

Supporting Information

Magnetic relaxation in $[\text{Ln}(\text{hfac})_4]^-$ anions with $[\text{Cu}(\text{hfac})\text{-Radical}]_n^{n+}$ cation chains as counterions

Juan Sun, Meng Yang, Lu Xi, Yue Ma, Licun Li*

Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry
and Tianjin Key Laboratory of Metal and Molecule-based Material Chemistry,
College of Chemistry, Nankai University, Tianjin 300071, China

Table S1. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for **1**.

<i>Bond distances</i>			
Gd(1)-O(7)	2.358(3)	Gd(1)-O(10)	2.363(3)
Gd(1)-O(9)	2.364(3)	Gd(1)-O(11)	2.362(2)
Gd(1)-O(12)	2.379(3)	Gd(1)-O(6)	2.383(3)
Gd(1)-O(5)	2.408(3)	Gd(1)-O(8)	2.417(3)
Cu(1)-O(4)	1.930(2)	Cu(1)-O(2)	1.964(3)
Cu(1)-N(3)	2.000(3)	Cu(1)-O(3)	2.192(3)
Cu(1)-N(2)	1.968(3)	O(2)-N(4)	1.306(4)
O(1)-N(5)	1.262(4)		
<i>Angles</i>			
O(7)-Gd(1)-O(10)	81.27(9)	O(7)-Gd(1)-O(9)	143.69(10)
O(10)-Gd(1)-O(9)	73.08(10)	O(7)-Gd(1)-O(11)	140.54(9)
O(10)-Gd(1)-O(11)	132.91(9)	O(9)-Gd(1)-O(11)	74.57(10)
O(7)-Gd(1)-O(12)	109.89(9)	O(10)-Gd(1)-O(12)	71.94(10)
O(9)-Gd(1)-O(12)	86.32(10)	O(11)-Gd(1)-O(12)	72.72(9)
O(7)-Gd(1)-O(6)	79.33(9)	O(10)-Gd(1)-O(6)	152.55(10)
O(9)-Gd(1)-O(6)	113.52(10)	O(11)-Gd(1)-O(6)	72.95(9)
O(12)-Gd(1)-O(6)	133.34(10)	O(7)-Gd(1)-O(5)	75.40(10)
O(10)-Gd(1)-O(5)	85.26(10)	O(9)-Gd(1)-O(5)	77.24(10)
O(11)-Gd(1)-O(5)	119.44(9)	O(12)-Gd(1)-O(5)	155.05(10)
O(6)-Gd(1)-O(5)	71.20(10)	O(7)-Gd(1)-O(8)	70.56(9)
O(10)-Gd(1)-O(8)	119.57(10)	O(9)-Gd(1)-O(8)	145.02(10)
O(11)-Gd(1)-O(8)	74.23(9)	O(12)-Gd(1)-O(8)	69.60(10)
O(6)-Gd(1)-O(8)	71.33(10)	O(5)-Gd(1)-O(8)	132.92(10)
O(4)-Cu(1)-O(2)	91.40(11)	O(4)-Cu(1)-N(2)	93.97(12)
O(2)-Cu(1)-N(2)	159.88(12)	O(4)-Cu(1)-N(3)	172.92(12)
O(2)-Cu(1)-N(3)	91.01(11)	N(2)-Cu(1)-N(3)	81.58(12)
O(4)-Cu(1)-O(3)	90.16(11)	O(2)-Cu(1)-O(3)	97.97(11)
N(2)-Cu(1)-O(3)	101.39(12)	N(3)-Cu(1)-O(3)	96.10(12)
N(4)-O(2)-Cu(1)	117.5(2)		

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

<i>Bond distances</i>			
Dy(1)-O(8)	2.328(3)	Dy(1)-O(12)	2.330(2)
Dy(1)-O(7)	2.335(3)	Dy(1)-O(10)	2.346(2)
Dy(1)-O(9)	2.348(3)	Dy(1)-O(6)	2.357(3)
Dy(1)-O(5)	2.379(3)	Dy(1)-O(11)	2.393(3)
Cu(1)-O(4)	1.934(2)	Cu(1)-O(2)	1.965(2)
Cu(1)-N(1)	1.968(3)	Cu(1)-N(3)	2.004(3)
Cu(1)-O(3)	2.187(3)	O(2)-N(4)	1.303(4)
O(1)-N(5)	1.266(4)		
<i>Angles</i>			
O(8)-Dy(1)-O(12)	143.36(9)	O(8)-Dy(1)-O(7)	73.74(10)
O(12)-Dy(1)-O(7)	80.47(9)	O(8)-Dy(1)-O(10)	74.34(9)
O(12)-Dy(1)-O(10)	140.98(9)	O(7)-Dy(1)-O(10)	133.49(9)
O(8)-Dy(1)-O(9)	86.51(10)	O(12)-Dy(1)-O(9)	109.76(9)
O(7)-Dy(1)-O(9)	71.75(9)	O(10)-Dy(1)-O(9)	73.40(9)
O(8)-Dy(1)-O(6)	113.05(11)	O(12)-Dy(1)-O(6)	79.71(9)
O(7)-Dy(1)-O(6)	152.24(10)	O(10)-Dy(1)-O(6)	72.68(9)
O(9)-Dy(1)-O(6)	133.76(9)	O(8)-Dy(1)-O(5)	76.59(10)
O(12)-Dy(1)-O(5)	75.39(10)	O(7)-Dy(1)-O(5)	84.44(10)
O(10)-Dy(1)-O(5)	119.41(9)	O(9)-Dy(1)-O(5)	153.96(9)
O(6)-Dy(1)-O(5)	71.87(10)	O(8)-Dy(1)-O(11)	144.78(9)
O(12)-Dy(1)-O(11)	71.22(9)	O(7)-Dy(1)-O(11)	119.62(10)
O(10)-Dy(1)-O(11)	74.10(9)	O(9)-Dy(1)-O(11)	69.79(9)
O(6)-Dy(1)-O(11)	71.34(10)	O(5)-Dy(1)-O(11)	133.69(9)
O(4)-Cu(1)-O(2)	91.44(10)	O(4)-Cu(1)-N(1)	94.02(12)
O(2)-Cu(1)-N(1)	159.65(12)	O(4)-Cu(1)-N(3)	172.88(12)
O(2)-Cu(1)-N(3)	90.99(11)	N(1)-Cu(1)-N(3)	81.47(12)
O(4)-Cu(1)-O(3)	90.22(11)	O(2)-Cu(1)-O(3)	97.86(10)
N(1)-Cu(1)-O(3)	101.70(12)	N(3)-Cu(1)-O(3)	96.08(11)
N(4)-O(2)-Cu(1)	117.45(19)		

Table S3. The substates and corresponding energy levels of **2** extracted from the $\chi_M T$ - T and M - H data.

$ M_J\rangle$	$E(\text{cm}^{-1})$
$\pm 13/2$	0
$\pm 11/2$	34.46
$\pm 1/2$	51.36
$\pm 3/2$	83.37
$\pm 9/2$	110.1
$\pm 5/2$	125.5
$\pm 7/2$	143.4
$\pm 15/2$	213.3

Table S4. The anisotropic energy barriers and the pre-exponential factors for compounds $[\text{Cs}\{\text{Dy}(\text{hfac})_4\}]$, $[\text{K}\{\text{Dy}(\text{hfac})_4\}]$ and the present work.

Compounds	Local symmetry	U_{eff}/K	τ_0/s
$[\text{Cs}\{\text{Dy}(\text{hfac})_4\}]$	D_{2d}	–	–
$[\text{K}\{\text{Dy}(\text{hfac})_4\}]$	D_{4d}	23.95 K,	3.12×10^{-9}
Compound 2	D_{4d}	15.74	6.74×10^{-7}

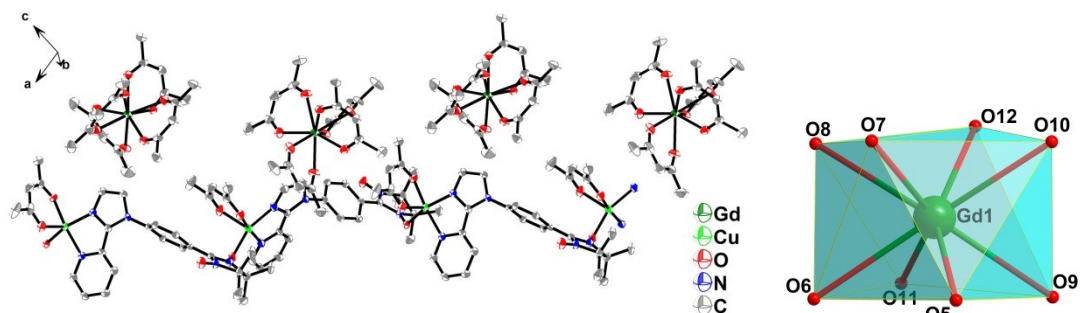


Fig. S1 (left) ORTEP diagram of **1**, showing 50% thermal ellipsoids (Hydrogen, fluorine atoms are not shown for the sake of clarity). (right) Local coordination geometry of Gd(III) ion.

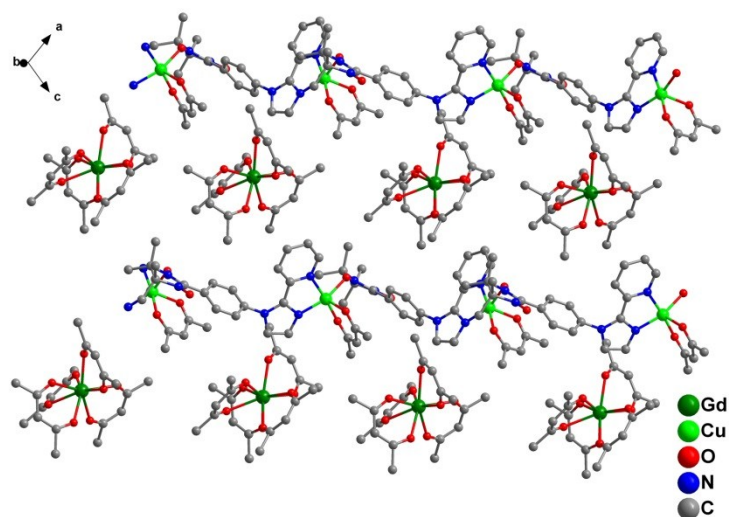


Fig. S2 Packing arrangement of **1** (H and F atoms are omitted for clarity).

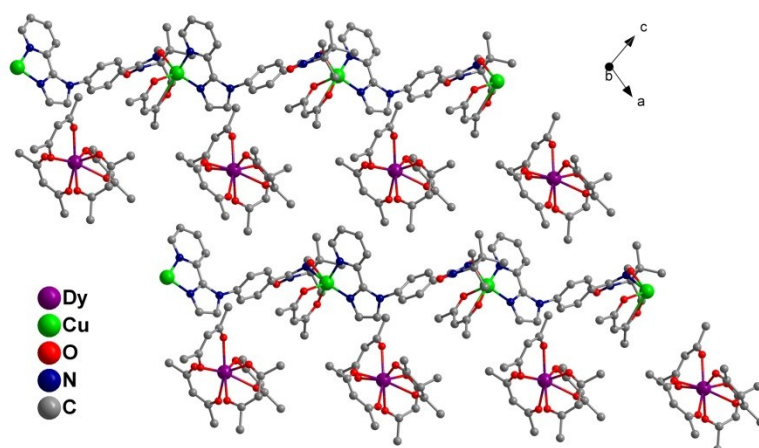


Fig. S3 Packing arrangement of **2** (H and F atoms are omitted for clarity).

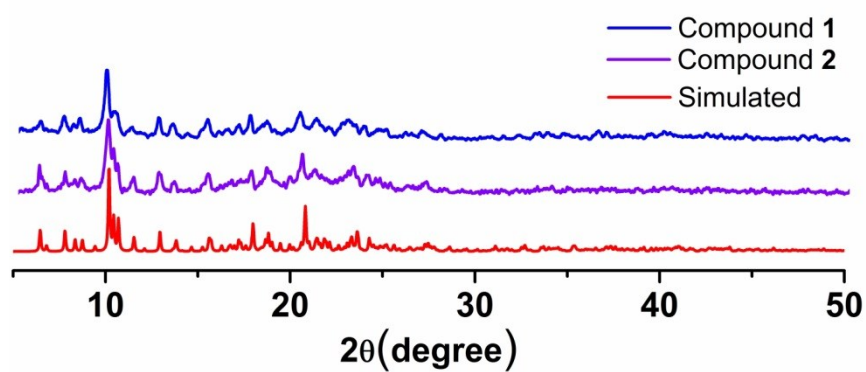


Fig. S4 Powder X-ray diffraction patterns of complexes **1** and **2**.

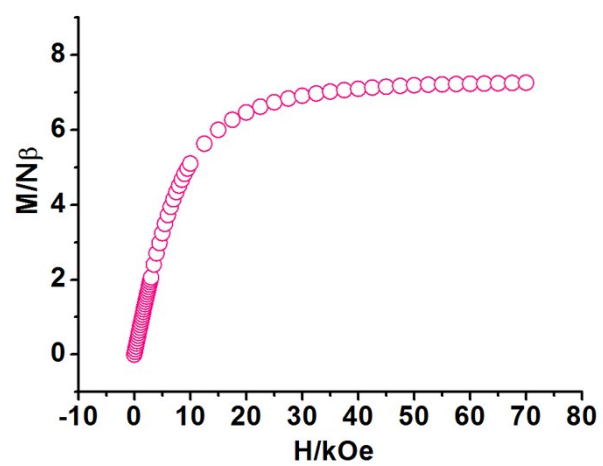


Fig. S5 M versus H curve for complex **1** at 2.0 K.