Supplementary Information for

Modulation of the magnetic dynamics in two air-stable sulfur-ligated dysprosium complexes via polymerization

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Table S1. Crystallographic data and structure refinement for complexes **1**·4CH_3OH, **2a**·sol and **2b**·sol.

Compound	**1**·4CH_3OH	**2a**·sol	**2b**·sol
Formula	$C_{46}Dy_2H_{48}N_9NaO_8S_8$	$C_{22.02}H_{25.52}DyN_4NaO_{6.74}S_4$	$C_{20.93}H_{25.87}DyN_4NaO_8S_4$
M, g mol^{-1}	1459.40	767.79	775.28
Temperature, K	150	150	150
Space group	$C2/c$	$P2_1/c$	$P2_1/n$
a, Å	33.071(2)	10.0840(8)	12.7198(11)
b, Å	11.0464(8)	13.8668(10)	13.9626(11)
c, Å	20.1342(12)	20.6024(14)	15.8515(13)
α, deg	90	90	90
β, deg	117.697(2)	97.591(3)	91.676(3)
γ, deg	90	90	90
V, Å^3	6512.5(7)	2855.6(4)	2814.0(4)
Z	4	4	4
d_{cal}, g cm^{-3}	1.488	1.786	1.830
2ϑ range, deg	3.94 to 50.018	3.988 to 50.02	3.888 to 55.052
Completeness	0.991	0.999	0.994
Final indices [$I>2\sigma(I)$]	R_1 = 0.0684, wR_2 = 0.1481	R_1 = 0.0470, wR_2 = 0.0894	R_1 = 0.0254, wR_2 = 0.0586
R indices (all data)	R_1 = 0.0737, wR_2 = 0.1510	R_1 = 0.0663, wR_2 = 0.0944	R_1 = 0.0299, wR_2 = 0.0609
Goodness-of-fit on F^2	1.058	1.103	1.104
Residual map, e Å^{-3}	1.50 / -2.00	0.88 / -1.21	0.94 / -1.62

***Table S2*.** Selected bond lengths (Å) and angles (deg) for complex **1**·4CH_3OH.

Dy1-S1	2.817(3)	S1-Dy1-S2	77.76(9)
Dy1-S2	2.833(3)	S2-Dy1-S3	157.94(9)
Dy1-S3	2.830(3)	S3-Dy1-S4	76.24(9)
Dy1-S4	2.821(3)	S4-Dy1-S1	70.19(8)
Dy1-O1	2.331(6)	O1-Dy1-S1	67.46(18)
Dy1-O2	2.347(6)	O2-Dy1-S2	67.57(18)
Dy1-O3	2.339(7)	O3-Dy1-S3	67.29(16)
Dy1-O4	2.284(7)	O4-Dy1-S4	68.68(19)
N1-O1	1.315(10)	O1-Dy1-S2	90.54(19)
N2-O2	1.358(10)	O2-Dy1-S1	129.92(19)
N3-O3	1.353(9)	O3-Dy1-S2	134.76(16)
N4-O4	1.364(10)	O1-Dy1-O2	77.6(2)
Na1-O1	2.304(7)	O2-Dy1-O3	67.8(2)
Na1-O2	2.340(6)	O3-Dy1-O4	86.1(2)
Na1-O3	2.315(6)	O4-Dy1-O1	153.8(2)
		Dy1-O1-Na1	93.3(2)
		Dy1-O2-Na1	91.9(2)
		Dy1-O3-Na1	92.8(2)

[a]Symmetry code: #1 1/2-x,1/2-y,1-z

Table S3. Selected bond lengths (Å) and angles (deg) for complex **2a**·sol.

Dy1-S1	2.8713(19)	S1-Dy1-S2	86.56(6)
Dy1-S2	2.8441(19)	S2-Dy1-S3	82.39(7)
Dy1-S3	2.860(2)	S3-Dy1-S4	78.22(6)
Dy1-S4	2.8306(19)	S4-Dy1-S1	81.47(6)
Dy1-O1	2.338(5)	O1-Dy1-S1	67.77(12)
Dy1-O2	2.304(5)	O2-Dy1-S2	67.47(13)
Dy1-O3	2.364(5)	O3-Dy1-S3	66.50(12)
Dy1-O4	2.317(4)	O4-Dy1-S4	67.94(12)
N1-O1	1.339(7)	O1-Dy1-S2	136.32(11)
N2-O2	1.340(7)	O2-Dy1-S1	84.08(14)
N3-O3	1.345(7)	O3-Dy1-S2	121.37(13)
N4-O4	1.336(7)	O1-Dy1-O2	74.97(17)
Na1-O1	2.454(5)	O1-Dy1-O3	67.11(16)
Na1-O2	2.430(6)	O2-Dy1-O3	76.07(17)
Na1-O3	2.409(5)	O4-Dy1-O1	81.90(16)
Na1-O5	2.374(6)	O4-Dy1-O3	89.77(16)
Na1-O6	2.300(7)	Dy1-O1-Na1	94.73(18)
Na1#1-S1	2.980(3)	Dy1-O2-Na1	96.24(17)
		Dy1-O3-Na1	95.23(17)
		O1-Na1-S1#2	163.50(17)
		O2-Na1-S1#2	93.51(15)
		O3-Na1-S1#2	107.04(15)
		Na1#1-S1-Dy1	134.24(9)

[a]Symmetry code: #1 -1-x,-1/2+y,-3/2-z; #2 -1-x,1/2+y,-3/2-z

Table S4. Selected bond lengths (Å) and angles (deg) for complex **2b**·sol.

Dy1-S1	2.8388(7)	S1-Dy1-S2	88.82(2)
Dy1-S2	2.8475(7)	S2-Dy1-S3	78.45(2)
Dy1-S3	2.8416(7)	S3-Dy1-S4	78.52(2)
Dy1-S4	2.8287(7)	S4-Dy1-S1	78.90(2)
Dy1-O1	2.3427(19)	O1-Dy1-S1	68.46(5)
Dy1-O2	2.3242(19)	O2-Dy1-S2	67.05(5)
Dy1-O3	2.3290(19)	O3-Dy1-S3	67.33(5)
Dy1-O4	2.3178(18)	O4-Dy1-S4	67.91(5)
N1-O1	1.342(3)	O1-Dy1-S2	136.35(5)
N2-O2	1.341(3)	O2-Dy1-S1	84.64(6)
N3-O3	1.345(3)	O3-Dy1-S2	120.38(5)
N4-O4	1.334(3)	O1-Dy1-O2	73.88(7)
Na1-O1	2.466(2)	O1-Dy1-O3	67.33(6)
Na1-O2	2.393(2)	O2-Dy1-O3	78.34(7)
Na1-O3	2.475(2)	O4-Dy1-O1	84.68(7)
Na1-O5	2.326(3)	O4-Dy1-O3	88.87(7)
Na1-O6	2.339(3)	Dy1-O1-Na1	94.10(7)
Na1#1-S1	2.9872(14)	Dy1-O2-Na1	96.56(7)
		Dy1-O3-Na1	94.22(7)
		O1-Na1-S1#2	160.71(6)
		O2-Na1-S1#2	91.23(6)
		O3-Na1-S1#2	106.75(6)
		Na1#1-S1-Dy1	140.41(3)

[a]Symmetry code: #1 3/2-x,1/2+y,3/2-z; #2 3/2-x,-1/2+y,3/2-z

Table S5. Continuous Shape Measures (CShM) calculations for complexes **1**·4CH_3OH, **2a**·sol and **2b**·sol.

Structure[a]	CShM (**1**)	CShM (**2a**)	CShM (**2b**)
OP-8	32.218	32.033	32.176
HPY-8	23.573	23.279	22.958
HBPY-8	13.628	12.993	13.641
CU-8	13.129	10.285	10.121
SAPR-8	4.211	3.698	3.585
TDD-8	2.363	3.359	3.233
JGBF-8	10.814	12.239	11.869
JETBPY-8	27.377	26.779	26.542
JBTP-8	3.969	3.439	3.229
BTPR-8	3.346	2.686	2.526
JSD-8	3.973	4.720	4.623
TT-8	13.929	10.979	10.853
ETBPY-8	24.084	22.177	22.027

[a] OP-8 = Octagon (D_{8h}); HPY-8 = Heptagonal pyramid (C_{7v}); HBPY-8 = Hexagonal bipyramid (D_{6h}); CU-8 = Cube (O_h); SAPR-8 = Square antiprism (D_{4d}); TDD-8 = Triangular dodecahedron (D_{2d}); JGBF-8 = Johnson - Gyrobifastigium (J26) (D_{2d}); JETBPY-8 = Johnson - Elongated triangular bipyramid (J14) (D_{3h}); JBTP-8 = Johnson - Biaugmented trigonal prism (J50) (C_{2v}); BTPR-8 = Biaugmented trigonal prism (C_{2v}); JSD-8 = Snub disphenoid (J84) (D_{2d}); TT-8 = Triakis tetrahedron (T_d); ETBPY-8 = Elongated trigonal bipyramid (D_{3h})

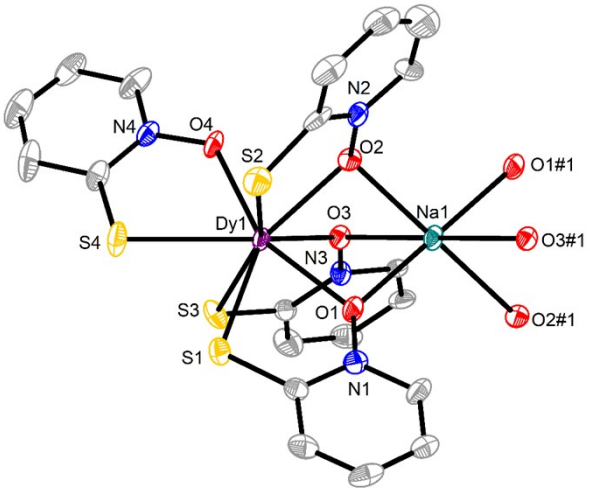

***Figure S1*.** Molecular structure of complex **1**·4CH_3OH. Hydrogen atoms are omitted for clarity. Symmetry code: #1 1/2-x,1/2-y,1-z.

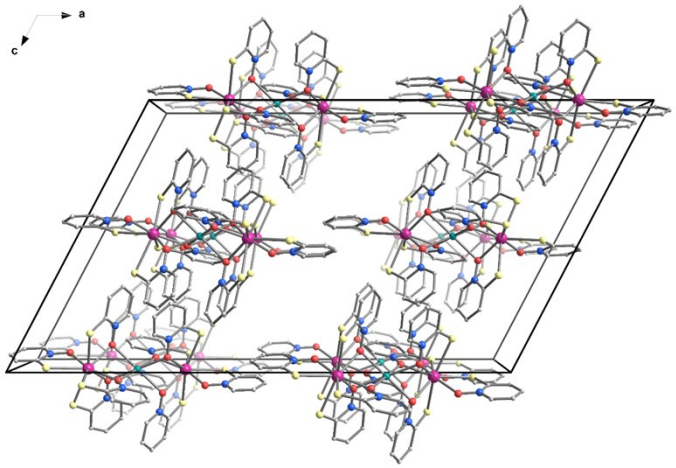

***Figure S2*.** Packing diagram of complex **1**·4CH_3OH. Hydrogen atoms are omitted for clarity.

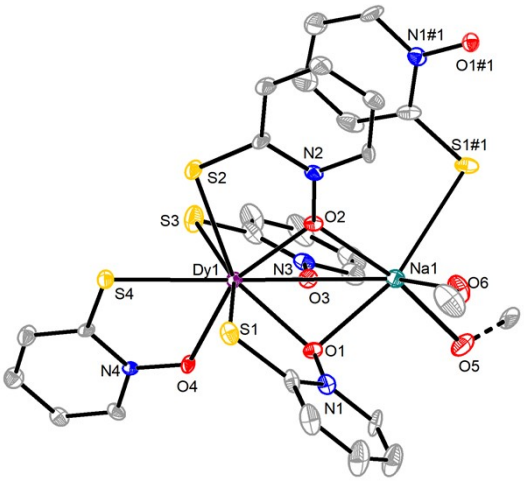

Figure S3. Molecular structure of complex **2a**·sol. O5 is disordered between methanol and water with the site occupancy factors (s.o.f) of 0.29:0.71. Hydrogen atoms are omitted for clarity. Symmetry code: #1 -1-x,1/2+y,-3/2-z.

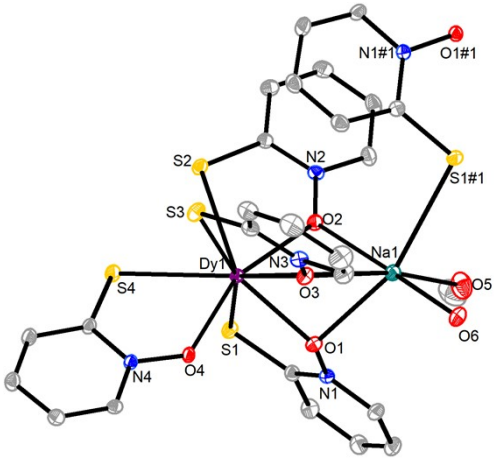

Figure S4. Molecular structure of complex **2b**·sol. O5 is disordered between methanol and water with the site occupancy factors (s.o.f) of 0.17:0.83. Hydrogen atoms are omitted for clarity. Symmetry code: #1 3/2-x,-1/2+y,3/2-z.

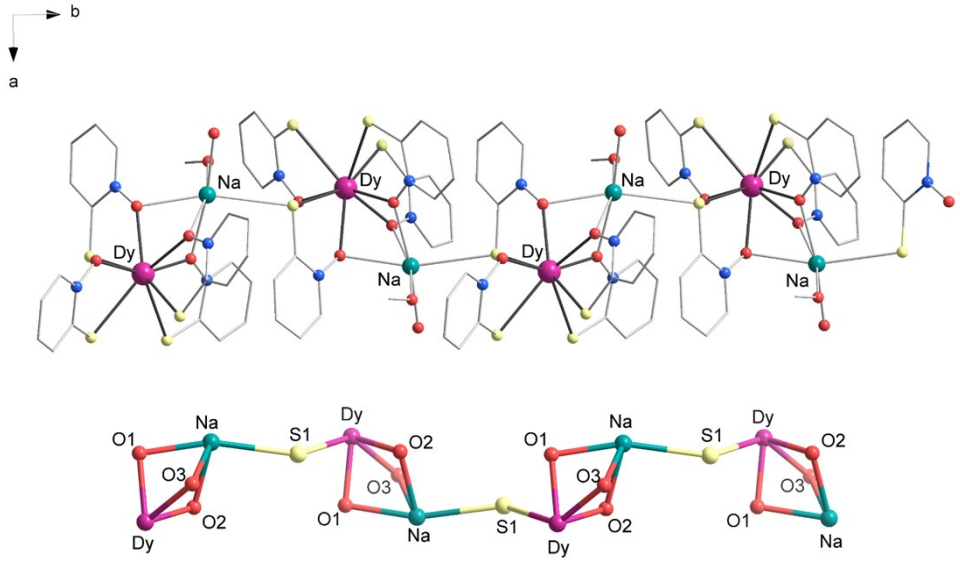

***Figure S5*.** The zig-zag type structure (top) and its enhanced view of the zig-zag core (bottom) of **2a**·sol. Disordered methanol coordinated to Na^+ with an occupancy of 0.29 are omitted for clarity.

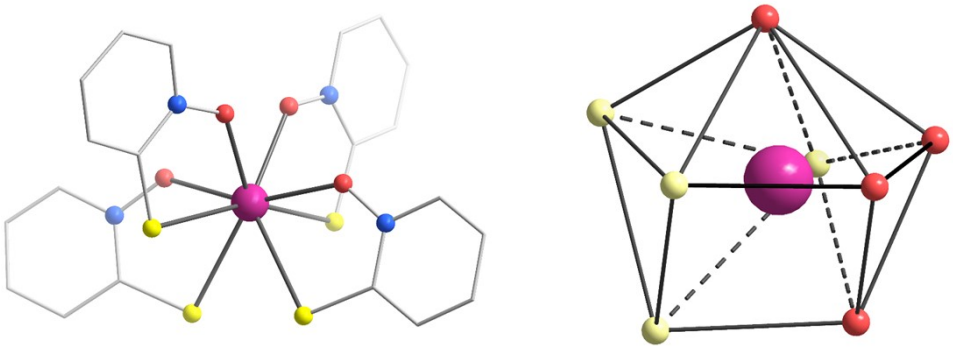

***Figure S6*.** The local structure of $[DyL_4]^-$ unit (left) and the coordination polyhedron of Dy^{3+} (right) in **2a**·sol.

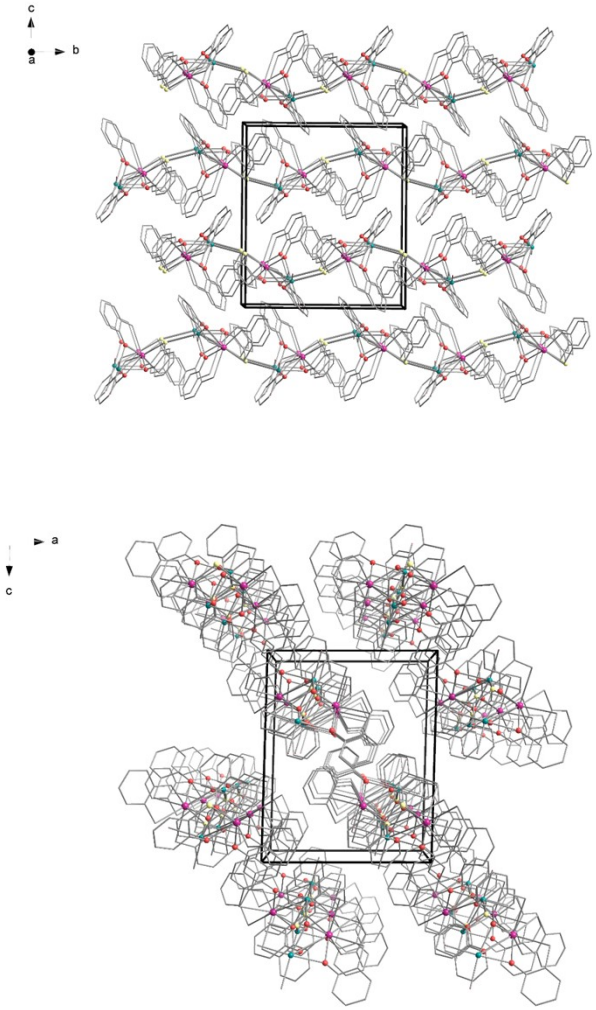

Figure S7. Packing diagram of complex **2b**·sol. Hydrogen atoms are omitted for clarity.

Magnetic measurements were performed on $[HN(Et)_3][Dy_2NaL_8]$ (**1**) and $[DyNaL_4(MeOH)_x(H_2O)_{2-x}]_n$ (**2**).

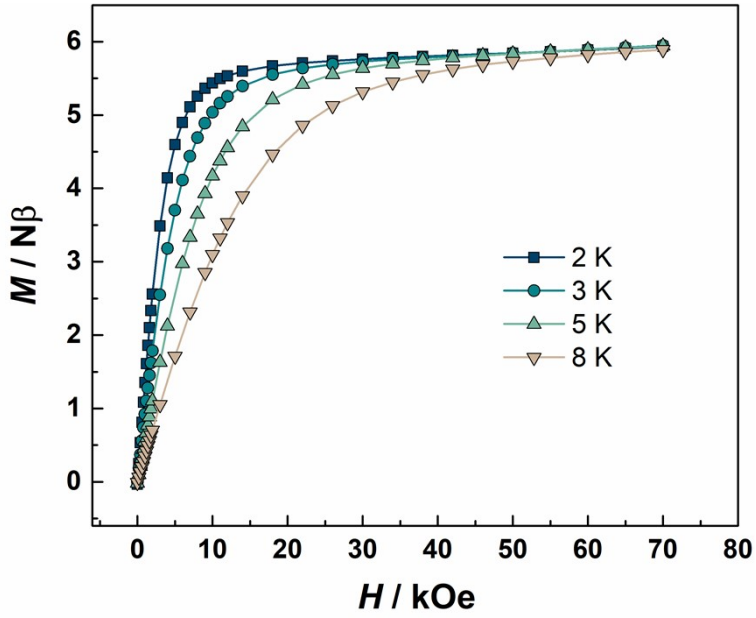

Figure S8. Plots of *M* versus *H* at various temperatures for **1**.

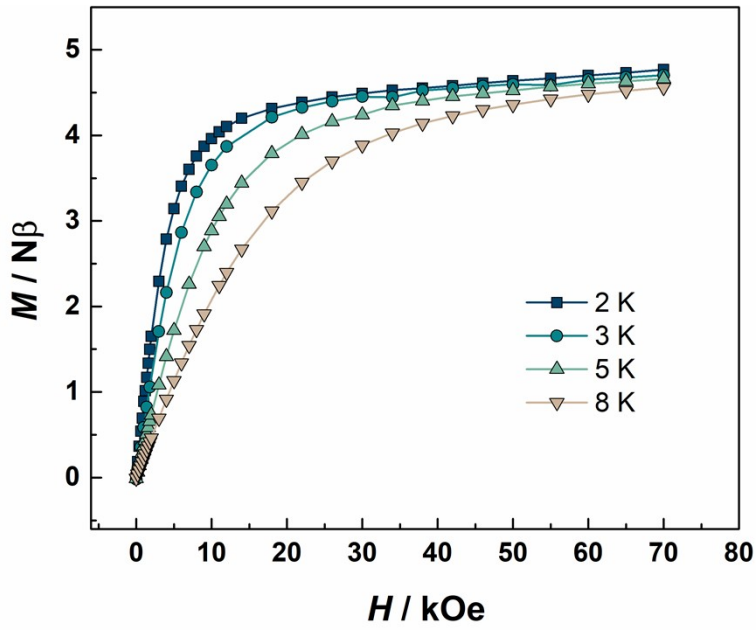

Figure S9. Plots of *M* versus *H* at various temperatures for **2**.

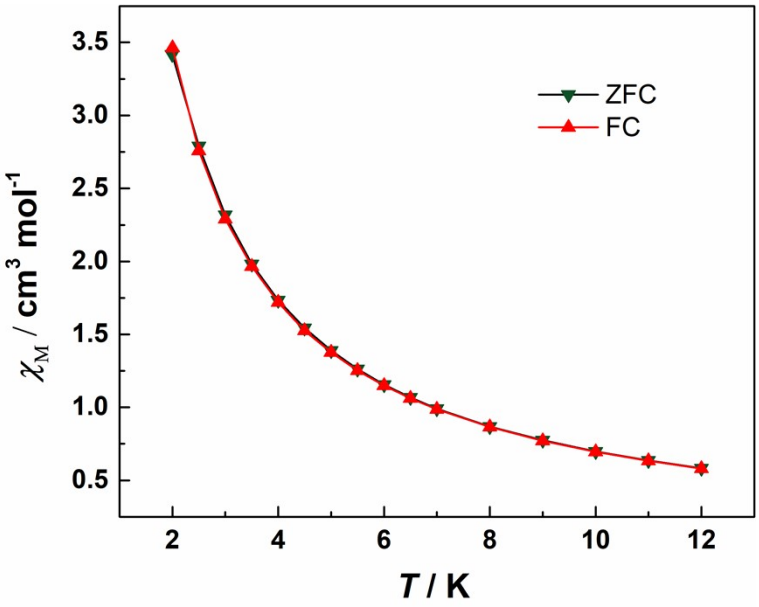

Figure S10. FC and ZFC of **1** at an applied field of 50 Oe.

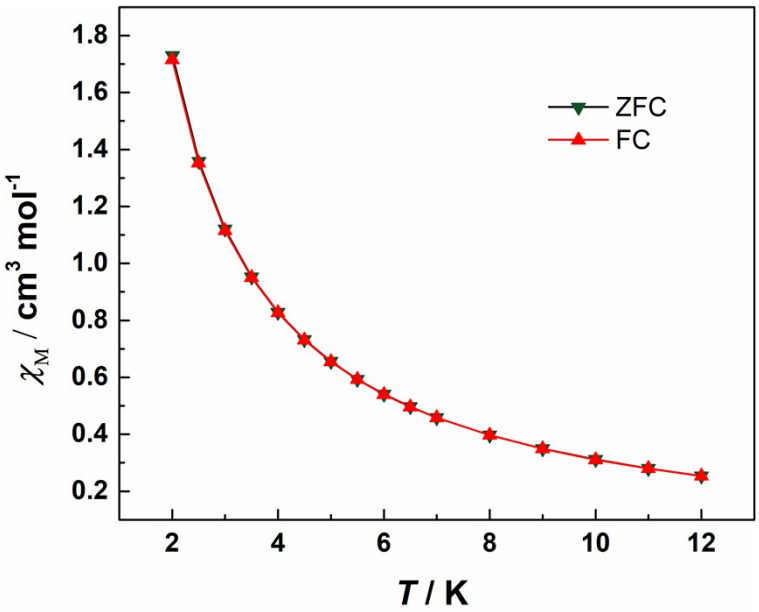

Figure S11. FC and ZFC of **2** at an applied field of 50 Oe.

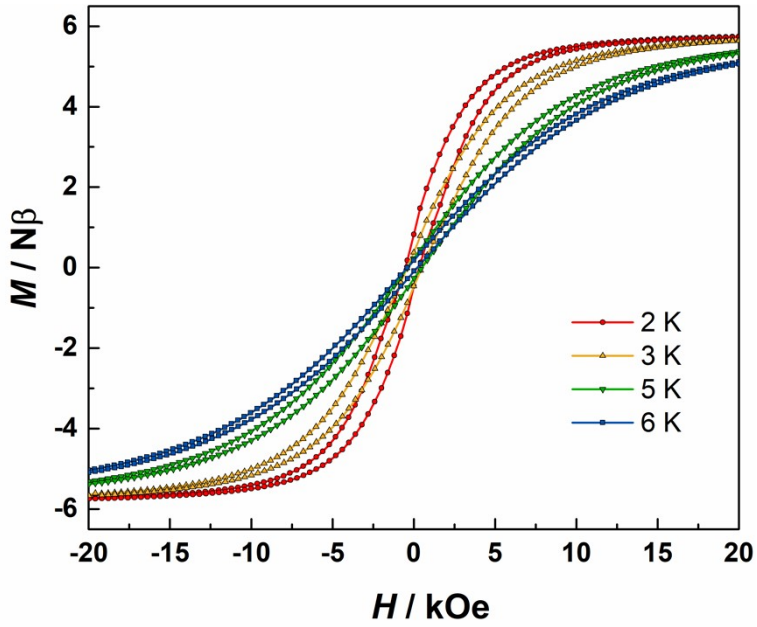

Figure S12. Magnetic hysteresis loops for **1** at an average sweep rate of 200 Oe s^{-1}.

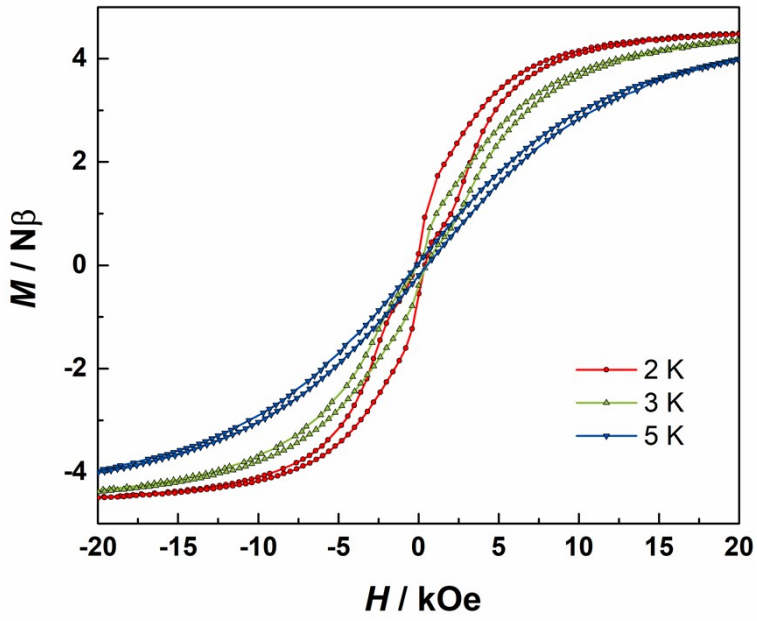

Figure S13. Magnetic hysteresis loops for **2** at an average sweep rate of 200 Oe s^{-1}.

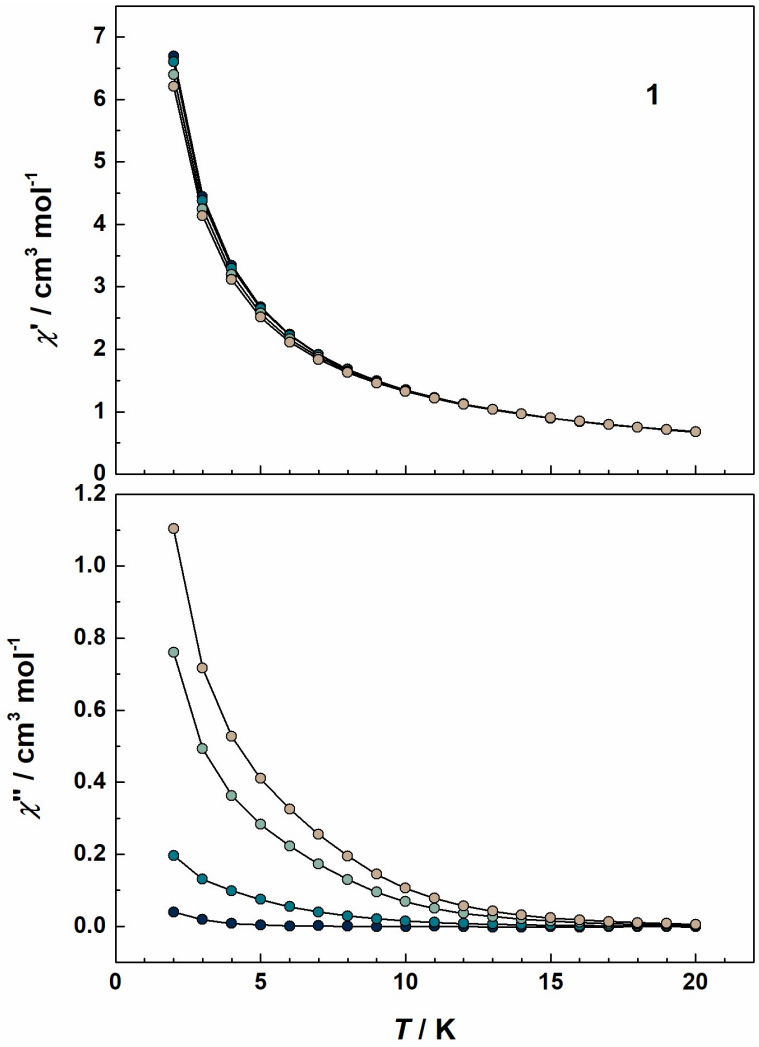

Figure S14. Temperature dependence of in-phase (χ') and out-of-phase (χ'') magnetic susceptibility under a zero dc field for **1** from 10 Hz (blue) to 800 Hz (khaki).

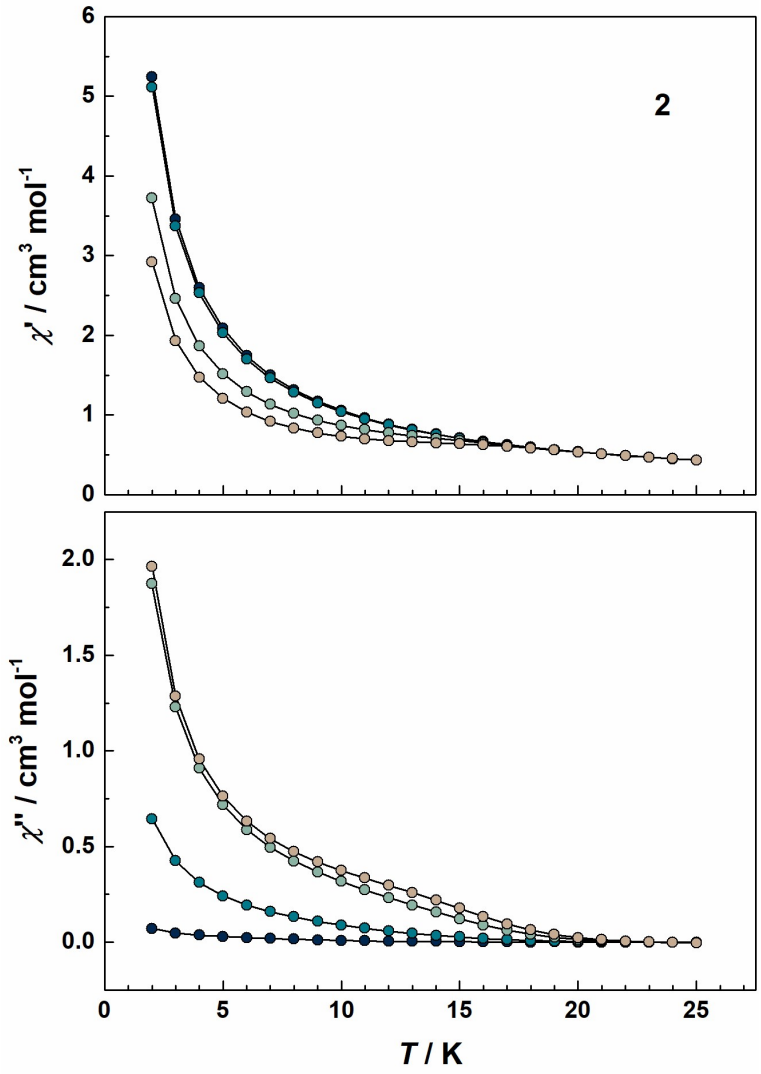

Figure S15. Temperature dependence of in-phase (χ') and out-of-phase (χ'') magnetic susceptibility under a zero dc field for **2** from 10 Hz (blue) to 800 Hz (khaki).

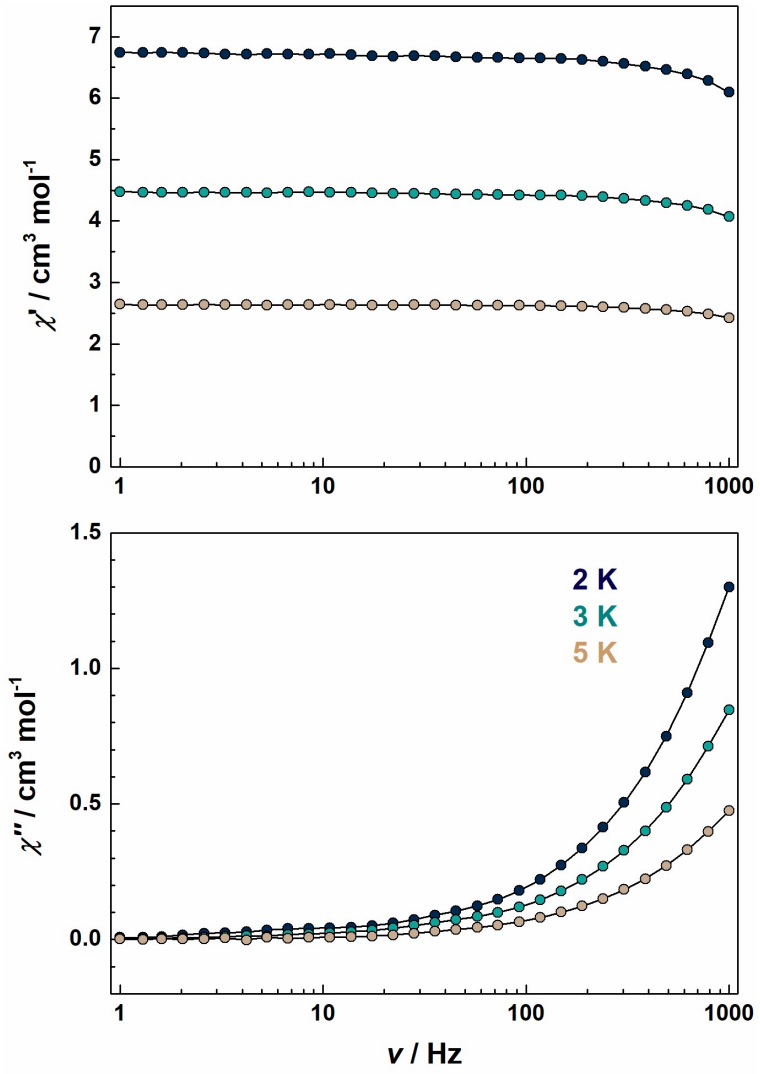

Figure S16. Frequency dependence of the ac susceptibility for **1** under zero dc field. The lines are guides for the eyes.

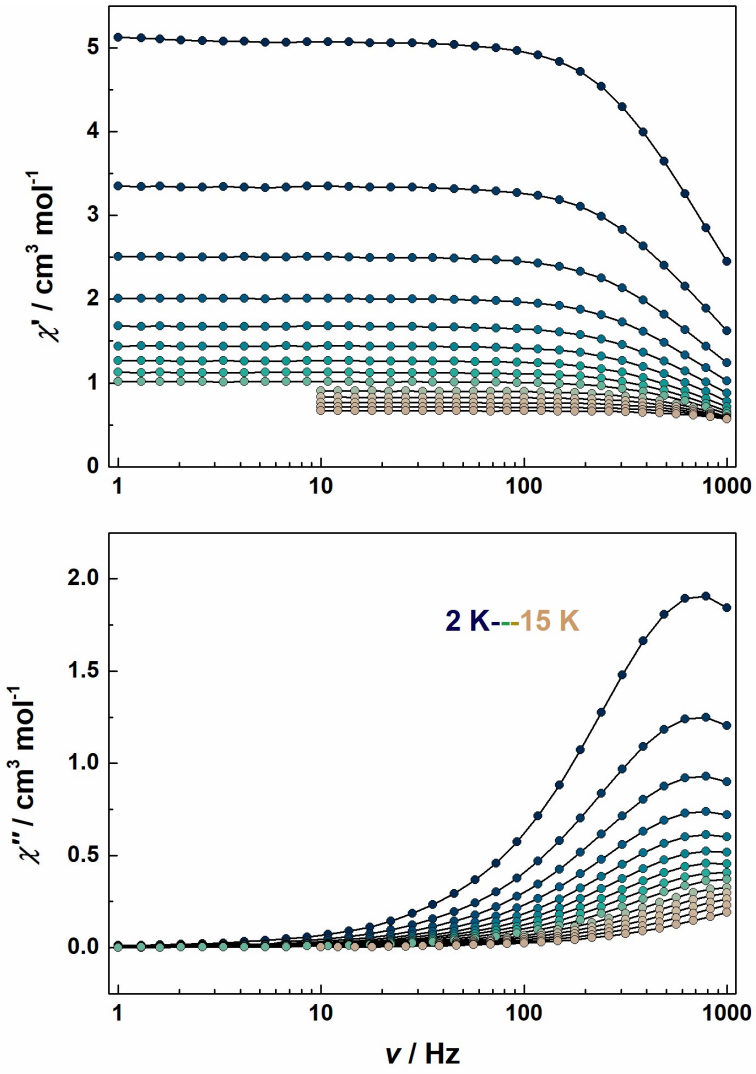

Figure S17. Frequency dependence of the ac susceptibility for **2** under zero dc field. The lines are guides for the eyes.

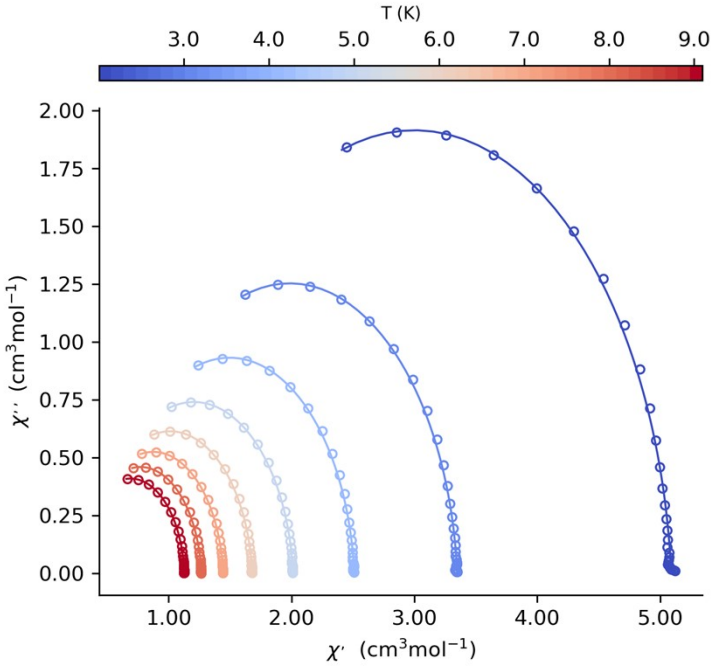

Figure S18. Cole–Cole plots of **2** at various temperatures under zero dc field. The solid lines represent fitting with the generalized Debye model.

Table S6. The best results fitted for **2** at zero dc field by using the generalized Debye model between 2 and 9 K.

T **/ K**	**τ / s**	**α**	***T*** **/ K**	**τ / s**	**α**
2.0	2.23E-04	0.06	6.0	2.05E-04	0.05
3.0	2.23E-04	0.05	7.0	1.96E-04	0.05
4.0	2.20E-04	0.05	8.0	1.86E-04	0.05
5.0	2.13E-04	0.05	9.0	1.73E-04	0.04

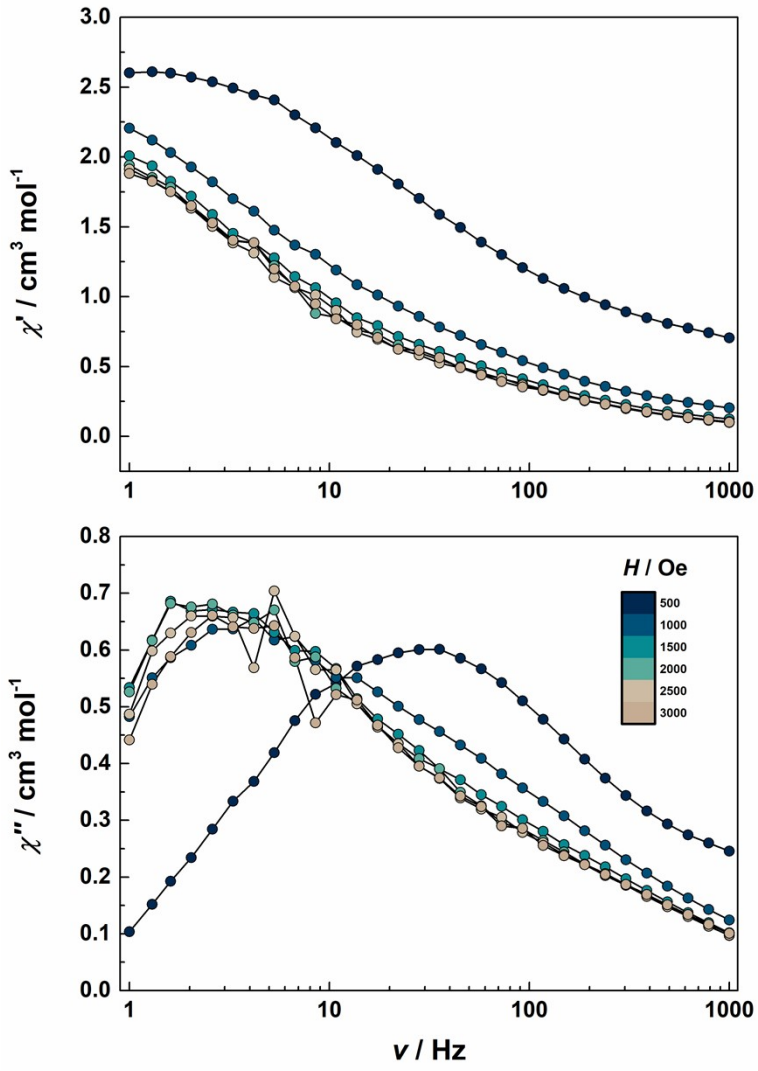

Figure S19. Frequency dependence of the ac susceptibility for **1** at 5 K under various dc fields. The lines are guides for the eyes.

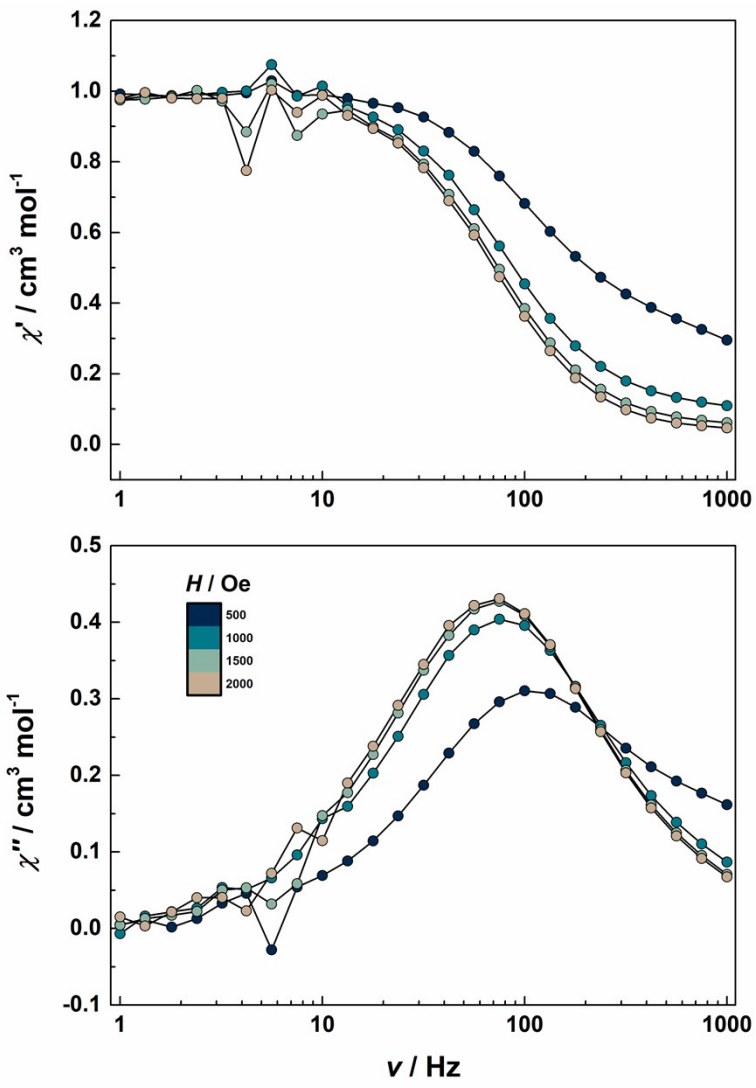

Figure S20. Frequency dependence of the ac susceptibility for **2** at 10 K under various dc fields. The lines are guides for the eyes.

Table S7. The best results fitted for **1** at 1 kOe dc field by using the generalized Debye model between 3 and 18 K.

T / K	***τ*** / s	***α***	***T*** / K	***τ*** / s	***α***
3.0	1.49E-01	0.43	11.0	1.18E-03	0.20
4.0	9.54E-02	0.51	12.0	8.58E-04	0.17
5.0	3.95E-02	0.52	13.0	6.53E-04	0.17
6.0	1.53E-02	0.46	14.0	4.96E-04	0.14
7.0	7.28E-03	0.40	15.0	3.85E-04	0.17
8.0	4.04E-03	0.33	16.0	3.01E-04	0.14
9.0	2.52E-03	0.28	17.0	2.40E-04	0.13
10.0	1.67E-03	0.24	18.0	1.93E-04	0.11

Table S8. The best results fitted for **2** at 1 kOe dc field by using the generalized Debye model between 6 and 15 K.

T / K	***τ*** / s	***α***	***T*** / K	***τ*** / s	***α***
6.0	3.82E-02	0.12	11.0	1.27E-03	0.07
7.0	1.44E-02	0.09	12.0	8.30E-04	0.06
8.0	6.58E-03	0.08	13.0	5.53E-04	0.07
9.0	3.49E-03	0.07	14.0	3.70E-04	0.08
10.0	2.02E-03	0.07	15.0	2.45E-04	0.09

Electronic Structure Calculations

Table S9. SA-CASSCF/RASSI calculated electronic states for Dy in **1'**.

Energy (cm^{-1})	g_x	g_y	g_z	g_z Angle (°)	Wavefunction
0.0	0.02	0.02	19.76	--	94%|±15/2>
171.5	0.25	0.36	16.84	11.4	85%|±13/2>
287.1	2.71	4.26	12.64	75.3	28%|±11/2> + 22%|∓1/2> + 21%|±3/2>
340.7	0.19	6.25	8.01	84.0	19%|±1/2> + 12%|±11/2> + 11%|∓5/2> + 10%|∓1/2>
355.6	1.47	3.26	6.01	37.0	34%|±11/2> + 17%|∓1/2> + 12%|±1/2>
390.3	0.62	3.87	12.81	68.3	28%|±9/2> + 22%|±3/2> + 14%|∓5/2> +12%|±7/2>
448.5	1.76	5.02	8.06	87.8	33%|±9/2> + 13%|∓9/2> + 10%|±3/2>
481.7	1.50	7.80	11.98	79.5	47%|±7/2> + 20%|±5/2> + 14%|∓5/2>

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

***Table S10*.** SA-CASSCF/RASSI calculated electronic states for Dy in **2b'**.

Energy (cm^{-1})	g_x	g_y	g_z	g_z Angle (°)	Wavefunction
0.0	0.01	0.02	19.76	--	95%|±15/2>
159.2	0.05	0.08	16.99	7.5	93%|±13/2>
303.0	1.07	6.36	8.55	75.4	50%|±1/2> + 29%|∓11/2>
321.4	1.46	5.83	7.99	41.7	35%|±11/2> + 21%|±3/2> + 18%|±1/2> + 16%|∓3/2>
367.9	0.96	3.36	9.56	67.1	31%|±3/2> + 24%|±11/2> + 11%|∓1/2>
405.5	1.54	3.86	12.94	73.0	27%|±5/2> + 20%|±7/2> + 18%|∓5/2> + 11%|∓9/2> + 11%|∓7/2>
451.5	0.91	6.49	8.54	54.0	50%|±9/2> + 14%|∓3/2> + 13%|∓5/2> + 12%|∓9/2>
492.0	1.77	3.30	15.03	54.8	58%|±7/2> + 16%|∓5/2>

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

Table S11. *Ab initio* calculated crystal field parameters for Dy in **1'**.

Crystal Field Parameter	Value / cm^{-1}
B_2^{-2}	-0.16129532658456E+00
B_2^{-1}	-0.85114953803481E-01
B_2^0	-0.20126848899970E+01
B_2^1	-0.94323735149704E-01
B_2^2	0.39904186794457E+00
B_4^{-4}	0.80643555705919E-02
B_4^{-3}	-0.31126697310434E-02
B_4^{-2}	-0.83709915538821E-02
B_4^{-1}	-0.20864853225299E-01
B_4^0	-0.63631819860152E-02
B_4^1	0.28840666168285E-02
B_4^2	-0.45278385423190E-02
B_4^3	0.19473254810021E-01
B_4^4	-0.41027673054578E-03
B_6^{-6}	-0.19825493291757E-03
B_6^{-5}	0.16829086003741E-03
B_6^{-4}	0.15293499980860E-03
B_6^{-3}	-0.19598607705620E-03
B_6^{-2}	-0.65377090416318E-05
B_6^{-1}	0.11830338651862E-03
B_6^0	0.22228962497249E-04
B_6^1	0.17987155567002E-03
B_6^2	-0.90026546565924E-04
B_6^3	0.45020726353990E-04
B_6^4	0.15396301523978E-04
B_6^5	0.17710019111883E-03
B_6^6	0.17144366475742E-03

Table S12. *Ab initio* calculated crystal field parameters for Dy in **2b'**.

Crystal Field Parameter	Value / cm^{-1}
B_2^{-2}	-0.20980553038568E-01
B_2^{-1}	-0.18485954382252E+00
B_2^0	-0.20670078116526E+01
B_2^1	-0.23337657033841E-01
B_2^2	0.39393107060609E+00
B_4^{-4}	-0.64972443622653E-02
B_4^{-3}	-0.22074700888074E-01
B_4^{-2}	0.13181332024597E-02
B_4^{-1}	0.97778860844905E-02
B_4^0	-0.71269102498518E-02
B_4^1	-0.11105697386755E-01
B_4^2	0.50435056050241E-02
B_4^3	0.20366347977141E-01
B_4^4	0.64301302609071E-02
B_6^{-6}	-0.12273964429901E-03
B_6^{-5}	-0.96782560932568E-04
B_6^{-4}	-0.45613360499897E-04
B_6^{-3}	-0.10981208180224E-03
B_6^{-2}	0.11004378874421E-04
B_6^{-1}	-0.38949841228988E-04
B_6^0	0.37660967810302E-04
B_6^1	-0.11313329160003E-04
B_6^2	0.14481463292536E-03
B_6^3	0.49690337112025E-04
B_6^4	0.11288492065028E-03
B_6^5	-0.11931388958425E-03
B_6^6	0.20583030266376E-03