Supplementary Information for

A Bis(silyldiamido) Dysprosium Single-Molecule Magnet

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Experimental Details

1. Materials

All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or in a glovebox. All solvents were dried and degassed by standard techniques. Anhydrous $DyCl_3$, $(HNAr)_2SiPh_2$ and $\{(NAr)_2SiPh_2\}_2K_2(THF)$ (Ar = 2,6-^{i}$Pr_2C_6H_3$) were prepared according to the literature procedure.[1–3] Elemental analyses were performed on Vario EL elemental analyzer.

1. J. B. Reed, B. Hopkins, L. Audrieth, P. Selwood, R. Ward and J. Dejong, *Inorganic Syntheses,* Volume 1, 28−33.
2. R. Murugavel, N. Palanisami and R. J Butcher, *J. Organomet. Chem.*, 2003, **675**, 65–71.
3. C.-L. Pan, W. Chen and J. Song, *Organometallics*, 2011, **30**, 2252–2260.

2. Synthesis of Complex

Synthesis of $[K(THF)_6][Dy\{(NAr)_2SiPh_2\}_2]$ (1).

$DyCl_3$ (1 mmol, 0.268 g) and $\{(NAr)_2SiPh_2\}_2K_2(THF)$ (2 mmol, 1.5 g) were combined in 10 mL THF. The resulting mixture was stirred overnight and was then filtered to remove any insoluble. The yellow solution obtained was concentrated to ca. 3 mL, and was then layered with hexane (10 ml). The solution was left at –35 °C for 3 days to give light yellow crystals of **1**. The crystals were collected and washed with hexane for 4 times (420 mg, 25 % yield). Elemental analysis calcd (%) for **1** ($C_{96}H_{136}DyKN_4O_6Si_2$): C 67.83, N 3.30, H 8.06; found: C 67.46, N 3.76, H 8.26.

3. Crystal Data and Structure

Single-crystal X-ray diffraction study was carried out on a Bruker D8 VENTURE diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 100 K. The structure was solved by direct method and refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrongen atom. Hydrogen atoms were located geometrically and refined isotropically. CCDC 2221344 (**1**) contains the supplementary crystallographic data, which 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).

Table S1. Crystallographic data and structure refinement for complex **1**.

Compound	**1**
Formula	$C_{96}H_{136}DyKN_4O_6Si_2$
M [g mol^{-1}]	1699.86
T (K)	100
Crystal system	tetragonal
Space group	$P4_2/n$
a [Å]	27.6854(7)
b [Å]	27.6854(7)
c [Å]	23.5921(5)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	18082.9(10)
Z	8
ρ_{calc} [g cm^{-3}]	1.249
2ϑ range [°]	4.506 to 54.944
Completeness	0.994
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ(I)]	R_1= 0.0489, wR_2 = 0.1063
Final R indexes [all data]	R_1= 0.0675, wR_2 = 0.1159
Largest diff. peak/hole [e Å^{-3}]	1.55/-0.79

Table S2. Selected bond lengths (Å) and angles (deg) for complex **1**.

Dy1-N1	2.294(3)	N1-Dy1-N2	69.79(9)
Dy1-N2	2.283(3)	N1A-Dy1-N2A	69.78(9)
Dy1-N1A	2.293(3)	N1-Dy1-N2A	106.21(9)
Dy1-N2A	2.283(3)	N1A-Dy1-N2	106.21(9)
Dy2-N3	2.265(3)	Si1-Dy1-Si1A	138.04(3)
Dy2-N4	2.296(3)	N3-Dy2-N4	70.13(9)
Dy2-N3B	2.265(3)	N3B-Dy2-N4B	70.12(9)
Dy2-N4B	2.296(3)	N3-Dy2-N4B	107.68(9)
		N3B-Dy2-N4	107.68(9)
		Si2-Dy2-Si2A	138.06(3)

[a]Symmetry code: A 3/2-X,-1/2-Y,+Z; B 3/2-X,1/2-Y,+Z

Table S3. Continuous Shape Measures (CShM) calculation for complex **1**.

Structure[a]	SP-4	T-4	SS-4	vTBPY-4
CShM (Dy1)	7.213	21.814	8.725	22.090
CShM (Dy2)	9.562	18.819	6.754	18.895

[a] SP-4 = Square (D_{4h}); T-4 = Tetrahedron (T_d); SS-4= Seesaw or sawhorse (C_{2v}); vTBPY-4 = Axially vacant trigonal bipyramid (C_{3v})

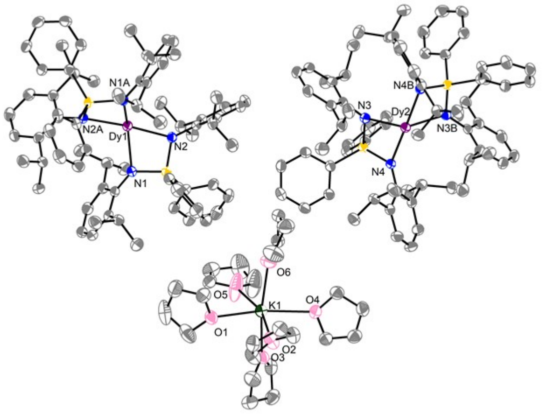


***Figure S1*.** Molecular structure of complex **1** drawn at 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry code: A 3/2-X,-1/2-Y,+Z; B 3/2-X,1/2-Y,+Z.

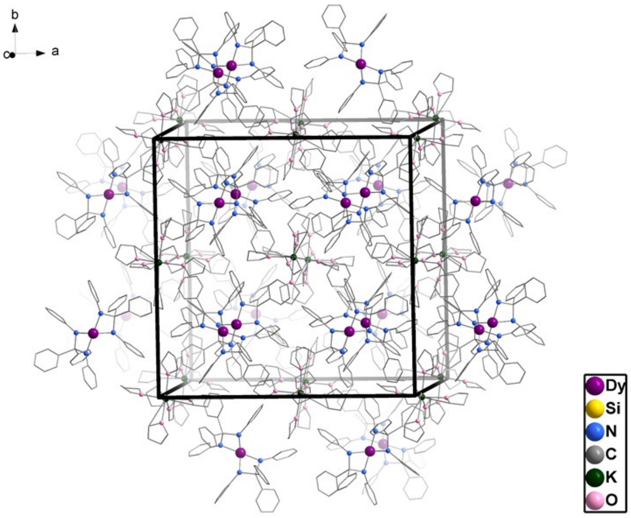


***Figure S2*.** Packing diagram of complex **1**. Hydrogen atoms and ^{i}Pr groups are omitted for clarity.

Magnetic Characterization

Direct-current (dc) magnetic susceptibilities were measured on a Quantum Design MPMS-3 SQUID magnetometer. Alternating-current (ac) magnetic susceptibility data were collected at frequencies up to 1000 Hz. Powder samples were embedded in eicosane to avoid any field induced crystal reorientation. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, eicosane and sample holder.

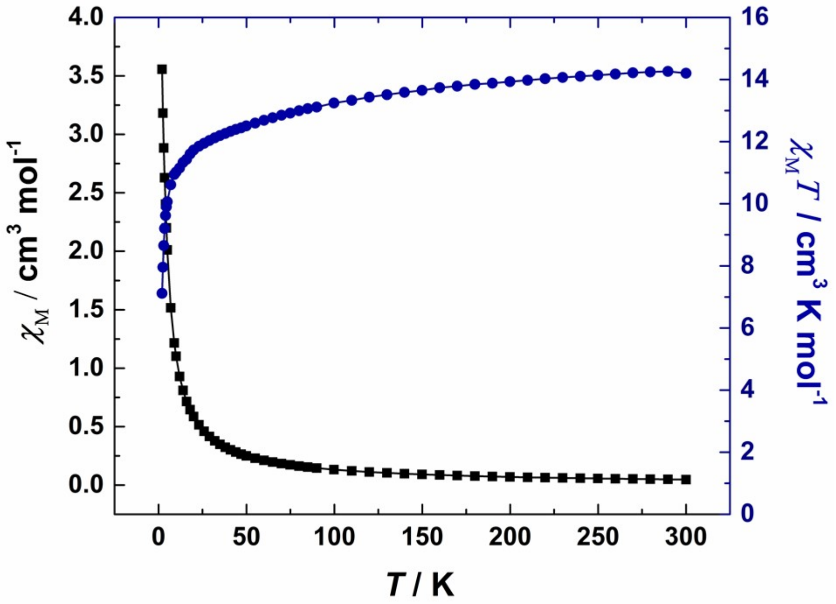


***Figure S3*.** Plots of χ_M and $\chi_M T$ versus T for **1** in an applied field of 1 kOe.

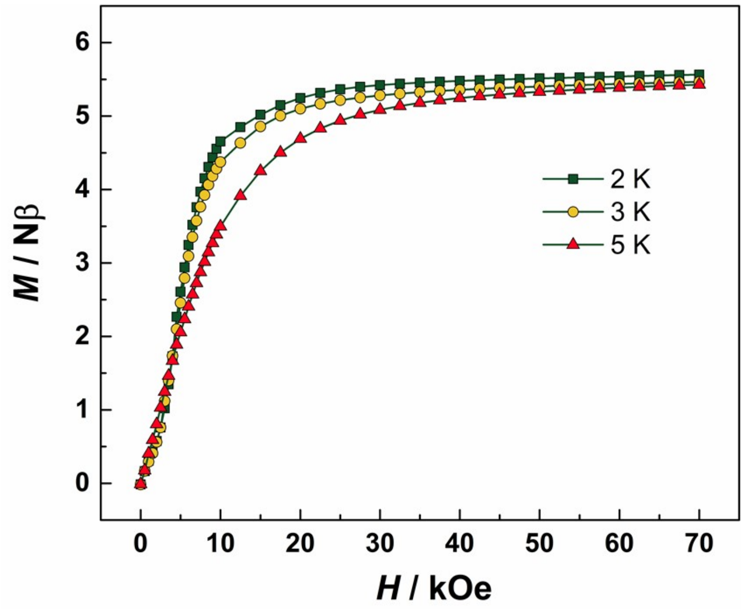


Figure S4. Plots of M versus H at various temperatures for **1**.

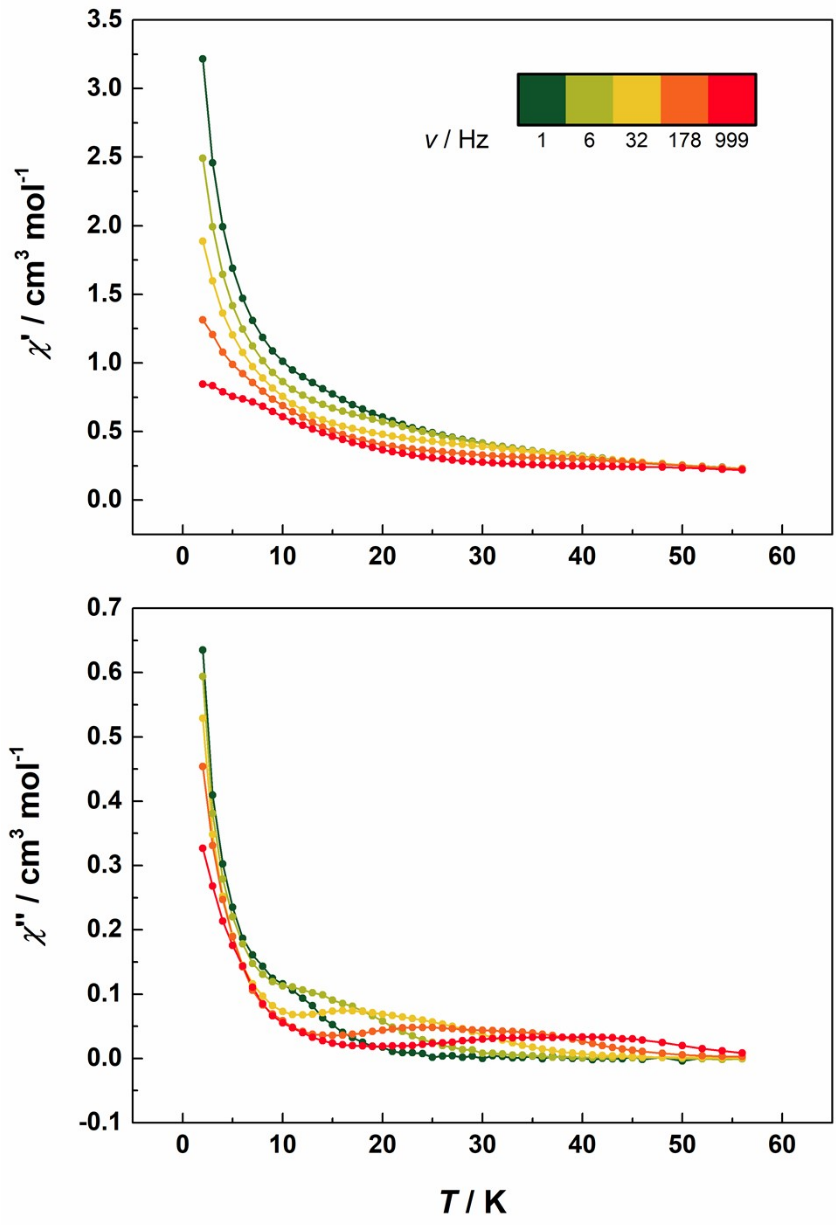


Figure S5. Temperature dependence of the in-phase (top) and out-of-phase (bottom) components of the ac magnetic susceptibility for **1** under zero magnetic field. The lines are guides for the eyes.

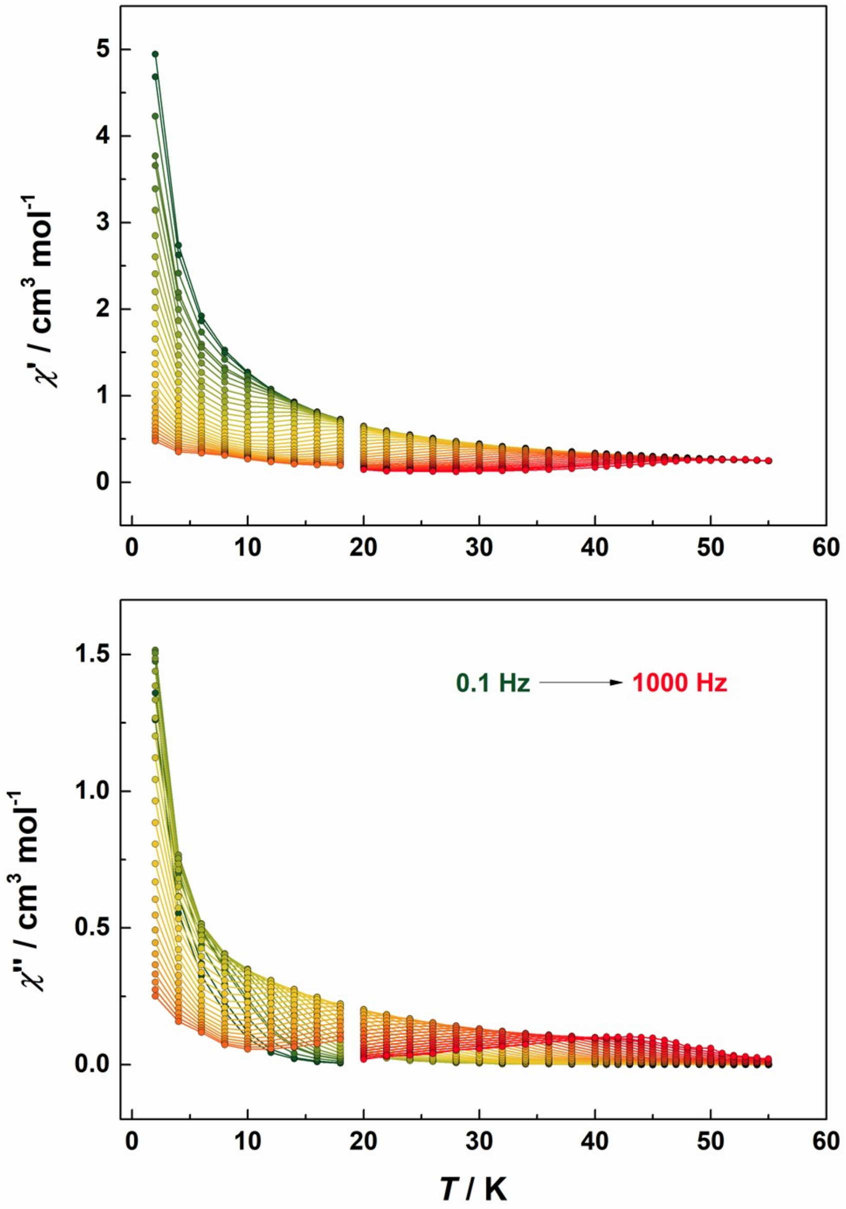


Figure S6. Temperature dependence of the in-phase (top) and out-of-phase (bottom) components of the ac magnetic susceptibility for **1** from Figure S7 and Figure 3a. The lines are guides for the eyes.

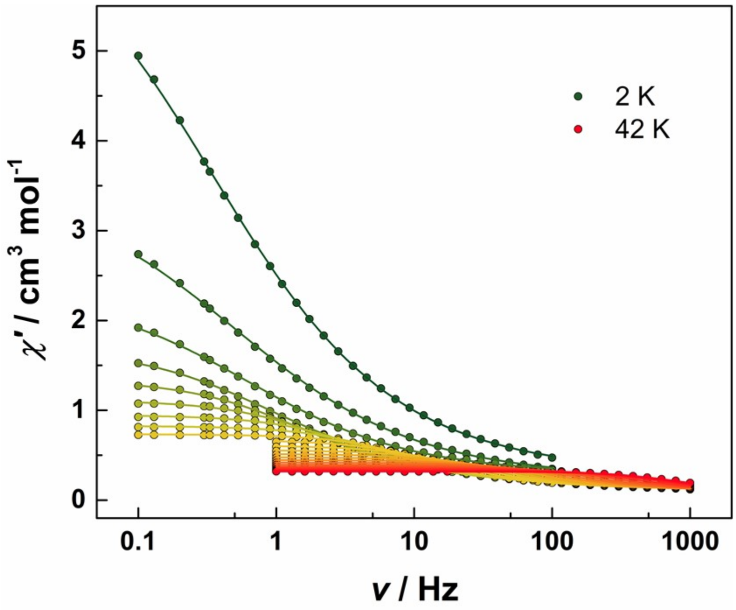


Figure S7. Frequency dependence of the in-phase ac susceptibility for **1** from 2 to 38 K at an interval of 2 K and from 40 to 42 K at an interval of 1 K under zero dc field. The solid lines represent simultaneous fit of χ' and χ'' data to the generalized Debye model.

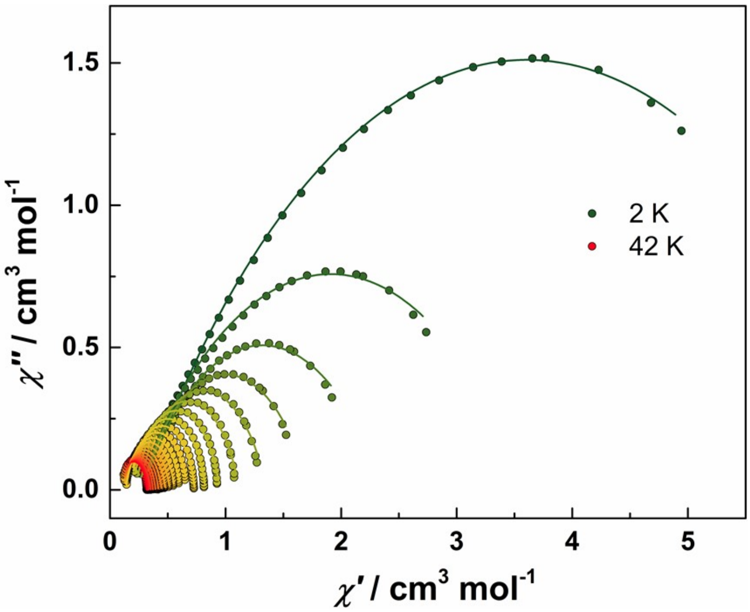


Figure S8. Cole–Cole plots of **1** at various temperatures. The solid lines represent fitting with the generalized Debye model.

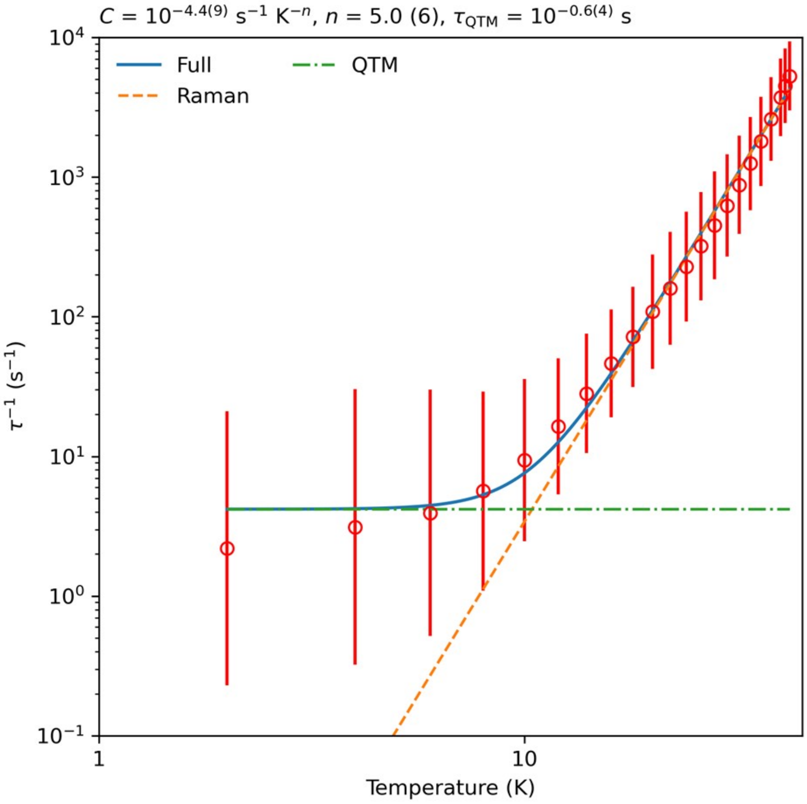
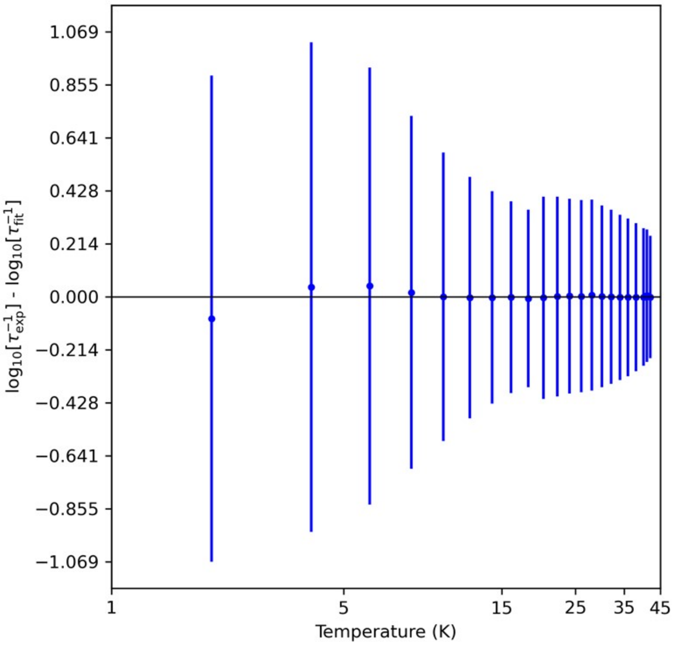


Figure S9. Plot of the magnetic relaxation rate *vs*. temperature for **1** under zero dc field. The solid blue line is the best fit by the CC-FIT2 program (Method 2), the green dashed line is the QTM component, and the yellow dashed line is the Raman component.



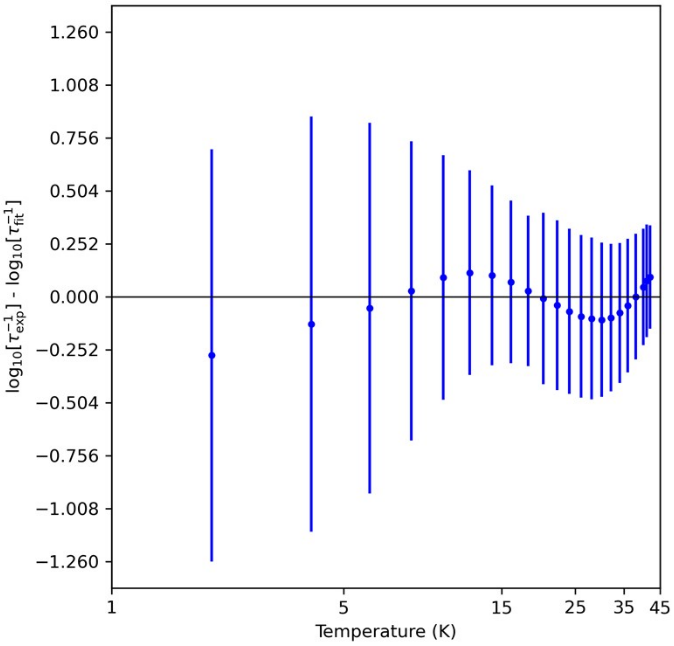


Figure S10. The residuals of fit for **1** by Method 1 (top) and Method 2 (bottom).

Table S4. The best results fitted for **1** at zero dc field by using the generalized Debye model between 2 and 42 K.

T **/ K**	$\boldsymbol{\tau_1}$ **/ s**	$\boldsymbol{\alpha_1}$	***T*** **/ K**	$\boldsymbol{\tau_1}$ **/ s**	$\boldsymbol{\alpha_1}$
2.0	4.54E-01	0.46	24.0	4.38E-03	0.17
4.0	3.20E-01	0.46	26.0	3.13E-03	0.17
6.0	2.54E-01	0.42	28.0	2.22E-03	0.17
8.0	1.77E-01	0.35	30.0	1.60E-03	0.15
10.0	1.07E-01	0.28	32.0	1.14E-03	0.14
12.0	6.09E-02	0.23	34.0	7.99E-04	0.13
14.0	3.55E-02	0.19	36.0	5.55E-04	0.12
16.0	2.16E-02	0.17	38.0	3.85E-04	0.11
18.0	1.39E-02	0.15	40.0	2.69E-04	0.10
20.0	9.20E-03	0.18	41.0	2.22E-04	0.09
22.0	6.25E-03	0.18	42.0	1.89E-04	0.08

Electronic Structure Calculations

Ab initio calculations with CASSCF/RASSI-SO/SINGLE_ANISO type using the OpenMolcas program package have been performed on the crystal structure of **1** without any optimizations. The basis sets were chosen from the ANO-RCC library with the paramagnetic ion treated with VTZP quality, the coordinated N atoms with VDZP quality and all other atoms (Si, C and H atoms) with VDZ quality. The state-averaged CASSCF orbitals of the sextets, quartets and doublets were optimized with 21, 224 and 490 states, respectively, with the RASSCF module. 21, 128 and 130 sextets, quartets and doublets were chosen to construct and diagonalize in spin-orbit (SO) coupling Hamiltonian with the RASSI module. These computed SO states were written into the SINGLE_ANISO program to compute the g-tensors, crystal field parameters and magnetic energy levels for the doublets of the ground $J = 15/2$ multiplet of the ^{6}H term for Dy(III). The two electron integrals were Cholesky decomposed with a threshold of 1×10^{-8} to account for the accuracy.

Table S5. SA-CASSCF/RASSI calculated electronic states for Dy1 in **1**.

Energy (cm^{-1})	g_x	g_y	g_z	g_z Angle (°)	Wavefunction
0.0	0.00	0.00	19.72	--	95%|±15/2>
289.3	0.08	0.13	16.69	30.2	41%|±13/2> + 23%|∓13/2>
469.3	0.34	0.46	14.33	51.7	28%|±13/2> + 13%|±5/2> + 13%|±3/2> + 11%|±1/2> + 10%|±7/2>
723.8	1.75	2.14	10.85	35.8	54%|±11/2> + 13%|±1/2>
973.4	7.08	6.71	3.97	40.4	21%|±9/2> + 16%|∓11/2> + 12%|∓9/2> + 12%|±5/2> + 10%|±3/2>
1219.7	2.66	3.33	12.61	90.0	28%|±7/2> + 25%|∓9/2> + 16%|∓1/2> +11%|±9/2>
1507.5	0.56	0.76	16.80	90.0	21%|±5/2> + 17%|±7/2> + 17%|∓7/2> + 12%|∓5/2> + 12%|∓3/2>
1755.8	0.09	0.13	19.72	90.0	23%|±1/2> + 19%|∓3/2> + 13%|±5/2> + 12%|∓1/2> + 11%|±3/2>

[a] Only components with > 10% contribution are given, rounded to the nearest percent.

Table S6. *Ab initio* calculated crystal field parameters for Dy1 in **1**.

Crystal Field Parameter	Value / cm^{-1}
B_2^{-2}	-6.66063729157970E-06
B_2^{-1}	6.22829555388050E+00
B_2^{0}	-7.14694682240600E+00
B_2^{1}	1.50359559066480E-05
B_2^{2}	1.09082288172030E+01
B_4^{-4}	-1.00178328169320E-07
B_4^{-3}	-7.75110263974170E-02
B_4^{-2}	-1.28833093422590E-07
B_4^{-1}	-5.14666127001530E-02
B_4^{0}	-9.43402447597890E-03
B_4^{1}	-2.11598521415320E-07
B_4^{2}	-9.97912990769090E-03
B_4^{3}	-5.64367841350580E-07
B_4^{4}	-3.28775702729310E-03
B_6^{-6}	-1.27266617706020E-09
B_6^{-5}	-3.94656401859730E-04
B_6^{-4}	-2.01630941014340E-09
B_6^{-3}	-4.45144223170660E-05
B_6^{-2}	-8.94829516918220E-10
B_6^{-1}	3.16915273455560E-05
B_6^{0}	6.11555993940880E-05
B_6^{1}	2.08484410745120E-09
B_6^{2}	3.45568351713530E-05
B_6^{3}	5.57090672584330E-10
B_6^{4}	7.57099185363040E-05
B_6^{5}	-1.97426158863010E-09
B_6^{6}	-4.85047654720500E-06

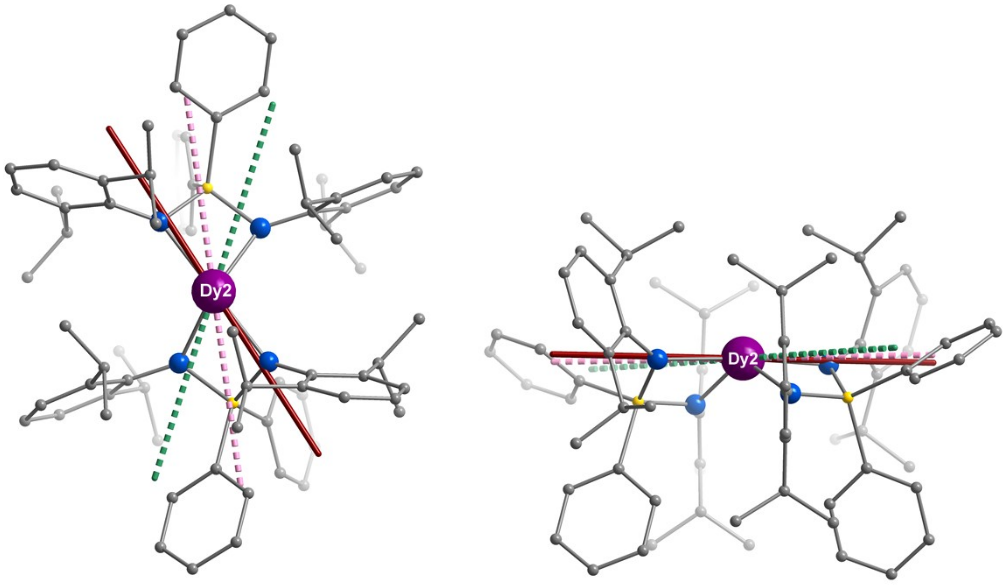


Figure S11. *Ab initio* calculated orientations of the main magnetic axes on Dy2 in the ground (red solid line), the first excited (pink dashed line) and the second excited (green dashed line) Kramers doublets in **1** from different directions.

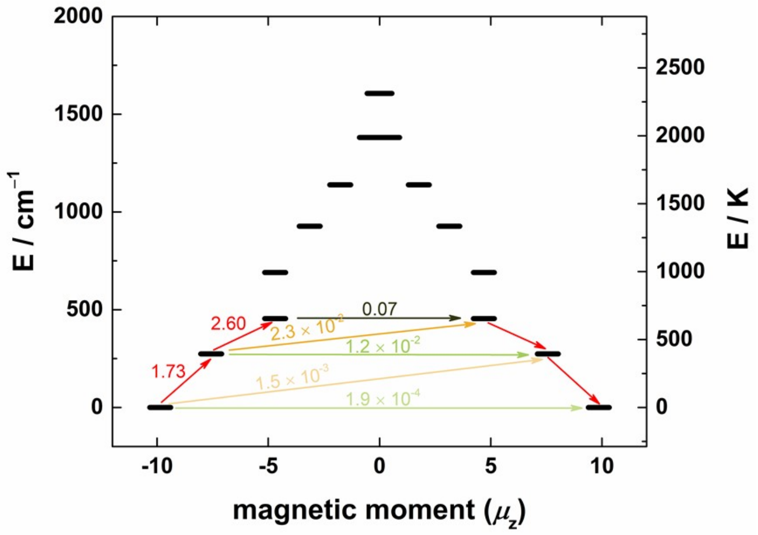


Figure S12. *Ab initio* calculated electronic states of Dy2 in **1** with the probability of transition between different sub-states. The thick black lines represent the Kramers doublets as a function of their magnetic moment along the main anisotropy axis. The green lines correspond to diagonal QTM. The yellow lines represent the Orbach process. The path shown by the red arrows represents the most probable path for magnetic relaxation.

Table S7. SA-CASSCF/RASSI calculated electronic states for Dy2 in **1**.

Energy (cm^{-1})	g_x	g_y	g_z	g_z Angle (°)	Wavefunction
0.0	0.00	0.00	19.71	--	78%|±15/2> +20%|∓15/2>
274.1	0.03	0.04	16.67	24.8	64%|±13/2>
454.6	0.16	0.19	14.72	50.4	24%|±13/2> + 16%|±5/2> + 14%|±7/2> + 12%|±3/2> + 11%|±11/2> + 10%|±1/2>
690.7	0.94	1.13	11.29	34.0	59%|±11/2> + 13%|±1/2>
926.8	3.37	4.79	8.05	43.6	28%|±9/2> + 16%|±11/2> + 14%|∓3/2> + 11%|±1/2>
1139.0	3.52	4.59	11.22	90.0	27%|±7/2> + 20%|±9/2> + 15%|∓1/2> + 13%|∓9/2> + 10%|±3/2>
1380.9	0.85	1.24	16.46	90.0	33%|±5/2> + 33%|∓7/2> + 15%|∓3/2>
1606.6	0.12	0.21	19.64	90.0	34%|±1/2> + 29%|∓3/2> + 22%|±5/2> + 10%|∓7/2>

[a] Only components with > 10% contribution are given, rounded to the nearest percent.

Table S8. *Ab initio* calculated crystal field parameters for Dy2 in **1**.

Crystal Field Parameter	Value / cm^{-1}
B_2^{-2}	-3.57504348634260E-05
B_2^{-1}	-6.48024879083480E+00
B_2^{0}	-6.76486793790950E+00
B_2^{1}	-1.50361347998700E-05
B_2^{2}	9.27854278894440E+00
B_4^{-4}	-1.83396879707460E-08
B_4^{-3}	6.25549226257270E-02
B_4^{-2}	1.46334101391620E-07
B_4^{-1}	5.69669105937930E-02
B_4^{0}	-8.00049811076060E-03
B_4^{1}	2.08495354804940E-07
B_4^{2}	-4.09791411196900E-03
B_4^{3}	4.02696757020340E-07
B_4^{4}	2.45267100747800E-03
B_6^{-6}	-5.61465203361130E-10
B_6^{-5}	1.66910612411780E-04
B_6^{-4}	-8.72558309531840E-10
B_6^{-3}	-1.50221699676600E-05
B_6^{-2}	-1.93942775255420E-09
B_6^{-1}	-1.31370131685420E-04
B_6^{0}	5.57769833095360E-05
B_6^{1}	-1.48364696884330E-09
B_6^{2}	5.72267621736330E-05
B_6^{3}	6.33367642084080E-10
B_6^{4}	8.30335664989920E-05
B_6^{5}	1.88156572781710E-09
B_6^{6}	3.27682978725460E-05