

Supporting Information

Supramolecular heptanuclear Ln-Cu complexes involving nitronyl nitroxide biradicals: structure and magnetic behavior

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Table S1. Selected bond distances (Å) and angles (°) for complex **1**.

1 YCu			
Y1-O4	2.353(7)	Y2-O23	2.368(7)
Y1-O2	2.362(7)	Y2-O18	2.336(7)
Y1-O9	2.383(8)	Y2-O16	2.353(7)
Y1-O6	2.296(8)	Y2-O17	2.348(7)
Y1-O3	2.344(7)	Y2-O22	2.376(8)
Y1-O5	2.374(7)	Y2-O20	2.303(8)
Y1-O7	2.296(8)	Y2-O21	2.295(8)
Y1-O8	2.346(9)	Y2-O19	2.357(8)
Cu1-O12	1.945(7)	Cu2-N14	1.980(8)
Cu1-O14	1.939(7)	Cu2-O26	2.060(7)
Cu1-O11	1.930(7)	Cu2-O25	2.198(7)
Cu1-O13	2.197(8)	Cu1-N7	1.979(8)
N2-O2	1.287(10)	N9-O16	1.304(10)
N3-O9	1.334(10)	N10-O23	1.319(10)
O2-Y1-O9	84.0(2)	O16-Y2-O23	86.6(2)
O12-Cu1-O13	89.6(3)	O26-Cu2-O25	87.3(3)
N2-O2-Y1	139.6(6)	N9-O16-Y2	140.1(6)
N3-O9-Y1	139.6(6)	N10-O23-Y2	136.7(6)

Table S2. Selected bond distances (Å) and angles (°) for complex **2**.

2 TbCu			
Tb1-O4	2.383(6)	Tb2-O23	2.393(6)
Tb1-O2	2.378(6)	Tb2-O18	2.359(7)
Tb1-O9	2.415(7)	Tb2-O16	2.362(7)
Tb1-O6	2.339(7)	Tb2-O17	2.371(6)
Tb1-O3	2.352(6)	Tb2-O22	2.390(7)
Tb1-O5	2.403(7)	Tb2-O20	2.340(7)
Tb1-O7	2.336(7)	Tb2-O21	2.327(7)
Tb1-O8	2.359(7)	Tb2-O19	2.355(7)
Cu1-O12	1.954(6)	Cu2-N14	1.974(7)
Cu1-O14	1.940(6)	Cu2-O26	2.072(7)
Cu1-O11	1.938(7)	Cu2-O25	2.198(7)
Cu1-O13	2.208(7)	Cu1-N7	1.971(7)
N2-O2	1.310(10)	N9-O16	1.300(10)
N3-O9	1.301(10)	N10-O23	1.318(10)
O2-Tb1-O9	83.7(2)	O16-Tb2-O23	46.18(8)

O12-Cu1-O13	89.6(3)	O26-Cu2-O25	87.3(3)
N2-O2-Tb1	138.5(5)	N9-O16-Tb2	139.2(5)
N3-O9-Tb1	139.2(5)	N10-O23-Tb2	137.1(5)

Table S3. Selected bond distances (Å) and angles (°) for complex **3**.

3 DyCu			
Dy1-O4	2.376(8)	Dy2-O23	2.389(8)
Dy1-O2	2.395(8)	Dy2-O18	2.368(9)
Dy1-O9	2.414(8)	Dy2-O16	2.359(9)
Dy1-O6	2.325(8)	Dy2-O17	2.369(8)
Dy1-O3	2.361(8)	Dy2-O22	2.414(9)
Dy1-O5	2.435(9)	Dy2-O20	2.321(9)
Dy1-O7	2.322(9)	Dy2-O21	2.334(9)
Dy1-O8	2.390(10)	Dy2-O19	2.391(8)
Cu1-O12	1.972(9)	Cu2-N14	1.990(9)
Cu1-O14	1.955(8)	Cu2-O26	2.083(9)
Cu1-O11	1.936(9)	Cu2-O25	2.201(9)
Cu1-O13	2.219(9)	Cu1-N7	1.988(9)
N2-O2	1.298(12)	N9-O16	1.318(12)
N3-O9	1.290(12)	N10-O23	1.296(13)
O2-Dy1-O9	84.1(3)	O16-Dy2-O23	86.7(3)
O12-Cu1-O13	89.4(3)	O26-Cu2-O25	87.7(3)
N2-O2-Dy1	138.8(7)	N9-O16-Dy2	140.9(7)
N3-O9-Dy1	140.0(7)	N10-O23-Dy2	138.0(7)
Dy1-O2-N2-C7	65.4(15)	Dy2-O16-N9-C54	62.0(17)
Dy1-O9-N3-C35	60.8(16)	Dy2-O23-N10-C82	57.0(17)

Table S4. Selected bond distances (Å) and angles (°) for complex **4**.

4 HoCu			
Ho1-O2	2.349(7)	Ho2-O22	2.384(8)
Ho1-O5	2.279(9)	Ho2-O23	2.361(8)
Ho1-O4	2.358(7)	Ho2-O18	2.344(8)
Ho1-O3	2.325(8)	Ho2-O17	2.348(8)
Ho1-O9	2.389(8)	Ho2-O19	2.339(7)
Ho1-O7	2.383(8)	Ho2-O21	2.300(9)
Ho1-O8	2.266(8)	Ho2-O16	2.330(7)
Ho1-O6	2.339(9)	Ho2-O20	2.301(8)
Cu1-N7	1.971(9)	Cu2-N14	1.985(8)
Cu1-O12	1.965(8)	Cu2-O26	2.083(9)

Cu1-O11	1.916(9)	Cu2-O25	2.170(9)
Cu1-O13	2.196(9)	Cu1-O14	1.943(8)
N2-O2	1.309(11)	N9-O16	1.297(11)
N3-O9	1.292(11)	N10-O23	1.308(12)
O2-Ho1-O9	83.5(3)	O16-Ho2-O23	86.6(3)
O12-Cu1-O13	89.9(3)	O26-Cu2-O25	87.0(3)
N2-O2-Ho1	138.1(6)	N9-O16-Ho2	140.2(6)
N3-O9-Ho1	138.7(6)	N10-O23-Ho2	136.9(6)

Table S5. Accurate geometry analysis by SHAPE 2.0 software.

Complex	TDD-8	JBTPR-8	BTPR-8	Complex	TDD-8	JBTPR-8	BTPR-8
1 Y1	1.347	1.662	0.853	1 Y2	2.007	1.591	0.783
2 Tb1	1.369	1.706	0.853	2 Tb2	2.007	1.652	0.738
3 Dy1	1.357	1.560	0.856	3 Dy2	1.976	1.549	0.775
4 Ho1	1.394	1.543	0.788	4 Ho2	1.889	1.581	0.738

Table S6. Selected magnetic parameters for four related Dy SMMs¹⁻⁴.

Complex	U_{eff}	$H_{\text{dc}}(\text{Oe})$	$\tau_0(\text{s})$	Closest ideal geometry	Ref.
[Dy(hfac) ₃ (NITmbis)] ₂	11.6 ± 0.3 K	0	2.3 × 10 ⁻⁸	C _{2v}	1
[Dy(hfac) ₃ Cu(hfac) ₂ (bisNITPhPyrim)]	8.13 K	500	1.07 × 10 ⁻⁸	C _{2v} ~D _{2d}	4
[DyNi(hfac) ₅ (NITPh-PyPzbis)]	23.3 K	2000	6.33 × 10 ⁻⁷	C _{2v}	2
[DyMn(hfac) ₅ (NITPh-PyPzbis)]	-	-	-	D _{2d}	2
[DyCo(hfac) ₅ (NITPh-PyPzbis)]·CH ₂ Cl ₂	14.91 K	2500	6.80 × 10 ⁻⁸	C _{2v}	3
[Dy ₂ Cu(hfac) ₈ Cu(NITPhTzbis) ₂][DyCu(hfac) ₅ (NITPhTzbis)] ₂	10.8 K	400	6.3 × 10 ⁻⁷	C _{2v}	This work

NITmbis = 1,3-bis-(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4,5-hydro-1H-imidazol-2-yl)benzene ; bisNITPhPyrim = [5-(5-pyrimidyl)-1,3-bis(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4,5-hydro-1H-imidazol-2-yl)]benzene ; NITPh-PyPzbis = 5-(3-(2-pyridinyl)-1H-pyrazol-1-yl)-1,3-bis(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4,5-hydro-1H-imidazol-2-yl)benzene ; NITPh-PyPzbis = 5-(3-(2-pyridinyl)-1H-pyrazol-1-yl)-1,3-bis(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4,5-hydro-1H-imidazol-2-yl)benzene ; NITPh-Tzbis = 5-(1,2,4-triazolyl)-1,3-bis(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4,5-hydro-1H-imidazol-2-yl)benzene.

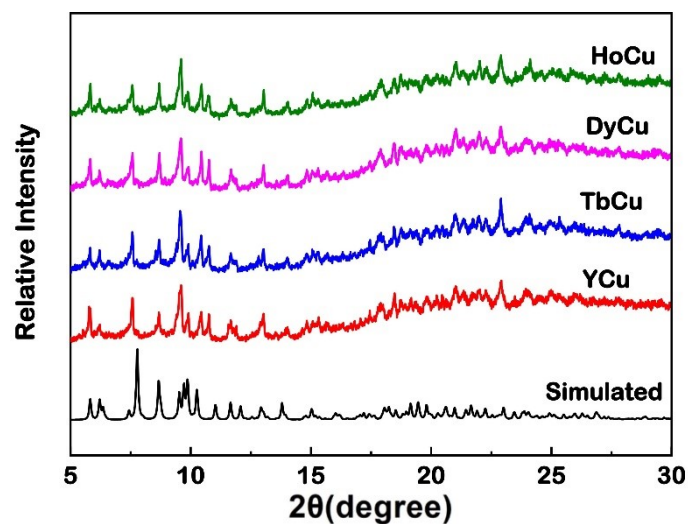
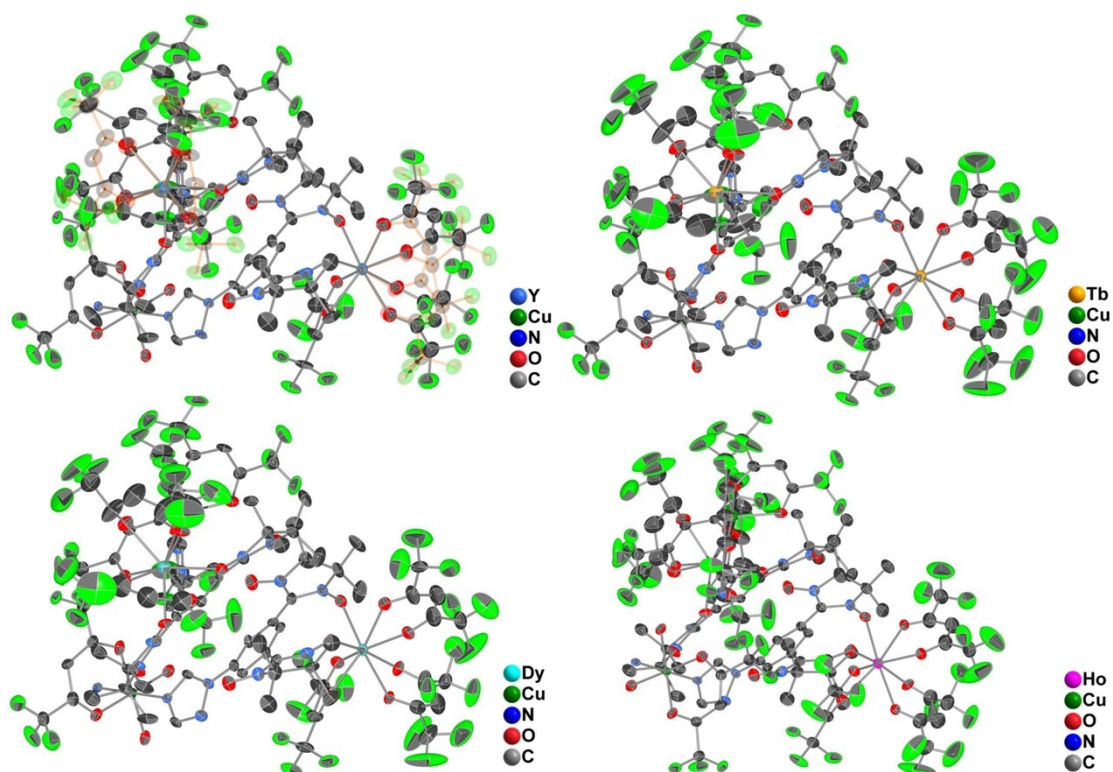


Figure S1. The Powder X-ray diffraction (PXRD) patterns for complexes 1–4 at room temperature.



1. **Figure S2.** X-ray crystal structure of complexes 1-4 with thermal ellipsoids drawn at the 30 % probability level.(The atoms contained in the disordered components of the YCu structure are shown with 80% transparency and linked by orange bonds.)

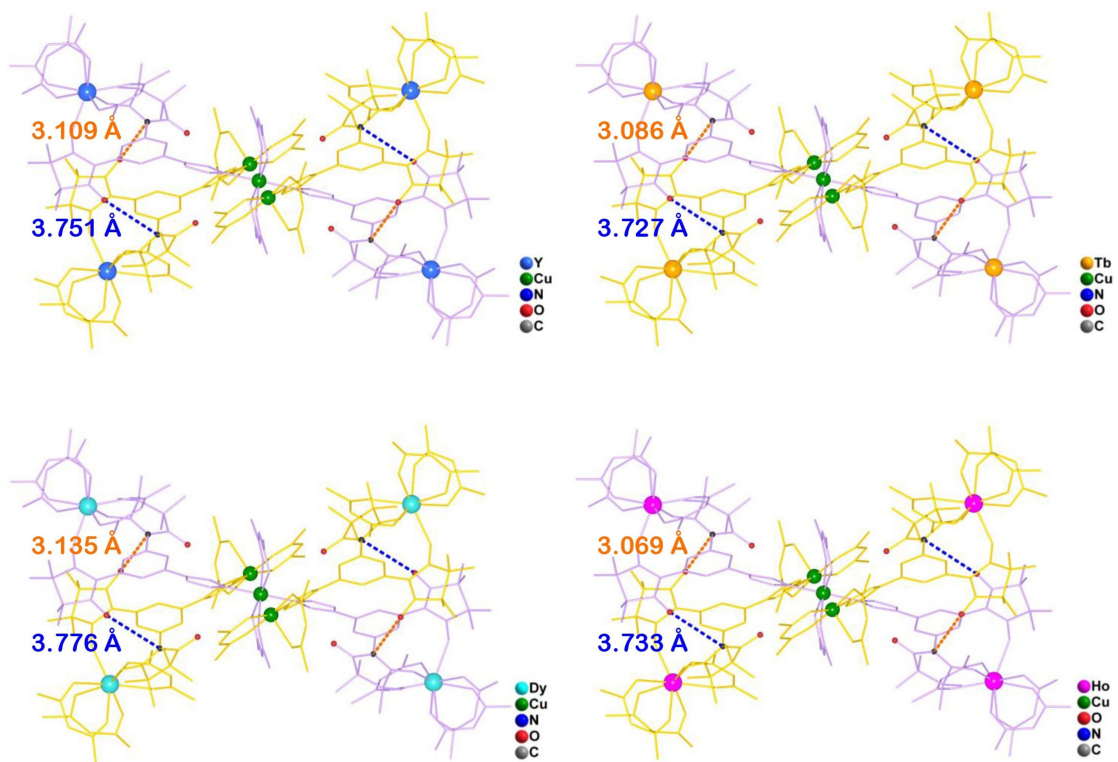


Figure S3. Schematic of short distances between the uncoordinated NO groups and the bridging sp^2 carbon atoms of the radicals in all complexes.

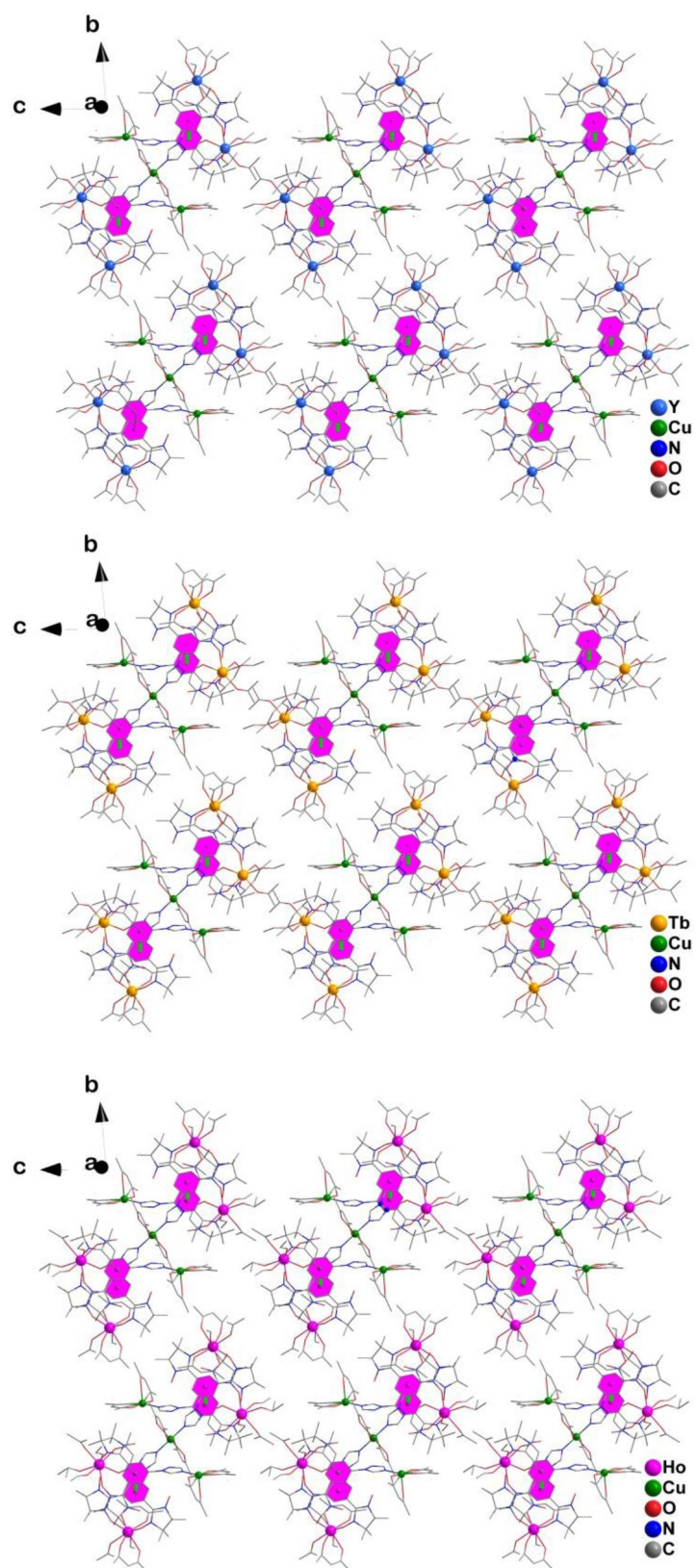


Figure S4. Packing arrangement for complexes **1** (top), **2** (middle), and **4** (bottom). Fluorine and hydrogen atoms are omitted for the sake of clarity.

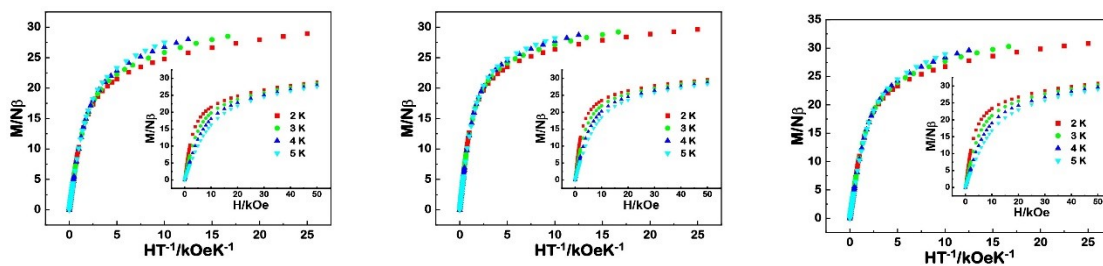


Figure S5. Field dependences of magnetization and plots of the reduced magnetization M vs. H/T (Insets) in the field range 0–50 kOe and at the temperature range of 2.0–5.0 K for complexes 2 (left), 3 (middle) and 4 (right).

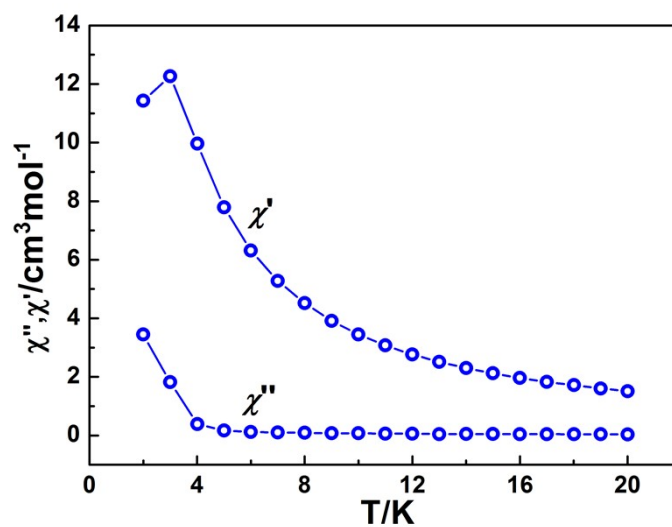


Figure S6. Temperature dependence of the in-phase and out-of-phase ac susceptibilities under zero dc field for **3**.

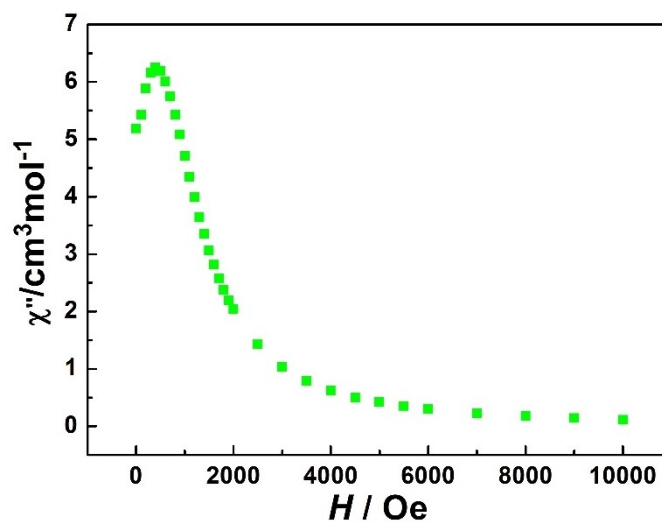


Figure S7. Field dependence of the out-of-phase ac susceptibilities for **3** under 2 K and a frequency of 997 Hz.

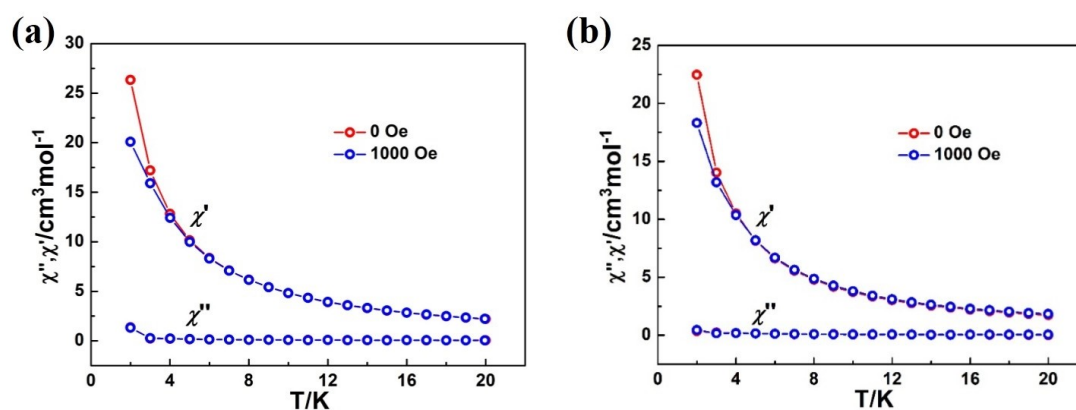


Figure S8. Temperature dependence of the in-phase and out-of-phase ac susceptibilities under zero dc field (red line) and 1000Oe dc field (blue line) for 2 and 4.

References

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