Supporting Information

Single-Molecule Magnet Behavior in One Cu^{II}-Decorated $\{Dy^{III}_2\}$ Complex with Nitronyl Nitroxide Biradical

Hongdao Li, Zan Sun, Juan Sun, Lu Xi, Jianni Guo, Guifang Sun, Jing Xie, Yue Ma, Licun Li*

Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry and Tianjin Key Laboratory of Metal and Molecule-based Material Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

Table S1. Crystallographic data and structure refinement summary for **1**

Complex	**1**
Empirical formula	$C_{25}H_{31}N_5O_5$
*M*r	481.55
T, (K)	113(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a /Å	7.784(3)
b /Å	12.896(3)
c /Å	13.706(5)
α /º	62.522(19)
β /º	88.17(4)
γ /º	79.78(4)
V /Å^3	1199.3(8)
Z	2
D_{calcd} /g cm^{-3}	1.333
μ /mm^{-1}	0.095
θ /º	3.02-25.35
F(000)	512
Reflections collected	12740
Unique reflns/R_{int}	4191/0.0829
GOF (F^2)	1.077
R_1, wR_2 ($I > 2\sigma(I)$)	0.1145, 0.2616
R_1, wR_2 (all data)	0.1731, 0.2941

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

1			
O(1)-C(9)	1.245(8)	O(2)-N(2)	1.272(6)
O(3)-N(3)	1.289(6)	O(4)-N(4)	1.269(6)
O(5)-N(5)	1.275(6)	N(2)-C(12)	1.350(8)
N(2)-C(14)	1.519(8)	N(3)-C(12)	1.344(8)
N(3)-C(13)	1.496(8)	N(4)-C(19)	1.359(8)
N(4)-C(21)	1.512(8)	N(5)-C(19)	1.369(8)
N(5)-C(20)	1.497(8)	C(7)-C(8)	1.326(9)
C(11)-C(10)	1.335(9)		
O(2)-N(2)-C(12)	127.2(5)	O(2)-N(2)-C(14)	120.0(5)
O(3)-N(3)-C(12)	127.3(5)	O(3)-N(3)-C(13)	118.7(5)
O(4)-N(4)-C(19)	126.6(5)	O(4)-N(4)-C(21)	120.8(5)
O(5)-N(5)-C(19)	126.2(5)	O(5)-N(5)-C(20)	121.9(5)
C(12)-N(2)-C(14)	112.5(5)	C(12)-N(3)-C(13)	113.6(5)
C(19)-N(4)-C(21)	112.2(5)	C(19)-N(5)-C(20)	111.4(5)
N(2)-C(12)-N(3)	108.9(5)	N(4)-C(19)-N(5)	107.8(5)

Description of the structure of 1

Single-crystal X-ray analysis reveals that compound **1** crystallizes in the triclinic space group $P\bar{1}$. The crystal structure of NITPhPyoebis biradical (**1**) is shown in Figure S1, the N-O bond lengths of two mono-radicals are in the range of 1.269-1.289 Å, corresponding to the typical N-O radical distances ranging from 1.25 to 1.32.[1] The C9-O1 bond length is 1.245 Å, which is typical of carbonyl group. And the neighboring N1-C7 and N1-C11 bond lengths are 1.366 and 1.377Å, respectively. Besides, the C7–C8, C8–C9, C9–C10 and C10–C11 bond lengths are 1.326, 1.448, 1.447 and 1.335 Å, respectively, the gap between the shortest and the longest C–C bond is large. The result suggests that biradical ligand contains a pyridinone ring.[2] The dihedral angles between benzene ring and five-membered heterocyclic rings of two mono-radicals are 18.48(2)° and 18.85(3)°, respectively, while the dihedral angle between the benzene ring and the pyridone ring is 42.72(2)°. In the intermolecular, the shortest separation between two nitroxide groups from the adjacent biradicals is 3.914 Å and the distances between the oxygen atom of NO group of one biradical and the bridging sp^2 carbon atom (C19#1, #1: 1-x, -y, 1-z) of the neighboring biradical are 3.031 and 3.271 Å, respectively, which imply the presence of non-negligible intermolecular interactions.

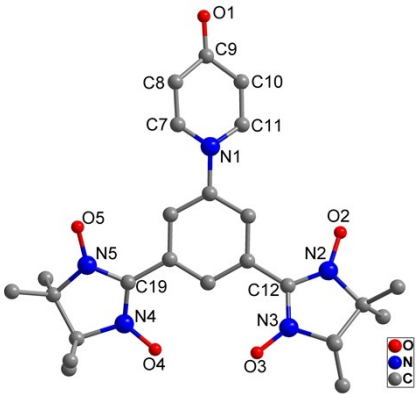

Figure S1. Crystal structure of complex **1** with the atom-labeling and all of the hydrogen atoms are omitted for clarity.

As shown in Figure S2, the stacking of neighboring phenyl rings of biradicals with centroid···centroid distances of 3.846 and 3.938 Å generates intermolecular π-π interactions to form an infinite pseudo 1D chain.

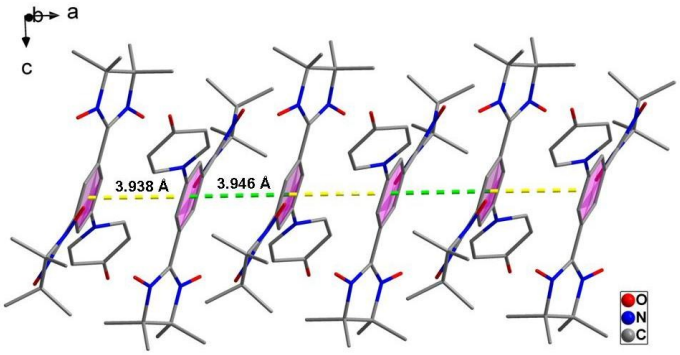

Figure S2. One-dimensional chain of complex **1** via π・・・π interactions and all of the hydrogen atoms are omitted for clarity.

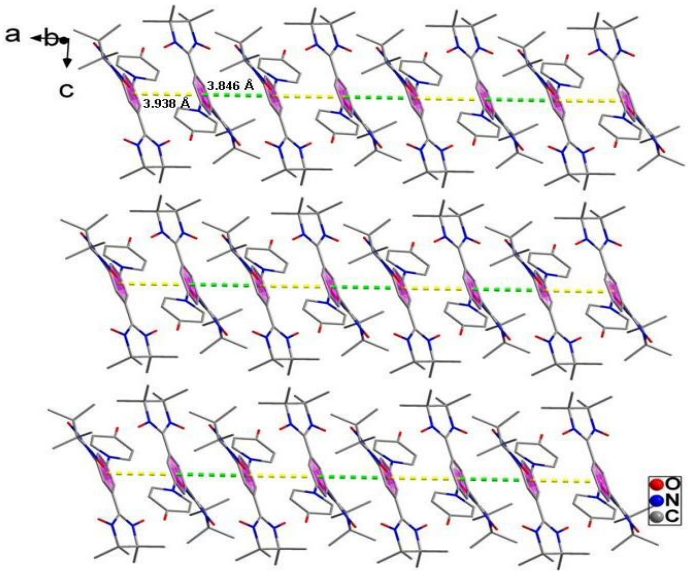

Figure S3. Packing arrangement of the chains in **1** and all of the hydrogen atoms are omitted for clarity.

References

1 (a) A. Caneschi, D. Gatteschi and P. Rey, *Prog. Inorg. Chem.* 1991, **39**, 331; (b) A. Caneschi, P. Chiesi, L. David, F. Ferraro, D. Gatteschi and R. Sessoli, *Inorg. Chem.* 1993, **32**, 1445; (c) E. V. Tretyakov and V. I. Ovcharenko, *Russ. Chem. Rev.* 2009, **78**, 971.

2 (a) Y. X. Zhu, Z. W. Wei, M. Pan, H. P. Wang, J. Y. Zhang and C. Y. Su, *Dalton Trans.* 2016, **45**, 943; (b) S. Y. Yin, Y. X. Zhu, M. Pan, Z. W. Wei, H. P. Wang, Y. N. Fan and C. Y. Su, *Eur. J. Inorg. Chem.* 2017, 646.

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

2 Gd		**3** Tb	
Gd(1)-O(5)	2.338(3)	Tb(1)-O(5)	2.351(4)
Gd(1)-O(3)	2.343(3)	Tb(1)-O(3)	2.339(4)
Gd(1)-O(4)	2.352(3)	Tb(1)-O(4)	2.356(4)
Gd(1)-O(7)#1	2.357(3)	Tb(1)-O(7)#1	2.377(3)
Gd(1)-O(6)	2.358(3)	Tb(1)-O(6)	2.370(3)
Gd(1)-O(2)	2.364(3)	Tb(1)-O(2)	2.358(3)
Gd(1)-O(1)	2.369(3)	Tb(1)-O(1)	2.377(3)
Gd(1)-O(7)	2.371(3)	Tb(1)-O(7)	2.376(3)
Cu(1)-O(8)	1.914(3)	Cu(1)-O(8)	1.923(3)
Cu(1)-O(11)	1.914(3)	Cu(1)-O(11)	1.923(3)
Cu(1)-O(12)	1.931(3)	Cu(1)-O(12)	1.937(3)
Cu(1)-O(9)	1.954(3)	Cu(1)-O(9)	1.955(3)
Cu(1)-O(10)	2.219(3)	Cu(1)-O(10)	2.231(4)
O(12)-N(2)	1.307(4)	O(12)-N(2)	1.306(4)
O(13)-N(3)	1.268(4)	O(13)-N(3)	1.266(5)
O(14)-N(4)	1.274(5)	O(14)-N(4)	1.276(6)
O(15)-N(5)	1.261(5)	O(15)-N(5)	1.266(5)
O(2)-Gd(1)-O(1)	71.84(11)	O(2)-Tb(1)-O(1)	71.72(12)
O(3)-Gd(1)-O(4)	71.57(13)	O(3)-Tb(1)-O(4)	71.90(14)
O(5)-Gd(1)-O(6)	72.51(12)	O(5)-Tb(1)-O(6)	71.88(13)
O(7)#1-Gd(1)-O(7)	69.08(10)	O(7)#1-Tb(1)-O(7)	68.89(11)
Gd(1)#1-O(7)-Gd(1)	110.92(10)	Tb(1)#1-O(7)-Tb(1)	111.11(11)
O(8)-Cu(1)-O(9)	92.26(14)	O(8)-Cu(1)-O(9)	92.69(15)
O(11)-Cu(1)-O(10)	88.05(13)	O(11)-Cu(1)-O(10)	87.92(14)
N(2)-O(12)-Cu(1)	119.6(2)	N(2)-O(12)-Cu(1)	119.0(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1 for **2** and **3**

Table S4. Selected bond lengths [Å] and angles [°] for complexes **4** and **5**.

4 Dy		**5** Ho	
Dy(1)-O(5)	2.346(4)	Ho(1)-O(5)	2.340(4)
Dy(1)-O(3)	2.314(4)	Ho(1)-O(3)	2.342(4)
Dy(1)-O(4)	2.349(4)	Ho(1)-O(4)	2.351(4)
Dy(1)-O(7)#1	2.369(3)	Ho(1)-O(7)#1	2.360(3)
Dy(1)-O(6)	2.349(4)	Ho(1)-O(6)	2.362(4)
Dy(1)-O(2)	2.347(4)	Ho(1)-O(2)	2.362(3)
Dy(1)-O(1)	2.366(4)	Ho(1)-O(1)	2.369(3)
Dy(1)-O(7)	2.357(3)	Ho(1)-O(7)	2.369(3)
Cu(1)-O(8)	1.920(4)	Cu(1)-O(8)	1.916(4)
Cu(1)-O(11)	1.921(3)	Cu(1)-O(11)	1.916(3)
Cu(1)-O(12)	1.937(3)	Cu(1)-O(12)	1.931(3)
Cu(1)-O(9)	1.958(4)	Cu(1)-O(9)	1.951(4)
Cu(1)-O(10)	2.228(4)	Cu(1)-O(10)	2.224(4)
O(12)-N(2)	1.307(5)	O(12)-N(2)	1.307(5)
O(13)-N(3)	1.260(5)	O(13)-N(3)	1.263(5)
O(14)-N(4)	1.274(6)	O(14)-N(4)	1.275(6)
O(15)-N(5)	1.269(5)	O(15)-N(5)	1.263(5)
O(2)-Dy(1)-O(1)	72.02(13)	O(2)-Ho(1)-O(1)	71.76(12)
O(3)-Dy(1)-O(4)	71.93(17)	O(3)-Ho(1)-O(4)	71.70(15)
O(5)-Dy(1)-O(6)	72.10(15)	O(5)-Ho(1)-O(6)	72.43(14)
O(7)#1-Dy(1)-O(7)	69.20(12)	O(7)#1-Ho(1)-O(7)	69.04(11)
Dy(1)#1-O(7)-Dy(1)	110.80(12)	Ho(1)#1-O(7)-Ho(1)	110.96(11)
O(8)-Cu(1)-O(9)	92.95(17)	O(8)-Cu(1)-O(9)	92.69(15)
O(11)-Cu(1)-O(10)	87.86(16)	O(11)-Cu(1)-O(10)	87.92(14)
N(2)-O(12)-Cu(1)	119.0(3)	N(2)-O(12)-Cu(1)	119.0(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1 for **4** and **5**

Table S5. SHAPE analysis for complexes **2**-**5**.

Complex	SAPR-8	TDD-8	BTPR-8
2 Gd	**0.580**	1.570	2.168
3 Tb	**0.594**	1.558	2.196
4 Dy	**0.562**	1.572	2.189
5 Ho	**0.590**	1.570	2.193

SAPR-8: Square antiprism; TDD-8: Triangular dodecahedron; BTPR-8: Biaugmented trigonal prism

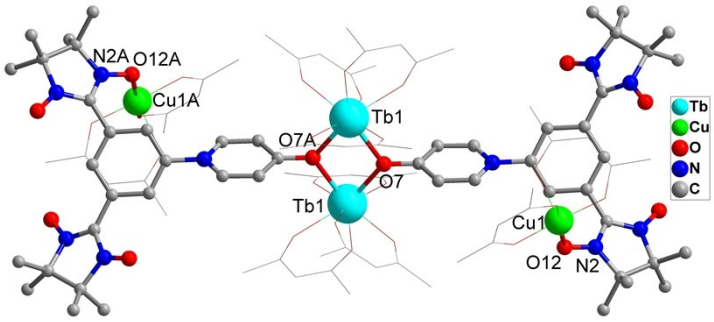

Figure S4. Molecular structure of complex **3** and all of the hydrogen and fluorine atoms are omitted for clarity.

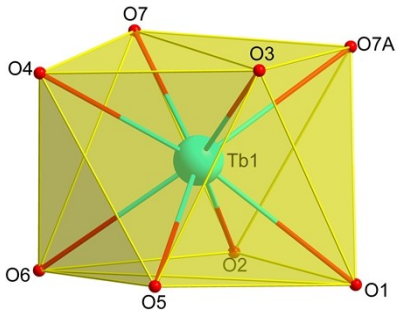

Figure S5. The coordination polyhedron of Tb(III) ion in complex **3**.

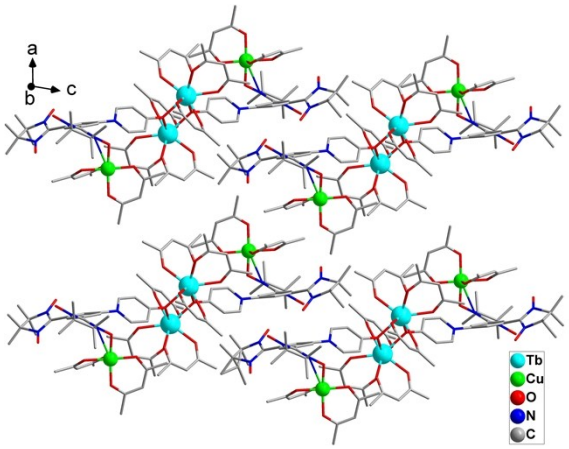

Figure S6. Packing diagram of complex **3** and all of the hydrogen and fluorine atoms are omitted for clarity.

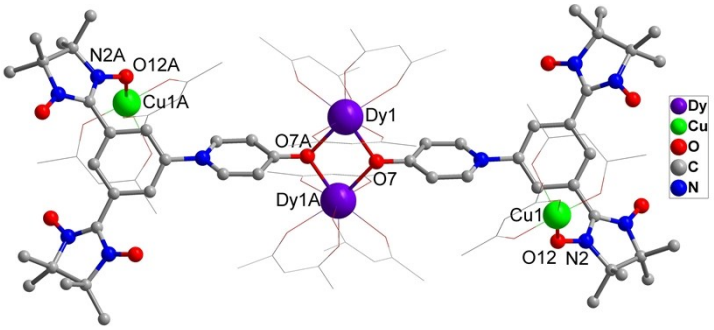

Figure S7. Molecular structure of complex **4** and all of the hydrogen and fluorine atoms are omitted for clarity.

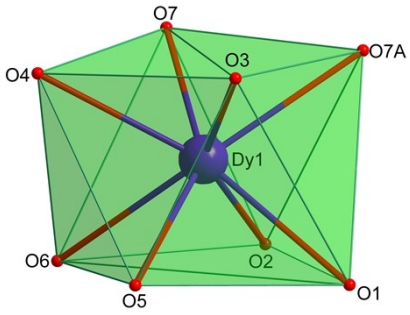

Figure S8. The coordination polyhedron of Dy(III) ion in complex **4**.

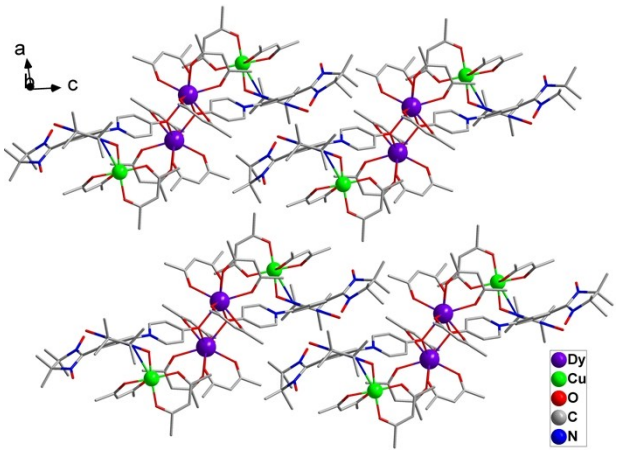

Figure S9. Packing diagram of complex **4** and all of the hydrogen and fluorine atoms are omitted for clarity.

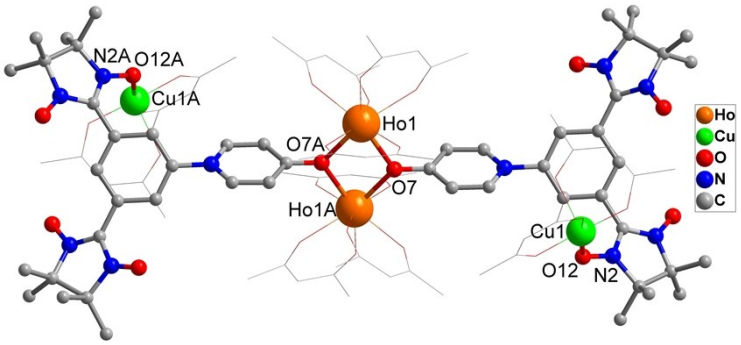

Figure S10. Molecular structure of complex **5** and all of the hydrogen and fluorine atoms are omitted for clarity.

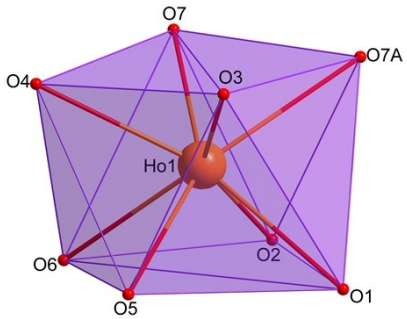

Figure S11. The coordination polyhedron of Ho(III) ion in complex **5**.

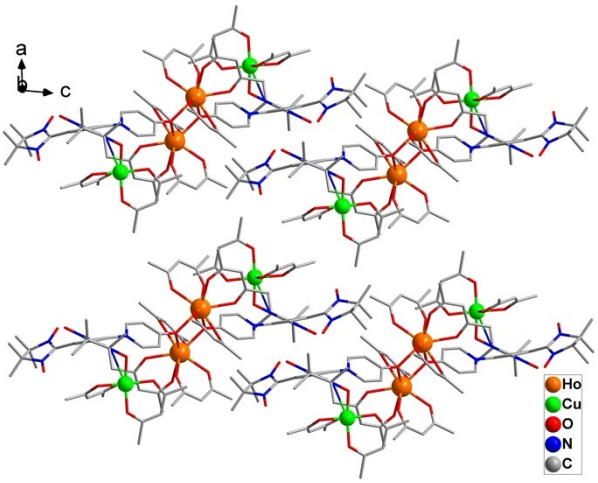

Figure S12. Packing diagram of complex **5** and all of the hydrogen and fluorine atoms are omitted for clarity.

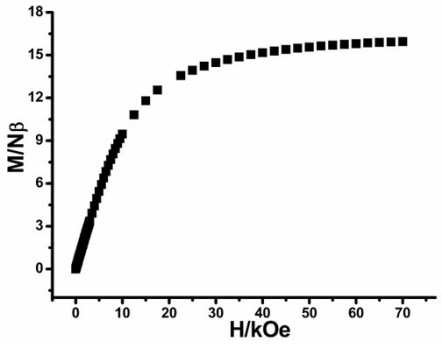

Figure S13. *M* versus *H* plot of complex **2** at 2.0K.

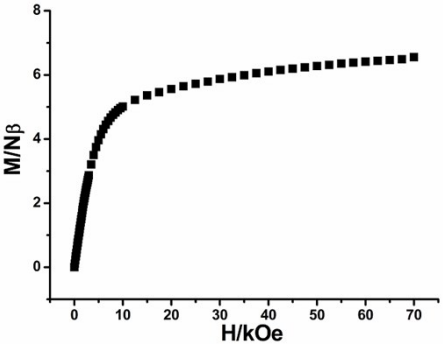

Figure S14. *M* versus *H* plot of complex **3** at 2.0K.

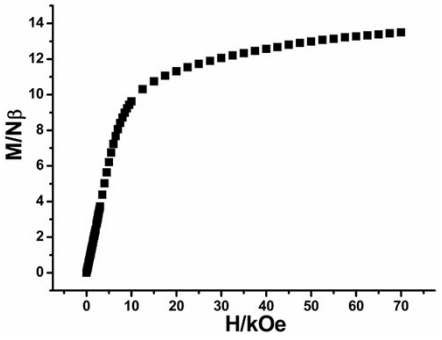

Figure S15. *M* versus *H* plot of complex **4** at 2.0K.

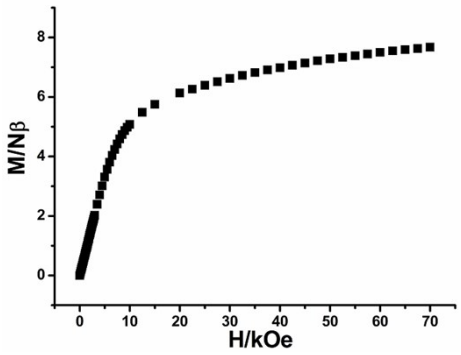

Figure S16. *M* versus *H* plot of complex **5** at 2.0K.

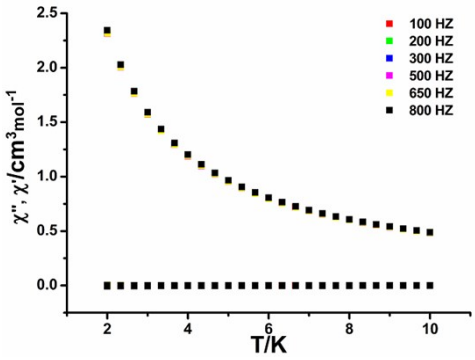

Figure S17. Temperature dependence of the in-phase and out-of-phase components of the ac magnetic susceptibilities for **3** in zero dc field with an oscillation of 3 Oe.

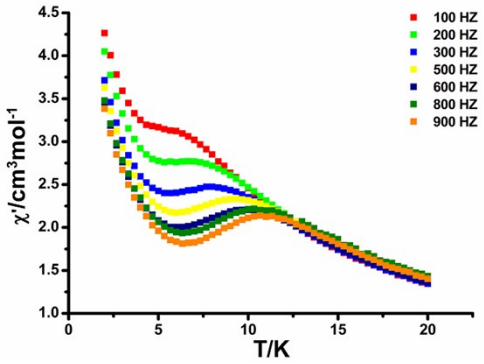

Figure S18. Temperature dependence of χ' for **4** in zero dc field with an oscillation of 3 Oe.

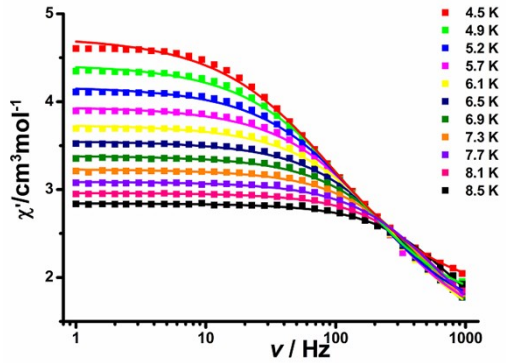

Figure S19. Frequency dependence of χ' for **4** under zero dc field in the temperature range 4.5-8.5 K. The solid line represents the fitting result.

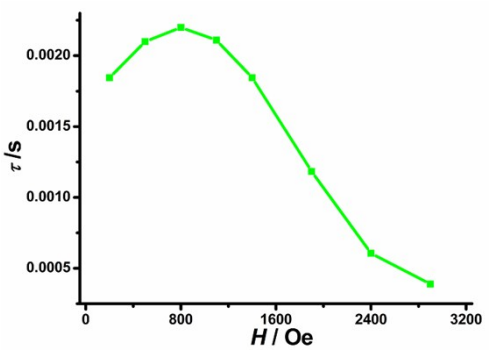

Figure S20. The τ versus H plot for complex **4** at 4.5 K under the applied dc field.

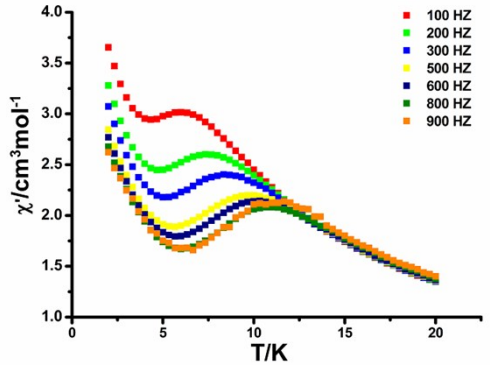

Figure S21. Temperature dependence of χ' for **4** in 800 Oe dc field with an oscillation of 3 Oe.

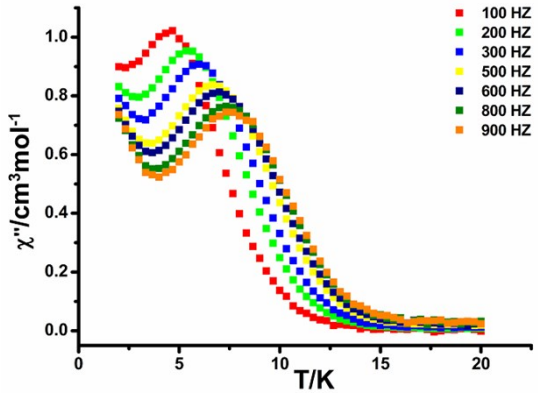

Figure S22. Temperature dependence of χ'' for **4** in 800 Oe dc field with an oscillation of 3 Oe.

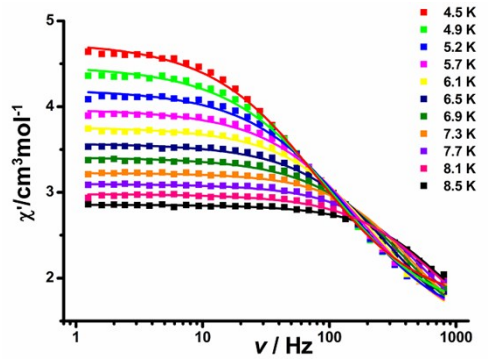

Figure S23. Frequency dependence of χ' for **4** under 800 Oe dc field in the temperature range 4.5-8.5 K. The solid line represents the fitting result.

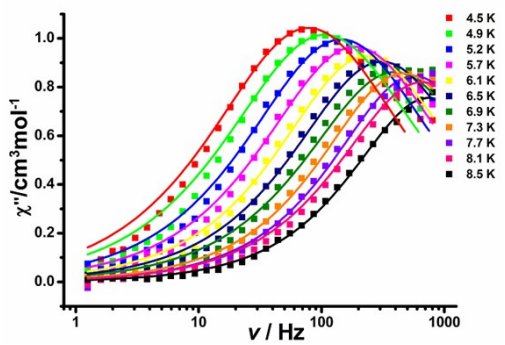

Figure S24. Frequency dependence of χ'' for **4** under 800 Oe dc field in the temperature range 4.5-8.5 K. The solid line represents the fitting result.

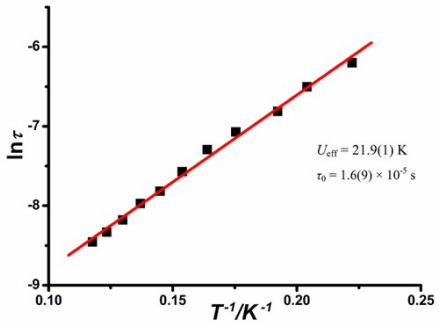

Figure S25. Plot of $\ln\tau$ vs $1/T$ of **4** under 800 Oe dc field. The solid line represents the fitting result.

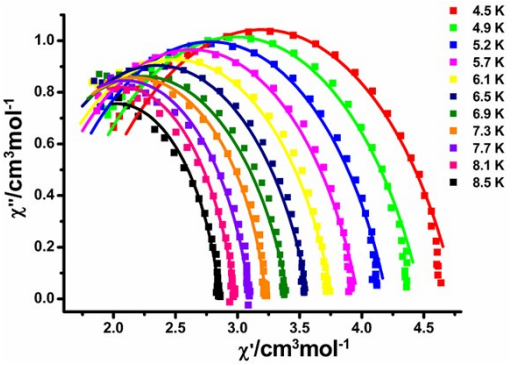

Figure S26. Cole−Cole plots at 800 Oe dc field for **4**. The solid lines represent the best fit to the measured results.

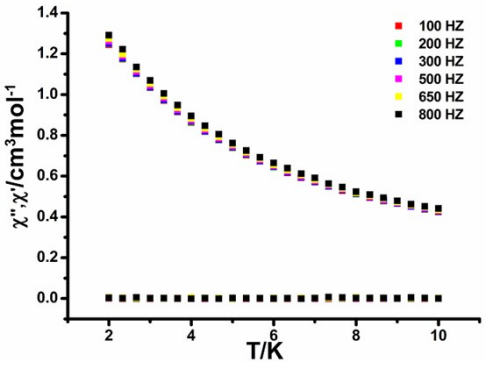

Figure S27. Temperature dependence of the in-phase and out-of-phase components of the ac magnetic susceptibilities for **5** in zero dc field with an oscillation of 3 Oe.