Supporting Information

Slow relaxation of the magnetization observed in mononuclear Ln-radical compounds with D_{4d} geometry configuration

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1. Crystallographic Data

Table S1. Crystallographic Data and Structure Refinement Details for **1**-**3**.

	1	**2**	**3**
formula	$C_{50}H_{36}F_{36}Gd_2N_8O_{16}$	$C_{50}H_{36}F_{36}N_8O_{16}Tb_2$	$C_{50}H_{36}Dy_2F_{36}N_8O_{16}$
Mr	2003.34	2006.71	2013.87
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1$/c
a (Å)	22.7171(4)	22.4759(11)	22.3377(12)
b (Å)	17.7935(3)	17.6489(7)	17.6000(7)
c (Å)	18.7601(4)	18.5888(9)	18.5483(10)
α(°)	90	90	90
β(°)	109.425(2)	108.609(5)	108.210(6)
γ(°)	90	90	90
V (Å^3)	7151.5(2)	6988.2(6)	6927.0(6)
Z	4	4	4
ρcalc (Mg/m^3)	1.861	1.907	1.931
μ (mm^{-1})	13.351	11.339	2.306
F(000)	3888	3896	3904
θ range(°)	3.52~67.08	3.54~67.08	2.071~25.008
GOF on F^2	1.021	1.047	1.030
R_1/wR_2[$I > 2\sigma(I)$]	0.0600, 0.1535	0.1074, 0.2835	0.0524, 0.1201
R_1/wR_2 (all data)	0.0841, 0.1696	0.1449, 0.3215	0.0822, 0.1475

Table S2. Lanthanide geometry analysis by *SHAPE* software

Ln(III)	D_{2d}-DD	C_{2v}-TP	D_{4d}-AP
Gd1(**1**)	1.273	2.420	0.647
Gd2(**1**)	1.378	2.097	0.534
Tb1(**2**)	1.483	1.714	0.564
Tb2(**2**)	1.620	2.007	0.380
Dy1(**3**)	1.538	1.730	0.536
Dy2(**3**)	1.749	2.066	0.333

Table S3. Selected bond lengths (Å) and bond angles (°) in complex **1**.

Gd(1)-O(1)	2.311(5)	O(3)-Gd(1)-O(4)	71.82(16)
Gd(1)-O(3)	2.360(5)	O(3)-Gd(1)-O(5)	77.16(16)
Gd(1)-O(4)	2.384(5)	O(3)-Gd(1)-O(7)	140.27(17)
Gd(1)-O(5)	2.402(5)	O(4)-Gd(1)-O(5)	123.99(16)
Gd(1)-O(6)	2.359(5)	O(4)-Gd(1)-N(3)	133.36(18)
Gd(1)-O(7)	2.371(4)	O(5)-Gd (1)-N(3)	74.22(18)
Gd(1)-O(8)	2.383(5)	O(6)-Gd(1)-O(3)	109.28(17)
Gd(1)-N(3)	2.546(6)	O(6)-Gd(1)-O(4)	75.39(16)
Gd(2)-O(9)	2.334(6)	O(6)-Gd(1)-O(8)	79.74(17)
Gd(2)-O(11)	2.359(5)	O(6)-Gd(1)-N(3)	145.32(17)
Gd(2)-O(12)	2.367(5)	O(8)-Gd(1)-N(3)	118.97(18)
Gd(2)-O(13)	2.380(5)	N(1)-O(1)-Gd(1)	141.3(4)
Gd(2)-O(14)	2.377(5)	O(9)-Gd(2)-O(11)	78.97(19)
Gd(2)-O(15)	2.379(5)	O(9)-Gd(2)-O(12)	81.9(2)
Gd(2)-O(16)	2.363(5)	O(9)-Gd(2)-O(14)	144.47(17)
Gd(2)-N(5)	2.542(6)	O(11)-Gd(2)-O(12)	71.61(17)
O(1)-Gd(1)-O(3)	82.38(19)	O(12)-Gd(2)-O(13)	119.15(17)
O(1)-Gd(1)-O(4)	77.27(18)	O(15)-Tb(2)-O(11)	138.0(3)
O(1)-Gd(1)-O(5)	142.39(16)	O(15)-Tb(2)-O(14)	111.9(3)
O(1)-Gd(1)-O(6)	144.76(17)	O(16)-Tb(2)-O(13)	119.2(3)
O(1)-Gd(1)-O(7)	110.4(20)	O(11)-Gd(2)-N(5)	134.04(18)
O(1)-Gd(1)-O(8)	74.02(18)	O(12)-Gd(2)-N(5)	71.37(17)
O(1)-Gd(1)-N(3)	69.57(18)	N(7)-O(9)-Gd(2)	138.8(4)

Table S4. Selected bond lengths (Å) and bond angles (°) in complex **2**.

Tb(1)-O(1)	2.289(8)	O(3)-Tb(1)-O(4)	72.0(3)
Tb(1)-O(3)	2.352(9)	O(3)-Tb(1)-O(6)	144.6(3)
Tb(1)-O(4)	2.346(8)	O(3)-Tb(1)-O(5)	79.2(3)
Tb(1)-O(5)	2.365(9)	O(4)-Tb(1)-O(6)	141.6(3)
Tb(1)-O(6)	2.357(7)	O(4)-Tb(1)-O(8)	109.3(3)
Tb(1)-O(7)	2.375(8)	O(4)-Tb(1)-O(5)	145.3(3)
Tb(1)-O(8)	2.335(8)	O(5)-Tb(1)-O(7)	136.5(3)
Tb(1)-N(3)	2.531(11)	O(5)-Tb(1)-O(6)	71.0(2)
Tb(2)-O(9)	2.329(8)	O(6)-Tb(1)-O(8)	80.7(3)
Tb(2)-O(11)	2.349(9)	O(4)-Tb(1)-N(3)	71.9(3)
Tb(2)-O(12)	2.342(9)	O(8)-Tb(1)-N(3)	144.9(3)
Tb(2)-O(13)	2.368(9)	N(1)-O(1)-Tb(1)	140.5(7)
Tb(2)-O(14)	2.345(9)	O(9)-Tb(2)-O(11)	112.8(3)

Tb(2)-O(15)	2.332(8)	O(9)-Tb(2)-O(12)	76.1(3)
Tb(2)-O(16)	2.349(8)	O(12)-Tb(2)-O(11)	72.5(3)
Tb(2)-N(7)	2.524(11)	O(14)-Tb(2)-O(11)	81.6(3)
O(1)-Tb(1)-O(3)	76.3(3)	O(14)-Tb(2)-O(16)	74.7(3)
O(1)-Tb(1)-O(4)	81.3(3)	O(15)-Tb(2)-O(11)	138.0(3)
O(1)-Tb(1)-O(5)	73.3(3)	O(15)-Tb(2)-O(14)	111.9(3)
O(1)-Tb(1)-O(7)	103.9(2)	O(16)-Tb(2)-O(13)	119.2(3)
O(1)-Tb(1)-O(8)	144.2(3)	O(11)-Tb(2)-N(7)	75.3(3)
O(1)-Tb(1)-O(6)	112.6(3)	O(13)-Tb(2)-N(7)	75.6(3)
O(1)-Tb(1)-N(3)	70.7(3)	N(5)-O(9)-Tb(2)	135.8(8)

Table S5. Selected bond lengths (Å) and bond angles (°) in complex **3**.

Dy(1)-O(1)	2.283(5)	O(3)-Dy(1)-O(6)	109.42(18)
Dy(1)-O(3)	2.316(5)	O(3)-Dy(1)-O(7)	141.13(17)
Dy(1)-O(4)	2.347(5)	O(3)-Dy(1)-O(8)	145.31(17)
Dy(1)-O(5)	2.368(5)	O(3)-Dy(1)-N(3)	72.42(19)
Dy(1)-O(6)	2.341(5)	O(4)-Dy(1)-O(7)	144.55(17)
Dy(1)-O(7)	2.342(5)	O(5)-Dy(1)-O(7)	141.13(17)
Dy(1)-O(8)	2.354(5)	O(4)-Dy(1)-N(3)	134.43(19)
Dy(1)-N(3)	2.516(6)	O(5)-Dy(1)-O(6)	73.09(17)
Dy(2)-O(9)	2.324(5)	O(6)-Dy(1)-O(7)	80.78(18)
Dy(2)-O(11)	2.333(5)	O(6)-Dy(1)-N(3)	145.69(18)
Dy(2)-O(12)	2.337(5)	N(1)-O(1)-Dy(1)	140.4(4)
Dy(2)-O(13)	2.350(5)	O(9)-Dy(2)-O(11)	113.03(18)
Dy(2)-O(14)	2.349(5)	O(9)-Dy(2)-O(12)	75.85(19)
Dy(2)-O(15)	2.330(5)	O(9)-Dy(2)-O(13)	143.69(17)
Dy(2)-O(16)	2.315(5)	O(9)-Dy(2)-O(14)	142.31(17)
Dy(2)-N(7)	2.499(6)	O(9)-Dy(2)-N(7)	70.53(18)
O(1)-Dy(1)-O(4)	76.66(18)	O(11)-Dy(2)-O(12)	72.56(17)
O(1)-Dy(1)-O(5)	142.72(17)	O(11)-Dy(2)-O(13)	81.56(18)
O(1)-Dy(1)-O(6)	143.56(17)	O(11)-Dy(2)-N(7)	74.77(19)
O(1)-Dy(1)-O(7)	112.92(19)	O(12)-Dy(2)-O(13)	77.64(19)
O(1)-Dy(1)-O(3)	81.55(19)	O(12)-Dy(2)-O(14)	136.66(18)
O(1)-Dy(1)-O(8)	72.88(19)	O(13)-Dy(2)-O(16)	72.64(17)
O(1)-Dy(1)-N(3)	70.48(19)	O(15)-Dy(2)-O(16)	72.64(17)
O(3)-Dy(1)-O(4)	72.28(16)	O(16)-Dy(2)-N(7)	72.20(18)
O(3)-Dy(1)-O(5)	76.76(17)	N(5)-(O9)-Dy(2)	135.4(4)

2. Powder X-ray Diffraction (PXRD)

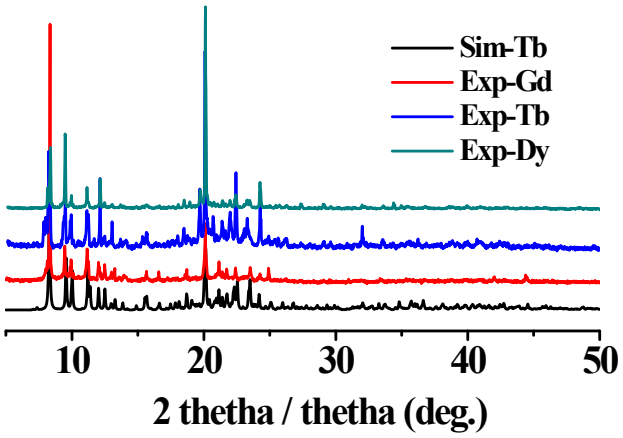

Figure S1. Powder X-ray diffractions of **1-3**.

3. Other crystal structure graphic

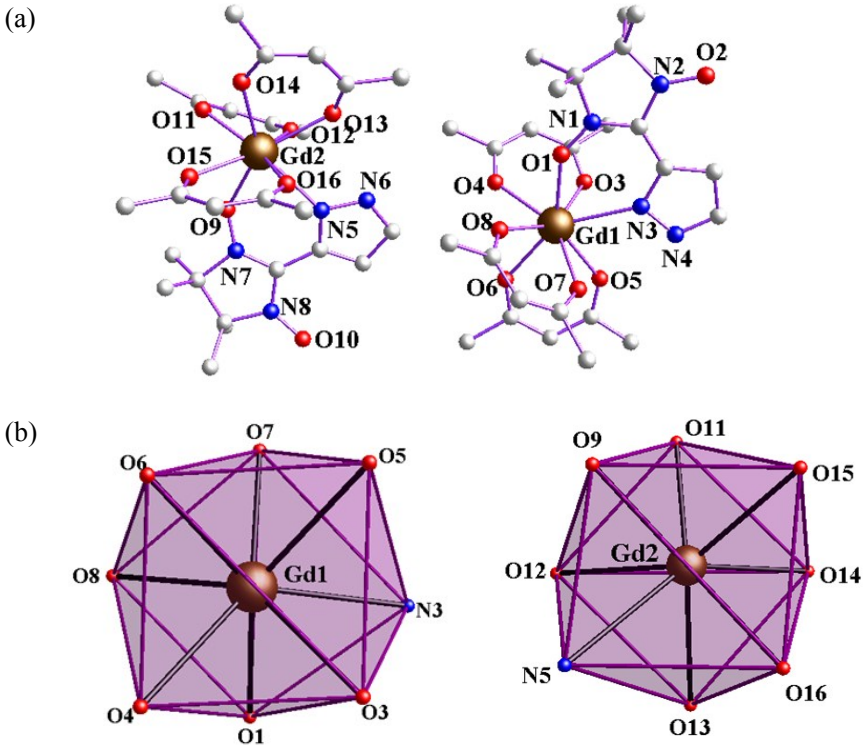

Figure S2. (a) Simplified view of the crystal structure of **1**. Fluorine and hydrogen atoms are omitted for clarity. (b) D_{4d}-symmetry polyhedral of the central gadolinium atoms.

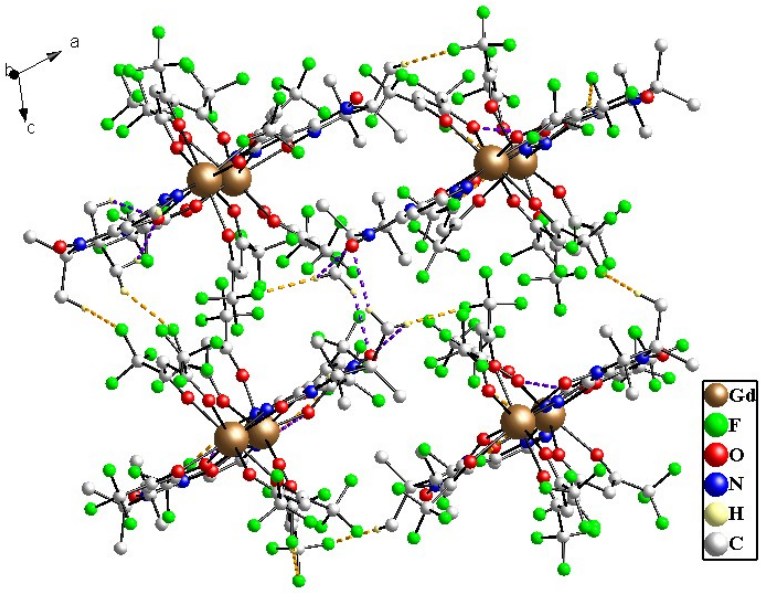

Figure S3. The 3D supermolecular framework via C–H··F (brown dashed lines) and C–H··O (purple dashed lines) hydrogen bonds in **1**.

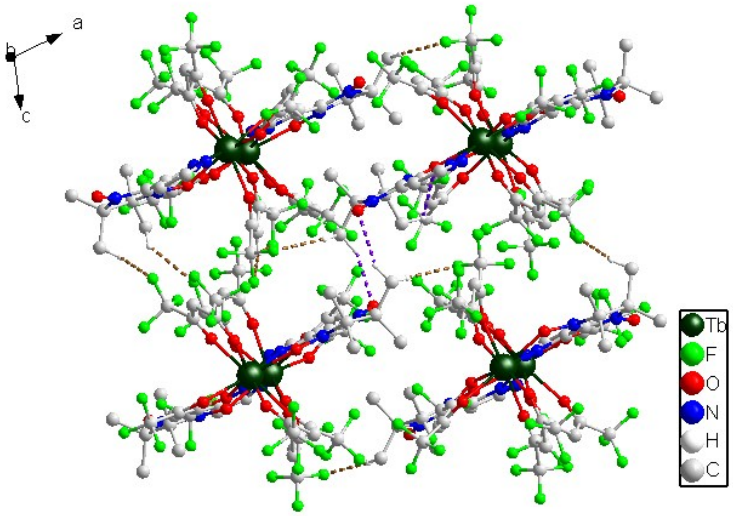

Figure S4. The 3D supermolecular framework via C–H···F (brown dashed lines) and C–H··O (purple dashed lines) hydrogen bonds in **2**.

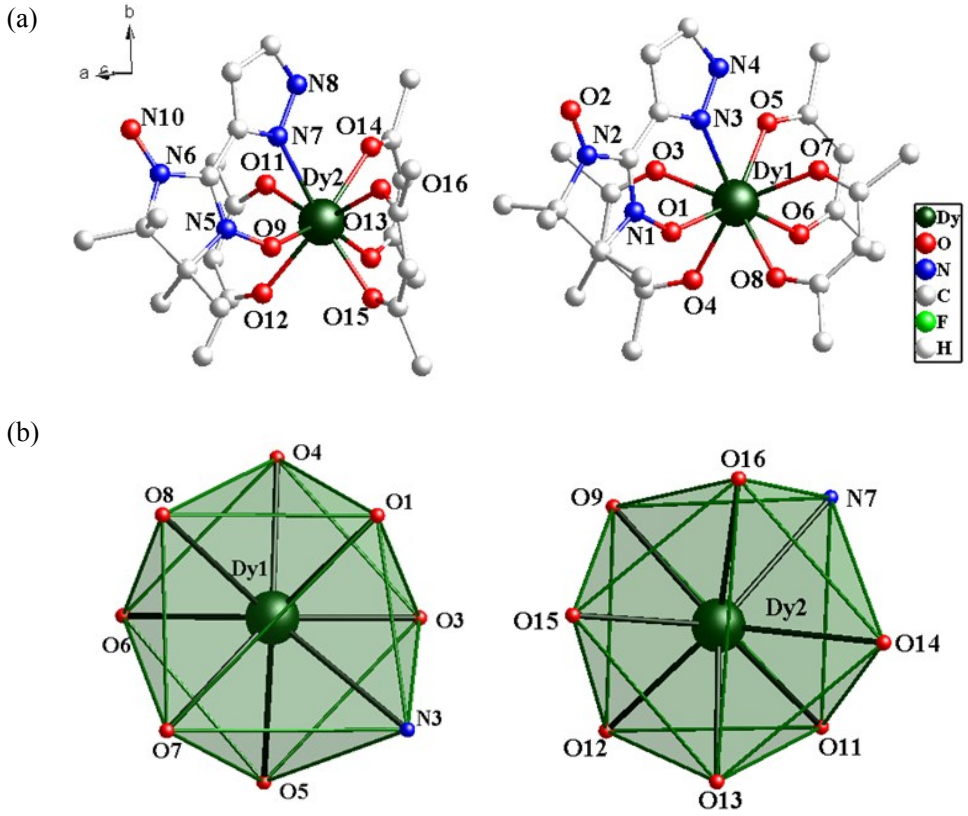

Figure S5. (a) Simplified view of the crystal structure of **3** Fluorine and hydrogen atoms are omitted for clarity. (b) D_{4d}-symmetry polyhedral of the central dysprosium atoms.

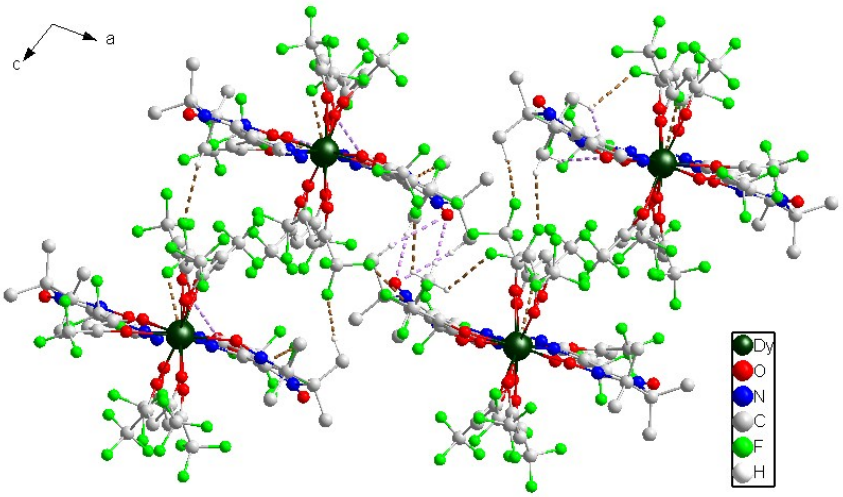

Figure S6. The 3D supermolecular framework via C–H··F (brown dashed lines) and C–H··O (purple dashed lines) hydrogen bonds in **3**.

4. Other Magnetic Data

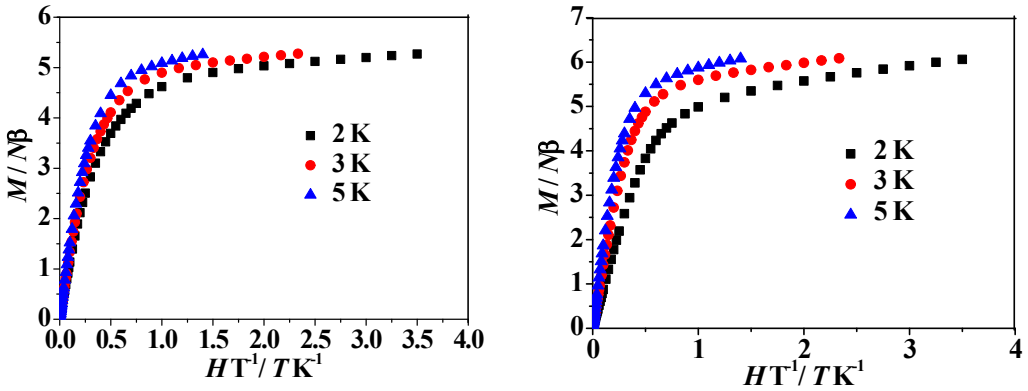

Figure S7. Field dependence of the magnetization at 2, 3, and 5 K for complexes **2** (left) and **3** (right).

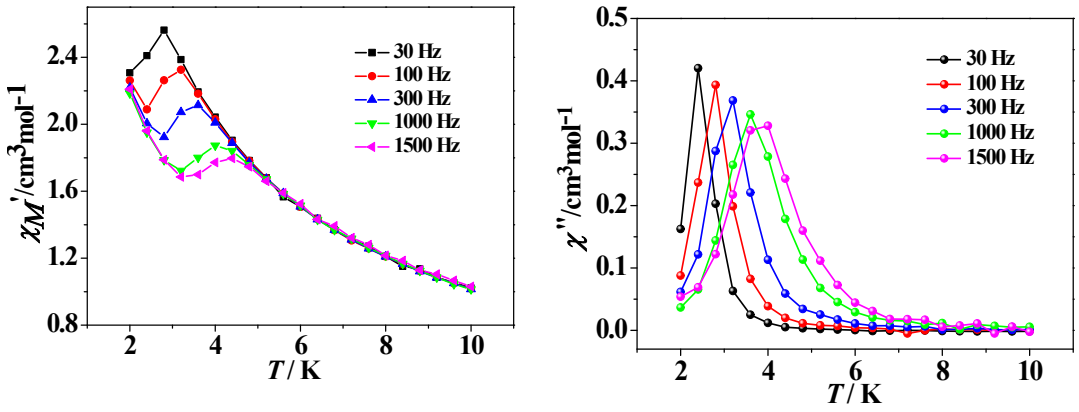

Figure S8. Temperature dependencies of the in-phase (χ′) and out-of-phase signals (χ″) components of the ac magnetic susceptibility for **2** at zero dc fields with an oscillation of 3.0 Oe.

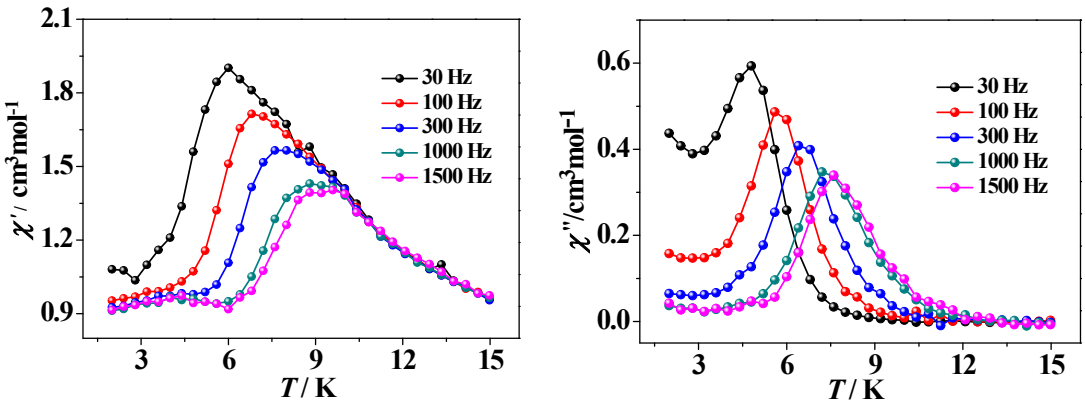

Figure S9. Temperature dependencies of the in-phase (χ′, left) and out-of-phase signals (χ″, right) components of the ac magnetic susceptibility for **3** at zero dc fields with an oscillation of 3.0 Oe.

Table S6. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **2** and **3** according to the generalized Debye model.

Compound **2**				
Temperature / K	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
2	2.3973	3.5204	0.0396	0.1817
2.2	2.2115	3.2885	0.0154	0.1381
2.4	2.2332	3.2685	0.0057	0.1145
2.6	2.4562	3.4438	0.0025	0.0981
2.8	2.4308	3.3692	0.0012	0.0799
3	2.4556	3.3444	6.8991E-4	0.0603
3.2	2.4753	3.3247	4.1230E-4	0.0477
3.4	2.1000	2.8999	2.6626E-4	0.0336
3.6	2.1148	2.8852	1.7771E-4	0.0252
3.8	2.3792	3.1208	1.1294E-4	0.0258
4.0	2.1419	2.8581	8.7743E-5	0.0169
Compound **3**				
Temperature / K	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
2	1.4288	3.5712	0.0280	0.0591
3	1.6726	3.3274	0.0229	0.0518
4	1.1813	3.1868	0.0130	0.0442
5	1.9227	3.0772	0.0048	0.0434
5.5	1.9674	3.0326	0.0026	0.0516
6	2.0023	2.9977	0.0014	0.0700
6.5	2.0357	2.9643	6.7595E-4	0.0927
7	2.0644	2.9356	3.4714E-4	0.1183
7.5	2.0897	2.9103	1.8298E-4	0.1433
8	2.1295	2.8705	1.0650E-4	0.1491
9	2.0347	2.6950	8.3596E-5	0.0455