For submission to *New J. Chem.* ***Revised Manuscript*** (NJ-ART-08-2018-004169)

Self-Assembly of Rare Octanuclear Quad(double-stranded) Cluster Helicates Showing Slow Magnetic Relaxation and Magnetocaloric Effect

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Table S1 Selected bond lengths (Å) and angles (°) for **1**.

Gd(1)-O(12)	2.217(5)	Gd(1)-O(13)	2.251(5)
Gd(1)-O(3)	2.373(5)	Gd(1)-O(6)	2.376(5)
Gd(1)-O(7)	2.386(5)	Gd(1)-O(2)	2.388(5)
Gd(1)-N(2)	2.537(6)	Gd(1)-N(5)	2.553(6)
Gd(2)-O(1)	2.234(5)	Gd(2)-O(34)	2.352(5)
Gd(2)-O(33)	2.353(5)	Gd(2)-O(11)	2.363(5)
Gd(2)-O(10)	2.393(5)	Gd(2)-O(20)	2.408(5)
Gd(2)-N(8)	2.550(6)	Gd(2)-O(1W)	2.611(5)
Gd(2)-O(35)	2.912(5)	Gd(3)-O(8)	2.256(5)
Gd(3)-O(34)	2.363(5)	Gd(3)-O(33)	2.365(5)
Gd(3)-O(14)	2.372(5)	Gd(3)-O(15)	2.385(5)
Gd(3)-O(21)	2.401(5)	Gd(3)-N(11)	2.532(6)
Gd(3)-O(1W)	2.624(5)	Gd(3)-O(36)	2.834(6)
Gd(4)-O(42)	2.307(5)	Gd(4)-O(41)	2.331(5)
Gd(4)-O(36)	2.339(5)	Gd(4)-O(33)	2.360(5)
Gd(4)-O(35)	2.367(5)	Gd(4)-O(37)	2.380(5)

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Gd(4)-O(16)	2.447(5)	Gd(4)-O(20)	2.448(5)
Gd(5)-O(39)	2.309(5)	Gd(5)-O(40)	2.329(5)
Gd(5)-O(38)	2.348(5)	Gd(5)-O(36)	2.350(5)
Gd(5)-O(35)	2.375(5)	Gd(5)-O(34)	2.385(5)
Gd(5)-O(9)	2.451(5)	Gd(5)-O(21)	2.472(5)
Gd(6)-O(25)	2.246(5)	Gd(6)-O(37)	2.359(5)
Gd(6)-O(18)	2.368(5)	Gd(6)-O(38)	2.380(5)
Gd(6)-O(9)	2.401(5)	Gd(6)-O(19)	2.417(5)
Gd(6)-N(14)	2.575(6)	Gd(6)-O(2W)	2.641(5)
Gd(6)-O(35)	2.704(5)	Gd(7)-O(29)	2.249(5)
Gd(7)-O(37)	2.360(5)	Gd(7)-O(23)	2.367(4)
Gd(7)-O(38)	2.372(5)	Gd(7)-O(16)	2.403(5)
Gd(7)-O(22)	2.405(5)	Gd(7)-N(17)	2.551(6)
Gd(7)-O(2W)	2.611(5)	Gd(7)-O(36)	2.917(6)
Gd(8)-O(17)	2.232(5)	Gd(8)-O(24)	2.238(5)
Gd(8)-O(27)	2.327(5)	Gd(8)-O(31)	2.382(5)
Gd(8)-O(26)	2.393(5)	Gd(8)-O(30)	2.418(5)
Gd(8)-N(20)	2.541(7)	Gd(8)-N(23)	2.547(6)
O(12)-Gd(1)-O(13)	107.97(17)	O(12)-Gd(1)-O(3)	83.77(18)
O(1)-Gd(2)-O(34)	80.63(17)	O(1)-Gd(2)-O(33)	134.53(17)
O(8)-Gd(3)-O(34)	133.71(17)	O(8)-Gd(3)-O(33)	81.10(17)
O(42)-Gd(4)-O(41)	73.85(17)	O(42)-Gd(4)-O(36)	153.68(19)
O(39)-Gd(5)-O(40)	74.23(17)	O(39)-Gd(5)-O(38)	136.73(17)
O(25)-Gd(6)-O(37)	79.16(17)	O(25)-Gd(6)-O(18)	92.33(17)
O(29)-Gd(7)-O(37)	133.79(17)	O(29)-Gd(7)-O(23)	90.59(17)
O(17)-Gd(8)-O(24)	108.15(18)	O(17)-Gd(8)-O(27)	86.52(18)

Table S2 Selected bond lengths (Å) and angles (°) for **2**.

Tb(1)-O(12)	2.225(3)	Tb(1)-O(13)	2.248(3)
Tb(1)-O(3)	2.375(3)	Tb(1)-O(6)	2.378(3)
Tb(1)-O(2)	2.395(3)	Tb(1)-O(7)	2.394(3)
Tb(1)-N(2)	2.548(3)	Tb(1)-N(5)	2.555(4)
Tb(2)-O(1)	2.240(3)	Tb(2)-O(34)	2.369(3)
Tb(2)-O(11)	2.374(3)	Tb(2)-O(33)	2.373(3)
Tb(2)-O(10)	2.401(3)	Tb(2)-O(20)	2.415(3)
Tb(2)-N(8)	2.555(4)	Tb(2)-O(1W)	2.628(3)
Tb(2)-O(35)	2.895(4)	Tb(3)-O(8)	2.261(3)
Tb(3)-O(14)	2.368(3)	Tb(3)-O(33)	2.368(3)
Tb(3)-O(34)	2.369(3)	Tb(3)-O(15)	2.398(3)
Tb(3)-O(21)	2.414(3)	Tb(3)-N(11)	2.544(4)
Tb(3)-O(1W)	2.630(3)	Tb(4)-O(42)	2.309(3)

Tb(4)-O(41)	2.344(3)	Tb(4)-O(36)	2.356(3)
Tb(4)-O(35)	2.368(3)	Tb(4)-O(33)	2.377(3)
Tb(4)-O(37)	2.396(3)	Tb(4)-O(20)	2.450(3)
Tb(4)-O(16)	2.463(3)	Tb(5)-O(39)	2.306(3)
Tb(5)-O(36)	2.343(3)	Tb(5)-O(40)	2.344(3)
Tb(5)-O(38)	2.369(3)	Tb(5)-O(35)	2.379(3)
Tb(5)-O(34)	2.391(3)	Tb(5)-O(9)	2.455(3)
Tb(5)-O(21)	2.482(3)	Tb(6)-O(25)	2.252(3)
Tb(6)-O(37)	2.360(3)	Tb(6)-O(18)	2.381(3)
Tb(6)-O(38)	2.387(3)	Tb(6)-O(9)	2.397(3)
Tb(6)-O(19)	2.426(3)	Tb(6)-N(14)	2.573(4)
Tb(6)-O(2W)	2.632(3)	Tb(6)-O(35)	2.760(4)
Tb(7)-O(29)	2.268(3)	Tb(7)-O(38)	2.371(3)
Tb(7)-O(37)	2.376(3)	Tb(7)-O(23)	2.385(3)
Tb(7)-O(16)	2.412(3)	Tb(7)-O(22)	2.410(3)
Tb(7)-N(17)	2.556(4)	Tb(7)-O(2W)	2.646(3)
Tb(7)-O(36)	2.865(4)	Tb(8)-O(24)	2.235(3)
Tb(8)-O(17)	2.238(3)	Tb(8)-O(27)	2.367(3)
Tb(8)-O(31)	2.378(3)	Tb(8)-O(26)	2.402(3)
Tb(8)-O(30)	2.413(3)	Tb(8)-N(20)	2.531(4)
Tb(8)-N(23)	2.549(4)	O(12)-Tb(1)-O(13)	108.01(11)
O(12)-Tb(1)-O(3)	84.21(12)	O(1)-Tb(2)-O(34)	80.61(11)
O(1)-Tb(2)-O(11)	90.81(11)	O(8)-Tb(3)-O(14)	90.24(11)
O(8)-Tb(3)-O(33)	81.33(11)	O(42)-Tb(4)-O(41)	74.46(12)
O(42)-Tb(4)-O(36)	152.54(12)	O(39)-Tb(5)-O(36)	151.00(13)
O(39)-Tb(5)-O(40)	74.10(11)	O(25)-Tb(6)-O(37)	79.69(11)
O(25)-Tb(6)-O(18)	91.80(11)	O(29)-Tb(7)-O(38)	79.63(11)
O(29)-Tb(7)-O(37)	133.41(11)	O(24)-Tb(8)-O(17)	108.66(12)
O(24)-Tb(8)-O(27)	154.76(12)		

Table S3 Selected bond lengths (Å) and angles (°) for **3**.

Dy(1)-O(12)	2.211(5)	Dy(1)-O(13)	2.244(4)
Dy(1)-O(6)	2.356(5)	Dy(1)-O(7)	2.360(5)
Dy(1)-O(2)	2.367(5)	Dy(1)-O(3)	2.374(5)
Dy(1)-N(2)	2.541(6)	Dy(1)-N(5)	2.549(5)
Dy(2)-O(1)	2.220(5)	Dy(2)-O(33)	2.332(5)
Dy(2)-O(34)	2.354(4)	Dy(2)-O(11)	2.365(4)
Dy(2)-O(10)	2.391(5)	Dy(2)-O(20)	2.418(4)

Dy(2)-N(8)	2.545(6)	Dy(2)-O(1W)	2.587(4)
Dy(3)-O(8)	2.257(5)	Dy(3)-O(34)	2.353(5)
Dy(3)-O(33)	2.366(4)	Dy(3)-O(14)	2.381(4)
Dy(3)-O(15)	2.393(5)	Dy(3)-O(21)	2.402(4)
Dy(3)-N(11)	2.528(6)	Dy(3)-O(1W)	2.636(4)
Dy(3)-O(36)	2.815(5)	Dy(4)-O(42)	2.310(4)
Dy(4)-O(36)	2.334(5)	Dy(4)-O(41)	2.329(5)
Dy(4)-O(35)	2.357(5)	Dy(4)-O(33)	2.367(4)
Dy(4)-O(37)	2.389(5)	Dy(4)-O(20)	2.440(5)
Dy(4)-O(16)	2.448(5)	Dy(5)-O(39)	2.299(4)
Dy(5)-O(40)	2.320(5)	Dy(5)-O(36)	2.332(5)
Dy(5)-O(38)	2.355(4)	Dy(5)-O(35)	2.366(4)
Dy(5)-O(34)	2.380(4)	Dy(5)-O(9)	2.446(5)
Dy(5)-O(21)	2.469(5)	Dy(6)-O(25)	2.238(5)
Dy(6)-O(37)	2.349(5)	Dy(6)-O(18)	2.371(5)
Dy(6)-O(38)	2.386(5)	Dy(6)-O(9)	2.411(4)
Dy(6)-O(19)	2.427(4)	Dy(6)-N(14)	2.554(6)
Dy(6)-O(35)	2.665(5)	Dy(6)-O(2W)	2.668(4)
Dy(7)-O(29)	2.245(4)	Dy(7)-O(37)	2.356(4)
Dy(7)-O(38)	2.360(4)	Dy(7)-O(23)	2.371(4)
Dy(7)-O(16)	2.396(4)	Dy(7)-O(22)	2.400(5)
Dy(7)-N(17)	2.533(6)	Dy(7)-O(2W)	2.594(4)
Dy(8)-O(17)	2.226(5)	Dy(8)-O(24)	2.231(5)
Dy(8)-O(27)	2.337(5)	Dy(8)-O(31)	2.385(5)
Dy(8)-O(26)	2.390(5)	Dy(8)-O(30)	2.402(5)
Dy(8)-N(20)	2.529(6)	Dy(8)-N(23)	2.547(6)
O(12)-Dy(1)-O(13)	107.06(16)	O(12)-Dy(1)-O(6)	153.99(17)
O(1)-Dy(2)-O(33)	135.09(16)	O(1)-Dy(2)-O(34)	81.07(16)
O(8)-Dy(3)-O(34)	133.68(16)	O(8)-Dy(3)-O(33)	81.35(16)
O(42)-Dy(4)-O(36)	154.11(17)	O(42)-Dy(4)-O(41)	73.99(17)
O(39)-Dy(5)-O(40)	74.02(16)	O(39)-Dy(5)-O(36)	149.32(18)
O(25)-Dy(6)-O(37)	78.73(16)	O(25)-Dy(6)-O(18)	91.98(16)
O(29)-Dy(7)-O(37)	134.96(17)	O(29)-Dy(7)-O(38)	81.19(16)
O(17)-Dy(8)-O(24)	107.62(17)	O(17)-Dy(8)-O(27)	86.83(17)

Table S4 Selected bond lengths (Å) and angles (°) for **4**.

Ho(1)-O(12)	2.217(5)	Ho(1)-O(13)	2.253(4)
Ho(1)-O(6)	2.378(5)	Ho(1)-O(3)	2.381(4)

Ho(1)-O(7)	2.396(4)	Ho(1)-O(2)	2.404(5)
Ho(1)-N(2)	2.540(5)	Ho(1)-N(5)	2.545(5)
Ho(2)-O(1)	2.234(4)	Ho(2)-O(34)	2.352(4)
Ho(2)-O(33)	2.355(5)	Ho(2)-O(11)	2.365(4)
Ho(2)-O(10)	2.399(5)	Ho(2)-O(20)	2.405(4)
Ho(2)-N(8)	2.544(6)	Ho(2)-O(1W)	2.623(4)
Ho(3)-O(8)	2.270(4)	Ho(3)-O(33)	2.362(4)
Ho(3)-O(14)	2.369(4)	Ho(3)-O(34)	2.368(4)
Ho(3)-O(15)	2.385(4)	Ho(3)-O(21)	2.405(4)
Ho(3)-N(11)	2.539(5)	Ho(3)-O(1W)	2.643(4)
Ho(3)-O(36)	2.876(6)	Ho(4)-O(42)	2.303(4)
Ho(4)-O(36)	2.328(4)	Ho(4)-O(41)	2.340(4)
Ho(4)-O(35)	2.364(5)	Ho(4)-O(33)	2.383(4)
Ho(4)-O(37)	2.399(4)	Ho(4)-O(16)	2.449(4)
Ho(4)-O(20)	2.453(4)	Ho(5)-O(39)	2.301(4)
Ho(5)-O(40)	2.336(5)	Ho(5)-O(36)	2.342(5)
Ho(5)-O(38)	2.366(4)	Ho(5)-O(35)	2.376(4)
Ho(5)-O(34)	2.387(4)	Ho(5)-O(9)	2.466(5)
Ho(5)-O(21)	2.483(4)	Ho(6)-O(25)	2.242(4)
Ho(6)-O(37)	2.354(4)	Ho(6)-O(38)	2.382(4)
Ho(6)-O(18)	2.383(5)	Ho(6)-O(9)	2.392(4)
Ho(6)-O(19)	2.423(5)	Ho(6)-N(14)	2.578(6)
Ho(6)-O(2W)	2.651(4)	Ho(6)-O(35)	2.735(5)
Ho(7)-O(29)	2.262(4)	Ho(7)-O(38)	2.358(4)
Ho(7)-O(23)	2.369(4)	Ho(7)-O(37)	2.373(4)
Ho(7)-O(16)	2.405(4)	Ho(7)-O(22)	2.411(4)
Ho(7)-N(17)	2.551(5)	Ho(7)-O(2W)	2.646(5)
Ho(8)-O(24)	2.232(4)	Ho(8)-O(17)	2.242(5)
Ho(8)-O(27)	2.355(5)	Ho(8)-O(31)	2.369(5)
Ho(8)-O(26)	2.408(5)	Ho(8)-O(30)	2.424(5)
Ho(8)-N(20)	2.537(6)	Ho(8)-N(23)	2.546(6)
O(12)-Ho(1)-O(13)	107.27(16)	O(12)-Ho(1)-O(6)	153.84(17)
O(1)-Ho(2)-O(34)	81.12(15)	O(1)-Ho(2)-O(33)	133.96(16)
O(8)-Ho(3)-O(33)	81.58(15)	O(8)-Ho(3)-O(14)	89.41(15)
O(42)-Ho(4)-O(36)	153.34(18)	O(42)-Ho(4)-O(41)	74.67(16)
O(39)-Ho(5)-O(40)	74.83(16)	O(39)-Ho(5)-O(36)	150.24(18)
O(25)-Ho(6)-O(37)	79.80(16)	O(25)-Ho(6)-O(38)	133.54(15)
O(29)-Ho(7)-O(38)	80.51(16)	O(29)-Ho(7)-O(23)	90.02(15)

O(24)-Ho(8)-O(17)	107.79(17)	O(24)-Ho(8)-O(27)	154.83(18)

Table S5. Results of the Continuous Shape Measure Analysisa geometry[a]

Compound	Geometry / Atoms	TDD-8	SAPR-8	HBPY-8	JGBF-8	JTCTPR-9	CSAPR-9
1	Gd1	**2.169**	3.572				
	Gd2					**1.557**	2.351
	Gd3					**1.587**	2.276
	Gd4	1.897	**1.707**				
	Gd5	2.176	**1.291**				
	Gd6					**1.806**	2.355
	Gd7					**1.598**	2.484
	Gd8	**2.254**	3.569				
2	Tb1			**10.756**	12.570		
	Tb2					**1.592**	2.317
	Tb3	2.715	**2.456**				
	Tb4	1.880	**1.612**				
	Tb5	2.139	**1.415**				
	Tb6					**1.787**	2.362
	Tb7					**1.635**	2.447
	Tb8	**2.258**	3.532				
3	Dy1	**2.074**	3.538				
	Dy2	66.780	**66.702**				
	Dy3					**1.588**	2.201
	Dy4	1.872	**1.780**				
	Dy5	2.182	**1.153**				
	Dy6					**1.802**	2.264
	Dy7	2.539	**2.529**				
	Dy8	**2.194**	3.469				
4	Ho1	**2.114**	3.543				
	Ho2	2.721	**2.469**				
	Ho3					**1.530**	2.345
	Ho4	1.911	**1.703**				
	Ho5	2.157	**1.297**				
	Ho6					**1.750**	2.372
	Ho7	2.682	**2.601**				
	Ho8	**2.219**	3.515				

[a]TDD-8 is the shape measure relative to the triangular dodecahedron (D_{2d}); SAPR-8 is the shape measure relative to the square antiprism (D_{4d}); HBPY-8 is the shape measure relative to the hexagonal bipyramid (D_{6h}); JGBF-8 is the shape measure relative to the Johnson gyrobifastigium J26 (D_{2d});

JTCTPR-9 is the shape measure relative to the tricapped trigonal prism J51 (D_{3h}); CSAPR-9 is the shape measure relative to the spherical capped square antiprism (C_{4v}); JCSAPR-9 is the shape measure relative to the capped square antiprism (C_{4v}); CCU-9 is the shape measure relative to the spherical-relaxed capped cube. The number in bold corresponds to the closer ideal geometry to the real complexes.

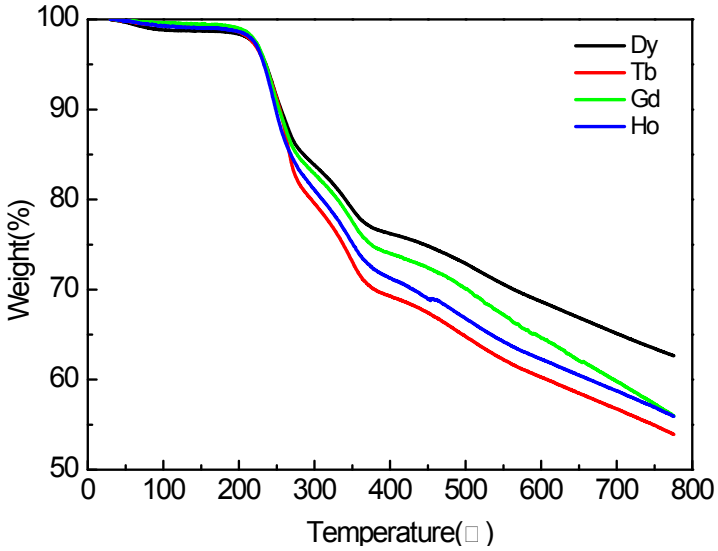

Figure S1. The thermogravimetry curves of all complexes in an N_2 atmosphere at a heating rate of 10 °C/min. The first weight loss occurred below 200 ºC can be attributed to the loss of two lattice methanol molecules. After that, the frameworks of these complexes began to decompose gradually. The loss between 200-260 ºC can be due to the loss of twelve free water molecules, two coordination water molecules, two $acac^-$ anions and six hydroxyl anions. The result is consistent with the ones of elemental analysis.

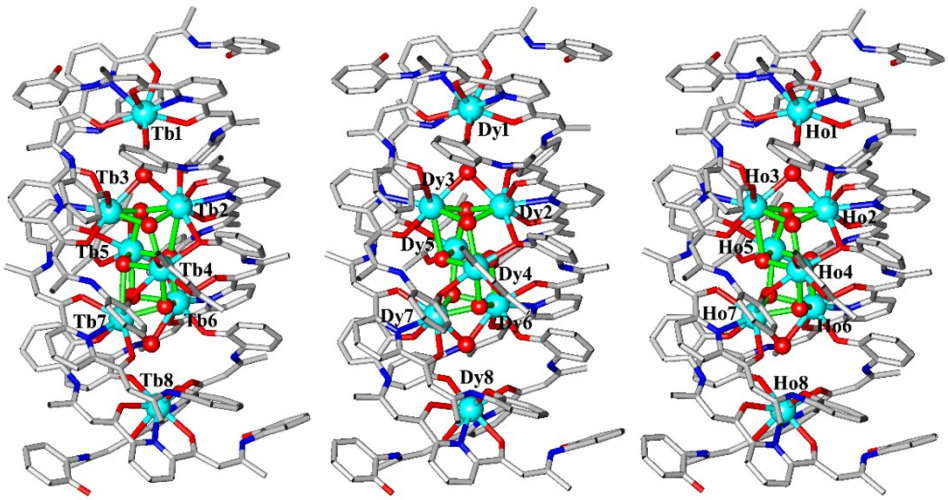

Figure S2. Perspective drawing of the cation section of **2** (left), **3** (middle) and **4** (right) showing

the atom numbering. H atoms are omitted for clarity.

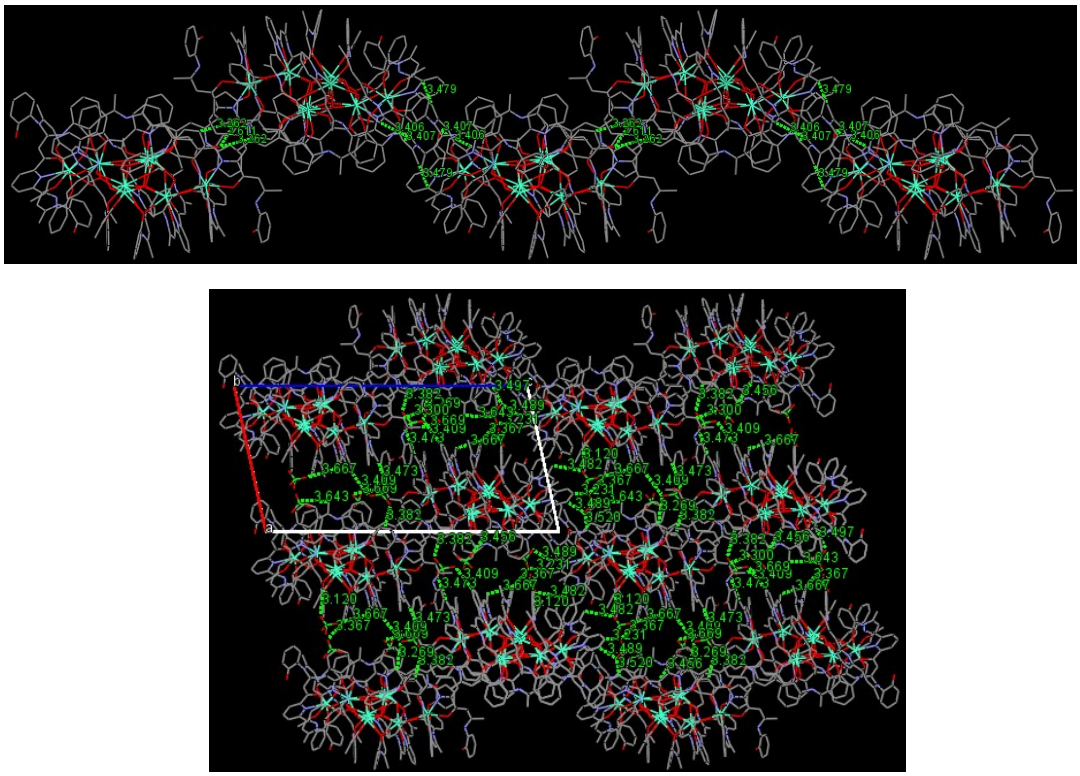

Figure S3. Up: One dimensional stacking diagram formed by intercluster hydrogen bonds along the b axis in **1–4**. Down: A view showing 3D structure in **1–4**.

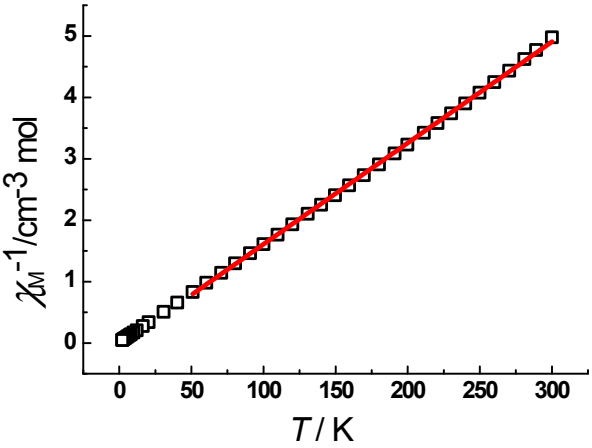

Figure S4. Plot of $1/\chi_M$ vs T for **1**. The red solid line is the fitting result by Curie-Weiss law.

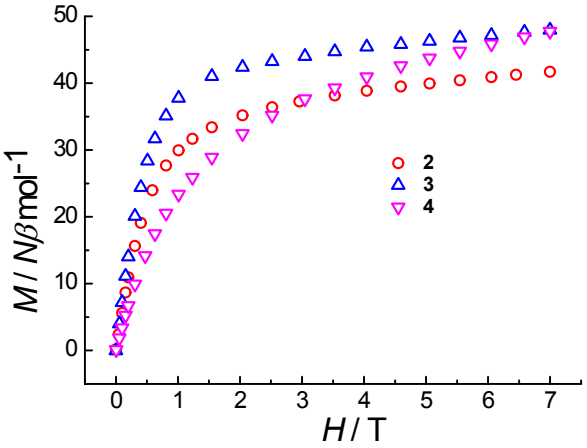

Figure S5. Field dependence of magnetization for **2-4** at 2.0 K.

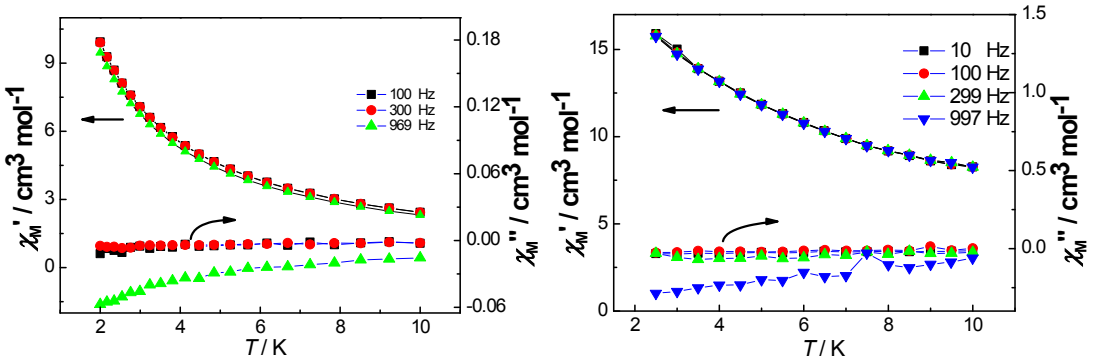

Figure S6. Temperature dependence of the in-phase χ' and out-of-phase χ'' at different frequencies in a 2.5 Oe ac field oscillating at 100–997 Hz without a dc field for **2** (left) and **4** (right).

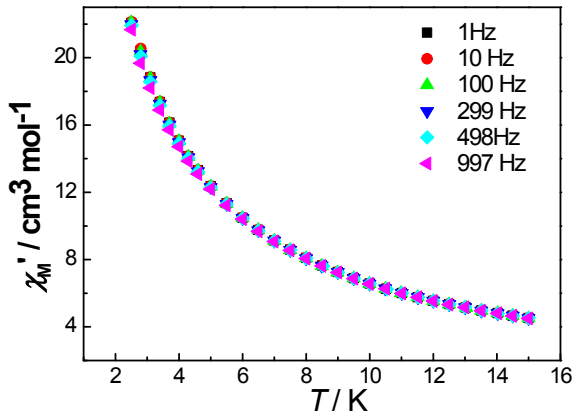

Figure S7.Temperature dependence of the in-phase χ' at different frequencies in a 2.5 Oe ac field oscillating at 1–1000 Hz with zero dc field for **3**.

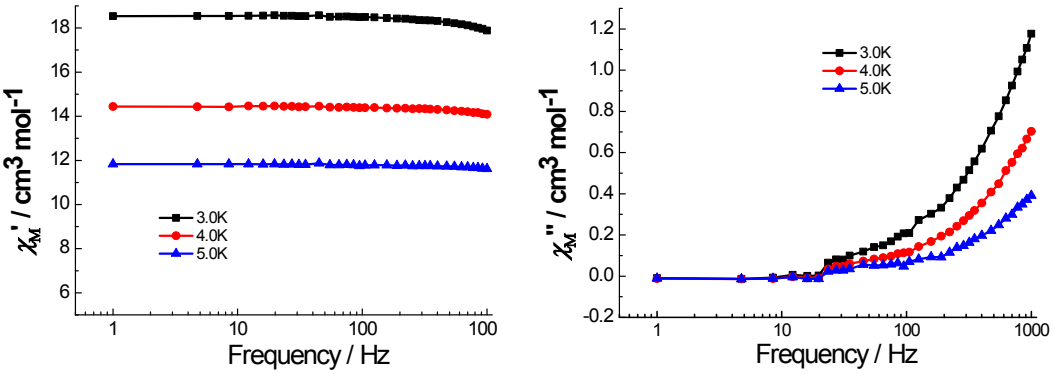

Figure S8. Frequency dependence of the in-phase χ' and out-of-phase χ'' in a 2.5 Oe ac field without a dc field for **3**.

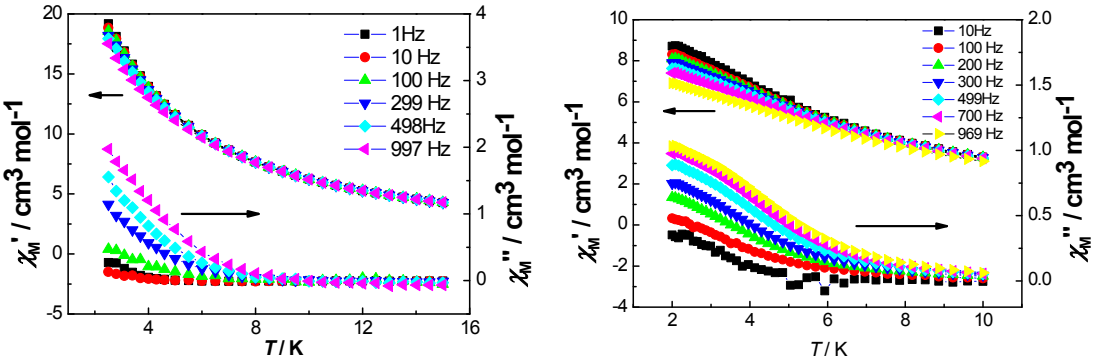

Figure S9. Temperature dependence of the in-phase χ' and out-of-phase χ'' at different frequencies oscillating at 1−1000 Hz with a dc field of 1000 Oe (left) in a 2.5 Oe ac field and 2000 Oe (right) in a 3.0 Oe ac field for **3**.