

## A novel nitronyl nitroxide and its two 1D chain Cu-Tb complexes: synthesis, structures and magnetic properties

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

<i>Bond distances</i>			
N(1)–O(1)	1.275(3)	N(1)–C(10)	1.354(3)
N(1)–C(11)	1.493(3)	N(2)–O(2)	1.290(2)
N(2)–C(10)	1.354(3)	N(2)–C(12)	1.500(3)
C(11)–C(13)	1.527(3)	C(11)–C(14)	1.523(3)
C(12)–C(15)	1.519(3)	C(12)–C(16)	1.534(3)
C(10)–C(1)	1.454(3)	C(4)–O(3)	1.380(3)
C(7)–O(3)	1.425(3)	C(7)–N(3)	1.433(3)
<i>Angles</i>			
O(1)–N(1)–C(10)	126.7(2)	O(2)–N(2)–C(10)	126.6(2)
N(1)–C(10)–N(2)	107.5(2)	C(10)–N(2)–C(12)	112.6(2)
C(10)–N(1)–C(11)	112.7(2)	C(11)–C(12)–C(15)	115.0(2)
C(11)–C(12)–C(16)	114.0(2)	C(12)–C(11)–C(13)	113.2(2)
C(12)–C(11)–C(14)	115.3(2)	C(3)–C(4)–O(3)	124.0(2)
C(4)–O(3)–C(7)	116.1 (2)	O(3)–C(7)–N(3)	107.1(2)
C(7)–N(3)–N(4)	120.4(2)	C(7)–N(3)–C(9)	129.8(2)
N(1)–C(11)–C(12)	101.2(2)	N(2)–C(12)–C(11)	100.3(2)
N(1)–C(11)–C(13)	106.1(2)	N(1)–C(11)–C(14)	109.4(2)
N(2)–C(12)–C(15)	110.0(2)	N(2)–C(12)–C(16)	106.4(2)

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

<i>Bond distances</i>			
Tb(1)–O(2)	2.345(3)	Tb(1)–O(4)	2.329(3)
Tb(1)–O(5)	2.354(4)	Tb(1)–O(6)	2.335(3)
Tb(1)–O(7)	2.361(4)	Tb(1)–O(8)	2.333(4)
Tb(1)–O(9)	2.340(3)	Tb(1)–N(5)	2.578(4)
Cu(1)–O(1)	2.409(4)	Cu(1)–O(10)	1.943(4)
Cu(1)–O(11)	1.952(3)	Cu(1)–O(12)	1.943(4)
Cu(1)–O(13)	1.951(3)	Cu(1)–N(4A)	2.467(4)
<i>Angles</i>			

O(2)-Tb(1)-O(4)	75.21(12)	O(2)-Tb(1)-O(5)	73.23(12)
O(2)-Tb(1)-O(6)	106.36(12)	O(2)-Tb(1)-O(7)	75.79(12)
O(2)-Tb(1)-O(8)	149.44(12)	O(2)-Tb(1)-O(9)	85.88(12)
O(2)-Tb(1)-N(5)	140.85(14)	N(5)-Tb(1)-O(4)	84.57(12)
N(5)-Tb(1)-O(5)	68.94(13)	N(5)-Tb(1)-O(6)	74.13(12)
N(5)-Tb(1)-O(7)	136.66(12)	N(5)-Tb(1)-O(8)	69.71(14)
N5(1)-Tb(1)-O(9)	119.77(13)	O(1)-Cu(1)-O(10)	94.38(16)
O(1)-Cu(1)-O(11)	88.46(14)	O(1)-Cu(1)-O(12)	88.31(16)
O(1)-Cu(1)-O(13)	91.22(14)	O(1)-Cu(1)-N(4A)	177.00(17)
N(4A)-Cu(1)-O(10)	88.31(16)	N(4A)-Cu(1)-O(11)	92.79(15)
N(4A)-Cu(1)-O(12)	89.03(16)	N(4A)-Cu(1)-O(13)	87.49(15)
Tb(1)-O(2)-N(2)	134.9(3)	Cu(1)-O(1)-N(1)	156.7(4)

A: x+1,y-1,z

**Table S3** SHAPE analysis for Ln ions in complexes **2a** and **2b**.

Complex	Ln	SAPR-8	TDD-8	JBTPR-8	BTPR-8
<b>2a</b>	<b>Tb</b>	<b>0.863</b>	2.247	2.206	1.440
<b>2b</b>	<b>Tb1</b>	<b>0.999</b>	1.180	2.492	1.837
	<b>Tb2</b>	<b>0.989</b>	1.521	2.483	1.891
	<b>Tb3</b>	<b>0.597</b>	1.418	2.569	1.952

**Table S4** SHAPE analysis for Cu ions in complex **2b**.

complex	VOC-5	TBTY-5	SPY-5	JTBPY-5
<b>Cu1</b>	0.985	4.327	<b>0.815</b>	7.194
<b>Cu2</b>	4.785	<b>2.254</b>	3.907	5.606
<b>Cu3</b>	2.788	3.128	<b>2.504</b>	6.214

**Table S5** Selected bond lengths (Å) and angles (°) for complex **2b**.

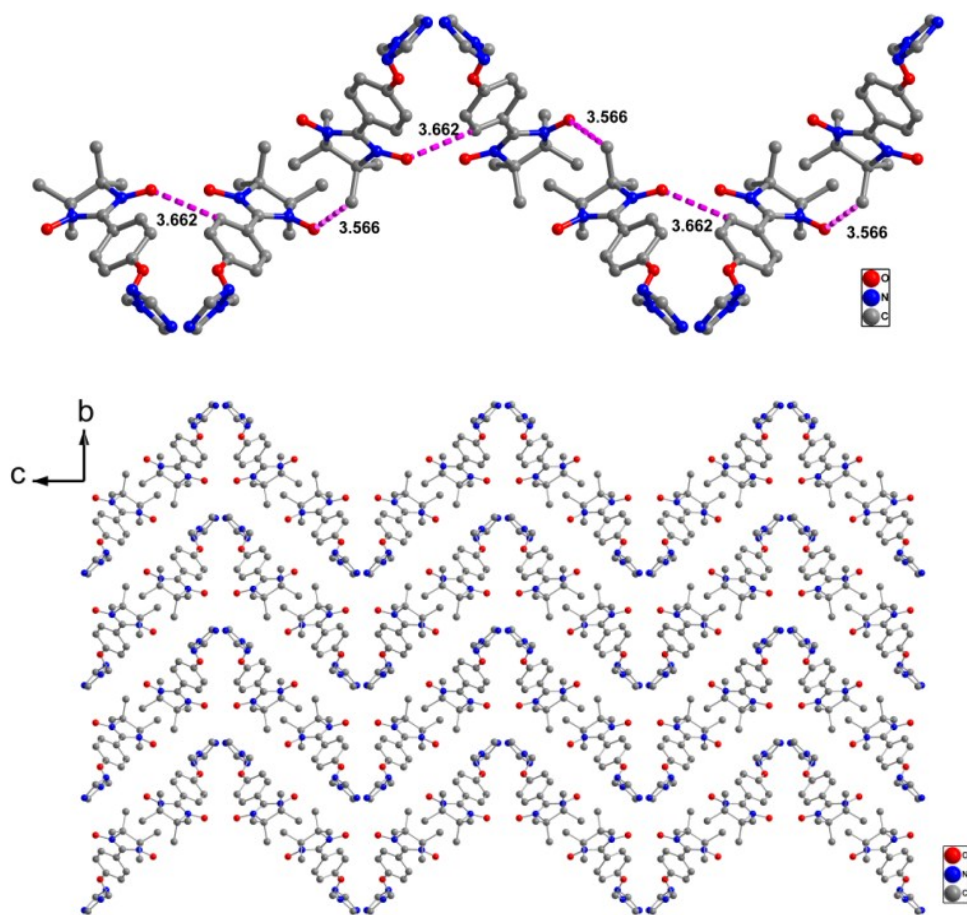
<i>Bond distances</i>			
Tb(1)–O(1)	2.343(5)	Tb(1)–O(2)	2.373(7)
Tb(1)–O(3)	2.356(7)	Tb(1)–O(4)	2.344(9)
Tb(1)–O(5)	2.322(7)	Tb(1)–O(6)	2.355(8)
Tb(1)–O(7)	2.396(6)	Tb(1)–O(21A)	2.380(6)
Tb(2)–O(8)	2.371(6)	Tb(2)–O(14)	2.352(6)
Tb(2)–O(15)	2.370(7)	Tb(2)–O(16)	2.370(8)
Tb(2)–O(17)	2.340(7)	Tb(2)–O(18)	2.369(7)
Tb(2)–O(19)	2.340(8)	Tb(2)–O(20)	2.375(6)
Tb(3)–O(27)	2.373(6)	Tb(3)–O(28)	2.371(6)
Tb(3)–O(29)	2.359(7)	Tb(3)–O(30)	2.374(6)
Tb(3)–O(31)	2.352(6)	Tb(3)–O(32)	2.358(7)

Tb(3)–O(33)	2.353(7)	Tb(3)–O(34)	2.370(5)
Cu(1)–N(5)	1.979(7)	Cu(1)–O(10)	1.911(6)
Cu(1)–O(11)	1.957(6)	Cu(1)–O(12)	2.158(9)
Cu(1)–O(13)	1.939(6)	Cu(2)–N(10)	1.956(8)
Cu(2)–O(23)	1.908(8)	Cu(2)–O(24)	2.102(9)
Cu(2)–O(25)	2.027(7)	Cu(2)–O(26)	1.908(7)
Cu(3)–N(15)	1.968(7)	Cu(3)–O(36)	1.918(8)
Cu(3)–O(37)	1.954(7)	Cu(3)–O(38)	2.167(10)
Cu(3)–O(39)	1.926(7)		

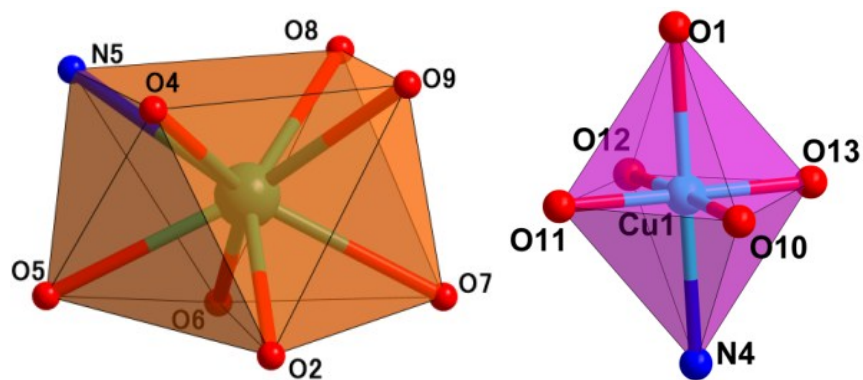
*Angles*

O(7)–Tb(1)–O(1)	85.4(2)	O(7)–Tb(1)–O(2)	138.9(2)
O(7)–Tb(1)–O(3)	102.4(2)	O(7)–Tb(1)–O(4)	69.9(3)
O(7)–Tb(1)–O(5)	74.8(2)	O(7)–Tb(1)–O(6)	78.3(2)
O(7)–Tb(1)–O(21A)	149.3(2)	O(21A)–Tb(1)–O(1)	104.1(2)
O(21A)–Tb(1)–O(2)	71.1(2)	O(21A)–Tb(1)–O(3)	86.3(2)
O(21A)–Tb(1)–O(4)	139.9(3)	O(21A)–Tb(1)–O(5)	80.5(2)
O(21A)–Tb(1)–O(6)	77.1(2)	O(8)–Tb(2)–O(14)	104.6(2)
O(8)–Tb(2)–O(15)	72.1(2)	O(8)–Tb(2)–O(16)	138.4(2)
O(8)–Tb(2)–O(17)	83.0(2)	O(8)–Tb(2)–O(18)	79.4(2)
O(8)–Tb(2)–O(19)	78.8(2)	O(8)–Tb(2)–O(20)	149.6(2)
O(20)–Tb(2)–O(14)	84.9(2)	O(20)–Tb(2)–O(15)	137.6(2)
O(20)–Tb(2)–O(16)	70.6(2)	O(20)–Tb(2)–O(17)	104.3(2)
O(20)–Tb(2)–O(18)	75.7(2)	O(20)–Tb(2)–O(19)	77.0(2)
O(27)–Tb(3)–O(28)	77.07(19)	O(27)–Tb(3)–O(29)	73.8(2)
O(27)–Tb(3)–O(30)	83.16(19)	O(27)–Tb(3)–O(31)	142.6(2)
O(27)–Tb(3)–O(32)	107.7(2)	O(27)–Tb(3)–O(33)	71.4(2)
O(27)–Tb(3)–O(34)	144.4(2)	O(34)–Tb(3)–O(28)	74.81(18)
O(34)–Tb(3)–O(29)	77.1(2)	O(34)–Tb(3)–O(30)	108.24(19)
O(34)–Tb(3)–O(31)	71.4(2)	O(34)–Tb(3)–O(32)	82.9(2)
O(34)–Tb(3)–O(33)	142.5(2)	N(5)–Cu(1)–O(10)	89.2(3)
N(5)–Cu(1)–O(11)	164.0(4)	N(5)–Cu(1)–O(12)	103.7(3)
N(5)–Cu(1)–O(13)	90.9(3)	N(10)–Cu(2)–O(23)	90.2(3)
N(10)–Cu(2)–O(24)	129.4(3)	N(10)–Cu(2)–O(25)	140.6(4)
N(10)–Cu(2)–O(26)	91.6(3)	N(15)–Cu(3)–O(36)	88.5(3)
N(15)–Cu(3)–O(37)	154.9(4)	N(15)–Cu(3)–O(38)	118.3(4)
N(15)–Cu(3)–O(39)	91.6(3)		

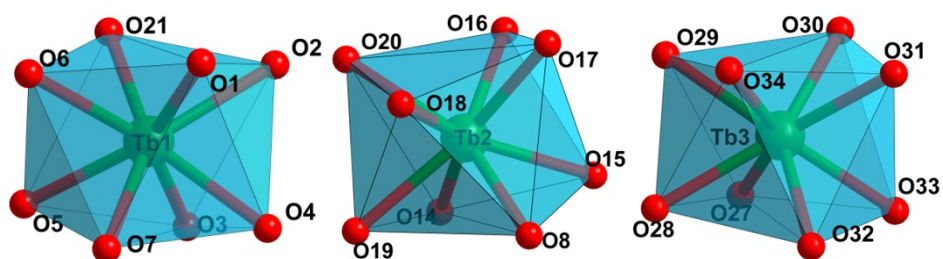
A: x,y+1,z



**Figure S1.** One-dimensional chain via hydrogen bonding and packing arrangement of 1.



**Figure S2** Local coordination geometry of Tb<sup>III</sup> ion and Cu<sup>II</sup> ion in complex 2a.



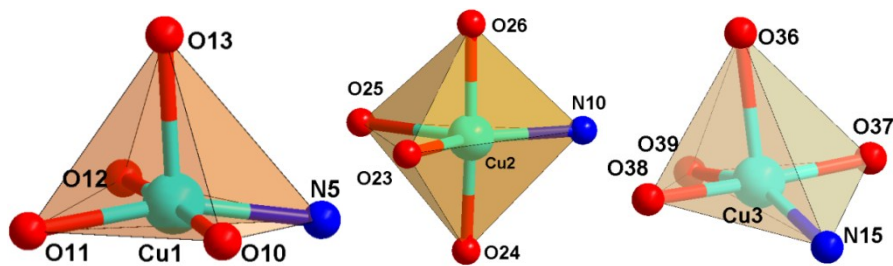


Figure S3 Local coordination geometry of Tb<sup>III</sup> ions and Cu<sup>II</sup> ions in complex **2b**.

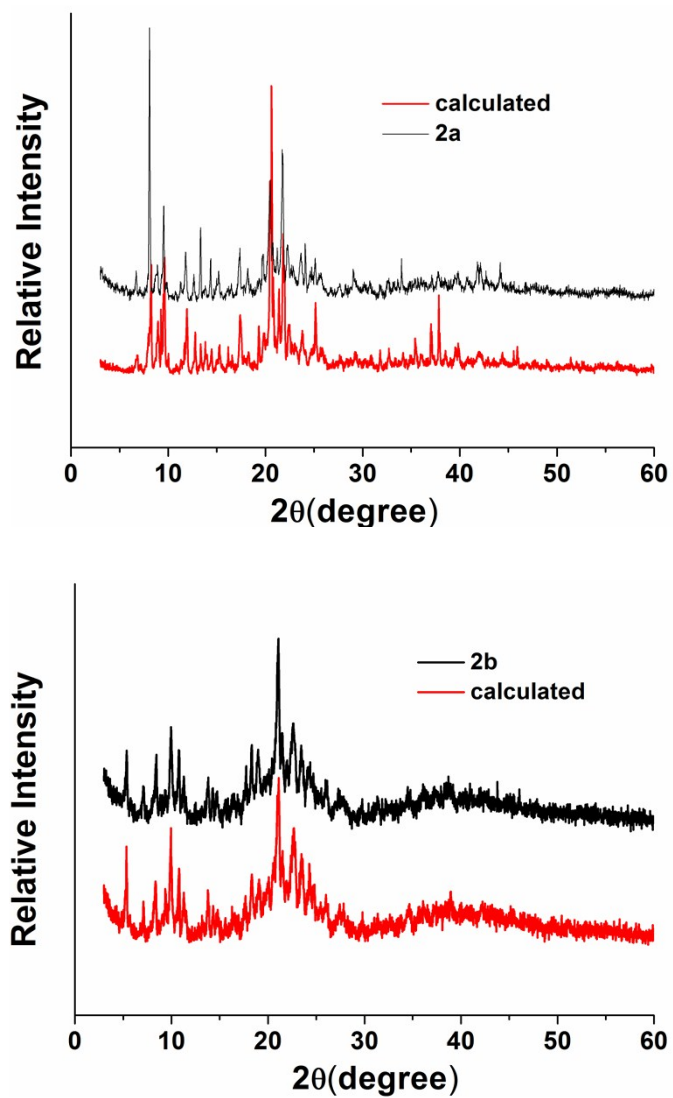


Figure S4 XRD patterns of complexes **2a** and **2b**.

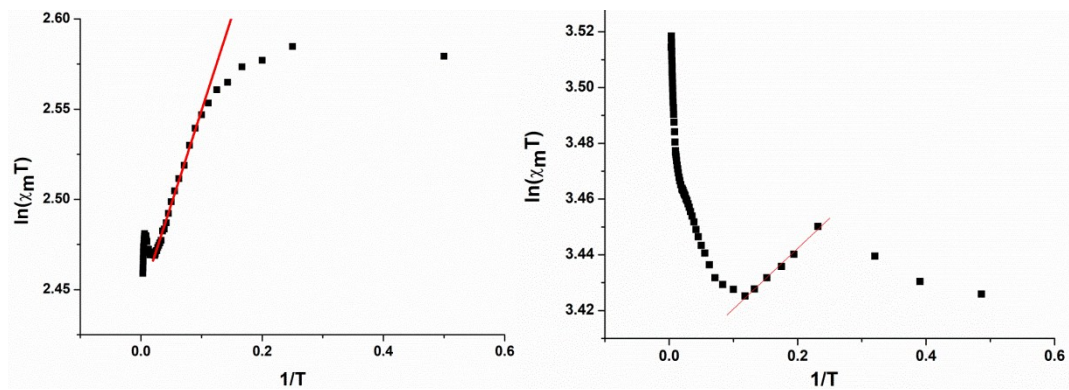


Figure S5  $\ln(\chi T)$  vs.  $1/T$  plot for **2a** (left) and **2b** (right).

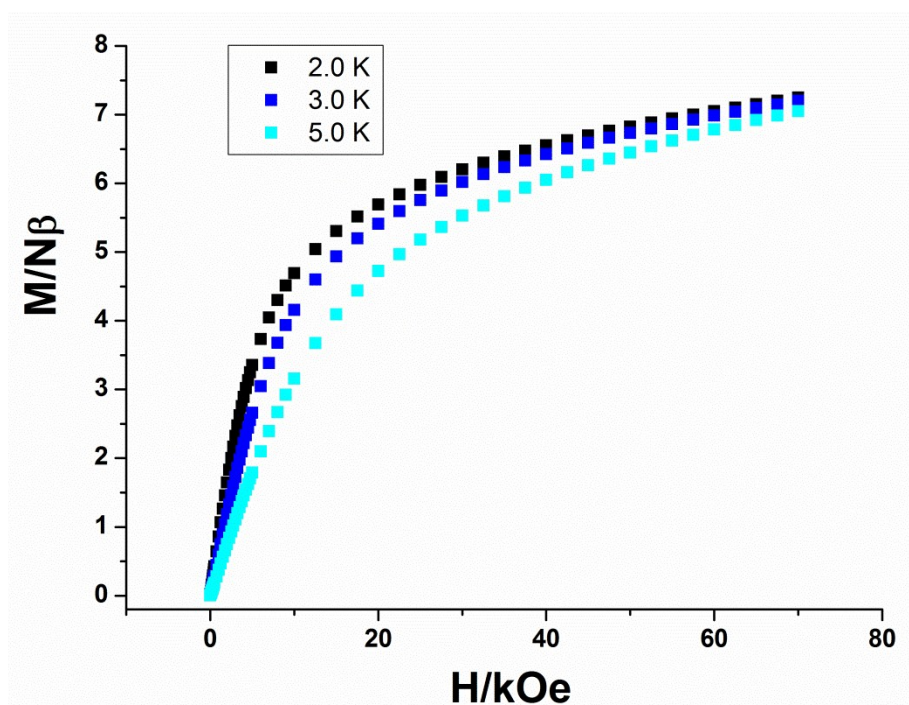
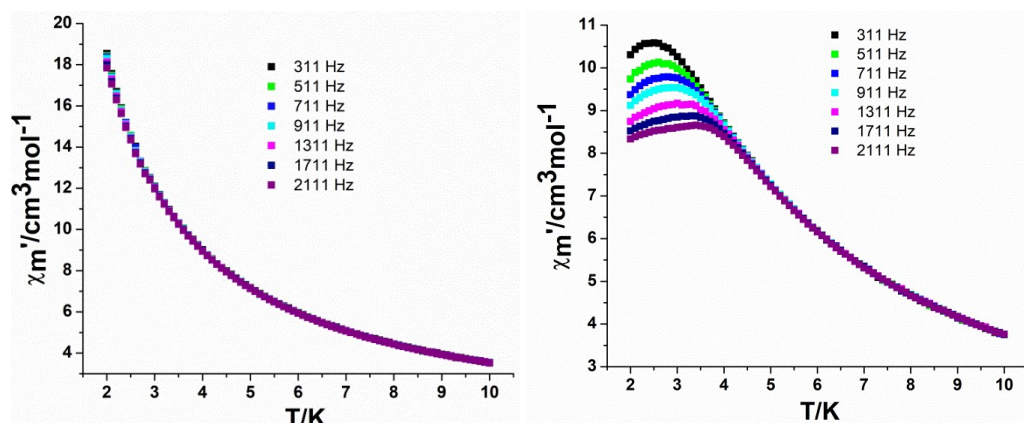
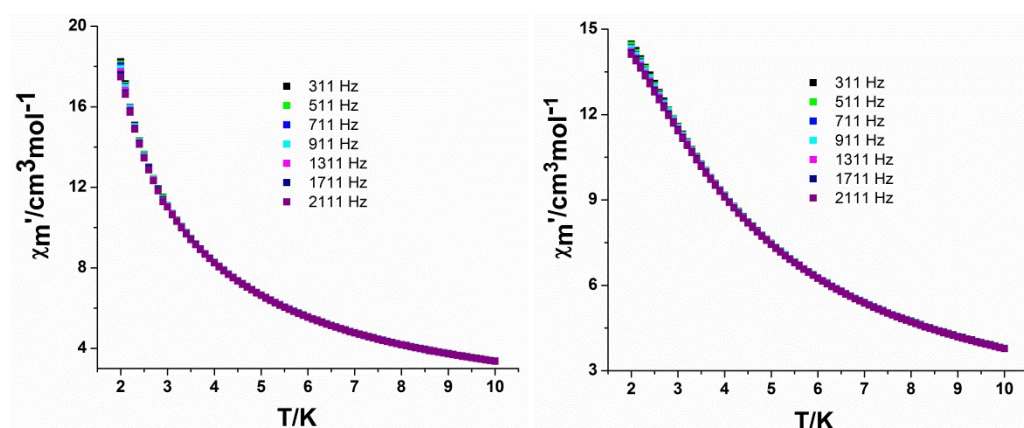


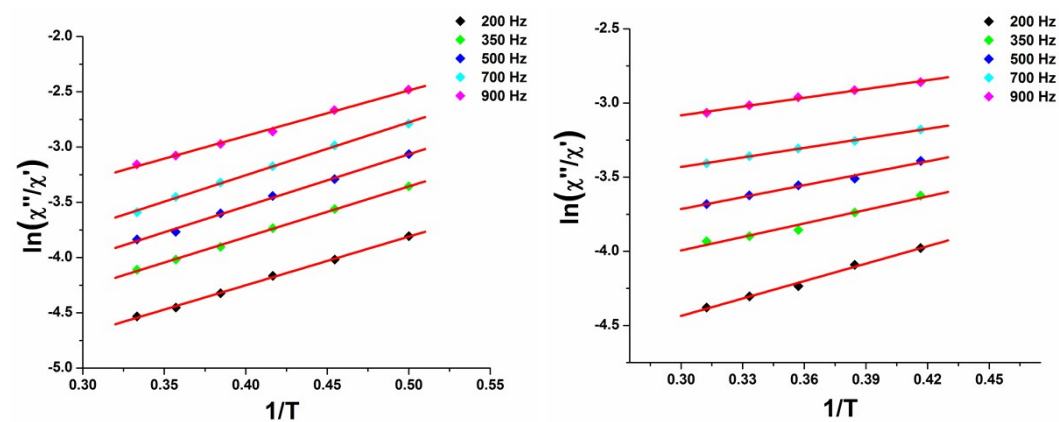
Figure S6  $M$  versus  $H$  plot at 2, 3, 5 K for complex **2a**.



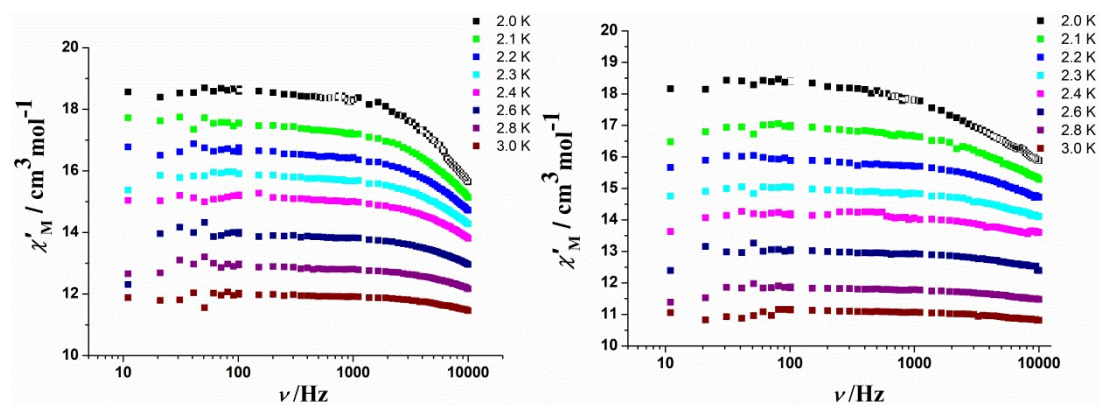
**Figure S7** Temperature dependence of the out-phase in zero (left) and 2 kOe field (right) for complex **2a**.



**Figure S8** Temperature dependence of the in-phase in zero (left) and 2 kOe field (right) for complex **2b**.



**Figure S9** Natural logarithm of the ratio of  $\chi''/\chi'$  vs.  $1/T$  for **2a** (left) and **2b** (right). The solid line represents the fitting results.



**Figure S10** Frequency dependence of the out-of-phase components for the ac magnetic susceptibility in a zero field for **2a** (left) and **2b** (right).