Probing the Magnetic Relaxation and Magnetic Moments Arrangement in a Series of Dy_4 Squares

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Table S1. Crystallographic data for complexes **1-3**.

	1	**2**	**3**
Formula	$C_{98}H_{149}Dy_8N_{11}O_{56}$	$C_{54}H_{88}Dy_4N_6O_{23}S_2$	$C_{52}H_{68}Dy_4N_6O_{23}S_2$
FW, $g\cdot mol^{-1}$	3677.28	1903.42	1859.24
crystal system	Monoclinic	Triclinic	Triclinic
space group	*C2/c*	*P-1*	*P-1*
T, K	273(2)	296(2)	273(2)
λ, Å	0.71073	0.71073	0.71073
a, Å	27.3361(9)	10.465(6)	10.1501(6)
b, Å	26.2199(9)	13.832(7)	12.5967(8)
c, Å	22.9128(8)	14.762(8)	13.2679(8)
α, °	90	68.793(9)	87.2500(10)
β, °	92.2230(10)	88.158(11)	82.0570(10)
γ, °	90	68.409(9)	68.6090(10)
V, $Å^3$	16410.4(10)	1839.8(16)	1564.38(17)
Z	4	1	1
ρ_{calcd}, $g\cdot cm^{-3}$	1.488	1.718	1.974
GOF on F^2	1.039	1.084	1.105
reflns collected	45670	11398	9792
R_1 ($I \geq 2\sigma(I)$)	0.0432	0.0393	0.0445
wR_2 (all data)	0.1355	0.1214	0.1375
CCDC	1432432	1432431	1432430

Table S2. Selected bond distances (Å) and angles (°) for complexes **1**, **2** and **3**.

Complex **1**		Complex **2**		Complex **3**	
Dy(1)-O(1)	2.4855(72)	Dy(1)-O(1)	2.4935(11)	Dy(1)-O(1)	2.4534(4)
Dy(2)-O(1)	2.4902(63)	Dy(2)-O(1)	2.4662(12)	Dy(2)-O(1)	2.5317(4)
Dy(3)-O(1)	2.5056(74)				
Dy(4)-O(1)	2.5274(66)				
Average Dy-O	2.5024(25)	Average Dy-O	2.4798(5)	Average Dy-O	2.4925(5)
Dy(1)-Dy(2)	3.5689(8)	Dy(1)-Dy(2)	3.4922(17)	Dy(1)-Dy(2)	3.5237(6)
Dy(2)-Dy(3)	3.5648(8)	Dy(1)-Dy(2)A	3.5219(19)	Dy(1)-Dy(2)A	3.5272(6)
Dy(3)- Dy(4)	3.5686(8)	Dy(1)-Dy(1)A	4.9870(22)	Dy(1)-Dy(1)A	4.9069(6)
Dy(4)- Dy(1)	3.5657(7)	Dy(2)-Dy(2)A	4.9323(23)	Dy(2)-Dy(2)A	5.0634(6)
Average Dy-Dy	3.5670	Average Dy-Dy	3.5077	Average Dy-Dy	3.5254
Dy(1)-O1-Dy(2)	91.658	Dy(1)-O1-Dy(2)	89.514(21)	Dy(1)-O1-Dy(2)	89.944(12)
Dy(2)-O1-Dy(3)	91.051	Dy(1)-O1-Dy(2)A	90.486(20)	Dy(1)-O1-Dy(2)A	90.056(12)
Dy(3)-O1-Dy(4)	90.289				
Dy(4)-O1-Dy(1)	90.656				
Average Dy-O-Dy	90.914	Average Dy-O-Dy	90	Average Dy-O-Dy	90
Dy(1)-O1-Dy(3)	164.861	Dy(1)-O1-Dy(1)A	180	Dy(1)-O1-Dy(1)A	180
Dy(2)-O1-Dy(4)	166.064	Dy(2)-O1-Dy(2)A	180	Dy(2)-O1-Dy(2)A	180
symmetry code:		A (1-x, 1-y, 1-z)		A (-x, 2-y, 1-z)	

Table S3. Bond valence sum calculations[1] for complexes **1**-**3** and [$Dy_4(\mu_4$-OH)] reported in the literature.

	[$Dy_4(\mu_4$-OH)] ref 25		Complex **1**		Complex **2**		Complex **3**	
Bond	R	S a)	R	S	R	S	R	S
Dy(1)-O(1)	2.506	0.2736	2.485	0.289	2.493	0.283	2.453	0.315
Dy(2)-O(1)	2.500	0.2779	2.490	0.285	2.466	0.304	2.531	0.257
Dy(3)-O(1)	2.513	0.2687	2.505	0.274				
Dy(4)-O(1)	2.529	0.2578	2.527	0.259				
BVS		1.078		1.107		1.174		1.144

S= $(R/R_1)^{-N}$, R_1=2.053 and N=6.5 for Dy^{3+}.

Table S4. The *CShM* values calculated by *SHAPE* 2.1 for **1** and [$Dy_4(\mu_4$-OH)] [ref 25].

Coordination Geometry	Complex **1**				[Dy_4(□$_4$-OH)] [ref 25]			
	Dy1	Dy2	Dy3	Dy4	Dy1	Dy2	Dy3	Dy4
Capped square antiprism J10 (C_{4v})	2.004	1.875	2.123	1.822	1.920	1.951	1.903	1.966
Spherical capped square antiprism (C_{4v})	1.363	1.175	1.424	1.146	1.179	1.218	1.081	1.200
Tricapped trigonal prism J51 (D_{3h})	3.630	3.458	3.748	3.252	3.318	3.386	3.057	3.463
Spherical tricapped trigonal prism (D_{3h})	1.882	1.785	1.857	1.857	1.875	1.867	2.036	1.788

Table S5. The *CShM* values calculated by *SHAPE* 2.1 for **2** and **3.**

Coordination Geometry		Complex **2**	Complex **3**
Capped square antiprism J10 (C_{4v})	Dy1	1.690	1.852
Spherical capped square antiprism (C_{4v})		1.064	0.965
Tricapped trigonal prism J51 (D_{3h})		1.333	2.268
Spherical tricapped trigonal prism (D_{3h})		0.782	0.934
Square antiprism (D_{4d})	Dy2	2.501	3.076
Triangular dodecahedron (D_{2d})		2.740	2.972
Biaugmented trigonal prism J50 (C_{2v})		2.395	2.438
Biaugmented trigonal prism (C_{2v})		2.168	3.725

Table S6. Minimal reorientation energies (cm^{-1}) calculated from Magellan program[2] for complexes **1-3**.

Complex **1**		Complex **2**		Complex **3**	
Dy(1)	266.0	Dy(1)	188.8	Dy(1)	124.1
Dy(2)	289.3	Dy(2)	589.8	Dy(2)	382.9
Dy(3)	294.7				
Dy(4)	266.2				

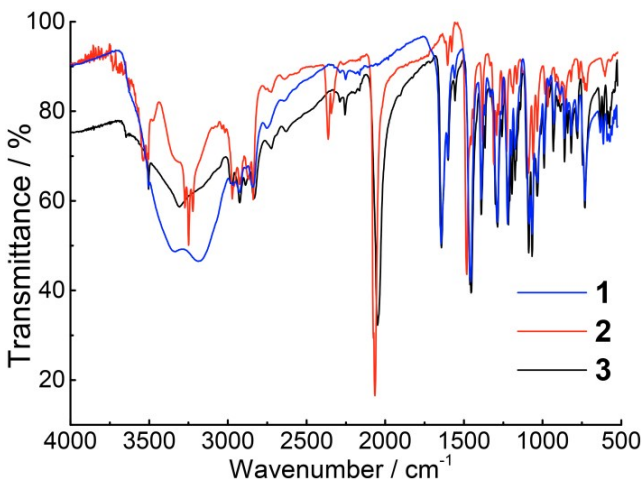

Fig. S1 IR spectra of complexes **1** (blue), **2** (red) and **3** (gray).

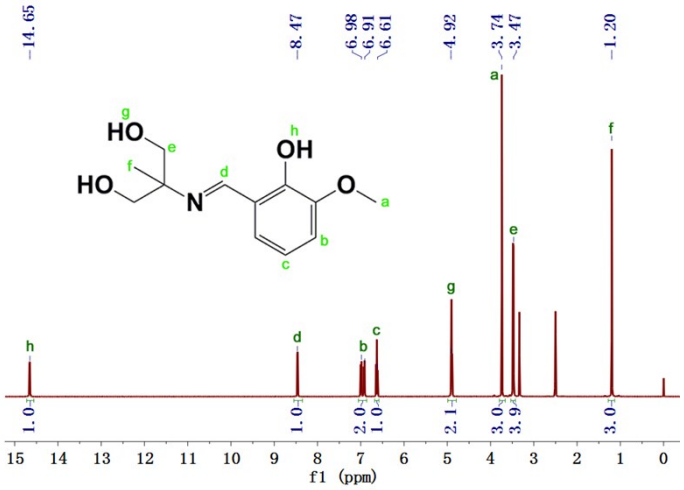

Fig. S2 ^{1}H NMR spectrum of ligand H_3L^1 at 295.0 K (DMSO, 400 MHz).

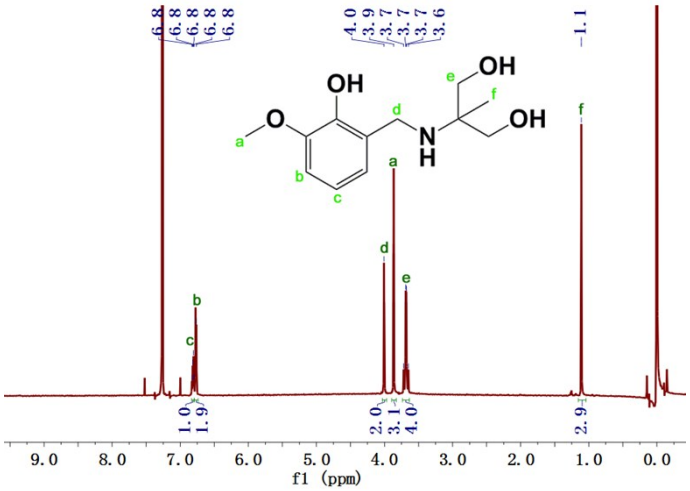

Fig. S3 ^{1}H NMR spectrum of ligand H_3L^2 at 295.0 K ($DCCl_3$, 400 MHz). The active hydrogen atoms are substituted by deuterated reagent.

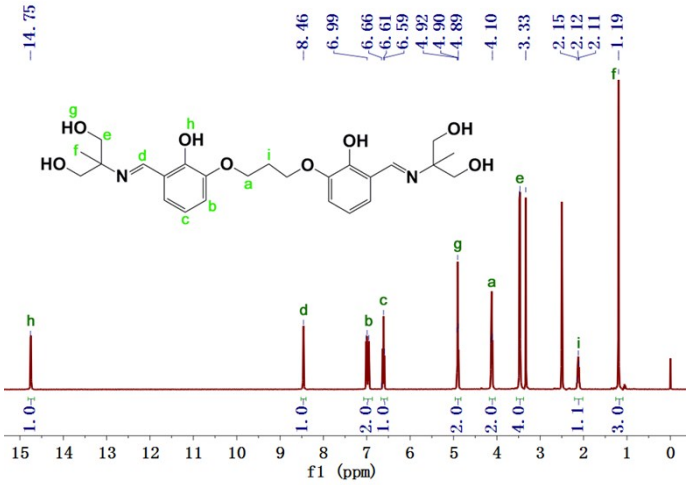

Fig. S4 ^{1}H NMR spectrum of ligand H_6L^3 at 295.0 K (DMSO, 400 MHz).

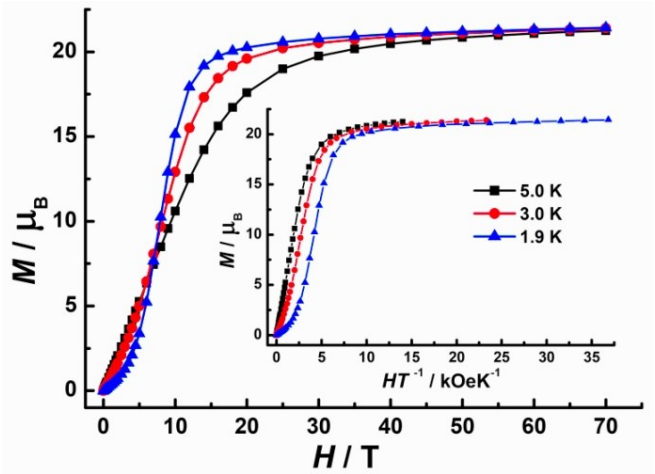

Fig. S5 Molar magnetization (*M*) versus magnetic field (*H*) for **1** at indicated temperature. Inset represents the plots of magnetization *M* versus *H*/*T*.

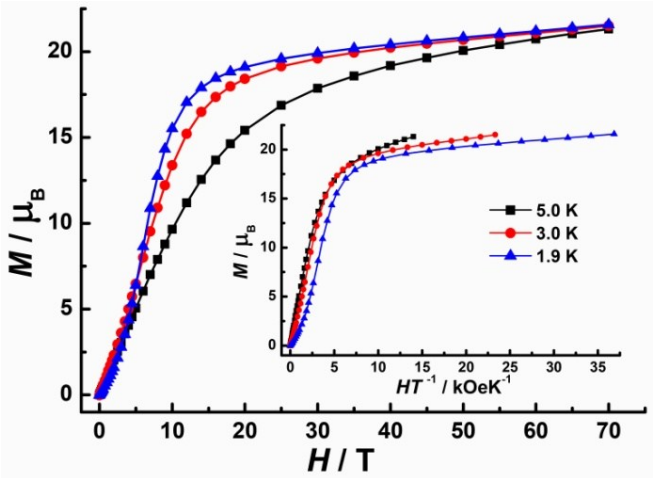

Fig. S6 Molar magnetization (*M*) versus magnetic field (*H*) for **2** at indicated temperature. Inset represents the plots of magnetization *M* versus *H*/*T*.

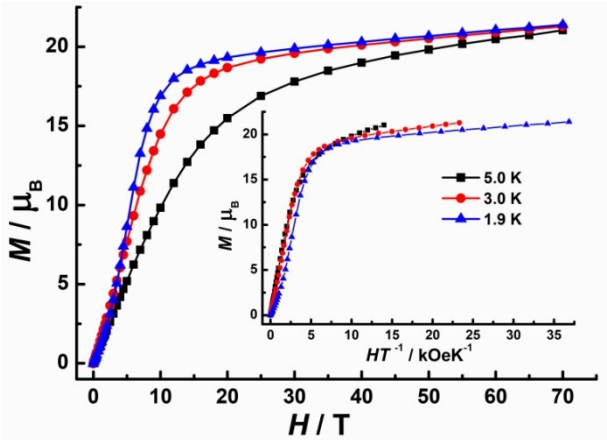

Fig. S7 Molar magnetization (*M*) versus magnetic field (*H*) for **3** at indicated temperature. Inset represents the plots of magnetization *M* versus *H*/*T*.

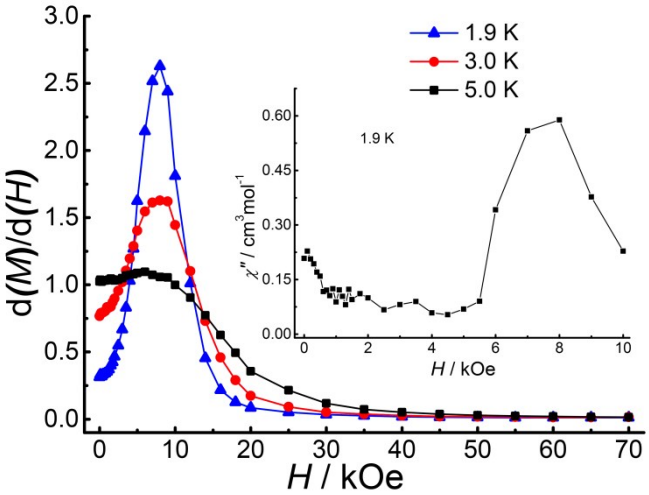

Fig. S8 d(*M/Ms*)/d*H* at different temperatures for **1**. Inset represents the plot of field dependent out-of-phase (χ'') susceptibility at 1.9 K.

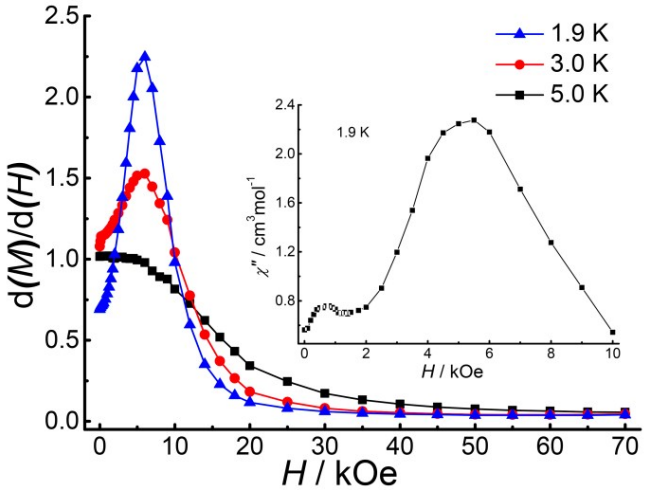

Fig. S9 d(*M/Ms*)/d*H* at different temperatures for **2**. Inset represents the plot of field dependent out-of-phase (χ'') susceptibility at 1.9 K.

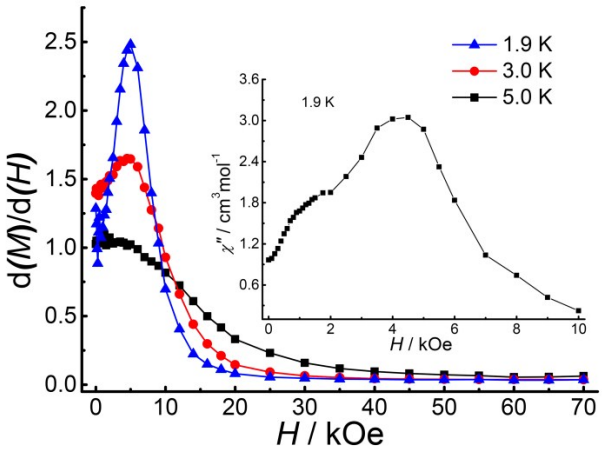

Fig. S10 d(*M/Ms*)/d*H* at different temperatures for **3**. Inset represents the plot of field dependent out-of-phase (χ'') susceptibility at 1.9 K.

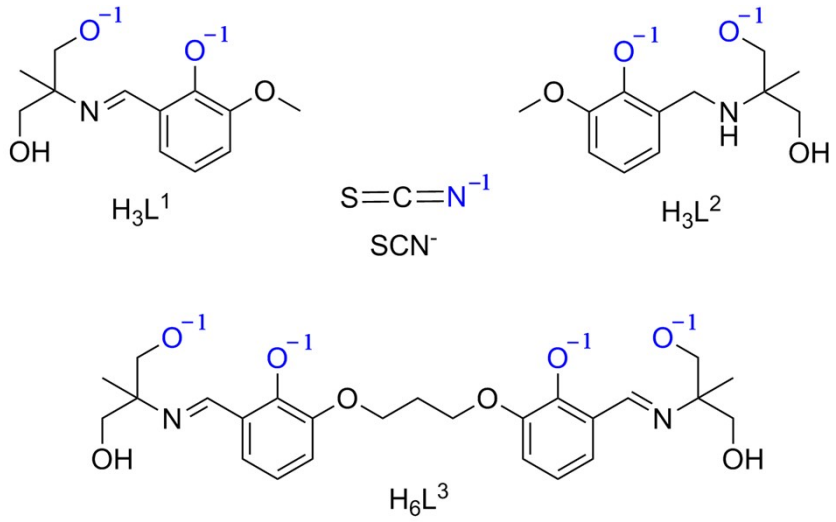

Fig. S11 Partial charges assigned to the formally charged ligands in complexes **1**-**3**.

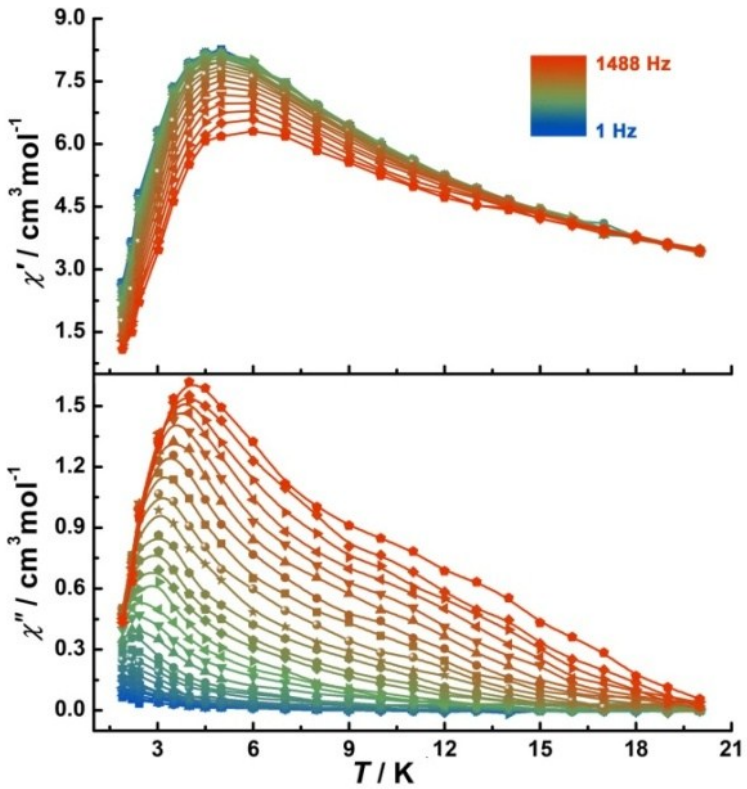

Fig. S12 Temperature dependent ac susceptibility for **1** under zero dc field.

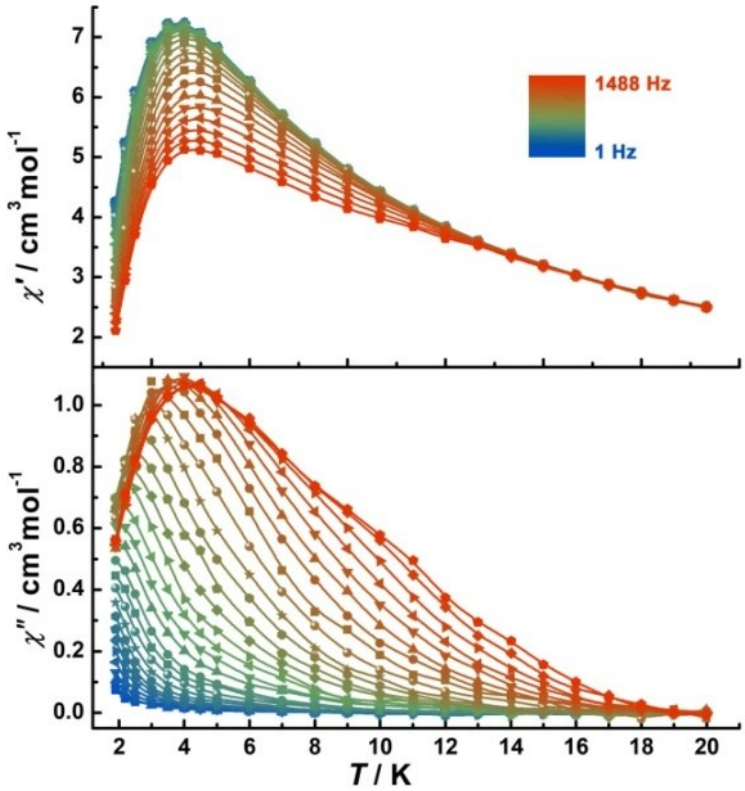

Fig. S13 Temperature dependent ac susceptibility for **2** under zero dc field.

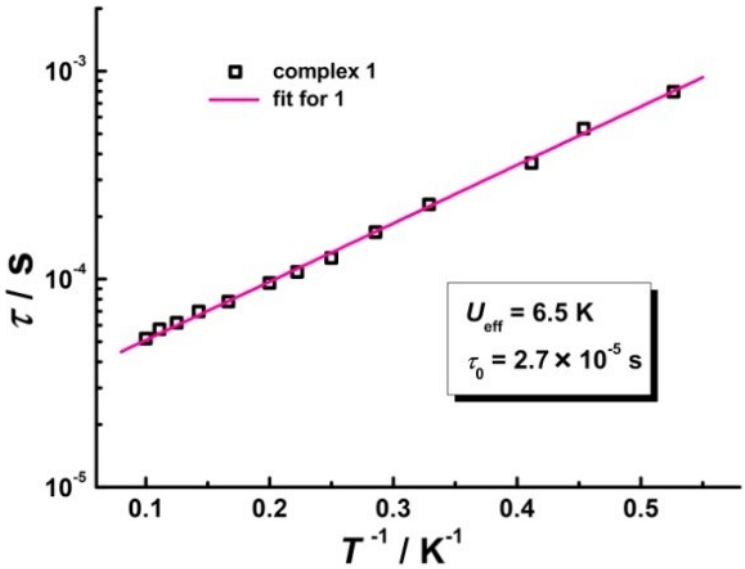

Fig. S14 Plot of τ *vs*. T^{-1} for **1**. The red line represents the Arrhenius fitted result.

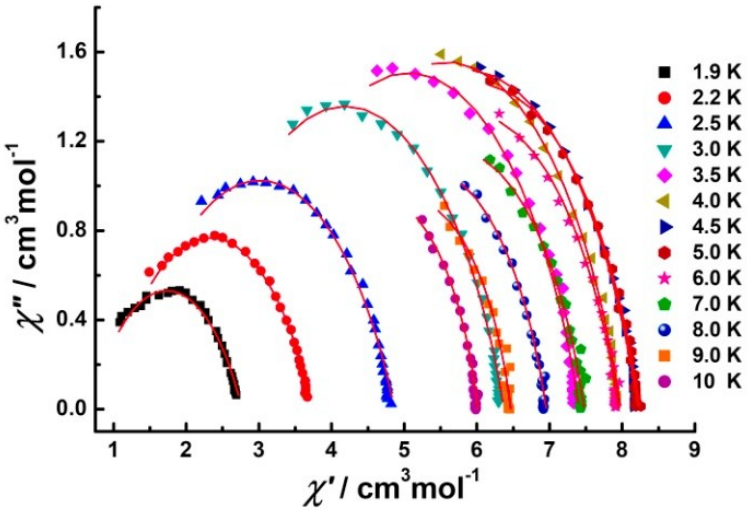

Fig. S15 Cole-Cole plots for **1** under indicated temperature. The solid lines indicate the best fits to the experiments with the generalized Debye model.

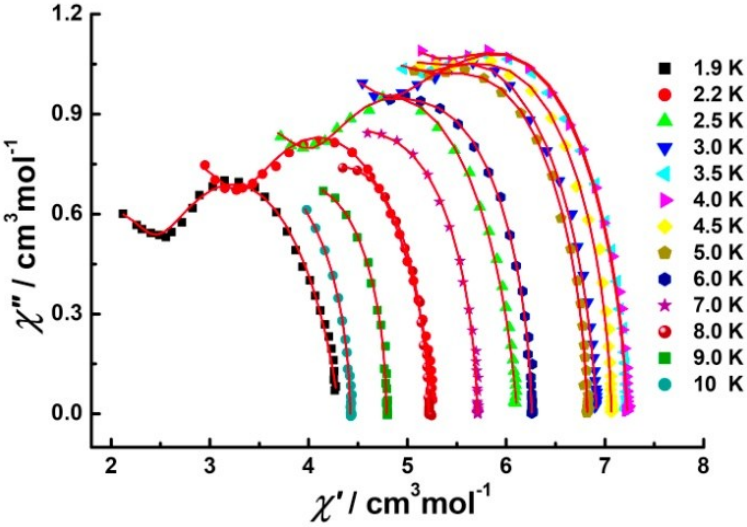

Fig. S16 Cole-Cole plots for **2** under indicated temperature. The solid lines indicate the best fits to the experiments with the double relaxation model.

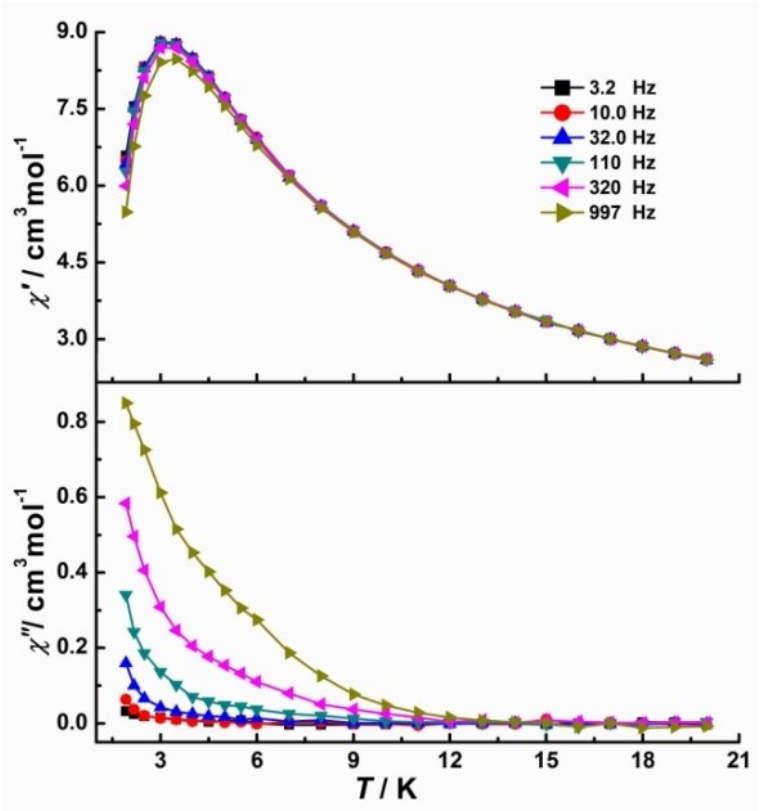

Fig. S17 Temperature-dependent ac susceptibility for **3** at indicated frequency, under zero dc field.

1. I. D. Brown and K. K. Wu, *Acta Crystallographica Section B*, 1976, B32, 1957-1959.
2. N. F. Chilton, D. Collison, E. J. L. McInnes, R. E. P. Winpenny and A. Soncini, *Nat Commun*, 2013, 4, 2551.