Supporting Information

Magnetic relaxation in unique nitronyl nitroxide biradical-Ln–Cu chains with Ln–bis(NIT)–Cu–bis(NIT)–Ln units

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Contents

Table S1. Selected bond lengths [Å] and angles [°] for **1**.

Bond distances			
Gd(1)-O(6)	2.422(2)	Cu(2)-O(3)	1.945(2)
Gd(1)-O(7)	2.358(2)	Cu(2)-O(3)#1	1.945(2)
Gd(1)-O(9)	2.382(2)	Cu(2)-O(4)	1.929(2)
Gd(1)-O(12)	2.406(3)	Cu(2)-O(4)#1	1.929(2)
Gd(1)-O(11)	2.340(3)	Cu(2)-O(5)#1	2.438(2)
Gd(1)-O(13)	2.327(2)	Cu(2)-O(5)	2.438(2)
Gd(1)-O(10)	2.399(3)	Cu(1)-O(1)	1.981(2)
Gd(1)-O(14)	2.380(3)	Cu(1)-O(2)	2.278(2)
O(6)-N(3)	1.297(3)	Cu(1)-N(1)#2	2.030(3)
O(7)-N(4)	1.304(4)	Cu(1)-N(1)	2.030(3)
O(8)-N(5)	1.269(5)	O(5)-N(2)	2.030(3)
Angles			
O(7)-Gd(1)-O(6)	82.96(8)	O(3)#1-Cu(2)-O(5)	79.66(9)
O(7)-Gd(1)-O(9)	118.09(8)	O(3)#1-Cu(2)-O(5)#1	100.34(9)
O(7)-Gd(1)-O(12)	69.22(8)	O(4)#1-Cu(2)-O(3)	87.69(10)
O(7)-Gd(1)-O(10)	70.83(9)	O(4)-Cu(2)-O(3)#1	92.31(10)
O(7)-Gd(1)-O(14)	137.66(9)	O(4)#1-Cu(2)-O(3)#1	92.31(10)
O(9)-Gd(1)-O(6)	71.79(8)	O(4)#1-Cu(2)-O(4)	87.69(10)
O(9)-Gd(1)-O(12)	140.39(9)	O(4)-Cu(2)-O(5)#1	180
O(9)-Gd(1)-O(10)	72.02(9)	O(4)#1-Cu(2)-O(5)	89.39(9)
O(12)-Gd(1)-O(6)	70.74(8)	O(4)-Cu(2)-O(5)	90.61(9)
O(11)-Gd(1)-O(6)	82.71(9)	O(4)#1-Cu(2)-O(5)#1	79.66(9)
O(11)-Gd(1)-O(9)	141.04(9)	O(1)-Cu(1)-O(1)#2	180
O(11)-Gd(1)-O(12)	91.15(9)	O(1)#2-Cu(1)-O(2)	92.04(9)
O(11)-Gd(1)-O(10)	71.86(9)	O(1)-Cu(1)-O(2)#2	87.96(9)
O(11)-Gd(1)-O(14)	147.10(10)	O(1)#2-Cu(1)-O(2)#2	92.04(9)
O(13)-Gd(1)-O(6)	73.10(10)	O(1)-Cu(1)-O(2)	87.96(9)
O(13)-Gd(1)-O(7)	144.68(9)	O(1)-Cu(1)-N(1)#2	90.95(10)
O(13)-Gd(1)-O(9)	84.47(9)	O(1)#2-Cu(1)-N(1)	180
O(13)-Gd(1)-O(12)	142.25(9)	O(1)-Cu(1)-N(1)	92.04(9)
O(13)-Gd(1)-O(10)	73.94(9)	O(3)-Cu(2)-O(5)	100.32(12)
O(13)-Gd(1)-O(14)	86.70(9)	N(1)#2-Cu(1)-O(2)#2	85.28(13)
O(10)-Gd(1)-O(6)	89.95(10)	N(1)-Cu(1)-O(2)#2	94.72(12)
O(10)-Gd(1)-O(12)	71.37(9)	N(1)#2-Cu(1)-O(2)	94.72(12)
O(14)-Gd(1)-O(6)	116.45(9)	N(1)#2-Cu(1)-N(1)	180
O(14)-Gd(1)-O(9)	138.00(9)	N(2)-O(5)-Cu(2)	150.8(3)
O(14)-Gd(1)-O(12)	135.51(9)	N(3)-O(6)-Gd(1)	138.0(3)
O(14)-Gd(1)-O(10)	71.97(9)	N(4)-O(7)-Gd(1)	140.4(3)
O(3)-Cu(2)-O(3)#1	131.35(9)	O(2)#2-Cu(1)-O(2)	180

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1; #2 -x+2,-y+1,-z+1.

Table S2. Selected bond lengths [Å] and angles [°] for **2**.

Bond distances			
Dy(1)-O(6)	2.407(2)	Cu(1)-O(2)	1.977(2)
Dy(1)-O(7)	2.335(2)	Cu(1)-O(2)#1	1.977(2)
Dy(1)-O(11)	2.379(2)	Cu(1)-O(1)#1	2.2805(19)
Dy(1)-O(13)	2.356(2)	Cu(1)-O(1)	2.2805(19)
Dy(1)-O(14)	2.366(2)	Cu(1)-N(1)	2.030(2)
Dy(1)-O(9)	2.290(2)	Cu(1)-N(1)#1	2.030(2)
Dy(1)-O(10)	2.357(2)	Cu(2)-O(4)#2	1.947(2)
Dy(1)-O(12)	2.311(2)	Cu(2)-O(4)	1.947(2)
O(7)-N(4)	1.299(3)	Cu(2)-O(3)#2	1.929(2)
O(5)-N(2)	1.273(3)	Cu(2)-O(3)	1.929(2)
O(8)-N(5)	1.270(4)	O(6)-N(3)	1.297(3)
Angles			
O(7)-Dy(1)-O(6)	83.23(7)	O(10)-Dy(1)-O(14)	74.61(9)
O(7)-Dy(1)-O(11)	69.00(7)	O(12)-Dy(1)-O(6)	82.43(8)
O(7)-Dy(1)-O(13)	118.10(7)	O(12)-Dy(1)-O(7)	141.35(8)
O(7)-Dy(1)-O(14)	70.81(8)	O(12)-Dy(1)-O(11)	72.38(8)
O(7)-Dy(1)-O(10)	137.85(8)	O(12)-Dy(1)-O(13)	90.77(7)
O(11)-Dy(1)-O(6)	70.41(7)	O(12)-Dy(1)-O(14)	146.75(8)
O(13)-Dy(1)-O(6)	71.61(7)	O(12)-Dy(1)-O(10)	72.86(9)
O(13)-Dy(1)-O(11)	140.02(8)	O(2)#1-Cu(1)-O(2)	180
O(13)-Dy(1)-O(14)	72.55(8)	O(2)-Cu(1)-O(1)	87.78(8)
O(13)-Dy(1)-O(10)	71.74(8)	O(2)-Cu(1)-O(1)#1	92.22(8)
O(14)-Dy(1)-O(6)	117.15(8)	O(2)#1-Cu(1)-O(1)#1	87.78(8)
O(14)-Dy(1)-O(11)	137.72(8)	O(2)#1-Cu(1)-O(1)	92.22(8)
O(9)-Dy(1)-O(6)	144.22(8)	O(2)#1-Cu(1)-N(1)#1	89.14(9)
O(9)-Dy(1)-O(7)	84.31(8)	O(2)#1-Cu(1)-N(1)	90.86(9)
O(9)-Dy(1)-O(11)	73.81(8)	O(2)-Cu(1)-N(1)#1	90.86(9)
O(9)-Dy(1)-O(13)	142.80(8)	O(2)-Cu(1)-N(1)	89.14(9)
O(9)-Dy(1)-O(14)	89.78(8)	O(1)-Cu(1)-O(1)#1	180.00(11)
O(9)-Dy(1)-O(10)	72.08(8)	N(1)-Cu(1)-O(1)#1	85.11(8)
O(9)-Dy(1)-O(12)	86.75(8)	N(1)-Cu(1)-O(1)	94.89(8)
O(10)-Dy(1)-O(6)	134.99(8)	N(1)#1-Cu(1)-O(1)#1	94.89(8)
O(10)-Dy(1)-O(11)	131.95(8)	N(1)#1-Cu(1)-O(1)	85.11(8)
O(7)-Dy(1)-O(6)	83.23(7)	N(1)#1-Cu(1)-N(1)	180
O(7)-Dy(1)-O(11)	69.00(7)	O(4)-Cu(2)-O(4)#2	180
O(7)-Dy(1)-O(13)	118.10(7)	O(4)#2-Cu(2)-O(5)	79.85(7)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1; #2 -x+1,-y,-z+1.

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

Bond distances			
Ho(1)-O(6)	2.391(2)	Cu(2)-O(3)#1	1.944(2)
Ho(1)-O(7)	2.322(2)	Cu(2)-O(3)	1.944(2)
Ho(1)-O(9)	2.346(2)	Cu(2)-O(4)#1	1.926(2)
Ho(1)-O(12)	2.375(3)	Cu(2)-O(4)	1.926(2)
Ho(1)-O(11)	2.301(3)	Cu(2)-O(5)	2.450(2)
Ho(1)-O(13)	2.282(2)	Cu(1)-O(1)	1.983(2)
Ho(1)-O(10)	2.362(3)	Cu(1)-O(1)#2	1.983(2)
Ho(1)-O(14)	2.354(3)	Cu(1)-O(2)	2.280(2)
O(6)-N(3)	1.295(4)	Cu(1)-O(2)#2	2.280(2)
O(7)-N(4)	1.298(5)	Cu(1)-N(1)	2.026(3)
O(8)-N(5)	1.267(5)	O(5)-N(2)	1.276(4)
Angles			
O(7)-Ho(1)-O(6)	83.32(9)	O(3)-Cu(2)-O(3)#1	180
O(7)-Ho(1)-O(9)	118.27(9)	O(3)-Cu(2)-O(5)	99.92(9)
O(7)-Ho(1)-O(12)	68.76(9)	O(3)#1-Cu(2)-O(5)	80.08(9)
O(7)-Ho(1)-O(10)	70.75(9)	O(4)#1-Cu(2)-O(3)#1	92.37(11)
O(7)-Ho(1)-O(14)	138.03(10)	O(4)-Cu(2)-O(3)	92.38(11)
O(9)-Ho(1)-O(6)	71.62(8)	O(4)-Cu(2)-O(3)#1	87.62(11)
O(9)-Ho(1)-O(12)	139.88(9)	O(4)#1-Cu(2)-O(3)	87.62(11)
O(9)-Ho(1)-O(10)	73.08(9)	O(4)#1-Cu(2)-O(4)	180
O(9)-Ho(1)-O(14)	71.70(9)	O(4)-Cu(2)-O(5)	89.49(9)
O(12)-Ho(1)-O(6)	70.20(8)	O(4)#1-Cu(2)-O(5)	90.51(9)
O(11)-Ho(1)-O(6)	82.59(9)	O(1)#2-Cu(1)-O(1)	180
O(11)-Ho(1)-O(7)	141.39(9)	O(1)-Cu(1)-O(2)	87.88(9)
O(11)-Ho(1)-O(9)	90.73(9)	O(1)#2-Cu(1)-O(2)#2	87.88(9)
O(11)-Ho(1)-O(12)	72.65(9)	O(1)-Cu(1)-O(2)#2	92.12(9)
O(11)-Ho(1)-O(10)	146.58(10)	O(1)#2-Cu(1)-O(2)	92.11(9)
O(11)-Ho(1)-O(14)	72.47(10)	O(1)-Cu(1)-N(1)	90.84(11)
O(13)-Ho(1)-O(6)	144.09(9)	O(1)#2-Cu(1)-N(1)	89.17(11)
O(13)-Ho(1)-O(7)	84.01(9)	O(1)#2-Cu(1)-N(1)#2	90.84(11)
O(13)-Ho(1)-O(9)	142.94(10)	O(1)-Cu(1)-N(1)#2	89.16(11)
O(13)-Ho(1)-O(12)	73.89(10)	O(2)-Cu(1)-O(2)#2	179.999(18)
O(13)-Ho(1)-O(11)	86.74(10)	N(1)-Cu(1)-O(2)	85.13(10)
O(13)-Ho(1)-O(10)	89.22(10)	N(1)#2-Cu(1)-O(2)	94.87(10)
O(13)-Ho(1)-O(14)	72.31(10)	N(1)#2-Cu(1)-O(2)#2	85.13(10)
O(10)-Ho(1)-O(6)	117.65(9)	N(1)-Cu(1)-O(2)#2	94.87(10)
O(10)-Ho(1)-O(12)	137.34(9)	N(1)-Cu(1)-N(1)#2	180

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1; #2 -x+2,-y+1,-z+1.

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

Bond distances			
Tb1-O(6)	2.441(9)	Cu(2)-O(3)#1	1.957(11)
Tb1-O(7)	2.335(12)	Cu(2)-O(3)	1.957(11)
Tb1-O(9)	2.382(10)	Cu(2)-O(4)#1	1.956(9)
Tb1-O(12)	2.406(12)	Cu(2)-O(4)	1.956(9)
Tb1-O(11)	2.310(13)	Cu(2)-O(5)	2.484(10)
Tb1-O(13)	2.334(10)	Cu(1)-O(1)#2	2.006(10)
Tb1-O(10)	2.324(16)	Cu(1)-O(1)	2.006(10)
Tb1-O(14)	2.361(11)	Cu(1)-O(2)#2	2.286(10)
O(8)-N(5)	1.290(16)	Cu(1)-O(2)	2.286(10)
O(6)-N(3)	1.310(14)	Cu(1)-N(1)	2.075(13)
O(7)-N(4)	1.299(15)	O(5)-N(2)	1.292(13)
Angles			
O(7)-Tb1-O(6)	84.0(4)	O(3)#1-Cu(2)-O(3)	180
O(7)-Tb1-O(9)	118.5(4)	O(3)-Cu(2)-O(5)	100.2(4)
O(7)-Tb1-O(12)	68.9(4)	O(3)#1-Cu(2)-O(5)	79.8(4)
O(7)-Tb1-O(14)	137.2(5)	O(4)#1-Cu(2)-O(3)	87.8(5)
O(9)-Tb1-O(6)	71.6(4)	O(4)#1-Cu(2)-O(3)#1	92.2(5)
O(9)-Tb1-O(12)	139.0(4)	O(4)-Cu(2)-O(3)	92.2(5)
O(12)-Tb1-O(6)	69.3(4)	O(4)-Cu(2)-O(3)#1	87.8(5)
O(11)-Tb1-O(6)	81.6(4)	O(4)#1-Cu(2)-O(4)	180
O(11)-Tb1-O(7)	141.7(4)	O(4)-Cu(2)-O(5)	89.3(4)
O(11)-Tb1-O(9)	90.1(4)	O(4)#1-Cu(2)-O(5)	90.7(4)
O(11)-Tb1-O(12)	72.7(4)	O(1)#2-Cu(1)-O(1)	180
O(11)-Tb1-O(13)	87.1(5)	O(1)#2-Cu(1)-O(2)#2	87.9(4)
O(11)-Tb1-O(10)	146.9(5)	O(1)-Cu(1)-O(2)	87.9(4)
O(11)-Tb1-O(14)	73.6(5)	O(1)#2-Cu(1)-O(2)	92.1(4)
O(13)-Tb1-O(6)	143.6(4)	O(1)-Cu(1)-O(2)#2	92.1(4)
O(13)-Tb1-O(7)	83.8(4)	O(1)-Cu(1)-N(1)#2	89.8(5)
O(13)-Tb1-O(9)	143.2(4)	O(1)#2-Cu(1)-N(1)	89.8(5)
O(13)-Tb1-O(12)	74.3(5)	O(1)-Cu(1)-N(1)	90.2(5)
O(13)-Tb1-O(14)	73.1(4)	O(1)#2-Cu(1)-N(1)#2	90.2(5)
O(10)-Tb1-O(6)	116.9(4)	O(2)-Cu(1)-O(2)#2	180
O(10)-Tb1-O(7)	70.6(5)	N(1)#2-Cu(1)-O(2)#2	85.0(4)
O(10)-Tb1-O(9)	72.2(5)	N(1)#2-Cu(1)-O(2)	95.0(4)
O(10)-Tb1-O(12)	138.0(5)	N(1)-Cu(1)-O(2)	85.0(4)
O(10)-Tb1-O(13)	90.8(5)	N(1)-Cu(1)-O(2)#2	95.0(4)
O(10)-Tb1-O(14)	74.1(5)	N(1)#2-Cu(1)-N(1)	180
O(14)-Tb1-O(6)	134.5(4)	O(3)#1-Cu(2)-O(3)	180
O(14)-Tb1-O(9)	71.0(4)	O(3)-Cu(2)-O(5)	100.2(4)

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

Table S5. SHAPE analysis for the Ln coordination spheres for **1–4**.

Complex	BTPR-8	JBTPR-8	SAPR-8	TDD-8
1 Gd	**0.858**	1.644	2.398	1.974
2 Dy	**0.830**	1.619	2.426	1.950
3 Ho	**0.815**	1.581	2.423	1.924
4 Tb	**0.931**	1.603	2.433	1.993

BTPR-8: Biaugmented trigonal prism; JBTPR-8: Biaugmented trigonal prism J50; TDD-8: Triangular dodecahedron; SAPR-8: Square antiprism.

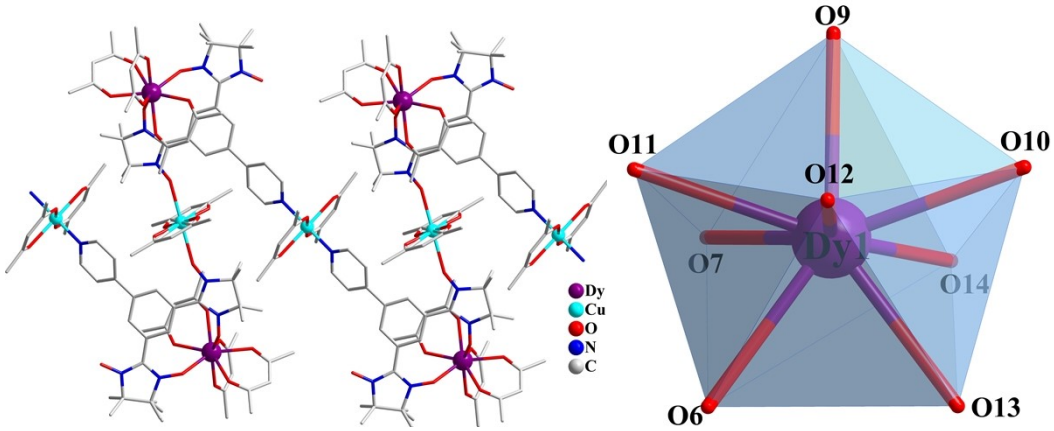

Fig. S1 (left) The crystal structure of complex **2** (F, H atoms are omitted). (right) The coordination polyhedron of Dy^{III} ion in **2**.

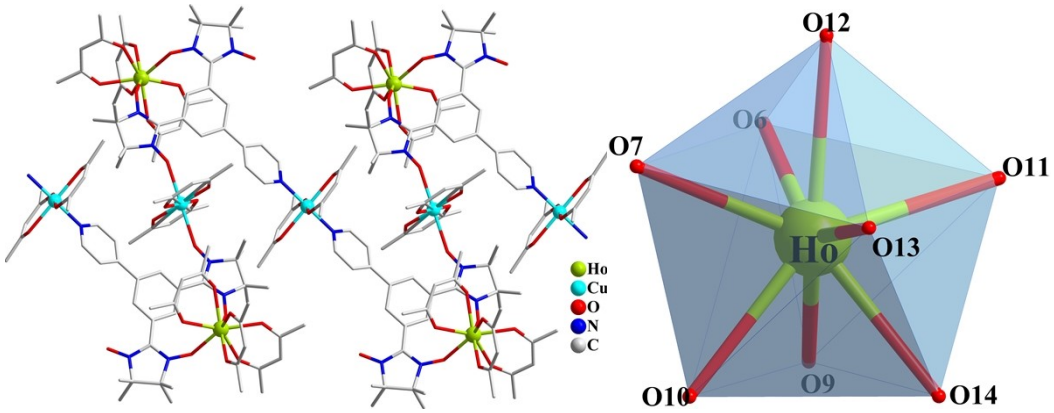

Fig. S2 (left) The crystal structure of complex **3** (F, H atoms are omitted). (right) The coordination polyhedron of Ho^{III} ion in **3**.

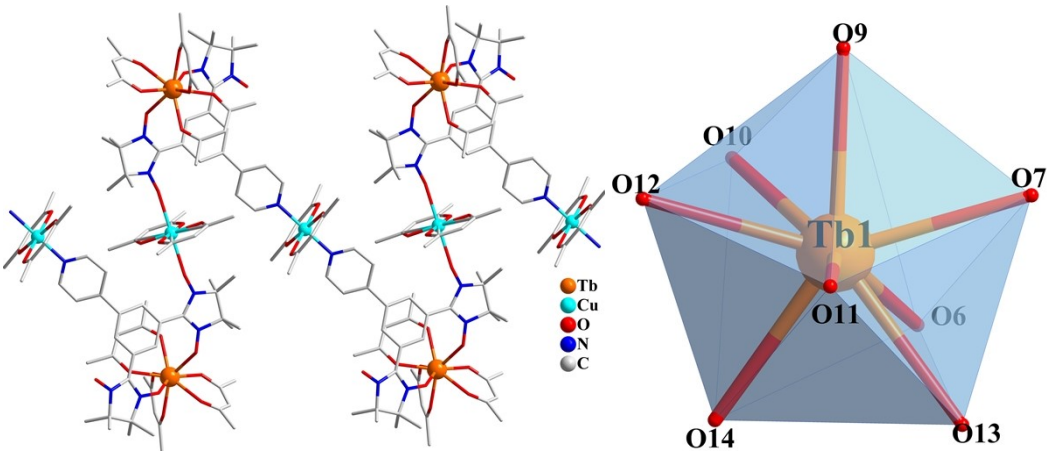

Fig. S3 (left) The crystal structure of complex **4** (F, H atoms are omitted). (right) The coordination polyhedron of Tb^{III} ion in **4**.

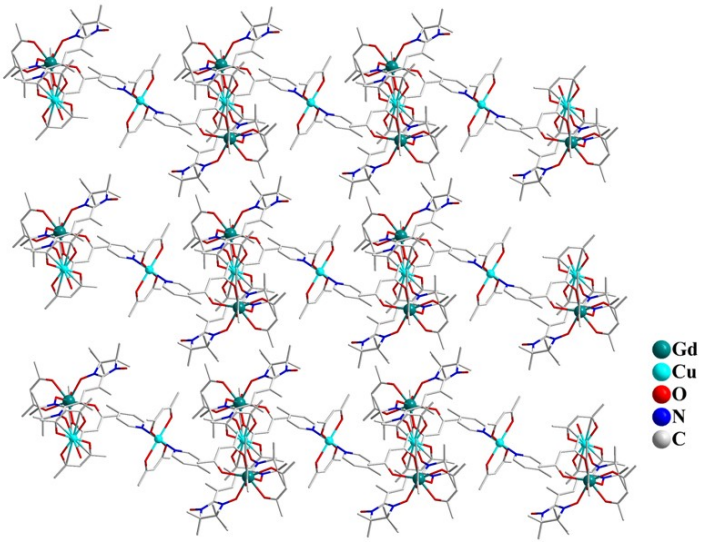

Fig. S4 Packing diagram of **1** (H and F atoms are omitted for clarity).

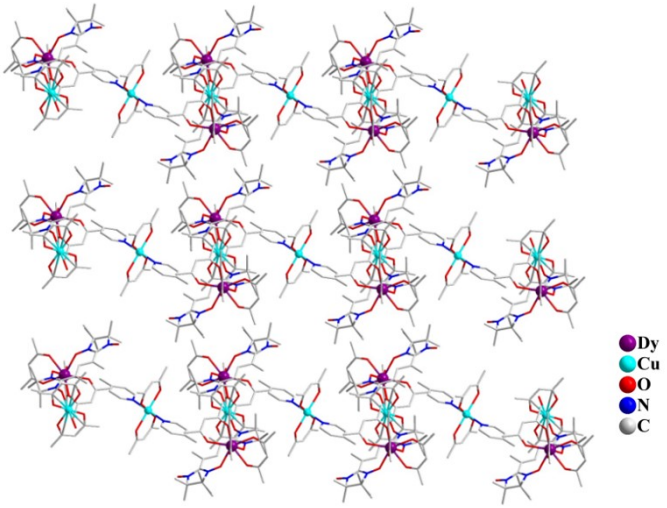

Fig. S5 Packing diagram of **2** (H and F atoms are omitted for clarity).

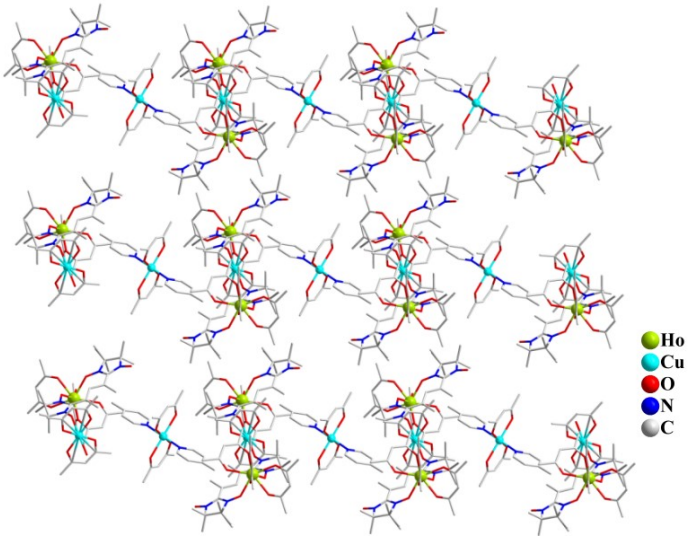

Fig. S6 Packing diagram of **3** (H and F atoms are omitted for clarity).

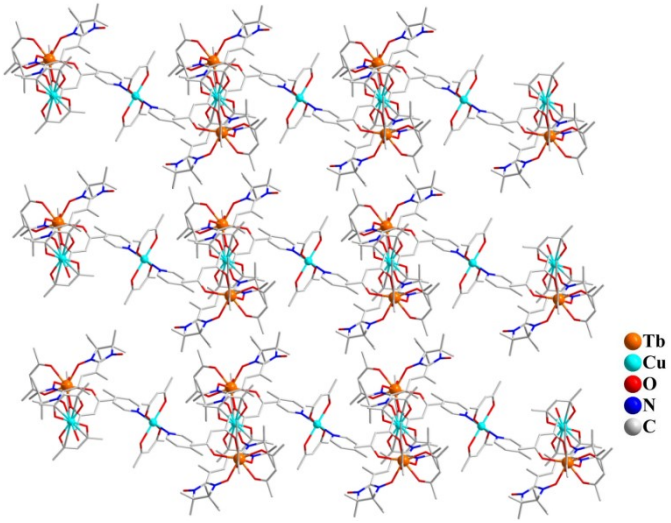

Fig. S7 Packing diagram of **4** (H and F atoms are omitted for clarity).

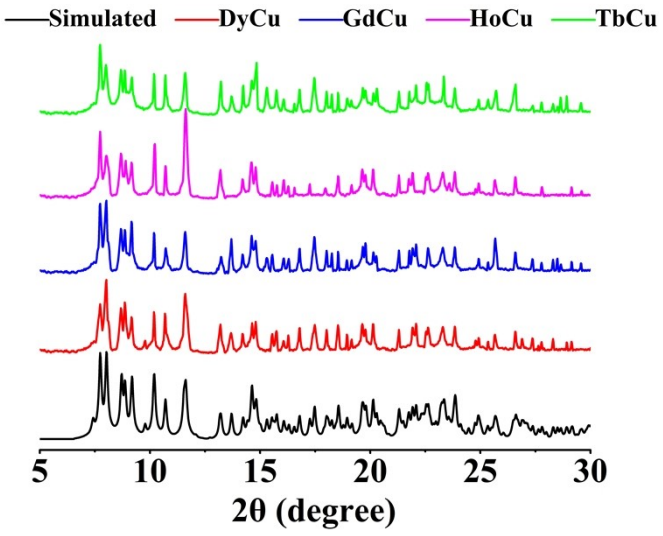

Fig. S8 Powder X-ray diffraction (PXRD) patterns of **1**-**4** at room temperature.

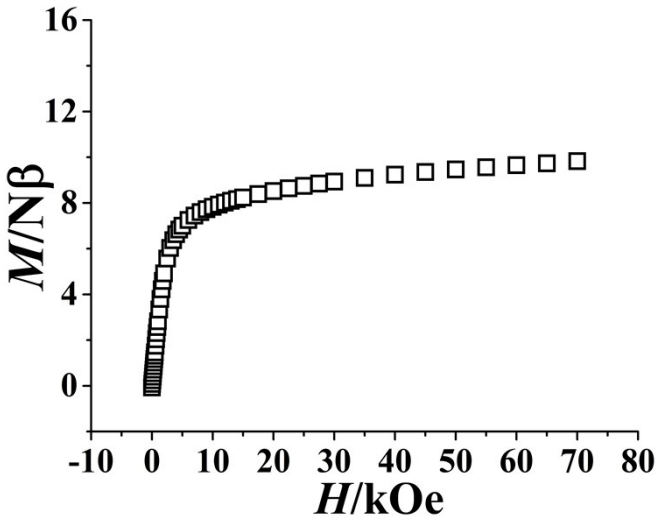

Fig. S9 Plot of magnetization *vs* field for **2** at 2 K

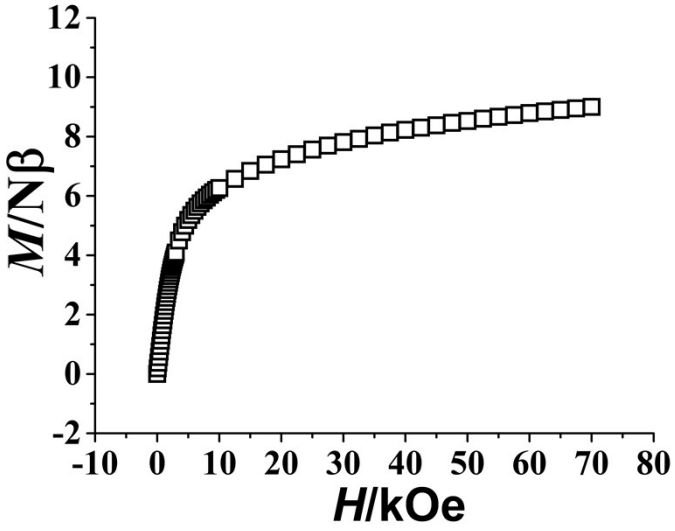

Fig. S10 Plot of magnetization *vs* field for **3** at 2 K.

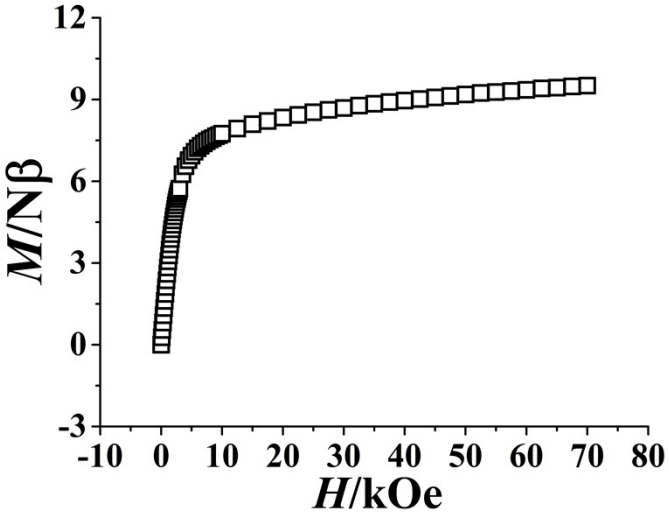

Fig. S11 Plot of magnetization *vs* field for **4** at 2 K.

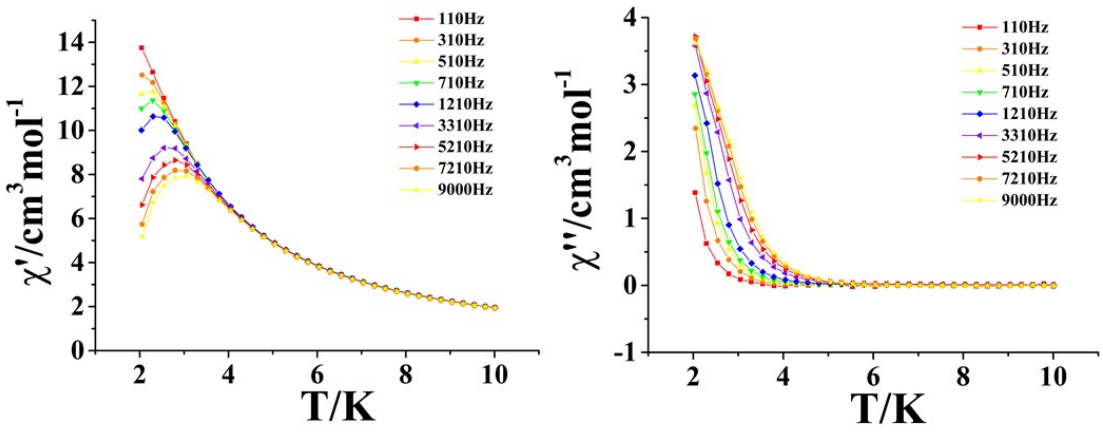

Fig. S12 Temperature-dependent ac signals of the χ′ and χ″ under zero dc field for compound **2**.

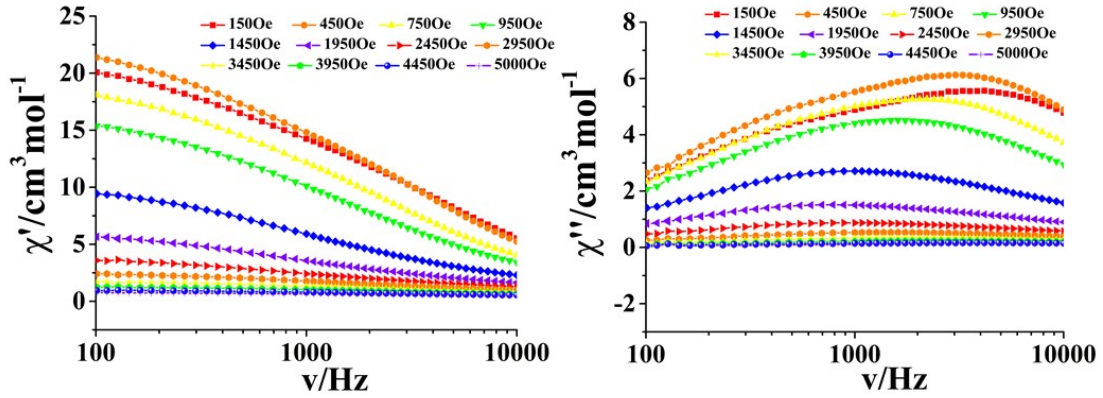

Fig. S13 Frequency-dependent ac signals of the χ′ and χ″ in the dc fields of 150-5000 Oe for compound **2**.

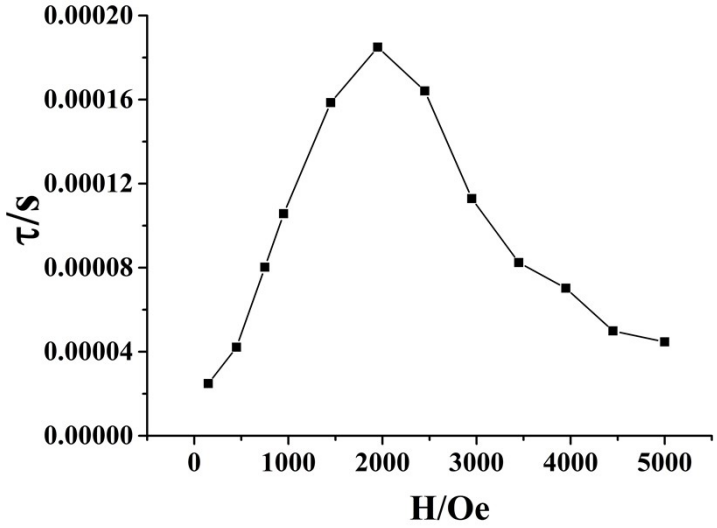

Fig. S14 The τ vs H plot for **2** at 2 K under applied dc fields

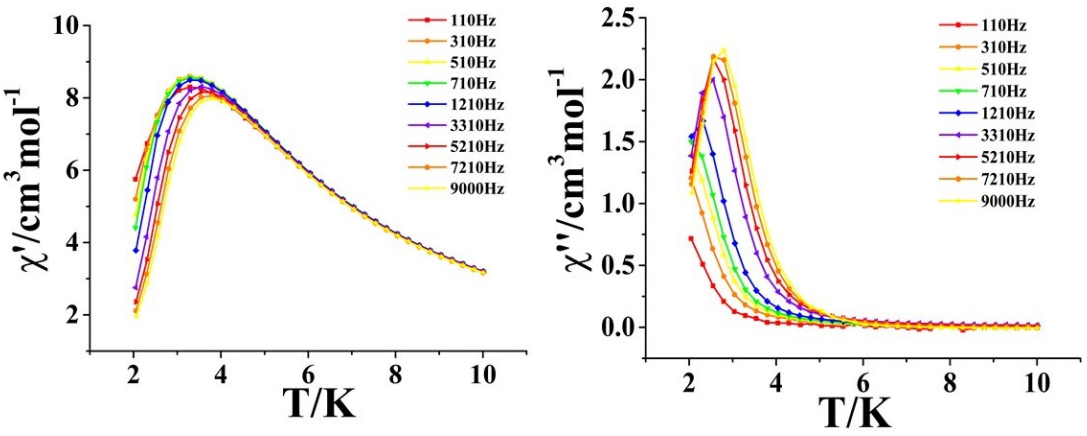

Fig. S15 Temperature-dependent ac signals for **2** under 1900 Oe dc field.

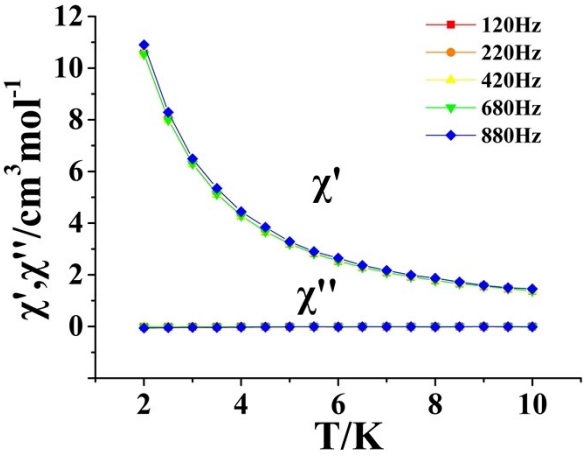

Fig. S16 Temperature-dependent ac signals of the χ′ (top) and χ″ (bottom) under zero dc field for compound **3**.

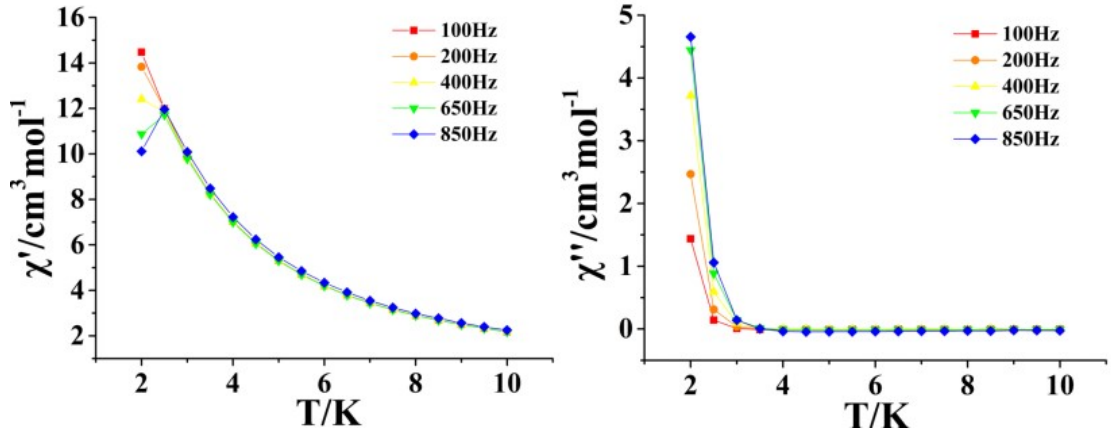

Fig. S17 Temperature-dependent ac signals of the χ′ and χ″ under zero dc field for compound **4**.

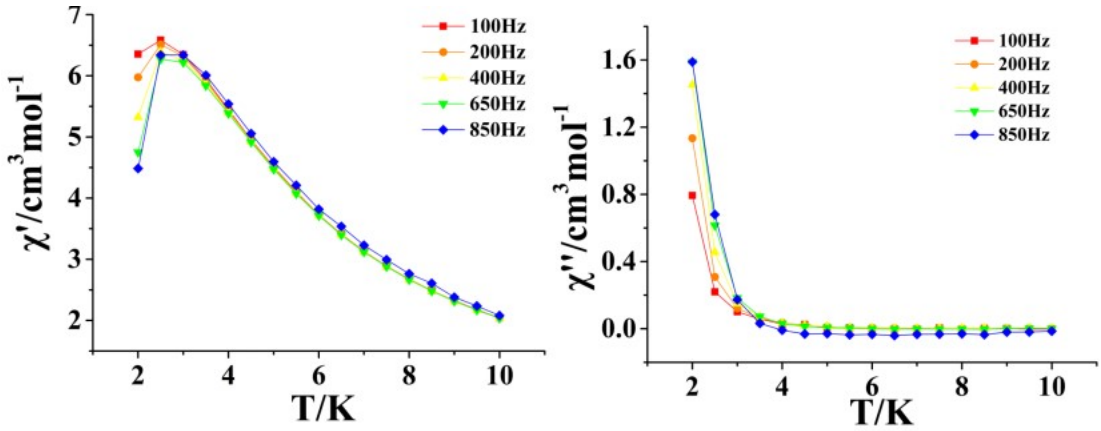

Fig. S18 Temperature-dependent ac signals of the χ′ and χ″ under 2000 Oe dc field for compound **4**.