Electronic Supporting Information

Net Toroidal Magnetic Moment in the Ground State of a {Dy_6}-triethanolamine ring

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Ab initio calculations of mononuclear Dy fragments in the {Dy_6} wheel

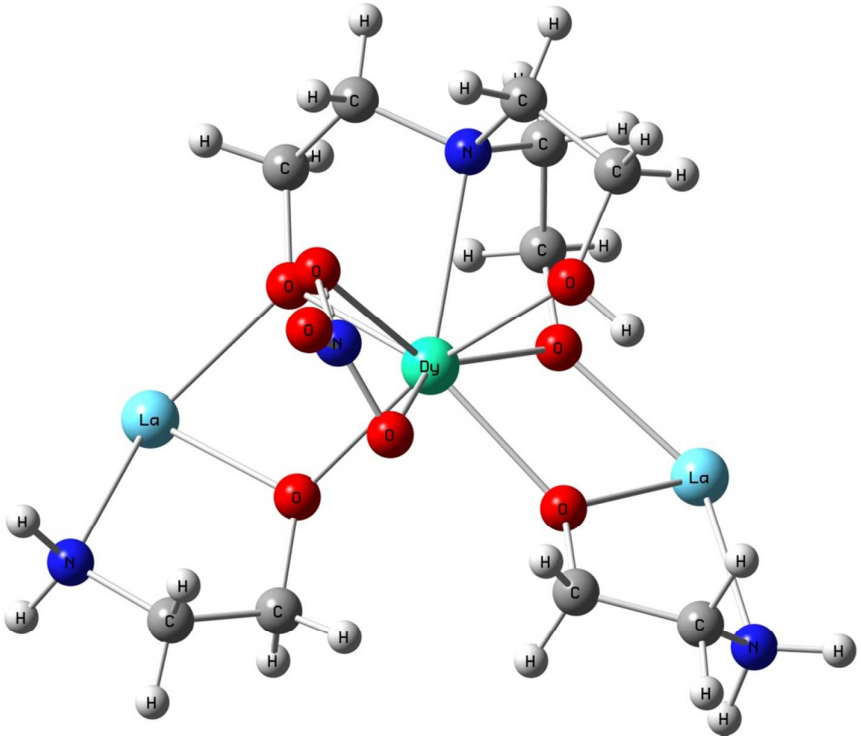

Figure S1. The structure of the calculated mononuclear Dy fragment (**structural model A**).

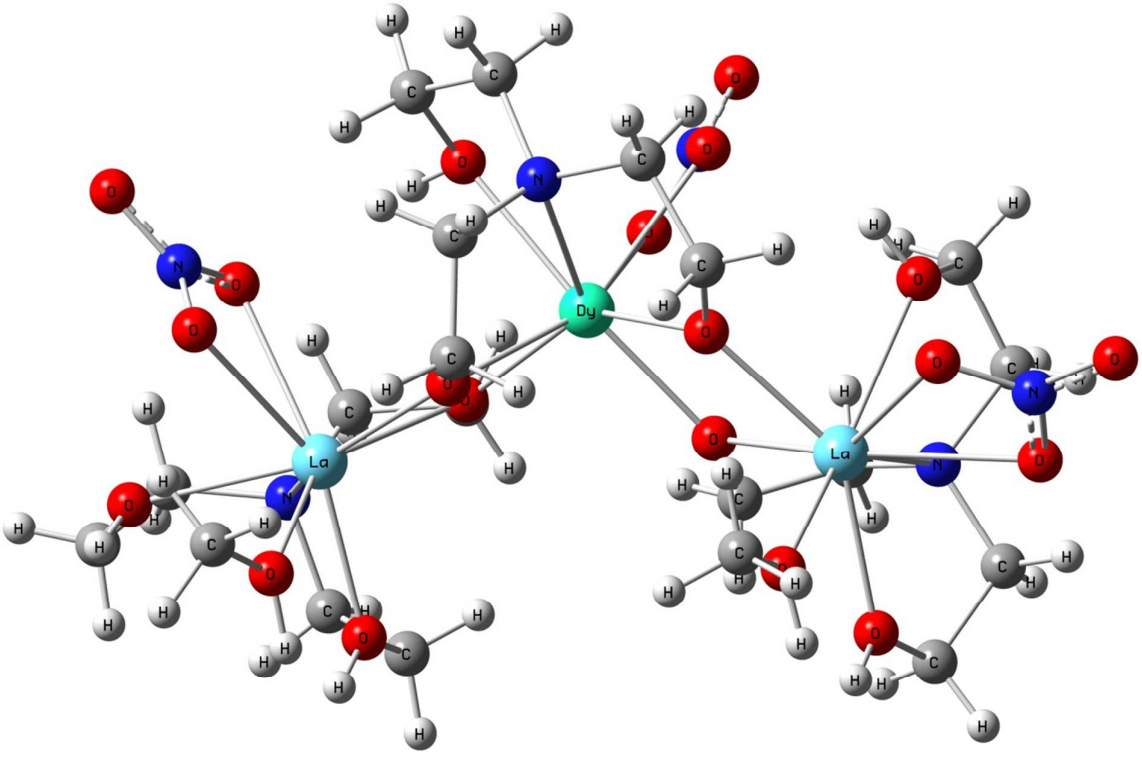

Figure S2. The structure of the calculated mononuclear Dy fragment (**structural model B**).

Computational details:

Basis Sets: All employed basis sets were taken from the standard ANO-RCC basis set library from MOLCAS. In order to ensure our results, two basis sets approximations were employed. The following contractions were used for the atoms in the **basis set approximation 1**:

Dy – 7s6p4d3f1g.
La – La.ECP.deGraaf.0s.0s.0e-La(LaMnO3).
O, N – 3s2p1d.
N, C – 3s2p. (for distant atoms)
H – 2s.

The following contractions were used for the atoms in the **basis set approximation 2**:

Dy – 8s7p5d4f2g1h.
La. – 7s6p4d3f1g.
O, N, C – 4s3p2d. (only for the first and second coordinated atoms)
O, N, C – 3s2p. (for distant atoms)
H – 3s1p. (for close atoms)
H – 2s. (for distant atoms)

So, for both structural approximations we have employed two different basis set approximations, therefore, in total we have 4 possible computational combinations:

- Structure **A** + basis set **1**=computational approximation **A1**.
- Structure **A** + basis set **2**=computational approximation **A2**.
- Structure **B** + basis set **1**=computational approximation **B1**.
- Structure **B** + basis set **2**=computational approximation **B2**.

Active space of the CASSCF method included 9 electrons in 7 orbitals.
The **spin-orbit interaction** was computed by mixing of 21 sextets, 128 quartets and 130 doublet spin free states.

Table S1. CASSCF energies of the lowest spin-free states (cm^{-1}) on the Dy1 center.

Spin multiplicity		A1	A2	B1	B2
6	H	0.000	0.000	0.000	0.000
		2.813	5.984	33.839	32.948
		87.460	80.527	78.671	73.146
		99.965	99.664	125.783	121.671
		218.556	203.493	226.389	221.337
		310.781	278.425	282.808	268.263
		375.717	343.460	348.845	324.955
		402.993	359.166	379.333	347.749
		420.016	393.081	447.047	432.272
		589.513	559.510	604.868	580.065
		594.723	566.101	611.216	590.705
	F	7591.110	7573.348	7592.014	7580.043
		7610.201	7588.608	7621.875	7604.796

		7717.278	7698.515	7735.365	7719.344
		7753.692	7731.429	7753.578	7736.791
		7770.193	7745.668	7768.476	7749.335
		7836.605	7806.477	7830.958	7812.451
		7877.319	7853.669	7883.121	7868.462
	P	34790.323	34817.115	34857.502	34851.899
		35016.278	34949.300	34933.665	34915.305
		35252.847	35203.084	35296.286	35245.964
4		24872.242	24857.533	24877.566	24863.755
		24878.375	24863.250	24884.450	24870.610
		24898.058	24879.834	24903.743	24886.628
		24904.177	24886.725	24921.736	24906.301
		24948.735	24925.788	24973.039	24953.426
		24969.305	24938.727	24982.337	24957.651
		24981.240	24957.685	25011.899	24988.491
		25019.631	24996.706	25047.377	25024.981
		25049.357	25021.988	25054.279	25032.225
		25079.259	25051.681	25072.897	25051.620
		25090.037	25063.430	25103.245	25079.978
		25117.223	25081.271	25107.982	25083.920
		25145.363	25113.258	25146.321	25123.696
		25170.417	25151.791	25180.793	25163.358
		25223.254	25204.431	25231.603	25215.774
		25259.386	25235.234	25277.825	25256.801
		25269.886	25242.616	25286.279	25263.513
		25283.388	25258.350	25297.740	25276.880
		25293.860	25268.599	25307.598	25286.158
		25321.264	25297.280	25331.318	25311.319
		…	…	…	…
2		37305.533	37280.567	37311.501	37292.088
		37308.189	37283.451	37313.487	37294.255
		37327.824	37296.513	37340.042	37316.517
		37333.284	37302.102	37344.958	37321.892
		37359.557	37325.515	37370.681	37344.574
		37383.828	37349.089	37394.206	37367.776
		37475.631	37443.549	37485.783	37462.164
		37489.328	37460.328	37495.525	37473.970
		37513.274	37482.764	37520.889	37496.987
		37519.641	37488.205	37523.300	37499.267
		37541.855	37508.443	37554.061	37529.052
		37580.686	37548.467	37588.233	37563.652
		37596.162	37562.932	37605.942	37580.647
		37607.027	37575.349	37612.321	37588.426
		37611.322	37579.636	37619.268	37595.512
		37648.078	37610.309	37639.373	37614.880
		37654.816	37616.965	37651.585	37626.276
		39000.380	38972.595	39003.208	38982.079
		39002.587	38975.287	39005.669	38985.026
		39036.826	39004.425	39041.994	39018.236
		…	…	…	…

Table S2. RASSI energies of the lowest spin-orbit states (cm^{-1}) on the Dy1 center.

A1	A2	B1	B2
0.000	0.000	0.000	0.000
66.374	49.690	62.794	56.026
162.274	128.870	129.707	113.761
185.501	156.367	189.344	174.275
246.529	216.895	256.899	237.215
340.054	287.985	277.482	252.476
365.221	321.059	368.993	343.248
501.270	459.815	505.294	477.160
3607.862	3601.467	3598.656	3592.254
3657.761	3642.690	3657.212	3651.403
3724.864	3689.476	3710.782	3694.899
3749.395	3712.670	3740.830	3718.960
3800.138	3754.489	3770.427	3747.339
3842.366	3797.486	3832.800	3807.225
3936.171	3890.517	3941.119	3908.277
6137.750	6130.894	6153.488	6143.054
6212.509	6181.081	6186.040	6174.245
6257.758	6214.491	6230.794	6210.323
6293.110	6256.654	6277.317	6256.204
6336.068	6297.936	6324.780	6304.388
6416.076	6367.487	6425.131	6389.356
8100.938	8087.159	8109.935	8096.654
8167.949	8127.629	8143.428	8125.794
8220.517	8180.341	8196.595	8175.853
8277.073	8243.188	8266.362	8247.190
8351.620	8303.888	8357.046	8322.820
9638.664	9620.292	9634.910	9619.560
9701.547	9660.583	9687.302	9669.261
9768.778	9731.182	9753.409	9732.427
9885.915	9839.860	9886.185	9853.795
10035.893	10006.554	10017.389	10001.915
10053.911	10017.478	10055.599	10031.261
10092.731	10056.420	10090.496	10067.686
10133.336	10096.028	10115.367	10093.698
10172.056	10137.081	10165.396	10139.933
10206.194	10164.715	10194.908	10175.056
10799.226	10782.872	10792.695	10782.508
10909.465	10859.953	10888.547	10861.697
11062.008	11014.841	11064.862	11032.772
11490.874	11454.424	11479.274	11457.286
11518.740	11484.295	11511.852	11489.869
11540.053	11504.213	11536.279	11514.691
11572.429	11531.188	11557.031	11532.912
11577.939	11540.162	11568.981	11545.863
13408.026	13371.140	13401.478	13378.184
13473.067	13434.691	13465.081	13441.565
13489.800	13452.003	13479.096	13455.907

13522.070	13483.731	13512.663	13489.391
14881.956	14843.350	14873.344	14849.120
14923.279	14884.811	14916.205	14892.249
14954.903	14916.093	14945.295	14921.322
15780.761	15741.578	15771.221	15746.957
15792.079	15752.930	15784.658	15759.958
16316.588	16276.650	16308.187	16283.192
24544.444	24507.464	24547.321	24521.567
24588.166	24550.238	24581.723	24555.722
24649.181	24609.450	24651.091	24623.067
24771.264	24729.061	24753.740	24726.970
24818.156	24776.668	24812.464	24784.456
25146.718	25119.335	25128.828	25110.769
25197.892	25167.493	25194.204	25174.661
25251.665	25201.292	25255.576	25222.253
25283.335	25247.785	25284.209	25258.785
25320.770	25284.944	25329.000	25304.461
25366.692	25322.653	25351.134	25320.698
25400.940	25349.626	25382.610	25354.777
25455.686	25404.988	25450.966	25414.981
27272.907	27252.155	27289.403	27264.821
27321.903	27283.224	27301.771	27280.827
27350.218	27305.761	27332.659	27309.556
…	…	…	…

Table S3. Main values of the *g*-tensor for the eight lowest Kramers doublets.

Kramers Doublet		A1	A2	B1	B2
1	g_X	0.1143	0.2408	0.1567	0.1844
	g_Y	0.2067	0.4898	0.4389	0.5321
	g_Z	19.2146	18.8850	19.3413	19.2573
2	g_X	0.1700	0.1315	0.4414	0.4080
	g_Y	0.4546	0.8835	0.7837	0.8540
	g_Z	18.0588	17.2766	18.0485	17.8196
3	g_X	0.7882	1.7776	0.7279	0.9380
	g_Y	3.1696	4.2030	2.2754	2.6503
	g_Z	13.2530	13.2501	15.1011	14.8621
4	g_X	3.0349	8.1736	2.9095	0.9836
	g_Y	5.8578	6.5911	4.5672	4.3107
	g_Z	8.6928	0.5647	10.3220	9.5553
5	g_X	3.2382	3.5100	8.9975	0.6662
	g_Y	3.6796	4.6350	6.3695	1.0554
	g_Z	11.8706	10.6726	1.0783	14.6864
6	g_X	10.3090	0.4778	1.8973	7.0792
	g_Y	7.2069	2.0244	4.7863	6.1644
	g_Z	0.9403	16.7788	13.3031	3.2045
7	g_X	10.4765	1.5816	0.9326	1.2147
	g_Y	8.1722	3.2178	1.4089	2.0924
	g_Z	1.5276	14.2349	16.2950	15.7287

8	g_X	0.0218	0.0095	0.0293	0.0513
	g_Y	0.0710	0.0823	0.1295	0.1774
	g_Z	19.2618	19.2331	19.2580	19.2163

Table S4. Directions of local anisotropy axes on Dy sites calculated in different approximations.

	A1	A2	B1	B2
Angle of the main anisotropy axis of the ground Kramers doublet ($_Z$) with the symmetry axis of the complex (S_6) (in degrees)				
	35.135	36.630	41.970	43.331
Angle between magnetic axes on two neighboring Dy centers				
	59.793	62.226	70.780	72.928

Table S5. Magnetic dipolar interaction constants (cm^{-1}) between Dy sites calculated in different approximations.

	A1	A2	B1	B2
(1-2) = (2-3) = (3-4) =(4-5) = (5-6) = (6-1)	-3.695	-3.611	-4.140	-4.168
(1-3) = (2-4) = (3-5) =(4-6) = (5-1) = (6-2)	0.127	0.091	-0.146	-0.196
(1-4) = (2-5) = (3-6)	-0.322	-0.372	-0.390	-0.387

Exchange interactions in the Dy_6 complex

There are two available measurements of the magnetism of the Dy6 complex:
Set 1.-- magnetism received the first time (several months before).
Set 2.-- magnetism received on 19 September 2011.

The χT at 300 K in both sets have quite different values: 74.16 cm^3Kmol^{-1} for set **1**, and 84.72 cm^3Kmol^{-1} for set **2**. (= 14.23% difference)
If set **1** is rescaled to reach the same saturation value as the set **2**, then the experimental curves differ significantly in the temperature region (0.0 K --- 130.0 K) – Figure 7.

The magnetic properties are described already quite well even when $J_{i,i+1}^{exch} = 0$. The only fitting parameters of the present *ab initio* description are the $J_{i,i+1}^{exch}$ parameters which were modeled by a single parameter J_{exch}, due to high symmetry of the complex.

The exchange parameter, within the Ising model, which gives the best description of the measured magnetic properties are:
J_{exch} = 0.050 cm^{-1}.

Table S6. Exchange spectrum of the Dy_6 complex (within B2 approximation) for the lowest 16 doublets, tunneling splitting and g_Z values for the lowest Ising doublets ($g_X = g_Y = 0$).

Nr	Energy (cm^{-1})	tunneling splitting	gz
1	0.000000000 0.000000000	0.0000E+00	0.00000000303108
2	4.389426111 4.389435587	9.4760E-06	0.00000000303108
3	4.390119911 4.390119911	0.0000E+00	0.00001010386068
4	4.390125127 4.390125127	0.0000E+00	1.05195465511169
5	4.391775363 4.391775363	0.0000E+00	1.15179136014907
6	4.391781618 4.391781618	0.0000E+00	1.05124198183064
7	4.393218925 4.393229768	1.0843E-05	1.15316519124157
8	4.612801449 4.614214440	1.4130E-03	0.00001010778324
9	4.614214440 4.616800664	2.5862E-03	22.99819824858233
10	4.617088144 4.617088144	0.0000E+00	0.04871524268167
11	4.617149620 4.617149620	0.0000E+00	0.07335995801889
12	4.617843293 4.617843293	0.0000E+00	0.10474053692468
13	4.618188306 4.618548899	3.6059E-04	0.10399366301543
14	4.808609646 4.809518119	9.0847E-04	0.00000000496571
15	4.809518119 4.811290490	1.7724E-03	26.38187642151797
16	4.811290490 4.812155464	8.6497E-04	27.74806885199575

17	8.398225429 8.398680811	4.5538E-04	26.28355055276091
18	8.398680811 8.399581350	9.0054E-04	0.03122013539049
19	8.399581350 8.400026542	4.4519E-04	0.04520692933095
20	8.589115378 8.589436811	3.2143E-04	0.03269509923026
21	8.589436812 8.589816617	3.7980E-04	15.28376882941397
22	8.589816618 8.589884584	6.7966E-05	21.41076768481282
23	8.591706723 8.591786539	7.9816E-05	14.99424487947897
24	8.591786540 8.592206260	4.1972E-04	15.09528494027239
25	8.592206261 8.592529847	3.2359E-04	21.14528114442143
26	8.752394021 8.752394024	3.0000E-09	14.80727155470471
27	8.753269697 8.753269700	3.0000E-09	55.88509673654480
28	8.753343581 8.753380061	3.6480E-05	55.94632887713033
29	8.754618157 8.754618160	3.0000E-09	55.74021794247896
30	8.755015443 8.755037285	2.1842E-05	55.66544176136265
31	8.755362116 8.755362119	3.0000E-09	55.86057840305874
32	13.080312272 13.080312276	4.0000E-09	55.72539731088926