Electronic Supplementary Information (ESI) for:

Single Molecule Magnet Behavior Observed in 1-D Dysprosium Chain with quasi-D_{5h} Symmetry

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Experimental Section

All preparations and manipulations were performed under aerobic conditions. The ligand H_2valdien was prepared according to a method described previously.[S1] Preparation of **$Na(PhO)_2PO_2$**. $(PhO)_2PO_2H$ (10 mmol, 0.25g) was added to the solution of NaOH (10 mmol, 0.4 g) in MeOH (20 mL), then the mixture was vigorously stirred for 2 hours at room temperature. The white solid ($Na(PhO)_2PO_2$) was obtained after evaporating the solution to dryness under reduced pressure without further purification for use directly.

$[DyNa(valdien)Cl((PhO)_2PO_2)]_n$ (1). To a solution of H_2valdien (0.15 mmol, 55 mg), Et_3N (0.30 mmol, 41.8 μL) in MeOH (3 mL) was added a MeOH solution (2 mL) of $DyCl_3·6H_2O$ (0.15 mmol, 57 mg). The solution was stirred for 3 min, and then a MeOH solution (2 mL) of $Na(PhO)_2PO_2$ (0.3 mmol, 81 mg) was added to the mixture. The resulting clear yellow solution was stirred briefly and filtered. The yellow block crystals suitable for X-ray diffraction studies were obtained by slow diffusion of isopropyl ether vapour into the yellow solution after 3 days. Yield: *ca*. 45%. Elemental analysis (%) calculated for $C_{32}H_{33}ClDyN_3NaO_8P$: C, 45.78; H, 3.96; N, 5.01. Found: C, 45.70; H, 3.85; N, 4.96. IR (KBr, cm^{-1}): 3439(w), 3200(w), 2916(w), 1626(vs), 1454(s), 1218(s), 1097(s), 899(m) and 741(m).

$[Dy(valdien)((PhO)_2PO_2)]_n$ (2). To a solution of H_2valdien (0.15 mmol, 55 mg), Et_3N (0.30 mmol, 41.8 μL) and $DyCl_3·6H_2O$ (0.15 mmol, 57 mg) in DMF/MeOH (5 mL, v/v = 1/4) was added a DMF/MeOH (5 mL, v/v = 1/4) solution of $(PhO)_2PO_2H$ (0.3 mmol, 112 mg) and Et_3N (0.45 mmol, 62.8 μL). The resulting clear yellow solution was stirred briefly and filtered. The yellow block crystals suitable for X-ray diffraction studies were obtained by slow diffusion of isopropyl ether vapour into the yellow solution after 3 days. Yield: *ca*. 30%. Elemental analysis (%) calculated for $C_{32}H_{33}DyN_3O_8P$: C, 49.21; H, 4.26; N, 5.38. Found: C, 49.11; H, 4.18; N, 5.22. IR (KBr, cm^{-1}): 3432(w), 3231(w), 2927(w), 1626(vs), 1449(m), 1225(vs), 1108(m),

939(m), 859(w), and 739(m).

[GdNa(valdien)Cl((PhO)$_2$PO$_2$)]$_n$ (3). The same procedure was used to synthesize **1** except that $DyCl_3 \cdot 6H_2O$ was used in place of $GdCl_3 \cdot 6H_2O$. Yield: *ca*. 53%. Elemental analysis (%) calculated for $C_{32}H_{33}ClGdN_3NaO_8P$: C, 46.07; H, 3.99; N, 5.04. Found: C, 46.14; H, 3.87; N, 5.18. IR (KBr, cm^{-1}): 3435(w), 3200(w), 2877(w), 1623(vs), 1450(m), 1220(vs), 1080(m), 901(m), 858(w), and 737(m).

[TbNa(valdien)Cl((PhO)$_2$PO$_2$)]$_n$ (4). The same procedure was used to synthesize **1** except that $DyCl_3 \cdot 6H_2O$ was used in place of $TbCl_3 \cdot 6H_2O$. Yield: *ca*. 48%. Elemental analysis (%) calculated for $C_{32}H_{33}ClTbN_3NaO_8P$: C, 45.98; H, 3.99; N, 5.03. Found: C, 45.76; H, 4.03; N, 5.11. IR (KBr, cm^{-1}): 3445(w), 3201(w), 2868(w), 1625(vs), 1446(m), 1213(vs), 1096(m), 901(m), 859(w), and 739(m).

[HoNa(valdien)Cl((PhO)$_2$PO$_2$)]$_n$ (5). The same procedure was used to synthesize **1** except that $DyCl_3 \cdot 6H_2O$ was used in place of $HoCl_3 \cdot 6H_2O$. Yield: *ca*. 42%. Elemental analysis (%) calculated for $C_{32}H_{33}ClHoN_3NaO_8P$: C, 45.65; H, 3.95; N, 4.99. Found: C, 45.77; H, 4.06; N, 4.88. IR (KBr, cm^{-1}): 3430(w), 3200(w), 2862(w), 1623(vs), 1449(m), 1220(vs), 1095(m), 911(m), 852(w), and 737(m).

[Ho(valdien)((PhO)$_2$PO$_2$)]$_n$ (6). The same procedure was used to synthesize **2** except that $DyCl_3 \cdot 6H_2O$ was used in place of $HoCl_3 \cdot 6H_2O$. Yield: *ca*. 25%. Elemental analysis (%) calculated for $C_{32}H_{33}HoN_3O_8P$: C, 49.05; H, 4.25; N, 5.36. Found: C, 48.89; H, 4.28; N, 5.22. IR (KBr, cm^{-1}): 3440(w), 3236(w), 2857(w), 1618(vs), 1458(m), 1215(vs), 1110(m), 931(m), 854(w), and 732(m).

Physical Measurements

Elemental analyses were carried out a Vario EL II Elementar. Infrared spectra were obtained on a Thermo Scientific Nicolet IS5 spectrometer. Powder X-ray diffraction (PXRD) were recorded at 298 K on a RINT2000 vertical goniometer with Cu Kα X-ray source (operated at 40kV and 100 mA). Magnetic measurements were performed on powdered samples with Quantum Design SQUID VSM magnetometers with field up to 7 T. All data were corrected for diamagnetism and the sample holder and of the constituent atoms using Pascal's constants.[S2]

X-ray data collection, structure solution and refinement for 1–6

The X-ray data of **1–6** were collected on a Bruker APEX II with a CCD area detector ($Mo_{K\alpha}$ radiation, λ = 0.71073 Å). The APEX II program was used to determine the unit cell parameters and for data collection. The data were integrated using SAINT [S3] and SADABS. [S4] The structures for two compounds were solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXTL program. [S5] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. Additional details of the data collections and structural refinement parameters are provided in Table S1 (**1** and **2**) and Table S2 (**3–6**). Selected bond lengths and bond angles for **1** and **2** are listed in Table S3. CCDC- 1415417 (**1**)， CCDC- 1415418 (**2**)，CCDC-1432155 (**3**), CCDC-1432156 (**4**), CCDC-1432157 (**5**) and CCDC-1432220 (**6**) contain 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.

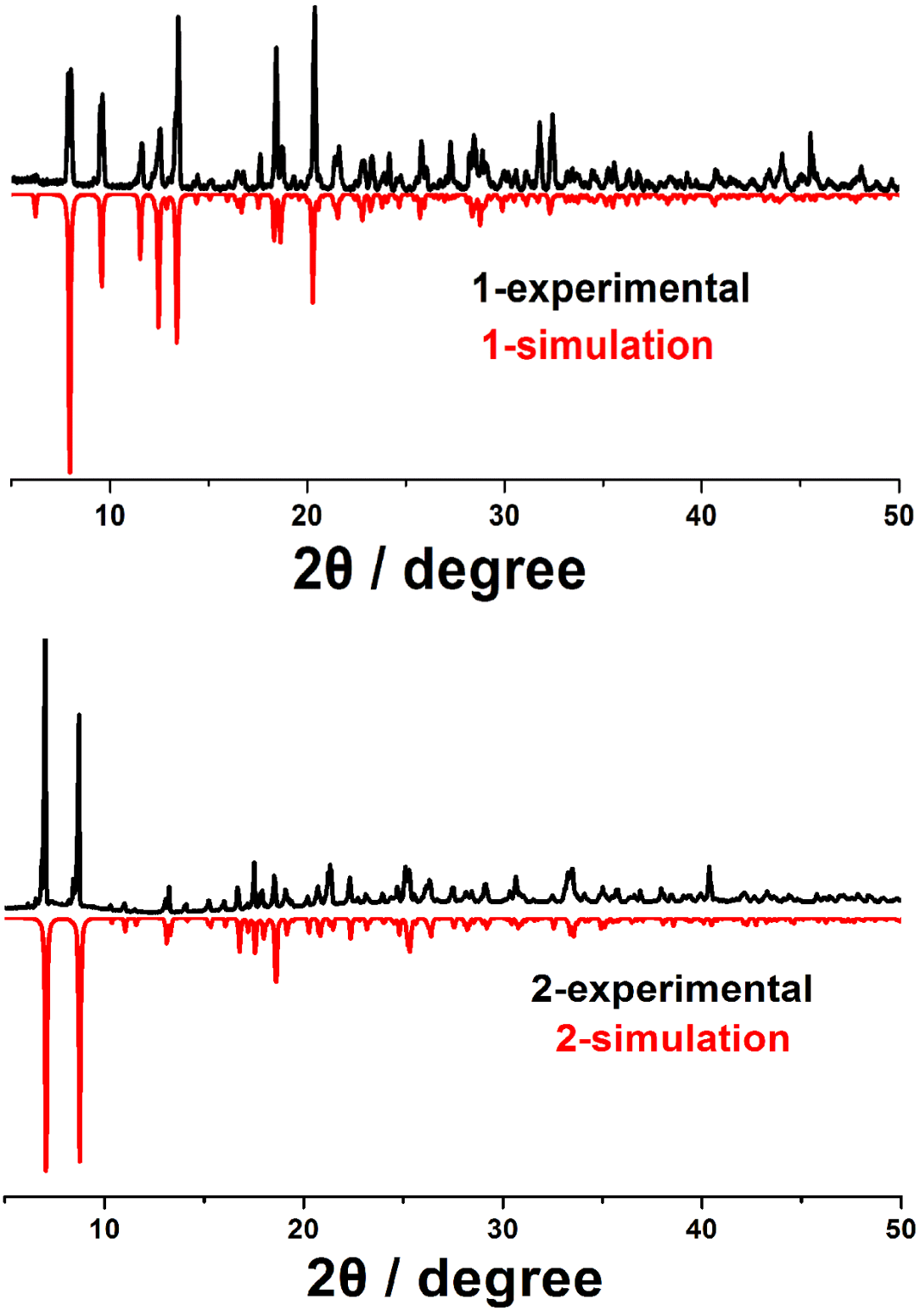

Figure S1. The powder XRD patterns for compound **1** and **2**. The pattern simulated from the single crystal data of compound **1** and **2** are also given.

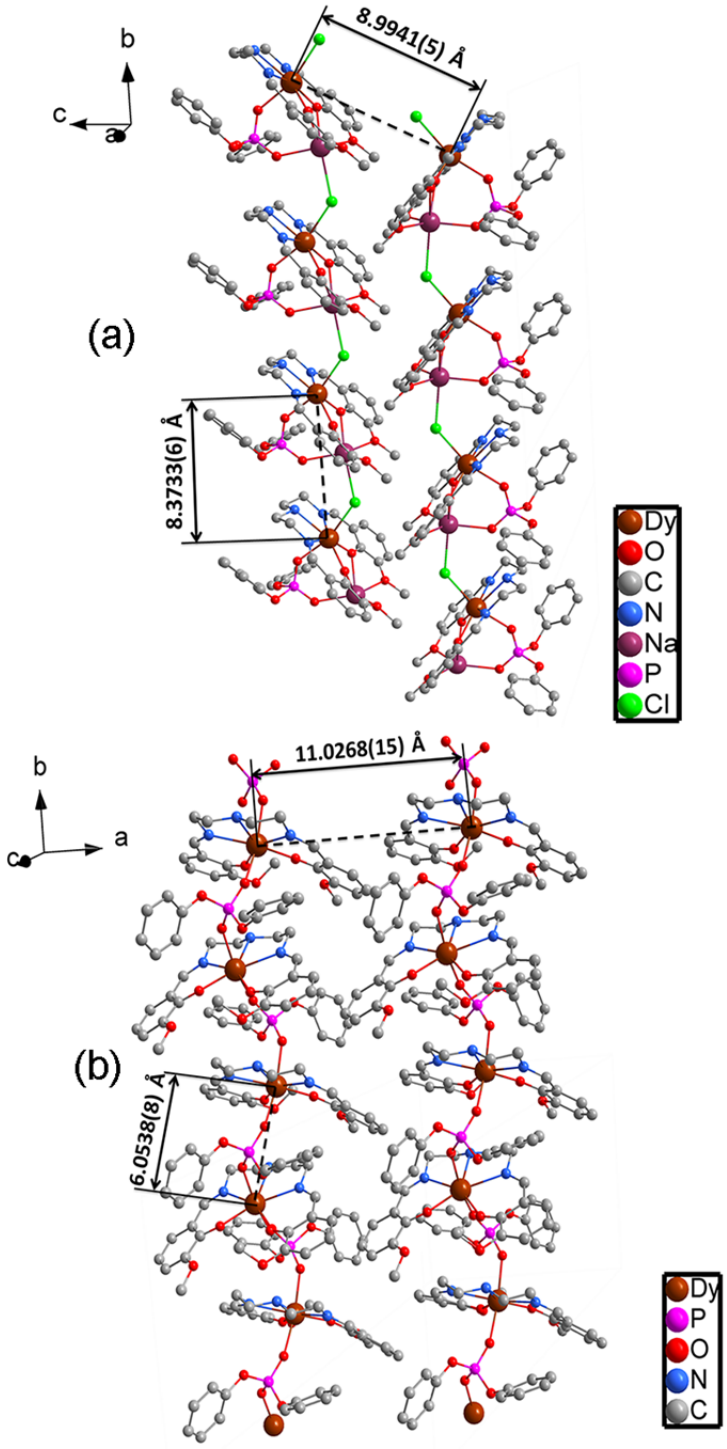

Figure S2. The crystal packing of **1** (**a**) and **2** (**b**). The shortest distances of Dy···Dy in the chain for **1** (a) and **2** (b) are 8.3733(6) and 6.0583(8) Å, respectively. And the nearest distances of Dy···Dy between the chain for **1** (a) and **2** (b) are 8.9941(5) and 11.0268(15) Å, respectively.

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

complex	**1**	**2**
Formula	$DyNaC_{32}H_{33}N_3O_8ClP$	$DyC_{32}H_{33}N_3O_8P$
*M*r [gmol^{-1}]	839.52	781.08
CCDC number	1415417	1415418
Crystal size[mm^3]	0.54×0.50×0.48	0.24× 0.21×0.16
Crystal system	Orthorhombic	Monoclinic
Space group	*P bca*	$P\ 2_1/_C$
a [Å]	22.2015(14)	11.0268(15)
b [Å]	8.3733(5)	11.6462(16)
c [Å]	36.918(2)	27.317(3)
α [˚]	90	90
β [˚]	90	113.808(4)
γ [˚]	90	90
V [Å^3]	6863.0(7)	3209.5(7)
Z	8	4
T , K	293(2)	293(2)
ρ_{calcd}[g cm^{-3}]	1.625	1.616
μ(Mo–*K*α) [mm^{-1}]	2.368	2.432
F (000)	3352	1564
θ range [˚]	1.83 – 27.63	1.93 – 27.62
Refl. collected / unique	43751 / 7952	20718 / 7318
R(int)	0.0311	0.0537
T_{max}/T_{min}	0.3961 / 0.3613	0.6969 / 0.5929
Data/restraints/parameters	7952 / 0 / 430	7318 / 0 / 408
R_1[a] /wR_2[b] ($I > 2\sigma(I)$)	0.0403 / 0.0792	0.0390 / 0.0808
R_1/wR_2 (all data)	0.0496 / 0.0823	0.0678 / 0.1016
GOF on F^2	1.239	1.032
Max/min [e Å^{-3}]	1.391 / -1.942	0.725 / -0.953

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S2. Crystallographic data and structure refinement for isostructural complexes **3**–**6**.

complex	**3**	**4**	**5**	**6**
Formula	$GdNaC_{32}H_{33}ClN_3O_8P$	$TbNaC_{32}H_{33}N_3O_8ClP$	$HoNaC_{32}H_{33}NO_8ClP$	$HoC_{32}H_{33}N_3O_8P$
*M*r [gmol^{-1}]	834.27	835.94	841.95	783.51
CCDC number	1432155	1432156	1432157	1432220
Crystal size[mm^3]	0.32 × 0.31 × 0.28	0.54 × 0.46 × 0.35	0.41 × 0.22 × 0.10	0.24 × 0.20 × 0.14
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*P bca*	*P bca*	*P bca*	$P\,2_1/_C$
a [Å]	22.267(3)	22.2076(17)	22.220(4)	10.990(2)
b [Å]	8.4192(13)	8.4021(7)	8.3683(16)	11.579(2)
c [Å]	36.839(6) A	36.877(3)	36.890(7)	27.216(5)
α [˚]	90.00	90.00	90.00	90.00
β [˚]	90.00	90.00	90.00	113.817(6)
γ [˚]	90.00	90.00	90.00	90.00
V [Å^3]	6906.3(18)	6880.9(10)	6859(2)	3168.4(10)
Z	8	8	8	4
T , K	293(2)	293(2)	293(2)	293(2)
ρ_{calcd}[g cm^{-3}]	1.605	1.614	1.631	1.643
μ(Mo–*K*α) [mm^{-1}]	2.110	2.245	2.497	2.603
F (000)	3336	3344	3360	1568
θ range [˚]	2.14 –27.47	2.14 – 27.45	1.43 – 27.47	1.94 – 26.00
Refl. collected / unique	42211 / 7834	41969 / 7836	42754 / 7821	33248 / 5992
R(int)	0.0438	0.0575	0.0726	0.0367
T_{max}/T_{min}	0.5896 / 0.5517	0.5071 / 0.3769	0.7883 / 0.4275	0.7120 /0.5739
Data/restraints/ parameters	7834 / 0 / 426	7836 / 0 / 426	7821 / 0 / 426	6206 / 144 / 408
R_1[a] /wR_2 [b] ($I > 2\sigma(I)$)	0.0415 / 0.0738	0.0425 / 0.0777	0.0367 / 0.0852	0.0357/0.0744
R_1/wR_2 (all data)	0.0561 / 0.0778	0.0651 / 0.0842	0.0722 / 0.1134	0.0480/ 0.0798
GOF on F^2	1.173	1.077	1.014	1.064
Max/min [e Å^{-3}]	0.821 /-2.064	1.045 / -1.489	0.532 / -0.697	1.460 / -1.869

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S3. Selected Bond Lengths (Å) and Angles (°) for **1** and **2**.

1					
Dy1-O1	2.211(3)	O1-Dy1-O5	89.49(10)	O3-Dy1-N3	72.36(11)
Dy1-O3	2.232(3)	O3-Dy1-O5	89.06(10)	O5-Dy1-N3	85.95(11)
Dy1-O5	2.294(3)	O1-Dy1-N2	140.60(11)	N2-Dy1-N3	68.06(12)
Dy1-N2	2.493(3)	O3-Dy1-N2	139.34(11)	N1-Dy1-N3	136.42(12)
Dy1-N1	2.515(4)	O5-Dy1-N2	79.41(10)	O1-Dy1-Cl1	103.71(8)
Dy1-N3	2.530(4)	O1-Dy1-N1	73.31(11)	O3-Dy1-Cl1	104.32(8)

Dy1-Cl1	2.6390(12)	O3-Dy1-N1	150.16(11)	O5-Dy1-Cl1	162.87(7)
Dy1-Na1	3.6270(16)	O5-Dy1-N1	86.20(11)	N2-Dy1-Cl1	83.46(8)
		N2-Dy1-N1	68.36(12)	N1-Dy1-Cl1	87.21(9)
O1-Dy1-O3	77.21(10)	O1-Dy1-N3	149.28(11)	N3-Dy1-Cl1	87.98(9)
O1-Dy1-Na1	40.57(8)	O3-Dy1-Na1	40.83(8)	O5-Dy1-Na1	75.05(7)
N2-Dy1-Na1	154.46(8)	N1-Dy1-Na1	109.82(9)	N3-Dy1-Na1	109.30(9)
Cl1-Dy1-Na1	122.08(4)				
2					
Dy1-O1	2.197(3)	O1-Dy1-O6[a]	99.69(13)	N3-Dy1-N2	66.78(14)
Dy1-O3	2.202(3)	O3-Dy1-O6[a]	91.83(13)	O1-Dy1-N1	72.52(14)
Dy1-O5	2.261(3)	O5-Dy1-O6[a]	163.10(13)	O3-Dy1-N1	153.81(14)
Dy1-O6[a]	2.279(3)	O1-Dy1-N3	152.56(14)	O5-Dy1-N1	86.58(13)
Dy1-N3	2.532(4)	O3-Dy1-N3	71.56(14)	O6[a]-Dy1-N1	85.61(13)
Dy1-N2	2.533(4)	O5-Dy1-N3	85.28(13)	N3-Dy1-N1	134.35(15)
Dy1-N1	2.536(4)	O6[a]-Dy1-N3	89.50(13)	N2-Dy1-N1	67.59(14)
		O1-Dy1-N2	139.87(14)	O3-Dy1-O5	101.69(13)
O1-Dy1-O5	92.21(13)	O3-Dy1-N2	137.85(13)	O6[a]-Dy1-N2	81.83(13)
O1-Dy1-O3	82.28(13)	O5-Dy1-N2	81.33(14)		

Symmetry transformations used to generate equivalent atoms: [a] x, y-1, z

Table S4. Continuous Shape Measures calculation for **1** and **2**.

Structure [ML7]	HP-7	HPY-7	PBPY-7	COC-7	CTPR-7	JPBPY-7	JETPY-7
1	33.490	25.169	0.775	8.133	6.113	4.712	23.157
2	33.887	24.701	0.496	6.561	4.970	3.056	23.699

HP-7 1 D7h Heptagon; HPY-7 2 C6v Hexagonal pyramid;

PBPY-7 3 D5h Pentagonal bipyramid; COC-7 4 C3v Capped octahedron;

CTPR-7 5 C2v Capped trigonal prism; JPBPY-7 6 D5h Johnson pentagonal bipyramid J13;

JETPY-7 7 C3v Johnson elongated triangular pyramid J7

Table S5. Crystal field parameters and anisotropy g-factors for **1** and **2** fitted from $\chi_M T$ *vs*. *T* and *M vs*. *H* data.

	1	**2**
B_2^0	-21.203	-17.096
B_4^0	-36.539	-26.606
B_6^0	56.616	55.275
g_x	1.320	1.927
g_y	1.373	0.128
g_z	1.189	1.342
Residual	0.038	0.041

Table S6. The substates and corresponding energy levels **1** and **2**.

1		**2**	
$\|m_J\rangle$	E(cm^{-1})	$\|m_J\rangle$	E(cm^{-1})
±13/2	0	±13/2	0
±11/2	41.63	±11/2	45.65
±1/2	53.49	±1/2	46.09
±3/2	87.11	±3/2	80.71
±9/2	119.8	±9/2	122.0
±5/2	131.8	±5/2	127.5
±7/2	152.3	±7/2	151.0
±15/2	200.7	±15/2	183.3

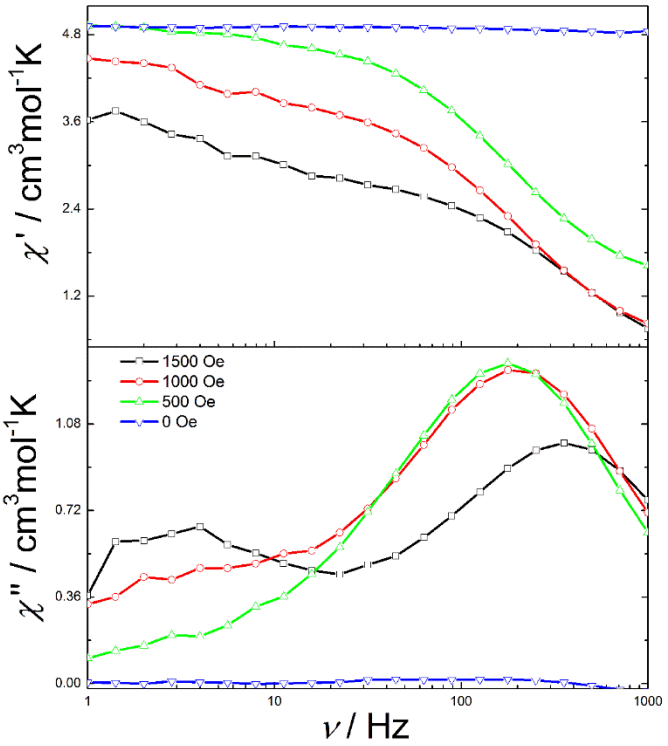

Figure S3. Frequency dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibility for **1** at 2 K under the applied static field from 0 to 1500 Oe. The solid lines are a guide for the eye.

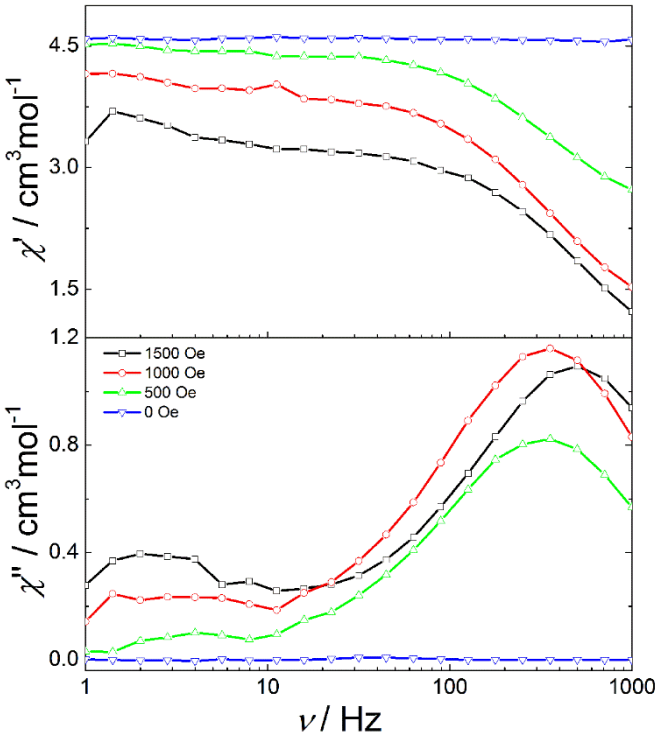

Figure S4. Frequency dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibility for **2** at 2 K under the applied static field from 0 to 1500 Oe. The solid lines are a guide for the eye.

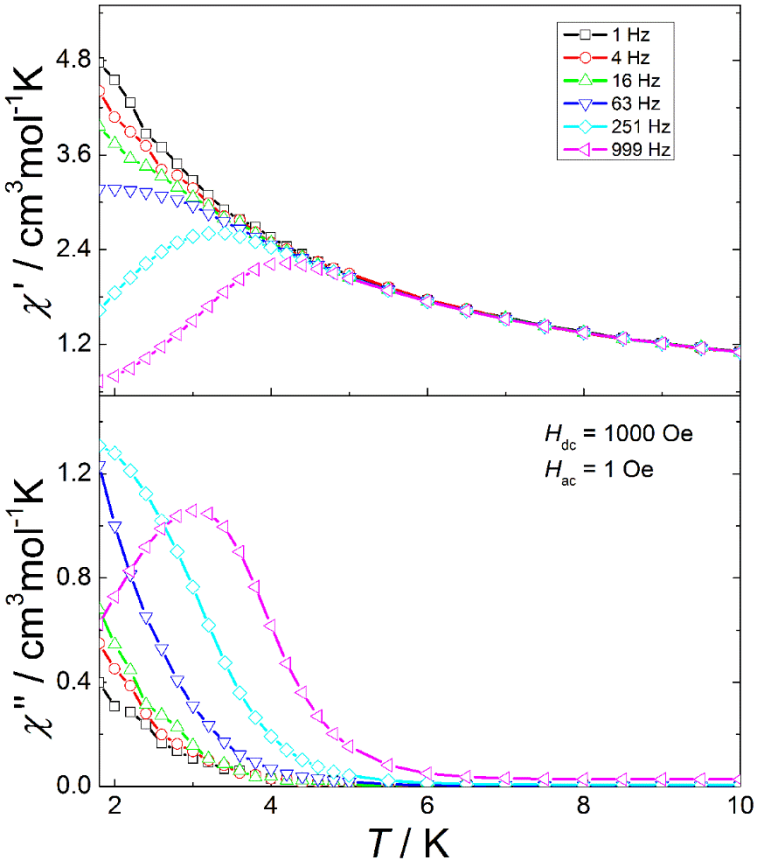

Figure S5. Temperature dependence of the in-phase and out-of-phase ac susceptibility data for **1** under 1000 Oe dc field range from 1.8 to 10 K (H_{ac}= 1 Oe). The solid lines are a guide for the eye.

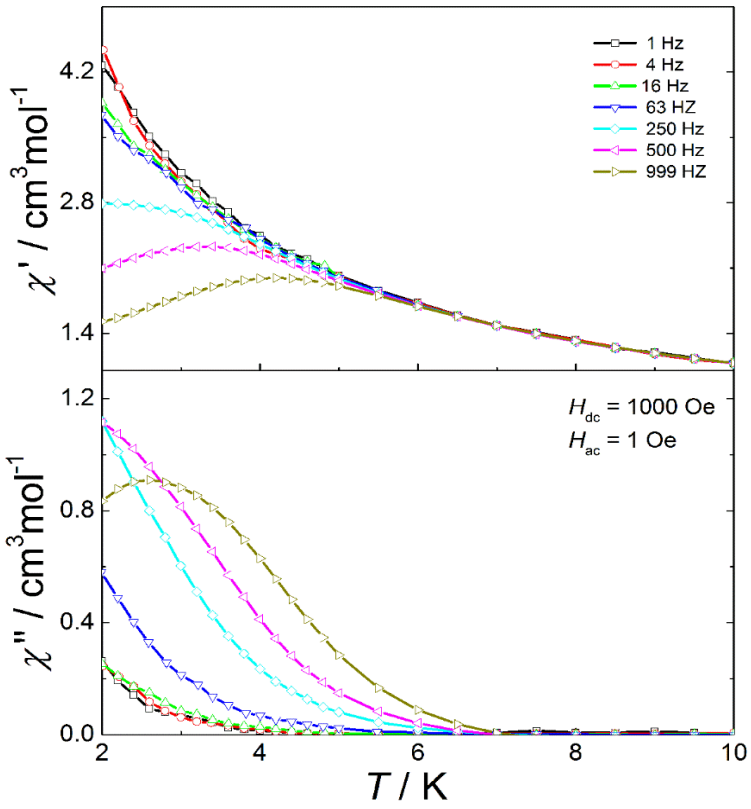

Figure S6. Temperature dependence of the in-phase and out-of-phase ac susceptibility data for **2** under 1000 Oe dc field range from 2 to 10 K (H_{ac}= 1 Oe). The solid lines are a guide for the eye.

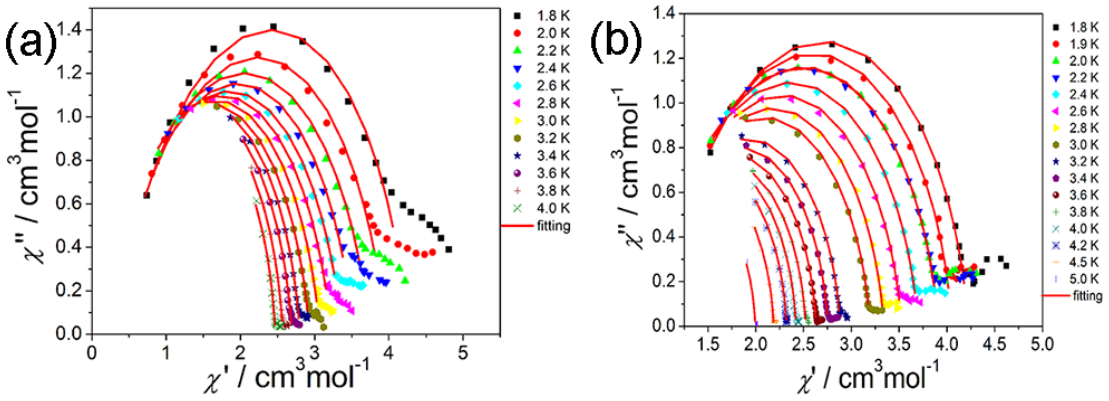

Figure S7. The Cole-Cole plots at 1.8–4.0 K of 1 (a) and at 1.8–5.0 K of 2 (c) measured under 1000 Oe dc field (H_{ac}= 1 Oe), and the red solid lines are the best fitting according to the generalized Debye model.

Table S7. Relaxation Fitting Parameters from the Least-Square Fitting of the Cole-Cole plots of **1** according to the Generalized Debye Model. [a]

Temperature / K	χ_S / cm^{3}mol^{-1}K	χ_T / cm^{3}mol^{-1}K	τ / s	α
1.8	0.3007	4.26079	0.00125	0.21613
2.0	0.24872	3.96021	9E-4	0.23388
2.2	0.08	3.75	6.3E-4	0.26204
2.4	0.17654	3.52561	4.8E-4	0.23201
2.6	0.09349	3.37062	3.4E-4	0.23747

2.8	0.05413	3.2255	2.5E-4	0.22901
3.0	0.07196	3.07289	1.9E-4	0.20791
3.2	0.07427	2.93357	1.4E-4	0.18789
3.4	0.09215	2.80117	1E-4	0.15851
3.6	0.12008	2.69382	8E-5	0.14092
3.8	0.15747	2.57161	6E-5	0.11322
4.0	0.15366	2.46967	4E-5	0.09959

[a]The Generalized Debye equation: $\chi'' = (\chi_S-\chi_T)\ \tanh[\alpha\pi/2]/2 + \{(\chi'-\chi_S)(\chi_T-\chi') + (\chi_T-\chi_S)^2\ \tanh^2[\alpha\pi/2]/4\}^{1/2}$ (1), where χ_S is the adiabatic magnetic susceptibility and χ_T is the isothermal magnetic susceptibility; χ' is in-phase susceptibility and χ'' is out-of-phase susceptibility.

Table S8. Relaxation Fitting Parameters from the Least-Square Fitting of the Cole-Cole plots of **2** according to the Generalized Debye Model. [a]

Temperature / K	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
1.8	1.05191	4.22402	5.9E-4	0.13751
1.9	1.00641	4.0556	5.3E-4	0.13933
2.0	0.91727	3.91552	4.8E-4	0.16110
2.2	0.94394	3.90885	4E-4	0.15365
2.4	0.89640	3.70188	3.3E-4	0.15746
2.6	0.91505	3.52592	2.9E-4	0.14628
2.8	0.90774	3.34191	2.4E-4	0.13855
3.0	0.90059	3.19673	2E-4	0.12951
3.2	0.89943	2.88249	1.7E-4	0.10524
3.4	0.90184	2.75335	1.5E-4	0.09352
3.6	0.88372	2.63081	1.3E-4	0.08295
3.8	0.85160	2.52265	1E-4	0.08740
4.0	0.78402	2.42057	9E-5	0.08155
4.2	0.74374	2.32119	7E-5	0.07072
4.5	0.68980	2.18606	5E-5	0.06711
5.0	0.68457	1.99502	3E-5	0.06768

Reference

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