Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2022

Supporting Information

Heterospin 2p-4f and 2p-3d-4f complexes constructed by a nitronyl nitroxide ligand: syntheses, structures and magnetic properties

Juan Sun,* Min Chen, Ying Li, Xingran Liu, Xinyang Fu, Lijun He, Chuanming Jin*

Hubei Key Laboratory of Pollutant Analysis & Reuse Technology, College of Chemistry and Chemical Engineering, Hubei Normal University, Huangshi 435002, P. R. China.

*E-mail: sunjuan@hbnu.edu.cn; cmjin@hbnu.edu.cn

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

Bond distances			
Gd(2)-O(4)	2.381(7)	Gd(1)-O(10)	2.393(7)
Gd(2)-O(3)	2.394(7)	Gd(1)-O(12)	2.399(7)
Gd(2)-O(1)	2.407(7)	Gd(1)-O(11)	2.400(7)
Gd(2)-O(6)	2.420(7)	Gd(1)-O(15)	2.407(7)
Gd(2)-O(7)	2.424(7)	Gd(1)-O(9)	2.416(7)
Gd(2)-O(2)	2.436(7)	Gd(1)-O(14)	2.437(7)
Gd(2)-O(5)	2.508(8)	Gd(1)-O(13)	2.509(8)
Gd(2)-N(4)	2.511(7)	Gd(1)-N(9)	2.512(8)
Gd(2)-N(5)	2.668(9)	Gd(1)-N(10)	2.656(8)
O(7)-N(1)	1.283(11)	O(15)-N(6)	1.305(10)
O(8)-N(2)	1.262(12)	O(16)-N(7)	1.272(11)
Angles			
O(4)-Gd(2)-O(3)	73.8(2)	O(10)-Gd(1)-O(12)	71.1(3)
O(4)-Gd(2)-O(1)	69.4(3)	O(10)-Gd(1)-O(11)	72.9(3)
O(3)-Gd(2)-O(1)	74.5(3)	O(12)-Gd(1)-O(11)	73.2(2)
O(4)-Gd(2)-O(6)	84.3(2)	O(10)-Gd(1)-O(15)	138.3(2)
O(3)-Gd(2)-O(6)	136.8(2)	O(12)-Gd(1)-O(15)	141.7(3)
O(1)-Gd(2)-O(6)	131.5(3)	O(11)-Gd(1)-O(15)	91.3(2)
O(4)-Gd(2)-O(7)	140.2(2)	O(10)-Gd(1)-O(9)	70.2(2)
O(3)-Gd(2)-O(7)	92.1(2)	O(12)-Gd(1)-O(9)	133.8(3)
O(1)-Gd(2)-O(7)	143.2(3)	O(11)-Gd(1)-O(9)	72.1(2)
O(6)-Gd(2)-O(7)	81.4(2)	O(15)-Gd(1)-O(9)	68.2(2)
O(4)-Gd(2)-O(2)	130.8(2)	O(10)-Gd(1)-O(14)	133.2(2)
O(3)-Gd(2)-O(2)	69.6(2)	O(12)-Gd(1)-O(14)	85.5(3)
O(1)-Gd(2)-O(2)	69.9(3)	O(11)-Gd(1)-O(14)	138.5(2)
O(6)-Gd(2)-O(2)	144.5(2)	O(15)-Gd(1)-O(14)	83.8(2)
O(7)-Gd(2)-O(2)	73.2(2)	O(9)-Gd(1)-O(14)	140.3(2)
O(4)-Gd(2)-O(5)	68.6(3)	O(10)-Gd(1)-O(13)	132.0(3)
O(3)-Gd(2)-O(5)	69.6(3)	O(12)-Gd(1)-O(13)	68.8(3)
O(1)-Gd(2)-O(5)	130.5(3)	O(11)-Gd(1)-O(13)	71.3(3)
O(6)-Gd(2)-O(5)	67.9(3)	O(15)-Gd(1)-O(13)	73.2(3)
O(7)-Gd(2)-O(5)	71.7(2)	O(9)-Gd(1)-O(13)	125.0(2)
O(2)-Gd(2)-O(5)	124.0(3)	O(14)-Gd(1)-O(13)	67.8(2)
O(4)-Gd(2)-N(4)	137.6(2)	O(10)-Gd(1)-N(9)	92.3(3)
O(3)-Gd(2)-N(4)	140.5(2)	O(12)-Gd(1)-N(9)	136.2(3)
O(1)-Gd(2)-N(4)	93.6(3)	O(11)-Gd(1)-N(9)	141.5(2)
O(6)-Gd(2)-N(4)	78.9(2)	O(15)-Gd(1)-N(9)	76.3(2)
O(7)-Gd(2)-N(4)	75.0(2)	O(9)-Gd(1)-N(9)	69.5(2)
O(2)-Gd(2)-N(4)	70.9(2)	O(14)-Gd(1)-N(9)	77.1(2)
O(5)-Gd(2)-N(4)	135.6(3)	O(13)-Gd(1)-N(9)	135.2(3)
O(4)-Gd(2)-N(5)	75.7(2)	O(10)-Gd(1)-N(10)	70.3(3)
O(3)-Gd(2)-N(5)	138.5(3)	O(12)-Gd(1)-N(10)	74.1(3)

O(1)-Gd(2)-N(5)	68.9(3)	O(11)-Gd(1)-N(10)	136.8(2)
O(6)-Gd(2)-N(5)	65.4(3)	O(15)-Gd(1)-N(10)	131.5(2)
O(7)-Gd(2)-N(5)	129.1(2)	O(9)-Gd(1)-N(10)	114.3(3)
O(2)-Gd(2)-N(5)	113.2(3)	O(14)-Gd(1)-N(10)	64.4(3)
O(5)-Gd(2)-N(5)	122.8(3)	O(13)-Gd(1)-N(10)	120.5(3)
N(4)-Gd(2)-N(5)	61.9(3)	N(9)-Gd(1)-N(10)	62.1(3)
N(1)-O(7)-Gd(2)	140.2(6)	N(6)-O(15)-Gd(1)	135.1(6)

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

Bond distances			
Tb(2)-O(4)	2.369(5)	Tb(1)-O(10)	2.369(5)
Tb(2)-O(3)	2.379(5)	Tb(1)-O(12)	2.372(5)
Tb(2)-O(1)	2.384(6)	Tb(1)-O(11)	2.382(5)
Tb(2)-O(6)	2.395(5)	Tb(1)-O(15)	2.397(5)
Tb(2)-O(7)	2.401(5)	Tb(1)-O(14)	2.407(5)
Tb(2)-O(2)	2.415(5)	Tb(1)-O(9)	2.417(5)
Tb(2)-N(4)	2.482(6)	Tb(1)-O(13)	2.499(5)
Tb(2)-O(5)	2.513(6)	Tb(1)-N(9)	2.503(6)
Tb(2)-N(5)	2.661(6)	Tb(1)-N(10)	2.649(6)
O(7)-N(1)	1.300(8)	O(16)-N(7)	1.285(8)
O(8)-N(2)	1.276(9)	O(15)-N(6)	1.284(8)
Angles			
O(4)-Tb(2)-O(3)	74.53(18)	O(10)-Tb(1)-O(12)	71.1(2)
O(4)-Tb(2)-O(1)	69.57(19)	O(10)-Tb(1)-O(11)	73.12(18)
O(3)-Tb(2)-O(1)	75.03(19)	O(12)-Tb(1)-O(11)	73.46(18)
O(4)-Tb(2)-O(6)	83.96(18)	O(10)-Tb(1)-O(15)	138.85(18)
O(3)-Tb(2)-O(6)	137.17(19)	O(12)-Tb(1)-O(15)	141.37(19)
O(1)-Tb(2)-O(6)	130.92(19)	O(11)-Tb(1)-O(15)	91.33(18)
O(4)-Tb(2)-O(7)	140.25(18)	O(10)-Tb(1)-O(14)	133.20(18)
O(3)-Tb(2)-O(7)	92.03(19)	O(12)-Tb(1)-O(14)	85.26(19)
O(1)-Tb(2)-O(7)	143.57(19)	O(11)-Tb(1)-O(14)	138.26(18)
O(6)-Tb(2)-O(7)	81.30(18)	O(15)-Tb(1)-O(14)	83.34(18)
O(4)-Tb(2)-O(2)	131.75(18)	O(10)-Tb(1)-O(9)	70.24(18)
O(3)-Tb(2)-O(2)	69.63(18)	O(12)-Tb(1)-O(9)	134.13(19)
O(1)-Tb(2)-O(2)	70.7(2)	O(11)-Tb(1)-O(9)	72.43(17)
O(6)-Tb(2)-O(2)	143.95(18)	O(15)-Tb(1)-O(9)	68.76(18)
O(7)-Tb(2)-O(2)	72.84(19)	O(14)-Tb(1)-O(9)	140.12(18)
O(4)-Tb(2)-N(4)	137.2(2)	O(10)-Tb(1)-O(13)	131.58(19)
O(3)-Tb(2)-N(4)	140.48(19)	O(12)-Tb(1)-O(13)	68.7(2)
O(1)-Tb(2)-N(4)	93.4(2)	O(11)-Tb(1)-O(13)	70.41(18)
O(6)-Tb(2)-N(4)	78.52(19)	O(15)-Tb(1)-O(13)	72.74(19)
O(7)-Tb(2)-N(4)	75.0(2)	O(14)-Tb(1)-O(13)	68.48(18)
O(2)-Tb(2)-N(4)	70.88(19)	O(9)-Tb(1)-O(13)	124.74(18)
O(4)-Tb(2)-O(5)	68.94(19)	O(10)-Tb(1)-N(9)	92.65(19)
O(3)-Tb(2)-O(5)	68.92(18)	O(12)-Tb(1)-N(9)	136.44(19)
O(1)-Tb(2)-O(5)	130.51(18)	O(11)-Tb(1)-N(9)	141.44(18)
O(6)-Tb(2)-O(5)	68.88(18)	O(15)-Tb(1)-N(9)	75.98(19)
O(7)-Tb(2)-O(5)	71.32(18)	O(14)-Tb(1)-N(9)	77.13(19)
O(2)-Tb(2)-O(5)	122.96(19)	O(9)-Tb(1)-N(9)	69.02(18)
N(4)-Tb(2)-O(5)	135.8(2)	O(13)-Tb(1)-N(9)	135.4(2)
O(4)-Tb(2)-N(5)	75.04(19)	O(10)-Tb(1)-N(10)	70.05(19)

O(3)-Tb(2)-N(5)	138.7(2)	O(12)-Tb(1)-N(10)	73.79(19)
O(1)-Tb(2)-N(5)	68.6(2)	O(11)-Tb(1)-N(10)	136.74(19)
O(6)-Tb(2)-N(5)	64.94(19)	O(15)-Tb(1)-N(10)	131.63(18)
O(7)-Tb(2)-N(5)	129.00(19)	O(14)-Tb(1)-N(10)	64.67(19)
O(2)-Tb(2)-N(5)	113.79(19)	O(9)-Tb(1)-N(10)	114.01(19)
N(4)-Tb(2)-N(5)	62.1(2)	O(13)-Tb(1)-N(10)	121.14(19)
O(5)-Tb(2)-N(5)	123.24(19)	N(9)-Tb(1)-N(10)	62.65(19)
N(1)-O(7)-Tb(2)	140.6(4)	N(6)-O(15)-Tb(1)	134.7(4)

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

Bond distances			
Tb(1)-O(10)	2.351(4)	Cu(2)-O(4)	1.931(4)
Tb(1)-O(11)	2.408(4)	Cu(2)-O(2)	1.962(4)
Tb(1)-O(5)	2.364(4)	Cu(2)-N(3)	2.009(5)
Tb(1)-O(12)	2.346(4)	Cu(2)-N(4)	1.970(5)
Tb(1)-O(6)	2.394(4)	Cu(2)-O(3)	2.191(5)
Tb(1)-O(7)	2.348(5)	O(2)-N(2)	1.306(6)
Tb(1)-O(8)	2.353(4)	O(1)-N(1)	1.262(6)
Tb(1)-O(9)	2.360(4)		
Angles			
O(10)-Tb(1)-O(11)	73.82(15)	O(7)-Tb(1)-O(9)	85.95(16)
O(10)-Tb(1)-O(5)	72.83(15)	O(8)-Tb(1)-O(11)	120.01(16)
O(10)-Tb(1)-O(6)	119.45(15)	O(8)-Tb(1)-O(5)	152.38(16)
O(10)-Tb(1)-O(8)	133.19(16)	O(8)-Tb(1)-O(6)	84.81(16)
O(10)-Tb(1)-O(9)	72.93(15)	O(8)-Tb(1)-O(9)	71.84(16)
O(5)-Tb(1)-O(11)	71.07(16)	O(9)-Tb(1)-O(11)	70.04(16)
O(5)-Tb(1)-O(6)	71.52(16)	O(9)-Tb(1)-O(5)	133.65(16)
O(12)-Tb(1)-O(10)	140.53(15)	O(9)-Tb(1)-O(6)	154.36(16)
O(12)-Tb(1)-O(11)	71.09(15)	O(4)-Cu(2)-O(2)	91.38(17)
O(12)-Tb(1)-O(5)	79.14(16)	O(4)-Cu(2)-N(3)	172.85(19)
O(12)-Tb(1)-O(6)	75.23(15)	O(4)-Cu(2)-N(4)	93.74(19)
O(12)-Tb(1)-O(7)	143.69(15)	O(4)-Cu(2)-O(3)	90.33(18)
O(12)-Tb(1)-O(8)	81.22(16)	O(2)-Cu(2)-N(3)	91.26(18)
O(12)-Tb(1)-O(9)	110.37(15)	O(2)-Cu(2)-N(4)	159.72(19)
O(6)-Tb(1)-O(11)	133.26(16)	O(2)-Cu(2)-O(3)	97.92(17)
O(7)-Tb(1)-O(10)	74.45(15)	N(3)-Cu(2)-O(3)	95.89(19)
O(7)-Tb(1)-O(11)	144.59(16)	N(4)-Cu(2)-N(3)	81.6(2)
O(7)-Tb(1)-O(5)	113.45(17)	N(4)-Cu(2)-O(3)	101.65(19)
O(7)-Tb(1)-O(6)	77.10(16)	N(2)-O(2)-Cu(2)	117.8(3)
O(7)-Tb(1)-O(8)	73.27(16)		

Table S4 SHAPE analysis for complexes **1** and **2**.

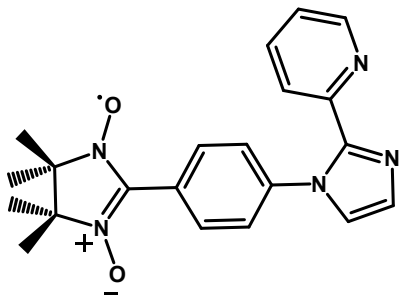
Compound	JCSAPR-9	CSAPR-9	JTCTPR-9	TCTPR-9	MFF-9
1 Gd1	1.722	**0.802**	1.804	**0.589**	1.465
1 Gd2	1.642	**0.809**	1.895	**0.695**	1.463
2 Tb1	1.638	**0.769**	1.725	**0.582**	1.465
2 Tb2	1.614	**0.821**	1.792	**0.693**	1.462

Table S5. SHAPE analysis for the Tb coordination sphere of **3**.

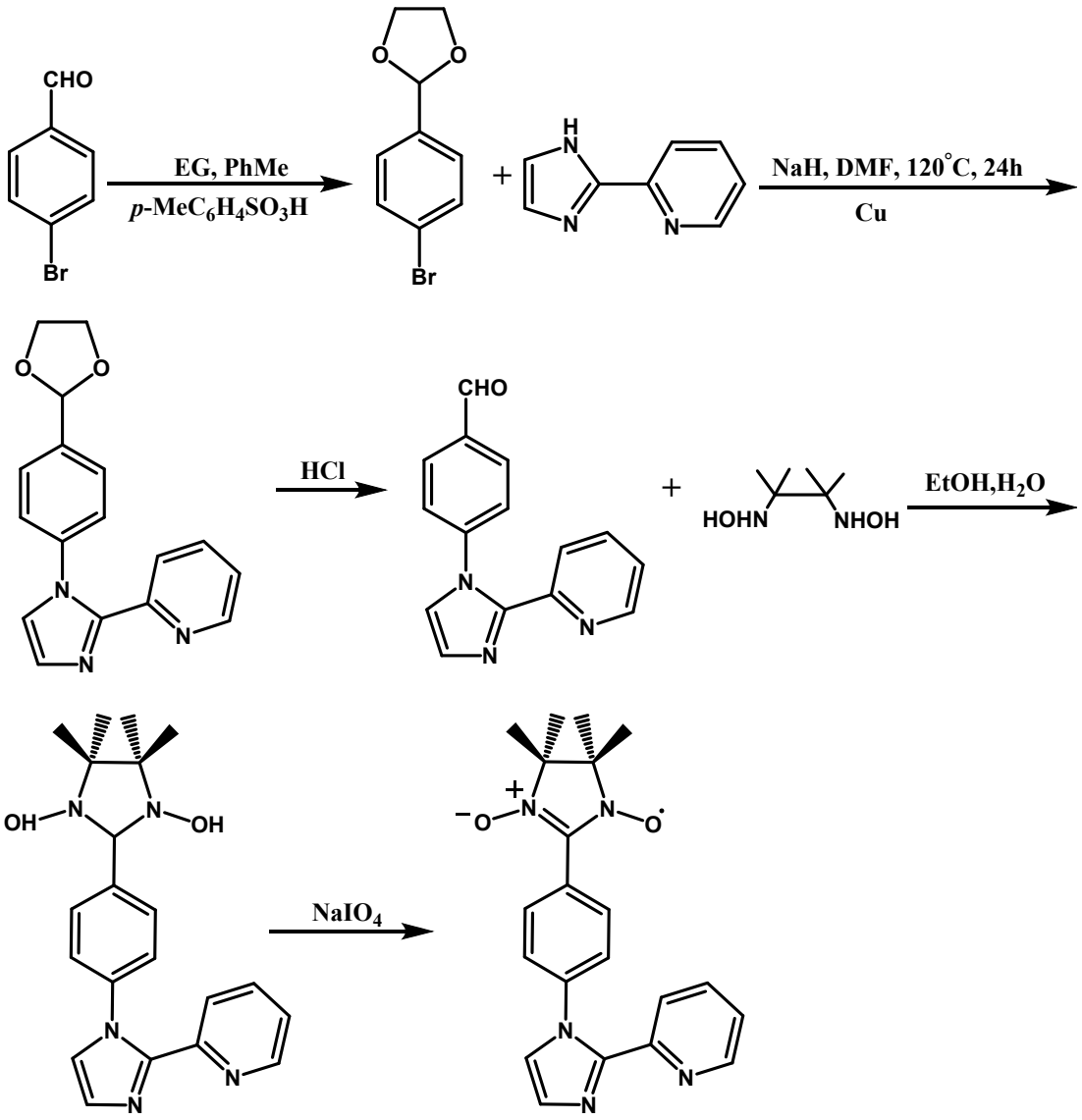
Compound	SAPR-8	TDD-8	JBTPR-8	BTPR-8
3	0.647	1.469	2.728	2.160

Table S6. The substates and corresponding energy levels **3.**

$\|M_J\rangle$	E(cm^{-1})
±6	0
±5	173.2
±4	214.0
±3	224.4
±2	237.7
±1	252.9
0	259.6



Scheme S1. Nit-Ph-PyIm radical ligand.



Scheme S2. The synthesis of Nit-Ph-PyIm biradical ligand (EG: ethylene glycol).

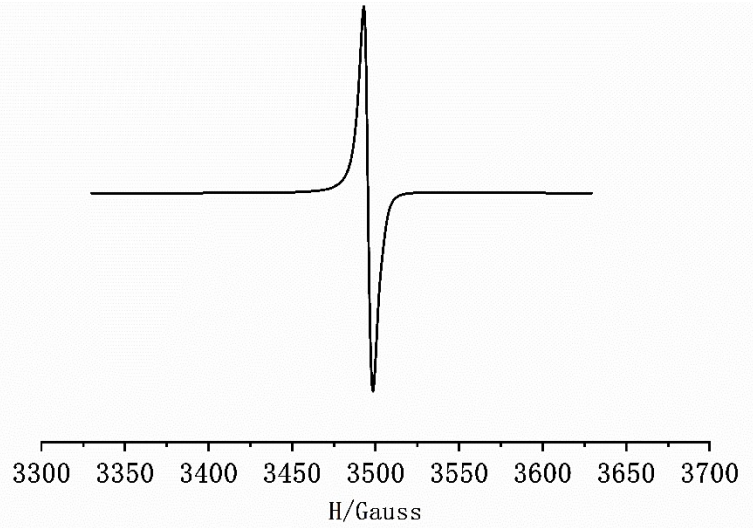


Fig. S1 EPR spectrum of the radical ligand Nit-Ph-PyIm.

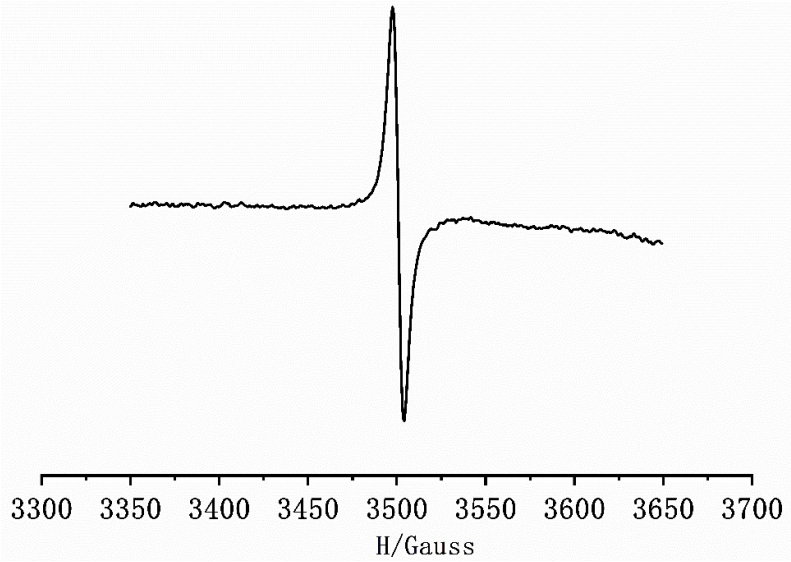


Fig. S2 EPR spectrum of the complex **1**.

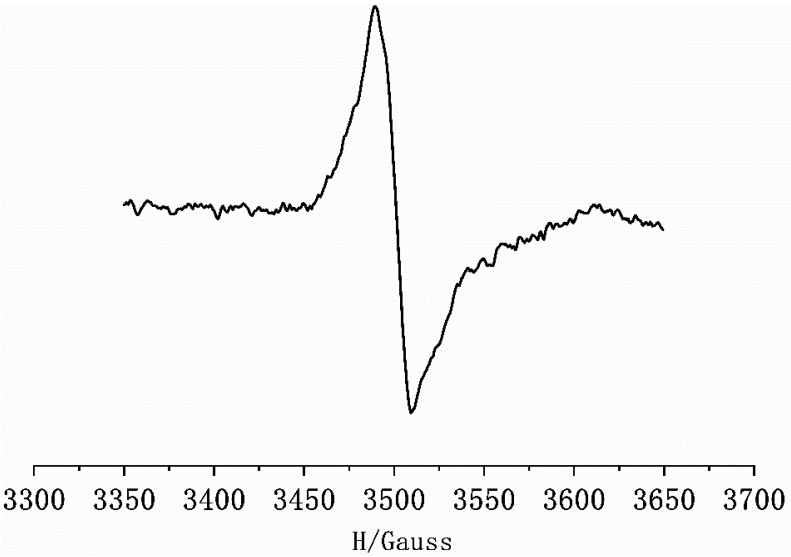


Fig. S3 EPR spectrum of the complex **2**.

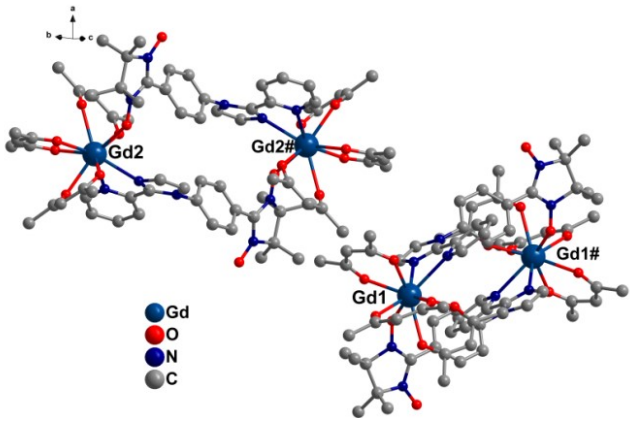


Fig. S4 Crystal structure of complex **1** (All hydrogen, fluorine atoms and $CHCl_3$ are omitted for clarity).

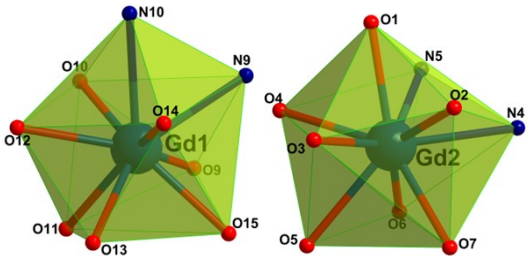


Fig. S5 Coordination polyhedron of Gd ions in complex **1**.

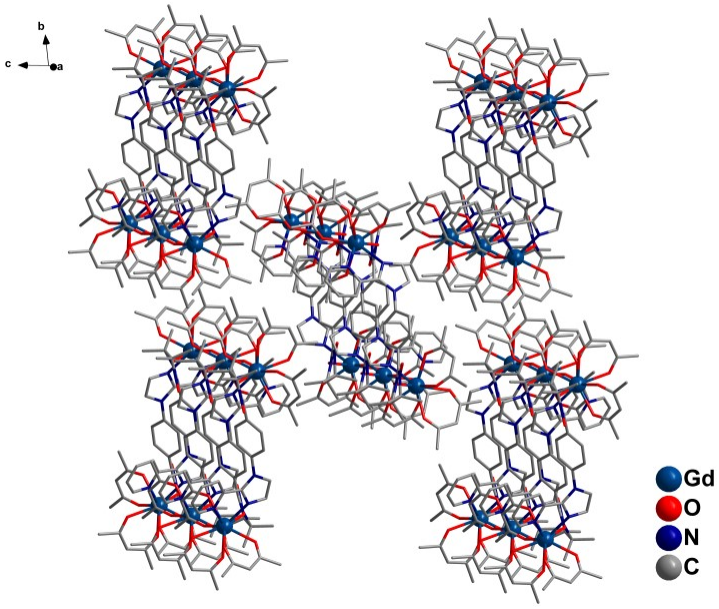


Fig. S6 Packing diagram of complex **1**, hydrogen, fluorine atoms and $CHCl_3$ are not shown for the sake of clarity.

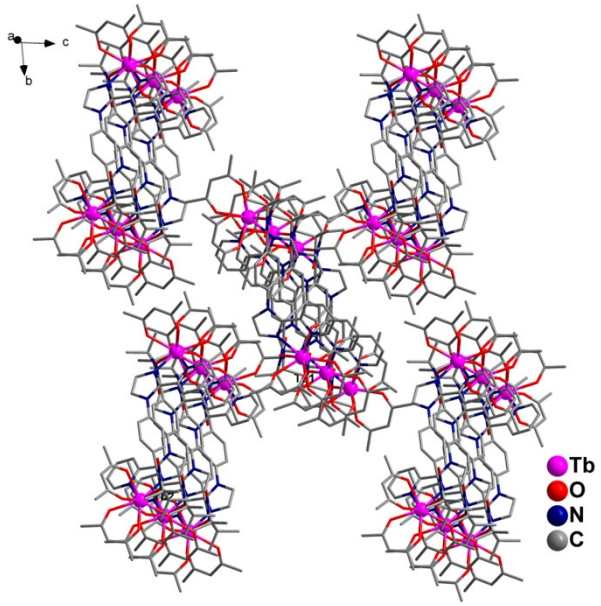


Fig. S7 Packing diagram of complex **2**, hydrogen, fluorine atoms and $CHCl_3$ are not shown for the sake of clarity.

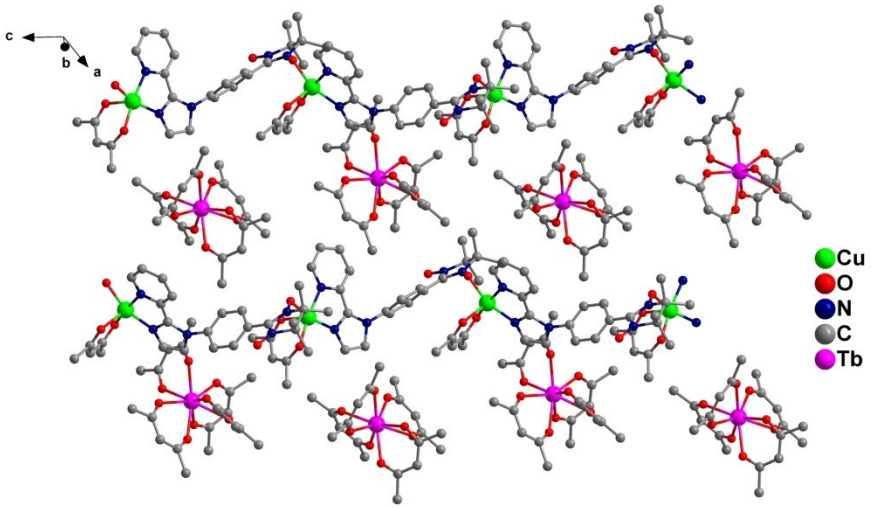


Fig. S8 Packing arrangement of **3** (H and F atoms are omitted for clarity).

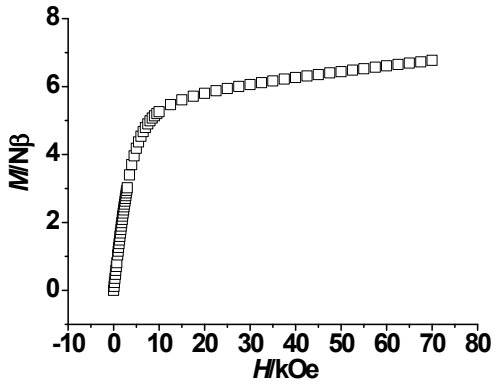


Fig. S9 *M* versus *H* curve for complex **2** at 2.0 K.

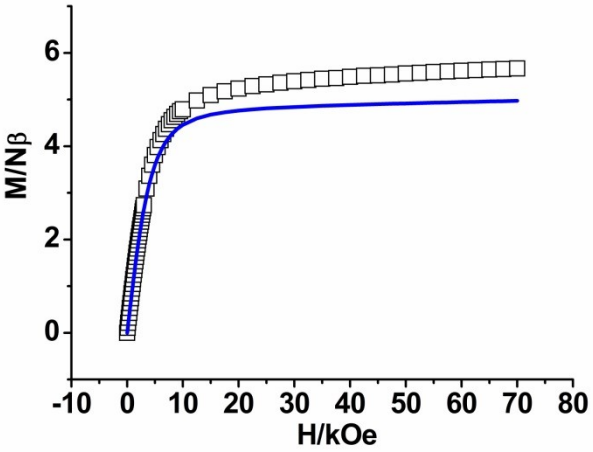


Fig. S10 *M* versus *H* curve for complex **3** at 2.0 K, the solid is fitted and simulated by the PHI program.

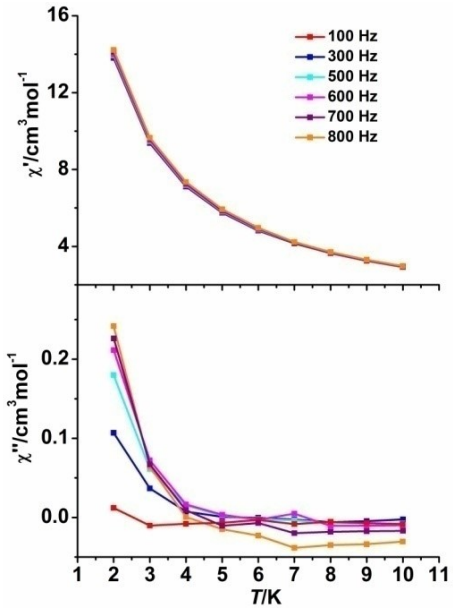


Fig. S11 Temperature dependence of the χ′ (top) and χ″ (bottom) under zero dc field for compound **2** at different frequencies.

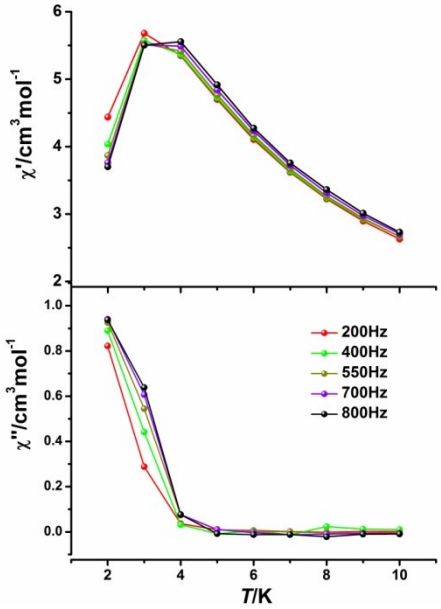


Fig. S12 Temperature dependence of the χ′ (top) and χ″ (bottom) under 3000 Oe dc field for compound **2** at different frequencies.

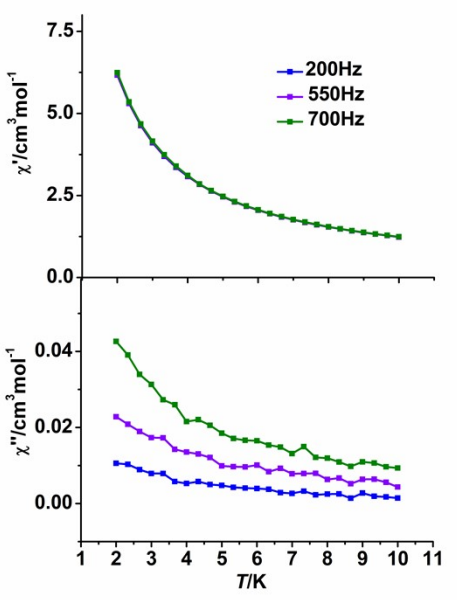


Fig. S13 Temperature dependence of the χ′ (top) and χ″ (bottom) under zero dc field for compound **3** at different frequencies.