Supporting Information

Slow relaxation of magnetization in lanthanide-biradical complexes based on a functionalized nitronyl nitroxide biradical

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Contents

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

Bond distances			
Gd(1)-O(2)	2.407(5)	O(2)-N(2)	1.312(8)
Gd(1)-O(3)	2.409(6)	O(3)-N(3)	1.312(8)
Gd(1)-O(10)	2.401(6)	O(1)-N(1)	1.282(8)
Gd(1)-O(6)	2.401(6)	O(4)-N(4)	1.286(8)
Gd(1)-O(5)	2.379(6)	Gd(3)-O(19)	2.413(6)
Gd(1)-O(8)	2.341(6)	Gd(3)-O(20)	2.390(6)
Gd(1)-O(7)	2.402(7)	Gd(3)-O(25)	2.426(6)
Gd(1)-O(9)	2.356(7)	Gd(3)-O(22)	2.387(6)
Gd(2)-O(17)	2.370(5)	Gd(3)-O(27)	2.407(7)
Gd(2)-O(12)	2.417(5)	Gd(3)-O(26)	2.366(6)
Gd(2)-O(13)	2.344(6)	Gd(3)-O(24)	2.336(6)
Gd(2)-O(11)	2.379(6)	Gd(3)-O(23)	2.389(6)
Gd(2)-O(14)	2.379(6)	O(19)-N(7)	1.301(8)
Gd(2)-O(16)	2.416(6)	O(20)-N(8)	1.289(9)
Gd(2)-O(15)	2.344(6)	O(18)-N(6)	1.276(9)
Gd(2)-N(5)	2.622(7)	O(21)-N(9)	1.296(9)
Angles			
O(2)-Gd(1)-O(3)	80.9(2)	O(11)-Gd(2)-N(5)	80.6(2)
O(10)-Gd(1)-O(2)	69.1(2)	O(14)-Gd(2)-O(12)	137.2(2)
O(10)-Gd(1)-O(3)	75.3(2)	O(14)-Gd(2)-O(16)	74.9(2)
O(6)-Gd(1)-O(2)	70.2(2)	O(14)-Gd(2)-N(5)	120.7(2)
O(6)-Gd(1)-O(3)	114.9(2)	O(16)-Gd(2)-O(12)	124.0(2)
O(6)-Gd(1)-O(10)	135.5(2)	O(16)-Gd(2)-N(5)	137.1(2)
O(6)-Gd(1)-O(7)	74.7(2)	O(15)-Gd(2)-O(17)	103.0(2)
O(5)-Gd(1)-O(2)	116.5(2)	O(15)-Gd(2)-O(12)	72.1(2)
O(5)-Gd(1)-O(3)	70.6(2)	O(15)-Gd(2)-O(11)	80.4(2)
O(5)-Gd(1)-O(10)	143.5(2)	O(15)-Gd(2)-O(14)	80.5(2)
O(5)-Gd(1)-O(6)	72.7(2)	O(15)-Gd(2)-O(16)	72.1(2)
O(5)-Gd(1)-O(7)	70.2(2)	O(15)-Gd(2)-N(5)	144.9(2)
O(8)-Gd(1)-O(2)	85.9(2)	N(2)-O(2)-Gd(1)	139.7(5)
O(8)-Gd(1)-O(3)	148.4(2)	N(3)-O(3)-Gd(1)	139.7(5)
O(8)-Gd(1)-O(10)	73.2(2)	O(19)-Gd(3)-O(25)	70.4(2)
O(8)-Gd(1)-O(6)	86.9(2)	O(20)-Gd(3)-O(19)	86.7(2)
O(8)-Gd(1)-O(5)	140.5(2)	O(20)-Gd(3)-O(25)	70.3(2)
O(8)-Gd(1)-O(7)	71.9(2)	O(20)-Gd(3)-O(27)	138.5(2)
O(8)-Gd(1)-O(9)	85.1(2)	O(22)-Gd(3)-O(19)	122.8(2)
O(7)-Gd(1)-O(2)	139.2(2)	O(22)-Gd(3)-O(20)	71.9(2)
O(7)-Gd(1)-O(3)	133.9(2)	O(22)-Gd(3)-O(25)	138.9(2)
O(7)-Gd(1)-O(10)	131.2(2)	O(22)-Gd(3)-O(27)	72.9(2)
O(9)-Gd(1)-O(2)	140.4(2)	O(22)-Gd(3)-O(23)	71.7(2)
O(9)-Gd(1)-O(3)	86.9(2)	O(27)-Gd(3)-O(19)	131.4(2)
O(9)-Gd(1)-O(10)	71.4(2)	O(27)-Gd(3)-O(25)	131.0(2)
O(9)-Gd(1)-O(6)	147.3(2)	O(26)-Gd(3)-O(19)	78.2(2)
O(9)-Gd(1)-O(5)	94.1(2)	O(26)-Gd(3)-O(20)	143.7(2)
O(9)-Gd(1)-O(7)	72.7(3)	O(26)-Gd(3)-O(25)	73.5(2)

O(17)-Gd(2)-O(12)	74.37(19)	O(26)-Gd(3)-O(22)	143.4(2)
O(17)-Gd(2)-O(11)	142.5(2)	O(26)-Gd(3)-O(27)	71.1(2)
O(17)-Gd(2)-O(14)	145.3(2)	O(26)-Gd(3)-O(23)	90.7(2)
O(17)-Gd(2)-O(16)	73.6(2)	O(24)-Gd(3)-O(19)	142.2(2)
O(17)-Gd(2)-N(5)	75.8(2)	O(24)-Gd(3)-O(20)	86.6(2)
O(12)-Gd(2)-N(5)	74.0(2)	O(24)-Gd(3)-O(25)	72.3(2)
O(13)-Gd(2)-O(17)	88.7(2)	O(24)-Gd(3)-O(22)	90.0(2)
O(13)-Gd(2)-O(12)	143.1(2)	O(24)-Gd(3)-O(27)	72.2(3)
O(13)-Gd(2)-O(11)	110.1(2)	O(24)-Gd(3)-O(26)	85.6(2)
O(13)-Gd(2)-O(14)	71.6(2)	O(24)-Gd(3)-O(23)	143.0(2)
O(13)-Gd(2)-O(16)	79.8(2)	O(23)-Gd(3)-O(19)	71.8(2)
O(13)-Gd(2)-O(15)	144.7(2)	O(23)-Gd(3)-O(20)	115.8(2)
O(13)-Gd(2)-N(5)	70.1(2)	O(23)-Gd(3)-O(25)	141.2(2)
O(11)-Gd(2)-O(12)	71.3(2)	O(23)-Gd(3)-O(27)	71.8(2)
O(11)-Gd(2)-O(14)	72.2(2)	N(7)-O(19)-Gd(3)	138.8(5)
O(11)-Gd(2)-O(16)	139.9(2)	N(8)-O(20)-Gd(3)	138.5(5)

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

Bond distances			
Tb(2)-O(11)	2.395(6)	O(2)-N(2)	1.305(10)
Tb(2)-O(16)	2.330(7)	O(3)-N(3)	1.358(10)
Tb(2)-N(5)	2.596(7)	N(4)-O(4)	1.284(10)
Tb(2)-O(15)	2.370(7)	O(1)-N(1)	1.294(11)
Tb(2)-O(12)	2.356(7)	Tb(3)-O(19)	2.404(7)
Tb(2)-O(14)	2.396(7)	Tb(3)-O(20)	2.356(7)
Tb(2)-O(17)	2.332(7)	Tb(3)-O(24)	2.340(7)
Tb(2)-O(13)	2.329(7)	Tb(3)-O(26)	2.411(7)
Tb(1)-O(2)	2.389(6)	Tb(3)-O(27)	2.311(7)
Tb(1)-O(10)	2.379(7)	Tb(3)-O(25)	2.393(8)
Tb(1)-O(3)	2.402(7)	Tb(3)-O(22)	2.364(7)
Tb(1)-O(6)	2.371(7)	Tb(3)-O(23)	2.366(7)
Tb(1)-O(8)	2.321(8)	O(19)-N(7)	1.288(10)
Tb(1)-O(7)	2.387(7)	O(20)-N(8)	1.304(10)
Tb(1)-O(9)	2.336(8)	N(6)-O(18)	1.268(10)
Tb(1)-O(5)	2.353(7)	O(21)-N(9)	1.277(12)
Angles			
O(11)-Tb(2)-N(5)	73.8(2)	O(7)-Tb(1)-O(3)	134.2(3)
O(16)-Tb(2)-O(11)	142.7(2)	O(9)-Tb(1)-O(2)	140.2(3)
O(16)-Tb(2)-N(5)	69.9(2)	O(9)-Tb(1)-O(10)	71.4(3)
O(16)-Tb(2)-O(15)	72.2(2)	O(9)-Tb(1)-O(3)	88.2(3)
O(16)-Tb(2)-O(12)	109.1(3)	O(9)-Tb(1)-O(6)	147.0(3)
O(16)-Tb(2)-O(14)	79.4(3)	O(9)-Tb(1)-O(7)	72.3(3)
O(16)-Tb(2)-O(17)	88.6(3)	O(9)-Tb(1)-O(5)	94.6(3)
O(15)-Tb(2)-O(11)	137.2(2)	O(5)-Tb(1)-O(2)	116.5(2)
O(15)-Tb(2)-N(5)	121.1(3)	O(5)-Tb(1)-O(10)	143.5(3)
O(15)-Tb(2)-O(14)	74.4(3)	O(5)-Tb(1)-O(3)	70.5(2)
O(12)-Tb(2)-O(11)	72.4(2)	O(5)-Tb(1)-O(6)	73.2(3)
O(12)-Tb(2)-N(5)	80.5(2)	O(5)-Tb(1)-O(7)	70.4(3)
O(12)-Tb(2)-O(15)	71.5(3)	N(2)-O(2)-Tb(1)	139.5(5)
O(12)-Tb(2)-O(14)	139.8(2)	N(3)-O(3)-Tb(1)	140.2(6)
O(14)-Tb(2)-O(11)	124.6(2)	O(19)-Tb(3)-O(26)	70.2(2)
O(14)-Tb(2)-N(5)	136.7(2)	O(20)-Tb(3)-O(19)	86.9(2)
O(17)-Tb(2)-O(11)	74.3(2)	O(20)-Tb(3)-O(26)	70.2(2)
O(17)-Tb(2)-N(5)	75.9(2)	O(20)-Tb(3)-O(25)	138.6(3)
O(17)-Tb(2)-O(15)	145.1(3)	O(20)-Tb(3)-O(22)	116.2(3)
O(17)-Tb(2)-O(12)	143.4(2)	O(20)-Tb(3)-O(23)	71.9(3)
O(17)-Tb(2)-O(14)	73.6(2)	O(24)-Tb(3)-O(19)	78.0(2)
O(13)-Tb(2)-O(11)	72.1(2)	O(24)-Tb(3)-O(20)	143.2(2)
O(13)-Tb(2)-O(16)	145.0(2)	O(24)-Tb(3)-O(26)	73.1(3)
O(13)-Tb(2)-N(5)	144.7(2)	O(24)-Tb(3)-O(25)	71.4(3)
O(13)-Tb(2)-O(15)	80.0(3)	O(24)-Tb(3)-O(22)	90.8(3)

O(13)-Tb(2)-O(12)	80.8(3)	O(24)-Tb(3)-O(23)	143.8(3)
O(13)-Tb(2)-O(14)	72.9(2)	O(27)-Tb(3)-O(19)	142.2(3)
O(13)-Tb(2)-O(17)	103.2(3)	O(27)-Tb(3)-O(20)	85.8(3)
O(2)-Tb(1)-O(3)	80.4(2)	O(27)-Tb(3)-O(24)	86.0(3)
O(10)-Tb(1)-O(2)	68.9(2)	O(27)-Tb(3)-O(26)	72.5(3)
O(10)-Tb(1)-O(3)	75.3(3)	O(27)-Tb(3)-O(25)	72.5(3)
O(10)-Tb(1)-O(7)	131.2(3)	O(27)-Tb(3)-O(22)	143.3(3)
O(6)-Tb(1)-O(2)	70.2(2)	O(27)-Tb(3)-O(23)	89.5(3)
O(6)-Tb(1)-O(10)	135.1(3)	O(25)-Tb(3)-O(19)	131.3(3)
O(6)-Tb(1)-O(3)	114.8(3)	O(25)-Tb(3)-O(26)	131.0(3)
O(6)-Tb(1)-O(7)	74.7(3)	O(22)-Tb(3)-O(19)	71.6(2)
O(8)-Tb(1)-O(2)	86.0(2)	O(22)-Tb(3)-O(26)	140.8(2)
O(8)-Tb(1)-O(10)	73.4(3)	O(22)-Tb(3)-O(25)	71.8(3)
O(8)-Tb(1)-O(3)	148.6(3)	O(22)-Tb(3)-O(23)	72.1(3)
O(8)-Tb(1)-O(6)	86.2(3)	O(23)-Tb(3)-O(19)	123.0(3)
O(8)-Tb(1)-O(7)	71.7(3)	O(23)-Tb(3)-O(26)	138.9(3)
O(8)-Tb(1)-O(9)	84.5(3)	O(23)-Tb(3)-O(25)	73.0(3)
O(8)-Tb(1)-O(5)	140.4(3)	N(7)-O(19)-Tb(3)	139.0(5)
O(7)-Tb(1)-O(2)	139.4(3)	N(8)-O(20)-Tb(3)	139.3(6)

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

Bond distances			
Dy(2)-O(11)	2.389(9)	O(2)-N(2)	1.302(15)
Dy(2)-O(16)	2.325(11)	O(3)-N(3)	1.316(16)
Dy(2)-N(5)	2.602(12)	N(4)-O(4)	1.265(16)
Dy(2)-O(15)	2.353(10)	O(1)-N(1)	1.290(17)
Dy(2)-O(12)	2.333(11)	Dy(3)-O(19)	2.374(10)
Dy(2)-O(14)	2.368(11)	Dy(3)-O(20)	2.352(11)
Dy(2)-O(17)	2.328(10)	Dy(3)-O(24)	2.335(11)
Dy(2)-O(13)	2.327(12)	Dy(3)-O(26)	2.398(11)
Dy(1)-O(2)	2.389(10)	Dy(3)-O(27)	2.297(13)
Dy(1)-O(10)	2.369(11)	Dy(3)-O(25)	2.394(12)
Dy(1)-O(3)	2.405(12)	Dy(3)-O(22)	2.334(12)
Dy(1)-O(6)	2.358(12)	Dy(3)-O(23)	2.366(11)
Dy(1)-O(8)	2.329(14)	O(19)-N(7)	1.312(15)
Dy(1)-O(7)	2.383(12)	O(20)-N(8)	1.295(15)
Dy(1)-O(9)	2.319(13)	N(6)-O(18)	1.264(16)
Dy(1)-O(5)	2.333(12)	O(21)-N(9)	1.289(18)
Angles			
O(11)-Dy(2)-N(5)	73.3(4)	O(7)-Dy(1)-O(3)	134.6(4)
O(16)-Dy(2)-O(11)	143.0(4)	O(9)-Dy(1)-O(2)	140.4(4)
O(16)-Dy(2)-N(5)	70.6(4)	O(9)-Dy(1)-O(10)	72.3(4)
O(16)-Dy(2)-O(15)	72.1(4)	O(9)-Dy(1)-O(3)	86.8(4)
O(16)-Dy(2)-O(12)	108.8(4)	O(9)-Dy(1)-O(6)	146.6(4)
O(16)-Dy(2)-O(14)	79.4(4)	O(9)-Dy(1)-O(7)	73.0(5)
O(16)-Dy(2)-O(17)	88.8(4)	O(9)-Dy(1)-O(5)	93.6(5)
O(16)-Dy(2)-O(13)	144.8(4)	O(5)-Dy(1)-O(2)	116.9(4)
O(15)-Dy(2)-O(11)	137.2(4)	O(5)-Dy(1)-O(10)	143.6(4)
O(15)-Dy(2)-N(5)	122.0(4)	O(5)-Dy(1)-O(3)	70.7(4)
O(15)-Dy(2)-O(14)	74.0(4)	O(5)-Dy(1)-O(6)	72.5(5)
O(12)-Dy(2)-O(11)	72.5(4)	O(5)-Dy(1)-O(7)	70.6(4)
O(12)-Dy(2)-N(5)	80.1(4)	N(2)-O(2)-Dy(1)	140.8(9)
O(12)-Dy(2)-O(15)	71.7(4)	N(3)-O(3)-Dy(1)	139.0(9)
O(12)-Dy(2)-O(14)	139.8(4)	O(19)-Dy(3)-O(26)	70.4(4)
O(14)-Dy(2)-O(11)	124.5(4)	O(19)-Dy(3)-O(25)	132.1(4)
O(14)-Dy(2)-N(5)	137.2(4)	O(20)-Dy(3)-O(19)	86.2(4)
O(17)-Dy(2)-O(11)	74.5(4)	O(20)-Dy(3)-O(26)	70.4(4)
O(17)-Dy(2)-N(5)	76.2(4)	O(20)-Dy(3)-O(25)	138.3(4)
O(17)-Dy(2)-O(15)	144.5(4)	O(20)-Dy(3)-O(23)	72.2(4)
O(17)-Dy(2)-O(12)	143.7(4)	O(24)-Dy(3)-O(19)	78.3(4)
O(17)-Dy(2)-O(14)	73.2(4)	O(24)-Dy(3)-O(20)	143.1(4)
O(17)-Dy(2)-O(13)	103.2(4)	O(24)-Dy(3)-O(26)	72.9(4)
O(13)-Dy(2)-O(11)	72.1(4)	O(24)-Dy(3)-O(25)	71.9(4)
O(13)-Dy(2)-N(5)	144.1(4)	O(24)-Dy(3)-O(23)	143.5(4)

O(13)-Dy(2)-O(15)	79.5(4)	O(26)-Dy(3)-O(25)	130.9(4)
O(13)-Dy(2)-O(12)	80.8(4)	O(27)-Dy(3)-O(19)	142.7(4)
O(13)-Dy(2)-O(14)	72.9(4)	O(27)-Dy(3)-O(20)	86.7(4)
O(2)-Dy(1)-O(3)	80.9(4)	O(27)-Dy(3)-O(24)	85.8(4)
O(10)-Dy(1)-O(2)	68.2(4)	O(27)-Dy(3)-O(26)	72.8(4)
O(10)-Dy(1)-O(3)	75.1(4)	O(27)-Dy(3)-O(25)	71.5(5)
O(10)-Dy(1)-O(7)	131.6(4)	O(27)-Dy(3)-O(22)	143.0(4)
O(6)-Dy(1)-O(2)	71.0(4)	O(27)-Dy(3)-O(23)	88.6(4)
O(6)-Dy(1)-O(10)	135.5(4)	O(22)-Dy(3)-O(19)	71.3(4)
O(6)-Dy(1)-O(3)	115.2(4)	O(22)-Dy(3)-O(20)	115.8(4)
O(6)-Dy(1)-O(7)	73.8(4)	O(22)-Dy(3)-O(24)	90.7(4)
O(8)-Dy(1)-O(2)	85.4(4)	O(22)-Dy(3)-O(26)	140.6(4)
O(8)-Dy(1)-O(10)	73.6(4)	O(22)-Dy(3)-O(25)	72.4(4)
O(8)-Dy(1)-O(3)	148.6(4)	O(22)-Dy(3)-O(23)	72.8(4)
O(8)-Dy(1)-O(6)	86.3(4)	O(23)-Dy(3)-O(19)	123.5(4)
O(8)-Dy(1)-O(7)	71.4(4)	O(23)-Dy(3)-O(26)	138.8(4)
O(8)-Dy(1)-O(9)	86.0(5)	O(23)-Dy(3)-O(25)	72.1(4)
O(8)-Dy(1)-O(5)	140.3(4)	N(7)-O(19)-Dy(3)	139.4(9)
O(7)-Dy(1)-O(2)	138.8(4)	N(8)-O(20)-Dy(3)	139.7(9)

Table S4. SHAPE analysis for the Ln coordination spheres.

Compound		SAPR-8	TDD-8	JBTPR-8	BTPR-8	JSD-8
1-Gd	Gd1	2.623	1.742	1.767	**0.992**	4.122
1-Gd	Gd2	**0.984**	1.270	2.117	1.490	3.248
1-Gd	Gd3	2.632	1.614	1.724	**0.922**	3.593
2-Tb	Tb1	2.706	1.775	1.782	**1.009**	4.140
2-Tb	Tb2	**0.992**	1.190	2.104	1.491	3.112
2-Tb	Tb3	2.579	1.615	1.671	**0.909**	3.513
3-Dy	Dy1	2.526	1.738	1.727	**0.953**	4.067
3-Dy	Dy2	**1.008**	1.167	2.158	1.500	3.060
3-Dy	Dy3	2.549	1.531	1.612	**0.881**	3.393

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 S5. Distances (Å) for the hydrogen bonds in all compounds.

D–H···A	Compound	d(D–H)	d(H···A)	d(D···A)
O17-H17A···O1	**1-Gd**	0.850	2.368	2.795
O17-H17A···O1	**2-Tb**	0.866	2.093	2.798
O17-H17A···O1	**3-Dy**	0.869	2.107	2.835

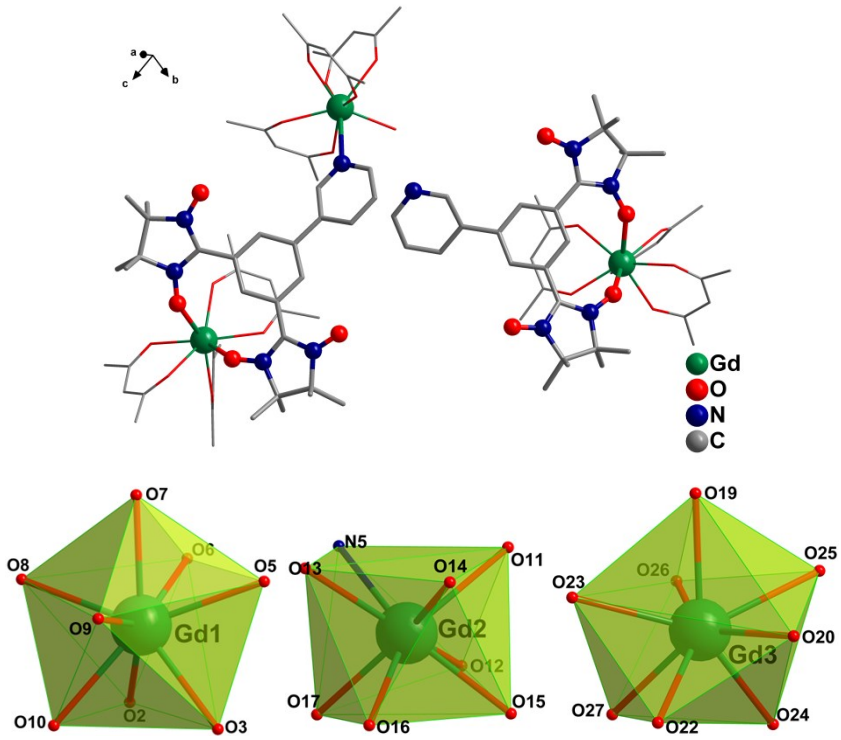

Fig. S1 Molecular structure of **1-Gd** and coordination polyhedrons of the Gd(III) ions (H and F atoms are omitted for clarity).

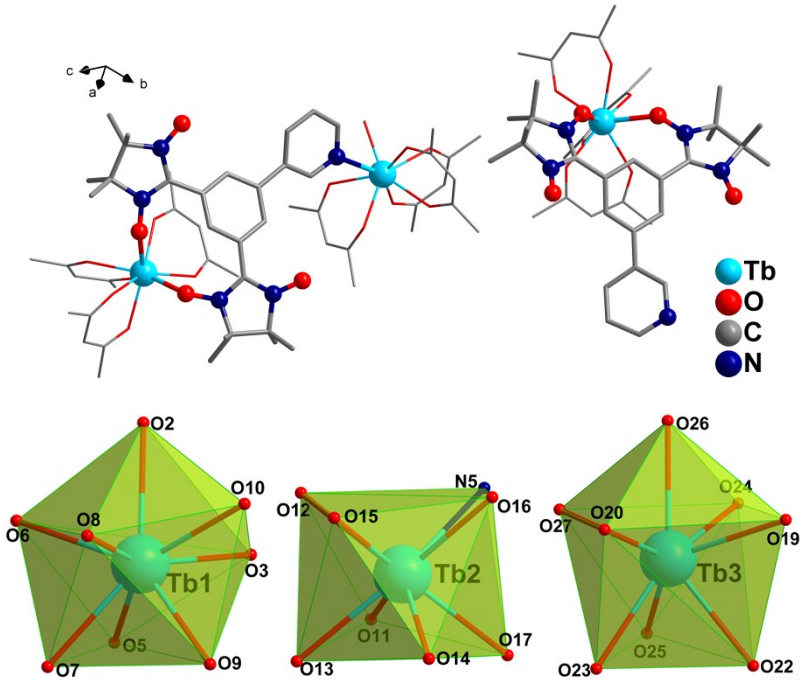

Fig. S2 Molecular structure of **2-Tb** and coordination polyhedrons of the Tb(III) ions (H and F atoms are omitted for clarity).

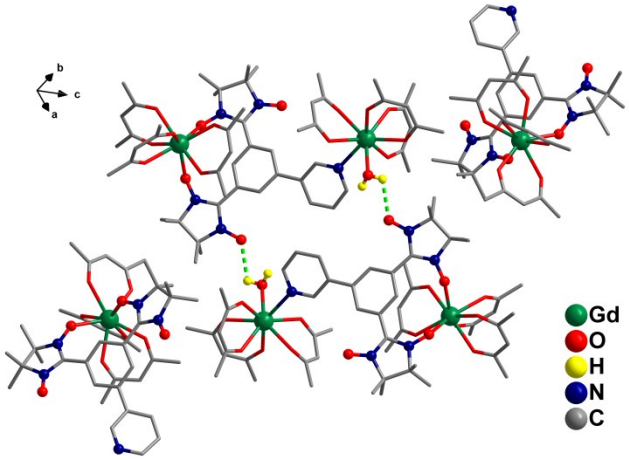

Fig. S3 Hydrogen bond-linked motifs in **1-Gd** (partial H and all F atoms are omitted for clarity).

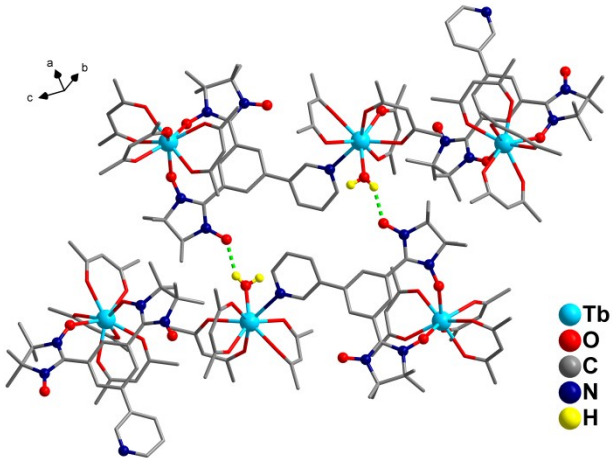

Fig. S4 Hydrogen bond-linked motifs in **2-Tb** (partial H and all F atoms are omitted for clarity).

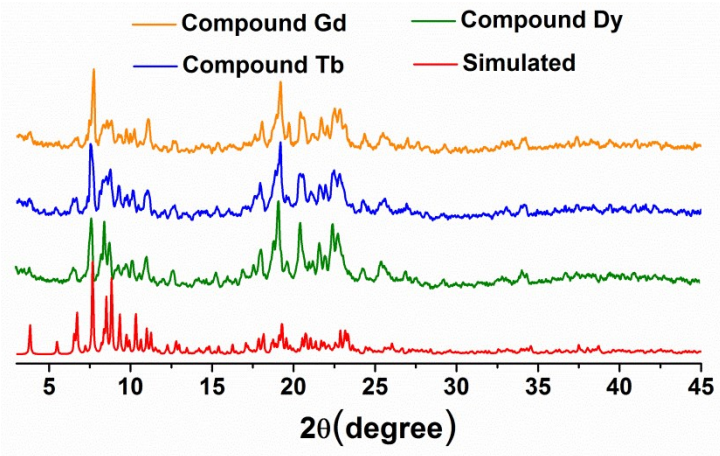

Fig. S5 Powder X-ray diffraction patterns of all complexes.

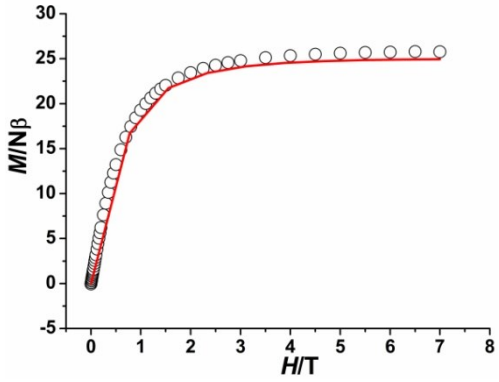

Fig. S6 Field-dependent magnetization at 2.0 K for **1-Gd**. The red line was simulated by the PHI program using the obtained magnetic parameters by the modeling of susceptibility data.

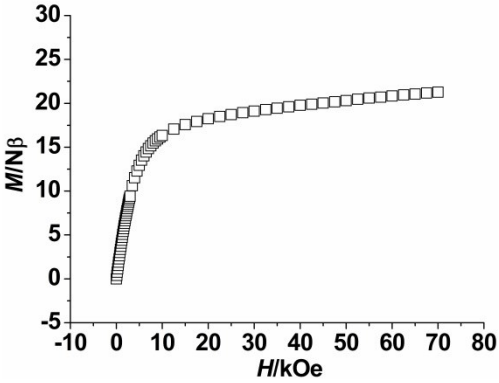

Fig. S7 *M* versus *H* plot at 2 K for complex **2-Tb**.

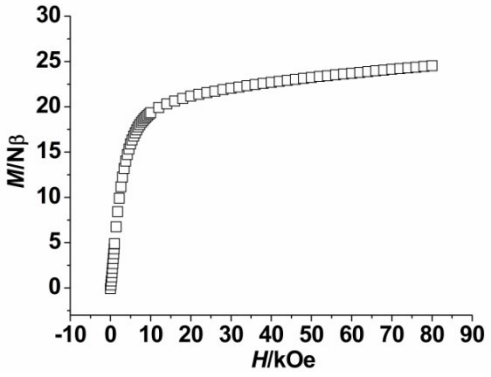

Fig. S8 *M* versus *H* plot at 2 K for complex **3-Dy**.

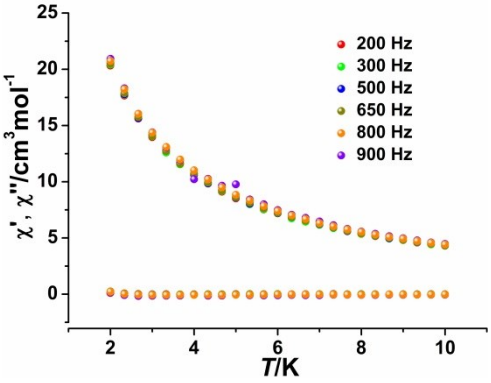

Fig. S9 Temperature dependence of the in-phase and out-of-phase components of the ac magnetic susceptibility in zero field with an oscillation 3 Oe for complex **2-Tb**.

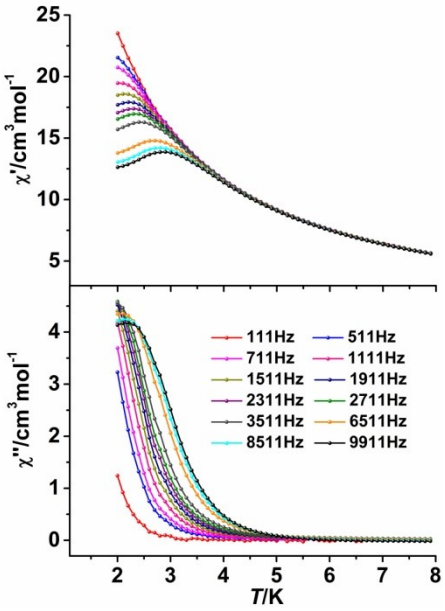

Fig. S10 Temperature-dependent ac signals under a zero dc field for **3-Dy**.

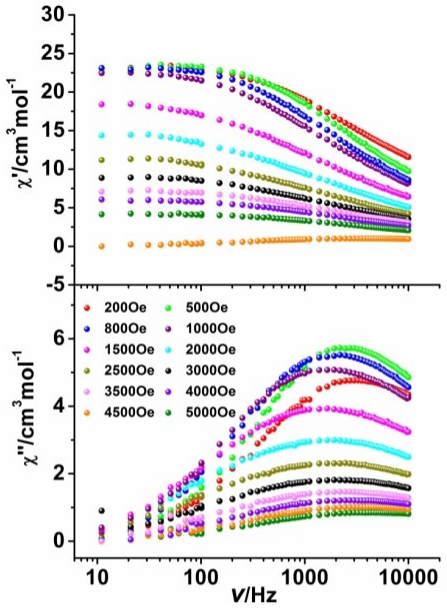

Fig. S11 Frequency dependence of the χ′ (top) and χ″ (bottom) components of the ac susceptibility, between 0 and 5000 Oe and between 10 and 10000 Hz, for **3-Dy** at 2 K.

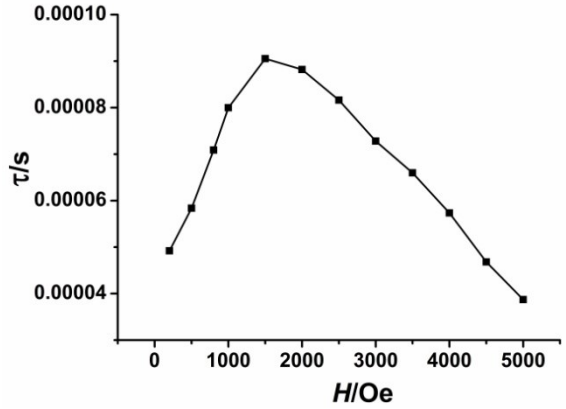

Fig. S12 The τ versus H plot for complex **3-Dy** at 2.0 K under the applied dc field.