Supporting Information

Heterometallic Ln-Cu complexes derived from phenyl pyrimidyl substituted nitronyl nitroxide biradical

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Table S1 Important bond lengths [Å] and angles [°] for **1**-**3**.

1 Gd			
Gd(1)-O(2)	2.425(4)	Gd(1)-O(3)	2.386(4)
Gd(1)-O(9)	2.400(4)	Gd(1)-O(10)	2.403(4)
Gd(1)-O(11)	2.379(5)	Gd(1)-O(12)	2.347(5)
Gd(1)-O(13)	2.364(5)	Gd(1)-O(14)	2.404(4)
O(1)-N(3)	1.261(7)	O(2)-N(4)	1.304(6)
O(3)-N(5)	1.306(7)	O(4)-N(6)	1.253(8)
Cu(1)-N(1)	2.414(5)	Cu(2)-N(2)	2.411(5)
Cu(1)-O(5)	1.951(4)	Cu(1)-O(6)	1.990(4)
Cu(2)-O(7)	1.962(5)	Cu(2)-O(8)	1.954(4)
N(4)-O(2)-Gd(1)	137.5(3)	N(5)-O(3)-Gd(1)	138.8(3)
O(3)-Gd(1)-O(2)	79.45(15)	O(9)-Gd(1)-O(10)	72.04(15)
O(12)-Gd(1)-O(11)	71.19(16)	O(13)-Gd(1)-O(14)	71.06(15)
O(5)-Cu(1)-O(6)	91.91(17)	O(8)-Cu(2)-O(7)	92.10(18)
2 Tb			
Tb(1)-O(2)	2.390(5)	Tb(1)-O(3)	2.396(6)
Tb(1)-O(9)	2.378(5)	Tb(1)-O(10)	2.390(5)
Tb(1)-O(11)	2.318(6)	Tb(1)-O(12)	2.351(6)
Tb(1)-O(13)	2.360(6)	Tb(1)-O(14)	2.353(5)
N(3)-O(1)	1.248(9)	O(2)-N(4)	1.307(8)
O(3)-N(5)	1.301(8)	N(6)-O(4)	1.262(9)
Cu(1)-N(1)	2.365(6)	Cu(2)-N(2)	2.394(5)
Cu(1)-O(5)	1.961(5)	Cu(1)-O(6)	1.970(5)
Cu(2)-O(7)	1.938(5)	Cu(2)-O(8)	1.968(5)
N(4)-O(2)-Tb(1)	137.9(5)	N(5)-O(3)-Tb(1)	139.1(4)
O(2)-Tb(1)-O(3)	79.8(2)	O(9)-Tb(1)-O(10)	72.15(17)
O(11)-Tb(1)-O(12)	73.0(2)	O(14)-Tb(1)-O(13)	71.72(18)
O(5)-Cu(1)-O(6)	92.3(2)	O(7)-Cu(2)-O(8)	92.4(2)
3 Dy			
Dy(1)-O(2)	2.404(9)	Dy(1)-O(3)	2.381(10)
Dy(1)-O(9)	2.367(8)	Dy(1)-O(10)	2.355(9)
Dy(1)-O(11)	2.289(12)	Dy(1)-O(12)	2.350(11)
Dy(1)-O(13)	2.354(9)	Dy(1)-O(14)	2.326(8)
O(1)-N(3)	1.231(15)	O(2)-N(4)	1.257(14)
O(3)-N(5)	1.285(14)	O(4)-N(6)	1.275(15)
Cu(1)-N(1)	2.350(9)	Cu(2)-N(2)	2.412(8)
Cu(1)-O(5)	1.954(9)	Cu(1)-O(6)	1.956(7)
Cu(2)-O(7)	1.939(8)	Cu(2)-O(8)	1.980(9)
N(4)-O(2)-Dy(1)	139.7(11)	N(5)-O(3)-Dy(1)	138.3(7)
O(3)-Dy(1)-O(2)	78.2(4)	O(10)-Dy(1)-O(9)	71.9(3)
O(11)-Dy(1)-O(12)	74.0(4)	O(14)-Dy(1)-O(13)	72.1(3)
O(5)-Cu(1)-O(6)	92.5(3)	O(7)-Cu(2)-O(8)	92.4(4)

Table S2 SHAPE analysis for the 8-coordinated Ln^{III} ions of **1**-**3**.

Compound	SAPR-8	**TDD-8**	JBTPR-8	**BTPR-8**	JSD-8
1 Gd	1.441	**0.998**	1.864	**1.075**	3.744
2 Tb	1.328	**1.180**	1.937	**1.115**	3.924
3 Dy	1.374	**1.203**	1.878	**1.145**	3.979

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

Table S3 Magnetic parameters and coordination geometry of Ln ion for complex **3** and the related nitronyl nitroxide biradical-Dy discrete complexes.

Compounds	Δ_{eff}/k_B (K)	τ_0 (s)	H_{dc}(Oe)	Closest ideal geometry	Ref.
$[Dy(hfac)_3(NITmbis)]_2$	11.6	2.3×10^{-8}	0	C_{2v}	11a
$[Dy(hfac)_3(NITPymbis)_2]_2 \cdot C_7H_{16}$	none	none	0	C_{2v}	11b
$[Dy(hfac)_3(NITFumbis)]_2$	15	1.25×10^{-6}	3000	C_{2v}	11c
$[Dy_2Co_2(hfac)_{10}(NITPhPybis)_2]$	6.03	5.2×10^{-5}	1000	C_{2v}	13b
$[Dy(hfac)_3Cu(hfac)_2(bisNITPhPyrim)]$	8.13	1.07×10^{-6}	500	$C_{2v} \sim D_{2d}$	this work

NIT*m*bis=1,3-bis-(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4,5-hydro-1*H*-imidazol-2-yl)benzene; NITPy*m*bis = 1,3-bis-(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4,5-hydro-1*H*-imidazol-2-yl) pyridine;NITFu*m*bis=2,5-bis-(1'-oxyl-3'-oxido-4',4',5',5'-tetramethyl-4,5-hydro-1*H*-imidazol-2-yl)furan;NITPhPybis=5-(4-pyridyl)-1,3-bis(1′-oxyl-3′-oxido-4′,4′,5′,5′-tetramethyl-4,5-hydro-1*H*-imidazol-2-yl)benzene.

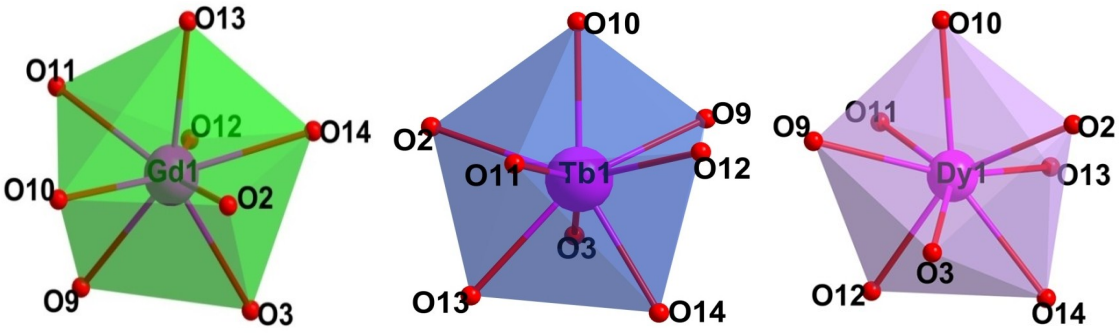


Fig.S1 Coordination polyhedrons of Ln^{III} ions for complexes **1**-**3**.

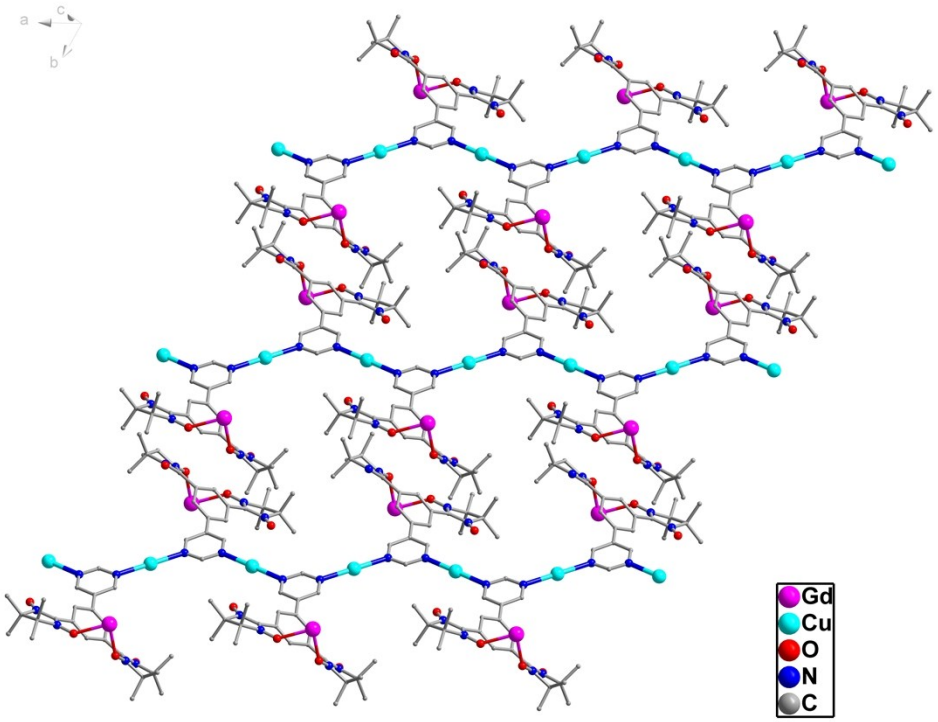


Fig.S2 Packing diagram of complex **1**. H atoms and hfac coligands are not shown for clarity.

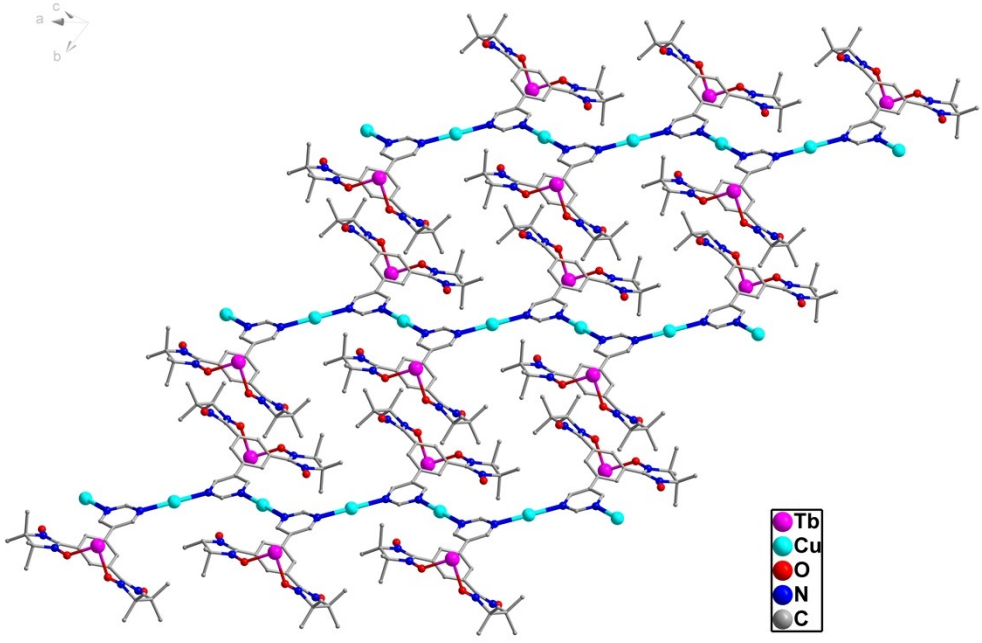


Fig.S3 Packing diagram of complex **2**. H atoms and hfac coligands are not shown for clarity.

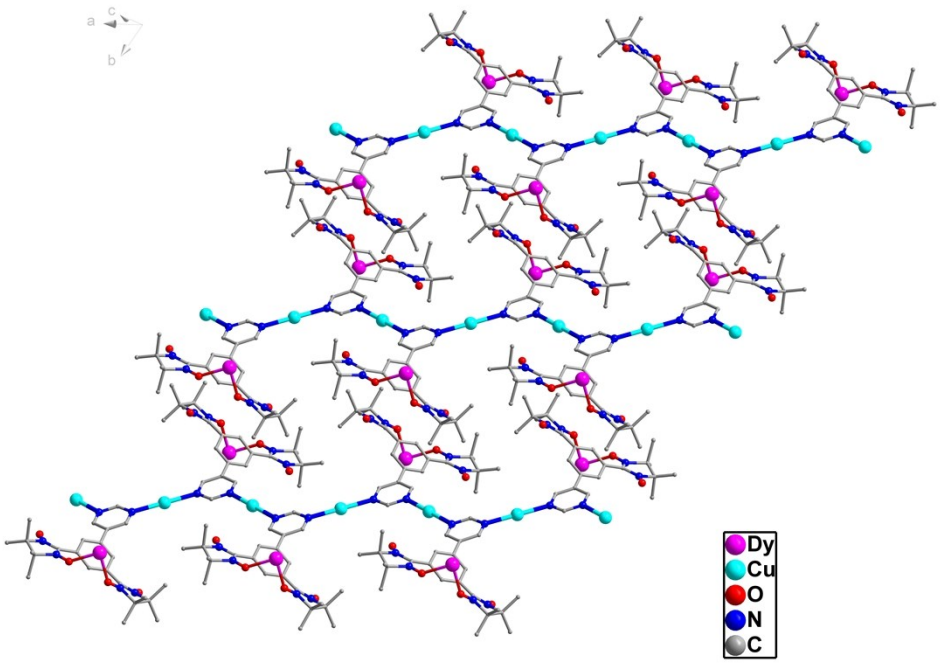
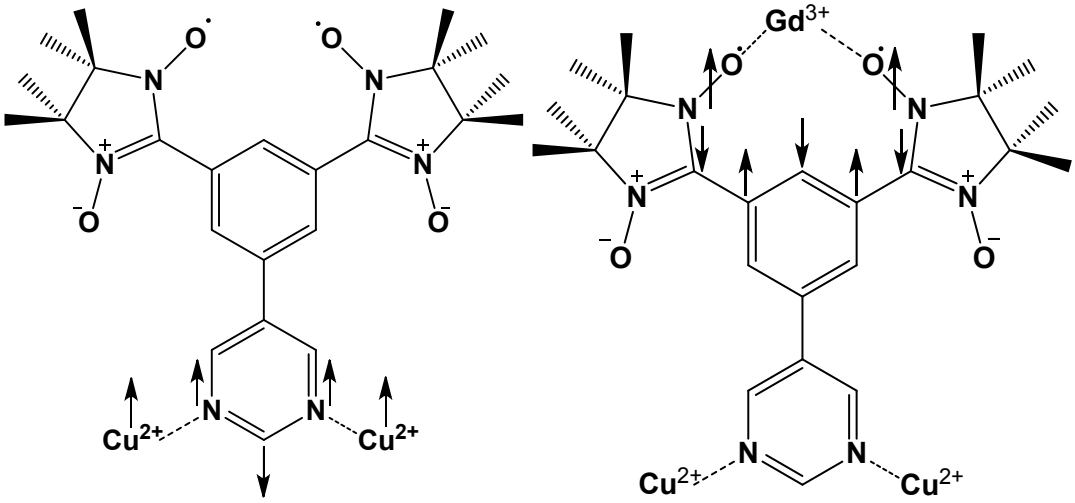


Fig.S4 Packing diagram of complex **3**. H atoms and hfac coligands are not shown for clarity.



Scheme S1 (left) Spin polarization mechanism for the magnetic coupling mediated by pyrimidyl ring; (right) Spin polarization mechanism for the magnetic coupling mediated by *m*-phenylene ring between two radicals.

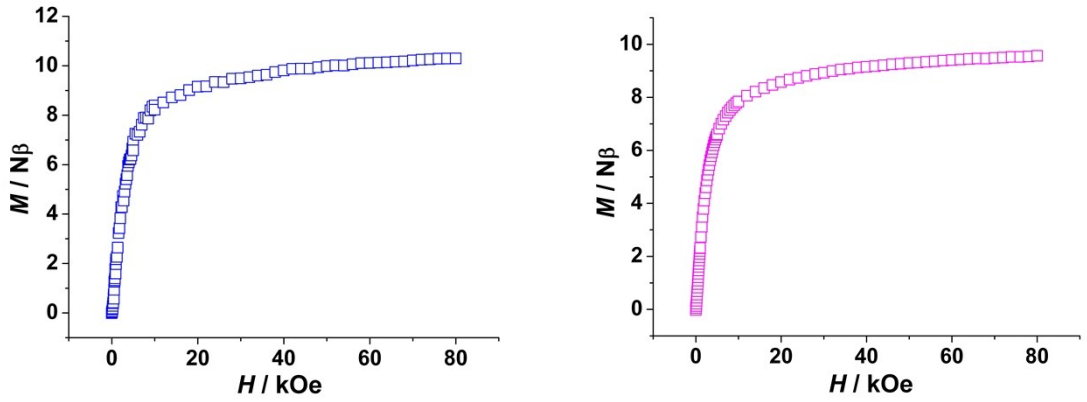


Fig.S5 *M* vs. *H* plots of **2** (blue) and **3** (pink) at 2.0 K.

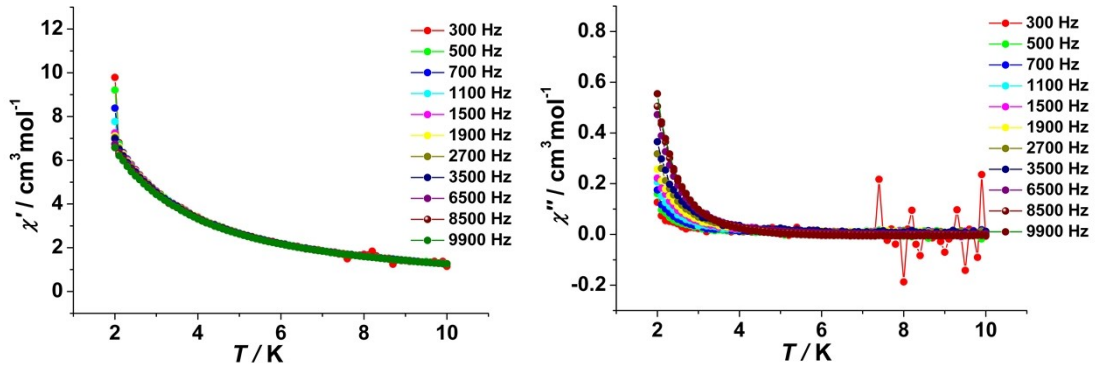


Fig.S6 Temperature dependence of χ′ (left) and χ″(right) ac susceptibility under zero dc field for **2**.

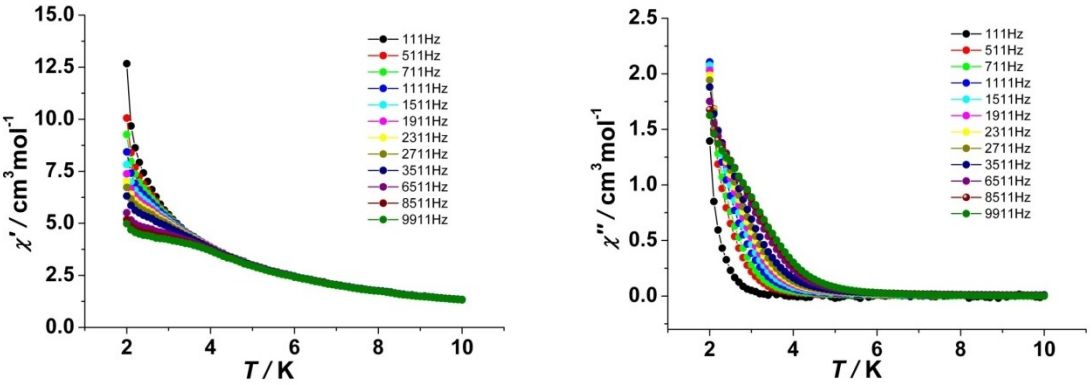


Fig.S7 Temperature dependence of χ′ (left) and χ″(right) ac susceptibility under zero dc field for **3**.

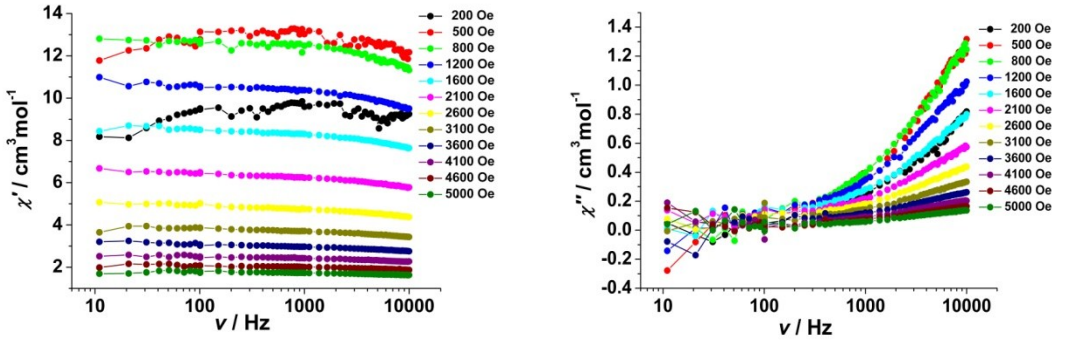


Fig.S8 Frequency dependence of χ′ (left) and χ″(right) ac susceptibility at 2 K under different dc fields for **2**.

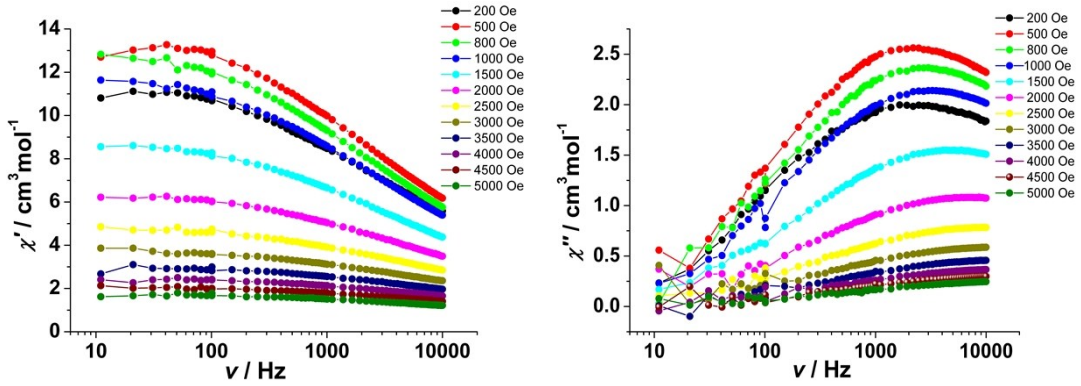


Fig.S9 Frequency dependence of χ′ (left) and χ″(right) ac susceptibility at 2 K under different dc fields for **3**.

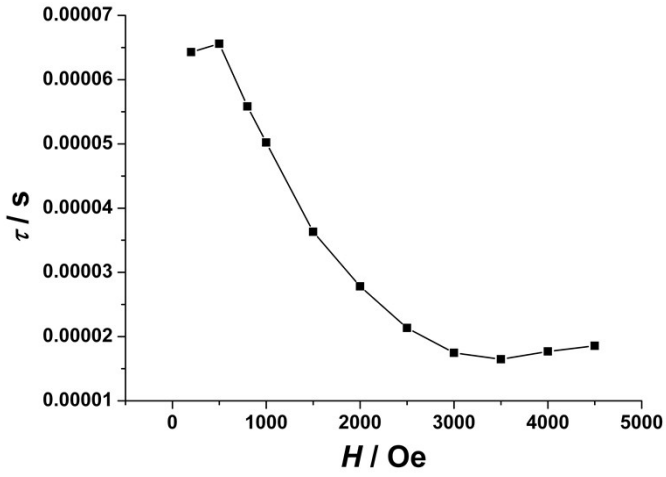


Fig.S10 The τ versus H plot for complex **3** at 2 K under applied dc fields.

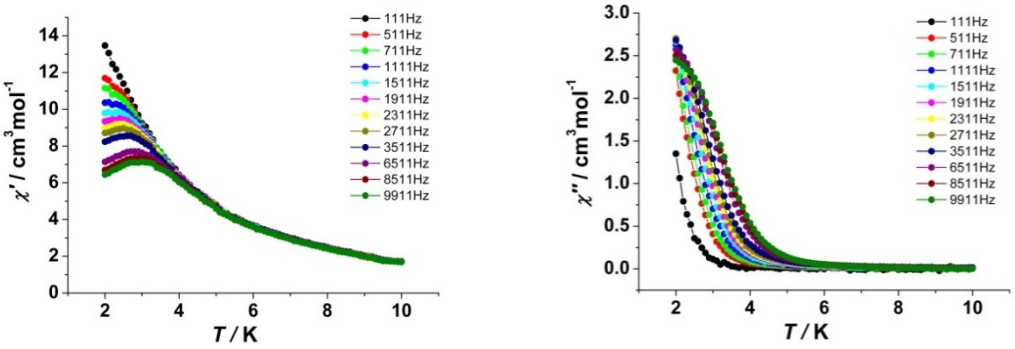


Fig.S11 Temperature dependence of χ' (left) and χ''(right) ac susceptibility under 500 Oe dc field for **3**.