Supporting Information

The First {Dy_4} Single-Molecule Magnet with a Toroidal Magnetic Moment in the Ground State

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Experimental Section

Materials and Physical Measurements. The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. Magnetic measurements were performed using a Quantum Design MPMS XL-7 SQUID magnetometer. For magnetization measurements, the samples were sealed in parafilm to avoid any orientation of the crystallites.

Synthesis of 1: A mixture of $Dy(NO_3)_3 \cdot 5H_2O$ (0.043 g, 0.1 mmol), 2,2'-bptH (0.023 g, 0.1 mmol), and triethylamine (0.030 g, 0.3 mmol) in ethanol was sealed in a 15mL Teflon-lined reactor and heated at 160 ^oC for 3 days and then cooled to room temperature at 5 $^oC\ h^{-1}$. Colorless transparent crystals were collected artificially in 20% yield based on Dy. Elemental analysis (%) calcd for $C_{52}H_{48}Dy_4N_{24}O_{18}$: C 32.08, H 2.48, N 17.26; found: C 31.52, H 2.72, N 16.92. IR data (KBr, cm^{-1}): 3401(br), 1601(s), 1472(s), 1382(vs), 1192(w), 1145(w), 1098(w), 1040(m), 806(m), 730(m), 637(m), 403(w).

X-Ray Crystallography. The intensity data of **1** were collected on a Rigaku R-AXIS SPIDER IP diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 293(2) K. The structure was solved with direct method and refined with full-matrix least-squares technique with the SHELXTL program package.[1,2] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically.

Crystal data of **1** at 293(2) K: $C_{52}H_{48}Dy_4N_{24}O_{18}$, M = 1947.14, monoclinic, a = 12.7886(7) Å, b = 10.9248(6) Å, c = 23.7340(12) Å, β = 104.032(1)°, V = 3217.0(3) Å^3, space group $P2_1/n$, Z = 2, μ(MoK_α) = 4.680 mm^{-1}, 20920 reflections measured, 6139 independent reflections (R_{int} = 0.0451). R_1 = 0.0388 for $I \geq 2\sigma(I)$ and wR_2 = 0.0884 for all data.

CCDC-848450 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Reference:

1 G. M. Sheldrick, *SADABS 2.05*, University of Göttingen.

2 *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, 2000.

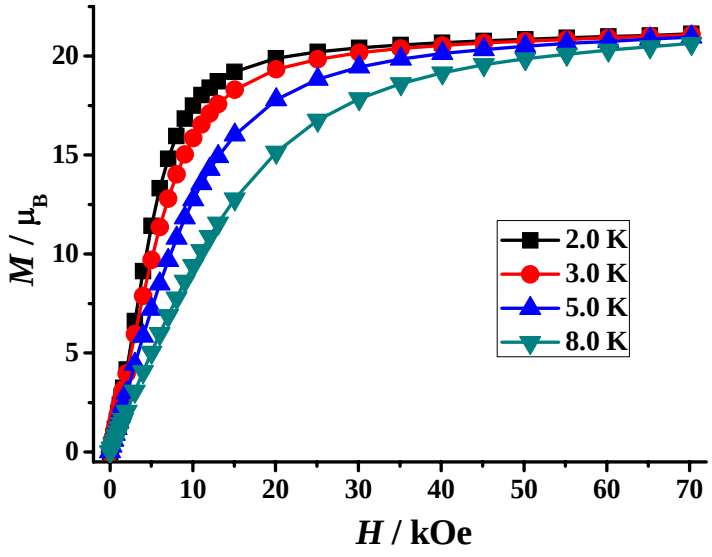

Fig. S1. *M* vs. *H* data at 2.0 K, 3.0 K, 5.0 K, 8.0 K for **1.**

Ab initio calculation of the magnetism in Complex 1.

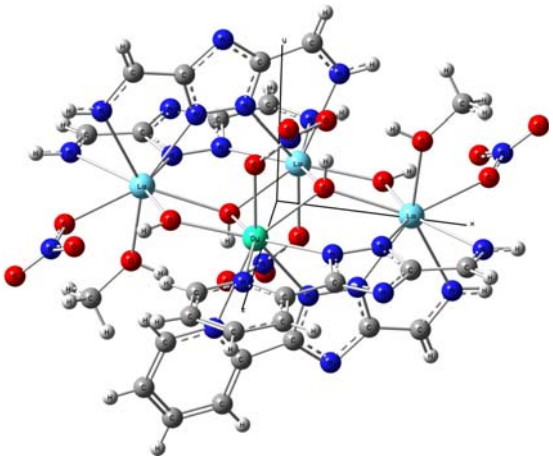

Fig. S2. Calculated structure of the Dy1 fragment in **1**.

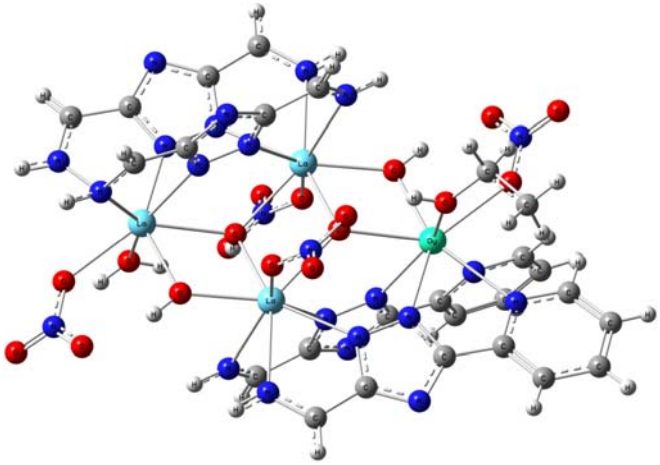

Fig. S3. Calculated structure of the Dy2 fragment in **1**.

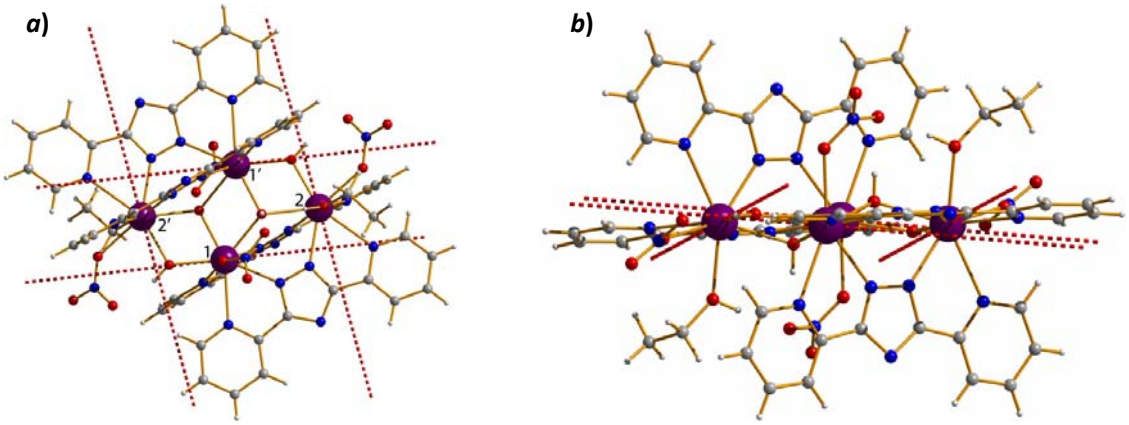

Fig. S4. Calculated magnetic axes corresponding to the lowest Kramers doublet on dysprosium sites of complex **1**. *a*) top view; *b*) side view. Color code for atoms: purple (Dy(III)), red (O), blue (N), grey (C).

Computational details:

Basis Sets: All employed basis sets were taken from the standard ANO-RCC basis set library from MOLCAS. The following contractions were used for the atoms:

Dy – 8s7p5d4f2g1h.

La – 7s6p4d3f1g.

O – 4s3p2d. (only for the first coordinated atoms, which make a bond with Dy)

N, O, C – 3s2p. (for distant atoms)

H – 3s1p. (only for the H connected to atoms from the first coordination sphere)

H – 2s. (for distant atoms)

Active space of the CASSCF method included 9 electrons in 7 orbitals.

The **spin orbit interaction** was computed by mixing of 21 sextets only. Mixing of states with other spin multiplicities is ongoing.

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

Spin multiplicity		**Spin free energies**		**Spin orbit energies**	
		Dy1	**Dy2**	**Dy1**	**Dy2**
6	H	0.000	0.000	0.000	0.000
		7.439	9.007	179.062	212.411
		235.684	271.596	293.657	305.464
		252.010	304.143	396.805	384.847
		412.475	414.121	457.952	434.101
		445.432	424.952	530.918	491.260
		497.104	494.887	634.412	583.822
		601.602	549.976	900.273	731.379
		631.018	570.327	3072.375	3096.351
		933.142	778.287	3219.570	3227.577
		941.657	783.708	3327.419	3318.879
	F	7764.722	7749.415	3392.223	3377.532
		7800.069	7766.834	3456.517	3421.773
		7859.787	7836.648	3571.312	3499.479
		7940.976	7898.327	3740.590	3615.737
		7988.775	7934.620	5718.604	5738.696
		8022.146	7956.878	5838.570	5836.935
		8026.012	7997.836	5927.533	5908.994
	P	34818.991	34843.844	5982.242	5962.886
		35138.133	35123.937	6102.826	6033.115
		35515.370	35391.169	6255.787	6154.500
4		--	--	7944.560	7955.056
2		--	--	8042.712	8030.736
				8116.594	8109.563
				8235.111	8175.703
				8399.797	8309.341

				9718.338	9723.847
				9774.777	9756.038
				9809.581	9784.152
				9836.091	9822.050
				9865.674	9839.021
				9906.975	9863.703
				9930.355	9883.417
				9958.978	9911.692
				9994.119	9947.359
				10183.291	10089.513
				11078.818	11095.821
				11326.091	11306.009
				11607.480	11497.090
				11990.728	11969.025
				12043.168	12001.171
				12059.056	12017.499
				12081.355	12032.361
				12110.379	12070.733
				13787.875	13748.406
				13805.000	13771.543
				13855.914	13821.564
				13892.004	13846.770
				15190.916	15148.223
				15213.850	15182.405
				15253.962	15213.232
				16201.264	16165.793
				16223.563	16181.508
				16808.905	16768.246
				38903.544	38911.547
				39005.119	38991.291
				39091.181	39061.258
				39259.252	39195.692
				40304.230	40298.826
				40470.356	40442.062
				40725.862	40625.116
				41472.270	41424.383
				41547.000	41485.259

Table S2. Main values of the *g* tensor for the lowest three Kramers doublets.

Kramers doublet		Main values of the g-tensor	
		Dy1	Dy2
1	gx	0.0000	0.0018
	gy	0.0017	0.0031
	gz	19.9026	19.8883
2	gx	0.0707	0.0442
	gy	0.1141	0.0731
	gz	17.0485	17.1050
3	gx	0.3281	0.7864
	gy	0.5656	1.0779
	gz	13.5228	14.5535

Table S3. Angles made by the main magnetic axes on Dy1 and Dy2 sites.

	Dy1	Dy2
Angle with the Dy4 plane	4.52°	10.77°
Angle with the shortest Dy-O bond	4.24°	14.04°
Angle between the main anisotropy axes	82.48°	

Model for the exchange coupling for complex 1:

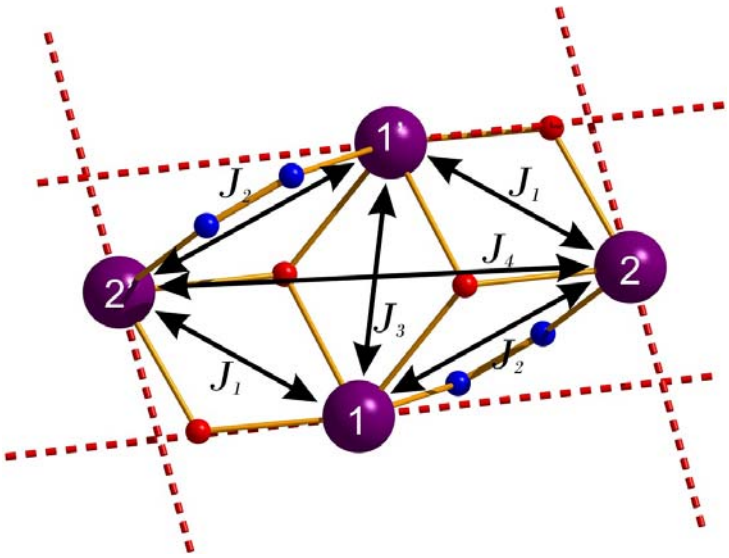

Fig. S5. The model for the exchange coupling employed for complex **1**.

Table S4. Exchange energies (cm^{-1}) and main values of the *g* tensor for the 8 lowest exchange doublets.

ID	Energy (cm^{-1})	Value of the main *g* factor ($g_{||}$)
1	0.000000000 0.000000000	0.0
2	2.966915216 2.966915216	59.8
3	3.033361282 3.033361290	39.8
4	3.033361498 3.033361506	39.8
5	4.365200362 4.365200378	0.06
6	4.365200381 4.365200397	0.06
7	5.638819046 5.638819046	0.0
8	6.191385967 6.191385967	52.5

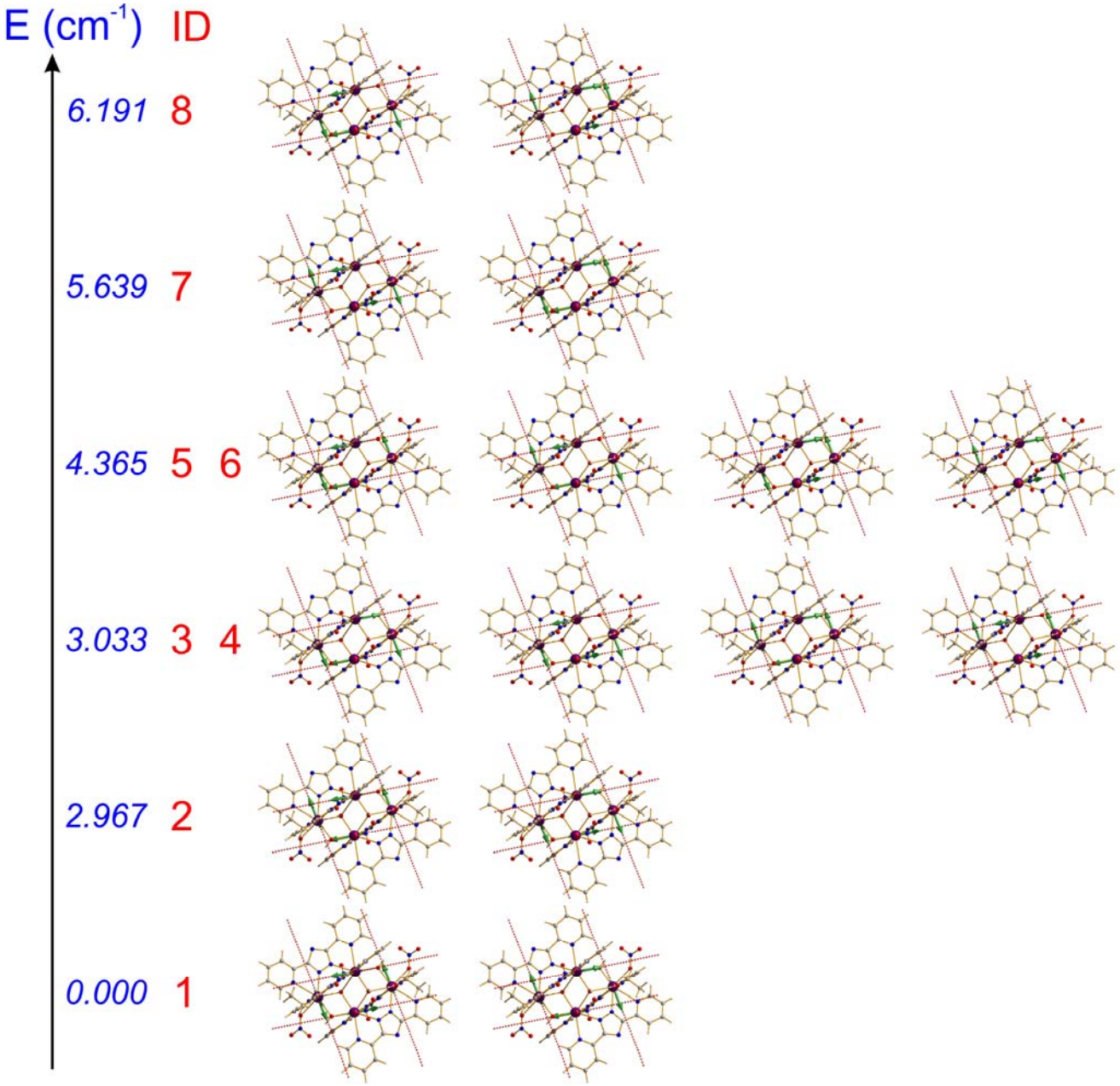

Fig. S6. Arrangements of the main magnetic moments on Dy(III) ions in the lowest excited states of complex **1**. The numbers in blue on the vertical axis are the calculated exchange energy (see Table S4). The red numbers stand for the number of the exchange doublet.

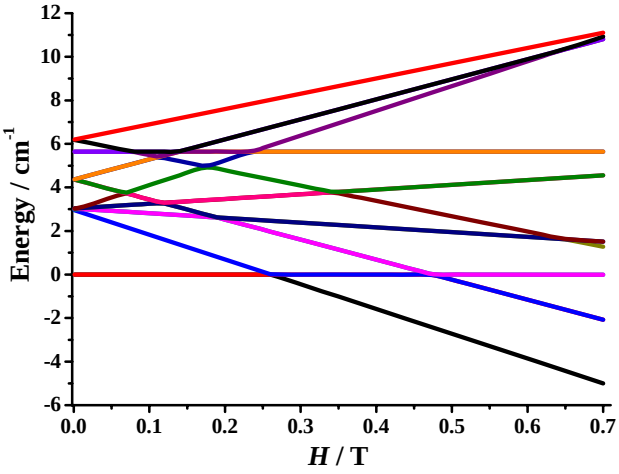

Fig. S7. Evolution of the lowest energy levels in applied magnetic field.

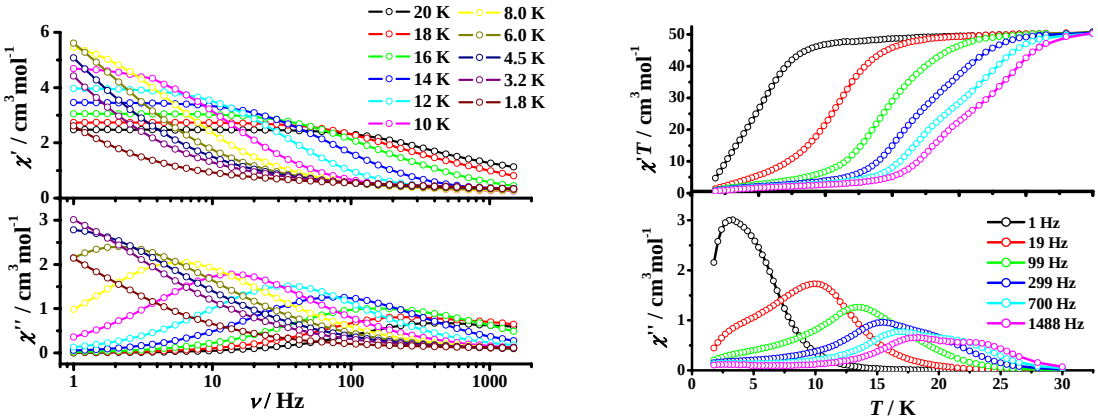

Fig. S8. Left: Variable-frequency ac susceptibility data for **1** collected under zero dc field at the indicated temperatures. Right: Temperature-dependence ac susceptibility data for **1** collected under zero dc field at the indicated frequency.

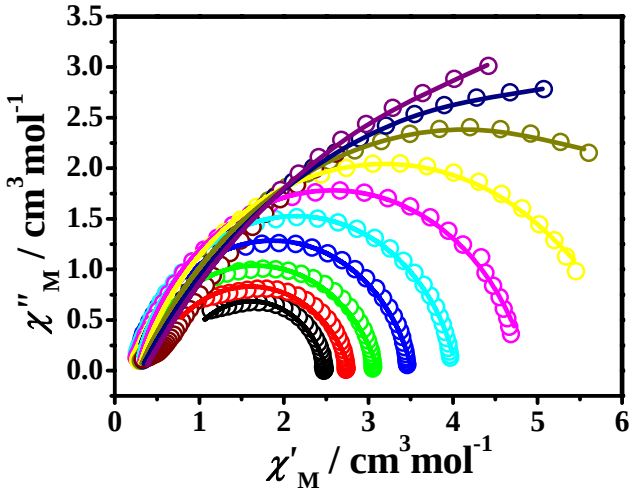

Fig. S9. Cole-Cole plots for **1** obtained from variable-frequency ac susceptibility data under a zero dc field in the temperature range. Solid lines represent fits to the data using a generalized Debye model. The α parameters were abstracted, giving 0.14-0.22.