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Tetranuclear Rare-Earth Complexes: Energy-Barrier Enhancement and Two-step Relaxation Activated by Ligand Substitution

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Content

Section S1 Supplementary Experimental Section

Synthesis of 5-(2-furanimino)-8-hydroxylquinoline (HL)

5-amino-8-hydroxylquinoline. 5-amino-8-hydroxyquinoline was synthesized with minor modifications compared to the method reported previously in the literature.[1] 5-nitryl-8-hydroxylquinoline (4.75 g, 0.025 mol) and 5% Pd/C (0.0625 g), the latter was used after dried with P_2O_5 and acted as catalyst, in a 1.3% ratio were added to absolute isopropanol. Then 5 mL of 80% hydrazine hydrate was dropped slowly into the solution at 70 °C over 30 minutes. The mixture was heated to 95 °C and refluxed for 4 h. Finally, the reaction system was filtered while hot, and the filtrate was allowed to stand still at 0 ° C for 6 h to crystallize. Subsequently, green needle crystals were obtained. (yield 2.5 g, 62.3%). Elemental analysis (%): calcd for $C_9H_8ON_2$ (fw = 160.42): C, 67.50; H, 5.00; N, 17.50. Found: C, 67.28; H, 4.73; N, 17.82. IR (cm^{-1}): 3344 (s), 1688 (s), 1626 (s), 1489 (s), 1346 (s), 915 (s), 746 (m).

5-(2-furanimino)-8-hydroxylquinoline (HL). 5-amino-8-hydroxylquinoline (0.80 g, 5 mmol) was dissolved in 30 mL of ethanol at 60 °C, 0.5 mL of freshly distilled 2-furaldehyde was added, and 3–4 drops of formic acid were dropped into the mixture as a catalyst. After that, the mixture was heated for 4 h at 83 °C. The product was isolated from the mixture and purified by recrystallization from a mixed solvent of ethanol and acetone (3/1, *v*/*v*). The purified product was obtained as a green solid (yield 1.00 g, 84.0%). Elemental analysis (%): calcd for $C_{14}H_{10}O_2N_2$ (fw = 238.24): C, 70.58; H, 4.20; N, 11.75; found: C, 70.63; H, 3.92; N, 11.52. IR (cm^{-1}): 3115 (w), 3048 (w), 1623 (s), 1575 (m), 1504 (vs), 1467 (s), 1415 (vs), 1282 (vs), 1235 (s), 1196 (s), 1080 (w), 1054 (w), 1011 (m), 938 (w), 813 (m), 790 (m), 703 (m), 650 (w), 592 (w), 411 (w). The ^{1}HNMR ($(CD_3)_2SO$) spectrum of 5-(2-furaldehyde)-amino-8-hydroxylquinoline (HL) is shown in Fig. S1†.

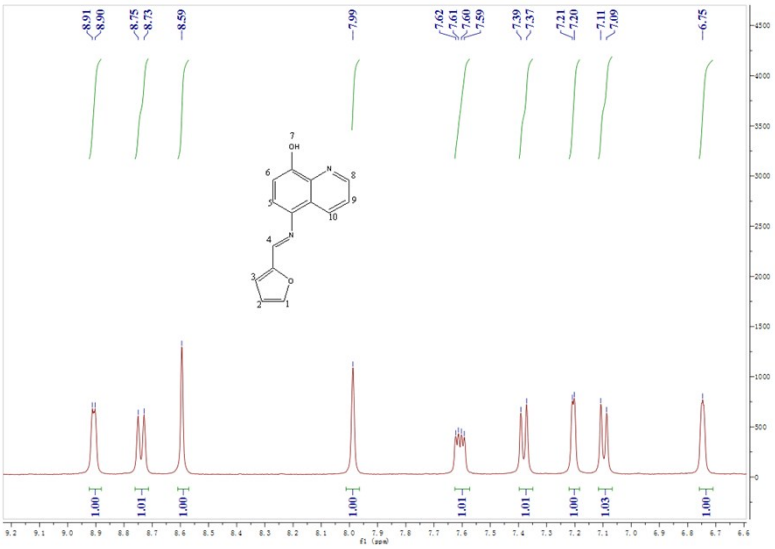


Fig. S1 The ^{1}HNMR spectrum of 5-(2-furanimino)-8-hydroxylquinoline (HL).

[1] A. Lilienkampf, J. L. Mao, B. J. Wan, Y. H. Wang, S. G. Franzblau and A. P. Kozikowski, *J. Med. Chem.,* 2009, 52, 2109–2118.

Section S2 Powder X-ray Diffraction and Thermogravimetric Analysis

To confirm the phase purity of the bulk samples for **1–6**, the experimental powder X-ray diffraction (PXRD) were carried out at room temperature (**Fig. S2**†). The main peaks

displayed in the measured patterns matched well with the simulated patterns generated from single-crystal X-ray diffraction data. Several missing or extra minor peaks could be attributed to the unavoidable loss of the solvent molecules in the unit cell during the sample preparation.

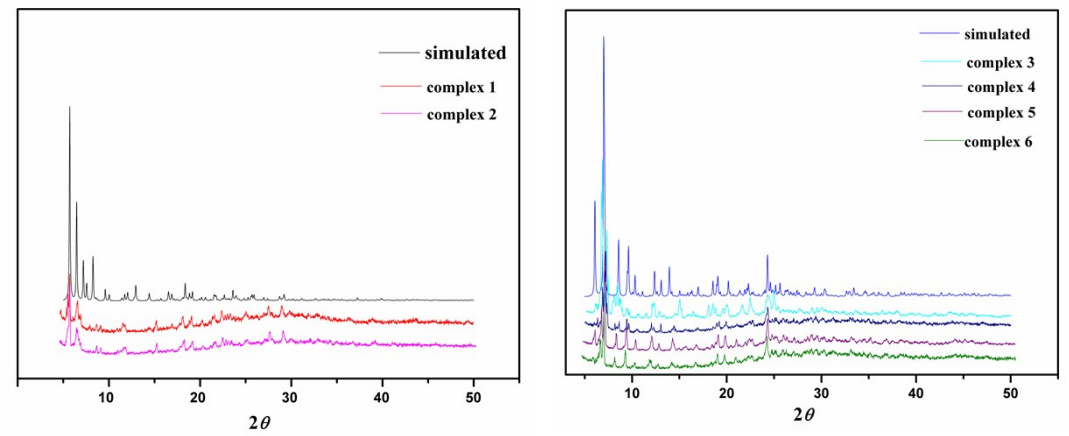


Fig. S2 The experimental and simulated PXRD patterns of complexes **1**−**6**.

To study further the thermal stability of the complexes **1**–**6**, the thermal behaviors were examined in the crystalline samples under an air atmosphere from 30 to 800 °C using thermo-gravimetric analyses (TGA). There are no solvent losses in the 30–100 °C range because of the spontaneous loss of solvent molecules resulted by the crystal-line samples being kept for an interval of time under ambient conditions (**Fig. S3**†). All of the TG curves are very similar, in which a main weight loss takes place between 300 and 500 °C, which is related to the release of the organic ligands.

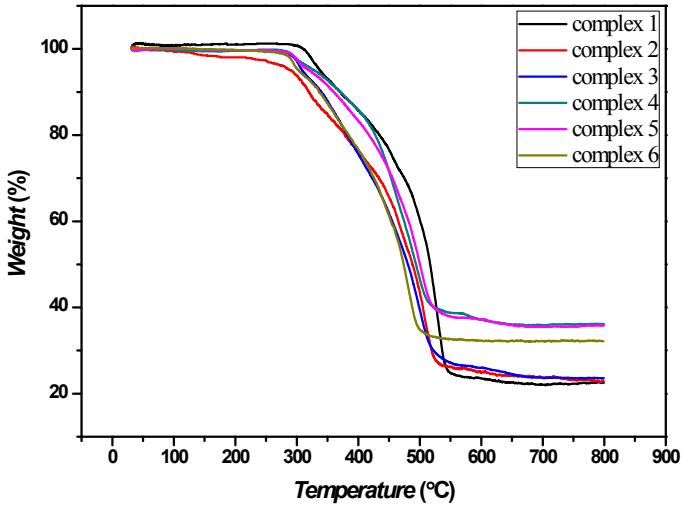


Fig. S3 TG curves of complexes **1**−**6**.

Section S3 Plots of Magnetic Data and Relaxation Fitting Parameters

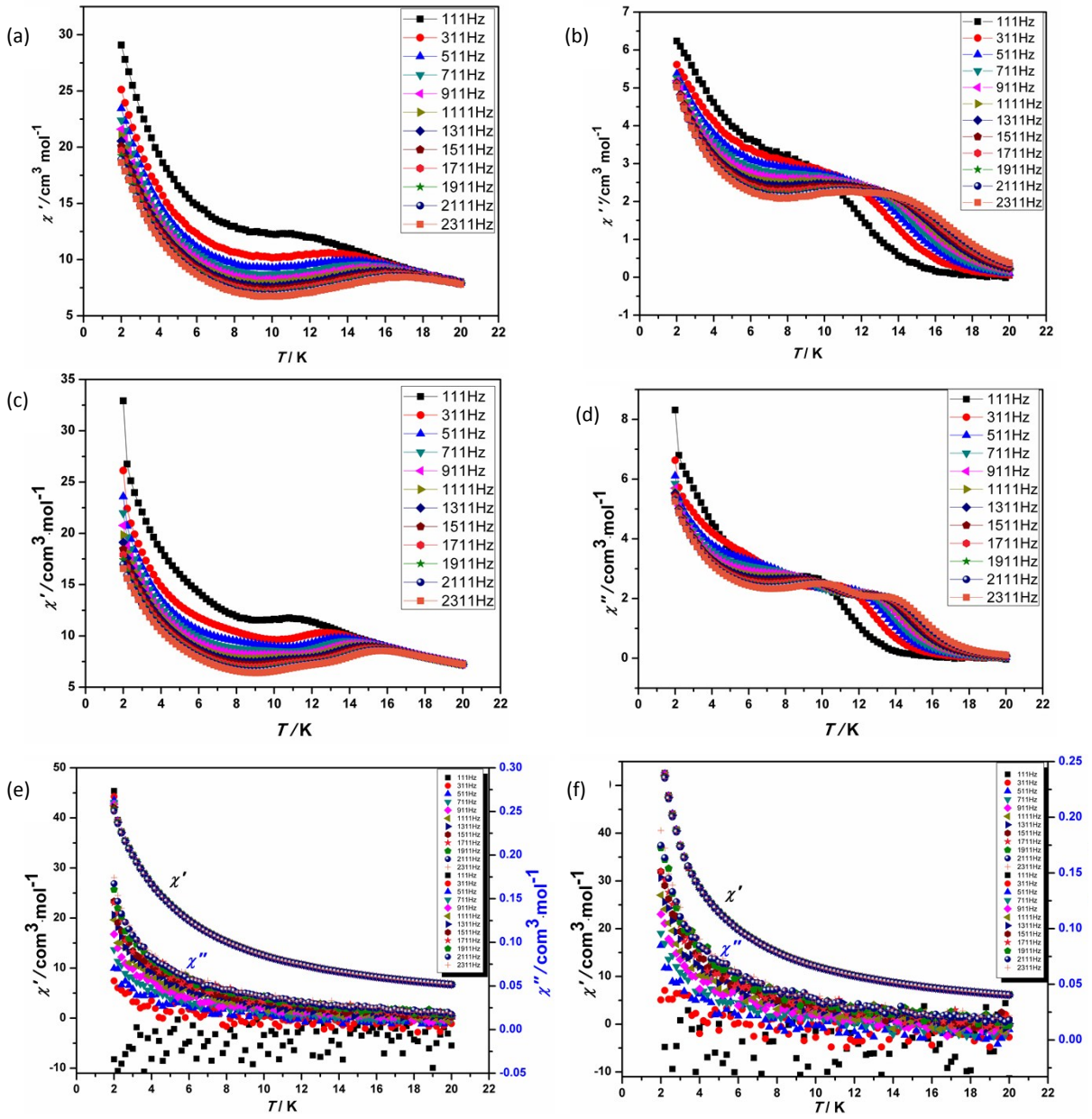


Fig. S4 Variable-temperature magnetic susceptibility in-phase (χ') and out-of-phase (χ'') for **2** ((a) and (b)), **4** ((c) and (d)), **5** (e) and **6** (f) with an oscillation of 3.0 Oe under a zero dc field.

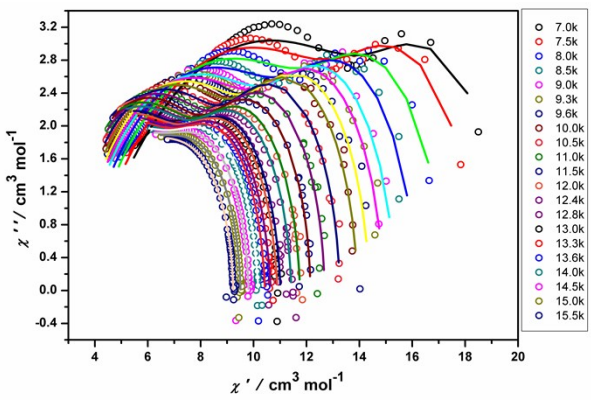
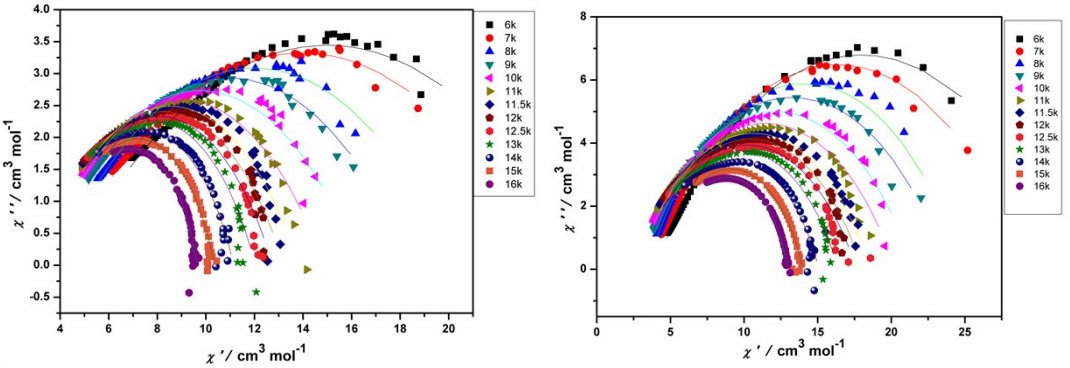


Fig. S5 The Cole-Cole plot for **4** measured in zero-dc field.



(a) (b)

Fig. S6 Cole-Cole plots for **2** under zero applied dc-field (a) or in 1500 Oe dc field (b).

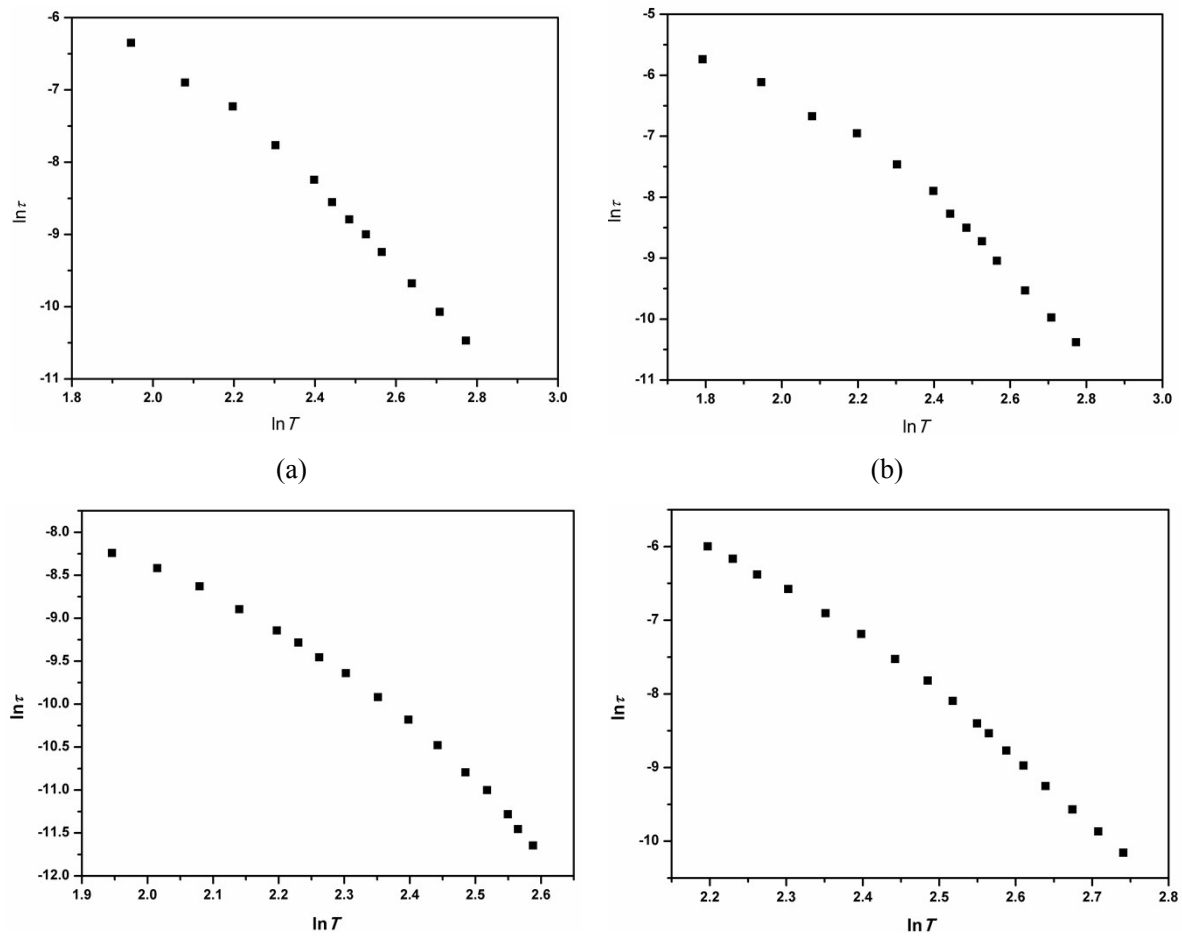


Fig. S7 The plots of lnτ vs. ln$T$. (a) For **2** without *dc* field; (b) For **2** in 1500 Oe *dc* field; (c) For **4** (FR); (d) For **4** (SR).

Table S1 Relaxation fitting parameters for Cole-Cole plots of **4** at varying temperatures under zero applied dc-field using the sum of two modified Debye model.

T/K	χ_S	$\Delta\chi_1$	α_1	$\Delta\chi_2$	α_2
7	3.55364	13.0628	0.465	3.31606	0.00294
7.5	3.50558	11.6668	0.429	3.51137	1.14E-08
8	3.36928	10.4937	0.403	3.51381	2.29E-08
8.5	3.29783	9.30755	0.366	3.63949	4.12E-08
9	3.22365	8.3991	0.329	3.77504	8.66E-08
9.3	3.14347	8.01509	0.314	3.79459	1.24E-07
9.6	3.12069	7.46623	0.286	3.81295	3.56E-07
10	3.00491	7.12506	0.270	3.81735	8.13E-07
10.5	2.91018	6.57574	0.239	3.78015	4.51E-06
11	2.72154	6.37559	0.233	3.59993	8.71E-06
11.5	2.58876	6.0862	0.219	3.48299	1.82E-05
12	2.17901	6.41402	0.260	3.16708	2.81E-05
12.4	2.20656	6.15357	0.252	3.07121	3.36E-05
12.8	2.05191	6.04111	0.256	2.92594	3.76E-05
13	1.72569	6.44699	0.297	2.74335	5.79E-05
13.3	1.6991	6.29437	0.296	2.66401	9.99E-05
13.6	2.07486	5.72541	0.267	2.64032	1.19E-04
14	2.24674	5.47243	0.275	2.46514	1.66E-04
14.5	3.2015	4.15002	0.176	2.45561	6.89E-04
15	3.50826	3.83005	0.162	2.16888	0.00102
15.5	3.76863	3.60137	0.146	1.86341	0.00198

Table S2 Relaxation fitting parameters for Cole-Cole plots of **2** at varying temperatures under zero applied dc-field using the Debye model of a single relaxation process.

T/K	χ_T	χ_S	α
6	25.6056	4.36386	0.60071
7	23.9087	3.9455	0.59047
8	20.2123	3.79129	0.54204
9	18.4534	3.42833	0.52572
10	16.3018	3.21761	0.49562
11	14.8382	3.14628	0.46903
11.5	13.8219	3.24616	0.43967
12	13.2005	3.28293	0.42484
12.5	12.743	3.33804	0.41387
13	12.0364	3.56339	0.37484
14	11.1393	3.76112	0.33718
15	10.3441	4.05312	0.28483
16	9.6365	4.29413	0.2364

Table S3 Relaxation fitting parameters for Cole-Cole plots of **2** at varying temperatures in 1500 Oe *dc* field using the Debye model of a single relaxation process.

T/K	χ_T	χ_S	α
6	32.0614	3.93975	0.4268
7	29.0311	3.59774	0.39936
8	24.7727	3.38247	0.35839
9	23.7187	2.88099	0.38556
10	21.4716	2.7176	0.37586
11	20.2449	2.62089	0.38442
11.5	18.5514	2.72828	0.36494
12	18.0099	2.77047	0.3679
12.5	17.6395	2.74496	0.38072
13	16.3909	3.13955	0.34229
14	15.0721	3.6466	0.30726
15	13.9783	4.19482	0.26572
16	12.9674	4.81656	0.20919

Table S4 Standard error for the extracted magnetic parameters

	Value for **2** in zero *dc* field	Standard error for **2** in zero *dc* field	Value for **2** in 1500 Oe *dc* field	Standard error for **2** in 1500 Oe *dc* field	Value for **4** (FR) in zero *dc* field	Standard error for **4** (FR) in zero *dc* field	Value for **4** (SR) in zero *dc* field	Standard error for **4** (SR) in zero *dc* field
τ_o	$1.79*10^{-8}$	$1.56*10^{-9}$	$1.45*10^{-8}$	$6.89*10^{-10}$	$8.54*10^{-11}$	$4.63*10^{-12}$	$1.14*10^{-9}$	$2.00*10^{-10}$
U_{eff}	117.4	8.1	123.3	5.5	162.1	13.9	165.3	2.5
C	5.30	1.20	2.12	0.26	0.931	0.100	0.00667	$8.51*10^{-5}$
n	2.5	0	2.8	0	4.2	0	5	0
A	0	0	0	0	0	0	0	0
m	1	0	1	0	1	0	1	0
τ_{QTM}	10^{29}	--	10^{29}	--	10^{29}	--	10^{29}	--

$\tau^{-1} = \tau_0^{-1}e^{-U\text{eff}/kBt} + CT^n + AT^m + \tau_{QTM}^{-1}$ (The four process respectively refer to Orbach process, Raman process, direct process and quantum tunneling of the magnetization)

Section S4 Crystallographic Data, Comparison of Magneto-Structural Correlation and Continuous Shape Measures Values

Table S5 Continuous shape measures (CSM) values for **1-6**

Configuration	CSM values for 1	CSM values for 2	CSM values for 3
Square antiprism (*D*4d)	0.988 for Y1; 1.363 for Y2	0.981 for Dy1; 1.571 for Dy2	0.761 for Y1;0.964 for Y2
bicapped trigonal-prismatic (*C*2v)	1.836 for Y1; 2.056 for Y2	1.785 for Dy1; 2.105 for Dy2	1.556 for Y1; 2.129 for Y2
Johnson - Biaugmented trigonal prism (*C*2v)	2.379 for Y1; 2.890 for Y2	2.314 for Dy1; 2.929 for Dy2	2.165 for Y1; 2.908 for Y2
Snub disphenoid (*D*2d)	4.896 for Y1; 4.525 for Y2	4.840 for Dy1; 4.408 for Dy2	4.825 for Y1; 4.840 for Y2
Configuration	CSM values for 4	CSM values for 5	CSM values for 6
Square antiprism (*D*4d)	0.779 for Dy1; 1.011 for Dy2	0.768 for Ho1; 0.949 for Ho2	0.758 for Tb1; 1.207 for Tb2
bicapped trigonal-prismatic (*C*2v)	1.536 for Dy1; 2.067 for Dy2	1.514 for Ho1; 2.089 for Ho2	1.605 for Tb1; 2.042 for Tb2
Johnson - Biaugmented trigonal prism (*C*2v)	2.153 for Dy1; 2.828 for Dy2	2.158 for Ho1; 2.859 for Ho2	2.361 for Tb1; 2.801 for Tb2
Snub disphenoid (*D*2d)	4.833 for Dy1; 4.653 for Dy2	4.771 for Ho1; 4.786 for Ho2	5.059 for Tb1; 4.744 for Tb2

Table S6 Comparison of some Dy^{III}_4-SMMs with similar coordination environment

complex[a]	Configuration/CSM values for Dy1 and Dy2[b]	U_{eff}/K under zero dc field	ref
$[Dy_4(dbm)_4(L)_6(\mu_3\text{-}OH)_2]$	SAPR-8 0.981 and 1.571	117.4	this work
$[Dy_4(acac)_4(L)_6(\mu_3\text{-}OH)_2]\cdot(CH_3CN)_2$	SAPR-8 0.779 and 1.011	162.1(FR) 165.3(SR)	this work
$[Dy_4(acac)_4(L1)_6(\mu_3\text{-}OH)_2]$	SAPR-8 0.867 and 1.158	48K(FR) 121K(SR)	11a
$[Dy_4(\mu_3\text{-}OH)_2(L2)_6(acac)_4]\cdot 2.5CH_3CN$	SAPR-8 0.895 and 0.863	99.29	11b
$[Dy_4(\mu_3\text{-}OH)_2(L2)_6(tmhd)_4]\cdot xCH_3CN\cdot yCH_3CH_2OH$	SAPR-8 0.778 and 1.341	64.56	11b
$[Dy_4(\mu_3\text{-}OH)_2(L2)_6(beac)_4]\cdot CH_3CN$	SAPR-8 0.885 and 1.241	61.05	11b
$[Dy_4(dbm)_4(L3)_6(\mu_3\text{-}OH)_2]\cdot xCH_3CN\cdot yCH_2Cl_2$	SAPR-8 0.914 and 1.469	93.23	11c
$[Dy_4(acac)_4(L3)_6(\mu_3\text{-}OH)_2]\cdot xCH_3CN$	SAPR-8 1.262 and 0.945	37.49(FR) 89.89(SR)	11c
$[Dy_4(dbm)_4(L4)_6(\mu_3\text{-}OH)_2]\cdot 4CH_3CN\cdot 2H_2O$	SAPR-8 0.945 and 1.462	89.38	11d
$[Dy_4(acac)_4(L5)_6(\mu_3\text{-}OH)_2]\cdot CH_3CN\cdot 0.5CH_2Cl_2$	SAPR-8 0.835 and 1.112	86.2	11e
$[Dy_4(\mu_3\text{-}OH)_2(\mu\text{-}OH)_2(2,2\text{-}bpt)_4(NO_3)_4(EtOH)_2]$	SAPR-8 1.309 and 1.872	80	7d
$[Dy_4(\mu_3\text{-}OH)_2(L6)_6(acac)_4]$	SAPR-8 0.817 and 0.965	79.15	11f
$[Dy_4(\mu_3\text{-}OH)_2(L7)_6(dppd)_4]\cdot 2CH_3CN$	SAPR-8 1.010 and 1.347	62.36	11g
$[Dy_4(dbm)_4(L1)_6(\mu_3\text{-}OH)_2]$	SAPR-8 0.922 and 1.445	56K	11h

[a] HL1 = 5-(4-fluorobenzylidene)-8-hydroxylquinoline;
HL2 = 5-(4-methoxybenzylidene)-8-hydroxylquinoline;
HL3 = 5-[(3-methyl-2-thiopheneformaldehyde)-amino]-8-hydroxylquinoline;
HL4 = 5-(4-pyridinecarboxaldehyde)amino-8-hydroxylquinoline;
HL5 = 5-(benzylidene)amino-8-hydroxyquinoline;
2,2-bptH = 3,5-bis(pyridin-2-yl)-1,2,4-triazol;
HL6 = 5-(4-phenylbenzylidene)-8-hydroxylquinoline;
HL7 = 5-(4-ethyoxylbenzylidene)-8-hydroxylquinoline
[b] SAPR-8: square antiprism

Table S7 Important bond angle and bond parameters for complex **1**

complex 1					
Bond lengths (Å)		Bond angles (°)		Bond angels (°)	
Y(1)-O(8)	2.285(6)	O(8)-Y(1)-O(7)	70.8(2)	O(1)-Y(1)-N(1)	66.6(2)
Y(1)-O(7)	2.311(5)	O(8)-Y(1)-O(11)	142.40(18)	O(11)#1-Y(1)-N(1)	77.8(2)
Y(1)-O(11)	2.320(4)	O(7)-Y(1)-O(11)	81.47(17)	O(3)-Y(1)-N(1)	77.19(19)
Y(1)-O(5)#1	2.350(5)	O(8)-Y(1)-O(5)#1	120.33(19)	O(10)-Y(2)-O(11)	131.0(2)
Y(1)-O(1)	2.358(5)	O(7)-Y(1)-O(5)#1	80.61(19)	O(10)-Y(2)-O(9)	74.0(2)
Y(1)-O(11)#1	2.371(5)	O(11)-Y(1)-O(5)#1	77.71(17)	O(11)-Y(2)-O(9)	73.26(17)
Y(1)-O(3)	2.412(5)	O(8)-Y(1)-O(1)	84.5(2)	O(10)-Y(2)-O(5)	145.2(2)
Y(1)-N(1)	2.512(6)	O(7)-Y(1)-O(1)	88.72(19)	O(11)-Y(2)-O(5)	72.54(16)
Y(1)-Y(2)#1	3.5352(13)	O(11)-Y(1)-O(1)	69.72(18)	O(9)-Y(2)-O(5)	140.45(19)
Y(1)-Y(1)#1	3.7971(17)	O(5)#1-Y(1)-O(1)	146.89(18)	O(10)-Y(2)-O(3)#1	137.9(2)
Y(1)-Y(2)	3.8367(11)	O(8)-Y(1)-O(11)#1	142.83(18)	O(11)-Y(2)-O(3)#1	71.15(17)
Y(2)-O(10)	2.281(6)	O(7)-Y(1)-O(11)#1	144.36(18)	O(9)-Y(2)-O(3)#1	82.8(2)
Y(2)-O(11)	2.312(4)	O(11)-Y(1)-O(11)#1	71.93(18)	O(5)-Y(2)-O(3)#1	67.76(18)
Y(2)-O(9)	2.318(5)	O(5)#1-Y(1)-O(11)#1	71.02(17)	O(10)-Y(2)-O(1)	86.0(2)
Y(2)-O(5)	2.323(5)	O(8)-Y(1)-O(3)	83.07(19)	O(1)-Y(2)-N(5)	80.20(19)
Y(2)-O(3)#1	2.355(6)	O(7)-Y(1)-O(3)	118.56(18)	O(10)-Y(2)-N(3)#1	76.7(3)
Y(2)-O(1)	2.373(5)	O(11)-Y(1)-O(3)	133.51(18)	O(11)-Y(2)-N(3)#1	133.9(2)
Y(2)-N(5)	2.514(7)	O(5)#1-Y(1)-O(3)	66.38(17)	O(9)-Y(2)-N(3)#1	84.47(19)
Y(2)-N(3)#1	2.565(6)	O(1)-Y(1)-O(3)	143.75(18)	O(5)-Y(2)-N(3)#1	105.7(2)
Y(2)-Y(1)#1	3.5353(13)	O(11)#1-Y(1)-O(3)	69.16(17)	O(3)#1-Y(2)-N(3)#1	66.4(2)
		O(8)-Y(1)-N(1)	72.1(2)	O(3)#1-Y(2)-O(1)	134.75(18)
		O(7)-Y(1)-N(1)	136.9(2)	O(10)-Y(2)-N(5)	79.1(2)
		O(11)-Y(1)-N(1)	118.05(18)	O(1)-Y(2)-N(3)#1	156.5(2)
		O(5)#1-Y(1)-N(1)	138.3(2)	N(5)-Y(2)-N(3)#1	81.0(2)
		O(9)-Y(2)-O(1)	106.16(19)	O(9)-Y(2)-N(5)	151.7(2)
		O(3)#1-Y(2)-N(5)	112.7(2)	O(11)-Y(2)-O(1)	69.60(17)
		O(1)-Y(1)-O(11)#1	103.30(18)	O(11)-Y(2)-N(5)	133.18(18)
		O(5)-Y(2)-O(1)	79.68(19)	O(5)-Y(2)-N(5)	67.3(2)

Table S8 Important bond angle and bond parameters for complex **2**

complex 2					
Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Dy(1)-O(8)	2.303(6)	O(8)-Dy(1)-O(11)	142.28(19)	O(11)#1-Dy(1)-O(5)#1	71.03(18)
Dy(1)-O(11)	2.341(5)	O(8)-Dy(1)-O(7)	70.5(2)	O(8)-Dy(1)-O(3)	83.64(19)
Dy(1)-O(7)	2.343(5)	O(11)-Dy(1)-O(7)	81.99(18)	O(11)-Dy(1)-O(3)	133.01(19)
Dy(1)-O(1)	2.353(6)	O(8)-Dy(1)-O(1)	83.9(2)	O(7)-Dy(1)-O(3)	117.62(18)
Dy(1)-O(11)#1	2.369(5)	O(11)-Dy(1)-O(1)	70.3(2)	O(1)-Dy(1)-O(3)	143.87(19)
Dy(1)-O(5)#1	2.382(5)	O(7)-Dy(1)-O(1)	89.5(2)	O(11)#1-Dy(1)-O(3)	69.35(17)
Dy(1)-O(3)	2.437(5)	O(8)-Dy(1)-O(11)#1	143.07(18)	O(5)#1-Dy(1)-O(3)	66.47(17)
Dy(1)-N(1)	2.511(7)	O(11)-Dy(1)-O(11)#1	71.65(18)	O(8)-Dy(1)-N(1)	72.6(2)
Dy(1)-Dy(2)#1	3.5558(10)	O(7)-Dy(1)-O(11)#1	144.4(2)	O(11)-Dy(1)-N(1)	118.15(19)
Dy(1)-Dy(1)#1	3.8189(8)	O(1)-Dy(1)-O(11)#1	103.1(2)	O(7)-Dy(1)-N(1)	137.8(2)
Dy(1)-Dy(2)	3.8547(8)	O(8)-Dy(1)-O(5)#1	121.1(2)	O(1)-Dy(1)-N(1)	66.9(2)
Dy(2)-O(10)	2.288(6)	O(11)-Dy(1)-O(5)#1	76.87(17)	O(11)#1-Dy(1)-N(1)	77.0(2)
Dy(2)-O(9)	2.322(5)	O(7)-Dy(1)-O(5)#1	80.2(2)	O(5)#1-Dy(1)-N(1)	137.9(2)
Dy(2)-O(5)	2.327(5)	O(1)-Dy(1)-O(5)#1	146.63(18)	O(3)-Dy(1)-N(1)	77.1(2)
Dy(2)-O(11)	2.339(5)	O(10)-Dy(2)-O(9)	73.1(2)	O(3)#1-Dy(2)-O(1)	134.76(19)
Dy(2)-O(3)#1	2.370(6)	O(10)-Dy(2)-O(5)	144.8(2)	O(10)-Dy(2)-N(5)	79.0(2)
Dy(2)-O(1)	2.390(6)	O(9)-Dy(2)-O(5)	141.64(19)	O(9)-Dy(2)-N(5)	151.3(2)
Dy(2)-N(5)	2.542(6)	O(10)-Dy(2)-O(11)	131.8(2)	O(5)-Dy(2)-N(5)	66.9(2)
Dy(2)-N(3)#1	2.562(6)	O(9)-Dy(2)-O(11)	73.42(17)	O(11)-Dy(2)-N(5)	132.72(17)
Dy(2)-Dy(1)#1	3.5558(10)	O(10)-Dy(2)-O(3)#1	137.2(2)	O(1)-Dy(2)-N(5)	79.6(2)
		O(9)-Dy(2)-O(3)#1	84.20(19)	O(10)-Dy(2)-N(3)#1	77.3(3)
		O(5)-Dy(2)-O(3)#1	68.44(18)	O(9)-Dy(2)-N(3)#1	85.63(18)
		O(11)-Dy(2)-O(3)#1	71.01(18)	O(5)-Dy(2)-N(3)#1	105.07(19)
		O(10)-Dy(2)-O(1)	86.7(2)	O(11)-Dy(2)-N(3)#1	132.7(2)
		O(9)-Dy(2)-O(1)	104.9(2)	O(3)#1-Dy(2)-N(3)#1	65.0(2)
		O(5)-Dy(2)-O(1)	79.1(2)	O(1)-Dy(2)-N(3)#1	157.6(2)
		O(11)-Dy(2)-O(1)	69.7(2)	N(5)-Dy(2)-N(3)#1	81.9(2)
		O(5)-Dy(2)-O(11)	72.53(16)	O(3)#1-Dy(2)-N(5)	113.2(2)

Table S9 Important bond angle and bond parameters for complex **3**

complex 3					
Bond lengths(Å)		Bond angles (°)		Bond angles (°)	
Y(1)-O(7)	2.298(2)	O(7)-Y(1)-O(11)	139.36(8)	O(1)-Y(1)-O(5)	146.66(8)
Y(1)-O(11)	2.313(2)	O(7)-Y(1)-O(8)	73.37(9)	O(11)#1-Y(1)-O(5)	71.82(7)
Y(1)-O(8)	2.314(2)	O(11)-Y(1)-O(8)	77.34(8)	O(7)-Y(1)-O(3)	86.74(8)
Y(1)-O(1)	2.340(2)	O(7)-Y(1)-O(1)	79.49(8)	O(11)-Y(1)-O(3)	133.36(8)
Y(1)-O(11)#1	2.352(2)	O(11)-Y(1)-O(1)	70.26(7)	O(8)-Y(1)-O(3)	123.10(8)
Y(1)-O(3)	2.389(2)	O(8)-Y(1)-O(1)	84.74(8)	O(1)-Y(1)-O(3)	143.82(7)
Y(1)-N(1)	2.559(3)	O(7)-Y(1)-O(11)#1	144.38(8)	O(11)#1-Y(1)-O(3)	70.36(8)
Y(2)-O(10)	2.286(2)	O(11)-Y(1)-O(11)#1	70.82(9)	O(5)-Y(1)-O(3)	66.95(7)
Y(2)-O(11)#1	2.288(2)	O(8)-Y(1)-O(11)#1	142.05(8)	O(7)-Y(1)-N(1)	75.48(8)
Y(2)-O(9)	2.305(2)	O(1)-Y(1)-O(11)#1	102.89(8)	O(11)-Y(1)-N(1)	114.18(8)
Y(2)-O(1)#1	2.360(2)	O(7)-Y(1)-O(5)	124.45(8)	O(8)-Y(1)-N(1)	140.86(9)
Y(2)-O(5)	2.360(2)	O(11)-Y(1)-O(5)	77.13(8)	O(1)-Y(1)-N(1)	66.65(8)
Y(2)-O(3)	2.384(2)	O(8)-Y(1)-O(5)	81.53(8)	O(11)#1-Y(1)-N(1)	73.21(8)
Y(2)-N(5)	2.506(3)	O(3)-Y(1)-N(1)	77.58(8)	O(5)-Y(1)-N(1)	136.55(8)
Y(2)-N(3)	2.528(3)	O(11)#1-Y(2)-O(1)#1	70.31(7)	O(1)#1-Y(2)-N(3)	155.60(8)
Y(2)-Y(1)#1	3.7987(5)	O(9)-Y(2)-O(1)#1	109.55(8)	O(5)-Y(2)-N(3)	105.85(9)
O(1)-Y(2)#1	2.360(2)	O(10)-Y(2)-O(5)	144.93(8)	O(3)-Y(2)-N(3)	66.60(8)
O(11)-Y(2)#1	2.288(2)	O(11)#1-Y(2)-O(5)	73.36(8)	N(5)-Y(2)-N(3)	77.56(9)
O(11)-Y(1)#1	2.352(2)	O(9)-Y(2)-O(5)	140.30(8)	O(10)-Y(2)-O(11)#1	128.80(8)
Y(1)-O(5)	2.383(2)	O(10)-Y(2)-O(3)	139.89(8)	O(11)#1-Y(2)-O(9)	73.98(8)
		O(11)#1-Y(2)-O(3)	71.53(8)	O(10)-Y(2)-O(1)#1	83.76(8)
		O(9)-Y(2)-O(3)	81.28(8)	O(5)-Y(2)-N(5)	66.84(9)
		O(1)#1-Y(2)-O(3)	135.08(8)	O(3)-Y(2)-N(5)	109.01(9)
		O(5)-Y(2)-O(3)	67.40(8)	O(10)-Y(2)-N(3)	78.50(9)
		O(10)-Y(2)-N(5)	80.73(9)	O(11)#1-Y(2)-N(3)	134.08(8)
		O(11)#1-Y(2)-N(5)	135.37(9)	O(1)#1-Y(2)-N(5)	83.19(8)
		O(9)-Y(2)-N(5)	150.39(9)	O(10)-Y(2)-O(9)	74.52(8)
		O(1)#1-Y(2)-O(5)	79.63(8)		

Table S10 Important bond angle and bond parameters for complex **4**

complex 4					
Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Dy(1)-O(7)	2.324(9)	O(7)-Dy(1)-O(11)#1	139.9(3)	O(11)-Dy(1)-O(3)#1	71.8(3)
Dy(1)-O(11)#1	2.335(8)	O(7)-Dy(1)-O(8)	73.0(3)	O(1)-Dy(1)-O(3)#1	146.9(3)
Dy(1)-O(8)	2.339(8)	O(11)#1-Dy(1)-O(8)	77.7(3)	O(7)-Dy(1)-O(5)#1	86.8(3)
Dy(1)-O(11)	2.344(8)	O(7)-Dy(1)-O(11)	144.6(3)	O(11)#1-Dy(1)-O(5)#1	132.6(3)
Dy(1)-O(1)	2.351(8)	O(11)#1-Dy(1)-O(11)	70.2(3)	O(8)-Dy(1)-O(5)#1	123.2(3)
Dy(1)-O(3)#1	2.403(8)	O(8)-Dy(1)-O(11)	142.2(3)	O(11)-Dy(1)-O(5)#1	70.4(3)
Dy(1)-O(5)#1	2.406(8)	O(7)-Dy(1)-O(1)	79.4(3)	O(1)-Dy(1)-O(5)#1	143.7(3)
Dy(1)-N(1)	2.563(9)	O(11)#1-Dy(1)-O(1)	71.1(3)	O(3)#1-Dy(1)-O(5)#1	66.9(3)
Dy(1)-Dy(2)#1	3.5465(8)	O(8)-Dy(1)-O(1)	84.6(3)	O(7)-Dy(1)-N(1)	75.9(3)
Dy(1)-Dy(2)	3.8205(8)	O(11)-Dy(1)-O(1)	102.9(3)	O(11)#1-Dy(1)-N(1)	114.1(3)
Dy(1)-Dy(1)#1	3.8267(11)	O(7)-Dy(1)-O(3)#1	124.3(3)	O(8)-Dy(1)-N(1)	140.6(3)
O(3)-Dy(1)#1	2.403(8)	O(11)#1-Dy(1)-O(3)#1	76.6(3)	O(11)-Dy(1)-N(1)	73.1(3)
Dy(2)-O(9)	2.294(9)	O(8)-Dy(1)-O(3)#1	81.9(3)	O(1)-Dy(1)-N(1)	66.4(3)
Dy(2)-O(10)	2.316(8)	O(5)#1-Dy(1)-N(1)	77.8(3)	O(3)#1-Dy(1)-N(1)	136.5(3)
Dy(2)-O(11)#1	2.321(8)	O(10)-Dy(2)-O(11)#1	74.0(3)	O(1)-Dy(2)-N(3)	82.9(3)
Dy(2)-O(3)	2.362(7)	O(9)-Dy(2)-O(3)	145.4(3)	O(5)-Dy(2)-N(3)	109.8(3)
Dy(2)-O(1)	2.382(8)	O(10)-Dy(2)-O(3)	140.7(3)	O(9)-Dy(2)-N(5)	78.5(3)
Dy(2)-O(5)	2.402(8)	O(11)#1-Dy(2)-O(3)	73.0(3)	O(10)-Dy(2)-N(5)	82.5(3)
Dy(2)-N(3)	2.508(10)	O(9)-Dy(2)-O(1)	83.9(3)	O(11)#1-Dy(2)-N(5)	133.6(3)
Dy(2)-N(5)	2.520(9)	O(10)-Dy(2)-O(1)	108.5(3)	O(3)-Dy(2)-N(5)	105.7(3)
Dy(2)-Dy(1)#1	3.5466(8)	O(11)#1-Dy(2)-O(1)	70.7(3)	O(1)-Dy(2)-N(5)	155.7(3)
O(11)-Dy(2)#1	2.320(8)	O(3)-Dy(2)-O(1)	79.8(3)	O(5)-Dy(2)-N(5)	66.5(3)
O(11)-Dy(1)#1	2.335(8)	O(9)-Dy(2)-O(5)	139.4(3)	N(3)-Dy(2)-N(5)	77.8(3)
O(5)-Dy(1)#1	2.406(8)	O(10)-Dy(2)-O(5)	81.9(3)	O(9)-Dy(2)-O(10)	73.6(3)
		O(11)#1-Dy(2)-O(5)	70.9(3)	O(9)-Dy(2)-N(3)	80.7(3)
		O(9)-Dy(2)-O(11)#1	129.2(3)	O(11)#1-Dy(2)-N(3)	135.4(3)
		O(3)-Dy(2)-O(5)	67.6(3)	O(3)-Dy(2)-N(3)	67.2(3)
		O(1)-Dy(2)-O(5)	135.2(3)	O(10)-Dy(2)-N(3)	150.2(3)

Table S11 Important bond angle and bond parameters for complex **5**

complex 5					
Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Ho(1)-O(7)	2.313(6)	O(7)-Ho(1)-O(11)#1	139.48(19)	O(7)-Ho(1)-O(5)	86.82(18)
Ho(1)-O(11)#1	2.316(5)	O(7)-Ho(1)-O(8)	73.3(2)	O(11)#1-Ho(1)-O(5)	133.13(18)
Ho(1)-O(8)	2.321(5)	O(11)#1-Ho(1)-O(8)	77.44(19)	O(8)-Ho(1)-O(5)	123.03(18)
Ho(1)-O(3)	2.340(5)	O(7)-Ho(1)-O(3)	79.26(18)	O(3)-Ho(1)-O(5)	143.83(17)
Ho(1)-O(11)	2.345(5)	O(11)#1-Ho(1)-O(3)	70.60(18)	O(11)-Ho(1)-O(5)	70.50(17)
O(11)-Ho(1)#1	2.316(5)	O(8)-Ho(1)-O(3)	84.69(18)	O(1)-Ho(1)-O(5)	67.00(18)
Ho(1)-O(1)	2.391(5)	O(7)-Ho(1)-O(11)	144.46(18)	O(7)-Ho(1)-N(3)	75.2(2)
Ho(1)-O(5)	2.392(5)	O(11)#1-Ho(1)-O(11)	70.6(2)	O(11)#1-Ho(1)-N(3)	114.45(18)
Ho(1)-N(3)	2.546(6)	O(8)-Ho(1)-O(11)	142.05(18)	O(8)-Ho(1)-N(3)	140.7(2)
Ho(1)-Ho(2)	3.5298(5)	O(3)-Ho(1)-O(11)	102.91(17)	O(3)-Ho(1)-N(3)	66.64(19)
Ho(1)-Ho(2)#1	3.8034(5)	O(7)-Ho(1)-O(1)	124.78(18)	O(11)-Ho(1)-N(3)	73.41(18)
Ho(1)-Ho(1)#1	3.8038(7)	O(11)#1-Ho(1)-O(1)	76.73(17)	O(1)-Ho(1)-N(3)	136.58(19)
Ho(2)-O(10)	2.283(6)	O(8)-Ho(1)-O(1)	81.68(18)	O(5)-Ho(1)-N(3)	77.60(18)
Ho(2)-O(11)	2.301(5)	O(3)-Ho(1)-O(1)	146.61(18)	O(10)-Ho(2)-O(11)	128.84(19)
Ho(2)-O(9)	2.307(5)	O(11)-Ho(2)-O(9)	73.97(18)	O(10)-Ho(2)-O(5)	139.81(19)
Ho(2)-O(1)	2.359(5)	O(10)-Ho(2)-O(1)	145.18(19)	O(11)-Ho(2)-O(5)	71.24(17)
Ho(2)-O(3)#1	2.366(5)	O(11)-Ho(2)-O(1)	73.02(17)	O(9)-Ho(2)-O(5)	81.43(19)
Ho(2)-O(5)	2.391(5)	O(9)-Ho(2)-O(1)	140.30(18)	O(1)-Ho(2)-O(5)	67.53(18)
Ho(2)-N(1)	2.496(6)	O(10)-Ho(2)-O(3)#1	83.90(19)	O(3)#1-Ho(2)-O(5)	134.94(18)
Ho(2)-N(5)	2.519(6)	O(11)-Ho(2)-O(3)#1	70.39(18)	O(10)-Ho(2)-N(1)	80.6(2)
Ho(2)-Ho(1)#1	3.8035(5)	O(9)-Ho(2)-O(3)#1	109.32(18)	O(10)-Ho(2)-O(9)	74.2(2)
O(3)-Ho(2)#1	2.366(5)	O(1)-Ho(2)-O(3)#1	79.35(18)	O(11)-Ho(1)-O(1)	71.66(17)
		O(9)-Ho(2)-N(1)	150.1(2)	O(9)-Ho(2)-N(5)	82.0(2)
		O(1)-Ho(2)-N(1)	67.3(2)	O(1)-Ho(2)-N(5)	106.1(2)
		O(3)#1-Ho(2)-N(1)	83.3(2)	O(3)#1-Ho(2)-N(5)	155.65(19)
		O(5)-Ho(2)-N(1)	109.3(2)	O(5)-Ho(2)-N(5)	66.70(19)
		O(10)-Ho(2)-N(5)	78.5(2)	N(1)-Ho(2)-N(5)	77.4(2)
		O(11)-Ho(2)-N(5)	133.95(19)	O(11)-Ho(2)-N(1)	135.6(2)

Table S12 Important bond angle and bond parameters for complex **6**

complex 6					
Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Tb(1)-O(7)	2.324(6)	O(7)-Tb(1)-O(11)#1	139.0(2)	O(11)#1-Tb(1)-O(3)	77.4(2)
Tb(1)-O(11)#1	2.337(6)	O(7)-Tb(1)-O(8)	72.9(2)	O(8)-Tb(1)-O(3)	83.0(2)
Tb(1)-O(8)	2.348(7)	O(11)#1-Tb(1)-O(8)	77.4(2)	O(11)-Tb(1)-O(3)	71.0(2)
Tb(1)-O(11)	2.385(6)	O(7)-Tb(1)-O(11)	144.4(2)	O(5)-Tb(1)-O(3)	147.0(2)
Tb(1)-O(5)	2.386(6)	O(11)#1-Tb(1)-O(11)	71.1(3)	O(7)-Tb(1)-O(1)	87.4(2)
O(11)-Tb(1)#1	2.337(6)	O(8)-Tb(1)-O(11)	142.6(2)	O(11)#1-Tb(1)-O(1)	133.2(2)
Tb(1)-O(3)	2.413(6)	O(7)-Tb(1)-O(5)	78.9(2)	O(8)-Tb(1)-O(1)	124.4(2)
Tb(1)-O(1)	2.435(7)	O(11)#1-Tb(1)-O(5)	70.3(2)	O(11)-Tb(1)-O(1)	69.4(2)
Tb(1)-N(5)	2.550(8)	O(8)-Tb(1)-O(5)	83.8(2)	O(5)-Tb(1)-O(1)	143.4(2)
Tb(1)-Tb(2)	3.5939(9)	O(11)-Tb(1)-O(5)	103.5(2)	O(3)-Tb(1)-O(1)	66.8(2)
Tb(1)-Tb(1)#1	3.8419(11)	O(7)-Tb(1)-O(3)	125.0(2)	O(7)-Tb(1)-N(5)	76.4(2)
O(5)-Tb(2)#1	2.395(6)	O(11)-Tb(2)-N(3)	134.0(3)	O(11)#1-Tb(1)-N(5)	113.1(2)
Tb(1)-Tb(2)#1	3.8603(10)	O(9)-Tb(2)-N(3)	150.3(3)	O(8)-Tb(1)-N(5)	140.6(2)
Tb(2)-O(10)	2.327(7)	O(3)-Tb(2)-N(3)	66.2(3)	O(11)-Tb(1)-N(5)	72.5(2)
Tb(2)-O(11)	2.333(6)	O(5)#1-Tb(2)-N(3)	83.1(2)	N(3)-Tb(2)-N(1)	78.7(3)
Tb(2)-O(9)	2.340(7)	O(1)-Tb(2)-N(3)	108.9(2)	O(1)-Tb(1)-N(5)	77.5(2)
Tb(2)-O(3)	2.384(7)	O(10)-Tb(2)-N(1)	78.4(3)	O(10)-Tb(2)-O(11)	131.0(2)
Tb(2)-O(5)#1	2.395(6)	O(11)-Tb(2)-N(1)	133.1(2)	O(10)-Tb(2)-O(9)	73.6(2)
Tb(2)-O(1)	2.411(6)	O(9)-Tb(2)-N(1)	82.8(2)	O(5)-Tb(1)-N(5)	66.4(2)
Tb(2)-N(3)	2.532(8)	O(3)-Tb(2)-N(1)	106.1(2)	O(3)-Tb(1)-N(5)	135.7(2)
Tb(2)-N(1)	2.558(8)	O(5)#1-Tb(2)-N(1)	156.7(2)	O(5)#1-Tb(2)-O(1)	134.6(2)
Tb(2)-Tb(1)#1	3.8603(10)	O(1)-Tb(2)-N(1)	66.2(2)	O(10)-Tb(2)-N(3)	80.0(3)
		O(11)-Tb(2)-O(9)	75.1(2)	O(9)-Tb(2)-O(5)#1	107.1(2)
		O(10)-Tb(2)-O(3)	143.7(2)	O(3)-Tb(2)-O(5)#1	79.3(2)
		O(11)-Tb(2)-O(3)	72.4(2)	O(10)-Tb(2)-O(1)	140.1(3)
		O(9)-Tb(2)-O(3)	142.3(2)	O(11)-Tb(2)-O(1)	70.7(2)
		O(10)-Tb(2)-O(5)#1	84.2(2)	O(9)-Tb(2)-O(1)	84.0(2)
		O(11)-Tb(2)-O(5)#1	70.2(2)	O(3)-Tb(2)-O(1)	67.6(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1.