Supporting Information

Linear hexanuclear helical dysprosium single-molecule magnets: the effect of axial substitution on magnetic interactions and relaxation dynamics

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Experimental Section.
General.
Unless otherwise specified, all the materials used in present work were commercially obtained and without further purification. Elemental analysis (C, H, and N) was determined on a PerkinElmer 2400 analyzer. Powder X-ray diffraction (PXRD) measurements were performed via a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. Infrared (IR) spectra were obtained on a Nicolet 6700 Flex FTIR spectrometer equipped with smart iTR™ attenuated total reflectance (ATR) sampling accessory in the range of 500-4000 cm^{-1}. Thermogravimetric analyses (TGA) were conducted using a STA 449 F3 simultaneous thermal analysis from room temperature to 800 °C under N_2 atmosphere with a heating rate of 10 °C·min^{-1}. Magnetic measurements were recorded on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet. The variable-temperature magnetization was measured between 2 and 300 K, with an applied field of 1000 Oe. The dynamics of the magnetization were investigated at different frequencies from 1 to 997 Hz, under a 3.0 Oe ac oscillating field and a zero dc field. The experimental magnetic data were corrected for the diamagnetism contribution of all the constituent atoms estimated from Pascal's tables[1] and sample-holder calibration.

Synthesis of the ligand H$_4$L.
The Schiff-base ligand [3,6-bis(2-hydroxy-3-methoxybenzylidene)hydrazinecarbonyl]-pyridazine (H$_4$L) was prepared according to the method reported in the literature.[2]

Synthesis of [Dy$_6$L$_3$(SCN)$_6$(DMF)$_8$]·4DMF (1).

The mixture of Dy(SCN)$_3$·6H$_2$O (0.10 mmol) and H$_2$L (0.05 mmol) in DMF (10 mL) in the presence of NEt$_3$ (0.10 mmol) was stirred at room temperature for 3 h and then subsequently filtered. Diethyl ether was allowed to diffuse slowly into the solution at room temperature. Red crystals of compound **1**, suitable for X-ray diffraction analysis, were collected after two months in ~37% yield. Anal. Calcd for C$_{108}$H$_{129}$Dy$_6$N$_{36}$O$_{30}$S$_6$: C, 36.22; H, 3.60; N, 14.08. Found: C, 36.27; H, 3.64; N, 14.02. Selected IR (cm^{-1}): 2931 (vw), 2057 (s), 1645 (vs), 1605 (s), 1562 (w), 1433 (vs), 1379 (s), 1319 (s), 1237 (s), 1212 (vs), 1150 (w), 1100 (w), 917 (s), 852 (w), 738 (s), 637 (w), 568 (s).

Synthesis of [Dy$_6$L$_3$(NO$_3$)$_6$(DMF)$_4$(H$_2$O)$_2$]·8DMF (2).

Compound **2** was synthesized by the similar procedure as compound **1** with the replacement of Dy(SCN)$_3$·6H$_2$O by Dy(NO$_3$)$_3$·6H$_2$O. Yield: ~49%. Anal. Calcd for C$_{102}$H$_{128}$Dy$_6$N$_{36}$O$_{50}$: C, 33.65; H, 3.52; N, 13.84. Found: C, 33.60; H, 3.56; N, 13.87. Selected IR (cm^{-1}): 3382 (br), 2935 (vw), 1645 (vs), 1606 (s), 1577 (w), 1432 (s), 1378 (s), 1320 (vs), 1239 (s), 1214 (vs), 1148 (w), 1099 (w), 918 (s), 861 (w), 738 (s), 672 (s), 637 (w), 571 (s).

X-ray crystal structure determinations.

Single crystal X-ray diffraction data (Table S1) for all compounds were collected at 173(2) K on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 with anisotropic thermal parameters for all non-H atoms by using the SHELXS (direct methods) and refined by ShelXL (full matrix least squares techniques) in the Olex2 package.[3, 4] All the non-H atoms were refined anisotropically and the H atoms were introduced geometrically and refined using the riding model. In addition, due to the presence of substantial badly disordered DMF molecules in compounds **1** and **2**, and which were poorly defined, the *SQUEEZE* routine[5] of the *PLATON* program[6] was employed to remove the contribution of the missing solvent molecules. The solvent content is further confirmed by thermogravimetric analyses (TGA) of these materials, as shown in Fig. S2. CCDC 1937074 (**1**) and 1937073 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
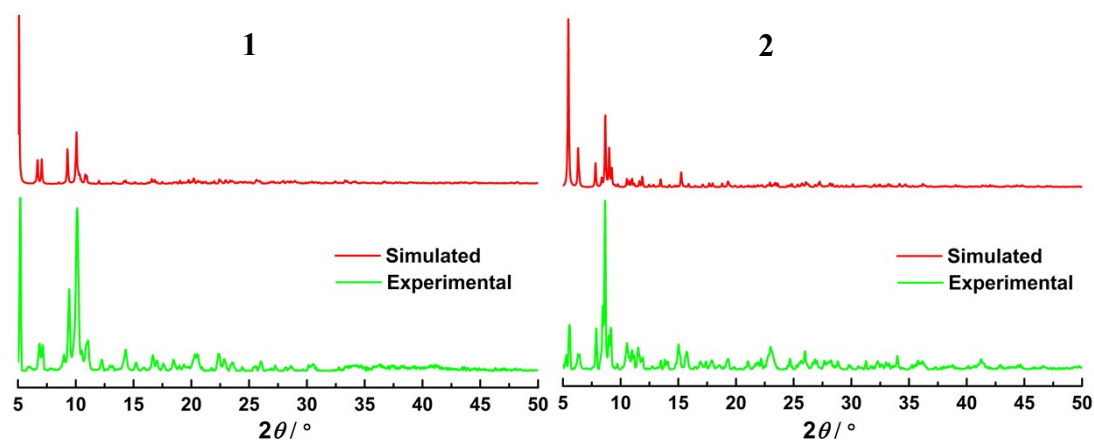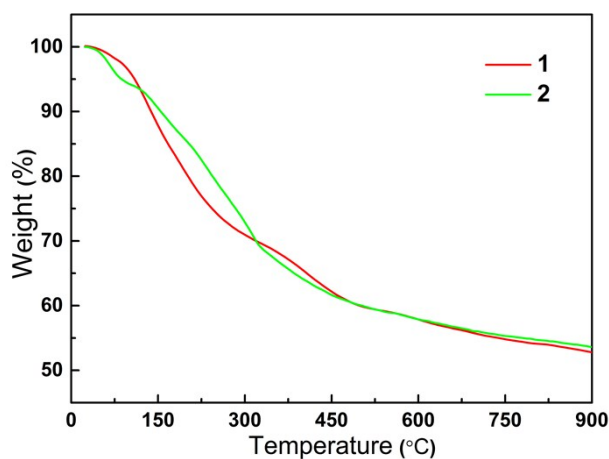

Fig. S1 Powder XRD analyses of compounds **1** and **2**.

Fig. S2 Thermogravimetric analyses of compounds **1** and **2**.

$5.1_12_{12}2_{23}2_{45}1_51_21_31_41_5$ $5.1_12_{12}2_{23}2_{45}2_{56}1_61_21_31_41_5$
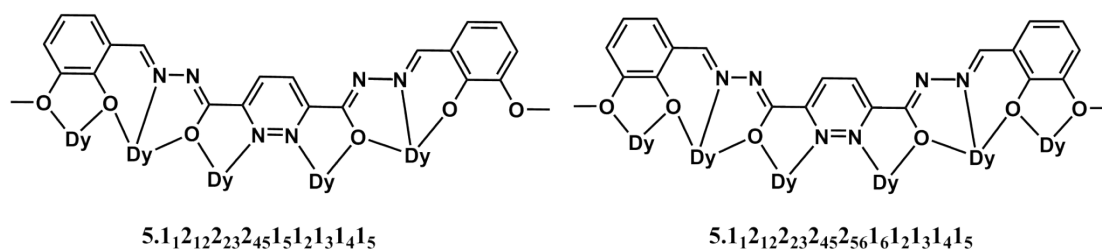
Scheme S1 Binding modes of the H$_4$L with deprotonated forms in compounds **1** and **2** indicated by the Harris notation.[7]

Λ   Δ   Λ   Δ
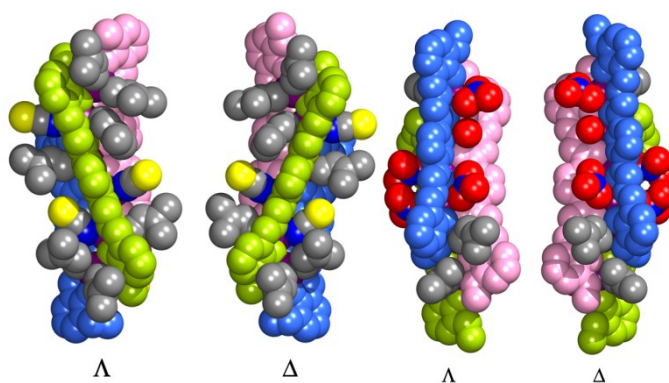
Fig. S3 Space-filling representations of left- (Λ) and right-hand (Δ) configurations for compounds **1** (left) and **2** (right).
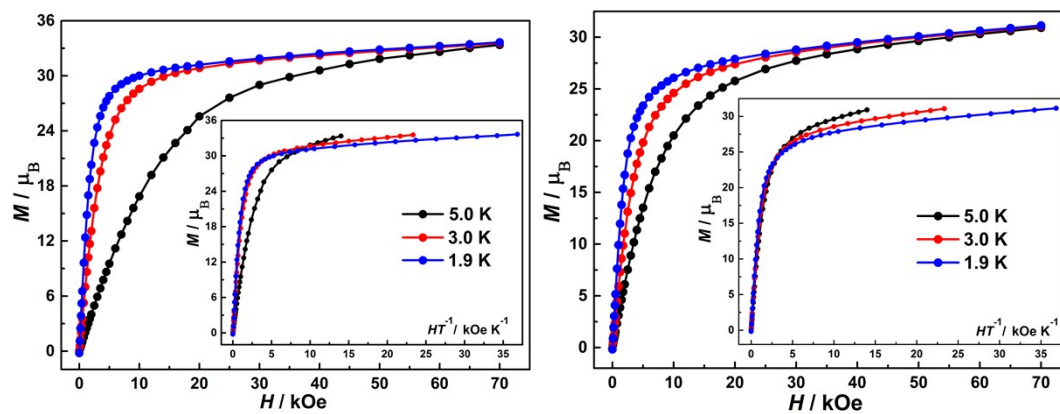
Fig. S4 Field dependence of magnetization in the range 0-70 kOe at 1.9, 3.0 and 5.0 K for compounds **1** (left) and **2** (right). Insets: Plots of the reduced magnetization M versus H/T.
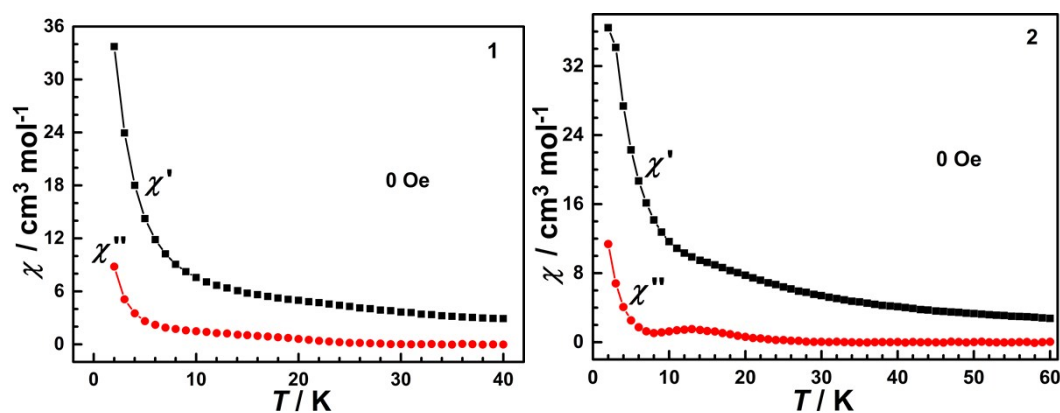
Fig. S5 Temperature dependence of the ac signals under zero dc field at 997 Hz ac frequency for compounds **1** (left) and **2** (right).
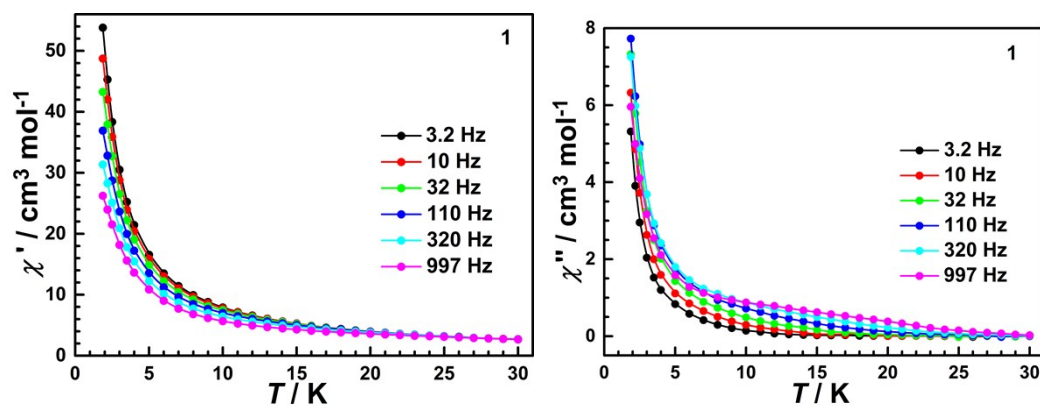
Fig. S6 Temperature dependence of the ac signals at different frequencies under zero dc field for compound **1**.
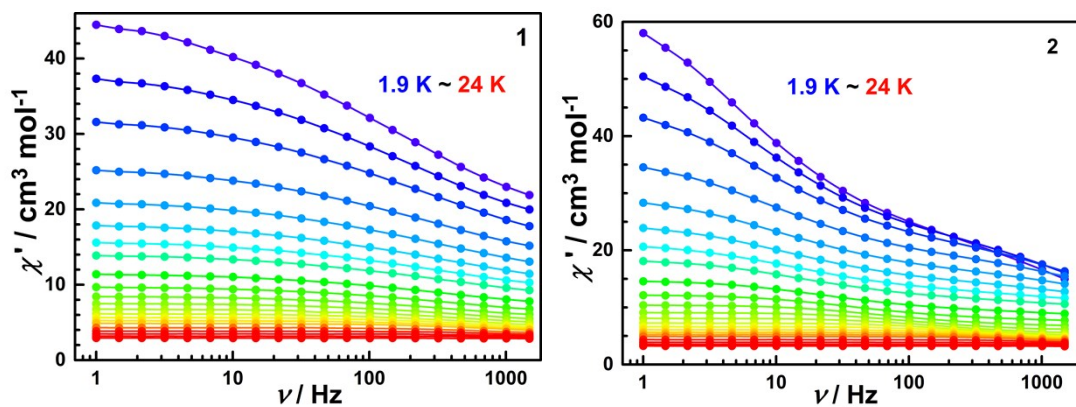
Fig. S7 Frequency dependence of the χ' ac signals under zero dc field for compounds **1** (left) and **2** (right).
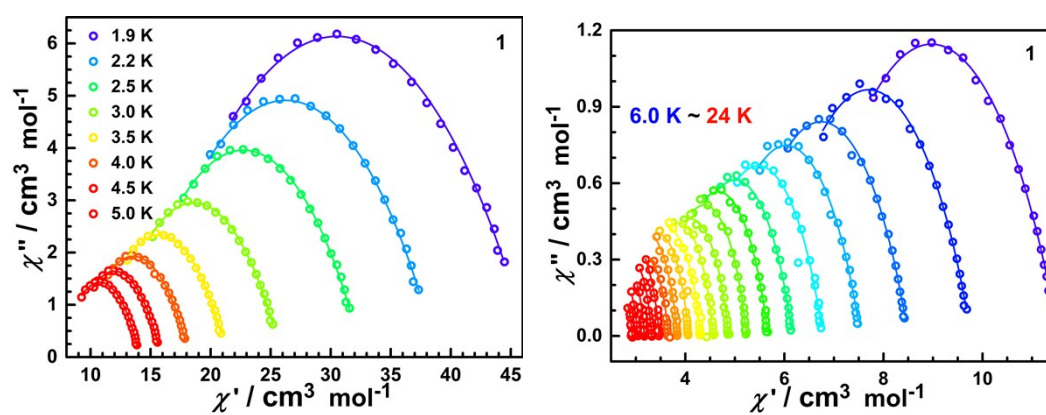
Fig. S8 Cole-Cole plots for **1** under a zero dc field. The solid lines represent the best fit to the data with the generalized Debye model.
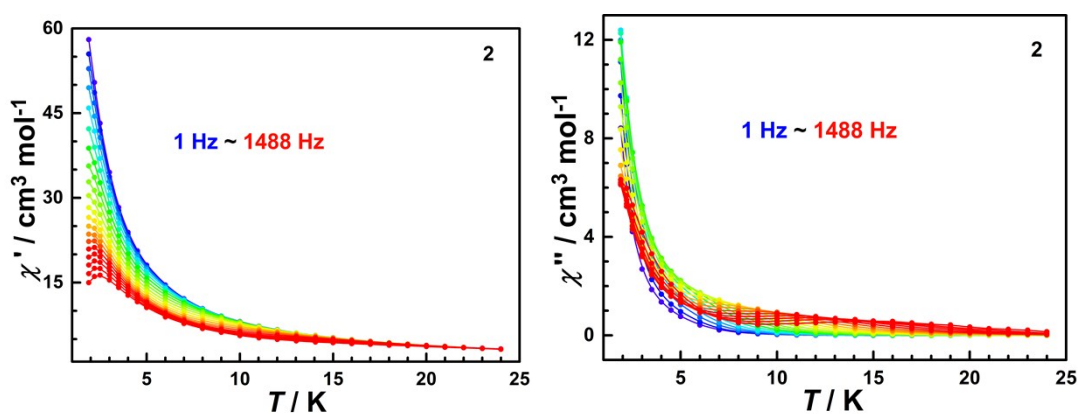
Fig. S9 Temperature dependence of the ac signals at different frequencies under zero dc field for compound **2**.
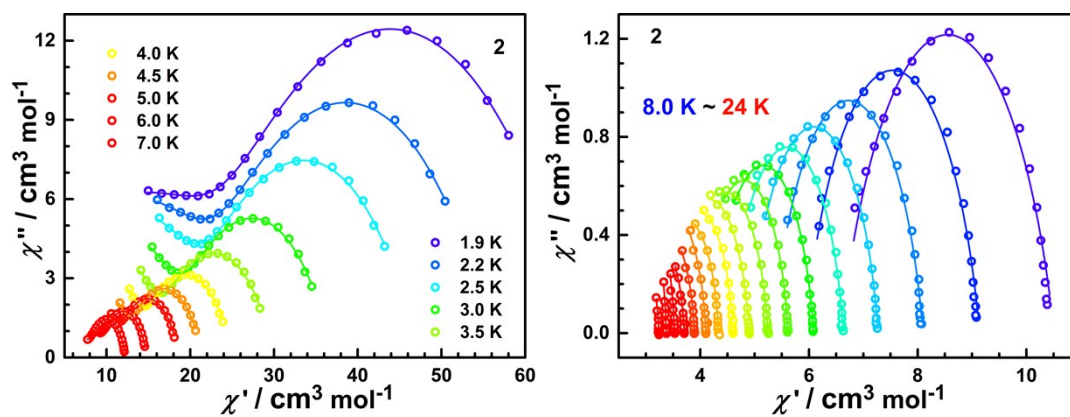
Fig. S10 Cole-Cole plots for **2** under a zero dc field. The solid lines represent the best fit to the data with the sum of two modified Debye functions (1.9-7.0 K), and the generalized Debye model (8.0-24 K), respectively.
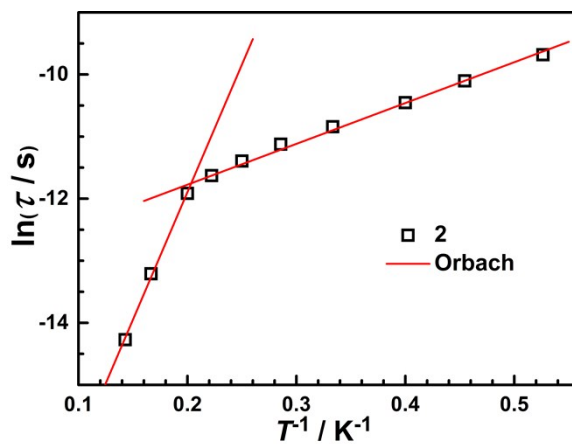
Fig. S11 Plots of $\ln(\tau)$ vs. T^{-1} for compound **2** under zero dc field, where τ corresponds to the fast relaxation time. The red lines correspond to the best fit to the Arrhenius law.

Table S1. Crystallographic data and structure refinement details for compounds **1** and **2**.

Compound	**1**	**2**
Formula	$C_{108}H_{129}Dy_6N_{36}O_{30}S_6$	$C_{102}H_{128}Dy_6N_{36}O_{50}$
Mr	3581.56	3640.71
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/n$	$R\bar{3}c$
T [K]	173(2)	173(2)
λ [Å]	0.71073	0.71073
a [Å]	19.1621(9)	55.955(4)
b [Å]	19.7925(9)	55.955(4)
c [Å]	36.6621(17)	20.8428(17)
α [°]	90	90
β [°]	96.3550(10)	90
γ [°]	90	120
V [Å^3]	13819.2(11)	56515(9)
Z	4	18
ρ_{calcd} [g·cm^3]	1.616	1.617
$F(000)$	6576	26568
R_{int}	0.0674	0.2081
GOF on F^2	1.089	1.045
Reflns collected	85352	116093
R_1, wR_2 [I ≥ 2σ(I)]	0.0551, 0.1520	0.0867, 0.1954
R_1, wR_2 (all data)	0.0768, 0.1648	0.1673, 0.2656
CCDC number	1937074	1937073

Table S2. Selected bond lengths [Å] and bond angles [°] for compound **1**.

Dy(1)-Dy(2)	3.9710(6)	Dy(4)-N(6)	2.514(7)
Dy(1)-N(13)	2.463(7)	Dy(4)-N(16)	2.457(7)
Dy(1)-N(32)	2.413(8)	Dy(4)-N(24)	2.482(7)
Dy(1)-O(1)	2.395(6)	Dy(4)-O(4)	2.442(6)
Dy(1)-O(7)	2.344(6)	Dy(4)-O(13)	2.394(5)
Dy(1)-O(11)	2.405(6)	Dy(4)-O(16)	2.343(5)
Dy(1)-O(12)	2.552(6)	Dy(4)-O(18)	2.278(5)
Dy(1)-O(20)	2.366(5)	Dy(4)-O(19)	2.281(5)
Dy(1)-O(21)	2.166(6)	Dy(5)-Dy(6)	3.9068(6)
Dy(2)-Dy(3)	3.8528(5)	Dy(5)-N(7)	2.530(7)
Dy(2)-N(4)	2.532(7)	Dy(5)-N(17)	2.520(7)
Dy(2)-N(12)	2.593(6)	Dy(5)-N(22)	2.465(7)
Dy(2)-N(23)	2.415(8)	Dy(5)-O(5)	2.370(6)
Dy(2)-O(2)	2.433(6)	Dy(5)-O(15)	2.404(6)

Dy(2)-O(9)	2.552(5)	Dy(5)-O(16)	2.289(5)
Dy(2)-O(10)	2.533(5)	Dy(5)-O(17)	2.295(5)
Dy(2)-O(11)	2.329(5)	Dy(5)-O(19)	2.533(5)
Dy(2)-O(14)	2.305(5)	Dy(5)-O(22)	2.553(6)
Dy(2)-O(20)	2.432(5)	Dy(6)-N(9)	2.489(8)
Dy(3)-Dy(4)	3.8089(5)	Dy(6)-N(26)	2.406(8)
Dy(3)-N(2)	2.449(7)	Dy(6)-O(8)	2.349(6)
Dy(3)-N(8)	2.547(6)	Dy(6)-O(15)	2.325(5)
Dy(3)-N(11)	2.511(7)	Dy(6)-O(17)	2.399(6)
Dy(3)-N(19)	2.504(7)	Dy(6)-O(23)	2.177(7)
Dy(3)-O(3)	2.418(6)	Dy(6)-O(24)	2.604(6)
Dy(3)-O(9)	2.280(5)	Dy(6)-O(26)	2.360(6)
Dy(3)-O(13)	2.277(5)	Dy(3)-Dy(2)-Dy(1)	151.889(14)
Dy(3)-O(14)	2.355(5)	Dy(4)-Dy(3)-Dy(2)	144.203(14)
Dy(3)-O(18)	2.376(5)	Dy(3)-Dy(4)-Dy(5)	145.126(14)
Dy(4)-Dy(5)	3.8200(5)	Dy(4)-Dy(5)-Dy(6)	155.180(15)
Dy(4)-N(5)	2.523(6)		

Table S3. Selected bond lengths [Å] and bond angles [°] for compound **2**.

Dy(3)-Dy(3)$^{\#1}$	3.8210(16)	Dy(2)-O(4)	2.320(12)
Dy(3)-Dy(2)	3.8229(12)	Dy(2)-O(7)	2.502(11)
Dy(3)-N(1)	2.523(13)	Dy(2)-O(8)	2.633(13)
Dy(3)-N(2)	2.535(14)	Dy(2)-O(13)	2.470(13)
Dy(3)-N(3)	2.445(14)	Dy(2)-O(18)	2.325(15)
Dy(3)-O(1)	2.350(11)	Dy(1)-N(6)	2.436(16)
Dy(3)-O(2)$^{\#1}$	2.269(11)	Dy(1)-N(10)	2.284(12)
Dy(3)-O(2)	2.384(11)	Dy(1)-O(3)	2.336(12)
Dy(3)-O(7)	2.233(12)	Dy(1)-O(4)	2.438(12)
Dy(3)-O(15)	2.453(18)	Dy(1)-O(6)	2.139(14)
Dy(3)-O(20)	2.42(2)	Dy(1)-O(9)	2.468(15)
Dy(2)-Dy(1)	3.8337(13)	Dy(1)-O(10)	2.409(19)
Dy(2)-N(7)	2.504(15)	Dy(1)-O(11)	2.202(17)
Dy(2)-N(8)	2.566(13)	Dy(1)-O(14)	145.29(3)
Dy(2)-O(1)	2.284(11)	Dy(3)$^{\#1}$-Dy(3)-Dy(2)	155.19(3)
Dy(2)-O(3)	2.343(11)	Dy(3)-Dy(2)-Dy(1)	

Symmetry code: #1 y-2/3, x+2/3, z+7/6

Table S4. Dy^{III} geometry analysis of compound **1** by *SHAPE* 2.1[8] software.

Dy center	Square antiprism (D_{4d})	Triangular dodecahedron (D_{2d})	Biaugmented trigonal prism J50 (C_{2v})	Biaugmented trigonal prism (C_{2v})	Snub diphenoid J84 (D_{2d})
Dy1	3.184	2.627	2.555	2.269	3.772
Dy6	3.184	2.764	2.724	2.430	4.151
Dy	Spherical-	Tricapped	Capped	Spherical	Spherical

center	relaxedcapped cube (C_{4v})	trigonal prism J51 (D_{3h})	Square antiprism J10 (C_{4v})	capped square antiprism (C_{4v})	tricapped trigonal prism (D_{3h})
Dy2	6.341	2.858	2.800	1.655	1.719
Dy3	7.854	3.422	1.775	0.742	1.296
Dy4	7.817	3.163	1.790	0.775	1.098
Dy5	6.522	2.455	2.250	1.576	1.227

Table S5. Dy^{III} geometry analysis of compound **2** by *SHAPE* 2.1[8] software.

Dy center	Square antiprism (D_{4d})	Triangular dodecahedron (D_{2d})	Biaugmented trigonal prism J50 (C_{2v})	Biaugmented trigonal prism (C_{2v})	Snub diphenoid J84 (D_{2d})
Dy1	3.619	2.580	3.592	3.144	3.591

Dy center	Spherical-relaxed capped cube (C_{4v})	Tricapped trigonal prism J51 (D_{3h})	Capped square antiprism J10 (C_{4v})	Spherical capped square antiprism (C_{4v})	Spherical tricapped trigonal prism (D_{3h})
Dy2	7.734	3.402	2.675	1.244	2.020
Dy3	7.395	3.092	1.722	0.782	1.431

Table S6. The best fitting parameters for compounds **1** and **2** from fitting of ac data at varying temperatures under zero applied dc field.

		Compound **1**		
T (K)	χ_s	χ_T	τ	α
1.9	0.142551E+02	0.467741E+02	0.107584E-02	0.539454
2.2	0.135922E+02	0.388808E+02	0.849015E-03	0.526953
2.5	0.128209E+02	0.326441E+02	0.752764E-03	0.514775
3	0.113262E+02	0.258779E+02	0.649167E-03	0.507534
3.5	0.100308E+02	0.213536E+02	0.589136E-03	0.499253
4	0.890018E+01	0.182327E+02	0.547408E-03	0.499624
4.5	0.813921E+01	0.158780E+02	0.538579E-03	0.487625
5	0.743422E+01	0.141069E+02	0.519673E-03	0.482676
6	0.640714E+01	0.115280E+02	0.497407E-03	0.462299
7	0.563295E+01	0.976625E+01	0.442262E-03	0.440685
8	0.498444E+01	0.849591E+01	0.366090E-03	0.428727
9	0.454052E+01	0.753213E+01	0.312505E-03	0.407104
10	0.416769E+01	0.677057E+01	0.263406E-03	0.393041
11	0.385916E+01	0.615725E+01	0.220814E-03	0.372614
12	0.366237E+01	0.566608E+01	0.201441E-03	0.340751
13	0.352871E+01	0.523564E+01	0.190810E-03	0.304247
14	0.336277E+01	0.487247E+01	0.165530E-03	0.299131
15	0.317115E+01	0.456398E+01	0.138976E-03	0.272791
16	0.292196E+01	0.430843E+01	0.102200E-03	0.291564
17	0.285873E+01	0.406040E+01	0.986144E-04	0.244907

18	0.255512E+01	0.384282E+01	0.582680E-04	0.274625
19	0.275532E+01	0.365343E+01	0.797702E-04	0.235341
20	0.237213E+01	0.347346E+01	0.389659E-04	0.249202
21	0.249580E+01	0.331595E+01	0.500636E-04	0.189688
22	0.243088E+01	0.317250E+01	0.337841E-04	0.192547
23	0.240388E+01	0.304046E+01	0.316419E-04	0.219069
24	0.234875E+01	0.292790E+01	0.210574E-04	0.251067

Compound **2**

T (K)	χ_s	$\Delta\chi_1$	τ_1	α_1	$\Delta\chi_2$	τ_2	α_2
1.9	0.243378E-26	24.6097	0.623298E-4	0.459569	41.5418	0.0303032	0.338378
2.2	0.445008E-26	23.4944	0.408963E-4	0.430491	32.4291	0.0242152	0.340932
2.5	0.999337E-26	21.8445	0.288266E-4	0.408507	25.1570	0.0204499	0.342107
3	0.113917E-25	19.0450	0.195596E-4	0.382956	17.8320	0.0169164	0.342891
3.5	0.198109E-25	16.4913	0.147605E-4	0.361439	13.4304	0.0146472	0.343703
4	0.340931E-25	14.4863	0.112459E-4	0.363972	10.5265	0.0130219	0.336167
4.5	0.736671E-25	12.7475	0.890497E-5	0.347384	8.70775	0.0113706	0.333329
5	0.197295E-24	11.5391	0.668548E-5	0.374846	7.13807	0.00997787	0.311131
6	0.811069E-25	9.89266	0.183174E-5	0.544578	4.95670	0.00718896	0.263356
7	0.309023E-24	8.31583	0.633893E-6	0.572300	3.97091	0.00433422	0.240769

T (K)	χ_s	χ_T	τ	α
8	0.658949E+01	0.105116E+02	0.211111E-02	0.288151E+00
9	0.593495E+01	0.913910E+01	0.136002E-02	0.243393E+00
10	0.535422E+01	0.809811E+01	0.870393E-03	0.223423E+00
11	0.491767E+01	0.727382E+01	0.588451E-03	0.203285E+00
12	0.456648E+01	0.663376E+01	0.415272E-03	0.187065E+00
13	0.423720E+01	0.608421E+01	0.294503E-03	0.180183E+00
14	0.399595E+01	0.561614E+01	0.222559E-03	0.157343E+00
15	0.370461E+01	0.524931E+01	0.154732E-03	0.177634E+00
16	0.345583E+01	0.490345E+01	0.113797E-03	0.172412E+00
17	0.332401E+01	0.460446E+01	0.936392E-04	0.149060E+00
18	0.321997E+01	0.433660E+01	0.808043E-04	0.126094E+00
19	0.284520E+01	0.410597E+01	0.479100E-04	0.145796E+00
20	0.290622E+01	0.389129E+01	0.482939E-04	0.120789E+00
21	0.282076E+01	0.370525E+01	0.397303E-04	0.113932E+00
22	0.167702E+01	0.352911E+01	0.115103E-04	0.124436E+00
23	0.151102E+01	0.337653E+01	0.990501E-05	0.839557E-01
24	0.270954E+01	0.323565E+01	0.307282E-04	0.235590E-01

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