Multifunctional Properties in $\{Cu^{II}_2Ln^{III}_2\}$ System Involving Nitrogen-Rich Nitronyl Nitroxide: Single-Molecule Magnet, Luminescence, Magnetocaloric Effect and Heat Capacity

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Table S1. The crystal data and refinement details of **1**

Ligand	**1**
Empirical formula	$C_{29}H_{36}Cl_2N_{12}O_4$
*M*r	687.60
T (K)	150(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a /Å	6.6243(8)
b /Å	15.4438(17)
c /Å	16.5551(17)
α /º	91.772(6)
β /º	101.017(6)

γ /º	100.690(6)
V /Å^3	1629.7(3)
Z	2
D_{calcd} /g cm^{-3}	1.405
θ /º	2.91-72.34
F(000)	720
Reflections collected	39190
Unique reflns/R_{int}	6755/0.0934
GOF (F^2)	0.999
R_1, wR_2 ($I > 2\sigma(I)$)	0.0924, 0.2031
R_1, wR_2 (all data)	0.1355, 0.2280

Table S2. Selected bond lengths [Å] and angles [°] for ligand **1**.

1 radical			
N(1)-C(4)	1.313(6)	N(7)-C(18)	1.317(6)
N(1)-C(1)	1.334(6)	N(7)-C(15)	1.346(7)
N(2)-C(2)	1.306(7)	N(8)-C(17)	1.315(6)
N(2)-C(3)	1.335(6)	N(8)-C(16)	1.341(7)
N(3)-N(4)	1.371(5)	N(9)-C(19)	1.347(6)
N(3)-C(5)	1.361(6)	N(9)-N(10)	1.383(5)
N(3)-C(4)	1.403(6)	N(9)-C(18)	1.408(6)
N(4)-C(6)	1.324(6)	N(10)-C(20)	1.322(6)
N(5)-O(1)	1.275(5)	N(11)-C(22)	1.353(6)
N(5)-C(8)	1.328(6)	N(11)-C(24)	1.506(6)
N(5)-C(10)	1.504(6)	N(12)-O(4)	1.277(5)
N(6)-O(2)	1.286(5)	N(12)-C(22)	1.346(6)
N(6)-C(8)	1.341(6)	N(12)-C(23)	1.505(6)
N(6)-C(9)	1.496(6)		
O(1)-N(5)-C(8)	125.7(4)	C(8)-N(6)-C(9)	112.7(4)
O(1)-N(5)-C(10)	121.4(4)	O(3)-N(11)-C(22)	125.1(4)
C(8)-N(5)-C(10)	112.7(4)	O(3)-N(11)-C(24)	122.0(4)
O(2)-N(6)-C(8)	125.3(4)	O(4)-N(12)-C(22)	125.0(4)
O(2)-N(6)-C(9)	121.9(4)	O(4)-N(12)-C(23)	122.6(4)

Table S3. Selected bond lengths [Å] and angles [°] for compounds **2** and **3**.

2 Gd		**3** Tb	
Gd(1)-O(7)	2.401(5)	Tb(1)-O(7)	2.376(4)
Gd(1)-O(8)	2.402(5)	Tb(1)-O(8)	2.395(5)
Gd(1)-O(9)	2.415(6)	Tb(1)-O(9)	2.372(4)
Gd(1)-O(10)	2.384(6)	Tb(1)-O(10)	2.388(4)
Gd(1)-O(11)	2.400(6)	Tb(1)-O(11)	2.369(4)
Gd(1)-O(12)	2.401(5)	Tb(1)-O(12)	2.396(4)
Gd(1)-O(13)	2.393(5)	Tb(1)-O(13)	2.389(4)
Gd(1)-N(3)	2.581(6)	Tb(1)-N(3)	2.570(5)
Gd(1)-N(5)	2.747(6)	Tb(1)-N(5)	2.743(5)
Cu(1)-O(6)	1.943(6)	Cu(1)-O(6)	1.948(5)
Cu(1)-O(5)	1.953(5)	Cu(1)-O(5)	1.960(4)
Cu(1)-O(3)	1.959(5)	Cu(1)-O(3)	1.961(4)
Cu(1)-O(4)	1.963(5)	Cu(1)-O(4)	1.965(4)
Cu(1)-O(1)	2.465(7)	Cu(1)-O(1)	2.464(5)
Cu(1)-N(6)	2.368(6)	Cu(1)-N(6)	2.368(5)
O(7)-Gd(1)-O(8)	73.16(18)	O(7)-Tb(1)-O(8)	70.53(16)
O(10)-Gd(1)-O(9)	72.78(18)	O(9)-Tb(1)-O(10)	73.63(14)
O(11)-Gd(1)-O(12)	70.52(19)	O(11)-Tb(1)-O(12)	73.05(15)
O(3)-Cu(1)-O(4)	92.2(2)	O(3)-Cu(1)-O(4)	91.91(19)
O(6)-Cu(1)-O(5)	92.4(2)	O(6)-Cu(1)-O(5)	92.1(2)
O(1)-Cu(1)-N(6)	165.2(2)	O(1)-Cu(1)-N(6)	165.1(2)

Table S4. Selected bond lengths [Å] and angles [°] for compound **4**.

	4 Dy
Dy(1)-O(7)	2.396(7)
Dy(1)-O(8)	2.352(7)
Dy(1)-O(9)	2.370(7)
Dy(1)-O(10)	2.361(7)
Dy(1)-O(11)	2.362(7)
Dy(1)-O(12)	2.371(6)
Dy(1)-O(13)	2.360(11)
Dy(1)-N(3)	2.564(8)
Dy(1)-N(5)	2.745(8)
Cu(1)-O(6)	1.954(7)
Cu(1)-O(5)	1.958(7)
Cu(1)-O(3)	1.948(7)
Cu(1)-O(4)	1.962(7)
Cu(1)-O(1)	2.468(8)
Cu(1)-N(6)	2.377(8)
O(7)-Dy(1)-O(8)	73.3(2)
O(10)-Dy(1)-O(9)	70.8(2)
O(11)-Dy(1)-O(12)	73.8(2)
O(3)-Cu(1)-O(4)	91.9(3)
O(6)-Cu(1)-O(5)	91.8(3)
O(1)-Cu(1)-N(6)	165.0(2)

Table S5. SHAPE analysis for complexes **2**-**4**.

Complex	JCSAPR-9	CSAPR-9	MFF-9
2 Gd	1.409	0.899	**0.671**
3 Tb	1.344	0.871	**0.659**
4 Dy	1.337	0.881	**0.654**

JCSAPR-9: Capped square antiprism J10; CSAPR-9: Spherical capped square antiprism; MFF-9: Muffin

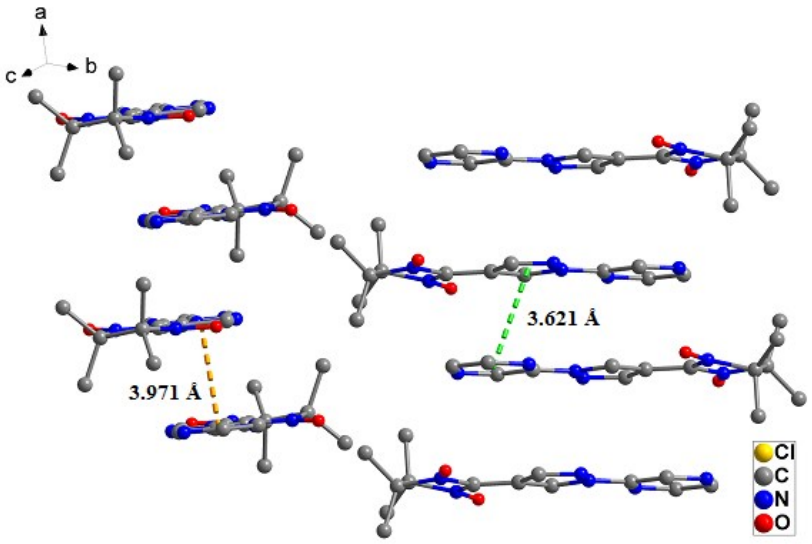

Figure S1. Packing diagram of ligand **1** and all of the hydrogen atoms are omitted for clarity.

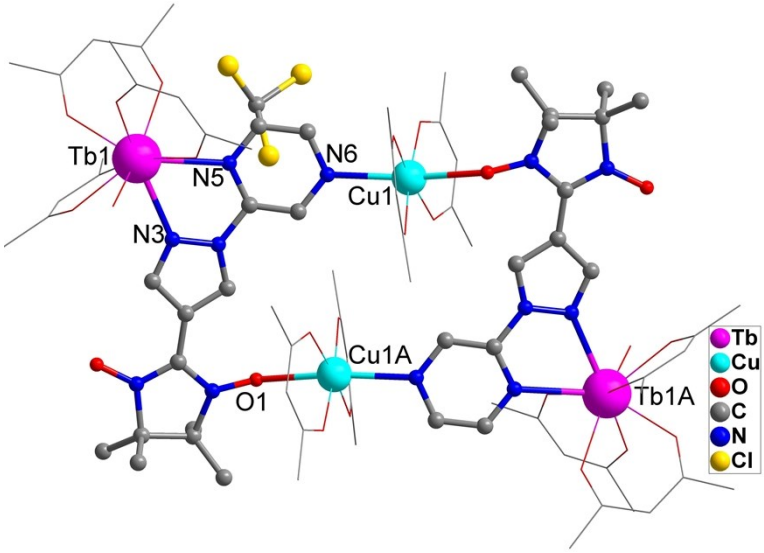

Figure S2. Crystal structure of complex **3**, in which H and F atoms are omitted for clarity.

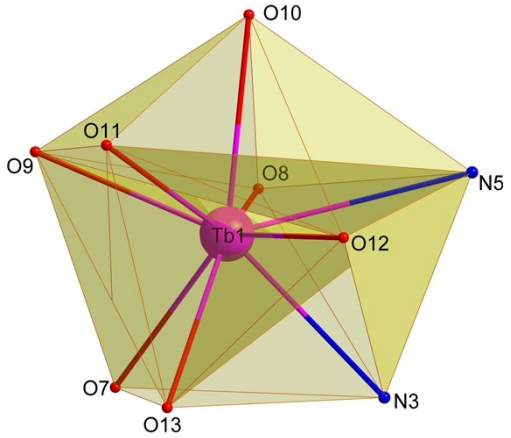

Figure S3. Coordination polyhedra around the Tb^{III} ion in **3**.

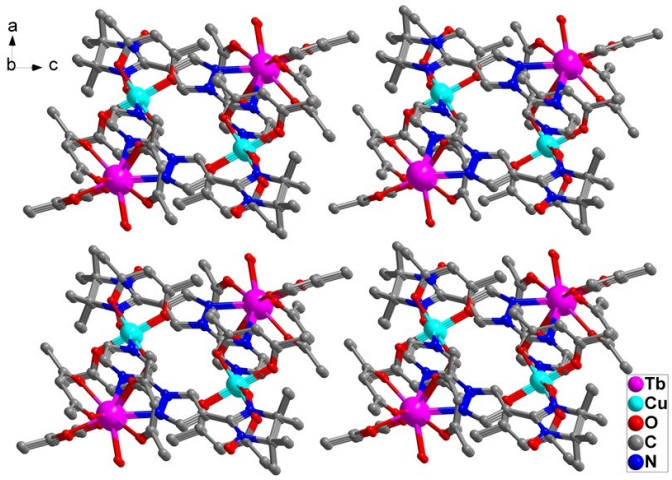

Figure S4. Packing diagram of complex **3**, where all the H and F atoms and trichloromethane solvent molecules are omitted for clarity.

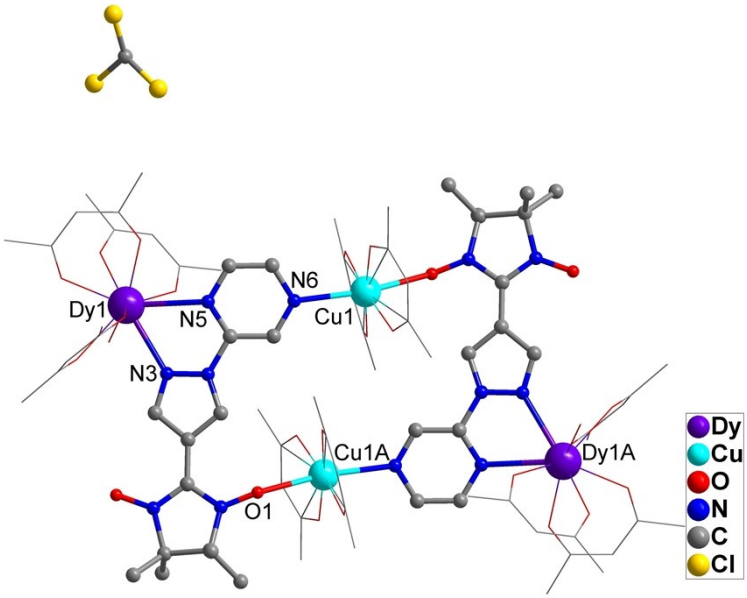

Figure S5. Crystal structure of complex **4**, in which H and F atoms are omitted for clarity.

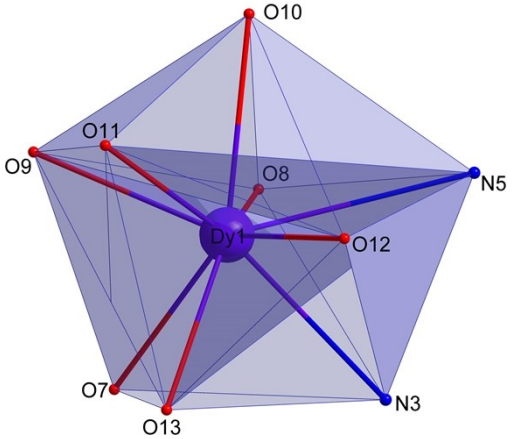

Figure S6. Coordination polyhedra around the Dy^{III} ion in **4**.

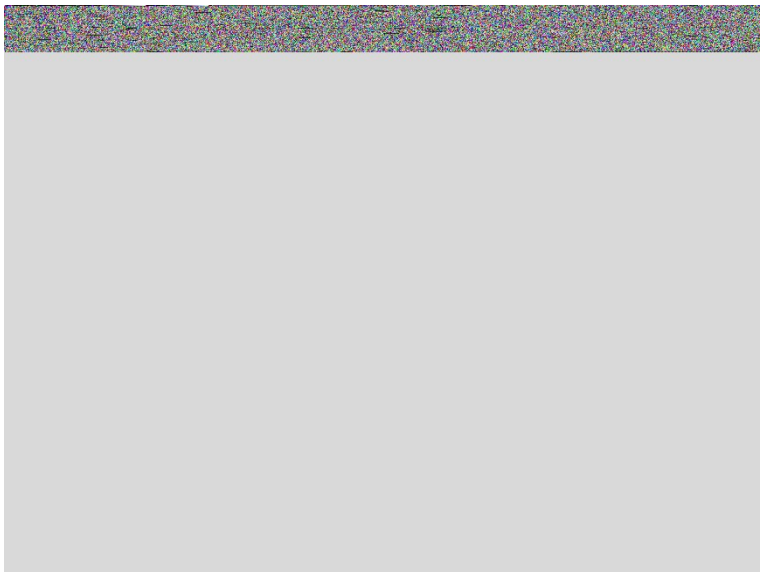

Figure S7. Packing diagram of complex **4**, where all the H and F atoms and trichloromethane solvent molecules are omitted for clarity.

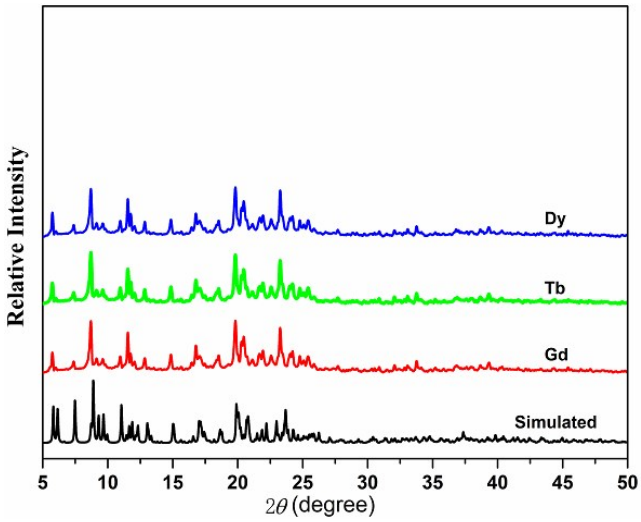

Figure S8. Powder X-ray diffraction (PXRD) patterns for complexes **2**-**4** at room temperature.

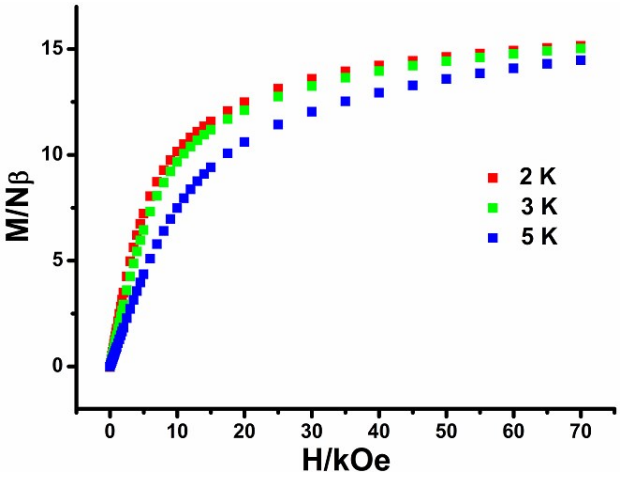

Figure S9. *M* versus *H* plot of complex **3** at 2.0, 3.0 and 5.0 K.

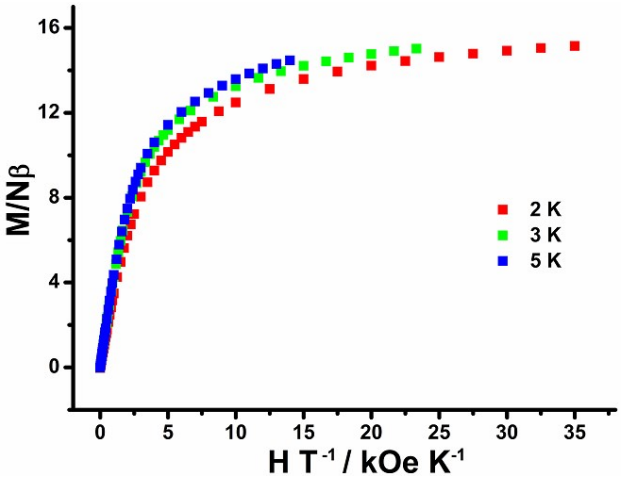

Figure S10. Plots of the reduced magnetization *M* versus HT^{-1} for compound **3**.

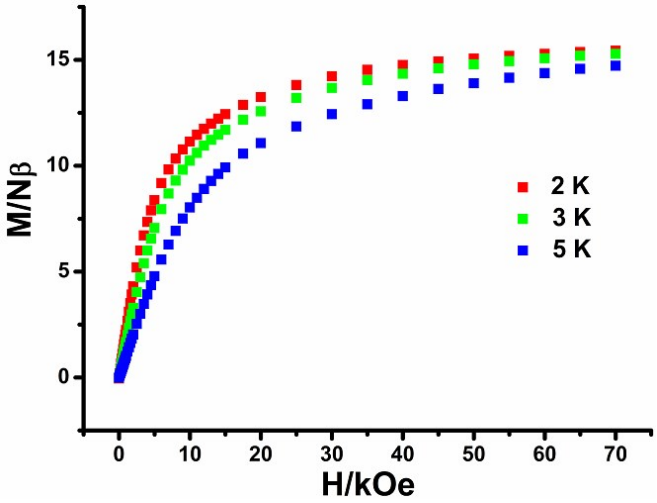

Figure S11. *M* versus *H* plot of complex **4** at 2.0, 3.0 and 5.0 K.

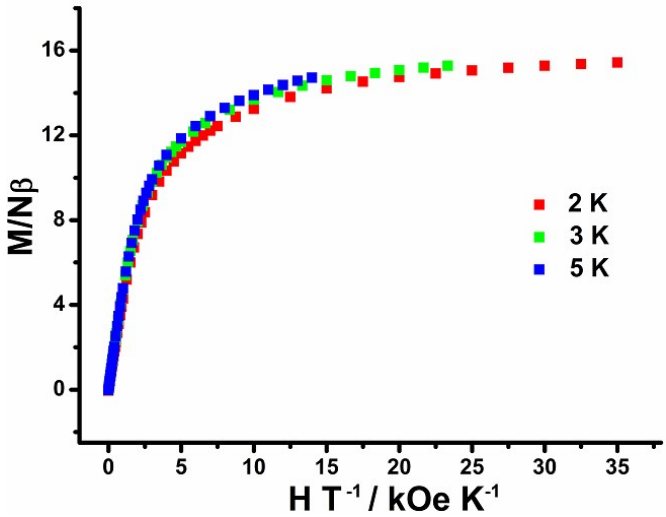

Figure S12. Plots of the reduced magnetization *M* versus HT^{-1} for compound **4**.

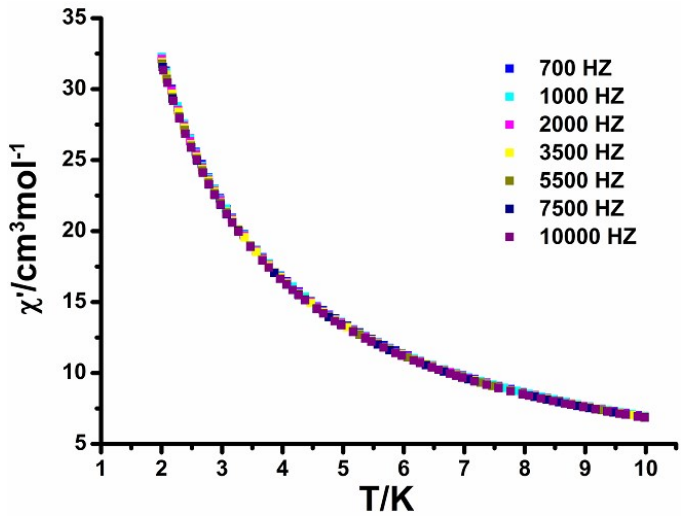

Figure S13. Temperature dependence of χ' for **3** in zero dc field with an oscillation of 3 Oe.

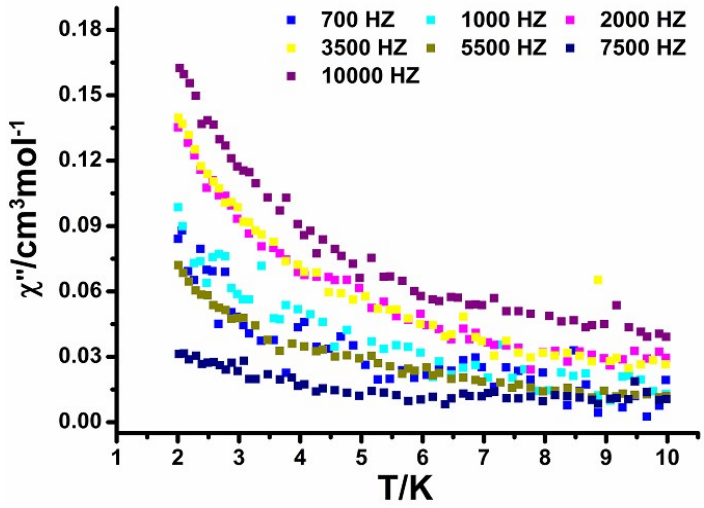

Figure S14. Temperature dependence of χ'' for **3** in zero dc field with an oscillation of 3 Oe.

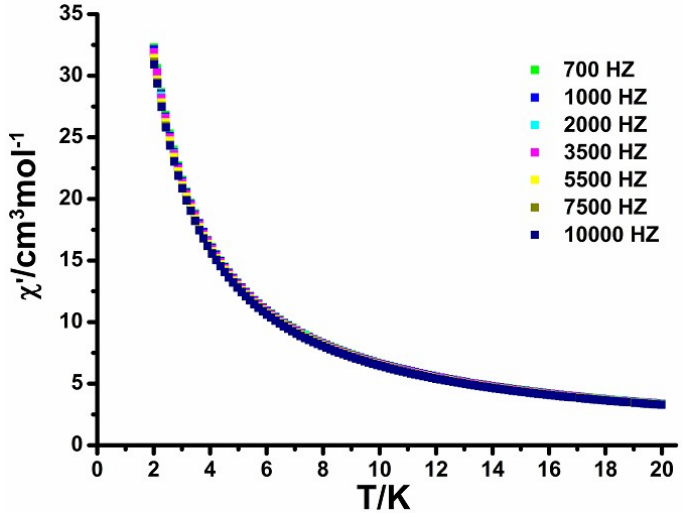

Figure S15. Temperature dependence of χ' for **4** in zero dc field with an oscillation of 3 Oe.

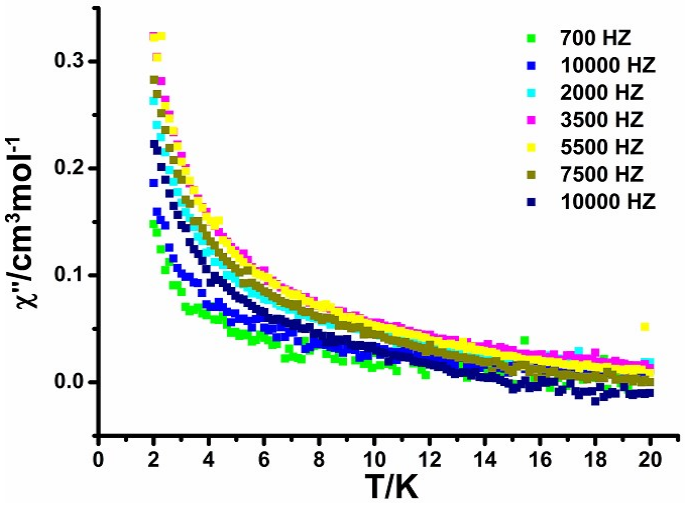

Figure S16. Temperature dependence of χ'' for **4** in zero dc field with an oscillation of 3 Oe.

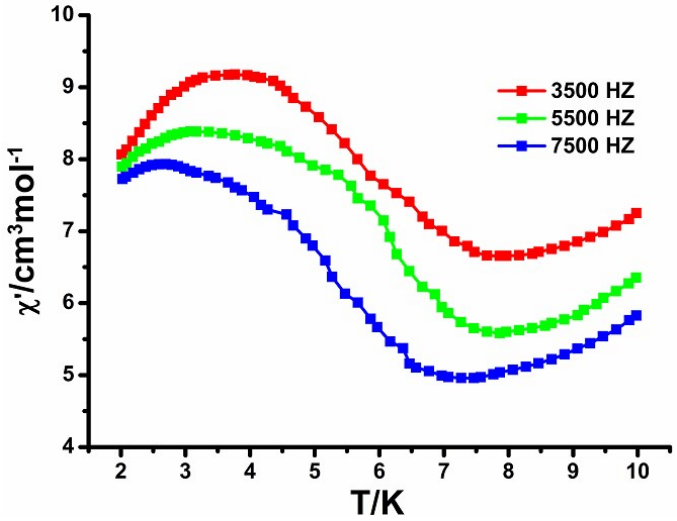

Figure S17. Temperature dependence of χ' for **4** in 1.5 kOe dc field with an oscillation of 3 Oe.

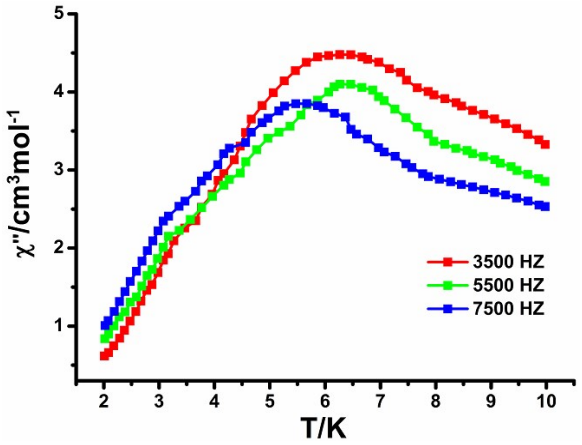

Figure S18. Temperature dependence of χ'' for **4** in 1.5 kOe dc field with an oscillation of 3 Oe.

Table S6. Selected parameters from the fitting result of the Cole-Cole plots for compound **4** under 1.5 kOe.

***Temp.* (K)**	***τ***	***α***
3.0 K	3.9E-4	0.38
3.5 K	2.33E-4	0.3595
4.0 K	1.5E-4	0.35
4.5 K	1.02E-4	0.33
5.0 K	6.6E-5	0.305
5.5 K	4.72E-5	0.274
6.0 K	3.86E-5	0.223
6.6 K	3.10E-4	0.218
7.0 K	2.86E-5	0.152

Table S7. Fitting parameters of the luminescence decay curve for compound **3**.

fitting parameter	compound **3**
τ_1	14.51
τ_2	52.06
A_1	1.21E4
A_2	397.5
B	3.16
R^2	0.997