Electronic Supplementary Information (ESI) for *NJC*

Syntheses, Crystal Structures, and Magnetic Properties of a Family of Heterometallic Octanuclear [Cu_6Ln_2] (Ln = Dy(III), Tb(III), Ho(III), Er(III), and Gd(III)) Complexes

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Table S1 Selected bond length of **1-5.**

bond	1	2	3	4	5
Cu(1)-Cl(1)	2.210(4)	2.192(8)	2.209(2)	2.210 (2)	2.209(3)
Cu(1)-O(1)	1.889(8)	1.895(16)	1.897(4)	1.889(4)	1.905(6)
Cu(1)-O(2)	1.939(8)	1.910(15)	1.945(4)	1.936(4)	1.936(6)
Cu(1)-N(2)	1.975(11)	1.94(2)	1.988(6)	1.987(6)	1.990(8)
Ln(1)-O(1)	2.259(8)	2.292(15)	2.252(4)	2.243(4)	2.291(5)
Ln(1)-O(1)^b	2.259(8)	2.292(15)	2.252(4)	2.243(4)	2.291(5)
Ln(1)-O(1)^d	2.259(8)	2.292(15)	2.252(4)	2.243(4)	2.291(5)
Ln(1)-O(2)	2.305(8)	2.306(15)	2.297(4)	2.278(4)	2.332(5)
Ln(1)-O(2)^b	2.305(8)	2.306(15)	2.297(4)	2.278(4)	2.332(6)
Ln(1)-O(2)^d	2.305(8)	2.306(15)	2.297(4)	2.278(4)	2.332(5)
Ln(1)-N(1)	2.509(16)	2.53(3)	2.492(8)	2.483(8)	2.514(14)

Symmetry code: a(0.33333+y, -0.33333+x, 0.16667-z), b(1-y, x-y, z), c(1.3333-x, 0.66667-x+y, 0.16667-z), d(1-x+y, 1-x, z), e(0.33333+x-y, 0.66667-y, 0.16667-z).

Table S2 Selected bond angles of **1-5.**

Angle	1	2	3	4	5
O(1)-Cu(1)-O(2)	82.8(3)	82.6(7)	82.80(18)	82.17(17)	83.7(2)
O(1)-Cu(1)-N(2)	164.7(4)	164.4(8)	164.8(2)	164.7(2)	165.4(3)
O(2)-Cu(1)-N(2)	82.3(4)	83.0(9)	82.1(2)	82.7(2)	81.8(3)
O(1)-Cu(1)-Cl(1)	98.4(3)	98.6(5)	97.92(14)	98.71(13)	97.43(18)
O(2)-Cu(1)-Cl(1)	178.7(3)	178.8(6)	179.20(14)	179.11(14)	178.4 (2)
N(2)-Cu(1)-Cl(1)	96.6(4)	95.9(8)	97.2(2)	96.42(19)	97.0(3)
O(1)-Ln(1)-O(1)^b	108.35(19)	108.0(4)	108.24(10)	108.60(10)	107.40(17)
O(1)-Ln(1)-O(1)^d	108.35(19)	107.9(4)	108.24(10)	108.60(10)	107.40(16)
O(1)^b-Ln(1)-O(1)^d	108.35(19)	107.9(4)	108.24(10)	108.60(10)	107.40(16)
O(1)-Ln(1)-O(2)	67.4(3)	66.2(6)	67.92(15)	67.56(14)	67.3(2)

O(1)-Ln(1)-O(2)^{b}	90.9(3)	91.5(6)	91.55(16)	91.84(16)	92.2(2)
O(1)-Ln(1)-O(2)^{d}	160.4(3)	160.5(6)	159.76(15)	159.01(16)	160.3(2)
O(1)^{b}-Ln(1)-O(2)^{d}	90.9(3)	91.5(6)	91.55(16)	91.84(16)	92.2(2)
O(1)^{b}-Ln(1)-O(2)	160.4(3)	160.5(6)	159.76(15)	159.01(16)	160.3(2)
O(1)b-Ln(1)-O(2)^{b}	67.4(3)	66.2(6)	67.92(15)	67.56(14)	67.3(2)
O(2)b-Ln(1)-O(2)^{d}	93.3(3)	94.8(5)	92.04(14)	91.66(14)	93.53(19)
O(1)d-Ln(1)-O(2)^{b}	160.4(3)	160.5(6)	159.75(15)	159.01(16)	160.3(2)
O(1)d-Ln(1)-O(2)^{d}	67.4(3)	66.2(6)	67.92(15)	67.56(14)	67.3(2)
O(1)d -Ln(1)-O(2)	90.9(3)	91.5(6)	91.55(16)	91.85(16)	92.2(2)
O(2)-Ln(1)-O(2)^{b}	93.3(3)	94.8(5)	92.04(14)	91.66(14)	93.5 (2)
O(2)-Ln(1)-O(2)^{d}	93.3(3)	94.8(5)	92.04(14)	91.66(14)	93.53(19)
O(1)-Ln(1)-N(1)	69.43(18)	69.0(4)	69.32(10)	69.67(10)	68.53(15)
O(1)^{b}-Ln(1)-N(1)	69.43(18)	69.0(4)	69.32(10)	69.67(10)	68.53(15)
O(1)^{d}-Ln(1)-N(1)	69.43(18)	69.0(4)	69.32(10)	69.67(10)	68.53(15)
O(2)-Ln(1)-N(1)	122.9(2)	121.8(4)	123.81(10)	124.08(10)	122.72(14)
O(2)^{b}-Ln(1)-N(1)	122.9(2)	121.8(4)	123.80(10)	124.08(10)	122.72(14)
O(2)^{d}-Ln(1)-N(1)	122.9(2)	121.8(4)	123.80(10)	124.09(10)	122.72(14)

Symmetry code: a(0.33333+y, -0.33333+x, 0.16667-z), b(1-y, x-y, z), c(1.3333-x, 0.66667-x+y, 0.16667-z), d(1-x+y, 1-x, z), e(0.33333+x-y, 0.66667-y, 0.16667-z).

Table S3 The possible geometries of nonacoordination metal centers.

geometry	point group	polyhedron
HP-7	D7h	Heptagon
HPY-7	C6v	Hexagonal pyramid
PBPY-7	D5h	Pentagonal bipyramid
COC-7	C3v	Capped octahedron
CTPR-7	C2v	Capped trigonal prism
JPBPY-7	D5h	Johnson pentagonal bipyramid (J13)
JETPY-7	C3v	Elongated triangular pyramid (J7)

Table S4 Deviation parameters[a] calculated by *SHAPE* from each ideal polyhedron for complexes **1**-**5**.

Structure	**1**	**2**	**3**	**4**	**5**
HP-7	48.277	47.953	47.484	47.605	47.968
HPY-7	32.489	32.341	40.790	40.874	32.486
PBPY-7	33.545	33.429	33.535	33.662	33.630
COC-7	27.691	27.629	30.486	30.547	27.892
CTPR-7	28.648	28.559	31.736	31.815	28.824
JPBPY-7	30.128	30.308	38.820	38.924	30.275
JETPY-7	32.459	32.245	40.323	40.332	32.349

[a] It should be noted that CShM values for **1**, **2** and **5** are slightly smaller than corresponding values for complexes **3** and **4**, which due to the crystal data were reduced using the resolution threshold of 0.88, 0.90 and 0.85 for **1**, **2** and **5**, respectively.

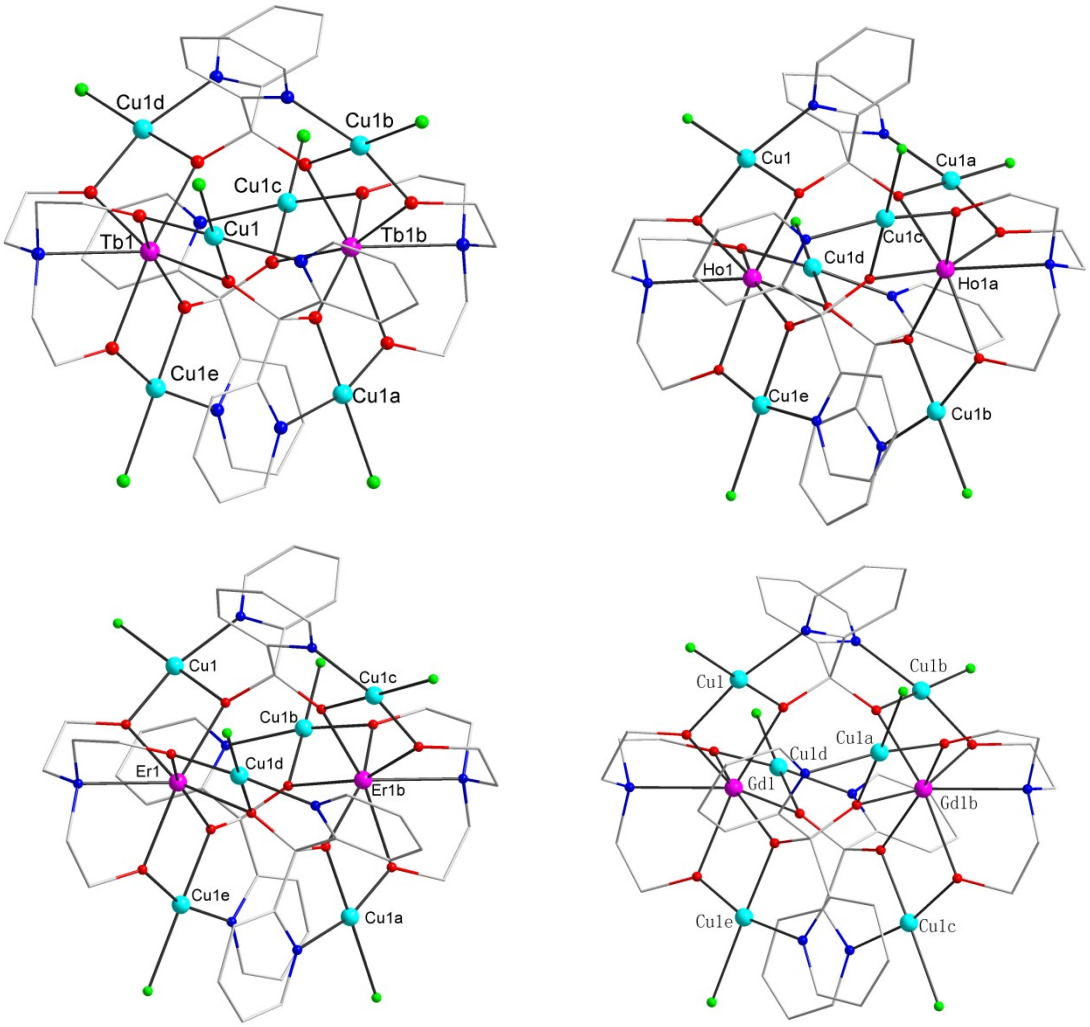


Fig. S1 Molecular structure of compound **2-5**. For clarity, the H atoms and the noncoordinated solvent molecules are omitted (symmetry code: a(0.33333+x-y, 0.66667-y, 0.16667-z), b(0.33333+y, -0.33333+x, 0.16667-z), c(1.3333-x, 0.66667-x+y, 0.16667-z), d(1-y, x-y, z), e(1-x+y, 1-x, z)), Cu^{II} turquiose, Dy^{III} pink**,** O red, N blue, C gray.

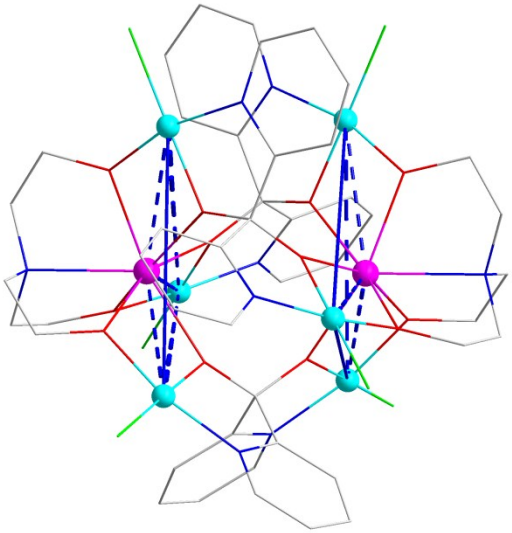


Fig. S2 Six Cu^{II} and two Dy^{III} ions form two tetrahedrons.

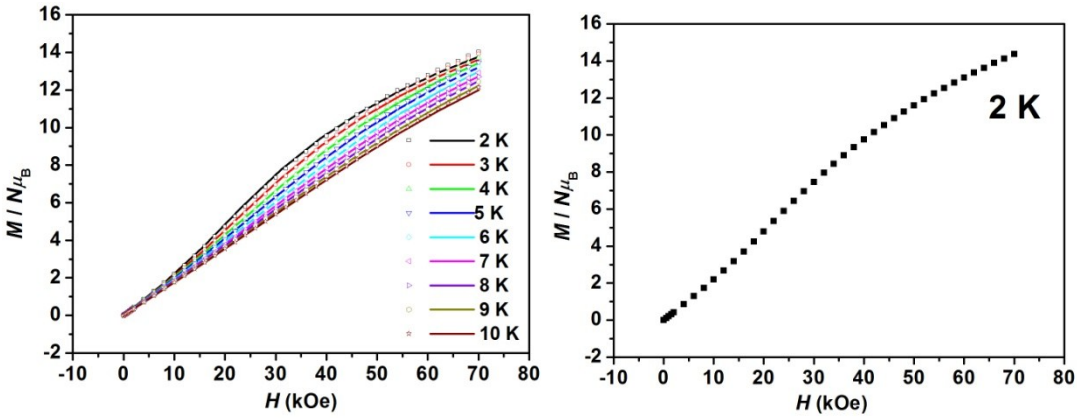


Fig. S3 Plot of the isothermal magnetization (*M* vs *H*) at different temperatures (left) and at 2 K (right) for **5**. The solid lines represent the simulated results by PHI program.

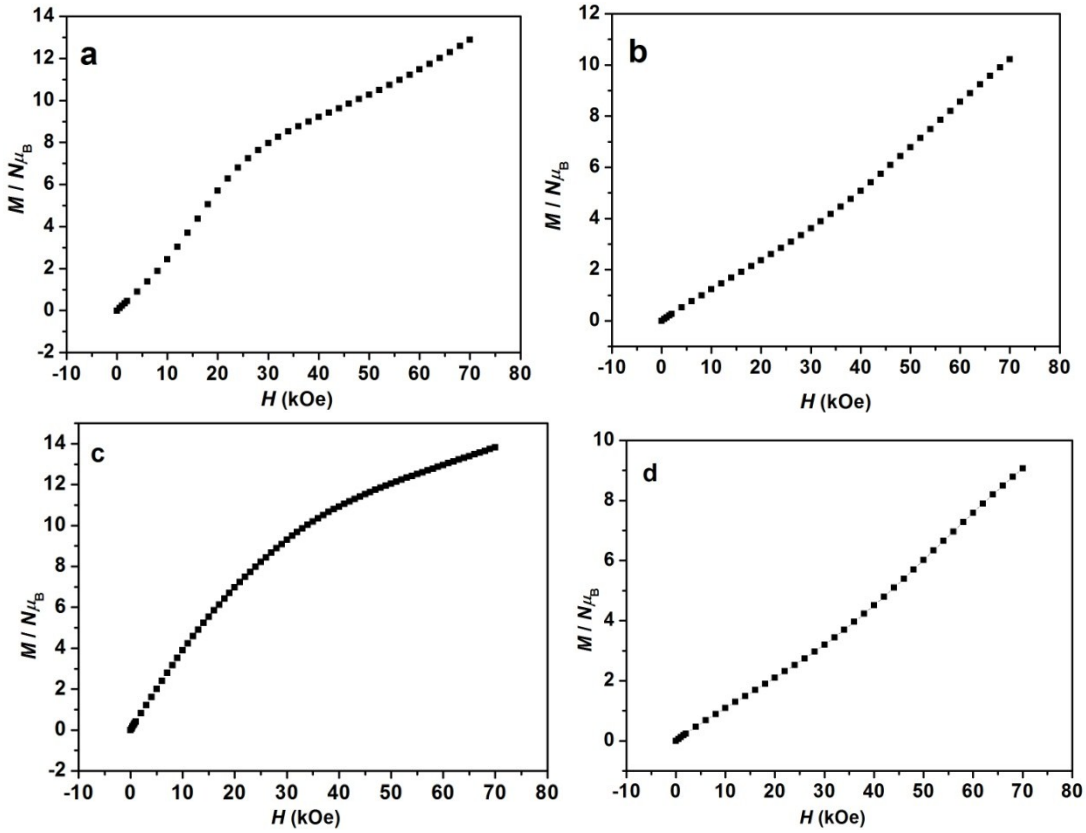


Fig. S4 *M* vs *H* plots at 2.0 K for **1**(Dy, a), **2**(Tb, b), **3**(Ho, c), **4**(Er, d).

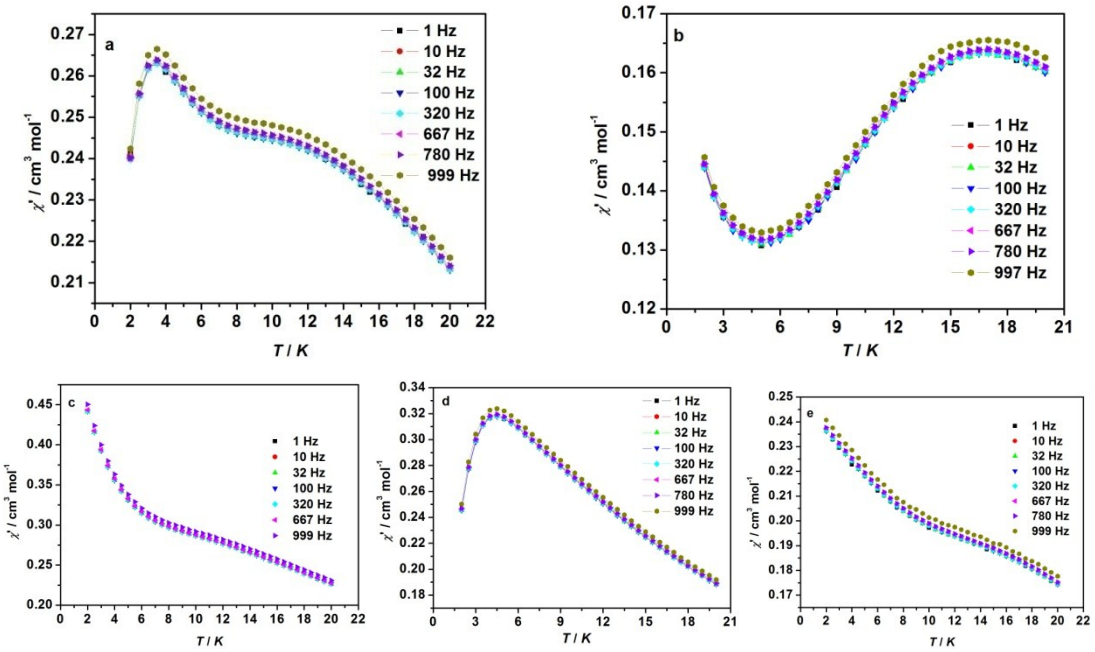


Fig. S5 Temperature dependence of the in-phase (χ_M') ac susceptibility signals in a 5 Oe ac field oscillating at 1-999 Hz with a zero applied dc field for **1**(a), **2**(b), **3**(c), **4**(d), **5**(e).

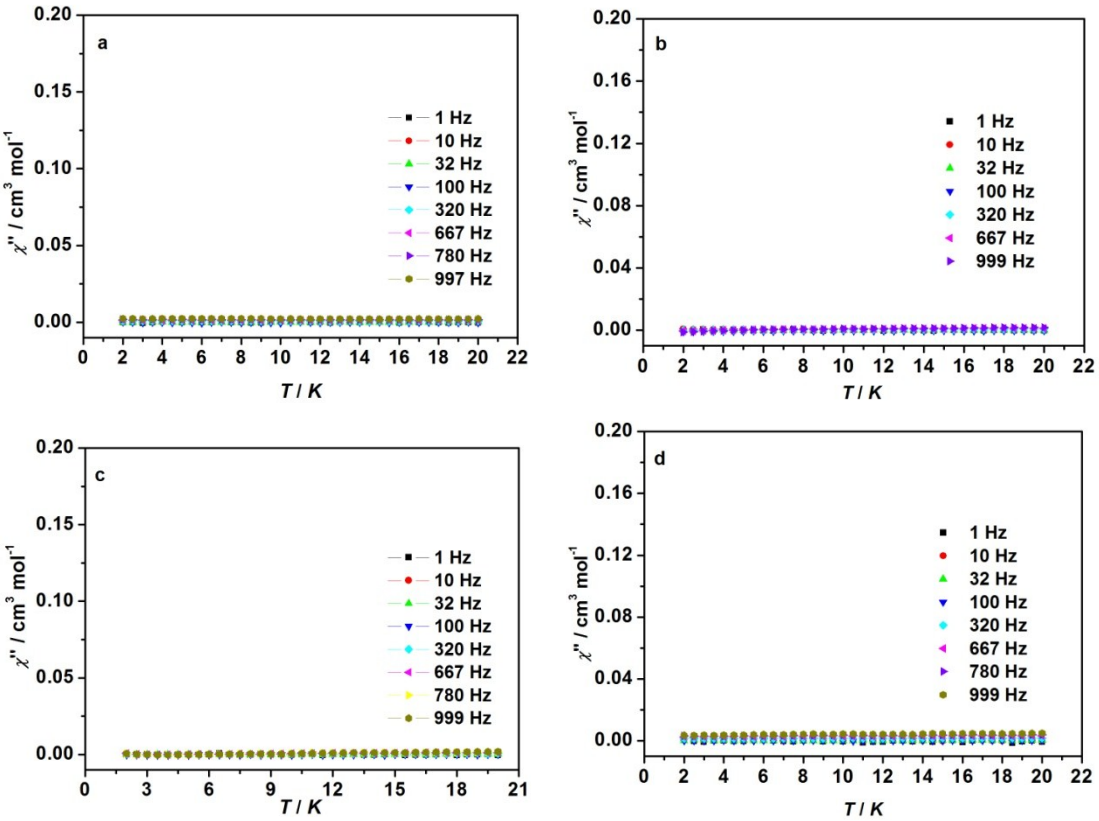


Fig. S6 Temperature dependence of the out-of-phase (χ_M'') ac susceptibility signals in a 5 Oe ac field oscillating at 1-999 Hz with a zero applied dc field for **2**(a), **3**(b), **4**(c), **5**(d).

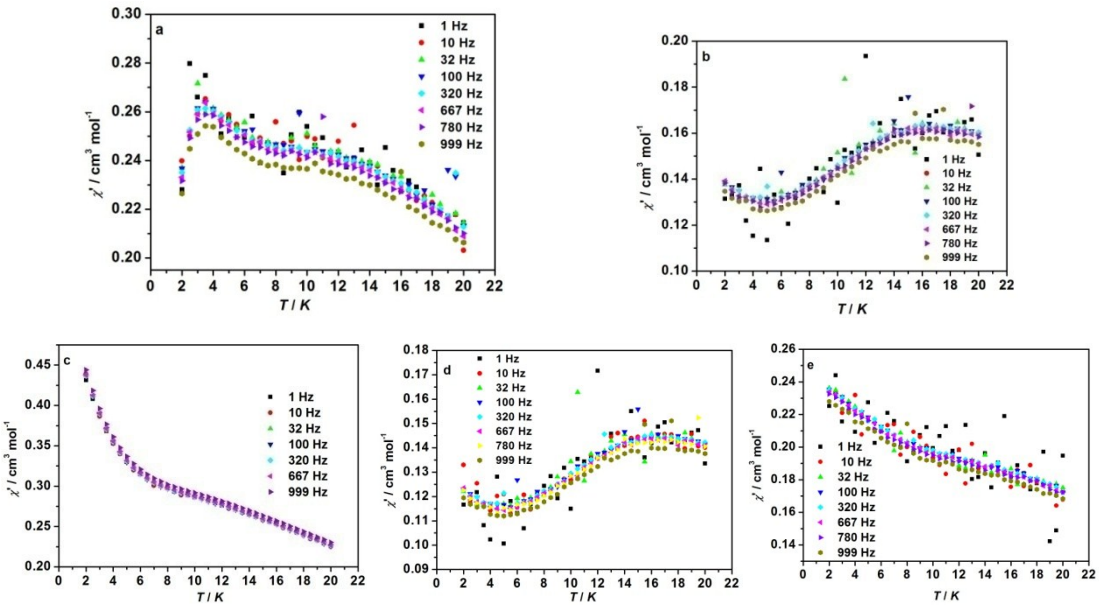
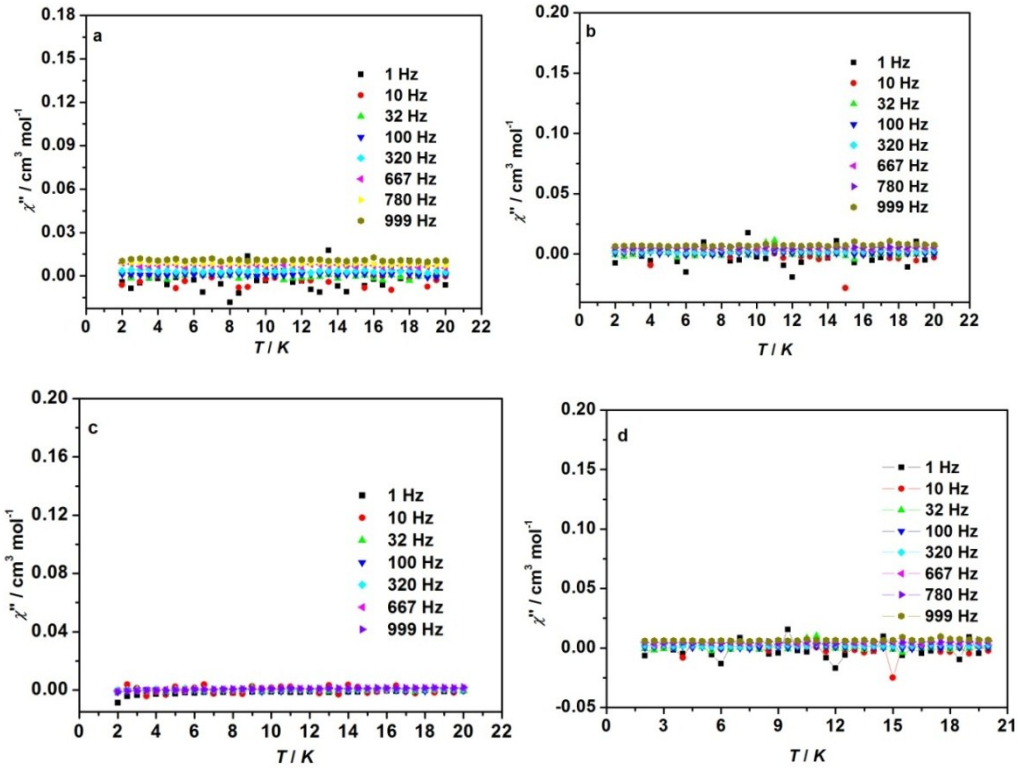


Fig. S7 Temperature dependence of the in-phase (χ_M') ac susceptibility signals in a 5 Oe ac field oscillating at 1-999 Hz with 2000 Oe dc field for **1**(a), **2**(b), **3**(c), **4**(d), **5**(e).



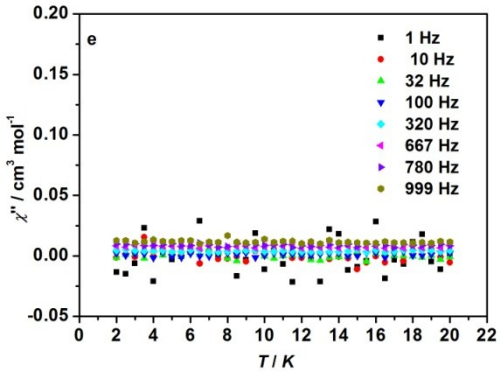


Fig. S8 Temperature dependence of the out-of-phase (χ_M'') ac susceptibility signals in a 5 Oe ac field oscillating at 1-999 Hz with 2000 Oe dc field for **1**(a), **2**(b), **3**(c), **4**(d), **5**(e).