## **Supporting Information**

## Loop chain and three-dimensional network assembled by multi-dentate nitronyl nitroxide radical and $M(hfac)_2$ (M = Co<sup>II</sup>, Cu<sup>II</sup>)

Juan Sun,<sup>a</sup> Lu Xi,<sup>a</sup> Jing Xie,<sup>a</sup> Kang Wang,<sup>a</sup> Licun Li,<sup>\*,a</sup> Jean-Pascal Sutter<sup>\*,b</sup>

<sup>a</sup> Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China
\*E-mail: llicun@nankai.edu.cn. (L.L.C.)
<sup>b</sup>LCC-CNRS, Université de Toulouse, CNRS, Toulouse, France
\*E-mail: sutter@lcc-toulouse.fr. (J.P.S.)

Bond distances			
Co(2)-O(9)	2.025(6)	Co(2)-O(7)	2.042(6)
Co(2)-O(8)	2.080(7)	Co(2)-O(10)	2.101(6)
Co(2)-N(1)#1	2.119(8)	Co(2)-O(6)	2.161(7)
Co(1)-O(1)	2.060(7)	Co(1)-O(4)	2.060(6)
Co(1)-O(3)	2.062(7)	Co(1)-N(4)	2.077(8)
Co(1)-O(2)	2.103(6)	Co(1)-O(5)	2.120(7)
O(5)-N(5)	1.287(9)	O(6)-N(6)	1.287(9)
Angles			
O(1)-Co(1)-O(4)	87.4(3)	O(1)-Co(1)-O(3)	87.4(3)
O(4)-Co(1)-O(3)	92.9(3)	O(1)-Co(1)-N(4)	96.2(3)
O(4)-Co(1)-N(4)	173.8(3)	O(3)-Co(1)-N(4)	92.3(3)
O(1)-Co(1)-O(2)	166.8(3)	O(4)-Co(1)-O(2)	88.7(3)
O(3)-Co(1)-O(2)	80.1(3)	N(4)-Co(1)-O(2)	88.8(3)
O(1)-Co(1)-O(5)	96.1(3)	O(4)-Co(1)-O(5)	86.7(3)
O(3)-Co(1)-O(5)	176.5(3)	N(4)-Co(1)-O(5)	87.9(3)
O(2)-Co(1)-O(5)	96.3(3)	O(9)-Co(2)-O(7)	175.9(3)
O(9)-Co(2)-O(8)	94.9(3)	O(7)-Co(2)-O(8)	88.2(3)
O(9)-Co(2)-O(10)	86.5(3)	O(7)-Co(2)-O(10)	91.1(2)
O(8)-Co(2)-O(10)	83.5(3)	O(9)-Co(2)-N(1)#1	84.0(3)
O(7)-Co(2)-N(1)#1	98.6(3)	O(8)-Co(2)-N(1)#1	92.7(3)
O(10)-Co(2)-N(1)#1	169.5(3)	O(9)-Co(2)-O(6)	84.3(3)
O(7)-Co(2)-O(6)	92.5(3)	O(8)-Co(2)-O(6)	175.6(2)
O(10)-Co(2)-O(6)	92.2(2)	N(1)#1-Co(2)-O(6)	91.5(3)
N(5)-O(5)-Co(1)	128.6(6)	N(6)-O(6)-Co(2)	122.0(5)

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

#1 x+1,y,z

Bond distances			
Cu(1)-O(6)	1.939(3)	Cu(1)-O(6)#1	1.939(3)
Cu(1)-O(7)	1.954(2)	Cu(1)-O(7)#1	1.954(2)
Cu(1)-O(5)	2.374(2)	Cu(1)-O(5)#1	2.374(2)
Cu(2)-O(10)	1.951(2)	Cu(2)-O(12)	1.956(3)
Cu(2)-N(6)	1.963(3)	Cu(2)-O(9)	1.967(2)
Cu(2)-O(11)	2.259(3)	Cu(2)-O(8)	2.402(2)
Cu(3)-O(16)	1.952(2)	Cu(3)-O(15)	1.959(3)
Cu(3)-N(9)	1.979(3)	Cu(3)-O(14)	1.990(3)
Cu(3)-O(13)	2.250(3)	Cu(4)-O(2)	1.936(3)
Cu(4)-O(4)	1.951(3)	Cu(4)-O(1)	1.974(3)
Cu(4)-N(1)	1.979(3)	Cu(4)-O(3)	2.175(3)
Cu(3)-O(17)	2.448(3)	O(5)-N(4)	1.284(4)
O(17)-N(8)	1.276(4)	O(8)-N(5)	1.280(4)
Angles			
O(6)-Cu(1)-O(6)#1	180.0	O(6)-Cu(1)-O(7)	92.53(11)
O(6)#1-Cu(1)-O(7)	87.47(11)	O(6)-Cu(1)-O(7)#1	87.48(11)
O(6)#1-Cu(1)-O(7)#1	92.53(11)	O(7)-Cu(1)-O(7)#1	180.0
O(6)-Cu(1)-O(5)#1	89.82(10)	O(6)#1-Cu(1)-O(5)#1	90.18(10)
O(7)#1-Cu(1)-O(5)#1	92.67(10)	O(7)-Cu(1)-O(5)#1	87.32(10)
O(6)-Cu(1)-O(5)	90.18(10)	O(6)#1-Cu(1)-O(5)	89.82(10)
O(7)#1-Cu(1)-O(5)	87.33(10)	O(7)-Cu(1)-O(5)	92.68(10)
O(5)#1-Cu(1)-O(5)	180.00(12)	O(10)-Cu(2)-O(12)	87.91(11)
O(10)-Cu(2)-N(6)	178.18(11)	O(12)-Cu(2)-N(6)	90.62(11)
O(10)-Cu(2)-O(9)	91.48(10)	O(12)-Cu(2)-O(9)	179.10(11)
N(6)-Cu(2)-O(9)	90.01(11)	O(10)-Cu(2)-O(11)	88.65(11)
O(12)-Cu(2)-O(11)	89.59(12)	N(6)-Cu(2)-O(11)	92.41(12)
O(9)-Cu(2)-O(11)	89.74(11)	O(10)-Cu(2)-O(8)	85.41(10)
O(12)-Cu(2)-O(8)	90.94(10)	N(6)-Cu(2)-O(8)	93.54(11)
O(9)-Cu(2)-O(8)	89.67(10)	O(11)-Cu(2)-O(8)	174.01(10)
O(16)-Cu(3)-O(15)	92.37(11)	O(16)-Cu(3)-N(9)	170.65(12)
O(15)-Cu(3)-N(9)	90.35(12)	O(16)-Cu(3)-O(14)	88.93(10)
O(15)-Cu(3)-O(14)	177.47(11)	N(9)-Cu(3)-O(14)	88.72(11)
O(16)-Cu(3)-O(13)	97.29(11)	O(15)-Cu(3)-O(13)	90.80(11)
N(9)-Cu(3)-O(13)	91.61(11)	O(14)-Cu(3)-O(13)	86.88(11)
O(2)-Cu(4)-O(4)	178.08(12)	O(2)-Cu(4)-O(1)	90.96(12)
O(4)-Cu(4)-O(1)	90.33(11)	O(2)-Cu(4)-N(1)	87.81(12)
O(4)-Cu(4)-N(1)	90.52(12)	O(1)-Cu(4)-N(1)	161.38(13)
O(2)-Cu(4)-O(3)	90.75(13)	O(4)-Cu(4)-O(3)	90.58(12)
O(1)-Cu(4)-O(3)	94.33(12)	N(1)-Cu(4)-O(3)	104.25(12)
N(5)-O(8)-Cu(2)	139.2(2)	N(4)-O(5)-Cu(1)	146.1(2)
N(8)-O(17)-Cu(3)	140.6(2)		

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

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



**Fig. S1** Packing arrangement of the chains in **1**. Hydrogen atoms, and fluorine atoms are omitted for clarity.



Fig. S2 View of 3D polymeric framework in 2 (All of the hfac ligands and H atoms are omitted for clarity).



Fig. S3 Compound 1: Experimental (dots) and calculated (full lines) magnetization versus H/T behaviors.



**Fig. S4** Compound 1: Temperature dependence of the ac magnetic susceptibility under zero and 1kOe dc field at 1kHz.



Fig. S5 Temperature dependence of the  $\chi'$  (left) and  $\chi''$  (right) under 3 kOe dc field for compound 1.



Fig. S6 Plot of  $\ln(\chi''/\chi')$  versus 1/T of 1, The solid line represents the fitting results.