Electronic Supplementary Information

Modulating single-molecule magnet behavior towards multiple magnetic relaxation processes through structural variation in Dy_4 clusters

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Tables S1 Selected bond lengths (Å) and angles (°) for cluster **1**[a].

Bond lengths			
Dy(1)-O(9)	2.305(6)	Dy(1)-O(6)	2.315(5)
Dy(1)-O(7)	2.321(5)	Dy(1)-O(11)	2.322(6)
Dy(1)-O(10)	2.344(5)	Dy(1)-O(8)	2.396(5)
Dy(2)-O(4)	2.294(6)	Dy(2)-O(5)	2.308(6)
Dy(2)-O(2)	2.320(5)	Dy(2)-O(1)	2.362(5)
Dy(2)-O(1)#1	2.385(5)	Dy(2)-O(12)	2.463(8)
Dy(2)-N(1)	2.477(6)	Dy(2)-N(2)	2.536(6)
Dy(1)-N(4)	2.548(6)	Dy(1)-N(3)	2.589(6)
Bond angles			
O(9)-Dy(1)-O(6)	110.2(2)	O(9)-Dy(1)-O(7)	82.0(2)
O(6)-Dy(1)-O(7)	71.44(18)	O(9)-Dy(1)-O(11)	90.2(2)
O(6)-Dy(1)-O(11)	139.33(18)	O(7)-Dy(1)-O(11)	148.31(18)
O(9)-Dy(1)-O(10)	78.6(2)	O(6)-Dy(1)-O(10)	145.5(2)
O(7)-Dy(1)-O(10)	77.16(19)	O(11)-Dy(1)-O(10)	71.19(19)
O(9)-Dy(1)-O(8)	71.36(19)	O(6)-Dy(1)-O(8)	75.3(2)
O(7)-Dy(1)-O(8)	126.27(18)	O(11)-Dy(1)-O(8)	78.8(2)
O(10)-Dy(1)-O(8)	137.0(2)	O(4)-Dy(2)-O(5)	71.5(2)
O(4)-Dy(2)-O(2)	80.0(2)	O(5)-Dy(2)-O(2)	95.7(2)
O(4)-Dy(2)-O(1)	92.6(2)	O(5)-Dy(2)-O(1)	91.0(2)
O(2)-Dy(2)-O(1)	167.84(19)	O(4)-Dy(2)-O(1)#1	73.9(2)
O(5)-Dy(2)-O(1)#1	140.1(2)	O(2)-Dy(2)-O(1)#1	97.52(19)
O(2)-Dy(2)-O(1)#1	71.0(2)	O(4)-Dy(2)-O(12)	138.5(3)
O(5)-Dy(2)-O(12)	148.2(2)	O(2)-Dy(2)-O(12)	83.1(3)
O(1)-Dy(2)-O(12)	96.5(3)	O(1)#1-Dy(2)-O(12)	71.0(2)

[a]Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y, -z

Tables S2 Selected bond lengths (Å) and angles (°) for cluster **2**[a].

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Bond lengths			
Dy(1)-O(2)	2.329(2)	Dy(1)-O(12)	2.334(2)
Dy(1)-O(1)	2.344(2)	Dy(1)-O(1)#1	2.367(2)
Dy(1)-O(4)	2.378(2)	Dy(1)-O(5)	2.397(2)
Dy(2)-O(11)	2.329(2)	Dy(2)-O(7)	2.336(2)
Dy(2)-O(10)	2.347(2)	Dy(2)-O(6)	2.350(2)
Dy(2)-O(8)	2.363(2)	Dy(2)-O(9)	2.369(2)
Dy(1)-N(1)	2.460(2)	Dy(1)-N(2)	2.556(2)
Dy(2)-N(3)	2.519(2)	Dy(2)-N(4)	2.532(3)
Bond angles			
O(2)-Dy(1)-O(12)	85.51(7)	O(2)-Dy(1)-O(1)	167.44(7)
O(12)-Dy(1)-O(1)	99.08(8)	O(2)-Dy(1)-O(1)#1	99.61(7)
O(12)-Dy(1)-O(1)#1	76.73(8)	O(1)-Dy(1)-O(1)#1	70.38(8)
O(2)-Dy(1)-O(4)	76.30(7)	O(12)-Dy(1)-O(4)	141.60(8)
O(1)-Dy(1)-O(4)	93.20(8)	O(1)#1-Dy(1)-O(4)	73.46(8)
O(2)-Dy(1)-O(5)	83.82(7)	O(12)-Dy(1)-O(5)	141.01(8)
O(1)-Dy(1)-O(5)	99.39(7)	O(1)#1-Dy(1)-O(5)	142.07(7)
O(4)-Dy(1)-O(5)	70.74(7)	O(11)-Dy(2)-O(7)	149.47(8)
O(11)-Dy(2)-O(10)	72.66(8)	O(7)-Dy(2)-O(10)	79.00(8)
O(11)-Dy(2)-O(6)	138.29(8)	O(7)-Dy(2)-O(6)	71.64(8)
O(10)-Dy(2)-O(6)	148.24(8)	O(11)-Dy(2)-O(8)	75.80(9)
O(7)-Dy(2)-O(8)	121.53(9)	O(10)-Dy(2)-O(8)	137.98(8)
O(6)-Dy(2)-O(8)	70.56(9)	O(11)-Dy(2)-O(9)	80.62(9)
O(7)-Dy(2)-O(9)	82.07(8)	O(10)-Dy(2)-O(9)	76.69(8)
O(6)-Dy(2)-O(9)	110.16(9)	O(8)-Dy(2)-O(9)	71.35(8)

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

Tables S3 Selected bond lengths (Å) and angles (°) for cluster **3**[a].

Bond lengths			
Dy(1)-O(4)	2.296(5)	Dy(1)-O(5)	2.322(5)
Dy(1)-O(10)#1	2.360(5)	Dy(1)-O(10)	2.386(5)
Dy(1)-O(2)	2.391(5)	Dy(1)-O(1)	2.436(5)
Dy(2)-O(6)	2.287(5)	Dy(2)-O(7)	2.298(5)
Dy(2)-O(1)#1	2.328(5)	Dy(2)-O(9)	2.340(5)
Dy(2)-O(8)	2.326(5)	Dy(2)-O(2)	2.359(5)
Dy(2)-O(10)	2.447(5)	Dy(1)-N(2)	2.554(6)
Dy(1)-N(1)	2.468(6)	Dy(2)-N(4)	2.585(6)
Bond angles			
O(4)-Dy(1)-O(5)	71.54(18)	O(4)-Dy(1)-O(10)#1	151.03(17)
O(5)-Dy(1)-O(10)#1	134.38(17)	O(4)-Dy(1)-O(10)	99.01(18)
O(5)-Dy(1)-O(10)	87.81(17)	O(10)#1-Dy(1)-O(10)	73.55(18)
O(4)-Dy(1)-O(2)	70.54(17)	O(10)#1-Dy(1)-O(2)	80.93(17)
O(5)-Dy(1)-O(2)	129.70(17)	O(10)-Dy(1)-O(2)	67.09(16)
O(4)-Dy(1)-O(1)	135.38(17)	O(5)-Dy(1)-O(1)	71.49(17)
O(10)#1-Dy(1)-O(1)	73.12(17)	O(10)-Dy(1)-O(1)	103.64(17)
O(2)-Dy(1)-O(1)	154.03(16)	O(4)-Dy(1)-N(1)	88.43(19)
O(5)-Dy(1)-N(1)	86.31(19)	O(2)-Dy(1)-N(1)	123.96(18)
O(10)#1-Dy(1)-N(1)	103.90(18)	O(1)-Dy(1)-N(1)	65.15(18)
O(4)-Dy(1)-N(2)	67.40(19)	O(10)#1-Dy(1)-N(2)	95.18(18)
O(5)-Dy(1)-N(2)	127.49(18)	O(10)-Dy(1)-N(2)	129.22(18)

[a]Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+2, -z+1

Table S4 The Dy^{III} geometry analysis by SHAPE 2.0 for clusters **1-3**.

$Dy1^{III}$	D_{4d}SAPR	D_{2d}TDD	C_{2v}JBTPR	C_{2v}BTPR	D_{2d}JSD
Cluster **1**	2.211	1.163	2.089	1.428	3.261
Cluster **2**	4.034	2.484	3.252	2.918	3.488
Cluster **3**	4.183	4.609	4.746	4.046	5.578

$Dy2^{III}$	D_{4d}SAPR	D_{2d}TDD	C_{2v}JBTPR	C_{2v}BTPR	D_{2d}JSD
Cluster **1**	3.394	2.626	3.507	3.137	3.686
Cluster **2**	1.322	1.220	2.231	1.722	3.754
Cluster **3**	4.536	1.902	2.727	2.564	4.085

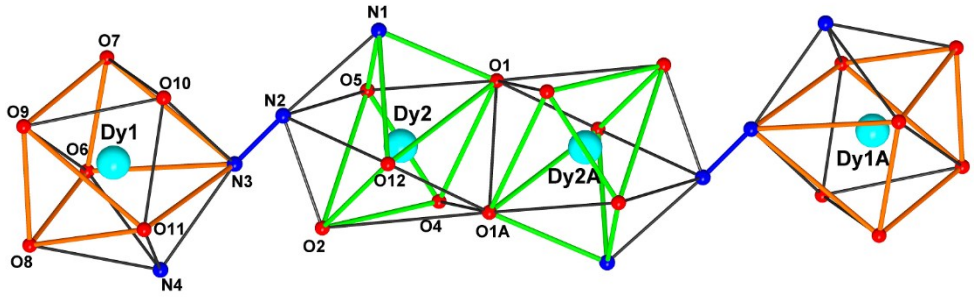

Fig. S1 Coordination polyhedra observed in cluster **1** showing distorted triangular dodecahedron geometry for Dy1 and Dy2. (Symmetry codes: A, -x+2, -y, -z).

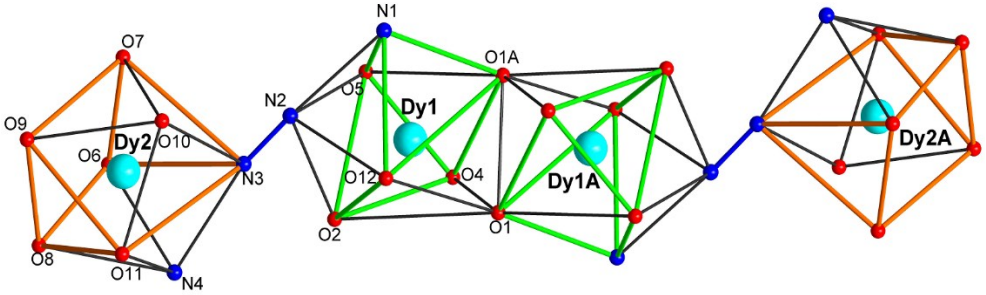

Fig. S2 Coordination polyhedra observed in cluster **2** showing distorted triangular dodecahedron geometry for Dy1 and Dy2. (Symmetry codes: A, -x+1, -y+1, -z).

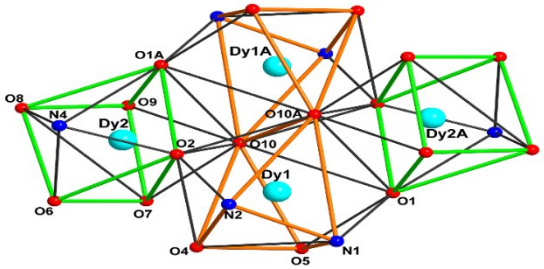

Fig. S3 Coordination polyhedra observed in cluster **3** showing distorted bicapped trigonal-prismatic geometry for Dy1 and Dy2. (Symmetry codes: A, -x+1, -y+2, -z+1).

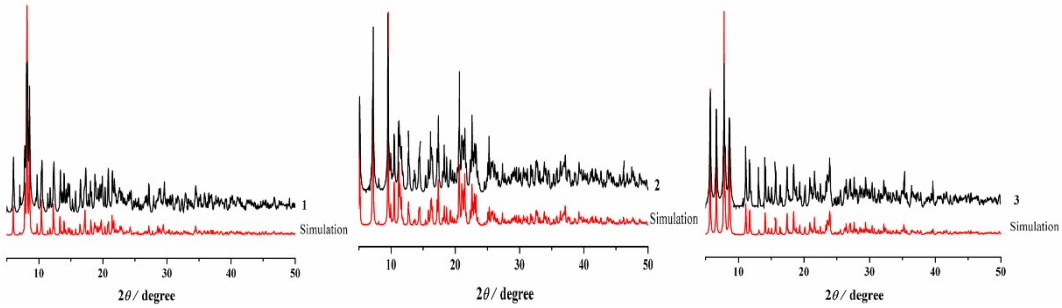

Fig. S4 The PXRD patterns for **1** (left)**, 2** (middle)**, 3** (right) and the corresponding simulated ones.

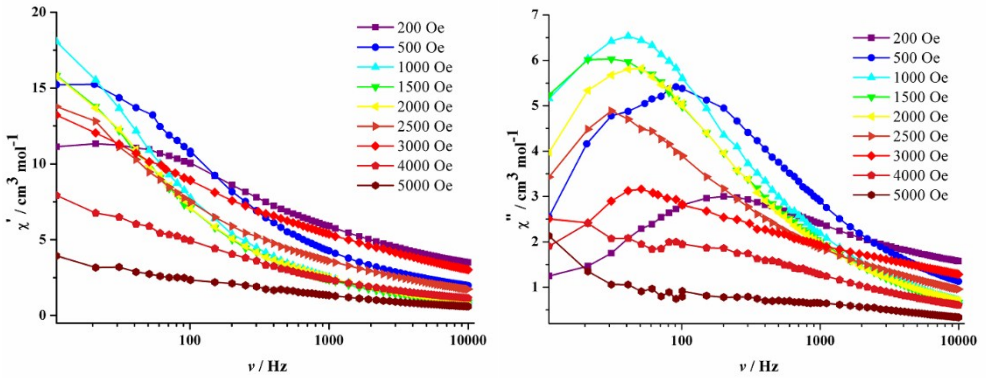

Fig. S5 The frequency dependency of the ac susceptibility was measured on cluster **2** under the applied field from 200 to 5000 Oe at 2.0 K.

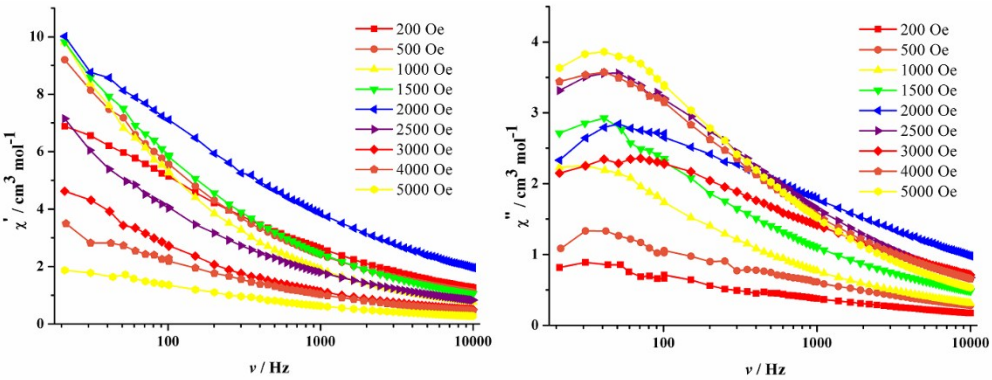

Fig. S6 The frequency dependency of the ac susceptibility was measured on cluster **3** under the applied field from 200 to 5000 Oe at 2.0 K.

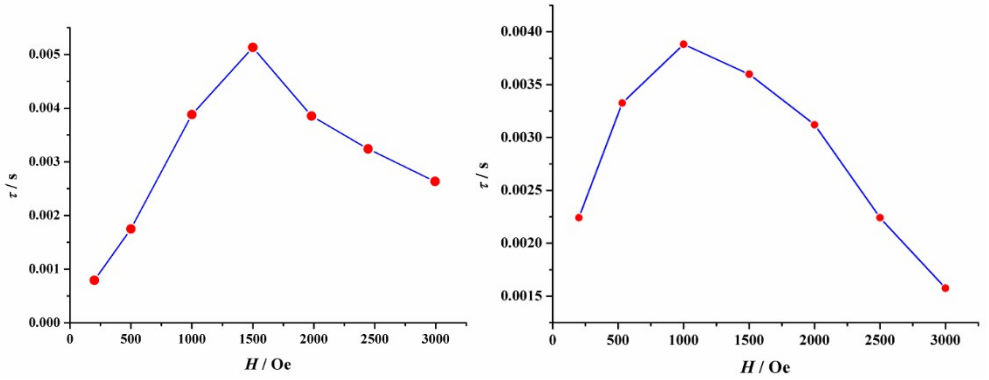

Fig. S7 The τ versus H plots for clusters **2** (left) and **3** (right) under different applied dc field.

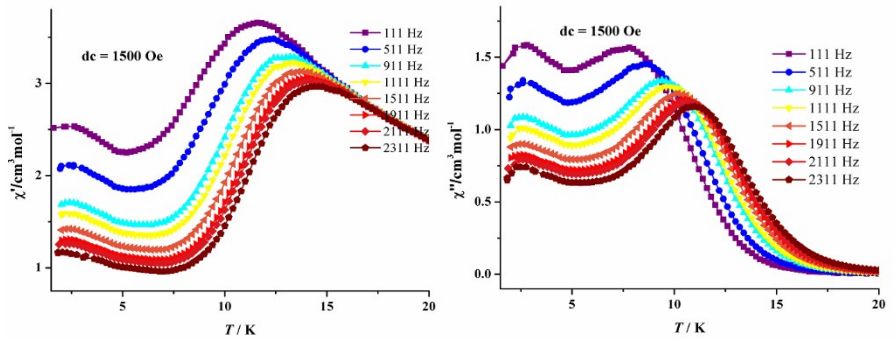

Fig. S8 The temperature dependence of χ' (left) and χ'' (right) for cluster **2** under a 1500 Oe dc field.

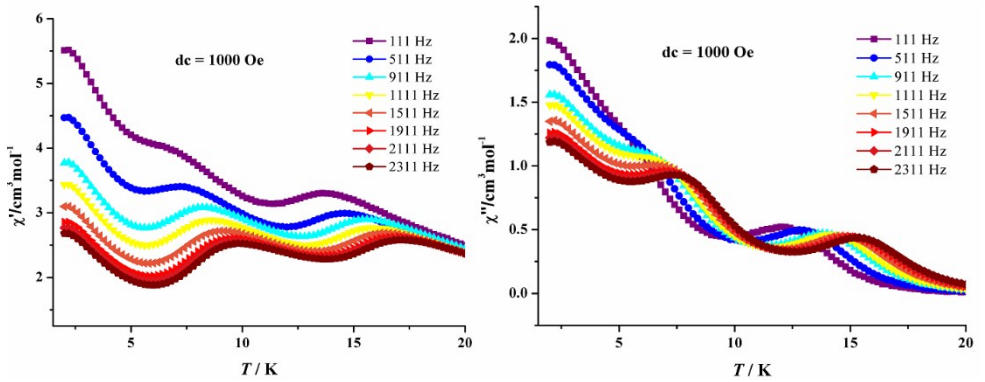

Fig. S9 The temperature dependence of χ' (left) and χ'' (right) for cluster **3** under a 1000 Oe dc field.

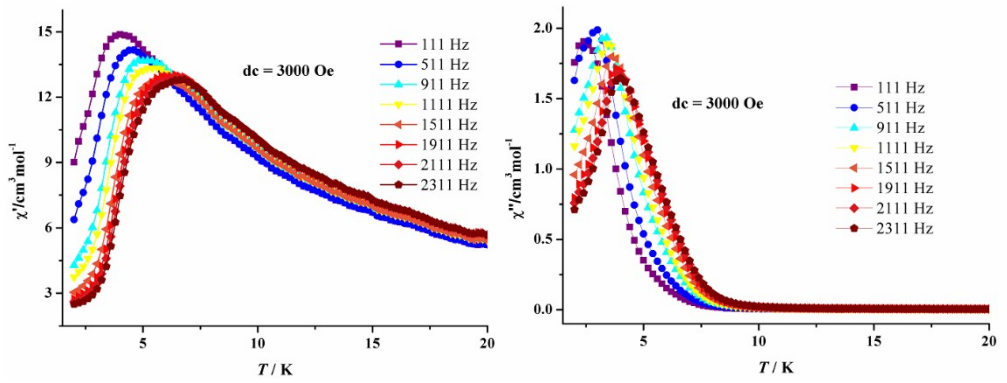

Fig. S10 The temperature dependence of χ' (left) and χ'' (right) for cluster **1** under a 3000 Oe dc field.

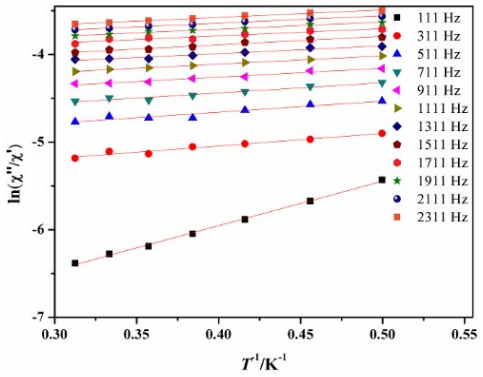

Fig. S11 Plots of natural logarithm of χ''/χ' versus $1/T$ for **1**, the red solid lines represent the fitting results over the range of 111−2311 Hz during the temperatures range 2.0 to 3.2 K.

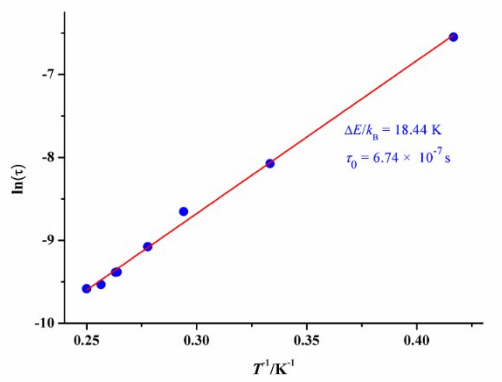

Fig. S12 ln (τ) vs 1/T plots for **1** under 3000 Oe dc filed (the red lines represents the best fit of the Arrhenius relationship).