Electronic supporting information

Bis-pyrazolone-based dysprosium(III) complexes: zero-field single-molecule magnet behavior in the [2 × 2] grid Dy$^{III}_4$ cluster

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Ligand synthesis Scheme
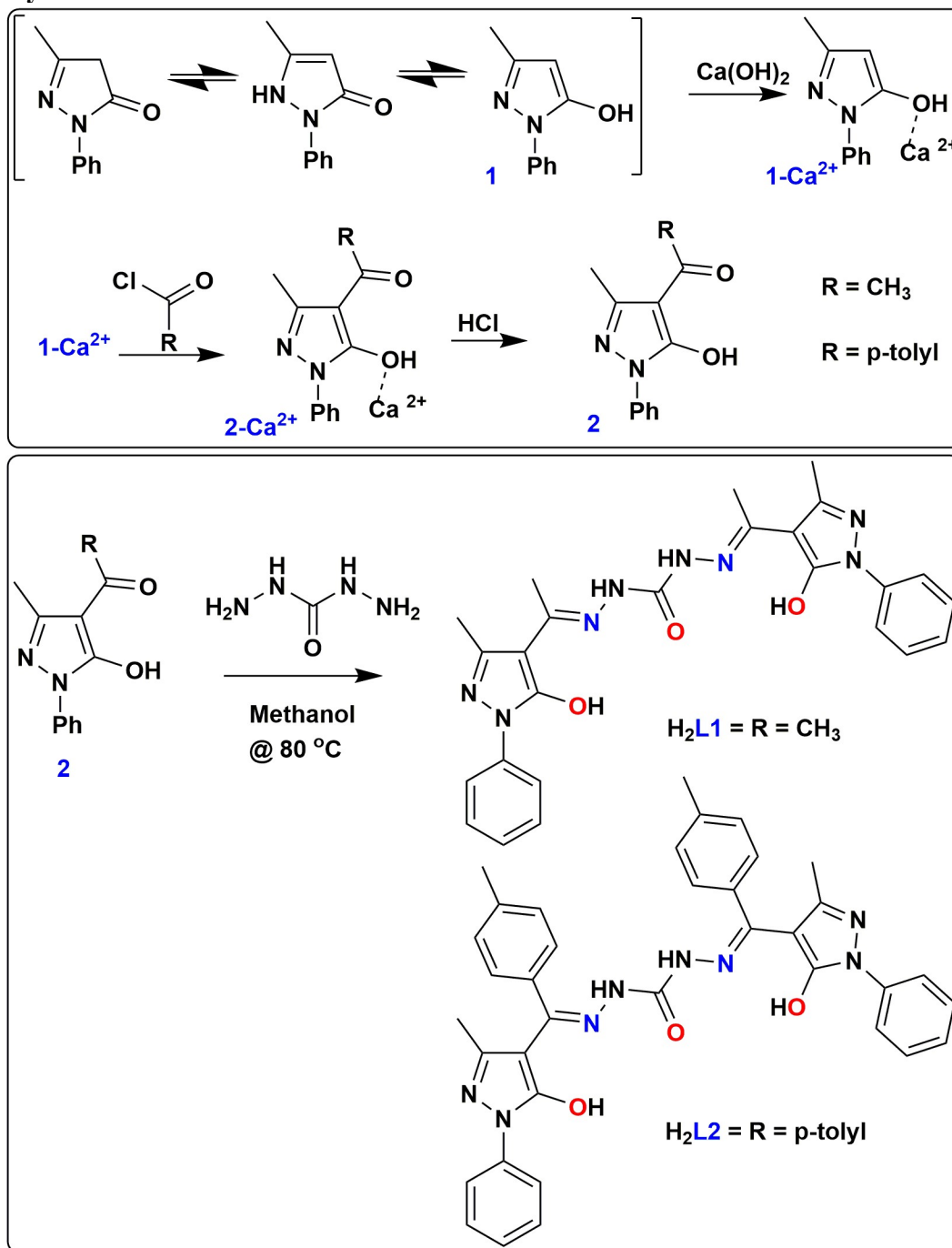
Scheme S1. Jensen's method[1] for pyrazolone-based ketones synthesis (top box) and ligands (H$_2$L1 and H$_2$L2) synthesis (bottom box).
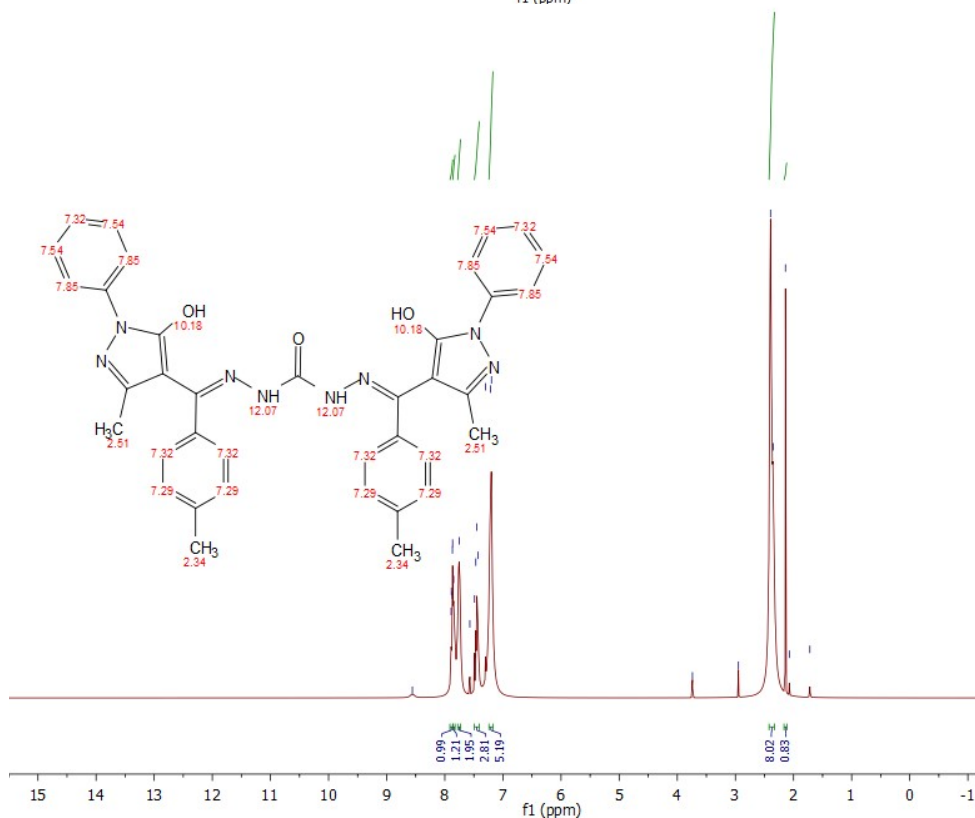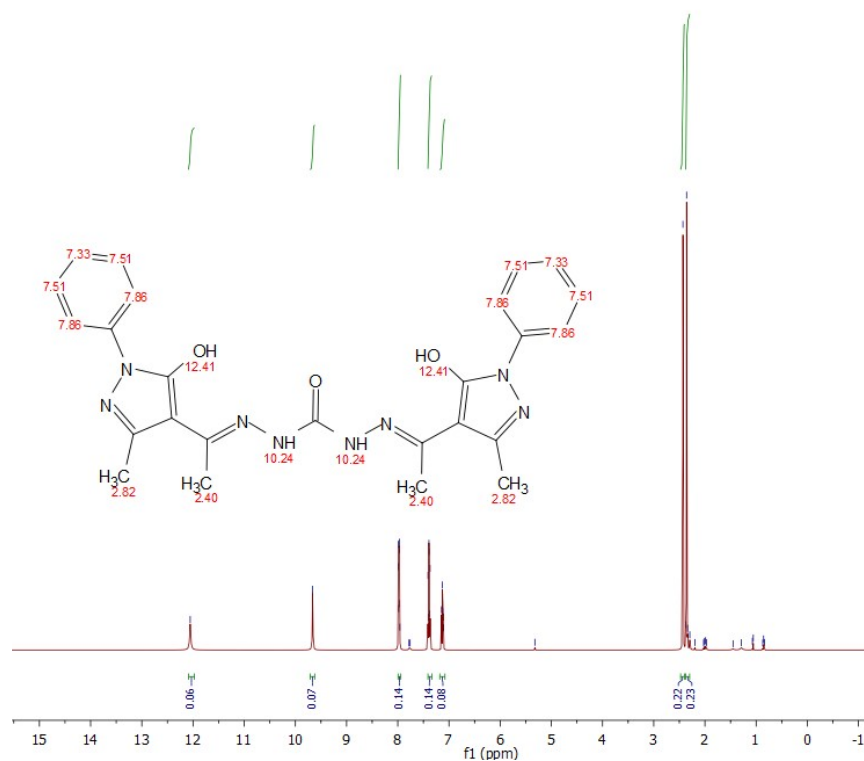
Fig. S1. ^{1}HNMR of H$_2$L1 in DMSO (top) and H$_2$L2 in CDCl$_3$ (bottom). Red numbers are the simulated chemical shifts (ppm).
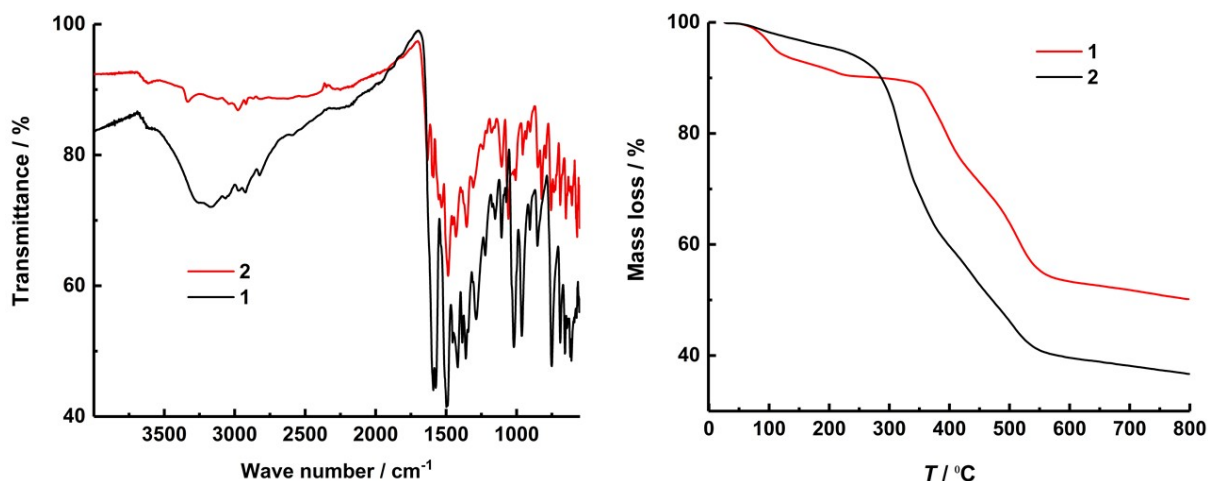
Fig. S2. FT-IR (ATR) spectrum of solid samples for complexes of **1** and **2** (left) and TGA curves in powder forms showing weight loss of co-crystallized solvents as well as masked solvents in the thermal stability range, and weight loss with degradation above 380 °C for **1** and 300°C for **2** at scan rate: 3 °C/min in N_2 atmosphere (right).
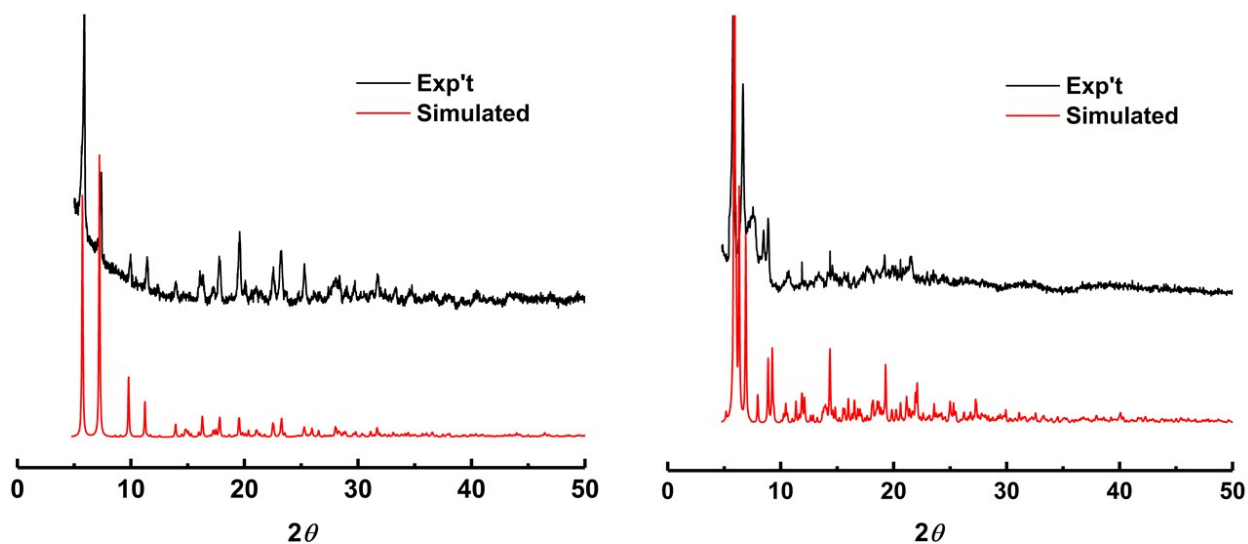

Fig. S3. Experimental and simulated X-ray powder diffraction (P-XRD) patterns for **1** (left) and **2** (right).

Crystal structure

Table S1 Crystallographic information for complexes **1** and **2**.[2a&b]

Compound reference	1	2
Chemical formula	$C_{102}H_{108}Dy_4N_{32}O_{18}$	$C_{164}H_{166}Dy_2N_{36}O_{12}$
Formula Mass g/mol	2720.2	3158.32
Crystal system	monoclinic	monoclinic
a (Å)	19.8689(16)	35.329(3)
b (Å)	31.487(3)	16.6830(14)
c (Å)	21.8015(16)	30.194(2)
α (°)	90	90
β (°)	116.894(3)	104.510(3)
γ (°)	90	90
Unit cell volume (Å^3)	12164.2(17)	17228(2)
Temperature (K)	300	180
Space group	$C2/c$ (no.15)	$C2/c$ (no.14)
Z	4	4
ρ_{calc} (g/cm^3)	1.483	1.218
F (000)	5400.0	6520.0
Radiation ($\lambda = 0.71073$)	Mo-Kα	Mo-Kα
Reflections collected	116732	66146
Independent reflections	16372	15339
R_{int}	0.0625	0.1414
GOF on F^2	1.518	1.013
R_1 (I $\geq$ 2 σ (I))	0.1195	0.0778
wR_2 (all data)	0.4113	0.2455
CCDC number	2181104	2181105

Table S2 Selected important bond distances and bond angles of **1** and **2**.

Complex 1			
Atoms	**Bond distances [Å]**	**Atoms**	**Bond angles [°]**
Dy1–O1	2.379(13)	O3–Dy1–O1	137.4(5)
Dy1–O2	2.4200(9)	O3–Dy1–O2	154.8(4)
Dy1–O3	2.270(15)	O4–Dy1–O5	135.8(5)
Dy1–O4	2.211(17)	O4–Dy1–O7^i	155.5(5)
Dy1–O5	2.345(12)	O5–Dy1–O1	135.3(5)
Dy1–O7^i	2.3387(8)	N3–Dy1–N1	141.5(5)
Dy1–N1	2.619(16)	O5^i–Dy2–O1	131.6(4)
Dy1–N3	2.592(17)	O6^i–Dy2–O5^i	133.0(5)
Dy2–O1	2.442(14)	O6^i–Dy2–O7	156.9(4)
Dy2–O2	2.3903(8)	O9–Dy2–O1	132.7(5)
Dy2–O5^i	2.412(13)	O9–Dy2–O2	160.3(4)
Dy2–O6^i	2.235(14)	N7–Dy2–N6	132.6(6)
Dy2–O7	2.2719(8)		
Dy2–O9	2.271(14)		
Dy2–N2	2.596(17)		
Dy2–N13^i	2.532(17)		
Dy1···Dy2	4.0086(15)		
Dy1···Dy2^i	3.8695(12)		
Dy···Dy$_{(packing-shortest)}$	9.9726(5)		

Complex 2			
Atoms	**Bond distances [Å]**	**Atoms**	**Bond angles [°]**
Dy1–O2	2.192(6)	O2–Dy1–O1	138.8(2)
Dy1–O3	2.262(6)	O3–Dy1–O5^i	150.2(2)
Dy1–O1	2.372(6)	O4^i–Dy1–O1	133.2(2)
Dy1–O4^i	2.360(5)	O5^i–Dy1–O4^i	138.1(2)
Dy1–O5^i	2.279(6)	N15^i–Dy1–N2	139.2(2)
Dy1–N2	2.565(7)	N1–Dy1–N2	135.5(3)
Dy1–N15^i	2.565(8)		
Dy1–N1	2.535(11)		
Dy1···Dy1^i	7.1451(9)		
Dy···Dy$_{(packing-shortest)}$	10.0499(11)		

Shape analysis

Table S3 The CShM values calculated by SHAPE 2.1 for complexes of **1** and **2** (highlighted are the shape of the complexes).[2c]

| Coordination Geometry	Complexes		
	1		**2**
	Dy1	Dy2	Dy1
Hexagonal bipyramid (D_{6h})	13.636	12.185	14.718
Cube (O_h)	11.053	10.217	12.691
Square antiprism (D_{4d})	3.027	4.740	3.150
Triangular dodecahedron (D_{2d})	1.888	2.653	1.315
Johnson gyrobifastigium J26 (D_{2d})	9.937	9.529	10.544
Johnson elongated triangular bipyramid J14 (D_{3h})	25.591	24.771	26.475
Biaugmented trigonal prism J50 (C_{2v})	2.482	3.645	2.237
Biaugmented trigonal prism (C_{2v})	2.254	3.142	2.028
Snub diphenoid J84 (D_{2d})	2.224	2.394	2.136

Crystal structure details
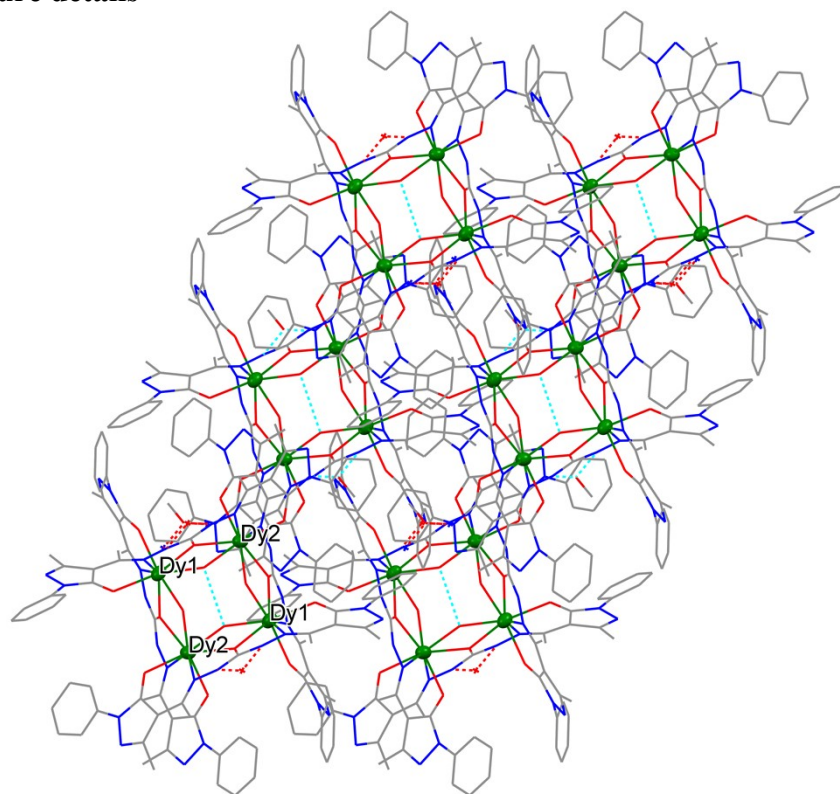
Fig. S4. Packing model along with b axis view of complex **1** respectively. Color code; green, Dy; red, O; blue, N; gray, C.
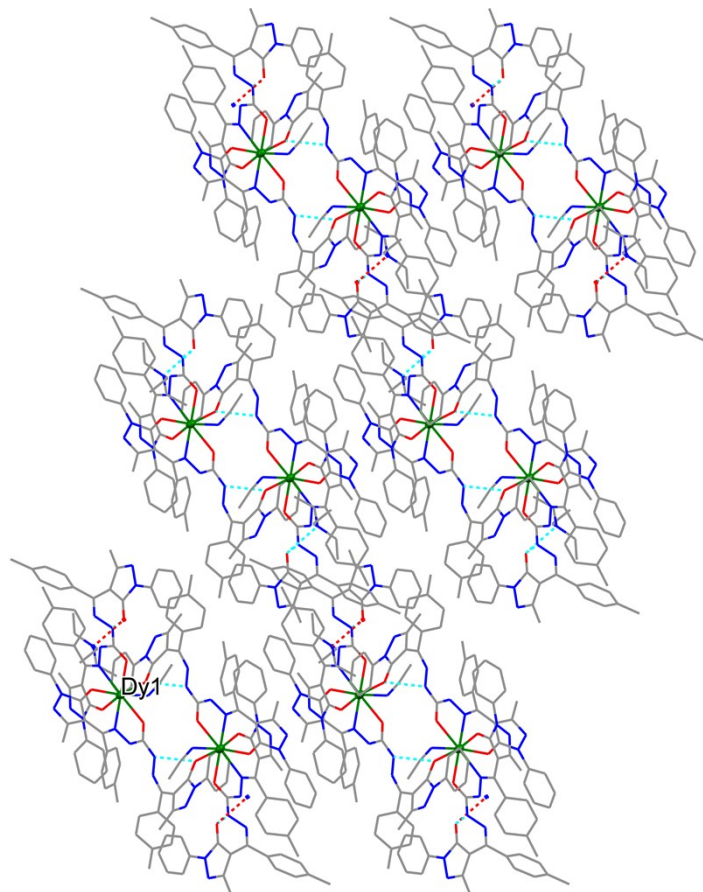
Fig. S5. Packing model along with b axis view of complex **2** respectively. Color code; green, Dy; red, O; blue, N; gray, C.
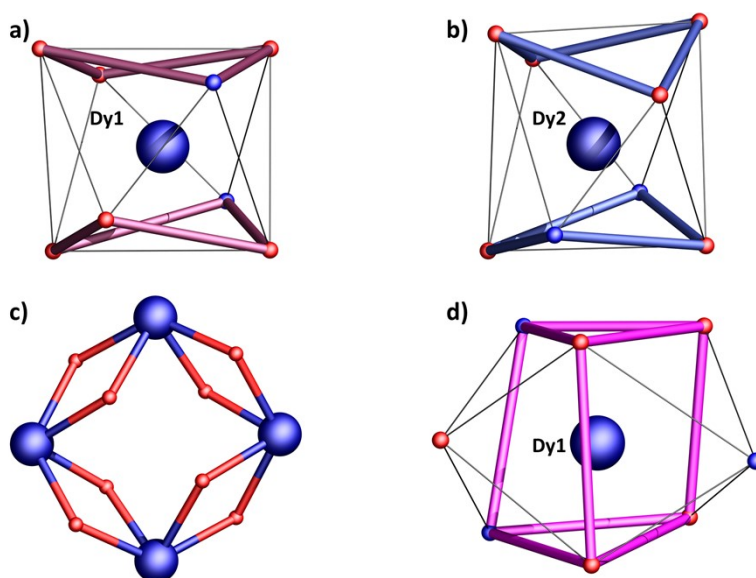

Fig. S6. (a, b) Coordination polyhedrons observed around the central metal atoms of complex of **1**. (c) μ_2−O$_{carbonyl}$ and μ_2−OH$^-$ bridging motifs for complex **1** in b axis view. (d) Coordination polyhedra observed in complex **2**. Color code; dark blue, Dy; red, O; blue, N.
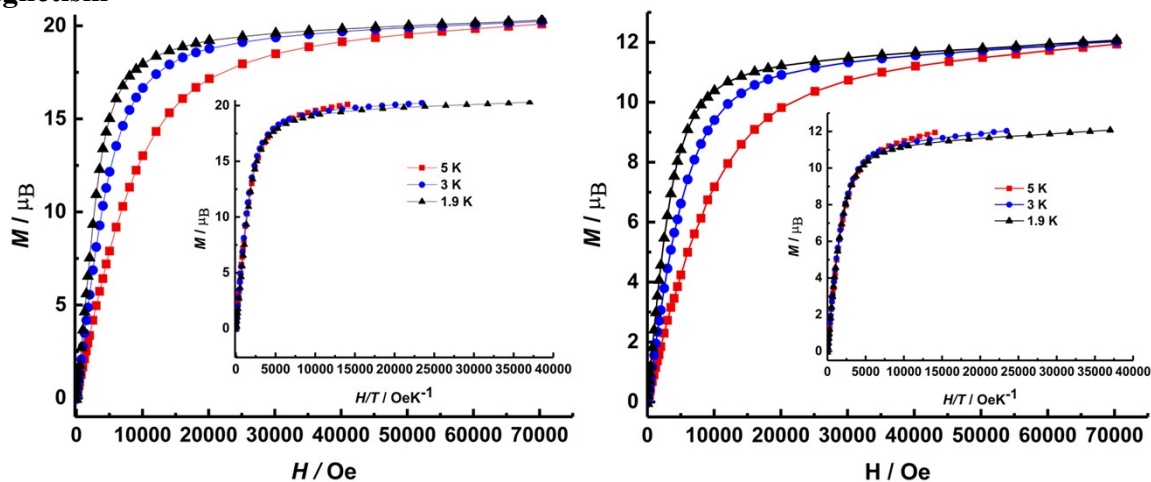
Magnetism

Fig. S7. Molar magnetization (*M*) *vs.* magnetic field (*H*) at 1.9, 3.0, and 5.0 K. for **1** (left) and **2** (right). Insets are the *M* vs *H*/T plots at the same temperature values.
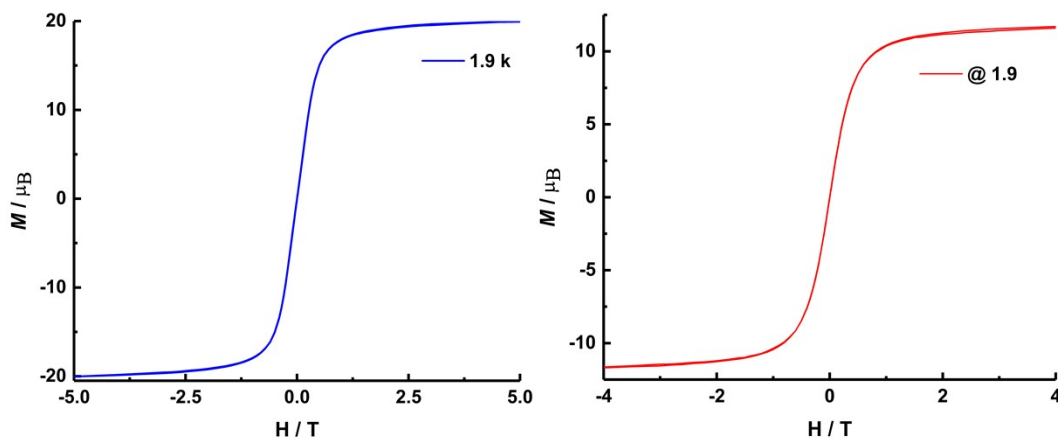

Fig. S8. Magnetic hysteresis loops at 1.9 K for **1** (left) and **2** (right) respectively.

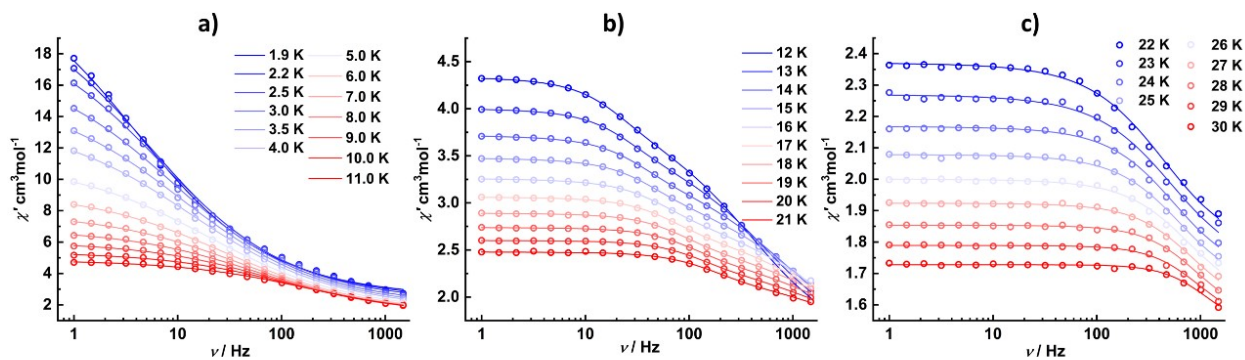

Fig. S9. Frequency-dependent in-phase (χ') plots for complex **1** (a; 1.9−11 K; b; 12−21 K; c; 22−30 K) where the solid lines represent fitting of the experimental data at different temperatures using the generalized Debye functions.

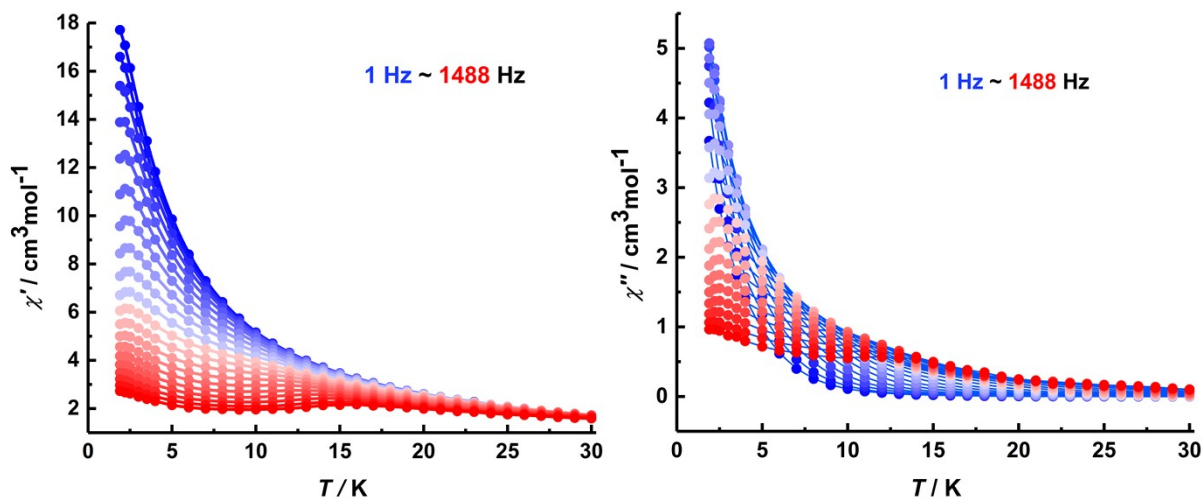**Fig. S10.** Plots of ac susceptibility vs. temperature oscillating at 1−1488 Hz for **1** in the temperature range of 1−30 K.
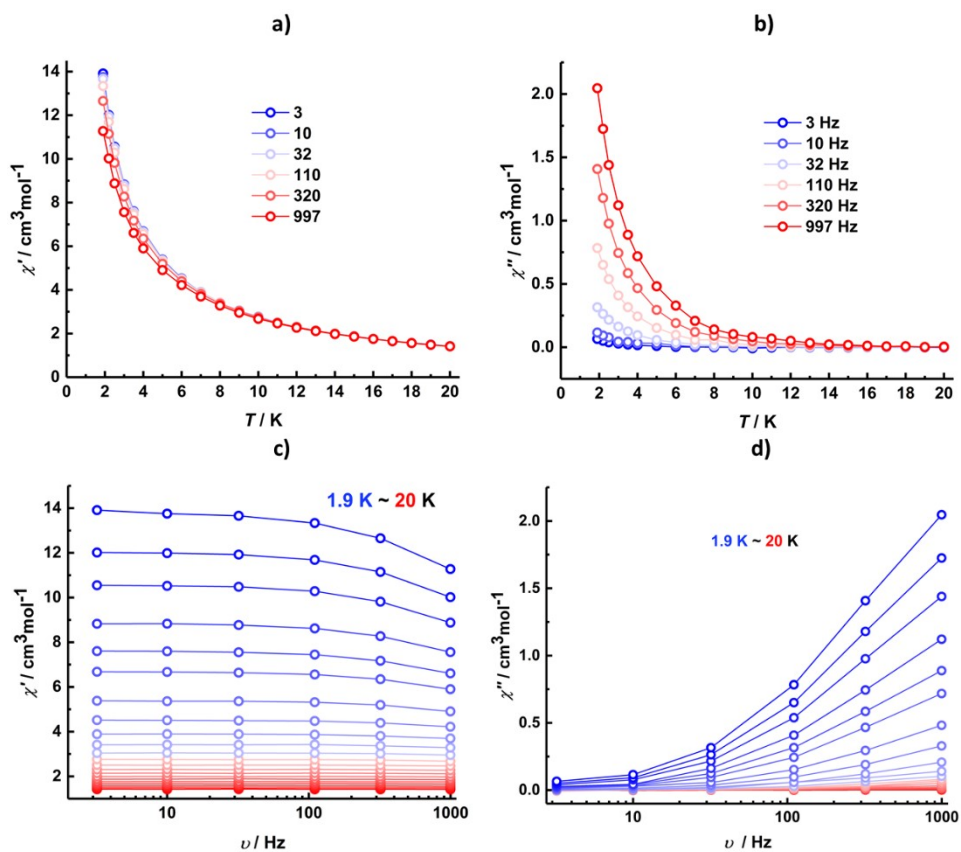

Fig. S11. Temperature- (a and b) and frequency- (c and d) dependent in-phase (χ') and out-phase (χ") plots for complex **2**.

Table S4 Relaxation fitting parameters for **1** from 1.9−11 K under a zero applied dc field.

T (K)	χ_S (cm³mol⁻¹)	χ_T (cm³mol⁻¹)	τ (s)	α
1.9	0.244302E+01	0.237250E+02	0.407292E-01	0.452653
2.2	0.230710E+01	0.219275E+02	0.300442E-01	0.451899
2.5	0.215060E+01	0.201494E+02	0.236667E-01	0.455965
3.0	0.193824E+01	0.176420E+02	0.178974E-01	0.463755
3.5	0.177603E+01	0.155958E+02	0.143137E-01	0.470324
4.0	0.166856E+01	0.138381E+02	0.117908E-01	0.474905
5.0	0.151163E+01	0.112150E+02	0.822111E-02	0.478405
6.0	0.141882E+01	0.931003E+01	0.569513E-02	0.473999
7.0	0.137936E+01	0.790958E+01	0.394733E-02	0.465300
8.0	0.138592E+01	0.684161E+01	0.278597E-02	0.451078
9.0	0.136839E+01	0.602635E+01	0.196012E-02	0.440453
10	0.134842E+01	0.537597E+01	0.135701E-02	0.433796
11	0.128974E+01	0.486046E+01	0.906202E-03	0.436270

Table S5. Relaxation fitting parameters for Cole-Cole plots of complex **1** from 12−20 K under zero applied dc-field using the sum of two modified Debye model.[3]

T (K)	$\chi_{S, tot}$	$\Delta\chi_1$	$\Delta\chi_2$	τ_1 (s)	α_1	τ_2 (s)	α_2
12	1.42510	2.40066	0.516387	0.391390E-03	0.318525	0.719803E-02	0.0153567
13	1.44414	2.08292	0.478638	0.277929E-03	0.312141	0.576194E-02	0.0213190
14	1.33835	1.97086	0.412387	0.178970E-03	0.352765	0.444365E-02	0.0120980
15	1.43628	1.63171	0.410770	0.147122E-03	0.337643	0.357631E-02	0.0229492
16	1.35527	1.53223	0.374984	0.986820E-04	0.369387	0.277951E-02	0.0244597
17	1.47811	1.20463	0.380564	0.945778E-04	0.322669	0.225593E-02	0.0315500
18	1.38198	1.16456	0.346569	0.657789E-04	0.354753	0.178916E-02	0.0173057
19	1.54859	8.59057	0.331244	0.817678E-04	0.308199	0.146326E-02	0.0225898
20	1.61308	6.79801	0.307738	0.914746E-04	0.276907	0.122509E-02	0.0277862

References
1. B. S. Jensen, *Acta Chem. Scand.*, 1959, **13**, 1668-1670.
2. (a) Sheldrick, G. M., *Acta Crystallogr. Sect. A* 2015, **71**, 3-8. (b) Sheldrick, G. M., *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71**, 3-8. (c) D. Casanova, M. Llunell, P. Alemany and S. Alvarez, *Chem. Eur. J.,* 2005, **11**, 1479-1494.
3. Y.-N. Guo, G.-F. Xu, Y. Guo and J. Tang, Dalton Trans., 2011, 40, 9953-9963.