figure S1: The optimized structures of (a) $\mathbf{1}_{Pm}$, (b) $\mathbf{1}_{Nd}$, (c) $\mathbf{1}_{Sm}$, (d) $\mathbf{1}_{Tb}$, (e) $\mathbf{1}_{Er}$, (f) $\mathbf{1}_{Ho}$, (g) $\mathbf{1}_{Tm}$ and (h) $\mathbf{1}_{Yb}$.

Table S4: Occupation of various orbitals in $Ln_2@C_{79}N$ complexes.*

Atom no.	Orbital	Ce	Pr	Nd	Pm	Sm	Gd
Alpha							
1	6S	0.002	0.001	0.001	0.001	0.001	0.221
1	6px	0.002	0.001	0.001	0.064	0.036	0.224
1	6py	0.018	0.016	0.014	0.022	0.013	0.027
1	6pz	0.018	0.015	0.014	0.024	0.013	0.022
1	5dxy	0.071	0.069	0.064	0.139	0.059	0.114
1	5dxz	0.071	0.066	0.062	0.150	0.050	0.117
1	5dyz	0.048	0.041	0.039	0.115	0.036	0.074
1	5dx2-y2	0.129	0.070	0.066	0.177	0.059	0.163
1	5dz2	0.079	0.050	0.047	0.103	0.045	0.102
1	4f0	0.028	0.302	0.640	0.878	0.997	1.000
1	4f+1	0.265	0.238	0.515	0.448	0.968	1.000
1	4f-1	0.134	0.675	0.512	0.281	0.628	1.000
1	4f+2	0.166	0.485	0.738	0.710	0.996	1.000
1	4f-2	0.599	0.449	0.435	0.625	0.997	1.000
1	4f+3	0.366	0.570	0.860	0.708	0.719	1.000
1	4f-3	0.119	0.232	0.269	0.426	0.673	1.000
2	6S	0.003	0.001	0.001	0.001	0.001	0.230
2	6px	0.095	0.001	0.001	0.043	0.001	0.223
2	6py	0.025	0.015	0.013	0.012	0.012	0.025
2	6pz	0.025	0.016	0.014	0.012	0.013	0.021
2	5dxy	0.112	0.068	0.062	0.069	0.054	0.108
2	5dxz	0.108	0.072	0.061	0.065	0.053	0.102
2	5dyz	0.076	0.036	0.038	0.047	0.034	0.081
2	5dx2-y2	0.164	0.071	0.066	0.099	0.064	0.157

2	5dz2	0.106	0.050	0.053	0.074	0.045	0.107
2	4f0	0.123	0.358	0.542	0.788	0.775	1.000
2	4f+1	0.125	0.346	0.730	0.739	0.568	1.000
2	4f-1	0.148	0.702	0.435	0.658	0.769	1.000
2	4f+2	0.111	0.294	0.694	0.866	0.982	1.000
2	4f-2	0.308	0.301	0.428	0.500	0.901	1.000
2	4f+3	0.263	0.359	0.564	0.379	0.993	1.000
2	4f-3	0.013	0.587	0.574	0.962	0.990	1.000
Beta							
1	6S	0.001	0.001	0.001	0.001	0.001	0.035
1	6px	0.001	0.001	0.001	0.047	0.036	0.031
1	6py	0.017	0.014	0.013	0.020	0.011	0.020
1	6pz	0.016	0.014	0.013	0.022	0.011	0.020
1	5dxy	0.061	0.054	0.051	0.117	0.045	0.082
1	5dxz	0.056	0.047	0.049	0.123	0.039	0.088
1	5dyz	0.040	0.032	0.032	0.090	0.026	0.057
1	5dx2-y2	0.066	0.056	0.054	0.125	0.046	0.079
1	5dz2	0.053	0.042	0.038	0.082	0.033	0.062
1	4f0	0.002	0.001	0.002	0.005	0.001	0.004
1	4f+1	0.003	0.005	0.003	0.012	0.001	0.002
1	4f-1	0.002	0.001	0.001	0.013	0.001	0.001
1	4f+2	0.003	0.002	0.001	0.007	0.001	0.004
1	4f-2	0.003	0.004	0.003	0.011	0.001	0.004
1	4f+3	0.003	0.002	0.001	0.005	0.002	0.003
1	4f-3	0.004	0.004	0.004	0.012	0.003	0.003
2	6S	0.002	0.001	0.001	0.001	0.001	0.036
2	6px	0.058	0.001	0.001	0.034	0.036	0.031
2	6py	0.023	0.014	0.012	0.011	0.011	0.018
2	6pz	0.023	0.014	0.013	0.012	0.012	0.019
2	5dxy	0.102	0.051	0.049	0.055	0.041	0.077
2	5dxz	0.094	0.051	0.048	0.050	0.041	0.079
2	5dyz	0.072	0.030	0.030	0.036	0.025	0.061
2	5dx2-y2	0.108	0.058	0.055	0.061	0.047	0.083
2	5dz2	0.085	0.040	0.041	0.046	0.035	0.066
2	4f0	0.005	0.002	0.001	0.001	0.001	0.004
2	4f+1	0.010	0.003	0.003	0.002	0.003	0.002
2	4f-1	0.003	0.001	0.001	0.001	0.001	0.002
2	4f+2	0.005	0.002	0.002	0.001	0.001	0.003
2	4f-2	0.008	0.002	0.003	0.002	0.001	0.005
2	4f+3	0.006	0.005	0.003	0.003	0.001	0.004
2	4f-3	0.009	0.003	0.002	0.001	0.001	0.002
		Tb	Dy	Ho	Er	Tm	Yb
Alpha							
1	6S	0.228	0.277	0.280	0.246	0.282	0.292
1	6px	0.225	0.203	0.202	0.224	0.202	0.197
1	6py	0.025	0.009	0.009	0.025	0.009	0.008
1	6pz	0.022	0.011	0.010	0.020	0.010	0.009

1	5dxy	0.108	0.031	0.030	0.097	0.028	0.027
1	5dxz	0.112	0.029	0.028	0.097	0.024	0.024
1	5dyz	0.075	0.018	0.017	0.056	0.015	0.015
1	5dx2-y2	0.156	0.060	0.055	0.127	0.053	0.047
1	5dz2	0.096	0.035	0.032	0.086	0.031	0.029
1	4f0	1.000	0.999	0.999	1.000	0.999	0.999
1	4f+1	1.000	0.999	0.999	1.000	0.998	0.998
1	4f-1	1.000	0.999	0.999	1.000	0.999	0.999
1	4f+2	1.000	0.999	0.999	1.000	0.999	0.999
1	4f-2	0.999	0.999	0.999	1.000	0.999	0.999
1	4f+3	1.000	0.998	0.998	1.000	0.998	0.998
1	4f-3	0.999	0.998	0.998	1.000	0.998	0.998
2	6S	0.243	0.279	0.282	0.255	0.282	0.292
2	6px	0.222	0.204	0.202	0.223	0.202	0.197
2	6py	0.023	0.009	0.009	0.023	0.008	0.008
2	6pz	0.020	0.011	0.011	0.018	0.011	0.010
2	5dxy	0.102	0.029	0.027	0.084	0.026	0.024
2	5dxz	0.092	0.028	0.027	0.082	0.027	0.025
2	5dyz	0.077	0.018	0.017	0.069	0.015	0.015
2	5dx2-y2	0.147	0.062	0.058	0.127	0.055	0.050
2	5dz2	0.107	0.034	0.032	0.085	0.029	0.027
2	4f0	1.000	0.999	0.999	1.000	0.999	0.999
2	4f+1	1.000	0.999	0.999	1.000	0.998	0.998
2	4f-1	1.000	0.999	0.999	1.000	0.999	0.999
2	4f+2	0.999	0.999	0.999	1.000	0.999	0.998
2	4f-2	1.000	0.999	0.999	1.000	0.999	0.999
2	4f+3	0.999	0.998	0.998	0.999	0.998	0.998
2	4f-3	1.000	0.998	0.998	1.000	0.998	0.998
Beta							
1	6S	0.036	0.020	0.020	0.037	0.020	0.02088
1	6px	0.029	0.023	0.021	0.024	0.017	0.01584
1	6py	0.019	0.009	0.009	0.019	0.008	0.00783
1	6pz	0.020	0.010	0.009	0.018	0.008	0.0079
1	5dxy	0.082	0.028	0.027	0.081	0.026	0.02527
1	5dxz	0.089	0.025	0.024	0.081	0.022	0.02166
1	5dyz	0.061	0.015	0.015	0.051	0.014	0.01407
1	5dx2-y2	0.077	0.027	0.026	0.072	0.025	0.02429
1	5dz2	0.059	0.022	0.021	0.063	0.021	0.02072
1	4f0	0.015	0.131	0.693	0.292	0.954	0.99863
1	4f+1	0.177	0.656	0.169	0.888	0.736	0.99768
1	4f-1	0.034	0.770	0.786	0.733	0.977	0.99889
1	4f+2	0.170	0.052	0.300	0.454	0.929	0.99873
1	4f-2	0.501	0.393	0.907	0.550	0.963	0.99814
1	4f+3	0.095	0.702	0.957	0.787	0.777	0.99779
1	4f-3	0.047	0.259	0.170	0.417	0.652	0.9979
2	6S	0.036	0.021	0.021	0.038	0.020	0.02107
2	6px	0.030	0.023	0.021	0.025	0.017	0.01599

2	6py	0.018	0.009	0.009	0.017	0.008	0.00789
2	6pz	0.018	0.009	0.009	0.017	0.008	0.0081
2	5dxy	0.073	0.026	0.024	0.072	0.024	0.02297
2	5dxz	0.076	0.024	0.023	0.072	0.023	0.0223
2	5dyz	0.062	0.016	0.016	0.061	0.016	0.01562
2	5dx2-y2	0.084	0.030	0.029	0.076	0.027	0.02766
2	5dz2	0.068	0.022	0.022	0.062	0.020	0.01964
2	4f0	0.010	0.353	0.003	0.444	0.909	0.99856
2	4f+1	0.050	0.063	0.993	0.639	0.827	0.9977
2	4f-1	0.026	0.804	0.991	0.758	0.992	0.9984
2	4f+2	0.845	0.425	0.409	0.809	0.812	0.99848
2	4f-2	0.062	0.519	0.394	0.281	0.977	0.99884
2	4f+3	0.016	0.244	0.602	0.395	0.586	0.9978
2	4f-3	0.033	0.560	0.589	0.800	0.886	0.99792

* Note here that the DFT-derived spin populations and orbital occupations reported here should be interpreted with caution, as single-determinant methods may not reliably capture the electronic structure of anisotropic lanthanide systems with partially filled 4f shells. These results are therefore provided for qualitative comparison, while the multireference CASSCF treatment offers a more robust description.

Table S8: Energies (atomic units) of HS, BS1 and BS2 for $Gd_2@C_{79}N$, $Tb_2@C_{79}N$, $Dy_2@C_{79}N$, $Ho_2@C_{79}N$, $Er_2@C_{79}N$, $Tm_2@C_{79}N$ and $Yb_2@C_{79}N$.

	Gd	Tb	Dy	Ho	Er	Tm	Yb
HS	−3287.274311	−3287.274178	−3287.236328	−3287.238511	−3287.272799	−3287.243251	−3287.243270
BS1	−3287.267225	−3287.267219	−3287.228261	−3287.230479	−3287.265824	−3287.235008	−3287.235052

Table S5: The orbital occupation of the one unpaired electron in $Gd_2@C_{79}N$. This has been computed for S = 15/2 state from *ab initio* calculation with CAS (15,15) active space.

Orbital	$Gd_2@C_{79}N$
6s	0.29
$5p_z$	0.10
$6p_z$	0.26
$5d_0$	0.35

Table S6: |V(r)|/G(r) for all the bond critical points properties for Ln−Ln in **1**$_{Ce}$−**1**$_{Yb}$. V(r) is the Virial Field function, G(r) is the electronic kinetic energy density, |V(r)|/G(r) is the ratio of Virial field function to Electronic kinetic energy.

Metal ion	|V(r)|/G(r)	Metal ion	|V(r)|/G(r)
1$_{Ce}$	1.142	**1**$_{Tb}$	3.001
1$_{Pr}$	0.918	**1**$_{Dy}$	1.927
1$_{Nd}$	0.861	**1**$_{Ho}$	1.984
1$_{Pm}$	0.801	**1**$_{Er}$	3.001
1$_{Sm}$	0.875	**1**$_{Tm}$	2.256
1$_{Gd}$	2.932	**1**$_{Yb}$	2.666

Table S7: The delocalisation indices δ(Ln, Ln) for Ln−Ln found in **1**$_{Ce}$−**1**$_{Yb}$.

Metal ion	δ(Ln, Ln)	Metal ion	δ(Ln, Ln)
1$_{Ce}$	0.428	**1**$_{Tb}$	0.512
1$_{Pr}$	0.223	**1**$_{Dy}$	0.534
1$_{Nd}$	0.194	**1**$_{Ho}$	0.529
1$_{Pm}$	0.163	**1**$_{Er}$	0.504
1$_{Sm}$	0.153	**1**$_{Tm}$	0.522
1$_{Gd}$	0.517	**1**$_{Yb}$	0.520

BS 2	−3287.259332	−3287.259368	−3287.222148	−3287.223962	−3287.257987	−3287.227285	−3287.227354

Table S9: S^2 of HS, BS1 and BS2 configurations for $Gd_2@C_{79}N$.	
	$<S^2>$
HS	63.7
BS1	7.7
BS2	49.7

Table S10: The relative energies (atomic units) of the different spin states are reported with respect to the ground state; State 1 corresponds to the low-spin configuration, while State 2 corresponds to the high-spin configuration.

State	Pr	Nd	Pm	Sm	Tb
State 1	0.028	0.066	0.069	0.015	0.021
State 2	0.089	0.164	0.124	0.203	0.158
	Dy	Ho	Er	Tm	
State 1	0.041	0.081	0.083	0.036	
State 2	0.211	0.146	0.208	0.122	

Table S11 :The energy of the all−possible spin states of $Gd_2@C_{79}N$.

Spin Multiplicity (2S+1)	Energy (a.u)	The difference in energy of the two roots divided by 2S+1 in cm^{-1} (B)
16	−25569.982	
14	−25569.981	442.9
	−25569.966	
12	−25569.967	442.9
	−25569.967	

10	−25569.965	442.9
	−25569.989	
8	−25569.966	442.9
	−25569.986	
6	−25569.988	442.9
	−25569.983	
4	−25569.985	442.9
	−25569.980	
2	−25569.982	

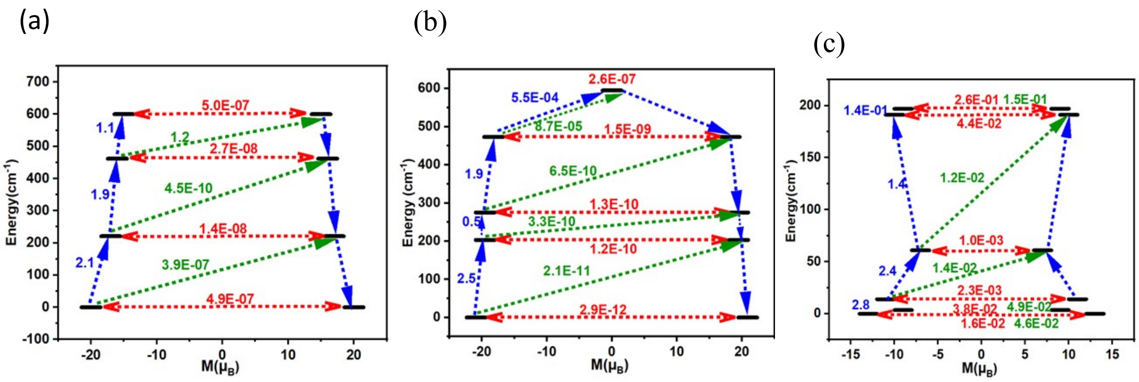


Figure S2: Relaxation mechanism of (a) $\mathbf{1}_{Tb}$ b) $\mathbf{1}_{Dy}$ and c) $\mathbf{1}_{Ho}$.

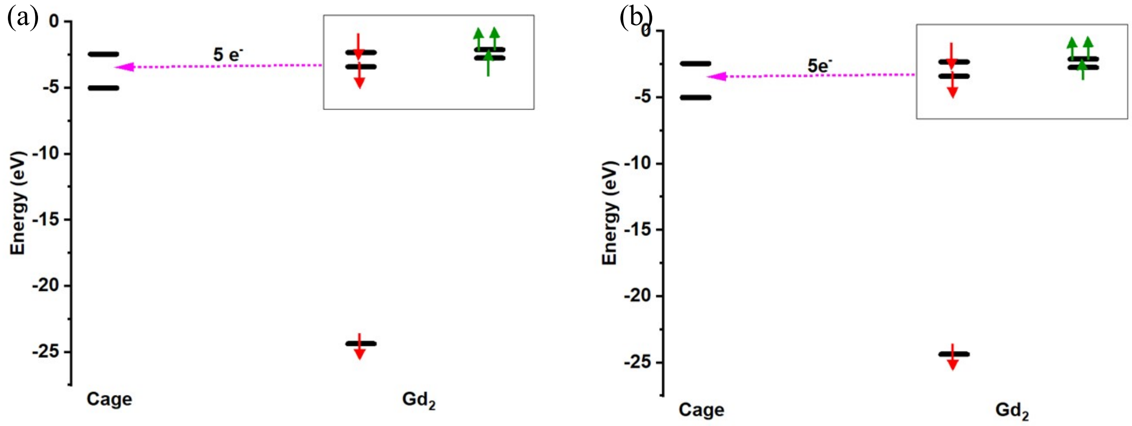


Figure S3: The MO diagrams corresponding to the formation of (a) $\mathbf{1}_{opt}$ and (b) $\mathbf{1}_{x+10}$ .Green arrows represent alpha electrons whereas red arrows represent beta electrons.

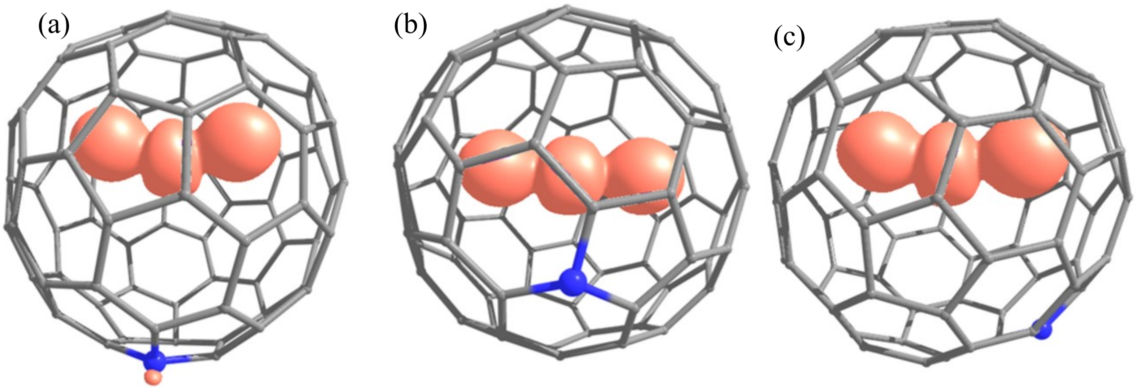


Figure S4: DFT computed spin population plot of (a) $\mathbf{1}_{z+10}$, (b) $\mathbf{1}_{opt}$, (c) $\mathbf{1}_{x+10}$ The corresponding spin population plots for the high spin state are given in figures (a-d) with an isosurface value of 0.006 e^{-} $bohr^{-3}$

Table S12: Gd−Gd bond distance and Electron density at the BCP between two Gd^{III} atoms under the application of OEEF.

Structure	**Gd−Gd bond distance (Å)**	**Electron Density ($eÅ^{-3}$)**	**Structure**	**Gd−Gd bond distance (Å)**	**Electron Density ($eÅ^{-3}$)**
$\mathbf{1}_{z+1}$	3.733	0.0204	$\mathbf{1}_{z-1}$	3.762	0.0201
$\mathbf{1}_{z+2}$	3.744	0.0202	$\mathbf{1}_{z-2}$	3.770	0.0200
$\mathbf{1}_{z+4}$	3.760	0.0201	$\mathbf{1}_{z-4}$	3.649	0.0219
$\mathbf{1}_{z+6}$	3.594	0.0224	$\mathbf{1}_{z-6}$	3.624	0.0224
$\mathbf{1}_{z+8}$	3.798	0.0194	$\mathbf{1}_{z-8}$	3.601	0.0209
$\mathbf{1}_{z+10}$	3.499	0.0251	$\mathbf{1}_{z-10}$	3.573	0.0235
$\mathbf{1}_{x+1}$	3.736	0.0188	$\mathbf{1}_{x-1}$	3.722	0.0193
$\mathbf{1}_{x+2}$	3.716	0.02067	$\mathbf{1}_{x-2}$	3.665	0.0210
$\mathbf{1}_{x+4}$	3.651	0.0207	$\mathbf{1}_{x-4}$	3.609	0.0026
$\mathbf{1}_{x+6}$	3.545	0.0237	$\mathbf{1}_{x-6}$	3.523	0.0242
$\mathbf{1}_{x+8}$	3.402	0.0263	$\mathbf{1}_{x-8}$	3.441	0.0263
$\mathbf{1}_{x+10}$	3.316	0.0290	$\mathbf{1}_{x-10}$	3.340	0.0287
$\mathbf{1}_{y+1}$	3.691	0.0211	$\mathbf{1}_{y-1}$	3.800	0.0196
$\mathbf{1}_{y+2}$	3.648	0.0218	$\mathbf{1}_{y-2}$	3.806	0.0195
$\mathbf{1}_{y+4}$	3.573	0.0234	$\mathbf{1}_{y-4}$	3.690	0.0207
$\mathbf{1}_{y+6}$	3.486	0.0253	$\mathbf{1}_{y-6}$	3.615	0.0227
$\mathbf{1}_{y+8}$	3.390	0.0263	$\mathbf{1}_{y-8}$	3.542	0.0244
$\mathbf{1}_{y+10}$	3.299	0.0290	$\mathbf{1}_{y-10}$	3.464	0.0261

Table S13: Electric field vectors and magnitudes at the Dy center estimated from a point−charge model using LoProp charges and optimized coordinates, for field−free and electric−field−perturbed structures.

Molecule	Electric Field experienced by Central metal ion (V/Å) on Dy1	E_x	E_y	E_z
1	1.008	0.145	−0.02084	0.998
$\mathbf{1}_{x+1}$	1.054	0.227	−0.07384	1.027
$\mathbf{1}_{x+2}$	1.079	0.229	−0.09746	1.051
$\mathbf{1}_{x+4}$	1.102	0.193	0.029	1.085
$\mathbf{1}_{x+6}$	1.238	0.365	0.097	1.180
$\mathbf{1}_{x+8}$	1.418	0.545	0.197	1.295
$\mathbf{1}_{x+10}$	1.471	0.573	0.229	1.336
$\mathbf{1}_{x-1}$	0.993	0.083	−0.01783	0.990
$\mathbf{1}_{x-2}$	0.971	−0.13651	−0.23057	0.933
$\mathbf{1}_{x-4}$	1.001	−0.06911	−0.16064	0.985
$\mathbf{1}_{x-6}$	0.987	−0.1624	−0.25065	0.941
$\mathbf{1}_{x-8}$	1.019	−0.16888	−0.26522	0.970
$\mathbf{1}_{x-10}$	1.063	−0.12151	−0.23921	1.028
$\mathbf{1}_{y+1}$	1.012	0.133	−0.05776	1.001
$\mathbf{1}_{y+2}$	1.010	0.099	−0.07732	1.002
$\mathbf{1}_{y+4}$	1.009	0.087	−0.08551	1.001
$\mathbf{1}_{y+6}$	1.024	0.084	−0.08393	1.017
$\mathbf{1}_{y+8}$	1.085	0.073	−0.03467	1.082
$\mathbf{1}_{y+10}$	1.157	0.113	−0.01897	1.152
$\mathbf{1}_{y-1}$	0.926	0.138	0.132	0.907
$\mathbf{1}_{y-2}$	0.943	0.186	0.130	0.916
$\mathbf{1}_{y-4}$	0.956	0.046	−0.1548	0.942
$\mathbf{1}_{y-6}$	0.949	−0.01632	−0.15344	0.937
$\mathbf{1}_{y-8}$	0.943	−0.02391	−0.14966	0.930
$\mathbf{1}_{y-10}$	0.963	−0.04329	−0.17646	0.946
$\mathbf{1}_{z+1}$	1.030	0.192	−0.09542	1.008
$\mathbf{1}_{z+2}$	1.035	0.196	−0.15393	1.004
$\mathbf{1}_{z+4}$	0.998	0.140	−0.33345	0.930
$\mathbf{1}_{z+6}$	0.965	0.115	−0.57026	0.770
$\mathbf{1}_{z+10}$	1.039	0.191	−0.709	0.735
$\mathbf{1}_{z-1}$	0.965	0.135	0.084	0.952
$\mathbf{1}_{z-2}$	0.938	0.121	0.119	0.923
$\mathbf{1}_{z-4}$	1.085	0.231	0.608	0.868
$\mathbf{1}_{z-6}$	1.099	0.257	0.637	0.858
$\mathbf{1}_{z-8}$	1.108	0.271	0.654	0.853
$\mathbf{1}_{z-10}$	1.124	0.281	0.672	0.856
Molecule	**Electric Field experienced by Central metal ion (V/Å) on Dy2**	**E_x**	**E_y**	**E_z**
1	0.966	0.029	−0.05099	−0.96396
$\mathbf{1}_{x+1}$	0.948	0.008	0.025	−0.9481
$\mathbf{1}_{x+2}$	0.950	0.035	0.063	−0.9471

$\mathbf{1}_{x+4}$	0.969	0.121	−0.0497	−0.9601
$\mathbf{1}_{x+6}$	0.973	0.078	−0.04239	−0.96873
$\mathbf{1}_{x+8}$	0.987	0.031	−0.02944	−0.98607
$\mathbf{1}_{x+10}$	0.996	−0.00067	−0.00808	−0.99596
$\mathbf{1}_{x-1}$	0.975	0.046	−0.06577	−0.97183
$\mathbf{1}_{x-2}$	0.958	0.242	0.151	−0.91457
$\mathbf{1}_{x-4}$	0.988	0.054	0.024	−0.98602
$\mathbf{1}_{x-6}$	0.952	0.199	0.130	−0.92205
$\mathbf{1}_{x-8}$	0.988	0.188	0.145	−0.95905
$\mathbf{1}_{x-10}$	1.045	0.138	0.111	−1.02992
$\mathbf{1}_{y+1}$	0.963	0.041	−0.01239	−0.96193
$\mathbf{1}_{y+2}$	0.964	0.070	0.006	−0.96164
$\mathbf{1}_{y+4}$	0.964	0.085	0.012	−0.9604
$\mathbf{1}_{y+6}$	0.977	0.096	0.010	−0.97266
$\mathbf{1}_{y+8}$	1.028	0.080	0.080	−1.02209
$\mathbf{1}_{y+10}$	1.074	0.073	0.085	−1.06847
$\mathbf{1}_{y-1}$	0.910	0.039	−0.22494	−0.88045
$\mathbf{1}_{y-2}$	0.891	0.015	−0.21634	−0.8646
$\mathbf{1}_{y-4}$	0.918	0.058	0.048	−0.91507
$\mathbf{1}_{y-6}$	0.922	0.099	0.019	−0.91635
$\mathbf{1}_{y-8}$	0.938	0.118	0.014	−0.93057
$\mathbf{1}_{y-10}$	0.974	0.124	−0.00623	−0.96571
$\mathbf{1}_{z+1}$	1.030	0.192	−0.09551	1.008
$\mathbf{1}_{z+2}$	0.937	−0.00146	0.092	−0.93238
$\mathbf{1}_{z+4}$	0.891	0.023	0.261	−0.852
$\mathbf{1}_{z+6}$	0.922	0.007	0.648	−0.65601
$\mathbf{1}_{z+10}$	0.980	−0.01879	0.678	−0.70792
$\mathbf{1}_{z-1}$	0.955	0.032	−0.17109	−0.93949
$\mathbf{1}_{z-2}$	0.936	0.046	−0.2069	−0.91192
$\mathbf{1}_{z-4}$	0.997	0.043	−0.59395	−0.7998
$\mathbf{1}_{z-6}$	0.997	0.033	−0.61562	−0.78365
$\mathbf{1}_{z-8}$	0.998	0.027	−0.62799	−0.77504
$\mathbf{1}_{z-10}$	1.006	0.021	−0.64047	−0.77513

Table S14: Variation of energy barrier as a function of OEEF.

Structure	**Energy Barrier (cm^{-1})**	**Structure**	**Energy Barrier (cm^{-1})**
$\mathbf{1}_{z+1}$	194.2	$\mathbf{1}_{z-1}$	431.7
$\mathbf{1}_{z+2}$	397.5	$\mathbf{1}_{z-2}$	445.6
$\mathbf{1}_{z+4}$	429.3	$\mathbf{1}_{z-4}$	302.9
$\mathbf{1}_{z+6}$	341.5	$\mathbf{1}_{z-6}$	310.3
$\mathbf{1}_{z+8}$	389.4	$\mathbf{1}_{z-8}$	307.1

$\mathbf{1}_{z+10}$	331.8	$\mathbf{1}_{z-10}$	301.6
$\mathbf{1}_{x+1}$	393.8	$\mathbf{1}_{x-1}$	472.4
$\mathbf{1}_{x+2}$	234.4	$\mathbf{1}_{x-2}$	317.9
$\mathbf{1}_{x+4}$	396.4	$\mathbf{1}_{x-4}$	389.2
$\mathbf{1}_{x+6}$	479.8	$\mathbf{1}_{x-6}$	357.4
$\mathbf{1}_{x+8}$	407.4	$\mathbf{1}_{x-8}$	353.7
$\mathbf{1}_{+10}$	456.4	$\mathbf{1}_{x-10}$	337.6
$\mathbf{1}_{y+1}$	476.7	$\mathbf{1}_{y-1}$	498.4
$\mathbf{1}_{y+2}$	308.9	$\mathbf{1}_{y-2}$	489.6
$\mathbf{1}_{y+4}$	331.6	$\mathbf{1}_{y-4}$	463.2
$\mathbf{1}_{y+6}$	335.5	$\mathbf{1}_{y-6}$	315.3
$\mathbf{1}_{y+8}$	323.1	$\mathbf{1}_{y-8}$	347.3
$\mathbf{1}_{y+10}$	294.0	$\mathbf{1}_{y-10}$	357.3

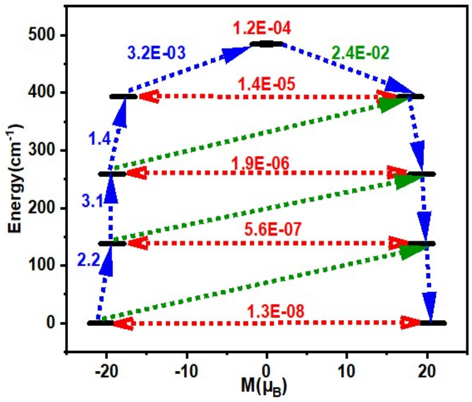


Figure S4: Relaxation mechanism of $\mathbf{1}_{opt}$.