Supporting Information for:

Synergistic effect of mixed-ligands on anisotropy axis of two dinuclear dysprosium complexes

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Table S1 *SHAPE*[1] analyses of compounds **1** and **2**

Configuration	Dy1	Dy2
Octagon(D_{8h})	30.356(31.031)	29.682(31.305)
Heptagonal pyramid(C_{7v})	23.032(23.879)	23.371(22.897)
Hexagonal bipyramid(D_{6h})	16.150(14.711)	15.372(15.232)
Cube(O_h)	10.032(9.071)	9.012(8.730)
Square antiprism(D_{4d})	2.527(3.172)	1.991(2.379)
Triangular dodecahedron(D_{2d})	**1.097(1.043)**	**1.203(0.942)**
Johnson gyrobifastigium J26(D_{2d})	13.799(14.254)	14.420(14.329)
Johnson elongated triangular bipyramid J14(D_{3h})	26.388(25.935)	25.243(27.038)
Biaugmented trigonal prism J50(C_{2v})	2.504(2.661)	2.530(2.823)
Biaugmented trigonal prism(C_{2v})	2.473(2.547)	2.535(2.735)
Snub diphenoid J84(D_{2d})	2.445(2.622)	2.729(2.734)
Triakis tetrahedron(T_d)	10.340(9.403)	9.302(9.091)
Elongated trigonal bipyramid(D_{3h})	22.302(21.171)	20.401(22.463)

Note: the values in the bracket represent the coordination geometry result of compound **2**.

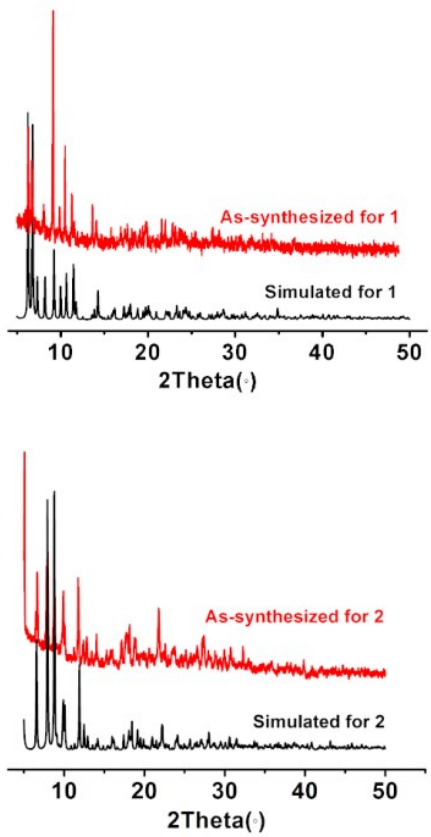

Fig. S1 Comparing the simulated PXRD (black) and experimental patterns (red) of complexes **1** (top) and **2** (bottom).

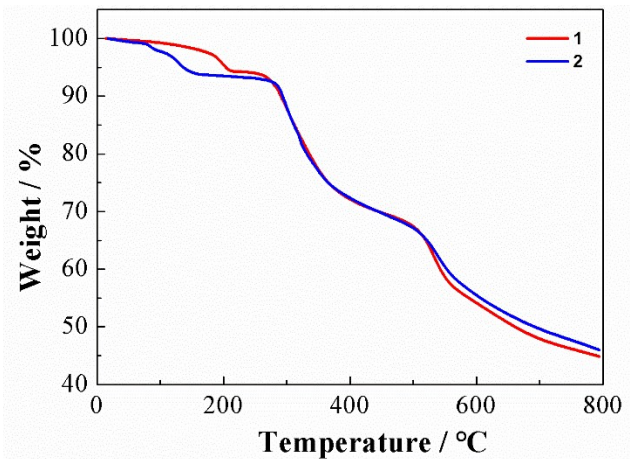

Fig. S2 The TGA plots for complexes **1** (red lines) and **2** (blue lines).

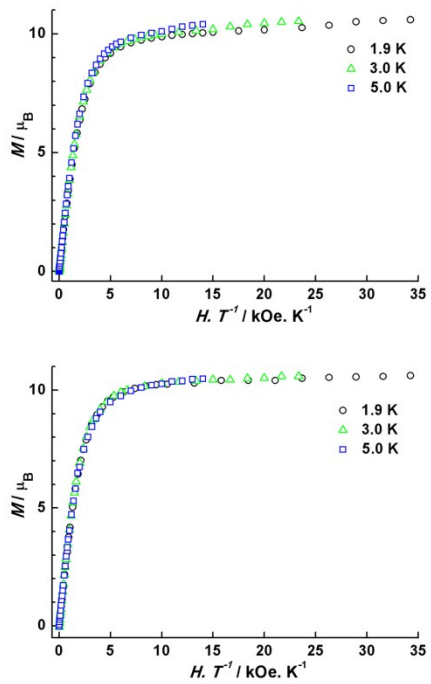

Fig. S3 Field dependence of the reduced magnetization data for complexes **1** (top) and **2** (bottom) at 1.9, 3, and 5 K.

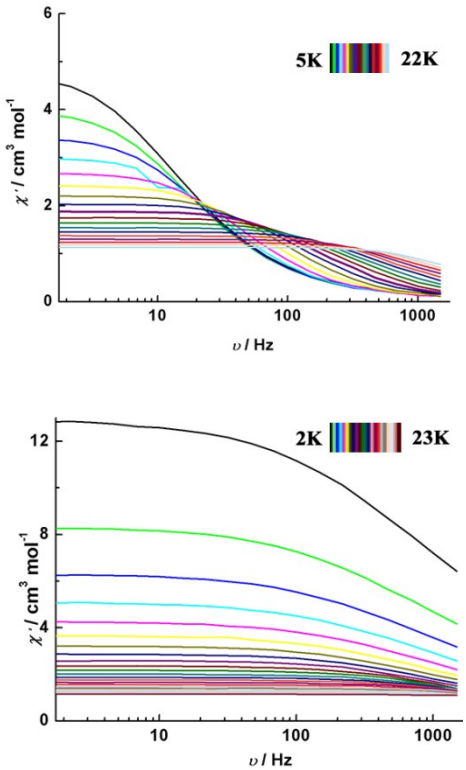

Fig. S4 Frequency dependence of the in-phase (χ') ac magnetic susceptibility data for **1** (top) and **2** (bottom) under zero applied dc field.

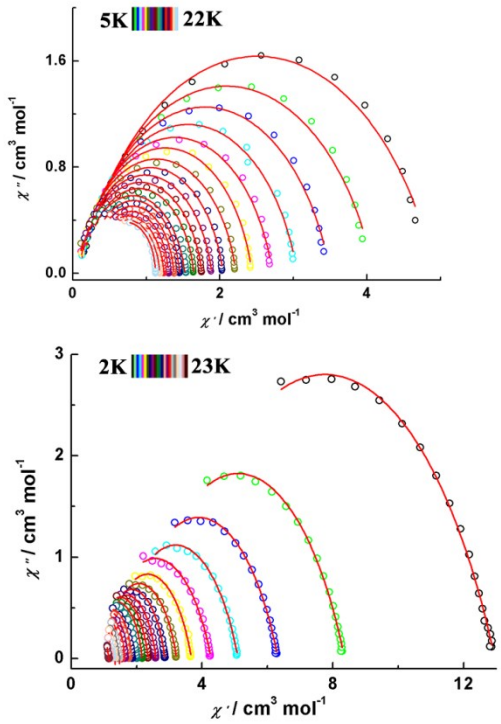

Fig. S5 Cole-Cole[2] plots for ac susceptibility collected under zero applied dc field for **1** (top) and **2** (bottom). Red solid lines represent the fits to the data.

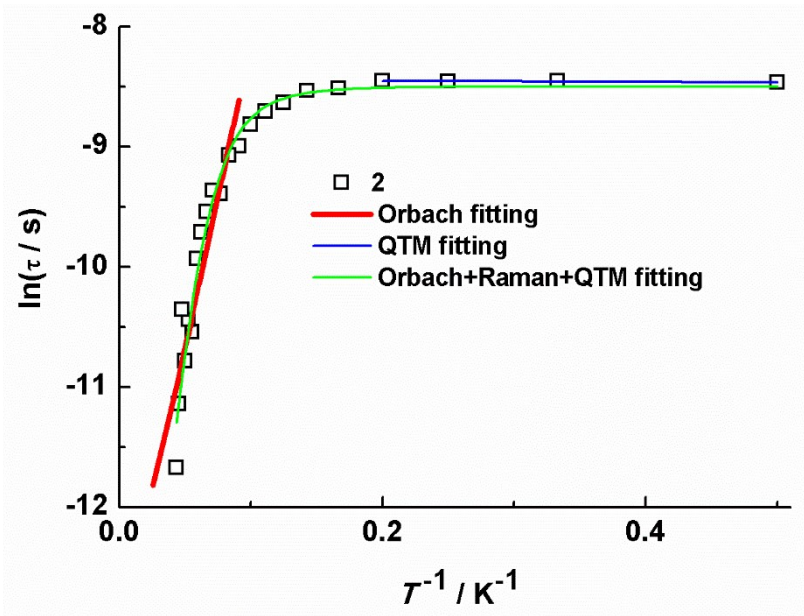

Fig. S6 ln(τ) vs. T^{-1} plots for **2** (hollow squares, 2-23 K).

Table S2 χ_T, χ_S, τ and α values of **1** and **2** estimated by theoretical calculations on the basis of the generalized Debye[3] model

				1				
T/K	5	6	7	8	9	10	11	12
χ_T/cm^3 mol^{-1}	4.946	4.116	3.519	3.069	2.730	2.454	2.234	2.058
χ_S/cm^3 mol^{-1}	0.12	0.11	0.11	0.089	0.085	0.086	0.0679	0.073
τ/μsec	10170	7940	5990	4400	3120	2200	1560	1130
α	0.236	0.214	0.191	0.184	0.163	0.149	0.152	0.154
T/K	13	14	15	16	17	18	19	20
χ_T/cm^3 mol^{-1}	1.901	1.769	1.657	1.553	1.463	1.381	1.306	1.242
χ_S/cm^3 mol^{-1}	0.070	0.072	0.105	0.108	0.147	0.197	0.250	0.266
τ/μsec	824	606	470	354	281	229	188	149
α	0.151	0.155	0.147	0.145	0.147	0.115	0.088	0.084
T/K	21	22						
χ_T/cm^3 mol^{-1}	1.182	1.123						
χ_S/cm^3 mol^{-1}	0.308	0.297						
τ/μsec	122	92.9						
α	0.056	0.045						
				2				
T/K	2	3	4	5	6	7	8	9
χ_T/cm^3 mol^{-1}	12.98	8.37	6.34	5.11	4.29	3.68	3.23	2.88
χ_S/cm^3 mol^{-1}	2.52	1.74	1.37	1.21	0.78	0.94	0.84	0.78
τ/sec	211	214	213	214	201	197	178	166
α	0.376	0.363	0.353	0.340	0.350	0.310	0.300	0.270
T/K	10	11	12	13	14	15	16	17
χ_T/cm^3 mol^{-1}	2.59	2.36	2.17	2.01	1.87	1.75	1.65	1.55
χ_S/cm^3 mol^{-1}	0.71	0.59	0.62	0.45	0.54	0.52	0.50	0.38
τ/μsec	149	124	115	83.3	86.0	71.8	60.5	48.4
α	0.254	0.234	0.208	0.232	0.189	0.178	0.180	0.177
T/K	18	19	20	21	22	23		
χ_T/cm^3 mol^{-1}	1.47	1.39	1.32	1.26	1.20	1.15		
χ_S/cm^3 mol^{-1}	0.36	0.20	0.18	0.48	0.12	0.15		
τ/μsec	26.4	29.2	20.7	31.8	14.5	8.55		
α	0.198	0.179	0.194	0.163	0.168	0.229		

Table S3 χ_S, χ_T, and α parameters of **1** and **2** derived from Cole-Cole[2] fitting

1								
T/K	5	6	7	8	9	10	11	12
χ_T/cm^3 mol^{-1}	4.924	4.097	3.498	3.051	2.713	2.438	2.221	2.042
χ_S/cm^3 mol^{-1}	0.097	0.086	0.09	0.088	0.071	0.080	0.058	0.078
α	0.241	0.220	0.193	0.175	0.160	0.140	0.144	0.133
T/K	13	14	15	16	17	18	19	20
χ_T/cm^3 mol^{-1}	1.888	1.756	1.644	1.521	1.453	1.372	1.300	1.239
χ_S/cm^3 mol^{-1}	0.080	0.086	0.145	0.110	0.206	0.257	0.297	0.274
α	0.127	0.125	0.101	0.119	0.082	0.062	0.0481	0.071
T/K	21	22						
χ_T/cm^3 mol^{-1}	1.180	1.125						
χ_S/cm^3 mol^{-1}	0.312	0.350						
α	0.050	0.047						
2								
T/K	2	3	4	5	6	7	8	9
χ_T/cm^3 mol^{-1}	12.95	8.35	6.32	5.10	4.27	3.67	3.22	2.87
χ_S/cm^3 mol^{-1}	2.56	1.85	1.47	1.28	0.87	1.00	0.93	0.85
α	0.37	0.349	0.337	0.326	0.331	0.291	0.27	0.24
T/K	10	11	12	13	14	15	16	17
χ_T/cm^3 mol^{-1}	2.58	2.36	2.17	2.01	1.85	1.75	1.64	1.55
χ_S/cm^3 mol^{-1}	0.81	0.63	0.67	0.48	0.66	0.51	0.68	0.27
α	0.22	0.22	0.186	0.216	0.13	0.177	0.12	0.20
T/K	18	19	20	21	22	23		
χ_T/cm^3 mol^{-1}	1.47	1.39	1.33	1.26	1.2	1.15		
χ_S/cm^3 mol^{-1}	0.3	0.28	0.24	0.42	0.1	0.17		
α	0.194	0.215	0.257	0.174	0.20	0.235		

Table S4 Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and m_J values of the lowest eight Kramers doublets (KDs) of individual Dy^{III} fragments with respect to the pseudospin $\tilde{S}$ = 1/2 in complexes **1** and **2** using CASSCF/RASSI with MOLCAS 8.2[4]

1

KDs	Dy1			Dy2		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
1	0.0	0.003 0.004 19.665	±15/2	0.0	0.006 0.008 19.709	±15/2
2	224.8	0.114 0.226 15.897	±13/2	221.5	0.218 0.419 16.132	±13/2
3	331.8	0.337 0.485 13.451	±11/2	325.6	0.767 1.051 13.571	±11/2
4	435.6	0.661 1.632 9.964	±9/2	413.8	0.197 1.818 9.709	±9/2
5	525.6	5.326 5.487 7.968	±7/2	493.2	4.897 5.980 9.005	±5/2

6	578.8	1.287 2.639 15.753	±3/2	562.0	0.731 1.401 14.488	±1/2
7	662.6	0.234 0.358 16.813	±1/2	647.0	0.078 0.117 18.952	±3/2
8	747.6	0.069 0.137 18.803	±5/2	732.5	0.005 0.017 19.453	±7/2

2

KDs	Dy1			Dy2		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
1	0.0	0.016 0.027 19.578	±15/2	0.0	0.001 0.001 19.667	±15/2
2	208.7	0.566 1.309 15.141	±13/2	226.0	0.014 0.022 16.272	±13/2
3	293.0	0.689 1.954 12.829	±11/2	367.4	0.445 0.690 13.323	±11/2

4	386.7	1.383 4.513 9.389	±9/2	462.7	2.130 2.501 9.546	±9/2
5	464.7	3.562 6.029 10.346	±5/2	560.9	4.805 5.304 8.772	±7/2
6	546.1	0.126 0.339 15.044	±1/2	644.5	0.916 1.729 15.264	±3/2
7	633.9	0.132 0.225 17.938	±3/2	701.8	0.190 0.305 17.305	±1/2
8	683.2	0.046 0.122 18.798	±7/2	769.6	0.129 0.190 18.384	±5/2

Table S5 Wave functions with definite projection of the total moment | m_J > for the lowest KDs of individual Dy^{III} fragments for complexes **1** and **2** using CASSCF/RASSI-SO with MOLCAS 8.2[4]

1		
	E/cm^{-1}	Wave functions
Dy1	0.0	96%|±15/2>
	224.8	80%|±13/2>+16%|±9/2>
Dy2	0.0	97%|±15/2>
	221.5	83%|±13/2>+14%|±9/2>
2		
Dy1	0.0	96%|±15/2>
	208.7	73%|±13/2>+18%|±9/2>
Dy2	0.0	96%|±15/2>
	226.0	83%|±13/2>+14%|±9/2>
	367.4	52%|±11/2>+30%|±7/2>

Table S6 Fitted exchange coupling J_{exch}, the calculated dipole-dipole interaction J_{dip} and the calculated total constant J_{total} of magnetic centers in **1** and **2** (cm^{-1}). The intermolecular interaction zJ' was fitted to -0.03 and -0.01 cm^{-1}, respectively

	1	**2**
J_{dip}	0.71	1.19
J_{exch}	-3.25	-3.25
J_{total}	-2.54	-2.06

Table S7 Exchange energies E (cm^{-1}), the energy difference between each exchange doublets Δ_t (cm^{-1}) and the main values of the g_z for the lowest two exchange doublets of **1** and **2**.

	E	Δ_t	g_z
1			
1	0.0	3.94×10^{-6}	23.020
2	0.1	4.17×10^{-6}	31.943
2			
1	0.0	2.48×10^{-5}	21.299
2	0.2	2.50×10^{-5}	32.747

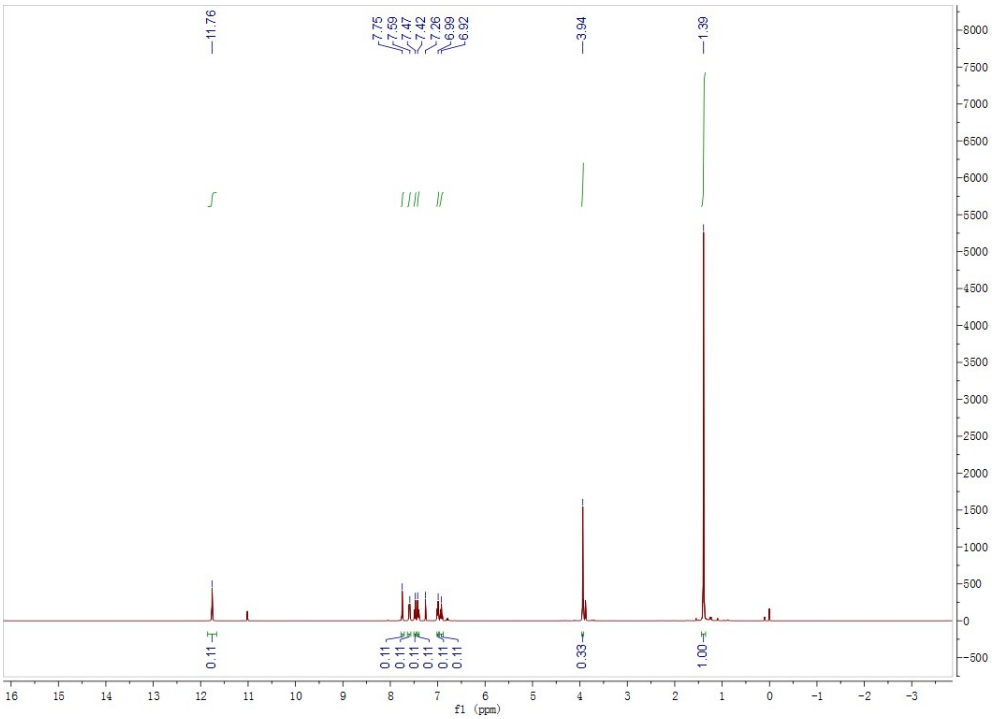

Figure S7 ^{1}H NMR spectra of the ligand HL_3 (400 MHz, $CDCl_3$, 298 K).

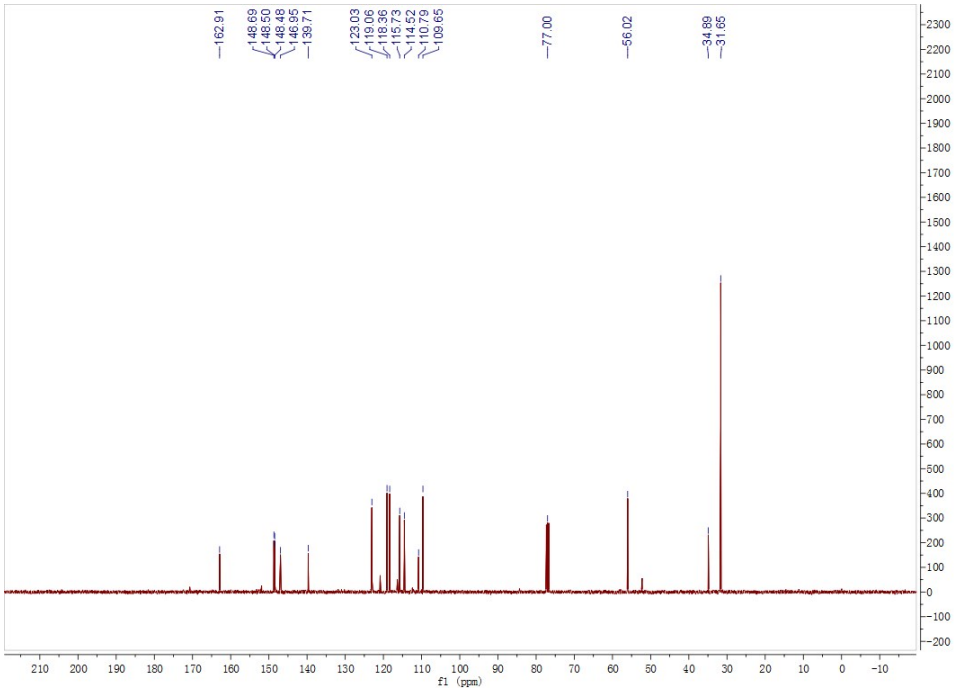

Figure S8 ^{13}C NMR spectra of the ligand HL_3 (400 MHz, $CDCl_3$, 298 K).

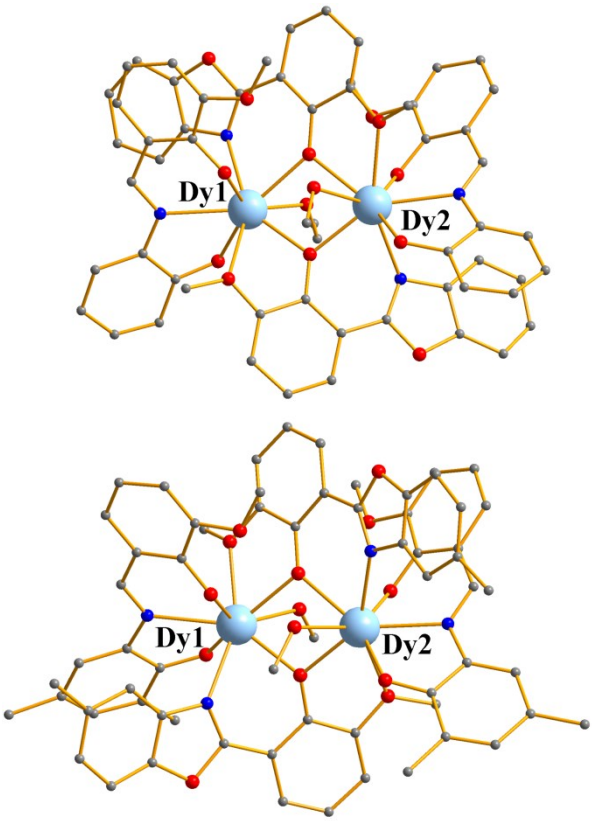

Figure S9 Calculated core structure of **1** (top) and **2** (bottom). H atoms are omitted. The tert-butyl groups in **1** and the methyl groups of each tert-butyl group in **2** are removed.

Table S8 Crystal data and structure refinements for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{91}H_{116}Dy_2N_4O_{14}$	$C_{83.5}H_{104}Dy_2N_4O_{15.5}$
Formula weight	1814.87	1736.70
Temperature (K)	296.98	150
Crystal system	trigonal	tetragonal
Space group	R3	$I4_1/a$
a (Å)	26.065(3)	40.7539(19)
b (Å)	26.065(3)	40.7539(19)
c (Å)	36.149(6)	20.1854(9)
α (°)	90	90
β (°)	90	90
γ (°)	120	90
Volume ($Å^3$)	21268(6)	33526(3)
Z	9	16
F(000)	8406.0	14224.0
ρ_{calg}/cm^3	1.275	1.376
μ/mm^{-1}	8.827	1.833
Radiation	CuKα	MoK\α
Reflections collected	20461	121120
Independent reflections	10693	15945
Data/restraints/parameters	10693/894/1129	15945/88/1045
Goodness of fit on ($F^{2)}$	1.185	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0595	R_1 = 0.0505
	wR_2 = 0.1585	wR_2 = 0.1004
R indexes (all data)	R_1 = 0.0728	R_1 = 0.0872
	wR_2 = 0.1663	wR_2 = 0.1163
Largest diff. peak/hole / e $Å^{-3}$	0.88/-0.50	1.18/-1.32

Table S9 Selected bond lengths (Å) and angles (°) for **1** and **2**

1		**2**	
Bond lengths (Å)			
Dy(1)-N(2)	2.487(11)	Dy(1)-N(2)	2.529(5)
Dy(1)-N(3)	2.497(13)	Dy(1)-N(3)	2.491(5)
Dy(1)-O(1)	2.595(11)	Dy(1)-O(1)	2.428(4)
Dy(1)-O(2)	2.308(9)	Dy(1)-O(2)	2.376(4)
Dy(1)-O(5)	2.392(10)	Dy(1)-O(5)	2.315(4)
Dy(1)-O(8)	2.239(11)	Dy(1)-O(8)	2.251(4)
Dy(1)-O(9)	2.222(10)	Dy(1)-O(9)	2.211(4)
Dy(1)-O(13)	2.490(10)	Dy(1)-O(14)	2.497(4)
Dy(2)-N(1)	2.543(13)	Dy(2)-N(1)	2.481(5)
Dy(2)-N(4)	2.484(12)	Dy(2)-N(4)	2.468(5)
Dy(2)-O(2)	2.298(9)	Dy(2)-O(2)	2.360(4)
Dy(2)-O(4)	2.465(11)	Dy(2)-O(4)	2.609(4)
Dy(2)-O(5)	2.401(10)	Dy(2)-O(5)	2.328(4)
Dy(2)-O(11)	2.206(11)	Dy(2)-O(11)	2.228(4)
Dy(2)-O(12)	2.213(10)	Dy(2)-O(12)	2.188(4)
Dy(2)-O(14)	2.517(10)	Dy(2)-O(13)	2.462(4)
Bond angles (°)			
Dy(1)-O(2)-Dy(2)	108.8(4)	Dy(1)-O(2)-Dy(2)	103.77(16)
Dy(1)-O(5)-Dy(2)	102.7(4)	Dy(1)-O(5)-Dy(2)	106.75(16)

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