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Supporting Information

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Coupling Dy_3 Triangles to Maximize the Toroidal Moment**

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Experimental Section

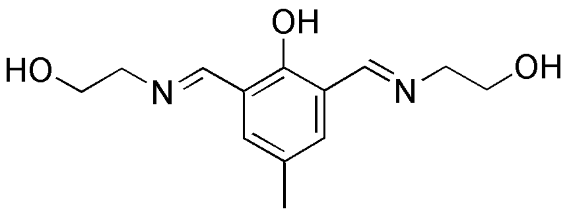
General. All starting materials were of A.R. Grade and were used as commercially obtained without further purification. 2, 6-diformyl-4-methylphenol (DFMP) were prepared according to a previously published method.[1] The Schiff-base ligand 2,6-bis((2-hydroxyethylimino)methyl)-4-methylphenol (H_3L, Scheme S1) was prepared by the *in-situ* condensation of 2, 6-diformyl-4-methylphenol and ethanolamine in a 1:2 ratio in methanol. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer 2400 analyzer. Fourier transform IR (FTIR) spectra were recorded with a Perkin-Elmer FTIR spectrophotometer using the reflectance technique (4000-300 cm^{-1}). Samples were prepared as KBr disks. All magnetization data were recorded on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet, except that Hysteresis loops were measured by a SQUID-VSM. The variable-temperature magnetization was measured with an external magnetic field of 1000 Oe in the temperature range of 1.9-300 K. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal's tables and sample holder calibration.

X-ray Crystallography. Crystallographic data and refinement details are given in Table S1. Suitable single crystal of **1** was selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at 185(2) K on a Bruker ApexII CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 with full-matrix least-squares techniques using SHELXS-97 and SHELXL-97 programs.[2] The locations of Dy atom were easily determined, and O, N, and C atoms were subsequently determined from the difference Fourier maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The H atoms were introduced in calculated positions and refined with a fixed geometry with respect to their carrier atoms. Crystal data for **1**: $C_{54}H_{68}Dy_6N_{12}O_{27}$, M = 2292.2 gmol^{-1}, T = 186(2) K, Triclinic space group P-1, a = 12.8711(5) Å, b = 15.8860(6) Å, c = 18.9783(7) Å, α = 70.4010(10)°, β = 83.2150(10)°, γ = 67.4600(10)°, V = 3376.2(2) $Å^3$, Z = 2, Theta range for data collection is 1.46-26.08°, ρ_{calcd} = 2.255 gcm^{-3}, R_1 = 0.0507, wR_2 = 0.1392 for 18872 reflections with $I>2\sigma(I)$, $F(000)$ = 2176, S = 1.077. CCDC 896054 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Referrences

1 R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies, A. K. Shiemke, *J. Am. Chem. Soc.* 1981, **103**, 4073.

2 (a) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**; (b) G. M. Sheldrick, *SHELXL-97. Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.



H_3L

Scheme S1 Structure of the H_3L ligand.

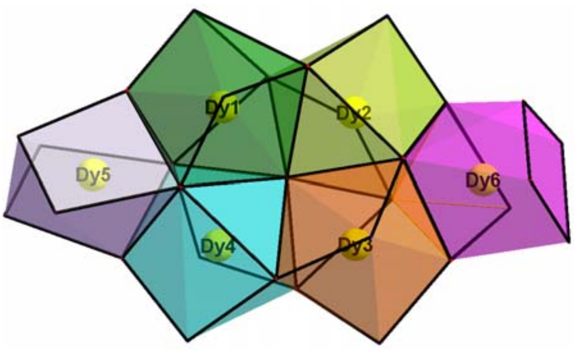


Figure S1. Coordination polyhedra observed in **1** showing distorted square antiprismatic geometries for Dy1/Dy2/Dy3/Dy4/Dy5 and a distorted tricapped trigonal-prismatic geometry for Dy6.

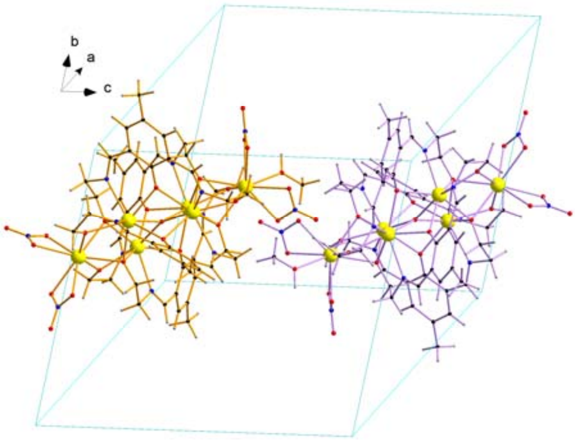


Figure S2. Crystal packing of complex **1** in unit cell. The right- and left-hand configurations coloured to emphasise the meso in unit cell.

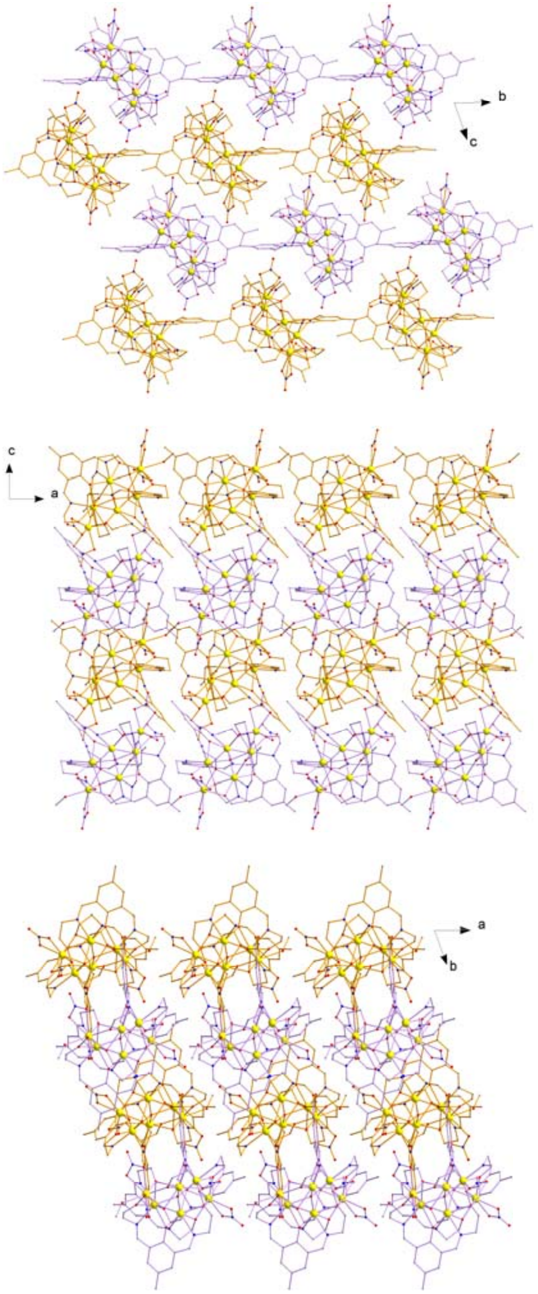


Figure S3. Crystal packing of arrangement complex **1** in different direction. Different colours are to emphasise the right- and left-hand configurations.

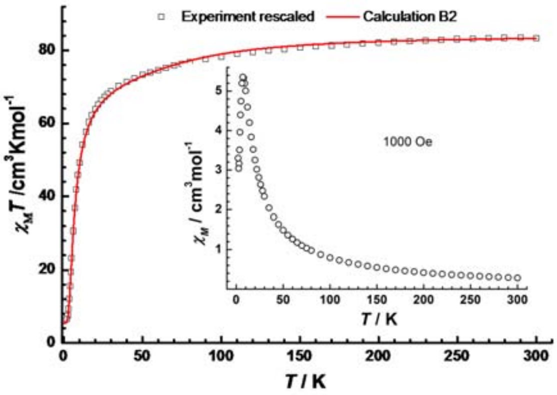


Figure S4. Plot of $\chi_M T$ vs T for **1**, the solid line corresponds to the best fit. The inset is a plot of temperature dependence of χ_M for **1**.

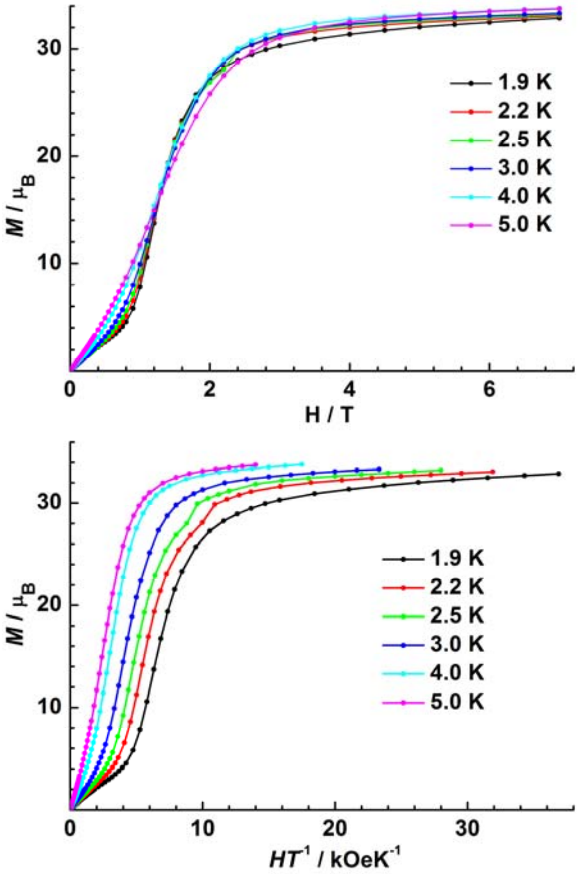


Figure S5. M versus H (Top) and M versus H/T (Bottom) plots at different temperatures below 5 K.

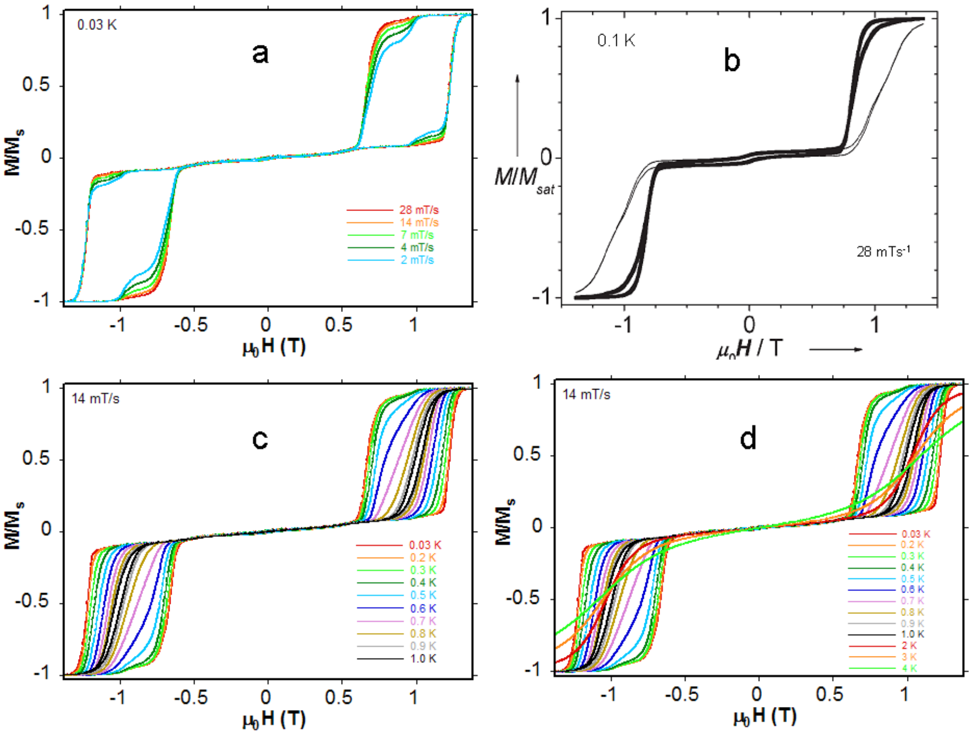


Figure S6. Hysteresis loops for **1** at different scan rates (a), and at different temperatures (c, d); Hysteresis loops for the prototype Dy_3 at 0.1 K and 28 mTs^{-1} (b). The observed larger hysteresis indicates that the “quantum mixing” in **1** is smaller than that in the prototype Dy_3.

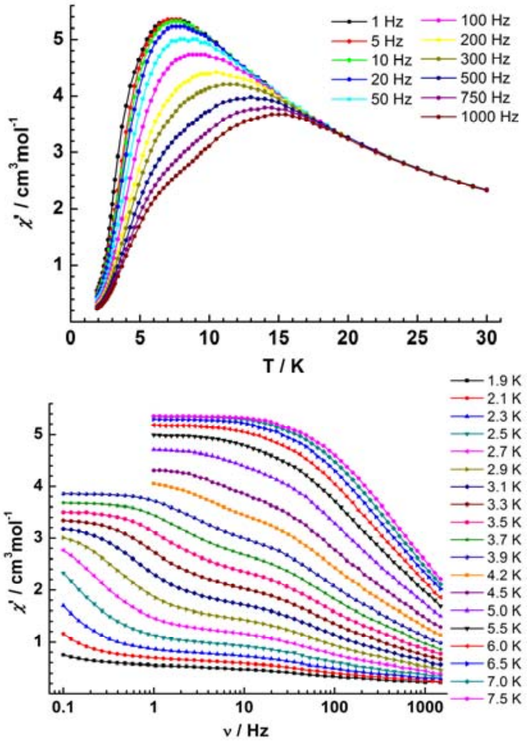


Figure S7. (Top): Temperature dependence of the in-phase ac susceptibility (χ') for **1** between 1 and 1000 Hz at H_{dc} = 0 Oe; (Bottom): Frequency dependence of the in-phase ac susceptibility for **1**, measured between 1.9 and 7.5 K at H_{dc} = 0 Oe. The solid lines are guides for the eyes.

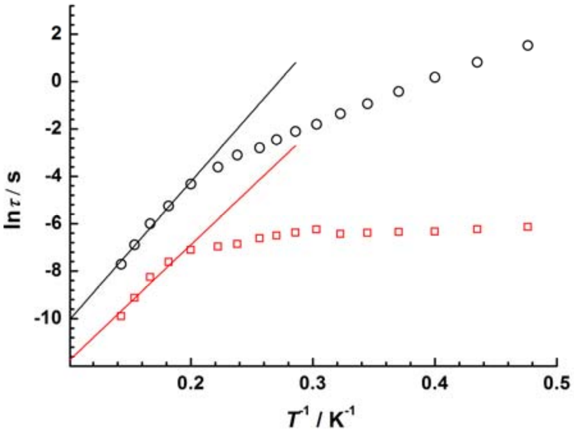


Figure S8. Plot of relaxation time (τ, natural logarithmic scale) *vs*. temperature (reciprocal scale) extracted from frequency-dependent data between 1.9 and 7.0 K under zero dc field. (red): relaxation phase in high frequency. (black): relaxation phase in low frequency. The solid lines represent linear fits to the Arrhenius equation based on the ac susceptibility data, affording effective energy barriers 33.9 and 40.7 K and pre-exponential factors (τ_0) of 5.8 × 10^{-8} and 1.2 × 10^{-7} s for two relaxation phases.

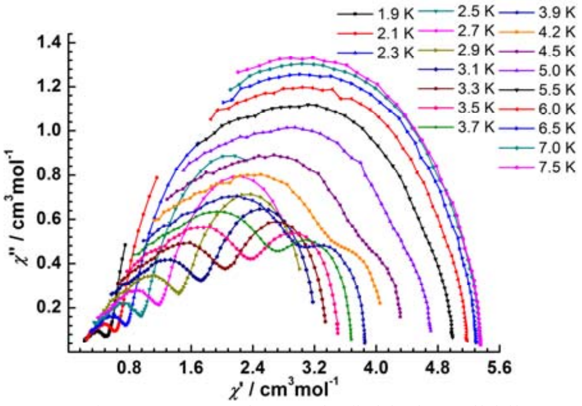


Figure S9. Cole-Cole diagram in the range of 1.9-7.5 K and zero-dc field, the solid lines are guides for the eyes.

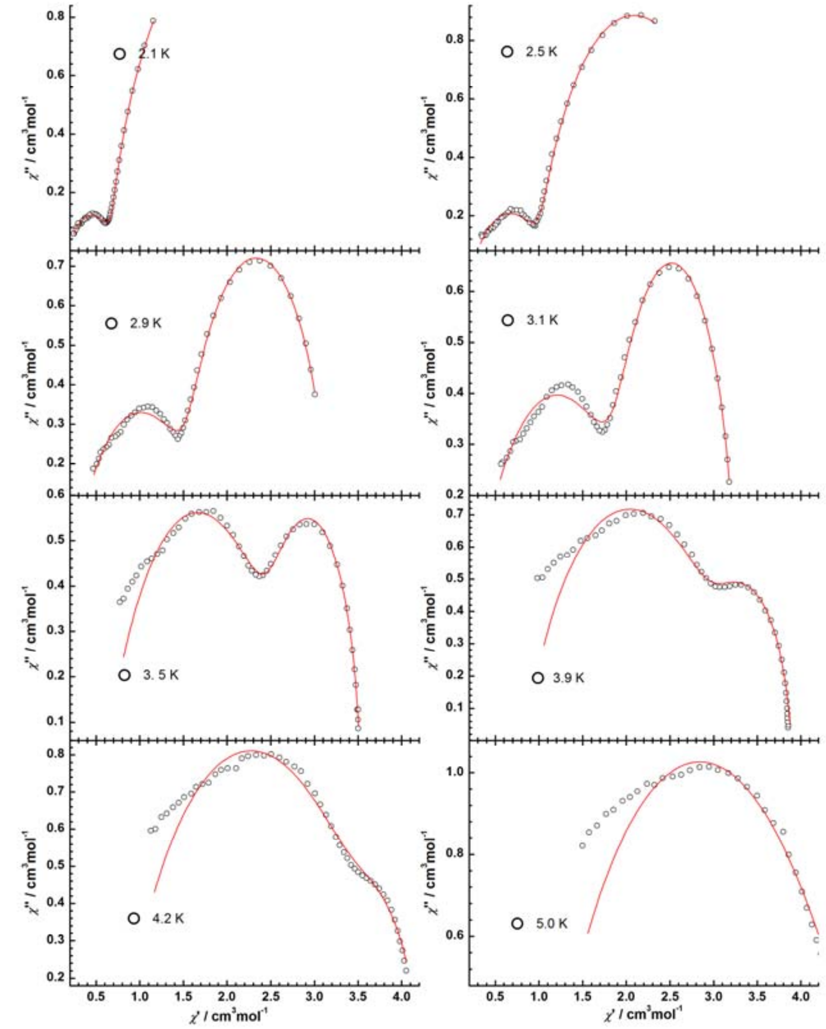


Figure S10. Cole-Cole diagram between 2.1 to 5.0 K for **1**, solid lines indicate fits to eq 1.

$$\chi_{\mathrm{AC}}(\omega)=\chi_{\mathrm{s,tot}}+\frac{\Delta\chi_1}{1+(i\omega\tau_1)^{(1-\alpha_1)}}+\frac{\Delta\chi_2}{1+(i\omega\tau_2)^{(1-\alpha_2)}} \quad \text{Eq. (1)}$$

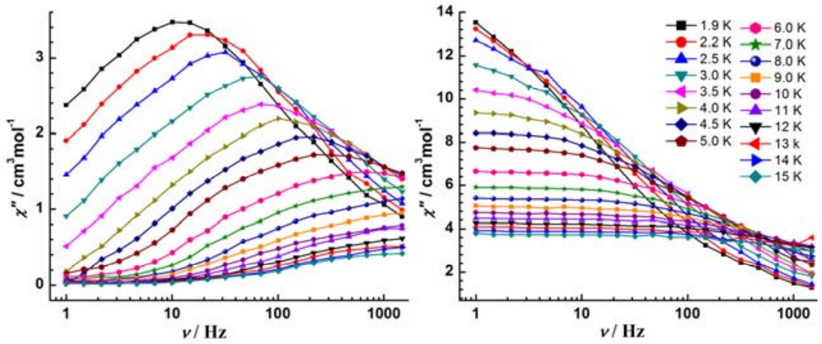


Figure S11. Frequency dependence of the ac susceptibility for **1**, measured between 1.9 and 15 K under 13 kOe dc field. The solid lines are guides for the eyes.

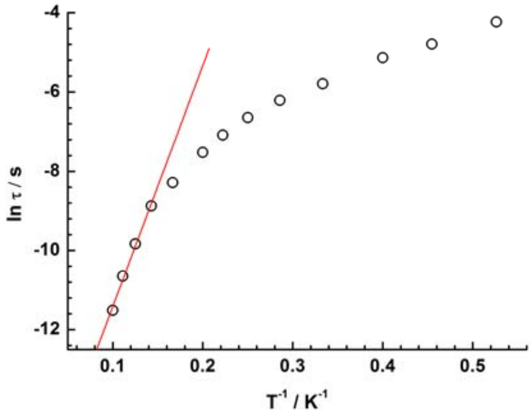


Figure S12. Arrhenius plot constructed from frequency-dependent data between 1.9 and 10 K under 13 kOe dc field. The solid line represents linear fit to the Arrhenius equation, affording an effective energy barrier of 42.3 K and pre-exponential factor (τ_0) of 2.5 × 10^{-8}.

Table S1. Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data.

T (K)	$\Delta\chi_s$ (cm^{3}mol^{-1})	$\Delta\chi_1$ (cm^{3}mol^{-1})	$\Delta\chi_2$ (cm^{3}mol^{-1})	τ_1 (s)	τ_2 (s)	α_1	α_2
1.9	0.171	2.846	0.395	10.967	2.65E-3	0.141	0.464
2.1	0.180	2.633	0.510	4.590	2.16E-3	0.129	0.447
2.3	0.197	2.333	0.647	2.252	1.97E-3	0.121	0.443
2.5	0.217	2.111	0.844	1.199	1.78E-3	0.122	0.437
2.7	0.260	1.817	1.064	0.658	1.75E-3	0.105	0.429
2.9	0.281	1.509	1.372	0.391	1.69E-3	0.0737	0.445
3.1	0.258	1.195	1.802	0.256	1.61E-3	0.0329	0.483
3.3	0.629	1.161	1.582	0.164	1.95E-3	0.0585	0.314
3.5	0.607	0.888	2.030	0.121	1.71E-3	0.0110	0.369
3.7	0.720	0.809	2.173	0.0864	1.50E-3	0.0371	0.336
3.9	0.850	0.762	2.274	0.0612	1.34E-3	0.0736	0.302
4.2	0.782	0.581	2.846	0.0451	1.05E-3	0.165	0.357
4.5	0.928	0.479	3.035	0.0270	9.47E-4	0.193	0.335
5.0	1.007	0.189	3.589	0.0134	8.18E-4	0.111	0.346
5.5	1.008	0.415	3.591	0.00521	4.89E-4	0.131	0.310
6.0	0.907	1.171	3.132	0.00248	2.59E-4	0.138	0.255
6.5	0.848	2.563	1.907	0.00101	1.09E-4	0.215	0.139
7.0	0.708	3.634	1.011	4.48E-4	5.03E-5	0.282	0.164

ab initio calculations for compound 1

Computational details

All calculations were done with MOLCAS 7.6 and are of CASSCF/RASSI/SINGLE_ANISO type.
The mononuclear Dy fragments have the same structure as the initial Dy_6 complex, in which all other five Dy ions were computationally substituted by diamagnetic Lu.
Two basis set approximations have been employed: **1** – small, and **2** – large. Table S1 shows the contractions of the employed basis sets for all elements.

Table S2. Contractions of the employed basis sets in computational approximations **1** and **2**.

Basis 1	Basis 2
Dy.ANO-RCC...7s6p4d3f1g.	Dy.ANO-RCC...8s7p5d4f2g1h.
Lu.ANO-DK3.Tsuchiya.27s23p15d10f.6s4p3d1f.	Lu.ANO-DK3.Tsuchiya.27s23p15d10f.6s4p3d1f.
O.ANO-RCC...3s2p1d. (close)	O.ANO-RCC...4s3p1d. (close)
O.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)	O.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)
N.ANO-RCC...3s2p1d. (close)	N.ANO-RCC...4s3p1d. (close)
N.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)	N.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)
C.ANO-DK3.Tsuchiya.12s8p.2s1p.	C.ANO-RCC...3s2p1d. (close)
H.ANO-DK3.Tsuchiya.6s.1s.	C.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)
	H.ANO-DK3.Tsuchiya.6s.1s.

Active space of the CASSCF method included 9 electrons in 7 orbitals (4*f* orbitals of Dy^{3+} ion).
We have mixed 21 sextets, 128 quartet and 130 doublet states by spin-orbit coupling.
On the basis of the resulting spin-orbital multiplets SINGLE_ANISO program computed local magnetic properties (g-tensors, magnetic axes, local magnetic susceptibility, etc.)

Electronic and magnetic properties of individual Dy centers

Table S3. Energies of the lowest Kramers doublets (cm^{-1}).

basis set 1 (small)					
Dy1	**Dy2**	**Dy3**	**Dy4**	**Dy5**	**Dy6**
0.000	0.000	0.000	0.000	0.000	0.000
181.863	166.890	152.485	173.820	249.668	193.695
239.395	234.944	219.692	216.556	390.278	356.121
285.142	281.495	262.782	249.408	434.192	458.560
331.937	326.298	302.344	294.643	474.181	480.261
386.465	359.801	355.412	321.768	508.419	555.116
494.977	447.148	486.589	400.812	567.980	601.860
523.379	509.576	520.492	496.853	638.330	704.672
3628.372	3632.043	3611.726	3636.196	3671.612	3634.795
3756.790	3740.851	3741.141	3724.129	3824.921	3808.054
3804.709	3789.054	3770.467	3768.541	3925.282	3905.257
3836.759	3829.401	3818.533	3803.979	3975.135	3978.942
3889.692	3879.011	3874.005	3848.673	4011.019	4045.402
3936.742	3918.772	3928.168	3877.130	4057.191	4088.067
3972.245	3934.788	3955.244	3915.765	4073.352	4168.278
6195.540	6198.474	6176.171	6195.067	6281.999	6233.159
6294.180	6278.139	6275.416	6262.096	6356.141	6352.715
6323.327	6309.763	6303.036	6291.947	6422.693	6428.699
6376.151	6357.419	6356.050	6326.208	6495.478	6515.697
6426.535	6408.344	6406.653	6376.531	6553.282	6599.435
6474.529	6451.921	6464.492	6425.191	6596.322	6654.694
8167.821	8165.025	8148.884	8155.123	8269.139	8233.058
8240.885	8229.983	8222.903	8211.699	8319.225	8328.871
8308.929	8281.894	8286.113	8260.399	8394.189	8406.717
8346.569	8336.451	8328.844	8307.792	8479.421	8517.483
8419.849	8399.071	8407.185	8371.967	8538.487	8590.793
9696.272	9693.551	9677.141	9680.910	9798.510	9776.995
9801.396	9773.283	9783.145	9753.728	9871.788	9876.689
9847.692	9845.203	9825.826	9821.674	9986.349	10003.509
9943.826	9920.022	9932.829	9891.940	10054.028	10120.980
…	…	…	…	…	…

Table S4. Energies (cm^{-1}) and *g* tensors of the lowest Kramers doublets (KD), basis set 1.

KD		Dy1		Dy2		Dy3		Dy4		Dy5		Dy6	
		E	*g*	E	*g*	E	*g*	E	*g*	E	*g*	E	*g*
1	g_X	0.000	0.0060	0.000	0.0058	0.000	0.0066	0.000	0.0102	0.000	0.0059	0.000	0.0066
	g_Y		0.0133		0.0101		0.0124		0.0177		0.0075		0.0084
	g_Z		19.7371		19.6730		19.7571		19.6940		19.8013		19.8127
2	g_X	181.863	0.4558	166.890	0.1498	152.485	0.4985	173.820	0.2245	249.668	0.1187	193.695	0.0199
	g_Y		0.6912		0.2087		0.7102		0.3248		0.2002		0.0353
	g_Z		17.2863		17.1060		17.8520		17.1761		16.6445		17.0623
3	g_X	239.395	3.1484	234.944	1.4247	219.692	3.7494	216.556	1.6762	390.278	3.1680	356.121	0.8215
	g_Y		4.3230		1.9514		5.2252		2.6288		3.6738		0.9191
	g_Z		11.9895		13.0575		11.1614		13.0607		11.0933		14.1224
4	g_X	285.142	9.3490	281.495	3.6426	262.782	10.2468	249.408	7.5269	434.192	1.0762	458.560	2.1024
	g_Y		6.7568		6.0630		7.3210		6.7741		5.5151		5.7926
	g_Z		2.1675		8.9313		0.6275		4.6806		11.7497		10.8394
5	g_X	331.937	1.7832	326.298	1.4204	302.344	0.3935	294.643	2.8256	474.181	0.8326	480.261	7.8389
	g_Y		2.0710		4.4170		2.7181		4.6224		3.4804		4.7769
	g_Z		11.1032		10.2205		11.8932		9.6386		9.6123		1.6724
6	g_X	386.465	1.5878	359.801	9.7386	355.412	1.9533	321.768	10.5305	508.419	1.6206	555.116	8.4795
	g_Y		2.9258		8.3234		3.6090		7.8681		6.2794		5.4626
	g_Z		14.8302		2.5014		14.2724		2.4982		12.5847		0.5766
7	g_X	494.977	1.3996	447.148	0.0250	486.589	1.2052	400.812	0.4290	567.980	0.3131	601.860	2.2129
	g_Y		4.9569		1.5127		2.8453		1.1652		0.6823		6.3168
	g_Z		12.1708		16.2311		14.9144		17.5584		19.0294		12.0767
8	g_X	523.379	0.8573	509.576	0.3825	520.492	0.6942	496.853	0.1443	638.330	0.0729	704.672	0.1271
	g_Y		6.2099		1.2582		3.9441		0.3460		0.2673		0.2700
	g_Z		13.7019		18.0951		15.9479		19.0712		19.3569		19.3883

Table S5. Energies of the lowest Kramers doublets (cm^{-1}) obtained with basis set 2.

basis set 2 (large)					
Dy1	**Dy2**	**Dy3**	**Dy4**	**Dy5**	**Dy6**
0.000	0.000	0.000	0.000	0.000	0.000
172.293	160.888	141.581	167.058	249.721	191.646
223.498	221.348	201.659	201.442	390.563	349.618
261.612	258.477	238.687	226.973	438.007	456.665
304.214	299.988	279.964	266.020	474.709	492.971
356.552	333.541	330.253	294.100	515.550	538.094
472.533	422.458	465.156	376.734	540.067	590.162
502.696	492.495	503.597	482.803	656.566	655.723
3620.826	3626.571	3604.523	3629.168	3670.604	3630.742
3741.414	3726.313	3720.731	3708.364	3822.047	3802.375
3778.644	3768.646	3747.401	3746.895	3922.554	3903.697
3814.019	3805.594	3797.480	3778.428	3972.780	3974.321
3863.744	3854.593	3850.640	3824.543	4013.969	4033.553
3913.102	3891.600	3905.790	3850.869	4035.106	4085.071
3942.316	3911.605	3930.828	3894.837	4087.140	4120.329
6183.020	6189.375	6163.784	6184.066	6281.166	6227.282
6275.781	6260.352	6252.268	6242.497	6351.631	6346.926
6299.493	6287.811	6283.775	6270.431	6418.698	6423.558
6349.207	6330.707	6331.587	6298.187	6488.424	6502.451
6396.116	6381.350	6377.354	6350.819	6543.211	6586.361
6446.207	6425.229	6440.526	6399.196	6600.764	6622.477
8151.429	8151.875	8132.696	8140.239	8266.986	8225.235
8219.699	8209.582	8201.186	8190.690	8313.618	8322.252
8281.072	8255.892	8260.278	8232.780	8386.957	8395.611
8318.108	8309.837	8301.837	8282.329	8468.405	8500.234
8389.861	8371.188	8380.644	8344.435	8539.459	8565.159
9678.179	9678.667	9659.251	9664.612	9795.560	9768.678
9776.694	9748.817	9757.680	9727.855	9862.668	9867.112
9819.315	9819.426	9800.259	9796.093	9975.890	9991.503
9913.535	9891.722	9905.457	9864.260	10052.408	10093.026
…	…	…	…	…	…

Table S6. Energies (cm^{-1}) and *g* tensors of the lowest Kramers doublets (KD), basis set 2.

KD		Dy1		Dy2		Dy3		Dy4		Dy5		Dy6	
		E	*g*	E	*g*	E	*g*	E	*g*	E	*g*	E	*g*
1	g_X	0.000	0.0078	0.000	0.0054	0.000	0.0074	0.000	0.0106	0.000	0.0047	0.000	0.0067
	g_Y		0.0152		0.0087		0.0127		0.0171		0.0069		0.0073
	g_Z		19.7343		19.6562		19.7393		19.6872		19.7828		19.8214
2	g_X	172.293	0.6270	160.888	0.1890	141.581	0.5943	167.058	0.3018	249.721	0.1879	191.646	0.0523
	g_Y		1.0125		0.2430		0.9257		0.3579		0.2572		0.0637
	g_Z		17.1926		17.0085		17.7579		17.0213		16.5851		17.0556
3	g_X	223.498	3.7516	221.348	1.6901	201.659	4.0860	201.442	2.4378	390.563	3.2211	349.618	0.6097
	g_Y		5.3515		2.4582		6.7192		3.9704		3.7606		0.6933
	g_Z		11.0200		12.6085		10.2507		11.9665		11.1241		14.1274
4	g_X	261.612	9.6494	258.477	2.3642	238.687	1.4185	226.973	7.3659	438.007	1.4803	456.665	2.9050
	g_Y		7.0852		5.5425		5.6026		6.6388		5.4050		3.2134
	g_Z		0.7877		9.5715		10.4051		2.6281		11.7121		10.0872
5	g_X	304.214	0.1924	299.988	0.3072	279.964	2.0176	266.020	1.1284	474.709	0.6780	492.971	1.2615
	g_Y		2.4746		4.1167		3.3455		3.6939		4.3789		3.0711
	g_Z		11.3959		10.8696		12.6143		11.7742		9.8525		16.5320
6	g_X	356.552	1.6108	333.541	11.0569	330.253	1.8272	294.100	10.9030	515.550	1.5850	538.094	0.4931
	g_Y		3.1253		6.7612		3.3259		7.2074		3.0983		4.3211
	g_Z		14.8195		2.2441		14.5049		2.3918		15.1808		11.0403
7	g_X	472.533	1.1577	422.458	0.1753	465.156	0.9251	376.734	0.3737	540.067	0.5451	590.162	1.8807
	g_Y		2.8958		1.1943		1.5001		0.9030		0.7570		3.3834
	g_Z		14.9198		17.2416		16.7395		18.0756		18.8934		13.4668
8	g_X	502.696	0.6693	492.495	0.2485	503.597	0.4904	482.803	0.0933	656.566	0.0080	655.723	0.2846
	g_Y		3.9041		0.7301		2.2805		0.2090		0.0481		0.7757
	g_Z		15.9273		18.6634		17.4694		19.2951		19.5855		18.5234

Table S7. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational approximations (degrees)

basis 1:

	Dy1	Dy2	Dy3	Dy4	Dy5	Dy6
Dy1	0.000	68.561	4.530	72.029	58.741	56.778
Dy2	68.561	0.000	66.940	3.579	56.913	60.694
Dy3	4.530	66.940	0.000	70.466	61.954	56.436
Dy4	72.029	3.579	70.466	0.000	54.097	57.196
Dy5	58.741	56.913	61.954	54.097	0.000	41.985
Dy6	56.778	60.694	56.436	57.196	41.985	0.000

basis 2:

	Dy1	Dy2	Dy3	Dy4	Dy5	Dy6
Dy1	0.000	69.608	4.658	73.312	58.340	57.536
Dy2	69.608	0.000	67.776	3.777	56.551	58.859
Dy3	4.658	67.776	0.000	71.528	61.799	57.404
Dy4	73.312	3.777	71.528	0.000	53.481	55.223
Dy5	58.340	56.551	61.799	53.481	0.000	42.091
Dy6	57.536	58.859	57.404	55.223	42.091	0.000

Table S8. Angles between the main magnetic axes of the lowest Kramers doublet on Dy centers obtained in two basis set approximations, i.e. angle between magnetic axis obtained with basis set 1 and magnetic axis obtained with basis set 2 (degrees).

	Dy1	Dy2	Dy3	Dy4	Dy5	Dy6
angle	0.442	0.627	0.219	0.846	0.364	1.229

Table S9. Angles between the main magnetic axes of the lowest Kramers doublet on Dy centers with the plane of the corresponding triangle (236 and 145).

	Dy1	Dy2	Dy3	Dy4	Dy5	Dy6
angle	7.088	9.754	5.106	8.411	7.037	5.368

Model of the exchange interaction in Dy_6 complex

Ising exchange Hamiltonian:

$$H = -\left(J_{dip} + J_{exch}\right)\left(\hat{\tilde{s}}_1\hat{\tilde{s}}_2 + \hat{\tilde{s}}_1\hat{\tilde{s}}_3 + \hat{\tilde{s}}_1\hat{\tilde{s}}_4 + \hat{\tilde{s}}_1\hat{\tilde{s}}_5 + \hat{\tilde{s}}_2\hat{\tilde{s}}_3 + \hat{\tilde{s}}_2\hat{\tilde{s}}_4 + \hat{\tilde{s}}_2\hat{\tilde{s}}_6 + \hat{\tilde{s}}_3\hat{\tilde{s}}_4 + \hat{\tilde{s}}_3\hat{\tilde{s}}_6 + \hat{\tilde{s}}_4\hat{\tilde{s}}_5\right) - J_{dip}\left(\hat{\tilde{s}}_1\hat{\tilde{s}}_6 + \hat{\tilde{s}}_2\hat{\tilde{s}}_5 + \hat{\tilde{s}}_3\hat{\tilde{s}}_5 + \hat{\tilde{s}}_4\hat{\tilde{s}}_6 + \hat{\tilde{s}}_5\hat{\tilde{s}}_6\right),$$

where $\tilde{s}_i = 1/2$ is the pseudospin corresponding to the lowest Kramers doublet on center Dy_i.

The dipolar part is considered exactly, while the exchange part is fitted. The best fitting of the magnetic properties is obtained with the following exchange parameter $J_{Lines} = -0.23980\ cm^{-1}$:

The relation between Lines and Ising parameters is:
$\tilde{J}_{Ising} = 25 \cdot J_{Lines} \cdot \cos\varphi$, where φ is the angle between local magnetic moments.

Table S10. Exchange interactions between Dy ions in the complex **Dy_6**.
Lines parameters (cm^{-1}):

interacting pair	J_{dip}	J_{exch}	$J_{total} = J_{dip} + J_{exch}$
1-2	0.80795	-0.23980	0.56815
1-3	0.12950	-0.23980	-0.11030
1-4	-0.75911	-0.23980	-0.99891
1-5	-0.36382	-0.23980	-0.60362
1-6	0.00742	0.00000	0.00742
2-3	-0.56520	-0.23980	-0.80500
2-4	0.13189	-0.23980	-0.10791
2-5	0.00353	0.00000	0.00353
2-6	-0.36084	-0.23980	-0.60064
3-4	0.88777	-0.23980	0.64797
3-5	0.00431	0.00000	0.00431
3-6	-0.34277	-0.23980	-0.58257
4-5	-0.30557	-0.23980	-0.54537
4-6	-0.00382	0.00000	-0.00382
5-6	-0.00823	0.00000	-0.00823

Ising parameters (cm^{-1}):

interacting pair	J_{dip}	J_{exch}	$J_{total} = J_{dip} + J_{exch}$
1-2	7.03823	-2.08895	4.94927
1-3	-3.22677	5.97520	2.74843
1-4	5.44950	1.72148	7.17098
1-5	4.77403	3.14664	7.92066
1-6	0.09964	0.00000	0.09964
2-3	5.34430	2.26746	7.61176
2-4	-3.29008	5.98198	2.69190
2-5	0.04859	0.00000	0.04859
2-6	4.66512	3.10026	7.76539
3-4	7.03220	-1.89949	5.13271
3-5	0.05094	0.00000	0.05094
3-6	4.61637	3.22955	7.84592
4-5	4.54610	3.56759	8.11369
4-6	-0.05444	0.00000	-0.05444
5-6	0.15268	0.00000	0.15268

Table S11. Energies (cm^{-1}) and the corresponding tunneling gaps and g_Z values of the lowest 15 exchange doublet states of the complex **Dy$_6$**.

energy	Δ_{tun}	g_Z
0.000000000000000 0.000000002168481	2.1685E-09	13.0935
7.558067632242402 7.558067632290340	4.7940E-11	8.6081
7.713037819690663 7.713037821218609	1.5279E-09	35.4153
7.896849969035810 7.896849969547637	5.1182E-10	38.5567
11.166996074010076 11.166996075057266	1.0472E-09	41.3632
11.181154005433775 11.181154006949349	1.5156E-09	40.1225
11.238374150494742 11.238374152851986	2.3572E-09	41.3057
11.291154064518341 11.291154065219398	7.0100E-10	34.1666
11.375024062528816 11.375024062669860	1.4100E-10	35.8569
11.396632854189331 11.396632855262746	1.0734E-09	36.3374
11.428097651792545 11.428097652199218	4.0670E-10	34.3780
11.462051783636159 11.462051785349974	1.7138E-09	43.8600
15.075414600881190 15.075414601473799	5.9260E-10	47.8474
15.208288138014147 15.208288139718729	1.7046E-09	47.4591
15.457464548030901 15.457464548159598	1.2860E-10	15.5414

Table S12. A comparison of the lowest calculated Kramers doublets, main values of g tensors, Ising exchange parameters, and the lowest magnetic excitation energies between the prototype Dy$_3$, Dy$_3$Cu, **Dy$_6$-1** and **1**.

		Lowest calculated Kramers doublets / cm^{-1}	Main values of the g tensor			Ising exchange parameters/ cm^{-1}	Lowest magnetic excitation energies / cm^{-1}
			g_x	g_y	g_z		
Dy$_3$	Dy1	234.2	0.003	0.005	19.844	J = 7.5	7.5
	Dy2	217.8	0.003	0.004	19.837		
	Dy3	150.2	0.064	0.089	19.740		
Dy$_3$Cu	Dy1	89.773	0.085	0.111	19.546	J = 5.8	5.4
	Dy2	94.571	0.032	0.049	19.648		
	Dy3	118.074	0.021	0.030	19.627		
Dy$_6$-1	Dy1	187	—	—	19.78	J_{12} = 5.3	0.4
	Dy2	119	—	—	19.66	J_{13} = 4.1	
	Dy3	80	—	—	19.32	J_{23} = 3.5	
						J_{int} = 0.8	
1	Dy1	181.863	0.006	0.013	19.737	J_{14} = 7.171	7.6
	Dy2	166.890	0.006	0.010	19.673	J_{15} = 7.921	
	Dy3	152.485	0.007	0.012	19.757	J_{23} = 7.612	
	Dy4	173.820	0.010	0.018	19.694	J_{26} = 7.765	
	Dy5	249.668	0.006	0.007	19.801	J_{36} = 7.846	
	Dy6	193.695	0.007	0.008	19.813	J_{45} = 8.114	
						J_{34} = 5.133	
						J_{12} = 4.949	

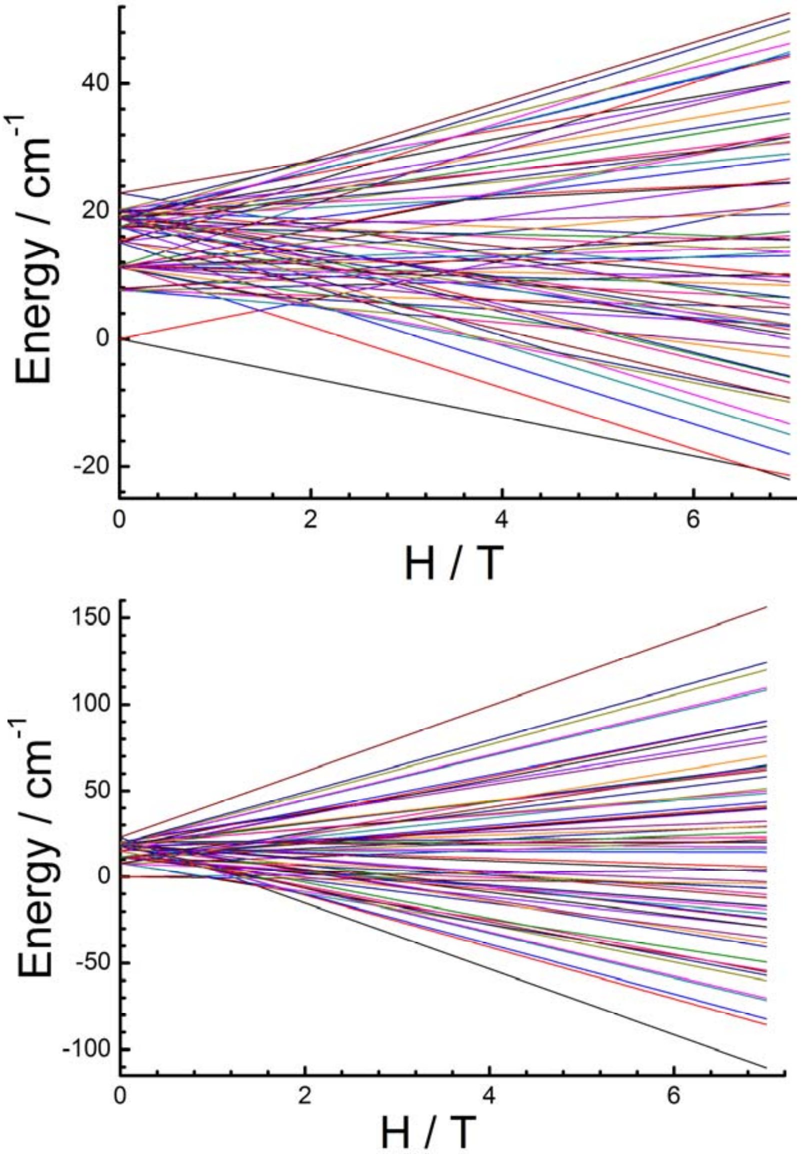


Figure S13. Zeeman splitting of the exchange energy levels in applied magnetic field in the direction of the g_Z of the *ground exchange doublet* (upper), and the *first excited exchange doublet* (bottom) of the Dy_6 complex.