Supporting Information

Role of Diamagnetic Ions on the Mechanism of Magnetization Relaxation in "Butterfly" $\{Co^{III}_2Ln^{III}_2\}$ (Ln =Dy, Tb and Ho) complexes

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Table S1. X-ray crystallographic data for **1** and **2**.

	1	**2**
Formula[a]	$Co_2Dy_2C_{42}H_{52}O_{20}N_4$	$Co_2Tb_2C_{42}H_{52}O_{20}N_4$
Mw, $gmol^{-1}$	1375.74	1368.59
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
a/Å	10.127(2)	10.092(2)
b/Å	10.631(2)	10.558(2)
c/Å	11.017(2)	11.080(2)
α/deg	90.13(3)	90.49 (3)
β/deg	91.28(3)	91.81(3)
γ/deg	90.31(3)	90.31(3)
V/$Å^3$	1185.8(4)	1179.6(4)
T/K	100(2)	100(2)
Z	1	1
ρ_{calc} [g cm^{-3}]	1.927	1.927
λ[b]/ Å	0.71073	0.71079
Data Measured	19162	26517
Ind. Reflns	5035	5561
R_{int}	0.0213	0.0368
Reflns with I I > 2σ(I)	4887	5478
Parameters	322	322
Restraints	1	0
R_1[c] (I > 2σ(I)), wR_2[c] (all data)	0.0302, 0.0612	0.0408, 0.0603
goodness of fit	1.042	1.102
Largest residuals/ e Å $^{-3}$	1.426, -1.639	0.831, -1.218

[a] Including solvate molecules. [b] Graphite monochromator. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

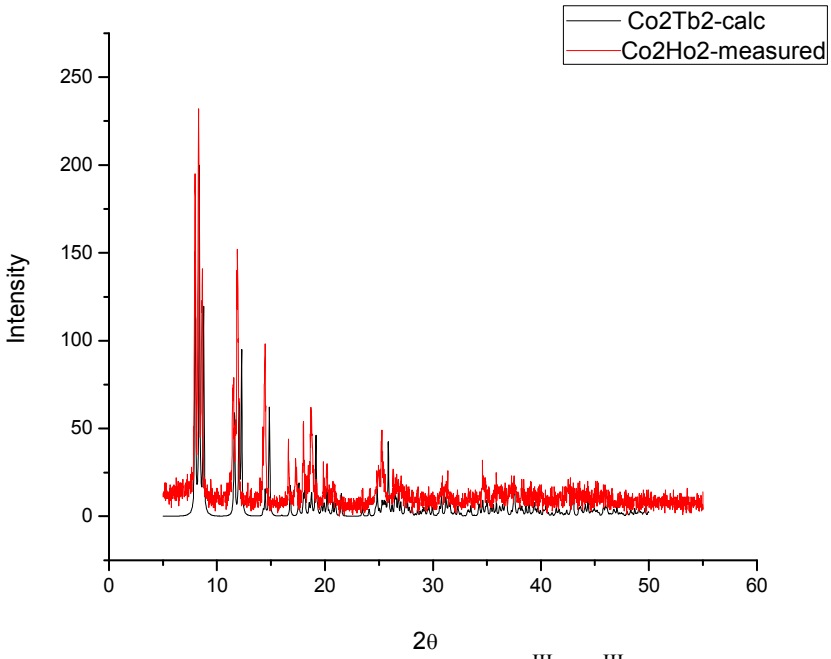

Figure S1. X-ray powder diffraction data for complex $\{Co^{III}_2Ho^{III}_2\}$(**3**). The data are compared to the simulated diffractogram of the $\{Co^{III}_2Tb^{III}_2\}$(**2**) analogue.

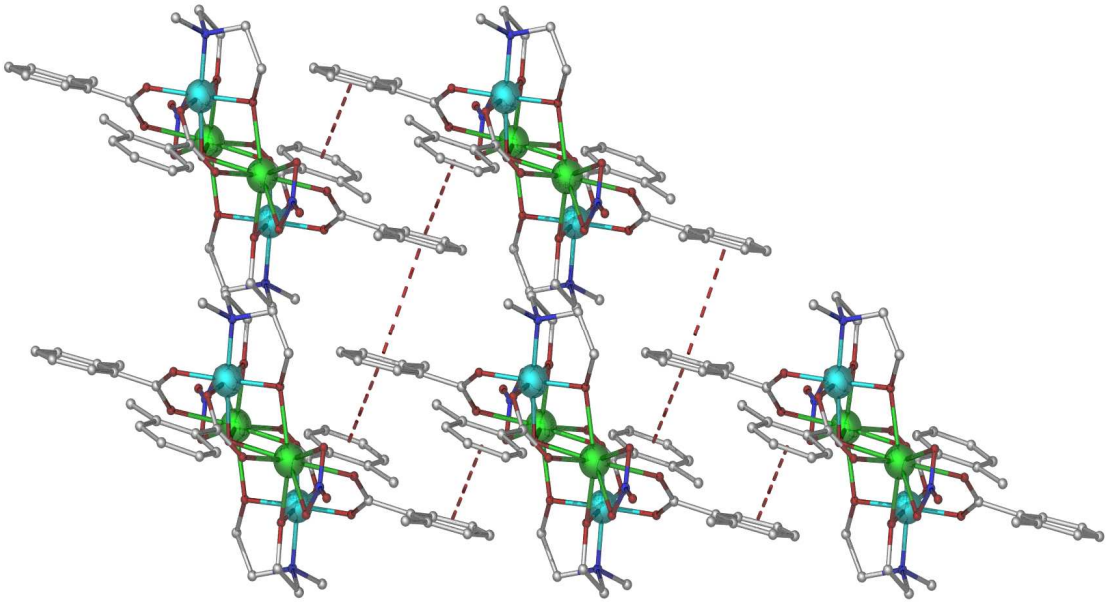

Figure S2. Packing diagram of compound **1**.

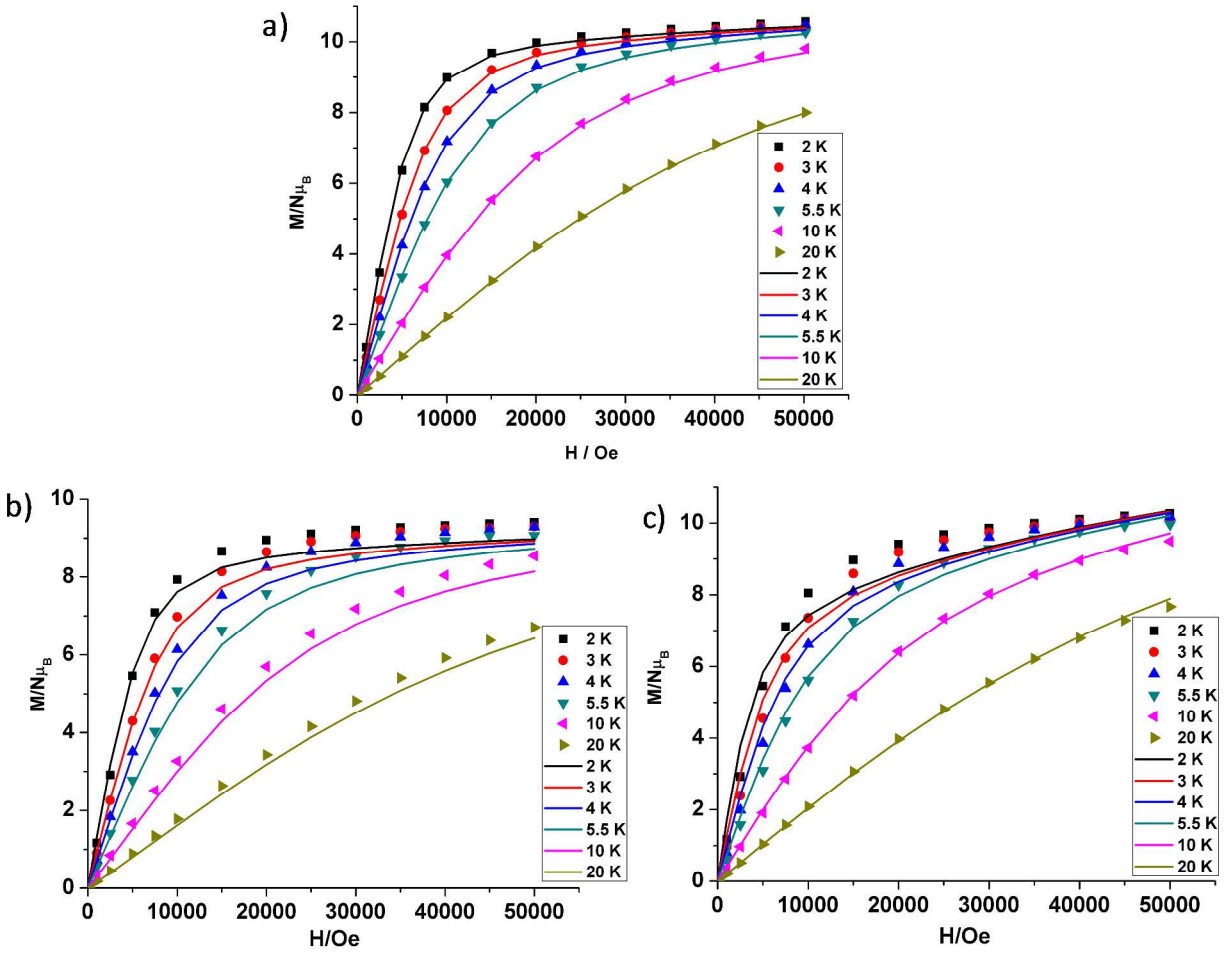

Figure S3. Plots of *M* versus *H* isotherms for complex (a) **1**, (b) **2** and (c) **3** at (top) 2, 3, 4, 5.5, 10 and 20 K (bottom). The solid lines are fits of the data using the Lines model employing the POLY_ANISO program.

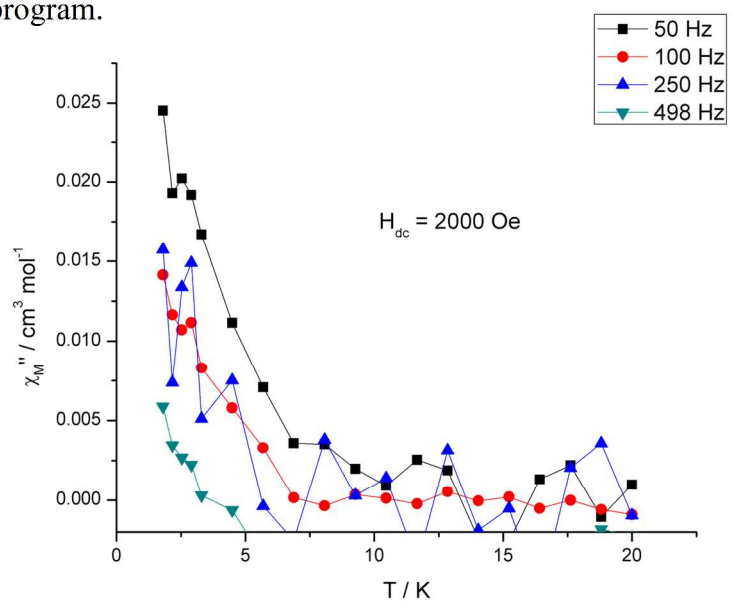

Figure S4. Plot of χ_M'' versus *T* at the frequencies indicated for **3**, with H_{dc} = 2000 Oe.

Table S2. RASSI energies of the lowest spin-orbit states (cm^{-1}) on each Ln^{III} centre in complexes **1-3**.

1		**2**		**3**	
Dy1	Dy2	Tb1	Tb2	Ho1	Ho2
0.000	0.000	0.000	0.000	0.000	0.000
77.518	77.944	0.180	0.180	4.496	2.803
187.362	188.428	138.003	138.003	30.500	21.383
245.927	247.047	143.825	143.825	47.445	35.528
273.979	275.357	224.498	224.498	66.331	81.147
350.793	351.836	275.607	275.607	97.271	112.692
414.201	415.025	301.178	301.178	109.880	128.906
675.248	675.816	430.456	430.456	155.589	181.827
3007.672	3007.902	432.902	432.902	161.296	189.002
3121.455	3122.368	586.366	586.366	194.535	209.606
3198.930	3199.791	586.853	586.853	210.938	220.977
3256.753	3257.755	732.414	732.414	254.550	256.444
3306.966	3308.139	732.466	732.466	264.661	268.214
3369.309	3370.135	2161.662	2161.662	305.168	309.663
3478.925	3479.550	2178.166	2178.166	306.250	310.466
5627.732	5628.189	2221.632	2221.632	366.092	362.572
5706.719	5707.658	2239.221	2239.221	366.748	363.786
5786.619	5787.527	2264.377	2264.377	5188.405	5197.063
5872.554	5873.578	2289.875	2289.875	5189.174	5197.523
5936.345	5936.914	2340.612	2340.612	5218.216	5208.616
5985.662	5986.595	2349.470	2349.470	5222.346	5209.709
7828.198	7828.836	2371.351	2371.351	5228.790	5239.317
7898.865	7899.763	2617.050	2617.050	5232.797	5241.561
8009.336	8010.307	2621.667	2621.667	5236.722	5262.527
8084.503	8084.997	3535.506	3535.506	5249.907	5263.074
8143.135	8144.165	3589.184	3589.184	5253.768	5268.806
9579.315	9580.044	3616.857	3616.857	5280.982	5289.543
9632.636	9633.338	3648.424	3648.424	5282.510	5291.517
9651.289	9652.040	3671.942	3671.942	5354.010	5359.470
9682.810	9683.755	3743.695	3743.695	5354.038	5359.586
9708.704	9709.541	3758.564	3758.564	5425.985	5428.731
9740.580	9741.416	3875.517	3875.517	5425.994	5428.741
9766.709	9767.663	3923.024	3923.024	8914.710	8915.277
9844.046	9844.838	4675.159	4675.159	8917.676	8916.051
9870.777	9871.459	4712.132	4712.132	8929.768	8945.049
9934.700	9935.602	4763.142	4763.142	8935.360	8949.052
10988.281	10988.865	4794.402	4794.402	8952.760	8963.304
11145.048	11146.198	4831.172	4831.172	8958.627	8965.480
11376.379	11377.106	4877.354	4877.354	8973.794	8984.922
11824.213	11825.057	4884.312	4884.312	8987.742	8987.682
11887.969	11888.803	5514.766	5514.766	8994.335	9002.859
11909.116	11909.897	5560.952	5560.952	9025.782	9032.015
11935.388	11936.162	5634.706	5634.706	9028.712	9037.794
11954.771	11955.643	5701.439	5701.439	9138.676	9143.316
13610.828	13611.678	5767.408	5767.408	9139.019	9143.834

13658.455	13659.238	6093.504	6093.504	11677.642	11680.385
13716.697	13717.545	6164.920	6164.920	11681.914	11680.563
13730.017	13730.828	6415.986	6415.986	11698.956	11714.717
15021.754	15022.568	6534.603	6534.603	11704.588	11717.850
15068.013	15068.846	24322.096	24322.096	11724.676	11738.695
15096.964	15097.791	24325.850	24325.850	11737.541	11740.852
16045.284	16046.122	24347.707	24347.707	11750.913	11757.443
16065.051	16065.862	24367.489	24367.489	11778.709	11783.177
16652.139	16652.967	24379.545	24379.545	11784.009	11792.302
38808.092	38808.777	24429.350	24429.350	11891.033	11895.420
38874.361	38874.855	24432.789	24432.789	11894.449	11899.352
38964.378	38965.038	24546.624	24546.624	13776.924	13789.510
39169.683	39170.847	24547.038	24547.038	13811.504	13820.204
40207.265	40208.009	29859.379	29859.379	13855.703	13854.742
40402.279	40403.423	29860.361	29860.361	13879.963	13874.385
40572.803	40573.613	29863.537	29863.537	13908.836	13924.367
41359.981	41360.819	29880.888	29880.888	13958.731	13974.371
41435.882	41436.817	29883.868	29883.868	13988.562	14006.559
		29909.217	29909.217	14076.099	14075.520
		29910.630	29910.630	14091.028	14091.505
		30168.744	30168.744	20594.734	20618.356
		30168.777	30168.777	20594.824	20618.687
		30174.148	30174.148	20638.872	20639.351
		30175.562	30175.562	20639.070	20639.816
		30246.842	30246.842	20695.296	20690.644
		30268.836	30268.836	20700.560	20702.837
		30274.012	30274.012	20748.020	20737.195
		30311.291	30311.291	20773.798	20780.270
		30318.874	30318.874	20792.623	20790.995
		30321.533	30321.533	20856.384	20876.491
		30345.039	30345.039	20858.511	20877.416
		30387.714	30387.714	23402.100	23408.959
		30395.086	30395.086	23402.682	23410.023
		30414.136	30414.136	23412.877	23420.960
		30414.284	30414.284	23416.097	23424.109
		30440.597	30440.597	23419.518	23425.827
		30440.947	30440.947	23769.682	23776.500
		30478.398	30478.398	23773.464	23781.230
		30478.452	30478.452	23875.354	23888.338
		30637.174	30637.174	23891.902	23895.325
		30637.181	30637.181	23896.330	23904.230
		31624.430	31624.430	23933.075	23926.486
		31626.506	31626.506	23936.436	23938.432
		……	…..	…..	…..

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Table S3. The *g*-tensor for the lowest Kramer's doublets in **1**and Ising doublets in **2** and **3**.

Kramers/ Ising doublet		**1**		**2**		**3**	
		Dy1	Dy2	Tb1	Tb2	Ho1	Ho2
1	g_x	0.0005	0.0004	3.2×10^{-8}	3.2×10^{-8}	6.5×10^{-8}	9.5×10^{-8}
	g_y	0.0043	0.0043	1.9×10^{-7}	2.1×10^{-7}	2.4×10^{-7}	1.8×10^{-7}
	g_z	19.9331	19.9282	17.2555	17.2515	16.1007	16.6344
2	g_x	0.1209	0.1189	3.2×10^{-8}	3.2×10^{-8}	3.2×10^{-8}	3.2×10^{-8}
	g_y	0.1274	0.1254	2.4×10^{-8}	7.5×10^{-8}	1.7×10^{-7}	0.0
	g_z	17.2964	17.2730	12.4492	12.4445	17.8588	15.0046
3	g_x	0.2067	0.2024	3.2×10^{-8}	3.2×10^{-8}	3.2×10^{-8}	3.2×10^{-8}
	g_y	0.2888	0.2859	1.2×10^{-7}	1.2×10^{-7}	3.6×10^{-8}	1.1×10^{-7}
	g_z	15.9508	15.9278	8.5401	8.5380	8.9640	7.3652
4	g_x	1.4846	1.4568	3.2×10^{-8}	3.2×10^{-8}	3.2×10^{-8}	3.2×10^{-8}
	g_y	4.7141	4.5711	0.0	3.2×10^{-8}	1.3×10^{-7}	1.7×10^{-7}
	g_z	11.5561	11.6391	12.5372	12.5335	12.1765	11.9757
5	g_x	1.4072	1.4965	3.2×10^{-8}	3.2×10^{-8}	3.2×10^{-8}	3.2×10^{-8}
	g_y	3.1583	3.1519	1.3×10^{-7}	1.0×10^{-8}	1.1×10^{-7}	5.4×10^{-8}
	g_z	13.1035	13.2205	16.8185	16.8135	18.5855	19.1770
6	g_x	7.5133	7.4378	3.2×10^{-8}	0.0	1.5×10^{-7}	1.5×10^{-7}
	g_y	5.0197	5.0307	3.2×10^{-8}	0.0	2.5×10^{-7}	2.4×10^{-7}
	g_z	0.6641	0.7445	17.8030	17.7957	17.8166	17.4206
7	g_x	1.8442	1.8543				
	g_y	5.3857	5.4626				
	g_z	12.5594	12.4749				
8	g_x	0.0257	0.0258				
	g_y	0.0389	0.0392				
	g_z	19.5155	19.5030				

Table S4. Lowest exchange doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel Splitting (Δ_{tun},cm^{-1}), and the g_z value of each doublet (g_x and $g_y = 0$) for complex **1**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.0000000000 0.0000000830	8.3×10^{-8}	0.042910380
2	2.9850281740 2.9850282655	9.1×10^{-8}	39.861241698
3	77.691630765 77.691634779	4.0×10^{-6}	3.318894283
4	78.210366470 78.210389731	2.3×10^{-5}	3.301448787
5	80.264333732 80.264375053	4.1×10^{-5}	37.094681630
6	80.727830551 80.727866581	3.6×10^{-5}	37.081141089
7	155.83770852 155.83779051	8.2×10^{-5}	0.045824643
8	158.06960269 158.06976539	1.6×10^{-4}	34.571262183
9	187.98787112 187.98788136	1.0×10^{-5}	13.604780627
10	189.05038362 189.05039360	9.9×10^{-6}	13.529755574
11	189.72105396 189.72106499	1.1×10^{-5}	33.415023211
12	190.79014407 190.79015437	1.0×10^{-5}	33.429460674

Table S5. Lowest exchange doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel Splitting (Δ_{tun},cm^{-1}), and the g_z value of each doublet (g_x and $g_y = 0$) for complex **2**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.000 0.013	1.30×10^{-2}	0.004192858
2	2.408 2.421	1.30×10^{-2}	34.412407005
3	138.859 138.928	6.90×10^{-2}	0.000935729
4	139.085 139.092	1.30×10^{-2}	0.001814626
5	144.964 145.017	5.30×10^{-2}	0.000866567
6	145.127 145.211	8.40×10^{-2}	0.000223544
7	277.000 282.200	5.2	0.003656115
8	283.519 288.719	5.2	18.568481433

Table S6. Lowest exchange doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel Splitting (Δ_{tun},cm^{-1}), and the g_z value of each doublet (g_x and $g_y = 0$) for complex **3**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.000 2.674	2.674	11.978425512
2	4.710 7.384	2.674	21.156552076
3	21.410 25.884	4.474	14.841768040
4	30.533 33.321	2.788	15.708578564
5	35.606 40.087	4.481	17.377038572
6	47.500 50.299	2.799	17.194496343
7	51.932 65.994	14.062	12.889115427
8	66.378 68.960	2.582	0.877467562
9	69.185 81.187	12.002	0.086043586
10	83.007 85.684	2.677	0.031005308
11	87.784 97.319	9.535	0.168581598
12	100.120 101.907	1.787	0.149776701

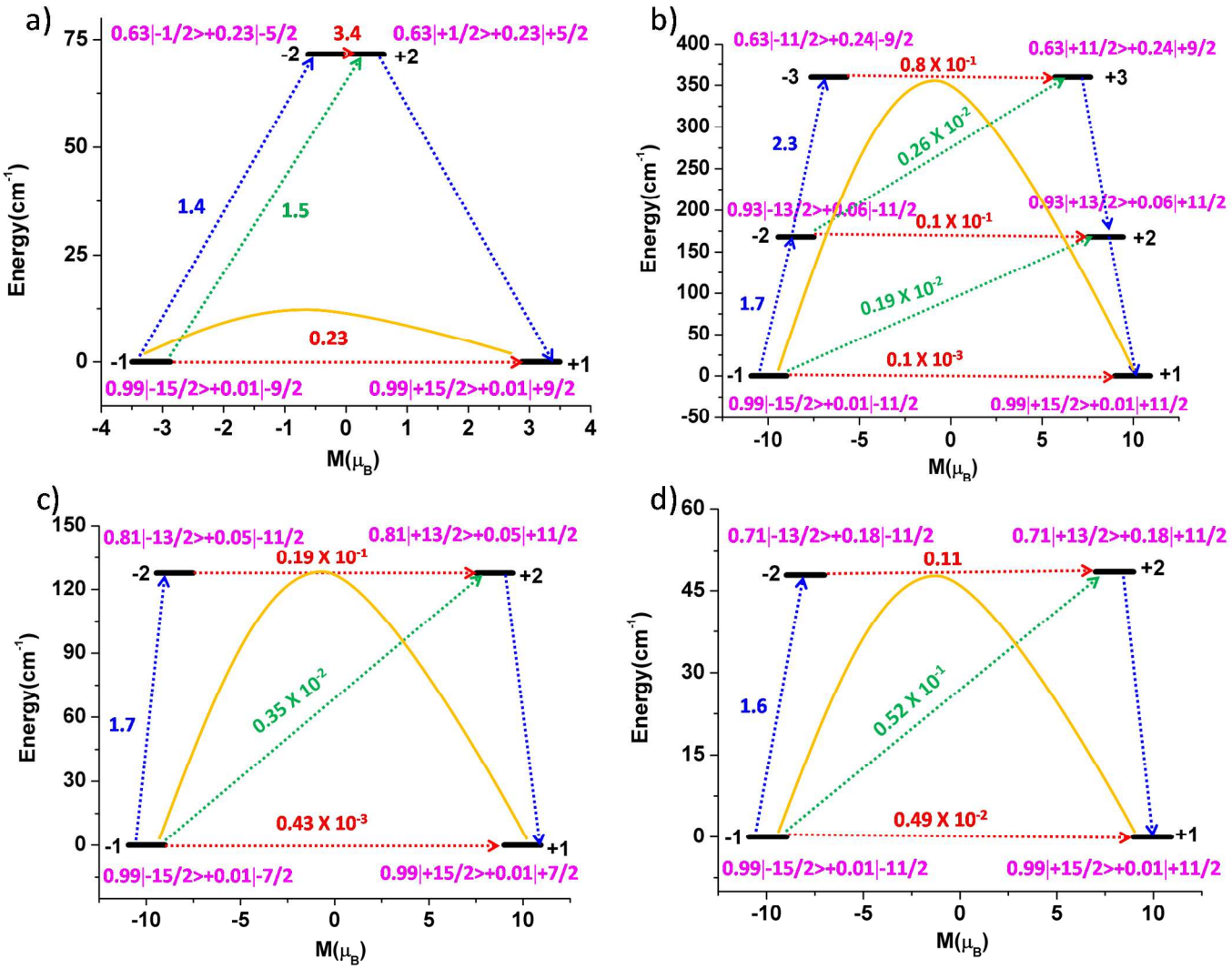

Figure S5. The magnetization blocking barrier for the Dy2 site in a) **1a**; b) **1b**; c) **1c** and d) **1d**. The thick black line indicates the Kramer's doublets (KDs) as a function of computed magnetic moment. The green/blue arrows show the possible pathway through Orbach/Raman relaxation. The dotted red lines represent the presence of QTM/TA-QTM between the connecting pairs. The numbers provided at each arrow are the mean absolute value for the corresponding matrix element of the transition magnetic moment. The yellow curve indicates the most possible relaxation pathway.

Table S7. Lowest exchange doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel Splitting (Δ_{tun},cm^{-1}), and the g_z value of each doublet (g_x and $g_y = 0$) for complex **1a**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.0000000000 0.0023882349	2.4×10^{-3}	0.042910380
2	1.8123182169 1.8157843368	3.5×10^{-3}	39.861241698
3	71.928431770 71.945416605	1.7×10^{-2}	3.318894283
4	72.978622183 73.002898334	2.4×10^{-2}	3.301448787
5	88.725281879 88.742178799	1.7×10^{-2}	37.094681630
6	90.080221324 90.105493908	2.5×10^{-2}	37.081141089

Table S8. Lowest exchange doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel Splitting (Δ_{tun},cm^{-1}), and the g_z value of each doublet (g_x and $g_y = 0$) for complex **1b**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.000000000000 0.000000000243	2.4×10^{-10}	0.104479167
2	1.994892922043 1.994892923003	9.6×10^{-10}	39.892042724
3	167.6776373148 167.6776373304	1.6×10^{-8}	4.219961858
4	168.2175909062 168.2175909362	3.0×10^{-8}	4.286837982
5	169.4037364685 169.4037365532	8.5×10^{-8}	37.131544760
6	169.8742618405 169.8742619391	9.7×10^{-8}	37.134609312
7	335.8322083599 335.8322084319	7.2×10^{-8}	0.124782737
8	337.3437292066 337.3437374757	8.3×10^{-6}	34.824950750
9	359.2747936948 359.2747937506	5.6×10^{-8}	8.958884184
10	360.1375076221 360.1375076772	5.5×10^{-8}	9.015377590
11	360.5946780043 360.5946786707	6.7×10^{-7}	33.885111929
12	361.4568824364 361.4575645633	6.8×10^{-4}	33.887696759
13	527.2379220221 527.2379442802	2.3×10^{-5}	2.722548976
14	527.8461702155 527.8462117816	4.2×10^{-5}	2.787940044

Table S9. Lowest exchange doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel Splitting (Δ_{tun},cm^{-1}), and the g_z value of each doublet (g_x and $g_y = 0$) for complex **1c**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.0000000000 0.0000000061	6.1×10^{-9}	0.048840651
2	1.9960091139 1.9960091318	1.8×10^{-8}	39.913186795
3	127.33080551 127.33080567	1.6×10^{-7}	4.148370298
4	127.86020862 127.86020873	1.1×10^{-7}	4.181403724
5	129.06121958 129.06122032	1.0×10^{-3}	37.152037493
6	129.51979445 129.51979519	7.4×10^{-7}	37.134609312
7	255.13094556 255.13094566	1.0×10^{-7}	0.085591161
8	256.64358915 256.64361905	3.0×10^{-5}	34.820489945
9	289.10290588 289.10290717	1.3×10^{-6}	9.985361010
10	289.96979606 289.96979739	1.3×10^{-6}	9.994438750
11	290.39364111 290.39364441	3.3×10^{-6}	33.798817570
12	291.26047274 291.26047603	3.3×10^{-6}	33.796915733

Table S10. Lowest exchange doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel Splitting (Δ_{tun}, cm^{-1}), and the g_z value of each doublet (g_x and $g_y = 0$) for complex **1d**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.0000000000 0.0000009510	9.5×10^{-7}	0.082042830
2	1.9599345907 1.9599367127	2.1×10^{-6}	39.703958941
3	48.044790561 48.044853866	6.3×10^{-5}	8.056773372
4	48.711645894 48.711665254	1.9×10^{-5}	7.986126667
5	49.634694760 49.635021350	3.2×10^{-4}	36.619339390
6	50.264643795 50.264656497	1.3×10^{-5}	36.601469246
7	94.341995637 94.342122942	1.3×10^{-4}	20.318636243
8	95.055255135 95.055323940	6.9×10^{-5}	31.118070269

Table S11. SINGLE_ANISO computed crystal field parameters for complexes **1-3**. The major components in the Table are in bold. B_k^q is the crystal field parameter and O_k^q is the extended Stevens operator. The quantization axis is chosen to be the main magnetic axis of the ground pseudo-Doublet.

k	q	B_k^q	B_k^q	B_k^q	B_k^q	B_k^q	B_k^q
		Complex **1**		Complex **2**		Complex **3**	
		Dy1	Dy2	Tb1	Tb2	Ho1	Ho2
2	-2	-0.83	-0.80	-1.31	**5.62**	-1.28	-1.16
	-1	**-4.59**	**-4.65**	-1.21	2.06	-1.35	1.41
	0	**-2.40**	**-2.40**	**-4.14**	**-4.14**	**-0.56**	**-0.82**
	1	2.47	2.39	2.58	1.98	**1.98**	**-0.72**
	2	-0.73	-0.75	**7.66**	**-5.33**	0.12	0.23
4	-4	0.01	0.005	4.08×10^{-4}	0.01	-0.001	0.001
	-3	9.65×10^{-4}	0.004	-0.12	0.07	-0.02	0.002
	-2	0.01	0.006	-0.03	0.05	-0.002	0.01
	-1	0.04	0.04	0.01	-0.02	0.01	-0.01
	0	-0.004	-0.004	-0.01	-0.01	-6.07×10^{-4}	9.33×10^{-4}
	1	-0.02	-0.02	-0.03	-0.02	-0.01	0.01
	2	0.005	0.005	0.05	-0.02	-3.85×10^{-4}	0.002
	3	-0.05	-0.05	0.05	-0.11	-0.03	0.002
	4	-0.004	-0.004	-0.01	-0.003	0.004	-0.004
6	-6	1.60×10^{-5}	-1.82×10^{-5}	2.07×10^{-4}	-2.23×10^{-4}	-2.02×10^{-4}	-2.80×10^{-4}
	-5	3.48×10^{-4}	2.99×10^{-4}	5.71×10^{-5}	3.71×10^{-5}	3.78×10^{-4}	2.98×10^{-4}
	-4	1.07×10^{-4}	1.11×10^{-4}	-2.63×10^{-5}	-3.23×10^{-4}	-7.39×10^{-5}	-2.34×10^{-5}
	-3	5.45×10^{-5}	4.74×10^{-5}	5.50×10^{-4}	-4.50×10^{-4}	-6.27×10^{-5}	1.29×10^{-4}
	-2	4.97×10^{-5}	4.97×10^{-5}	1.57×10^{-4}	-4.74×10^{-4}	-1.70×10^{-4}	2.46×10^{-4}
	-1	-1.89×10^{-4}	-1.90×10^{-4}	-9.53×10^{-5}	2.15×10^{-4}	-2.13×10^{-5}	-2.13×10^{-4}
	0	4.18×10^{-5}	4.20×10^{-5}	5.97×10^{-5}	5.97×10^{-5}	-2.27×10^{-5}	2.40×10^{-6}
	1	8.39×10^{-5}	7.72×10^{-5}	2.54×10^{-4}	1.65×10^{-4}	-8.27×10^{-5}	2.35×10^{-4}
	2	-1.03×10^{-5}	-7.89×10^{-6}	-4.64×10^{-4}	2.02×10^{-4}	-8.70×10^{-5}	5.54×10^{-5}
	3	1.42×10^{-4}	1.40×10^{-4}	1.55×10^{-5}	3.07×10^{-4}	-1.01×10^{-4}	-4.82×10^{-5}
	4	-4.83×10^{-5}	-4.03×10^{-5}	3.31×10^{-4}	7.61×10^{-5}	1.93×10^{-4}	-6.09×10^{-7}
	5	4.74×10^{-3}	5.08×10^{-3}	7.15×10^{-4}	7.13×10^{-4}	8.88×10^{-4}	-1.88×10^{-5}
	6	2.68×10^{-3}	2.67×10^{-3}	-3.07×10^{-4}	-2.96×10^{-4}	-1.35×10^{-4}	-2.03×10^{-5}

Table S12. SINGLE_ANISO computed crystal field parameters for complexes **1a** and **1b**. The major components in the Table are in bold. B_k^q is the crystal field parameter and O_k^q is the extended Stevens operator. The quantization axis is chosen to be the main magnetic axis of the ground pseudo-Doublet.

k	q	B_k^q	B_k^q	B_k^q	B_k^q
		Complex **1a**		Complex **1b**	
		Dy1	Dy2	Dy1	Dy2
2	-2	-0.58	2.07	-0.09	-0.1
	-1	-0.06	-0.07	**-5.91**	**-5.93**
	0	-3.45	-3.14	**-3.35**	**-3.36**
	1	**-6.79**	**-7.08**	0.59	0.47
	2	**6.0**	**6.11**	-0.98	-0.96
4	-4	-0.002	0.01	-0.01	0.006
	-3	-0.001	-0.03	-0.04	0.04
	-2	0.004	-0.001	-0.001	-0.001
	-1	-0.002	0.003	-0.03	0.03
	0	-0.003	-0.003	-0.01	-0.007
	1	0.03	0.03	-0.001	-0.001
	2	0.02	0.02	-0.001	-0.001
	3	-0.07	-0.07	-0.01	-0.001
	4	-0.02	-0.02	-0.005	0.005
6	-6	2.20×10^{-5}	1.12×10^{-5}	-0.89×10^{-4}	-0.87×10^{-4}
	-5	2.75×10^{-4}	-0.001	-0.78×10^{-3}	-0.77×10^{-3}
	-4	3.70×10^{-5}	1.34×10^{-4}	0.50×10^{-4}	0.49×10^{-4}
	-3	-4.89×10^{-5}	2.90×10^{-5}	0.82×10^{-4}	0.85×10^{-4}
	-2	-1.87×10^{-5}	-3.59×10^{-5}	0.28×10^{-4}	0.26×10^{-4}
	-1	-9.68×10^{-6}	-3.14×10^{-5}	0.68×10^{-4}	0.68×10^{-4}
	0	2.66×10^{-5}	2.37×10^{-5}	0.51×10^{-4}	0.51×10^{-4}
	1	9.92×10^{-5}	1.11×10^{-4}	-0.52×10^{-4}	-0.43×10^{-4}
	2	-1.83×10^{-4}	-2.2×10^{-4}	-0.32×10^{-4}	-0.34×10^{-4}
	3	-2.43×10^{-4}	-2.05×10^{-4}	0.21×10^{-4}	0.17×10^{-4}
	4	1.91×10^{-4}	1.45×10^{-4}	0.15×10^{-3}	0.15×10^{-3}
	5	-1.69×10^{-4}	3.88×10^{-4}	0.39×10^{-3}	0.37×10^{-3}
	6	3.78×10^{-4}	2.90×10^{-4}	-0.69×10^{-4}	-0.71×10^{-4}

Table S13. SINGLE_ANISO computed crystal field parameters for complexes **1c** and **1d**. The major components in the Table are in bold. B_k^q is the crystal field parameter and O_k^q is the extended Stevens operator. The quantization axis is chosen to be the main magnetic axis of the ground pseudo-Doublet.

k	q	B_k^q	B_k^q	B_k^q	B_k^q
		Complex **1c**		Complex **1d**	
		Dy1	Dy2	Dy1	Dy2
2	-2	-0.206	-0.23	-0.68	-0.68
	-1	**-5.83**	**-5.84**	**-3.37**	**-3.33**
	0	**-2.90**	**-2.91**	-1.29	-1.29
	1	0.83	0.82	**4.44**	**4.47**
	2	-1.09	-1.08	-0.16	-0.15
4	-4	0.006	0.01	-0.7×10^{-5}	-0.11×10^{-3}
	-3	0.04	0.04	-0.06	-0.06
	-2	-5.26×10^{-4}	-5.77×10^{-4}	-0.003	-0.003
	-1	0.04	0.04	0.02	0.02
	0	-0.01	-0.006	-0.005	-0.005
	1	-0.003	-0.004	-0.02	-0.02
	2	0.002	0.002	0.002	0.002
	3	-0.02	-0.02	-0.01	-0.01
	4	0.004	0.004	0.001	0.001
6	-6	-1.73×10^{-4}	-1.74×10^{-4}	0.75×10^{-4}	0.71×10^{-4}
	-5	-6.78×10^{-4}	-6.69×10^{-4}	0.26×10^{-3}	0.26×10^{-3}
	-4	6.13×10^{-5}	6.44×10^{-5}	-0.1×10^{-3}	-0.1×10^{-3}
	-3	1.54×10^{-5}	2.03×10^{-5}	0.81×10^{-4}	0.75×10^{-4}
	-2	3.75×10^{-5}	3.50×10^{-5}	0.11×10^{-3}	0.11×10^{-3}
	-1	-2.70×10^{-5}	-2.74×10^{-5}	-0.60×10^{-5}	-0.81×10^{-5}
	0	5.02×10^{-5}	5.02×10^{-5}	0.39×10^{-4}	0.39×10^{-4}
	1	-3.09×10^{-5}	-2.79×10^{-5}	-0.9×10^{-4}	-0.94×10^{-4}
	2	1.28×10^{-5}	1.06×10^{-5}	-0.61×10^{-4}	-0.6×10^{-4}
	3	5.01×10^{-5}	4.73×10^{-5}	-0.11×10^{-4}	-0.13×10^{-4}
	4	1.27×10^{-4}	1.26×10^{-4}	-0.11×10^{-3}	-0.11×10^{-3}
	5	4.28×10^{-4}	4.42×10^{-4}	-0.4×10^{-3}	-0.42×10^{-3}
	6	-9.13×10^{-5}	-8.77×10^{-5}	-0.3×10^{-3}	-0.3×10^{-3}

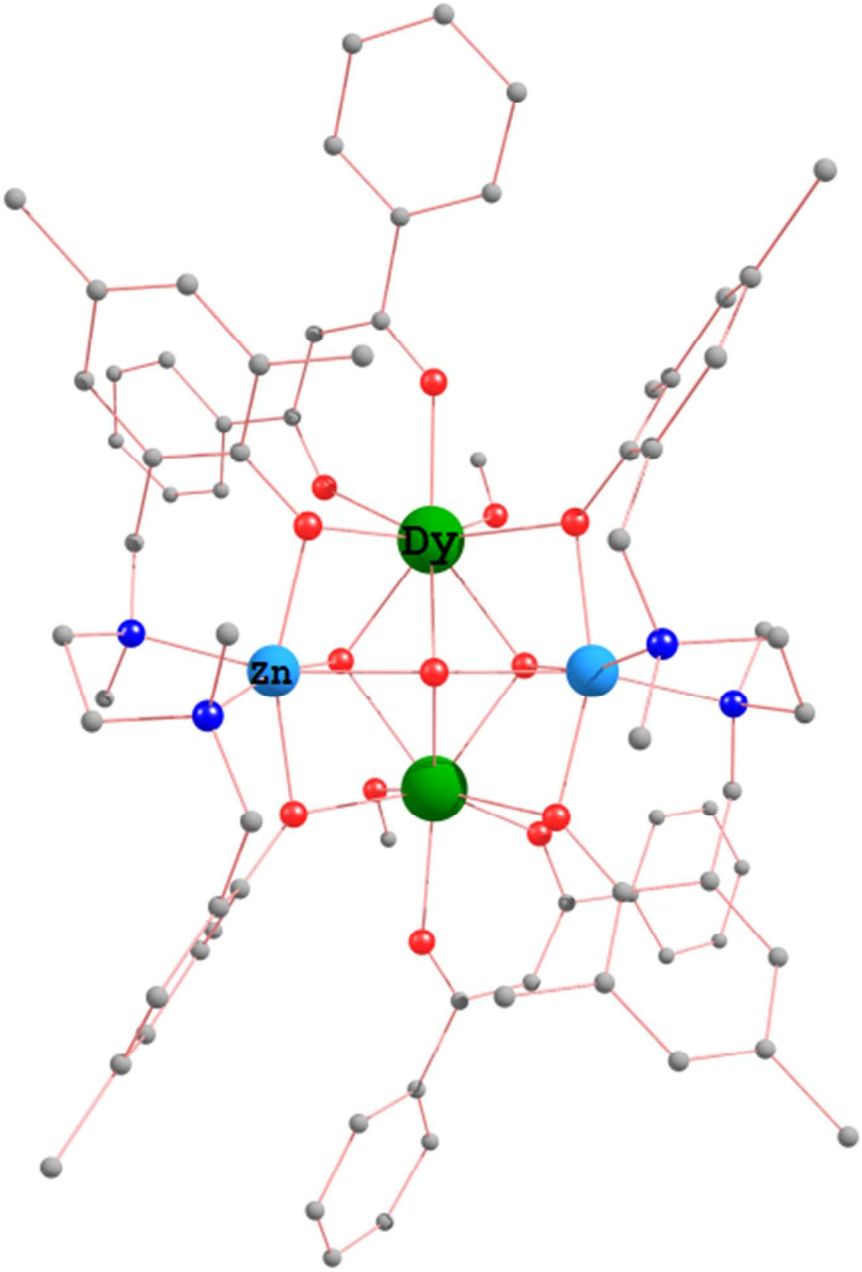

Figure S6. Molecular structure ofthe reported{$Dy^{III}_2Zn^{III}_2$} complex (See ref.45b, *Inorg. Chem.* **2012,***51*, 10211-10221).

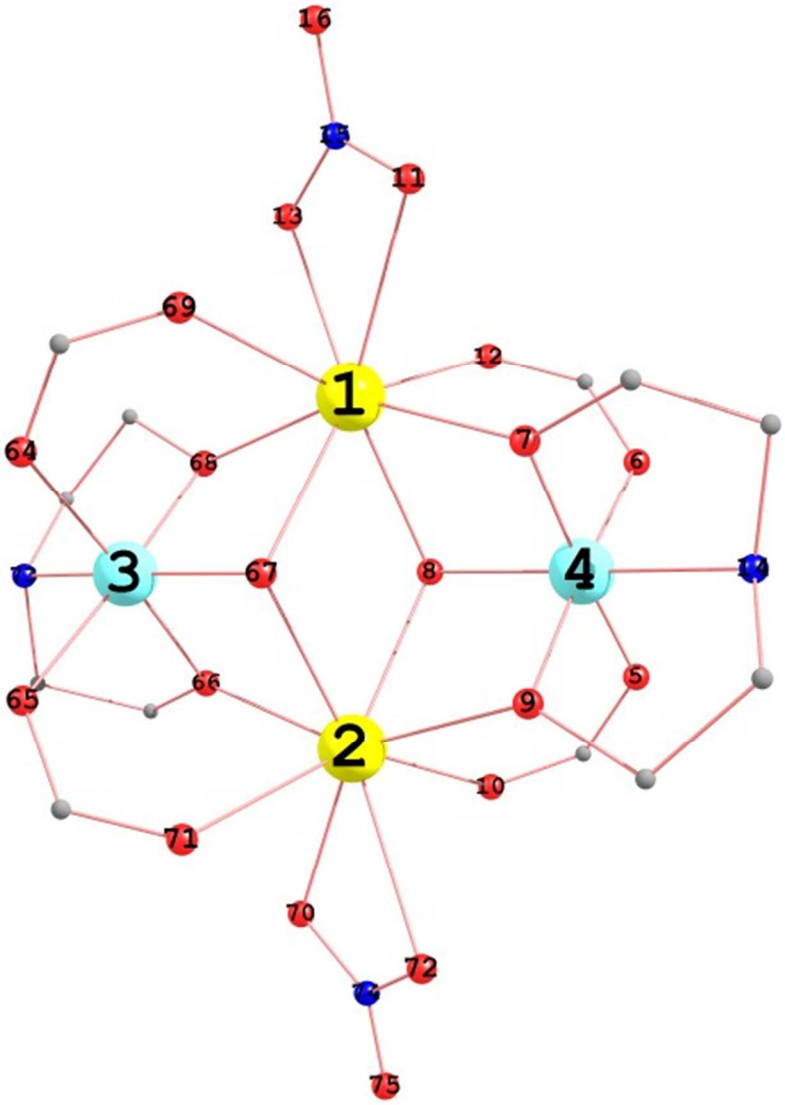

Figure S7. Labelled core structure of **1e** which can be directly compared to the numbering scheme used in the DFT calculated parameters given in Table S14, below.

Table S14. DFT computed Mulliken charges on the donor atoms of complex **1e** (with the hydrogen's summed in to heavy atoms)

1 Gd 1.791392	31 C 0.004480	73 N -0.488643
2 Gd 1.791143	33 C 0.022097	74 N 0.738469
3 Co 0.752310	34 C 0.023970	75 O -0.418449
4 Co 0.752141	35 C 0.182094	76 C 0.334148
5 O -0.533304	38 C 0.072736	79 C 0.522165
6 O -0.526966	39 C -0.067799	80 C 0.007508
7 O -0.688757	41 C 0.033732	82 C 0.527023
8 O -0.691544	45 C 0.020699	83 C 0.353286
9 O -0.423542	47 C -0.004810	86 C 0.077098
10 O -0.539708	49 C -0.059476	87 C 0.196542
11 O -0.505498	51 C 0.046408	90 C 0.004046
12 O -0.550244	55 C -0.009460	92 C 0.021766
13 O -0.501798	57 C 0.018538	93 C 0.023757
14 N -0.488477	59 C 0.296527	94 C 0.182065
15 N 0.739013	64 O -0.533392	97 C 0.072927
16 O -0.418432	65 O -0.527423	98 C -0.068607
17 C 0.334484	66 O -0.688693	100 C 0.033730
20 C 0.522108	67 O -0.691745	104 C 0.021105
21 C 0.007011	68 O -0.423444	106 C -0.004484
23 C 0.526941	69 O -0.540062	108 C -0.059569
24 C 0.353203	70 O -0.505169	110 C 0.046548
27 C 0.076135	71 O -0.550091	114 C -0.009456
28 C 0.196317	72 O -0.501552	116 C 0.018549
		118 C 0.296386

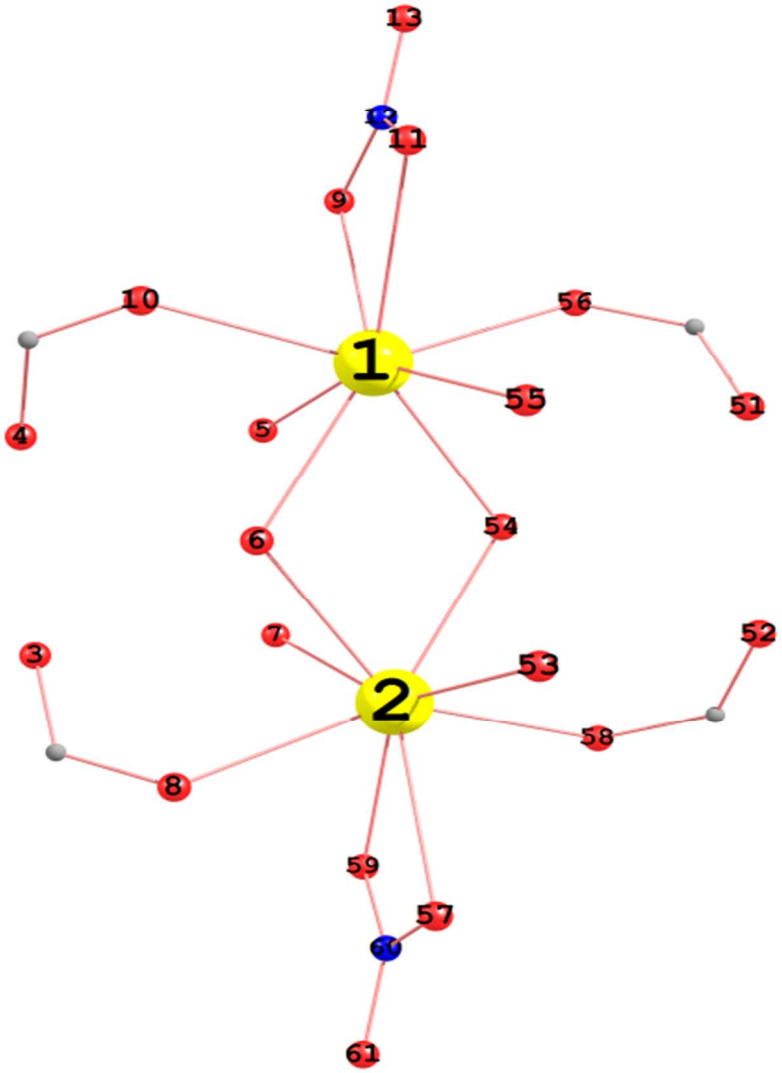

Figure S8. Labelled core structure of **1f** which can be directly compared to the numbering scheme used in the DFT calculated parameters given in Table S15, below.

Table S15. DFT computed Mulliken charges on the donor atoms of complex **1f** (with the hydrogen's summed in to heavy atoms)

1 Gd 1.634181	32 C 0.017456	73 C -0.045175
2 Gd 1.625078	36 C -0.046165	75 C 0.040175
3 O -0.512982	38 C -0.003121	76 C 0.045285
4 O -0.505334	40 C -0.113404	77 C 0.064830
5 O -0.189510	42 C 0.006248	78 C -0.115439
6 O -0.388328	46 C -0.058096	80 C 0.009058
7 O -0.223776	48 C -0.049398	84 C -0.043221
8 O -0.593940	51 O -0.529195	86 C 0.004946
9 O -0.510638	52 O -0.524832	88 C -0.104291
10 O -0.605709	53 O -0.199492	90 C 0.017893
11 O -0.506071	54 O -0.393063	94 C -0.048598
12 N 0.746002	55 O -0.188475	96 C -0.038107
13 O -0.459902	56 O -0.591929	93 C 0.023757
14 C 0.244152	57 O -0.506538	94 C 0.182065
17 C 0.449667	58 O -0.583120	97 C 0.072927
18 C -0.029589	59 O -0.510078	98 C -0.068607
20 C 0.439120	60 N 0.744960	100 C 0.033730
21 C 0.297224	61 O -0.456581	104 C 0.021105
24 C 0.069830	62 C 0.228311	106 C -0.004484
25 C -0.048577	65 C 0.454094	108 C -0.059569
27 C 0.041572	66 C -0.022515	110 C 0.046548
28 C 0.047906	68 C 0.442248	114 C -0.009456
29 C 0.063169	69 C 0.254579	116 C 0.018549
30 C -0.115004	72 C 0.072208	118 C 0.296386

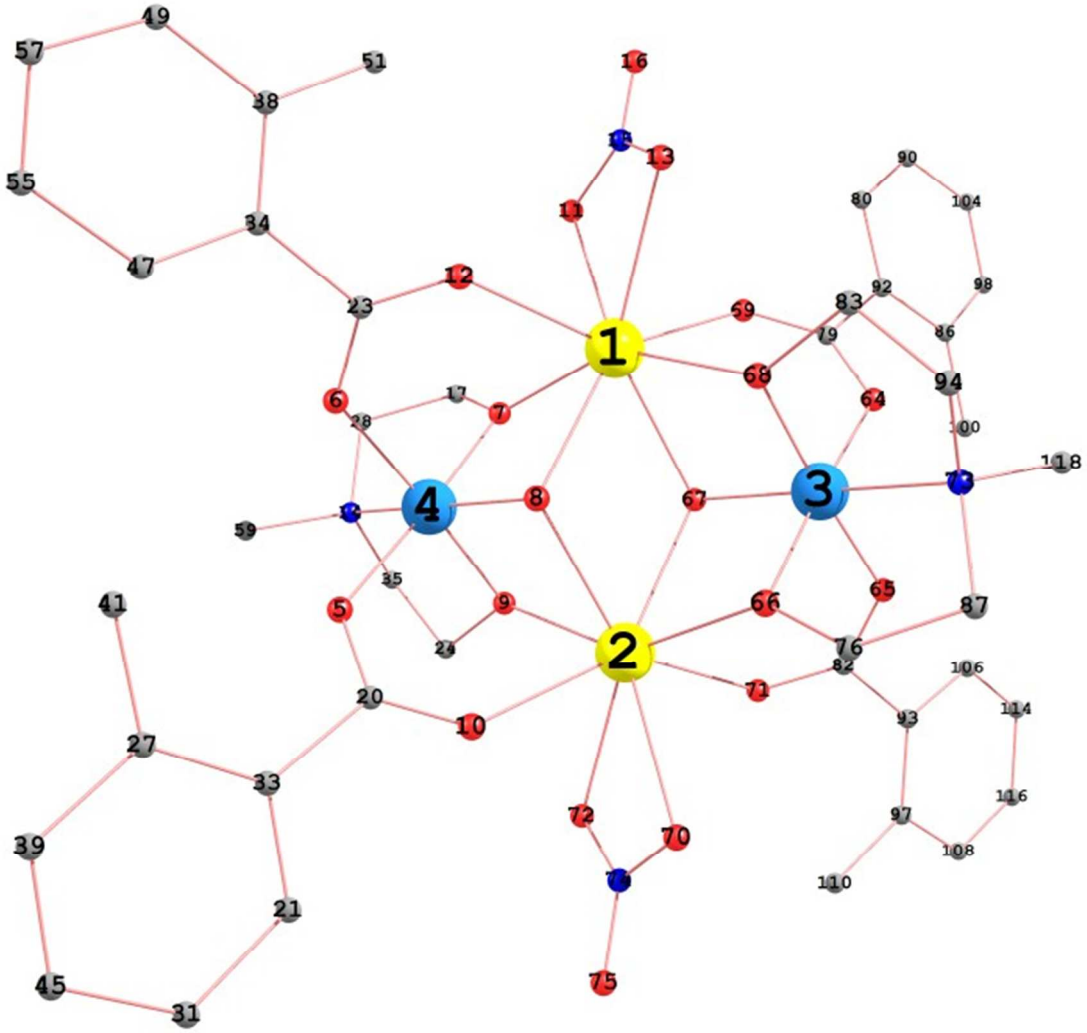

Figure S9. Labelled core structure of **1g** which can be directly compared to the numbering scheme used in the DFT calculated parameters given in Table S16, below.

Table S16. DFT computed Mulliken charges on the donor atoms of complex **1g** (with the hydrogen's summed in to heavy atoms)

1 Gd 1.857599	33 C -0.250231	75 O -0.203987
2 Gd 1.856632	34 C -0.203047	76 C 0.057434
3 Zn 1.538131	35 C 0.072244	79 C 0.052902
4 Zn 1.538470	38 C 0.206934	80 C 0.319860
5 O -0.411593	39 C -0.169534	82 C 0.047592
6 O -0.434212	41 C -0.068317	83 C 0.052524
7 O -0.714453	45 C 0.060591	86 C 0.275935
8 O -0.795743	47 C 0.373799	87 C 0.003831
9 O -0.705751	49 C -0.089260	90 C -0.155919
10 O -0.394161	51 C -0.063868	92 C -0.254545
11 O -0.252331	55 C -0.215490	93 C -0.205283
12 O -0.406999	57 C 0.045710	94 C 0.072036
13 O -0.250443	59 C 0.085807	97 C 0.208071
14 N -0.305988	64 O -0.411710	98 C -0.176113
15 N 0.044486	65 O -0.434608	100 C -0.066903
16 O -0.203227	66 O -0.714146	104 C 0.065416
17 C 0.057074	67 O -0.796027	106 C 0.376651
20 C 0.055240	68 O -0.706197	108 C -0.090899
21 C 0.313225	69 O -0.394475	110 C -0.063187
23 C 0.048103	70 O -0.251700	114 C -0.216999
24 C 0.052626	71 O -0.406695	116 C 0.047149
27 C 0.269977	72 O -0.250124	118 C 0.085829
28 C 0.004149	73 N -0.305482	
31 C -0.150826	74 N 0.044446	