

Supporting Information

A thermochromic macrocyclic materials exhibiting slow relaxation of the magnetization: support for magnetic response and visualization applications

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Table S1 Crystallographic data for complexes **1**, **2**, **3-Dy** and **3-Dy***.

	1	2	3-Dy	3-Dy*
formula	C ₁₆ H ₂₇ Cl ₃ DyN ₅ O ₅	C ₂₈ H ₂₉ Cl ₅ DyN ₇ O ₇	C ₃₆ H ₅₈ Cl ₄ Dy ₂ N ₁₀ O ₁₂	C ₃₆ H ₅₈ Cl ₄ Dy ₂ N ₁₀ O ₁₂
FW (g.mol ⁻¹)	638.27	915.33	1289.72	1289.72
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ /n	<i>C</i> 2/c	<i>C</i> 2/c
Temperature (K)	213(2)	293(2)	293.15	293(2)
a (Å)	8.7379(3)	15.4334(7)	18.4652(16)	18.5354(12)
b (Å)	11.3821(4)	11.5838(3)	21.993(2)	22.0457(19)
c (Å)	11.4772(4)	20.6732(10)	11.7138(11)	11.7708(8)
α (°)	92.571(2)	90	90	90
β (°)	99.667(3)	111.779(5)	94.456(8)	95.201(7)
γ (°)	90.403(3)	90	90	90
V (Å ³)	1124.01(7)	3432.1(3)	4742.7(7)	4790.1(6)
ρ _{calc} (Mg.m ⁻³)	1.886	1.771	1.806	1.788
μ (mm ⁻¹)	21.399	15.708	3.420	3.386
F (000)	630.0	1812.0	2560.0	2560
Collected reflections	10919	36464	13097	15735
Independent reflections	3975	6115	4149	4207
R _{int}	0.0580	0.1371	0.0847	0.0725
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0345	0.0611	0.1028	0.0707
wR ₂ (all data)	0.0875	0.1866	0.2344	0.1558
GOF	1.051	1.071	1.182	1.116
CCDC number	2344863	2344862	2344861	

Table S2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

1		2	
Dy-Cl1	2.7065(10)	Dy-Cl	2.7736(19)
Dy-Cl2	2.7104(10)	Dy-O1	2.259(5)
Dy-O	2.432(3)	Dy-O4	2.341(5)

Dy-N1	2.459(3)	Dy-N1	2.474(5)
Dy1-N2	2.455(3)	Dy-N2	2.539(6)
Dy1-N3	2.508(3)	Dy-N4	2.470(6)
Dy1-N4	2.481(3)	Dy-N6	2.461(6)
Dy1-N5	2.436(3)	Dy-N7	2.522(6)
Cl1-Dy-Cl2	146.78(3)	O1-Dy-Cl	145.29(16)
O1-Dy-Cl1	143.66(8)	O1-Dy-O4	78.0(2)
O1-Dy-Cl2	69.54(8)	O4-Dy-Cl	136.59(15)

Table S3 Selected bond lengths (Å) and angles (°) for complexes **3-Dy** and **3-Dy***.

3-Dy		3-Dy*	
Dy1-Cl1	2.678(5)	Dy*1-Cl1	2.690(3)
Dy1-O1	2.192(17)	Dy*1-O1	2.214(9)
Dy1-O1'	2.245(15)	Dy*1-O1'	2.222(9)
Dy1-N1	2.452(17)	Dy*1-N1	2.427(12)
Dy1-N2	2.408(18)	Dy*1-N2	2.455(10)
Dy1-N3	2.471(14)	Dy*1-N3	2.442(11)
Dy1-N4	2.443(18)	Dy*1-N4	2.434(10)
Dy1-N5	2.394(18)	Dy*1-N5	2.443(10)
O1-O2	1.43(3)	O1-O2	1.431(19)
O1-Dy1-Cl	158.3(4)	O1-Dy*1-Cl1	157.9(3)
O2-Dy1-Cl	164.2(5)	O2-Dy*1-Cl1	164.4(3)
O1-Dy1-O2	37.5(8)	O1-Dy*1-O2	37.6(8)
Dy1-O1-Dy2	142.4(8)	Dy*1-O1-Dy2	142.4(5)

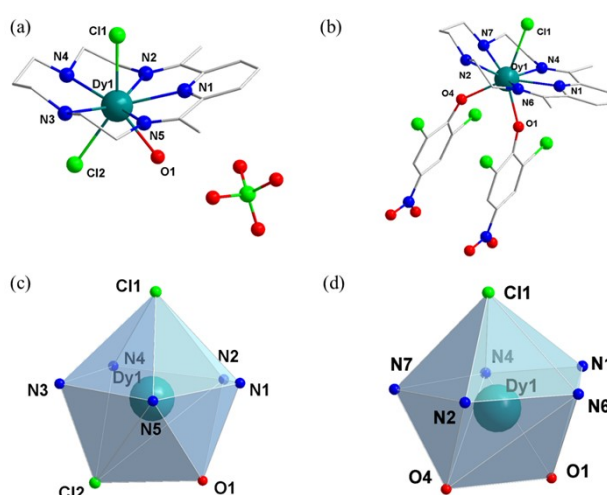


Fig. S1 Structure of complexes **1** (a) and **2** (b). Coordination polyhedra for complexes **1** (c) and **2** (d).

Table S4 Continuous Shape Measures (CSHMs) of the coordination geometry for Dy^{III} ion in complexes **1-3**. (CSHMs

values calculated with the Shape program). The CShMs values indicated the proximity to the ideal polyhedron, thus, CShMs = 0 corresponds to the non-distorted polyhedron. The three closer ideal geometries to the real complexes are listed and below are the symmetry and description for each polyhedron.

	CShMs		Polyhedron	
1	1.788	TDD-8	D_{2d}	Triangular dodecahedron
	2.733	BTPR-8	C_{2v}	Biaugmented trigonal prism
	3.928	JBTPR-8	C_{2v}	Biaugmented trigonal prism J50
2	2.101	TDD-8	D_{2d}	Triangular dodecahedron
	2.720	BTPR-8	C_{2v}	Biaugmented trigonal prism
	3.695	JBTPR-8	C_{2v}	Biaugmented trigonal prism J50
3	4.898	TDD-8	D_{2d}	Triangular dodecahedron
	6.474	BTPR-8	C_{2v}	Biaugmented trigonal prism
	7.055	JBTPR-8	C_{2v}	Biaugmented trigonal prism J50

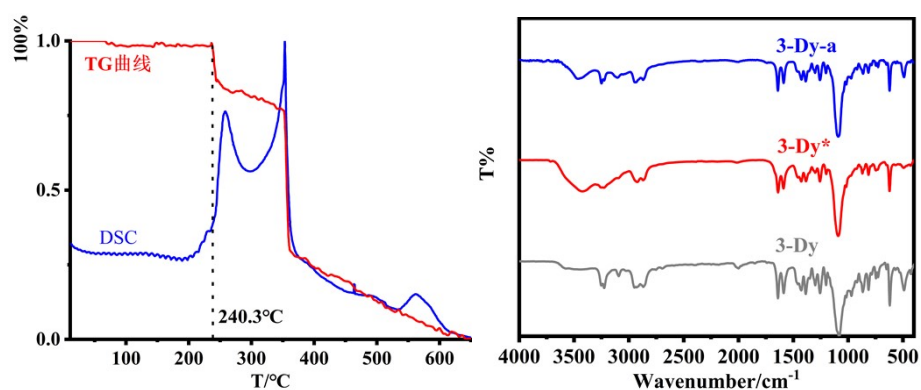


Fig. S2 TG (red line) and DSC (blue line) curve of **3-Dy** in 12-600 °C (left). Infrared spectra for **3-Dy**, **3-Dy***, **3-Dy-a** (after heating exposure to air for 3 weeks) in the coloration process (right).

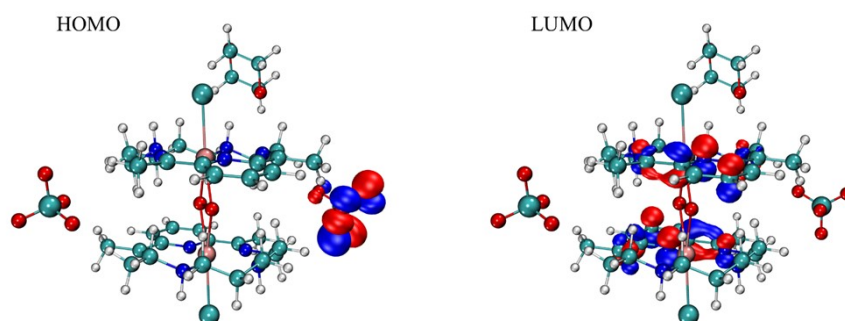


Fig. S3 HOMO and LUMO energy levels for **3**.

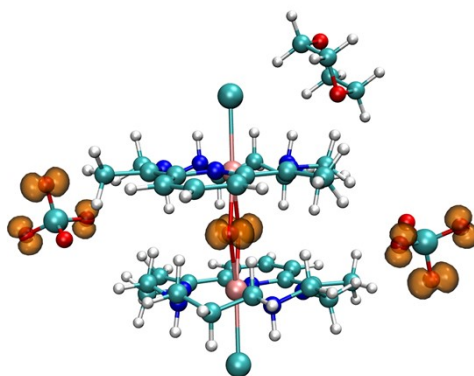


Fig. S4 Spin population analysis for complex **3**.

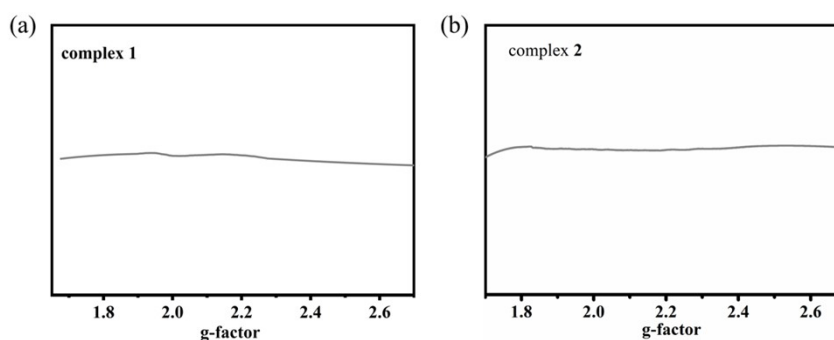


Fig. S5 EPR spectra of **1** (a), **2** (b) in the solid state after heating.

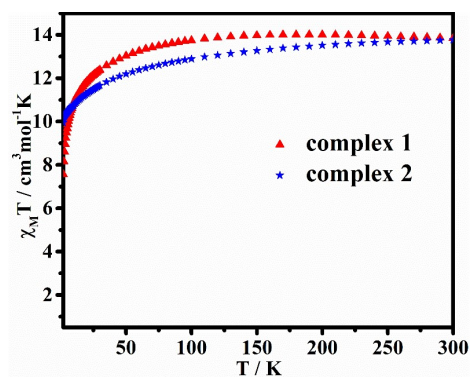


Fig. S6 Temperature dependence of the magnetic susceptibility $\chi_M T$ at 1000 Oe for complexes **1** and **2**.

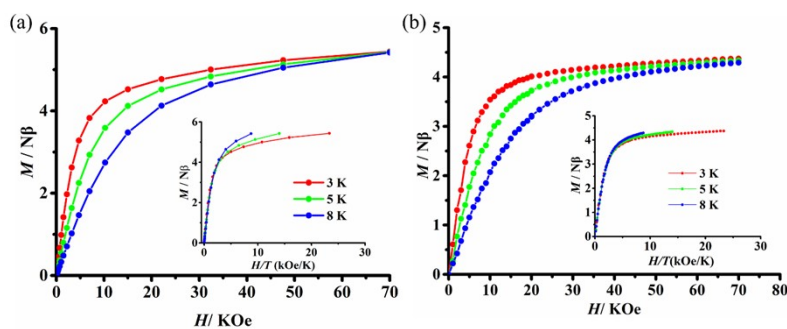


Fig. S7 Field dependences of magnetization in the field range 0–70 kOe and temperature range 3–8 K for complexes **1** (a) and **2** (b).

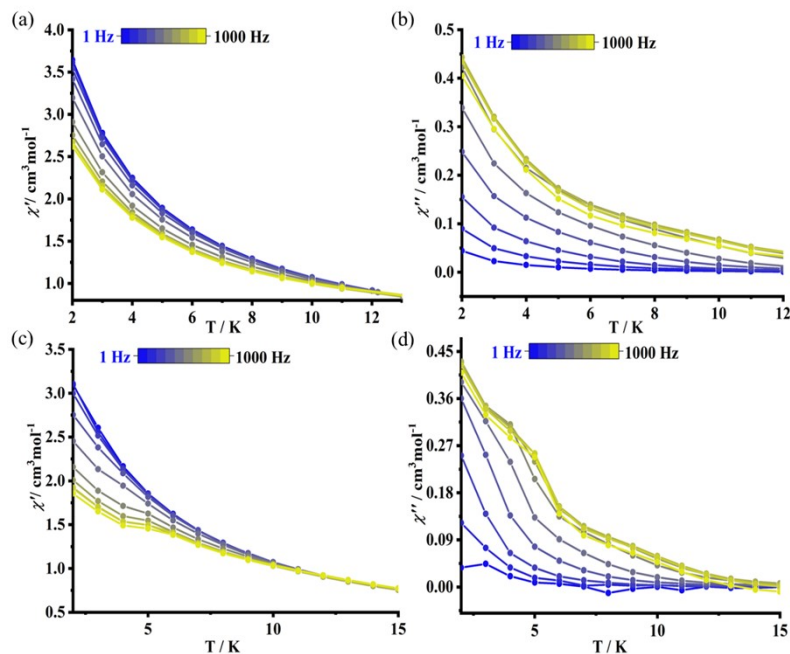


Fig. S8 Temperature dependence of the in-phase (χ') ac susceptibility (a) and out-of-phase (χ'') ac susceptibility (b) in the temperature range 2-12 K of complex **1** under 0 Oe. Temperature dependence of the in-phase (χ') ac susceptibility (c) and out-of-phase (χ'') ac susceptibility (d) in the temperature range 2-15 K of complex **1** under 1500 Oe.

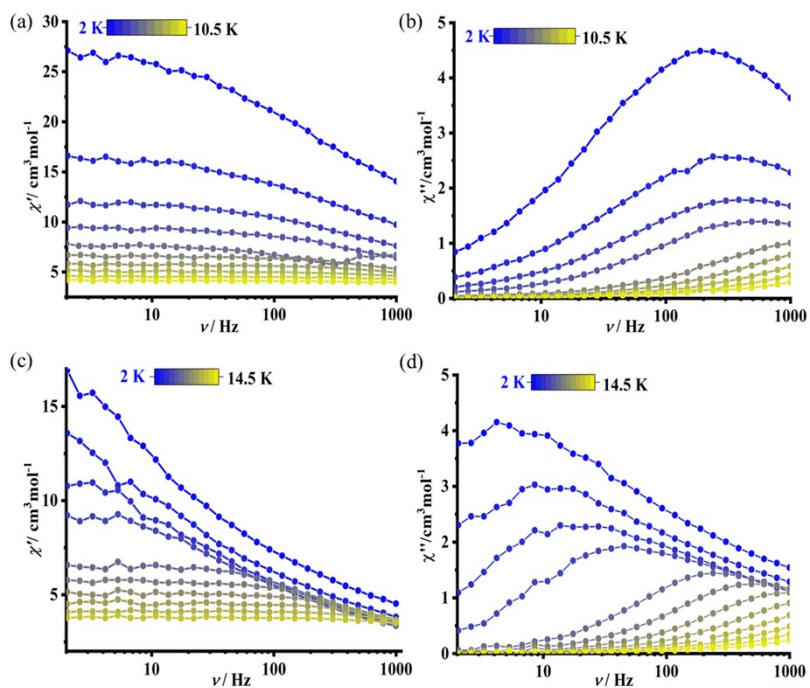


Fig. S9 Frequency dependence of the in-phase (χ') ac susceptibility (a) and the out-of-phase (χ'') ac susceptibility (b) in the temperature range 2-10.5 K of **2** under 0 Oe. Frequency dependence of the in-phase (χ') ac susceptibility (c) and out-of-phase (χ'') ac susceptibility (d) in the temperature range 2-14.5 K of complex **2** under 1000 Oe.

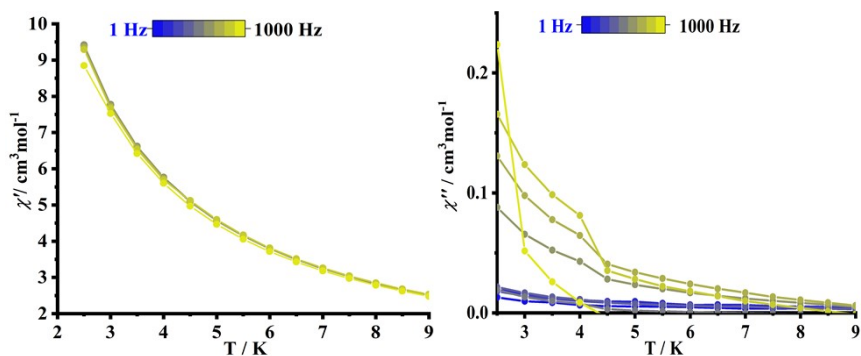


Fig. S10 Temperature dependence of the in-phase (χ') ac susceptibility (left) and the out-of-phase (χ'') ac susceptibility (right) in the temperature range 2.5-9 K of **3-Dy** under 0 Oe.

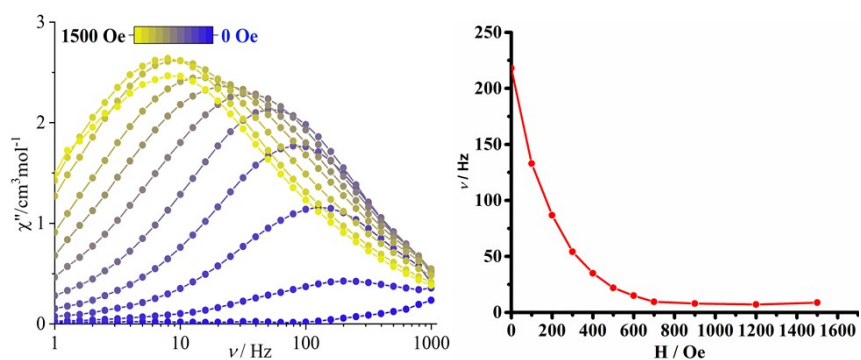


Fig. S11 Plot of the frequency dependence of the out-of-phase (χ'') ac susceptibility component under indicated dc field at 3 K for **3-Dy**(left). Plot of $1/\tau$ vs. H for **3-Dy** under different dc fields at 3 K (right), the solid line is guide for eyes.

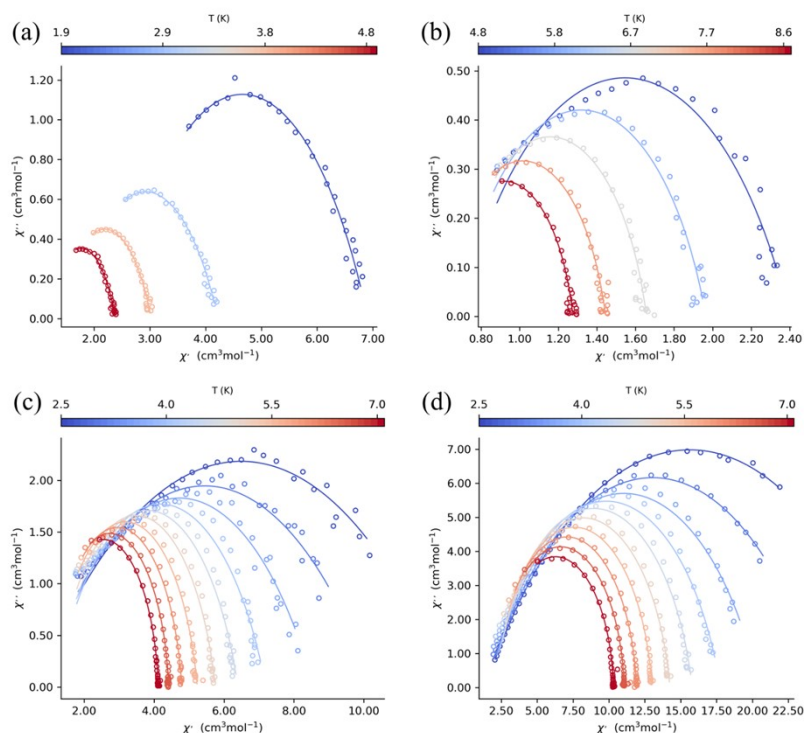


Fig. S12 Cole-Cole plots for **2** under 0 Oe (a) and 1000 Oe (b). Cole-Cole plots for **3-Dy** (c) and **3-Dy*** (d) under 1200 Oe. The solid lines are the best fit for the generalized Debye model.

Table S5. Best fitted parameters (χ_T , χ_S , τ and α) with the extended Debye model for complex **2** at 0 Oe in the temperature range 1.9-4.8 K.

T/ K	χ_S / cm ³ mol ⁻¹	χ_T / cm ³ mol ⁻¹	τ /s	α
1.9	2.41334	6.90768	0.00074	0.40782
2.9	1.62330	4.22096	0.00047	0.41834
3.8	1.35562	3.02534	0.00039	0.37031
4.8	1.15479	2.37991	0.00029	0.33339

Table S6. Best fitted parameters (χ_T , χ_S , τ and α) with the extended Debye model for complex **2** at 1000 Oe in the temperature range 4.8-8.6 K.

T/ K	χ_S / cm ³ mol ⁻¹	χ_T / cm ³ mol ⁻¹	τ /s	α
4.8	0.69354	2.39632	0.00240	0.33991
5.7	0.67393	1.96474	0.00113	0.26517
6.7	0.65801	1.65696	0.00058	0.19543
7.7	0.58629	1.44511	0.00030	0.19098
8.6	0.56281	1.27589	0.00017	0.16285

Table S7. Best fitted parameters (χ_T , χ_S , τ and α) with the extended Debye model for complex **3-Dy** at 1200 Oe in the temperature range 2.5-7 K.

T/ K	χ_S / cm ³ mol ⁻¹	χ_T / cm ³ mol ⁻¹	τ /s	α
2.5	1.39560	29.86939	0.04330	0.41950
3.0	1.40983	24.68399	0.02045	0.37975
3.5	1.63150	20.45429	0.00894	0.30641
4.0	1.86695	17.77609	0.00436	0.23267
4.5	2.06496	15.81021	0.00230	0.16799
5.0	2.15188	14.24521	0.00129	0.12203
5.5	2.19636	12.99291	0.00077	0.08665
6.0	2.21196	11.92472	0.00049	0.05917
6.5	2.19863	11.06543	0.00032	0.04439
7.0	2.22403	10.30955	0.00022	0.03218

Table S8. Best fitted parameters (χ_T , χ_S , τ and α) with the extended Debye model for complex **3-Dy*** at 1200 Oe in the temperature range 2.5-7 K.

T/ K	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	τ/s	α
2.5	0.60109	12.37717	0.00968	0.54786
3.0	0.64208	10.25542	0.00541	0.51016
3.5	0.88848	8.56849	0.00318	0.43425
4.0	1.16754	7.19940	0.00191	0.32422
4.5	1.21407	6.39964	0.00123	0.25762
5.0	1.22301	5.75390	0.00080	0.19492
5.5	1.14080	5.23607	0.00052	0.15616
6.0	1.11194	4.79474	0.00035	0.11105
6.5	1.06478	4.42118	0.00025	0.07680
7.0	0.97395	4.11916	0.00017	0.06131

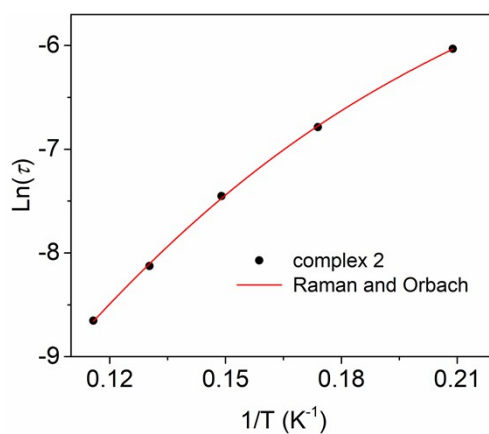


Fig. S13 Plots of $\ln(\tau)$ curves of $1/T$ at applying dc field for **2**.

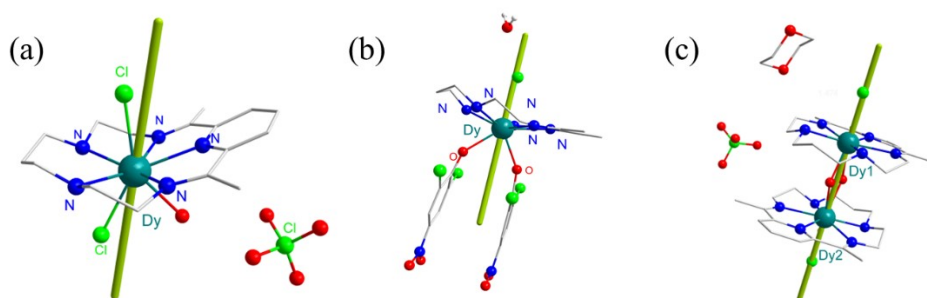


Fig. S14 Orientations of the anisotropy axes for Dy^{III} ions in **1** (a), **2** (b) and **3** (c) as calculated by MAGELLAN.