Supporting Information

Single-chain magnet behavior in 2p-3d-4f spin array with nitronyl nitroxide biradical

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Contents

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

Bond distances			
Gd(1)-O(3)	2.393(5)	Cu(2)-O(9)#1	1.927(6)
Gd(1)-O(2)	2.386(5)	Cu(2)-O(1)	2.386(6)
Gd(1)-O(13)	2.355(6)	Cu(2)-O(1)#1	2.386(6)
Gd(1)-O(18)	2.379(5)	Cu(2)-O(10)#1	1.934(6)
Gd(1)-O(15)	2.318(5)	Cu(2)-O(10)	1.934(6)
Gd(1)-O(17)	2.320(6)	Cu(3)-O(12)	1.927(5)
Gd(1)-O(16)	2.385(5)	Cu(3)-O(11)	1.936(6)
Gd(1)-O(14)	2.381(6)	Cu(3)-O(4)	2.611(6)
Cu(1)-O(8)	1.936(6)	Cu(3)-O(4)#1	2.611(6)
Cu(1)-O(5)	1.981(7)	O(3)-N(4)	1.293(8)
Cu(1)-N(1)	2.033(7)	O(2)-N(3)	1.302(8)
Cu(1)-O(7)	2.136(6)	N(5)-O(4)	1.271(8)
Cu(1)-O(6)	1.930(6)	N(2)-O(1)	1.275(8)
Cu(2)-O(9)	1.927(5)		
Angles			
O(2)-Gd(1)-O(3)	82.42(18)	O(6)-Cu(1)-O(8)	173.8(3)
O(13)-Gd(1)-O(3)	71.38(17)	O(6)-Cu(1)-O(5)	90.7(3)
O(13)-Gd(1)-O(2)	115.51(18)	O(6)-Cu(1)-N(1)	93.3(3)
O(13)-Gd(1)-O(18)	139.54(18)	O(6)-Cu(1)-O(7)	87.4(3)
O(13)-Gd(1)-O(16)	73.1(2)	O(9)#1-Cu(2)-O(9)	180
O(13)-Gd(1)-O(14)	72.3(2)	O(9)#1-Cu(2)-O(1)#1	93.2(2)
O(18)-Gd(1)-O(3)	70.70(17)	O(9)#1-Cu(2)-O(1)	86.8(2)
O(18)-Gd(1)-O(2)	72.57(18)	O(9)-Cu(2)-O(1)	93.2(2)
O(18)-Gd(1)-O(16)	130.95(18)	O(9)-Cu(2)-O(1)#1	86.8(2)
O(18)-Gd(1)-O(14)	140.5(2)	O(9)-Cu(2)-O(10)	87.6(2)
O(15)-Gd(1)-O(3)	83.7(2)	O(9)#1-Cu(2)-O(10)#1	87.6(2)
O(15)-Gd(1)-O(2)	146.57(19)	O(9)-Cu(2)-O(10)#1	92.4(2)
O(15)-Gd(1)-O(13)	88.3(2)	O(9)#1-Cu(2)-O(10)	92.4(2)
O(15)-Gd(1)-O(18)	74.15(18)	O(1)#1-Cu(2)-O(1)	180
O(15)-Gd(1)-O(17)	88.8(2)	O(10)-Cu(2)-O(1)	98.3(3)
O(15)-Gd(1)-O(16)	71.8(2)	O(10)#1-Cu(2)-O(1)#1	98.3(3)
O(15)-Gd(1)-O(14)	141.4(2)	O(10)#1-Cu(2)-O(1)	81.7(3)
O(17)-Gd(1)-O(3)	142.73(19)	O(10)-Cu(2)-O(1)#1	81.7(3)
O(17)-Gd(1)-O(2)	84.1(2)	O(10)#1-Cu(2)-O(10)	180
O(17)-Gd(1)-O(13)	145.0(2)	O(12)-Cu(3)-O(11)#2	86.8(2)
O(17)-Gd(1)-O(18)	72.13(19)	O(11)-Cu(3)-O(4)	78.8(2)
O(17)-Gd(1)-O(16)	72.9(2)	O(11)#2-Cu(3)-O(4)	101.2(2)
O(17)-Gd(1)-O(14)	89.0(2)	O(11)-Cu(3)-O(11)#2	180
O(16)-Gd(1)-O(3)	137.0(2)	O(12)#2-Cu(3)-O(4)	97.4(2)
O(16)-Gd(1)-O(2)	135.5(2)	O(12)-Cu(3)-O(4)	82.6(2)
O(14)-Gd(1)-O(3)	118.80(19)	O(12)#2-Cu(3)-O(12)	180
O(14)-Gd(1)-O(2)	71.3(2)	O(12)-Cu(3)-O(11)	93.2(2)
O(14)-Gd(1)-O(16)	70.7(2)	O(12)#2-Cu(3)-O(11)#2	93.2(2)
O(8)-Cu(1)-O(5)	85.3(3)	O(12)#2-Cu(3)-O(11)	86.8(2)
O(8)-Cu(1)-N(1)	92.7(3)	N(4)-O(3)-Gd(1)	139.2(4)
O(8)-Cu(1)-O(7)	89.3(3)	N(3)-O(2)-Gd(1)	136.8(5)
O(5)-Cu(1)-N(1)	143.7(3)	N(2)-O(1)-Cu(2)	149.2(6)
O(5)-Cu(1)-O(7)	107.6(3)	N(5)-O(4)-Cu(3)	144.3(5)
N(1)-Cu(1)-O(7)	108.6(3)		

#1 -x,-y+2,-z+1 #2 -x+1,-y+2,-z+1

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

Bond distances			
Tb(1)-O(3)	2.391(6)	Cu(2)-O(10)	1.923(8)
Tb(1)-O(2)	2.383(6)	Cu(2)-O(10)#2	1.923(8)
Tb(1)-O(15)	2.312(6)	Cu(2)-O(1)#2	2.383(7)
Tb(1)-O(18)	2.384(6)	Cu(2)-O(1)	2.383(7)
Tb(1)-O(13)	2.365(7)	Cu(1)-O(6)	1.932(7)
Tb(1)-O(16)	2.379(6)	Cu(1)-O(8)	1.932(7)
Tb(1)-O(17)	2.328(7)	Cu(1)-O(7)	2.143(8)
Tb(1)-O(14)	2.384(7)	Cu(1)-O(5)	1.977(8)
Cu(3)-O(12)	1.922(6)	Cu(1)-N(1)	2.031(8)
Cu(3)-O(11)#1	1.941(6)	O(3)-N(4)	1.291(9)
Cu(3)-O(11)	1.941(6)	O(2)-N(3)	1.296(9)
Cu(3)-O(4)	2.610(7)	O(4)-N(5)	1.258(10)
Cu(2)-O(9)#2	1.927(6)	O(1)-N(2)	1.246(10)
Cu(2)-O(9)	1.927(6)		
Angles			
O(2)-Tb(1)-O(3)	81.8(2)	O(12)#1-Cu(3)-O(4)	97.0(3)
O(2)-Tb(1)-O(18)	72.4(2)	O(11)#1-Cu(3)-O(11)	180
O(2)-Tb(1)-O(14)	71.3(2)	O(11)#1-Cu(3)-O(4)	79.3(2)
O(15)-Tb(1)-O(3)	83.9(2)	O(11)-Cu(3)-O(4)	100.7(2)
O(15)-Tb(1)-O(2)	146.5(2)	O(9)#2-Cu(2)-O(9)	180
O(15)-Tb(1)-O(18)	74.3(2)	O(9)#2-Cu(2)-O(1)	93.8(3)
O(15)-Tb(1)-O(13)	88.0(3)	O(9)-Cu(2)-O(1)	86.2(3)
O(15)-Tb(1)-O(16)	71.5(2)	O(9)#2-Cu(2)-O(1)#2	86.2(3)
O(15)-Tb(1)-O(17)	88.8(3)	O(9)-Cu(2)-O(1)#2	93.8(3)
O(15)-Tb(1)-O(14)	141.5(3)	O(10)#2-Cu(2)-O(9)#2	92.9(3)
O(18)-Tb(1)-O(3)	71.1(2)	O(10)-Cu(2)-O(9)#2	87.1(3)
O(18)-Tb(1)-O(14)	140.1(3)	O(10)-Cu(2)-O(9)	92.9(3)
O(13)-Tb(1)-O(3)	71.1(2)	O(10)#2-Cu(2)-O(9)	87.1(3)
O(13)-Tb(1)-O(2)	115.3(2)	O(10)-Cu(2)-O(10)#2	180.0(5)
O(13)-Tb(1)-O(18)	139.6(2)	O(10)#2-Cu(2)-O(1)#2	97.8(4)
O(13)-Tb(1)-O(16)	72.9(3)	O(10)-Cu(2)-O(1)	97.8(4)
O(13)-Tb(1)-O(14)	72.8(3)	O(10)-Cu(2)-O(1)#2	82.2(4)
O(16)-Tb(1)-O(3)	136.7(3)	O(10)#2-Cu(2)-O(1)	82.2(4)
O(16)-Tb(1)-O(2)	136.3(2)	O(1)-Cu(2)-O(1)#2	180
O(16)-Tb(1)-O(18)	130.8(2)	O(6)-Cu(1)-O(8)	173.9(3)
O(16)-Tb(1)-O(14)	71.0(3)	O(6)-Cu(1)-O(7)	87.1(3)
O(17)-Tb(1)-O(3)	143.3(2)	O(6)-Cu(1)-O(5)	90.5(3)
O(17)-Tb(1)-O(2)	84.9(3)	O(6)-Cu(1)-N(1)	93.5(3)
O(17)-Tb(1)-O(18)	72.3(2)	O(8)-Cu(1)-O(7)	89.6(3)
O(17)-Tb(1)-O(13)	144.6(2)	O(8)-Cu(1)-O(5)	85.5(3)
O(17)-Tb(1)-O(16)	72.7(3)	O(8)-Cu(1)-N(1)	92.5(3)
O(17)-Tb(1)-O(14)	88.5(2)	O(5)-Cu(1)-O(7)	107.3(3)
O(14)-Tb(1)-O(3)	118.8(2)	O(5)-Cu(1)-N(1)	143.7(3)
O(12)-Cu(3)-O(12)#1	180	N(1)-Cu(1)-O(7)	108.9(3)
O(12)#1-Cu(3)-O(11)	92.8(3)	N(4)-O(3)-Tb(1)	139.3(5)
O(12)#1-Cu(3)-O(11)#1	87.2(3)	N(3)-O(2)-Tb(1)	137.9(6)
O(12)-Cu(3)-O(11)	87.2(3)	N(5)-O(4)-Cu(3)	145.0(6)
O(12)-Cu(3)-O(11)#1	92.8(3)	N(2)-O(1)-Cu(2)	150.1(8)
O(12)-Cu(3)-O(4)	83.0(3)		

#1 -x,-y,-z #2 -x+1,-y,-z

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

Bond distances			
Ho(1)-O(3)	2.362(4)	Cu(2)-O(10)	1.934(5)
Ho(1)-O(2)	2.359(4)	Cu(2)-O(10)#2	1.934(5)
Ho(1)-O(15)	2.284(4)	Cu(2)-O(1)	2.372(4)
Ho(1)-O(16)	2.366(4)	Cu(2)-O(1)#2	2.372(4)
Ho(1)-O(18)	2.363(4)	Cu(1)-O(7)	2.140(4)
Ho(1)-O(14)	2.341(4)	Cu(1)-O(6)	1.945(4)
Ho(1)-O(13)	2.333(4)	Cu(1)-O(8)	1.937(4)
Ho(1)-O(17)	2.296(4)	Cu(1)-O(5)	1.986(5)
Cu(3)-O(12)	1.940(4)	Cu(1)-N(1)	2.025(5)
Cu(3)-O(11)	1.930(4)	O(3)-N(4)	1.293(6)
Cu(3)-O(4)#1	2.583(4)	O(2)-N(3)	1.298(6)
Cu(3)-O(4)	2.583(4)	O(4)-N(5)	1.278(7)
Cu(2)-O(9)#2	1.940(4)	O(1)-N(2)	1.264(7)
Cu(2)-O(9)	1.940(4)		
Angles			
O(3)-Ho(1)-O(16)	137.62(15)	O(11)-Cu(3)-O(12)	92.98(17)
O(3)-Ho(1)-O(18)	69.80(13)	O(11)#1-Cu(3)-O(12)	87.02(17)
O(2)-Ho(1)-O(3)	82.45(13)	O(11)-Cu(3)-O(11)#1	180
O(2)-Ho(1)-O(16)	135.01(15)	O(11)-Cu(3)-O(4)#1	97.47(16)
O(2)-Ho(1)-O(18)	72.26(13)	O(11)#1-Cu(3)-O(4)	97.47(16)
O(15)-Ho(1)-O(3)	83.75(14)	O(11)-Cu(3)-O(4)	82.53(16)
O(15)-Ho(1)-O(2)	146.00(14)	O(4)#1-Cu(3)-O(4)	180
O(15)-Ho(1)-O(16)	72.43(15)	O(9)-Cu(2)-O(9)#2	180
O(15)-Ho(1)-O(18)	73.83(13)	O(9)#2-Cu(2)-O(1)#2	87.94(17)
O(15)-Ho(1)-O(14)	142.06(15)	O(9)#2-Cu(2)-O(1)	92.06(17)
O(15)-Ho(1)-O(13)	88.23(15)	O(9)-Cu(2)-O(1)	87.94(17)
O(15)-Ho(1)-O(17)	88.50(16)	O(10)#2-Cu(2)-O(9)#2	92.60(19)
O(18)-Ho(1)-O(16)	131.59(13)	O(10)-Cu(2)-O(9)	92.60(19)
O(14)-Ho(1)-O(3)	119.24(14)	O(10)-Cu(2)-O(9)#2	87.40(19)
O(14)-Ho(1)-O(2)	70.97(16)	O(10)-Cu(2)-O(10)#2	180
O(14)-Ho(1)-O(16)	70.58(15)	O(10)#2-Cu(2)-O(1)	81.5(2)
O(14)-Ho(1)-O(18)	140.13(16)	O(10)-Cu(2)-O(1)	98.5(2)
O(13)-Ho(1)-O(3)	71.61(13)	O(10)#2-Cu(2)-O(1)#2	98.5(2)
O(13)-Ho(1)-O(2)	116.25(13)	O(1)-Cu(2)-O(1)#2	180
O(13)-Ho(1)-O(16)	73.08(15)	O(6)-Cu(1)-O(7)	87.17(19)
O(13)-Ho(1)-O(18)	138.78(14)	O(6)-Cu(1)-O(5)	90.8(2)
O(13)-Ho(1)-O(14)	73.29(17)	O(6)-Cu(1)-N(1)	92.79(19)
O(17)-Ho(1)-O(3)	142.84(14)	O(8)-Cu(1)-O(7)	89.74(18)
O(17)-Ho(1)-O(2)	84.08(15)	O(8)-Cu(1)-O(6)	174.27(19)
O(17)-Ho(1)-O(16)	72.31(17)	O(8)-Cu(1)-O(5)	85.5(2)
O(17)-Ho(1)-O(18)	73.13(14)	O(8)-Cu(1)-N(1)	92.75(19)
O(17)-Ho(1)-O(14)	88.24(16)	O(5)-Cu(1)-O(7)	107.0(2)
O(17)-Ho(1)-O(13)	144.57(15)	O(5)-Cu(1)-N(1)	144.9(2)
O(12)#1-Cu(3)-O(12)	180	N(1)-Cu(1)-O(7)	108.0(2)
O(12)-Cu(3)-O(4)	78.50(16)	N(4)-O(3)-Ho(1)	138.7(3)
O(12)#1-Cu(3)-O(4)	101.50(16)	N(3)-O(2)-Ho(1)	136.6(4)
O(12)#1-Cu(3)-O(4)#1	78.50(16)	N(5)-O(4)-Cu(3)	143.8(4)
O(11)-Cu(3)-O(12)#1	87.02(17)	N(2)-O(1)-Cu(2)	147.3(5)
O(11)#1-Cu(3)-O(12)#1	92.98(17)		

#1 -x,-y+1,-z #2 -x+1,-y+1,-z

Table S4. SHAPE analysis for the Ln coordination spheres for **1-3**.

Compound	SAPR-8	TDD-8	JBTPR-8	BTPR-8	JSD-8
1 Gd	2.090	1.884	1.540	0.771	3.718
2 Tb	2.059	1.792	1.526	0.754	3.689
3 Ho	2.134	1.918	1.474	0.744	3.712

SAPR-8: Square antiprism; TDD-8: Triangular dodecahedron; JBTPR-8: Biaugmented trigonal prism J50; BTPR-8: Biaugmented trigonal prism; JSD-8: Snub diphenoid J84.

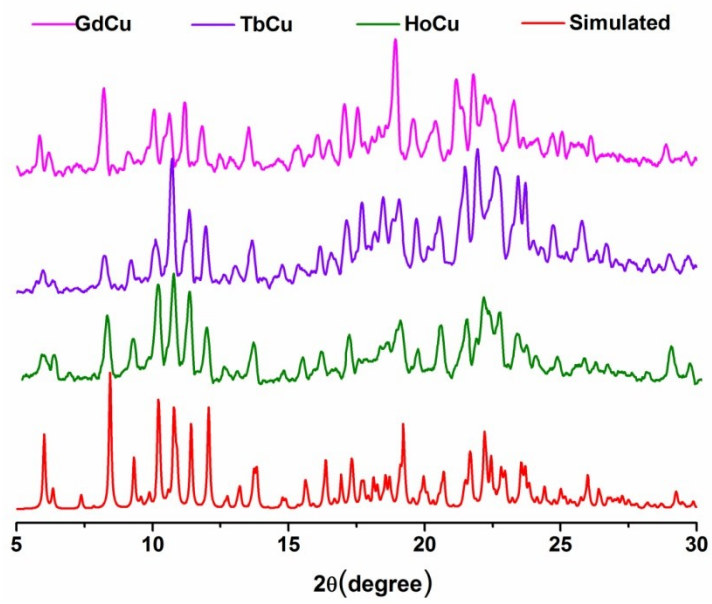

Fig. S1 Powder X-ray diffraction patterns of complexes **1-3**.

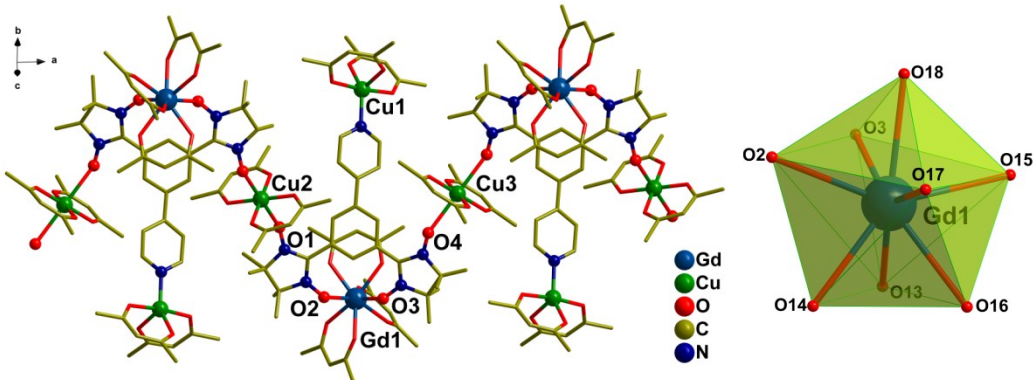

Fig. S2 One-dimensional structure of **1** and local coordination geometry of Gd(III) ion (Fluorine and Hydrogen atoms are omitted for the sake of clarity).

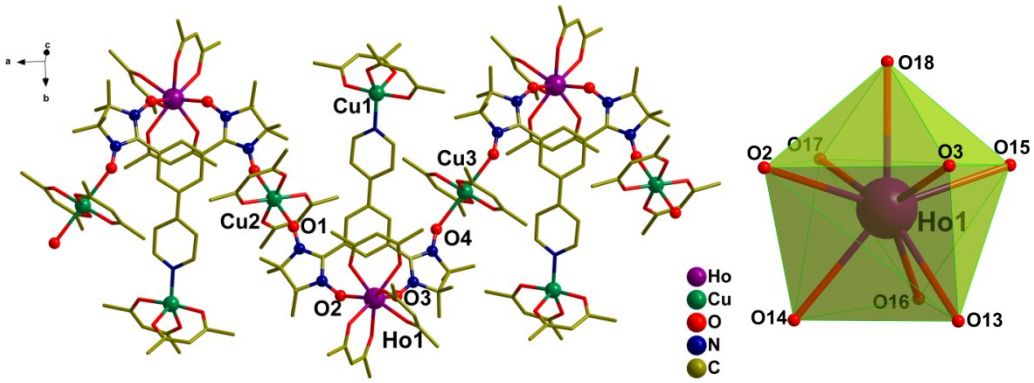

Fig. S3 One-dimensional structure of **3** and local coordination geometry of Ho(III) ion (Fluorine and Hydrogen atoms are omitted for the sake of clarity).

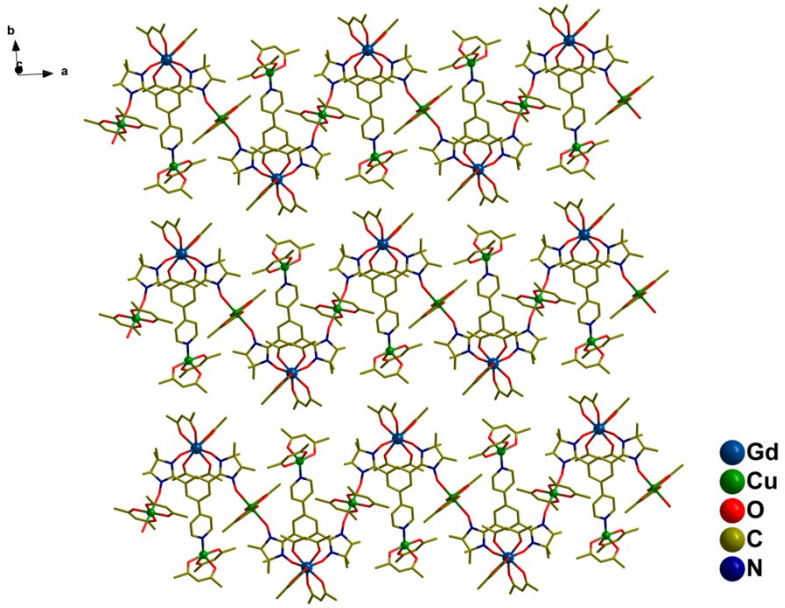

Fig. S4 Packing arrangement of the chains in **1** (H and F atoms are omitted for clarity).

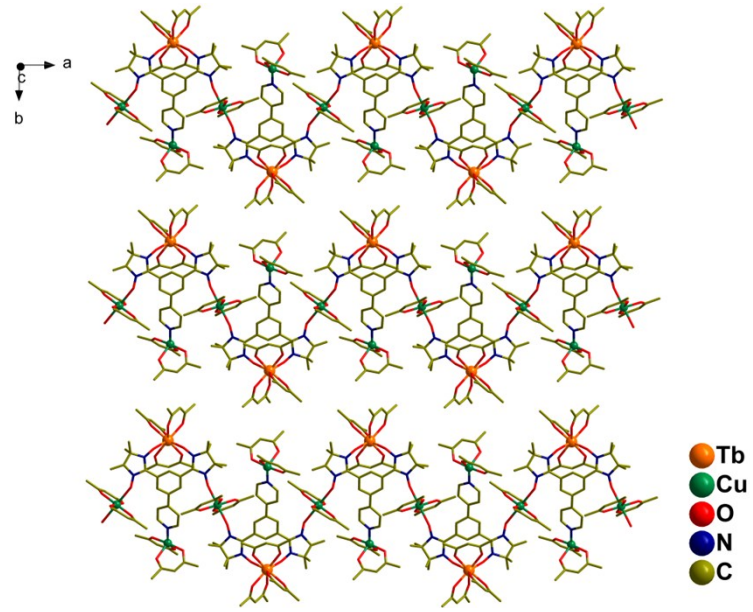

Fig. S5 Packing arrangement of the chains in **2** (H and F atoms are omitted for clarity).

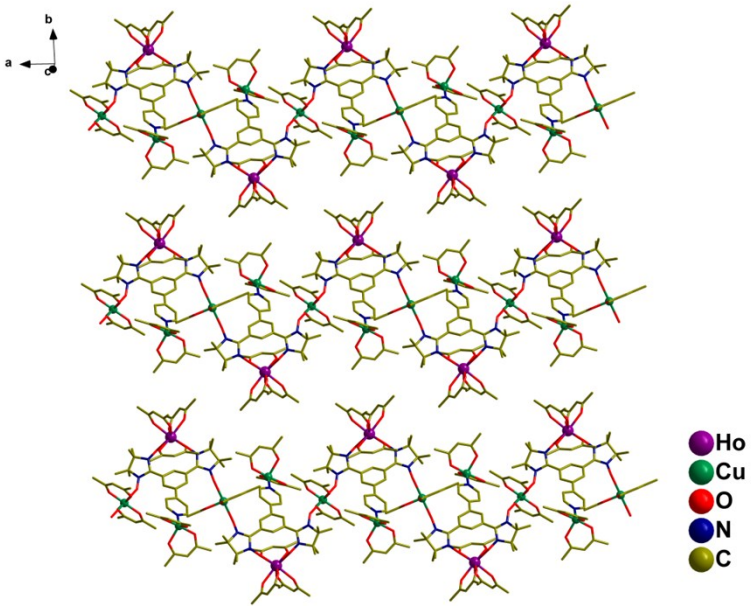

Fig. S6 Packing arrangement of the chains in **3** (H and F atoms are omitted for clarity).

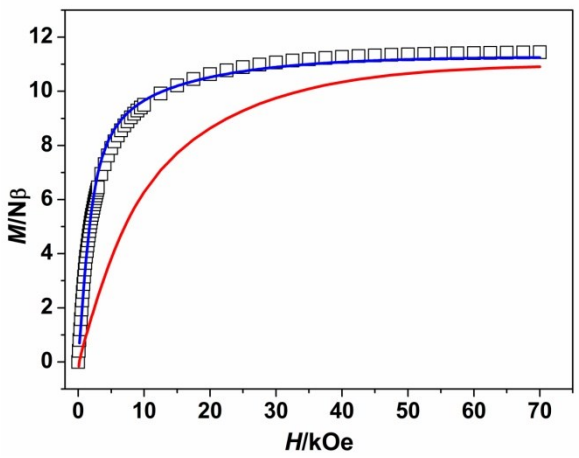

Fig. S7 Plot of magnetization *vs* field for **1** at 2 K. The blue line is the calculated curve using Magpack program, and the red line shows the theoretical behavior for one $S = 7/2$ and four $S = 1/2$ non-coupled spins (see the text).

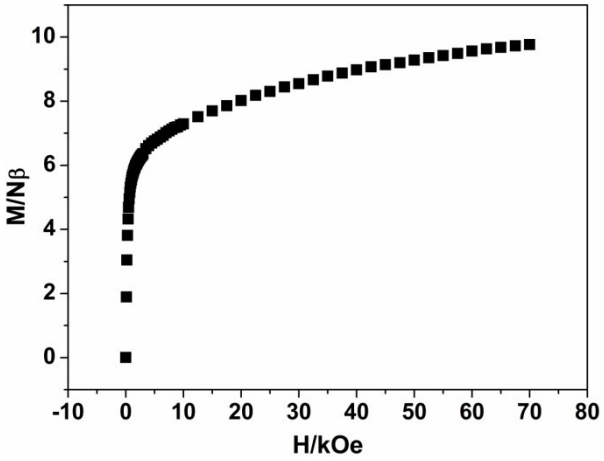

Fig. S8 Plot of magnetization *vs* field for **2** at 2 K.

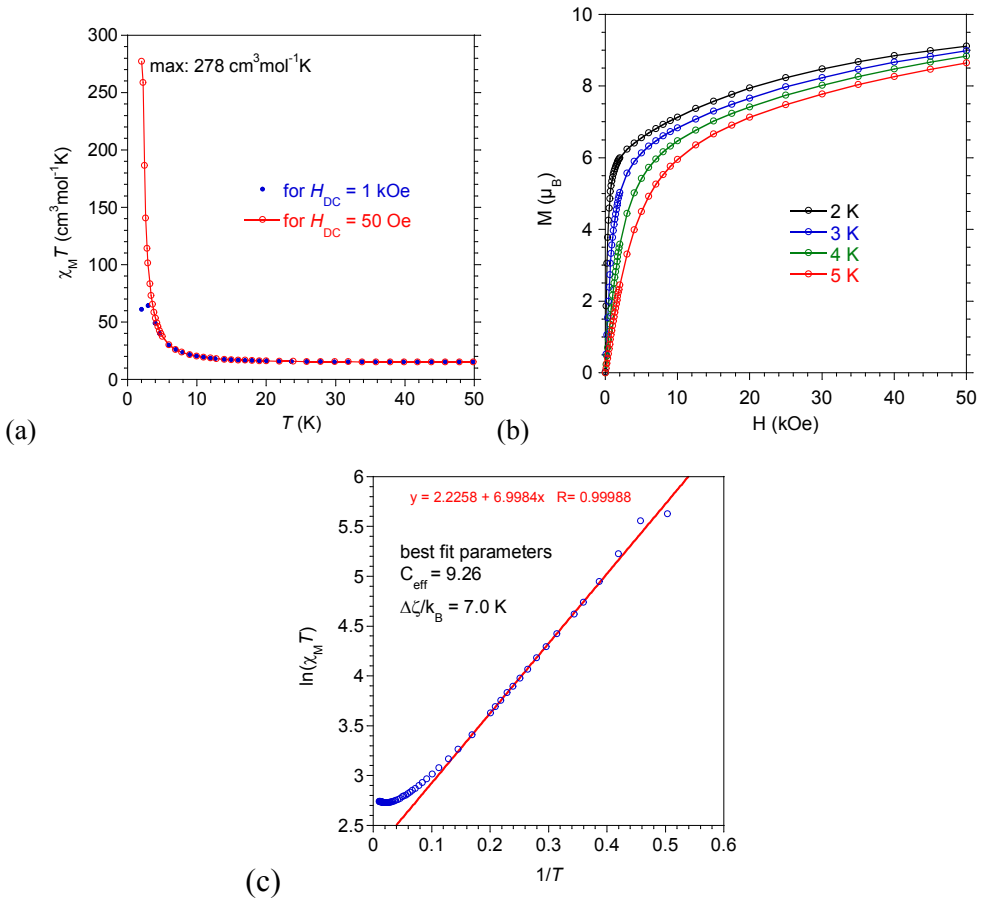

Fig. S9 Compound **3**: (a) $\chi_M T = f(T)$ for susceptibility data obtained in a field of 50 Oe (in red) and 1 kOe (in blue); (b) magnetization *vs* field at 2 K, 3 K, 4 K and 5 K; (c) $\ln(\chi_M T) = f(1/T)$ and best fit of the linear section between 2.5 and 5 K.

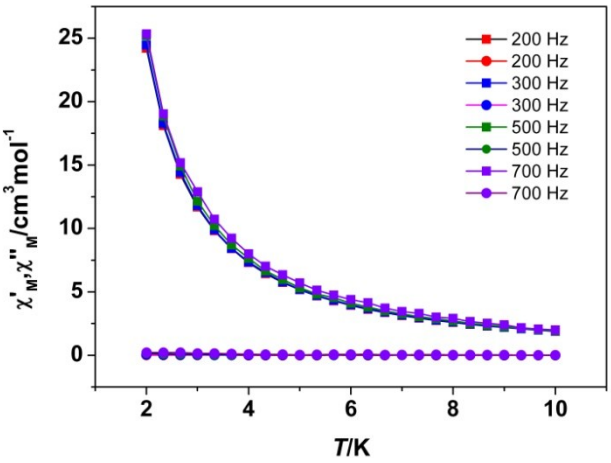

Fig. S10 Temperature dependence of in phase (χ') and out of phase (χ'') of **1** in 0 Oe dc field with an oscillation of 3 Oe.

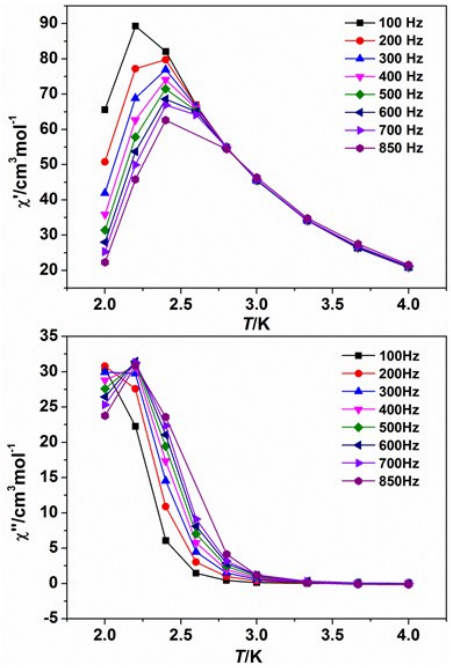

Fig. S11 Temperature-dependent ac signals under a zero dc field for compound **2**.

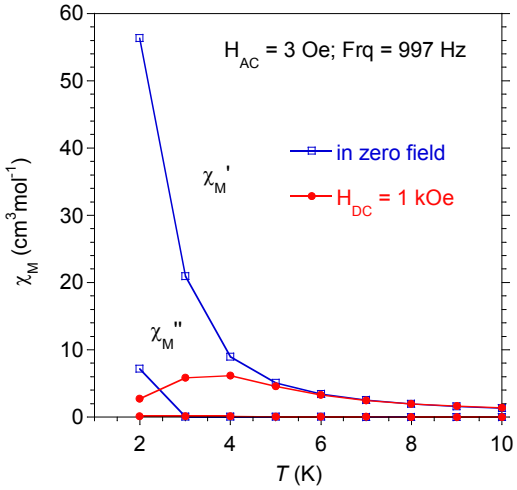

Fig. S12. Compound **3**: χ_M' and $\chi_M'' = f(T)$ in zero and 1 kOe dc field between 2-10 K.