SUPPORTING INFORMATION FOR

Control of Magnetic Anisotropy by Macrocyclic Ligand Distortion in a Family of Dy^{III} and Er^{III} Single Molecule Magnets

Yolimar Gil,[a,b] Pablo Fuentealba,[a] Andrés Vega,[b,c] Evgenia Spodine,[*a,b]

Daniel Aravena.[*d]

[a] *Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile.*

[b] *Centro para el Desarrollo de la Nanociencia y Nanotecnología (CEDENNA)*

[c] *Departamento de Ciencias Químicas, Universidad Andrés Bello, Santiago, Chile.*

[d] *Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile.*

Table S1. Crystal data and structure refinement details for Dy^{III} and Er^{III} complexes.

	1-Dy	**2-Dy**	**3-Dy**	**1-Er**	**2-Er**	**3-Er**
Chemical formula	$C_{21}H_{18}DyN_9S_3$	$C_{23}H_{22}DyN_9S_3$	$C_{29}H_{18}DyN_9S_3$, C_2H_3N	$C_{21}H_{18}ErN_9S_3$	$C_{23}H_{22}ErN_9S_3$	$C_{29}H_{18}ErN_9S_3$, C_2H_3N
M_r	655.12	683.17	792.26	659.88	687.94	796.01
Cr. Syst.	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space gr.	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	7.9518(10)	8.449(15)	22.428(4)	8.003(11)	8.453(6)	22.426(8)
b (Å)	12.835(15)	12.612(2)	8.3139(14)	12.842(17)	12.586(9)	8.327(3)
c (Å)	12.866(15)	13.166(2)	18.411(3)	12.857(17)	13.169(9)	18.470(7)
α (°)	100.522(1)	97.249(2)	90	99.871(1)	97.086(1)	90
β (°)	98.214(1)	105.438(2)	108.319(2)	104.272(1)	105.583(1)	108.591(5)
γ (°)	104.071(1)	97.531(2)	90	98.376(1)	97.529(1)	90
V (Å^3)	1228.0(3)	1321.6(4)	3259.0(10)	1236.9(3)	1319.43(16)	3269(2)
Z	2	2	4	2	2	4
Radiation	Mo K_α	Mo K_α	Mo K_α	Mo K_α	Mo K_α	Mo K_α
μ (mm^{-1})	3.327	3.095	2.521	3.675	3.449	2.797
Crystal size (mm)	0.09 × 0.15 × 0.24	0.11 × 0.12 × 0.25	0.04 × 0.06 × 0.22	0.24 × 0.26 × 0.31	0.05 × 0.08 × 0.13	0.06 × 0.07 × 0.12
T_{min}	0.455	0.184,	0.824	0.146	0.716	0.374
T_{max}	1.000	0.250	0.916	0.265	0.850	0.746
Total, unique, observed data [I > 2σ(I)]	9626, 4817, 4572	10386, 5196, 4180	24630, 6403, 5131	9677, 4845, 4519	10369, 5186, 4839	24695, 6414, 4233
R_{int}	0.025	0.056	0.059	0.028	0.017	0.145
R, wR, S	0.0197, 0.0473, 1.03	0.0406, 0.0837, 0.99	0.0456, 0.1148, 1.12	0.0232,0.0568, 1.05	0.0193,0.0428, 1.03	0.0565, 0.1382, 1.04
N. Ref, N. Par	4817, 308	5196, 325	6403, 408	4845, 307	5186, 325	6414, 408
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	-0.88, 0.99	-0.81, 0.64	-1.15, 1.06	-0.63, 1.01	-0.74, 0.97	-1.51, 1.21

Table S2. Ln-N bond distances (Å) for dysprosium(III) and erbium(III) complexes.

	Bond Distances (Å)					
	1-Dy	**2-Dy**	**3-Dy**	**1-Er**	**2-Er**	**3-Er**
Ln - N1[a]	2.609(2)	2.591(5)	2.630(5)	2.618(3)	2.570(2)	2.628(7)
Ln - N2	2.608(2)	2.582(5)	2.638(5)	2.531(3)	2.544(2)	2.606(7)
Ln - N3	2.548(3)	2.613(5)	2.598(5)	2.598(3)	2.603(3)	2.629(7)
Ln - N4[a]	2.629(2)	2.578(5)	2.619(5)	2.595(3)	2.579(2)	2.613(6)
Ln - N5	2.636(2)	2.549(5)	2.640(5)	2.543(3)	2.562(3)	2.589(7)
Ln - N6	2.553(2)	2.613(5)	2.621(5)	2.618(3)	2.611(2)	2.617(7)
Ln - N7[b]	2.400(3)	2.412(5)	2.401(6)	2.382(4)	2.399(3)	2.373(7)
Ln - N8[b]	2.411(3)	2.417(5)	2.386(7)	2.391(4)	2.394(3)	2.344(7)
Ln - N9[b]	2.373(3)	2.407(5)	2.358(7)	2.348(4)	2.390(3)	2.325(8)

[a] N atom from pyridine ring. [b] N atom corresponding to the isothiocyanate ligands, where N9 is in trans position to the other two nitrogen atoms.

Table S3. Continuous Shape Measurement calculations (CShM) of the first coordination sphere of Dy^{III} and Er^{III} complexes, referring to all standard 9 vertices of the polyhedron.

Structure [ML9]	**1-Dy**	**2-Dy**	**3-Dy**	**1-Er**	**2-Er**	**3-Er**
Enneagon	31.902	33.325	30.737	32.017	33.361	30.764
Octagonal pyramid	20.384	21.872	21.385	20.407	21.970	21.350
Heptagonal bipyramid	14.367	15.898	14.483	14.564	16.139	14.539
Johnson triangular cupola	14.352	14.525	14.452	14.384	14.501	14.518
Capped cube J8	7.891	7.362	5.247	8.076	7.456	5.228
Spherical-relaxed capped cube	6.872	6.255	4.108	7.065	6.391	4.127
Capped square antiprism J10	5.632	4.165	10.083	5.363	4.026	9.929
Spherical capped square antiprism	4.434	3.098	8.892	4.193	2.983	8.792
Tricapped trigonal prism J51	5.634	4.798	9.225	5.482	4.682	9.062
Spherical tricapped trigonal prism	5.209	3.814	10.032	4.904	3.687	9.896
Tridiminished icosahedron J63	11.534	11.333	11.798	11.647	11.331	12.057
Hula Hoop	4.292	6.323	**2.338**	4.480	6.534	**2.426**
Muffin	**3.171**	**2.045**	6.898	**3.002**	**1.955**	6.819

Table S4. Deviation from the ideal HH geometry for nitrogen atoms in Dy^{III} and Er^{III} complexes.

N atom	Deviation ideal HH for Nitrogen atoms (Å)					
	1-Dy	**1-Er**	**2-Dy**	**2-Er**	**3-Dy**	**3-Er**
py	0.382	0.397	0.294	0.296	0.618	0.622
	0.375	0.385	0.260	0.270	0.568	0.573
imine	0.483	0.489	0.761	0.774	0.132	0.131
	0.600	0.630	0.737	0.750	0.290	0.306
	0.492	0.498	0.830	0.850	0.104	0.114
	0.539	0.575	0.818	0.823	0.188	0.209
SCN	0.630	0.626	0.666	0.667	0.350	0.347
	0.700	0.686	0.665	0.661	0.338	0.336
SCN [a]	0.354	0.349	0.286	0.290	0.446	0.455

[a] SCN in trans position respect to the other two thiocyanate ligands.

Table S5. Parameters from the fit of Cole-Cole plots for **1-Dy**, **2-Dy**, **2-Er** and **3-Er**.

Complex	**T**				
1-Dy	1.8	7.33E-01	4.30	1.42E-03	1.24E-01
	1.9	6.88E-01	4.12	1.29E-03	1.40E-01
	2	6.64E-01	3.90	1.11E-03	1.38E-01
	2.1	6.34E-01	3.79	9.68E-04	1.40E-01
	2.3	5.86E-01	3.61	7.41E-04	1.40E-01
	2.5	5.46E-01	3.43	5.29E-04	1.30E-01
	2.7	5.12E-01	3.28	3.67E-04	1.15E-01
	2.9	4.76E-01	3.15	2.50E-04	1.00E-01
	3.2	4.07E-01	2.99	1.39E-04	8.06E-02
	3.5	2.68E-01	2.94	7.57E-05	7.32E-02
	3.8	3.28E-05	3.02	3.99E-05	7.29E-02
	4.1	3.28E-05	2.86	2.45E-05	5.69E-02
	4.5	3.28E-05	2.67	1.14E-05	1.03E-01
	5	3.28E-05	2.44	5.47E-06	8.67E-02
	5.5	3.28E-05	2.25	2.76E-06	7.02E-02
	6	3.28E-05	2.08	7.46E-07	1.66E-01
2-Dy	1.8	6.90E-01	3.72	3.35E-03	1.22E-01
	1.9	6.59E-01	3.55	2.89E-03	1.29E-01
	2	6.39E-01	3.33	2.27E-03	1.14E-01
	2.1	6.12E-01	3.20	1.79E-03	1.05E-01
	2.3	5.69E-01	3.02	1.13E-03	9.17E-02
	2.5	5.28E-01	2.86	6.76E-04	7.76E-02
	2.7	4.91E-01	2.72	4.10E-04	6.67E-02
	2.9	4.51E-01	2.61	2.54E-04	5.89E-02

	3.1	4.14E-01	2.52	1.62E-04	5.22E-02
	3.3	3.65E-01	2.44	1.05E-04	4.75E-02
	3.5	3.01E-01	2.39	6.96E-05	4.33E-02
	3.7	2.47E-01	2.33	4.74E-05	3.82E-02
	4	1.26E-01	2.31	2.64E-05	4.85E-02
	4.3	5.81E-02	2.24	1.61E-05	4.10E-02
	4.6	4.86E-02	2.12	9.45E-06	5.73E-02
	5	4.42E-02	1.98	5.34E-06	5.23E-02
	5.5	4.13E-02	1.81	2.65E-06	4.60E-02
	6	3.99E-02	1.68	1.23E-06	3.97E-02
2-Er	1.8	9.58E-01	6.28	2.37E-03	7.32E-02
	1.9	9.08E-01	6.03	1.97E-03	8.02E-02
	2	8.58E-01	5.73	1.51E-03	8.01E-02
	2.1	8.14E-01	5.44	1.12E-03	7.74E-02
	2.2	7.91E-01	5.29	9.14E-04	7.20E-02
	2.3	7.47E-01	5.05	6.18E-04	6.70E-02
	2.4	7.03E-01	4.86	4.25E-04	6.32E-02
	2.5	6.54E-01	4.70	2.86E-04	6.00E-02
	2.6	5.83E-01	4.59	1.88E-04	5.94E-02
	2.7	4.79E-01	4.52	1.21E-04	6.02E-02
	2.8	3.12E-01	4.52	7.59E-05	6.11E-02
	2.9	1.89E-02	4.65	4.58E-05	5.96E-02
	3	1.21E-07	4.57	2.96E-05	7.41E-02
	3.1	1.21E-07	4.44	1.95E-05	7.39E-02
	3.2	1.21E-07	4.31	1.27E-05	7.96E-02
	3.4	1.21E-07	4.08	5.16E-06	1.03E-01
	3.6	1.21E-07	3.88	1.90E-06	1.39E-01
	3.8	1.21E-07	3.70	1.02E-06	9.04E-02
	4	1.21E-07	3.53	3.92E-07	5.64E-02
3-Er	1.8	1.32E-01	5.19	9.62E-02	4.10E-01
	1.9	1.28E-01	4.94	8.44E-02	4.09E-01
	2	1.31E-01	4.68	7.20E-02	4.03E-01
	2.1	1.35E-01	4.41	6.05E-02	3.94E-01
	2.3	1.45E-01	3.95	4.33E-02	3.69E-01
	2.5	1.57E-01	3.53	3.01E-02	3.37E-01
	2.7	1.67E-01	3.18	2.12E-02	3.03E-01
	2.9	1.73E-01	2.90	1.53E-02	2.72E-01
	3.1	1.76E-01	2.67	1.12E-02	2.44E-01
	3.3	1.78E-01	2.48	8.43E-03	2.20E-01
	3.5	1.78E-01	2.32	6.43E-03	1.98E-01
	3.7	1.77E-01	2.19	4.96E-03	1.80E-01
	3.9	1.76E-01	2.07	3.86E-03	1.64E-01
	4.1	1.75E-01	1.96	3.06E-03	1.51E-01

4.3	1.73E-01	1.87	2.46E-03	1.39E-01
4.5	1.70E-01	1.79	1.98E-03	1.30E-01
4.7	1.69E-01	1.71	1.61E-03	1.20E-01
4.9	1.66E-01	1.64	1.32E-03	1.13E-01
5.1	1.63E-01	1.58	1.08E-03	1.06E-01
5.3	1.61E-01	1.51	8.95E-04	9.97E-02
5.5	1.60E-01	1.46	7.42E-04	9.42E-02
5.7	1.60E-01	1.40	6.16E-04	8.91E-02
5.9	1.60E-01	1.35	5.10E-04	8.45E-02
6.1	1.62E-01	1.31	4.23E-04	7.95E-02
6.3	1.67E-01	1.26	3.51E-04	7.44E-02
6.5	1.72E-01	1.21	2.89E-04	6.90E-02
6.7	1.81E-01	1.16	2.38E-04	6.22E-02
6.9	1.89E-01	1.11	1.95E-04	5.57E-02
7.1	2.02E-01	1.07	1.59E-04	4.93E-02
7.3	2.15E-01	1.02	1.29E-04	4.35E-02
7.5	2.33E-01	0.97	1.06E-04	3.68E-02
7.7	2.42E-01	0.93	8.58E-05	3.73E-02
7.9	2.74E-01	0.87	7.17E-05	2.31E-02
8.1	2.91E-01	0.83	5.82E-05	2.31E-02
8.4	3.09E-01	0.77	4.22E-05	2.29E-02
8.7	3.66E-01	0.68	3.25E-05	2.32E-02

Table S6. Fitting parameters for two generalised Debye models for **1-Dy** and **2-Dy**. Relaxation times for single Debye model to the dominant Cole-Cole semicircle is presented for comparison (τ_{ref}).

Complex	T	$\chi_{s,tot}$	χ_{T1}	τ_1	α_1	χ_{T2}	τ_2	α_2	τ_{ref}
1-Dy	1.8	7.60E-01	4.21	1.39E-03	1.09E-01	0.66	9.24E-02	1.00E-02	1.42E-03
	1.9	7.27E-01	4.00	1.25E-03	1.18E-01	0.76	9.91E-02	5.10E-02	1.29E-03
	2	7.01E-01	3.73	1.06E-03	1.15E-01	1.08	1.59E-01	2.62E-01	1.11E-03
	2.1	6.71E-01	3.63	9.35E-04	1.17E-01	1.05	1.82E-01	2.58E-01	9.68E-04
	2.3	6.26E-01	3.48	7.22E-04	1.18E-01	0.85	1.46E-01	2.62E-01	7.41E-04
	2.5	5.90E-01	3.32	5.22E-04	1.08E-01	0.67	1.23E-01	2.54E-01	5.29E-04
	2.7	5.62E-01	3.17	3.66E-04	9.31E-02	0.58	1.29E-01	2.90E-01	3.67E-04
	2.9	5.36E-01	3.04	2.52E-04	7.74E-02	0.51	1.43E-01	3.35E-01	2.50E-04
2-Dy	1.8	7.09E-01	3.52	3.15E-03	1.01E-01	0.56	6.52E-02	1.74E-01	3.35E-03
	1.9	6.85E-01	3.32	2.69E-03	1.00E-01	0.66	7.48E-02	2.09E-01	2.89E-03
	2	6.57E-01	3.14	2.14E-03	9.18E-02	0.76	9.89E-02	2.68E-01	2.27E-03
	2.1	6.33E-01	3.03	1.70E-03	8.20E-02	0.76	1.09E-01	2.80E-01	1.79E-03
	2.3	5.94E-01	2.89	1.09E-03	6.80E-02	0.64	9.72E-02	2.96E-01	1.13E-03
	2.5	5.58E-01	2.75	6.61E-04	5.55E-02	0.50	8.56E-02	2.76E-01	6.76E-04
	2.7	5.25E-01	2.64	4.07E-04	4.66E-02	0.40	8.93E-02	2.82E-01	4.10E-04
	2.9	4.90E-01	2.54	2.55E-04	4.12E-02	0.32	9.94E-02	2.90E-01	2.54E-04

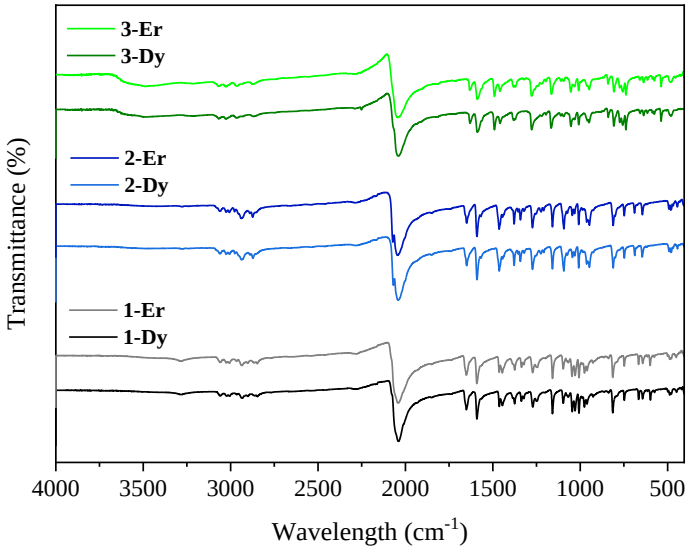

Figure S1. FTIR spectra for Dy^{III} and Er^{III} complexes.

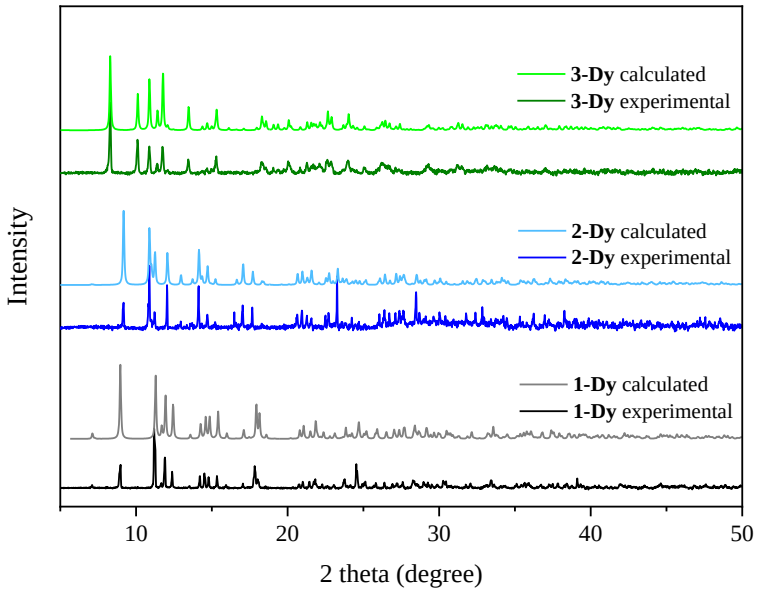

Figure S2. Comparison between experimental and calculated X-ray diffraction (XRD) patterns for dysprosium(III) complexes.

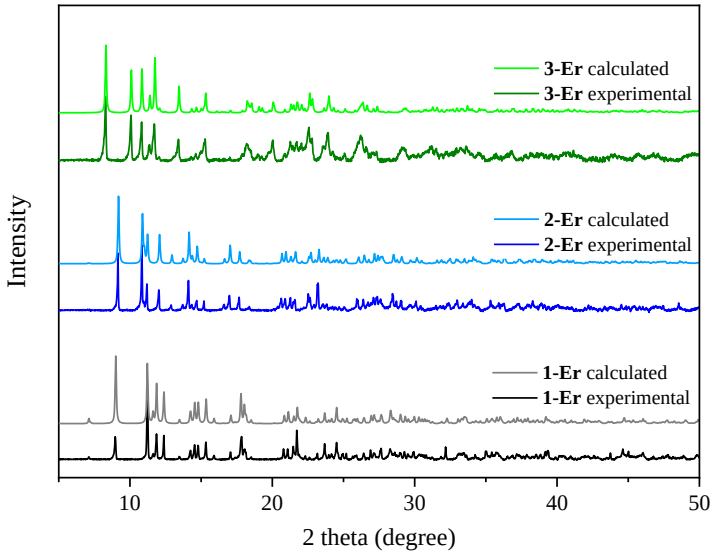

Figure S3. Comparison between experimental and calculated X-ray diffraction (XRD) patterns for erbium(III) complexes.

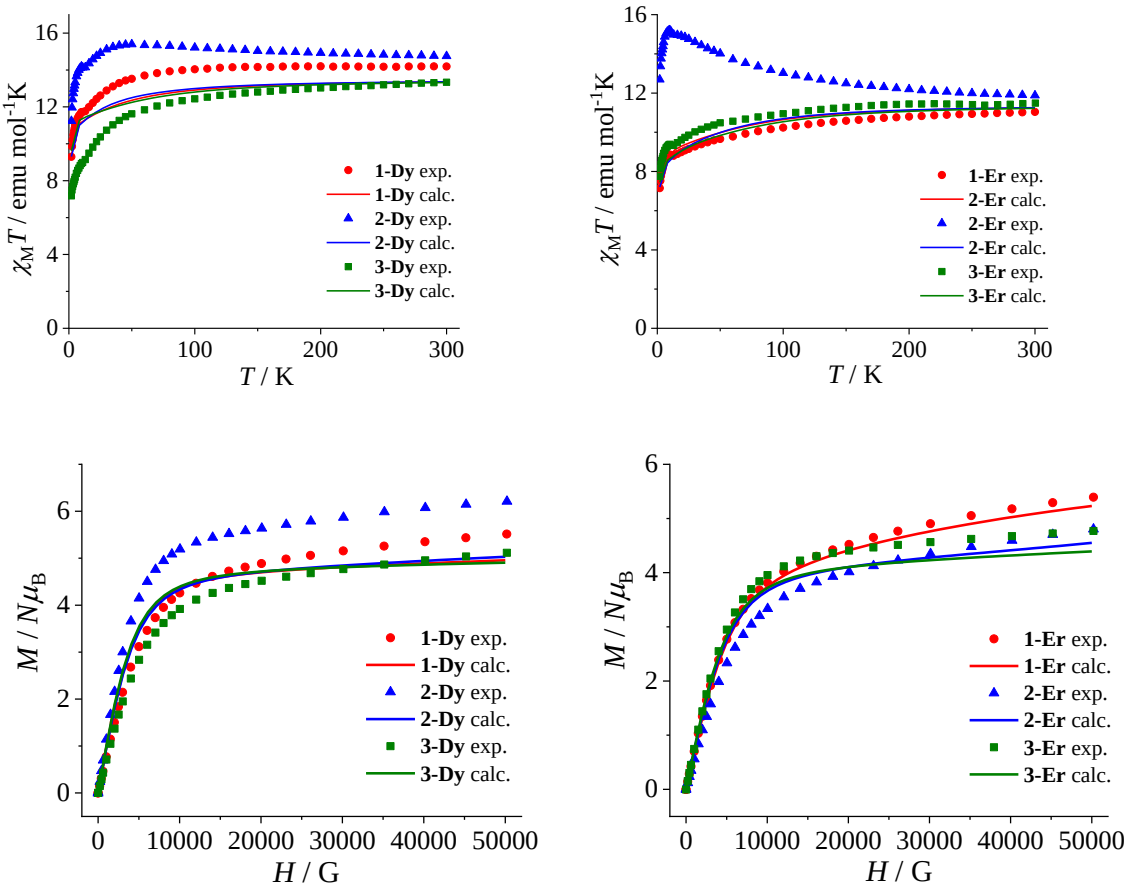

Figure S4. Comparison of experimental (symbols) and ab initio calculated (solid lines) temperature dependence of the product $\chi_M T$ with an applied field of 3 KOe (top), and molar magnetization as a function of applied magnetic field at 2 K(bottom), for Dy^{III} (left) and Er^{III} (right) complexes.

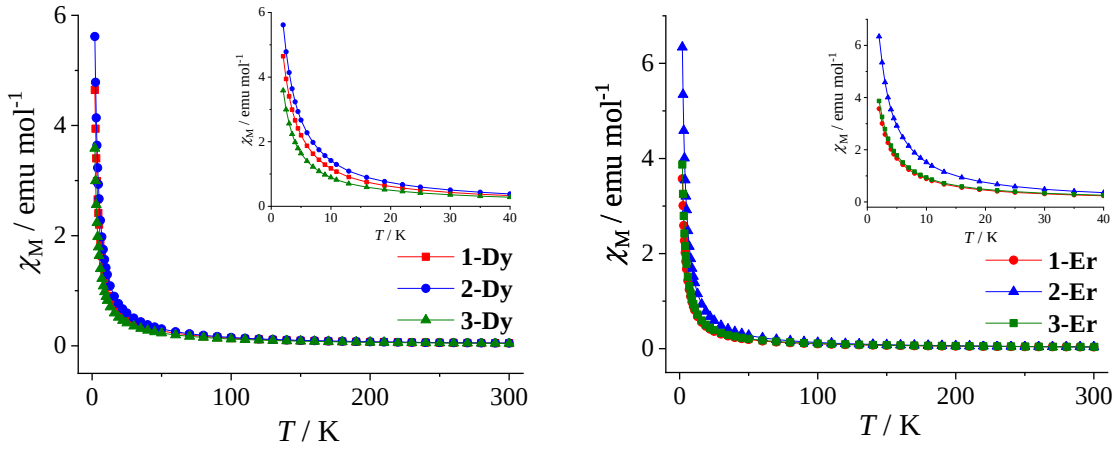

Figure S5. Dependence of the molar susceptibility with the temperature for Dy^{III} (left) and Er^{III} (right) complexes, with an applied field of 3 KOe. Inset: magnification of curves at low temperatures.

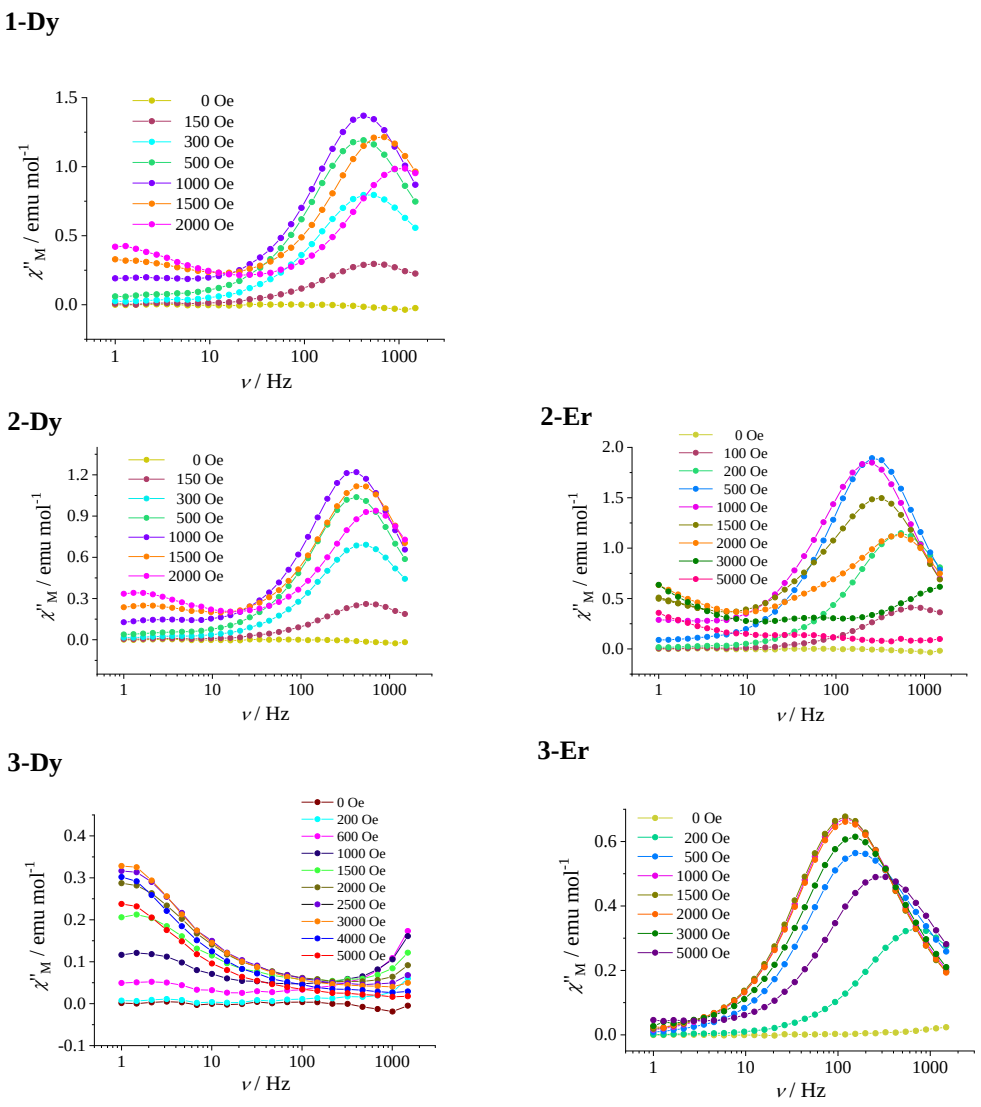

Figure S6. Dependence of the out-of-phase susceptibility with the frequency at different static fields. Left: **1-Dy** (top), **2-Dy** (center) at 2.7 K and **3-Dy** (bottom) at 2 K. Right: **2-Er** (center) and **3-Er** (bottom) at 2.3 and 5 K, respectively.

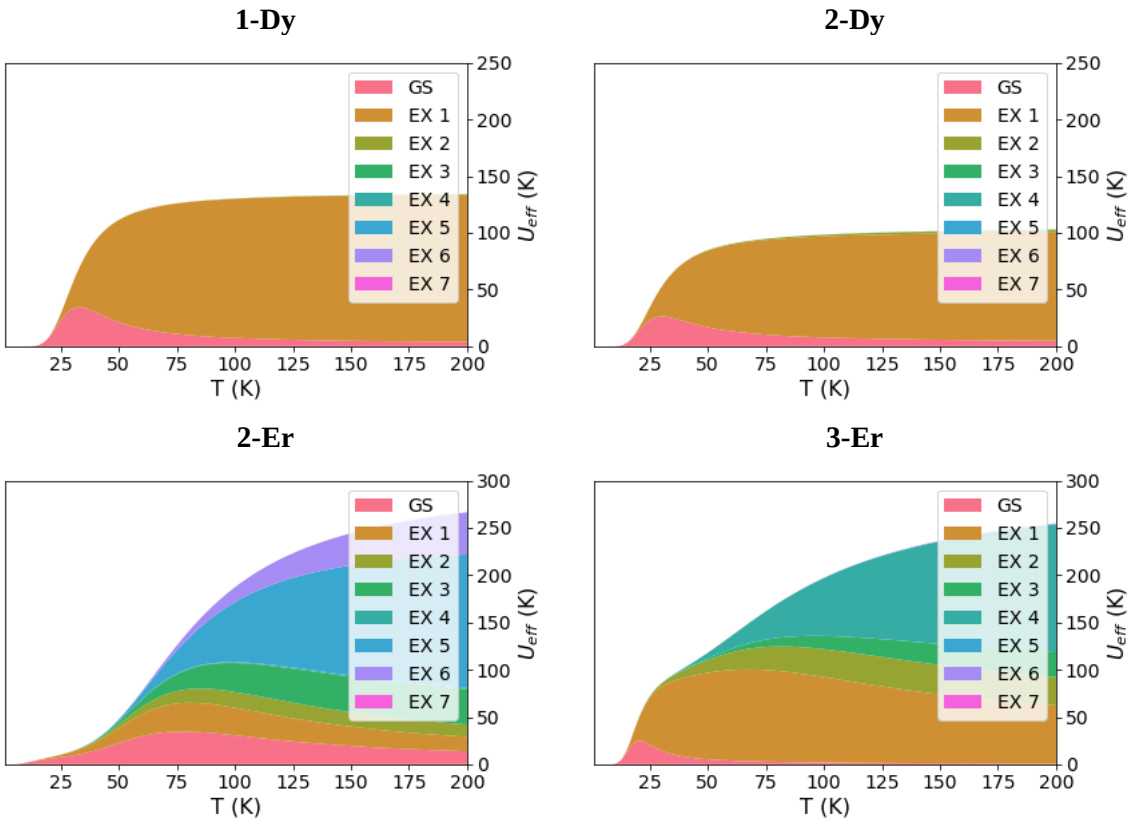

Figure S7. Calculated thermally assisted tunnelling pathways for **1-Dy**, **2-Dy**, **2-Er** and **3-Er**. Ground and excited state contributions are labelled as GS and EXn, respectively.

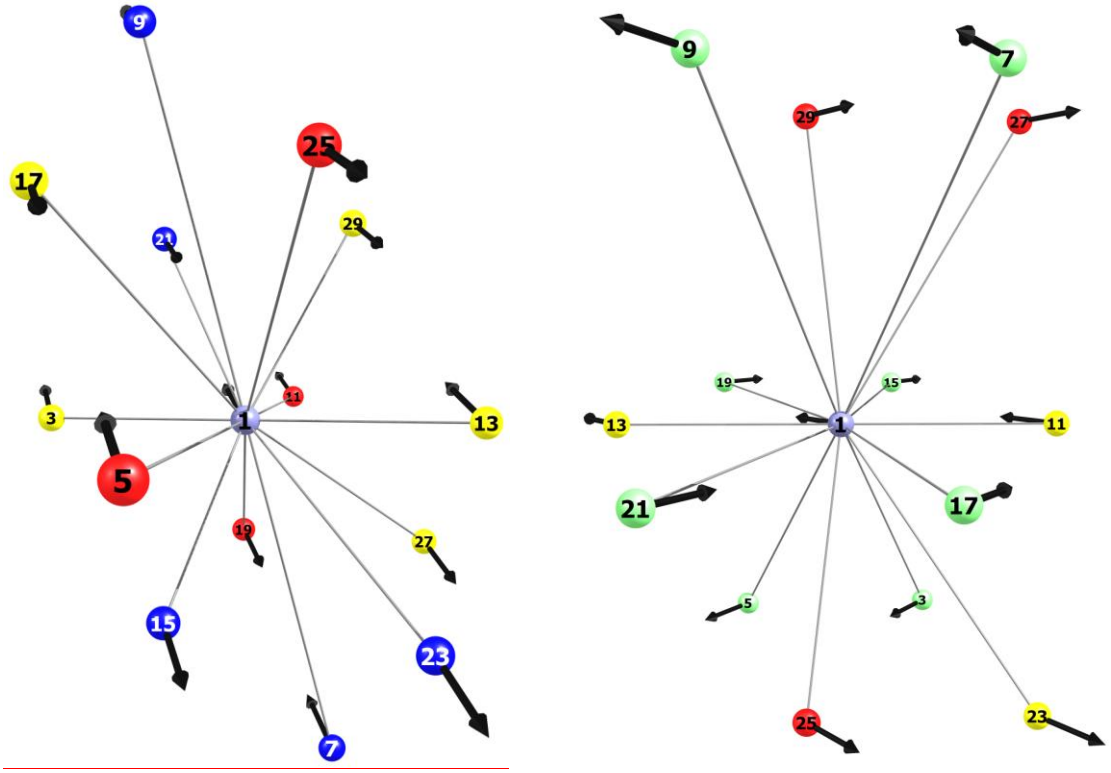

Figure S8. Dipolar interaction model for a central Dy1 centre and 14 neighbours for **1-Dy**, **2-Dy** (left) and **3-Dy** (right). Orientation of the g_z component of the magnetic moment is indicated by a black arrow. The type of dipolar interaction is indicated by different colours: Ferromagnetic (blue); Antiferromagnetic (red); Weak (yellow); Non-collinear (light green).

Table S7. Distances between Dy-Dy centres, angles between the calculated magnetic moment of the ground state and the vector connecting the two Ln ions (θ) and between magnetic moments (μ_z), and sign of the magnetic interaction for Dy^{III} complexes. In the case of non-collinear magnetic moments, there are two θ angles, each one corresponding to a different magnetic centre. Magnetic centre numbering corresponds to Figure S7. Contacts with a Dy-Dy distance lower than 10Å are highlighted in bold.

Complex	centers	Distance Dy-Dy (Å)	θ (°)		μ_z angle (°)	Interaction
1-Dy	**3;13**	**7.95**	**52.3**		**0**	**Weak**
	5;11	12.87	68.1		0	Antiferromagnetic
	7;9	12.84	38.6		0	Ferromagnetic
	15	**7.43**	**44.0**		**0**	**Ferromagnetic**
	17	**9.99**	**62.0**		**0**	**Weak**
	19	10.70	87.0		0	Antiferromagnetic
	21	**9.95**	**18.0**		**0**	**Ferromagnetic**
	23	10.48	13.0		0	Ferromagnetic
	25	10.25	89.0		0	Antiferromagnetic
	27	11.83	62.7		0	Weak
	29	**8.65**	**57.0**		**0**	**Weak**
2-Dy	**3;13**	**8.45**	**50.7**		**0**	**Weak**
	5;11	12.61	67.3		0	Antiferromagnetic
	7;9	13.17	37.9		0	Ferromagnetic
	15	**7.91**	**43.6**		**0**	**Ferromagnetic**
	17	10.04	61.9		0	Weak
	19	10.17	85.1		0	Antiferromagnetic
	21	**9.99**	**16.3**		**0**	**Ferromagnetic**
	23	11.34	12.1		0	Ferromagnetic
	25	10.37	86.5		0	Antiferromagnetic
	27	11.89	58.4		0	Weak
	29	**8.87**	**61.5**		**0**	**Weak**
3-Dy	**11;13**	**8.31**	**46.6**		**0**	**Weak**
	23	12.78	55.8		0	Weak
	25	10.76	82.2		0	Antiferromagnetic
	27	13.71	76.5		0	Antiferromagnetic
	29	11.85	77.7		0	Antiferromagnetic
	3	11.95	83.1	53.1	86.9	Non-Collinear
	5	11.95	53.2	83.0	86.9	Non-Collinear
	7	13.58	54.4	80.8	86.9	Non-Collinear
	9	13.58	80.7	54.4	86.9	Non-Collinear
	15	**9.63**	**60.8**	**26.4**	**86.9**	**Non-Collinear**
	17	**9.63**	**26.4**	**60.8**	**86.9**	**Non-Collinear**
	19	10.70	13.2	74.2	86.9	Non-Collinear
	21	10.70	74.2	15.8	86.9	Non-Collinear

Sample input for the calculation of tunnelling rates. Energies are expressed in cm^{-1} as presented in the ORCA ouput and g-values and g-vectors can be similarly obtained from the "ELECTRONIC G-MATRIX" section. This file is accompanied with the cif file DyDAPSCN.cif to consider the molecular orientation in the crystal frame.

```
>RUNMODE single
>NEWJOB
-> ncenters 1
-> dilution_ratio 1
-> dilution_repetitions 1
-> print low
-> InputMode gfactors
-> ciffile DyDAPSCN.cif
-> jobtitle DyDAPSCNUandtau

---> center 0
--> ncoord 1
Dy 0.160189 2.384948 3.152365
--> end ncoord
--> energies 8
    0.00
   73.10
  136.46
  214.30
  269.65
  279.40
  340.99
  435.15
--> end energies
--> NKD 8
    0.351527     0.945294    18.470900 iso =     6.589240
  X           0.6603557   -0.2936693   -0.6911503
  Y           0.6668114    0.6526112    0.3598072
  Z           0.3453880   -0.6984676    0.6267776
    2.474579     5.060902    11.933642 iso =     6.489708
  X           0.7111898   -0.1601832   -0.6845074
  Y           0.5931315    0.6593947    0.4619455
  Z           0.3773647   -0.7345338    0.5639645
    3.221964     4.857807     6.251583 iso =     4.777118
  X          -0.2052585   -0.7749651   -0.5977441
  Y          -0.5232736    0.6030215   -0.6021211
  Z           0.8270754    0.1891932   -0.5292941
    0.673594     1.286523     9.723510 iso =     3.894542
  X          -0.3129877    0.7445394   -0.5896607
  Y           0.6630092   -0.2732611   -0.6969557
  Z          -0.6800423   -0.6090890   -0.4081091
    0.512957     2.302658    12.461119 iso =     5.092245
  X          -0.7659419    0.3556570    0.5355755
  Y           0.1938663   -0.6665023    0.7198546
  Z           0.6129836    0.6551968    0.4415521
    0.394483     2.684671    13.741105 iso =     5.606753
  X           0.5676599    0.1490360   -0.8096607
  Y          -0.4338526   -0.7816729   -0.4480619
  Z          -0.6996672    0.6056202   -0.3790647
    0.019457     0.031537    16.696782 iso =     5.582592
  X           0.7360315    0.4514181   -0.5044594
  Y          -0.0750819   -0.6861619   -0.7235638
  Z          -0.6727707    0.5704415   -0.4711434
    0.010433     0.011273    18.454265 iso =     6.158657
  X           0.2375840    0.5207780    0.8199659
  Y          -0.5337537   -0.6352862    0.5581383
  Z           0.8115792   -0.5702646    0.1270334
--> end NKD
---> end center 0
>ENDJOB
```