

SUPPORTING INFORMATION

Single-molecule magnet behaviour in a Dy(III) pentagonal bipyramidal complex with a quasi linear Cl-Dy-Cl sequence

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EXPERIMENTAL SECTION

General Procedure. All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen filled glovebox. After drying over KOH, THF was purified by distillation from sodium/benzophenoneketyl. Unsolvated DyCl₃ was synthesized according to a standard procedure by the way of subliming the mixture of DyCl₃ and NH₄Cl.¹ NaBPh₄ was purchased from Aldrich and was used without further purification. Lanthanide metal analysis was carried out by complexometric titration.² IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer. Elemental analysis was performed in the microanalytical laboratory of IOMC.

Synthesis of [DyCl₂(THF)₅][B(C₆H₅)₄]·0.5(THF) (1). Anhydrous DyCl₃ (1.15 g, 4.30 mmol) was suspended in THF (10 mL) and stirred at room temperature for 12 h. Then dry NaBPh₄ (1.47 g, 4.30 mmol) was added to the suspension and the solution was quickly heated to 70 °C. The resulting cloudy solution was stirred at 40 °C for 24 h. Then, the solution was brought to room temperature and filtered from the insoluble precipitate of NaCl. Complex **1** was isolated as colorless crystals by slow diffusion of hexane into the THF solution of the complex, in an almost quantitative yield 86 % (3.36 g). Complex **1** crystallized as a solvate [DyCl₂(THF)₅][B(C₆H₅)₄]·0.5(THF). Elemental analysis calcd. (%) for C₄₆H_{63.50}BCl₂DyO_{5.50} (948.67 g·mol⁻¹): C, 58.21; H, 6.80; Dy, 17.12; found (%): C, 58.02; H, 6.87; Dy, 17.24. IR (Nujol, KBr) ν/cm⁻¹: 1952 (w), 1884 (w), 1821 (w), 1576 (m), 1560 (w), 1344 (m), 1295 (w), 1245 (m), 1177 (s), 1017 (s), 919 (s), 846 (s), 703 (m), 672 (m), 606 (m).

X-Ray crystallography.

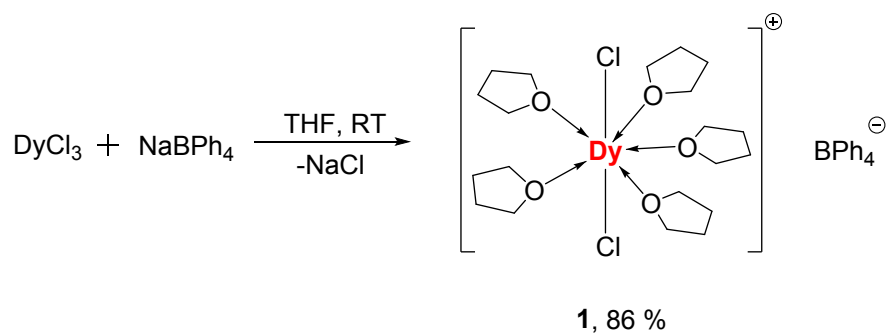
Crystals of **1** [C₄₆H_{63.50}BCl₂DyO_{5.50}, FW= 948.67, cryst. from THF-hexane] are triclinic, space group P-1, at 120(2) K $a = 12.5166(5)\text{\AA}$, $b = 12.7218(5)\text{\AA}$, $c = 29.2642(12)\text{\AA}$, $\alpha = 79.4431(9)^\circ$, $\beta = 79.7267(10)^\circ$, $\gamma = 82.1866(9)^\circ$, $V = 4481.8(3)\text{\AA}^3$, $Z(Z') = 4(2)$, $d_{\text{calc}} = 1.406\text{gcm}^{-3}$, $\lambda(\text{MoK}\alpha) = 18.31\text{ cm}^{-1}$. Intensities of 109457 reflections were measured with Bruker APEX-II CCD [$\lambda(\text{MoK}\alpha) = 0.71072\text{\AA}$, $2\theta < 58$] and 23822 independent reflections ($R_{\text{int}} = 0.0574$) were used in the further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Analysis of the Fourier density synthesis as well as displacement parameters clearly show that two of THF molecules are disordered. The refinement of the disordered part has been performed with restraints (DFIX and EADP). The refinement converged to $wR_2 = 0.0777$ and $\text{GOF} = 1.023$ for all independent reflections ($R_1 = 0.0388$ was calculated against F for 18731 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL-2014/6. Crystallographic data for the structure **1** was deposited at the Cambridge Crystallographic Data Centre as supplementary no. CCDC 1867504.

Magnetic Measurements.

Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer working in the range 1.8 – 350 K with the magnetic field up to 7 Tesla. The sample were prepared in a glove box. The data were corrected for the sample holder and the diamagnetic contributions calculated from the Pascal's constants. The ac magnetic susceptibility measurements were carried out in the presence of a 3 Oe oscillating field in zero or applied external dc field.

Photoluminescence measurements

The solid sample was sealed in a quartz tube in an argon atmosphere (glove box). The emission and excitation spectra were recorded at 77 K and 295 K using a spectrofluorimeter Edinburgh FLS-920. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter. Low temperature measurements (77 K) were performed using a liquid nitrogen dewar (quartz).



Scheme 1: Synthesis of complex **1**.

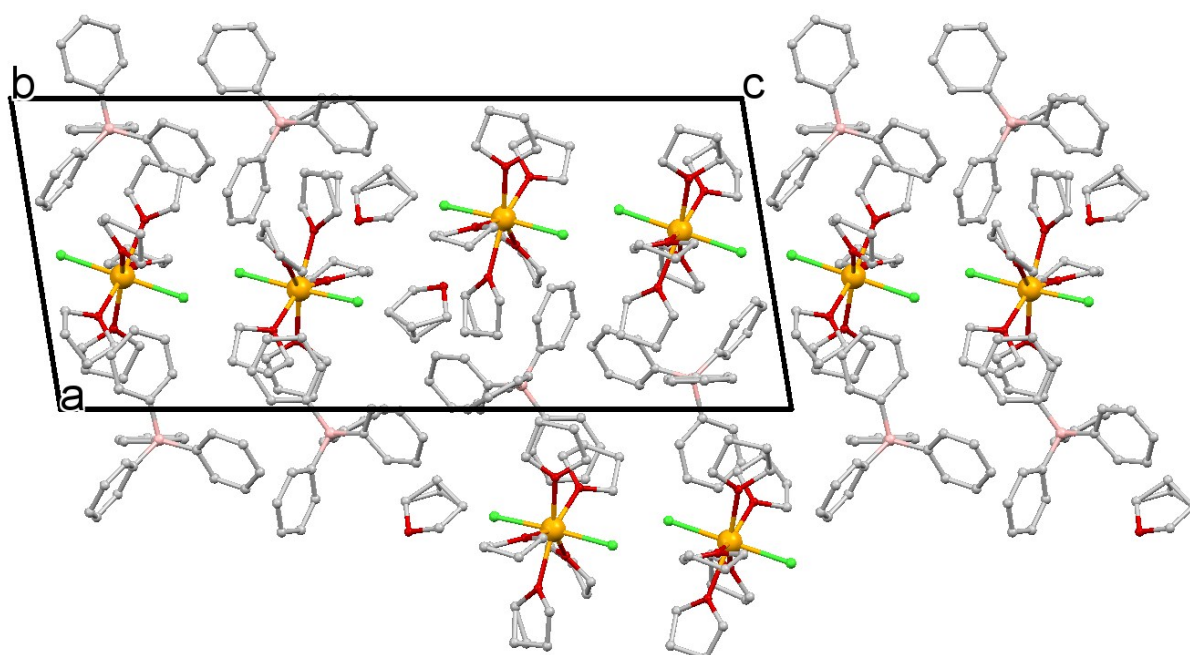


Figure S1: Perspective view of the crystal packing for **1** along the *a* crystallographic axis. Hydrogen atoms have been omitted for clarity.

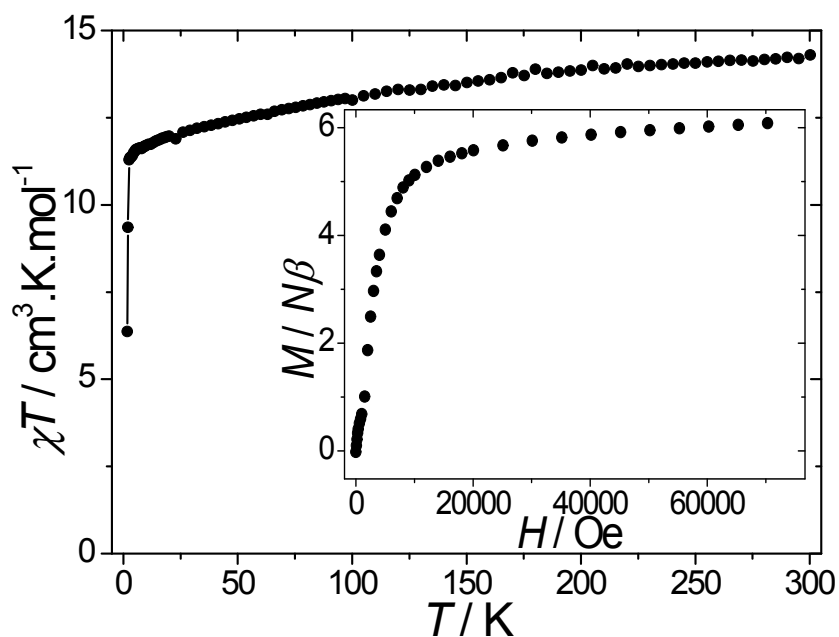


Figure S2: Temperature dependence of χT under an applied magnetic field of 1000 Oe for **1**. Inset: field dependence of the magnetization at 1.8 K for **1**.

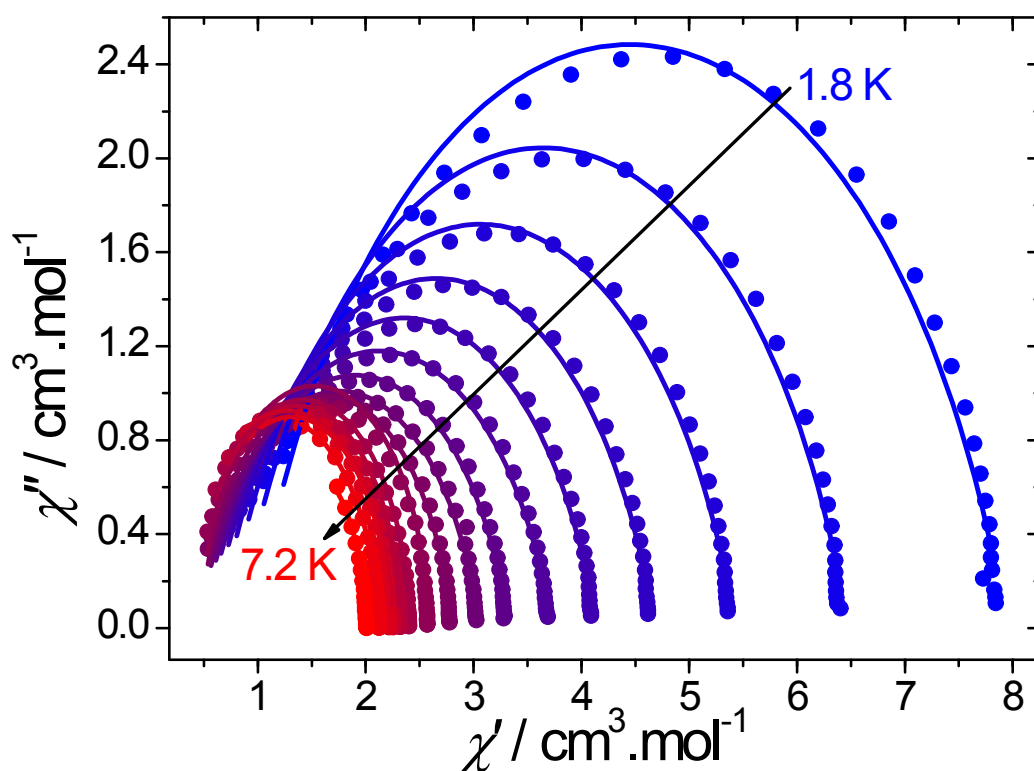


Figure S3: Cole-Cole (Argand) plots obtained using the ac susceptibility data for **1** (0 Oe). The solid lines correspond to the best fit obtained with a generalized Debye model.

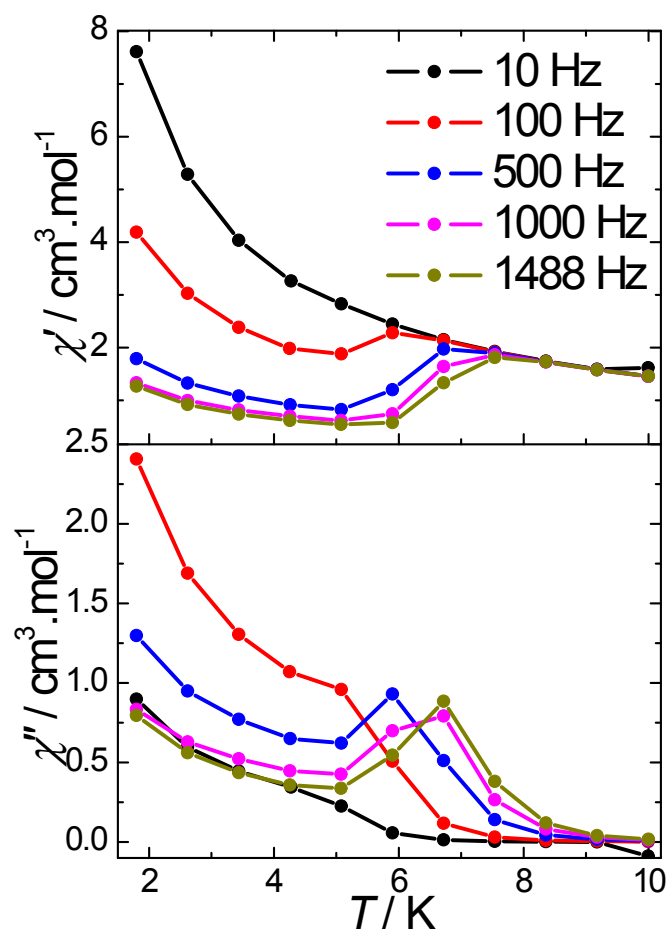


Figure S4: Temperature dependence of χ' and χ'' for **1** for different frequencies.

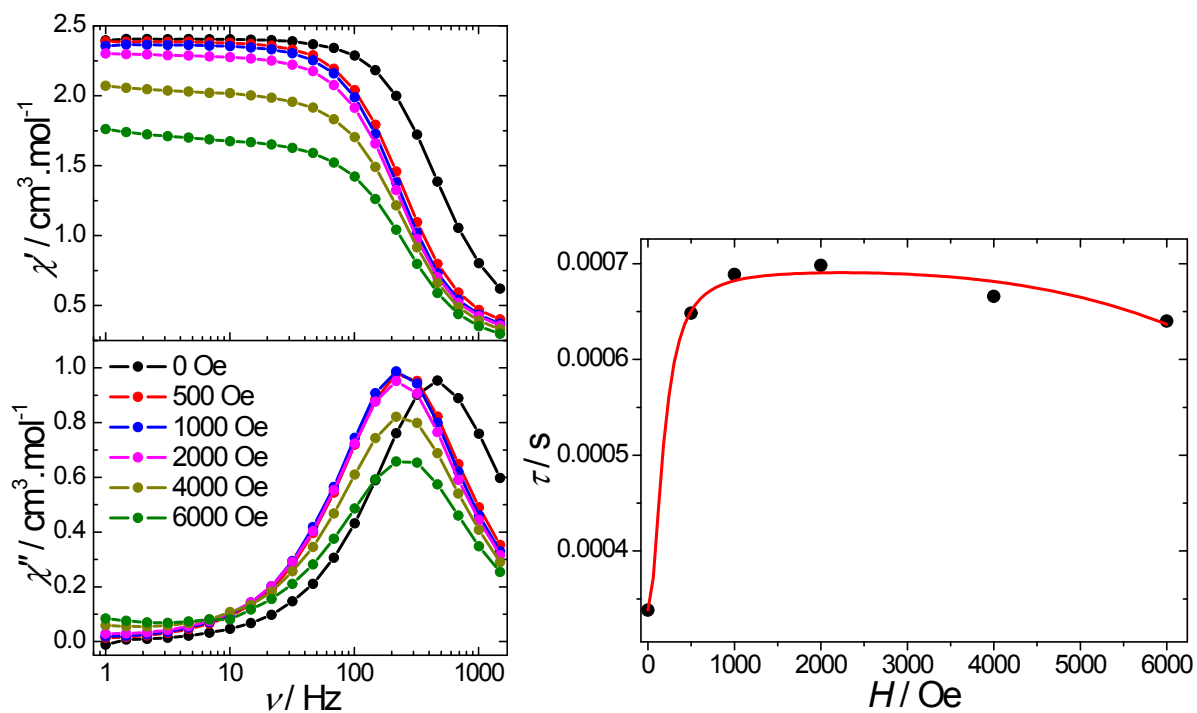


Figure S5: Left: Frequency dependence of χ' and χ'' for **1** for various dc fields at 6 K. Right: Field dependence of the relaxation time for **1** at 6 K. The red solid line represents the fit with Eq. 2.

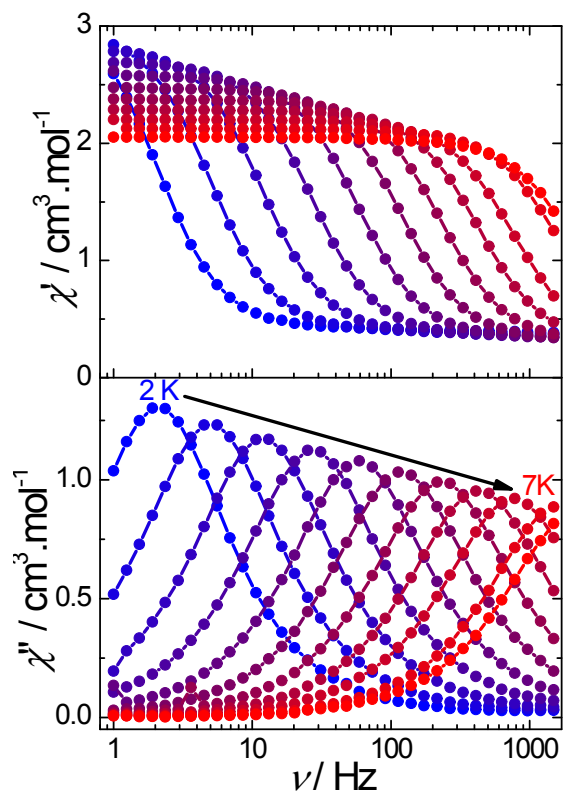


Figure S6: Frequency dependence of χ' and χ'' for **1** under a 1000 Oe dc field.

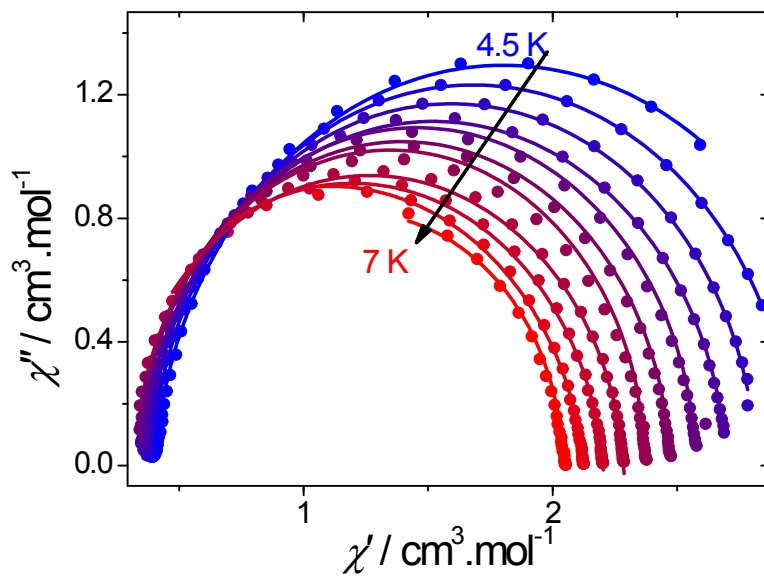


Figure S7: Cole-Cole (Argand) plot obtained using the ac susceptibility data for 1 (1000 Oe). The solid lines correspond to the best fit obtained with a generalized Debye model.

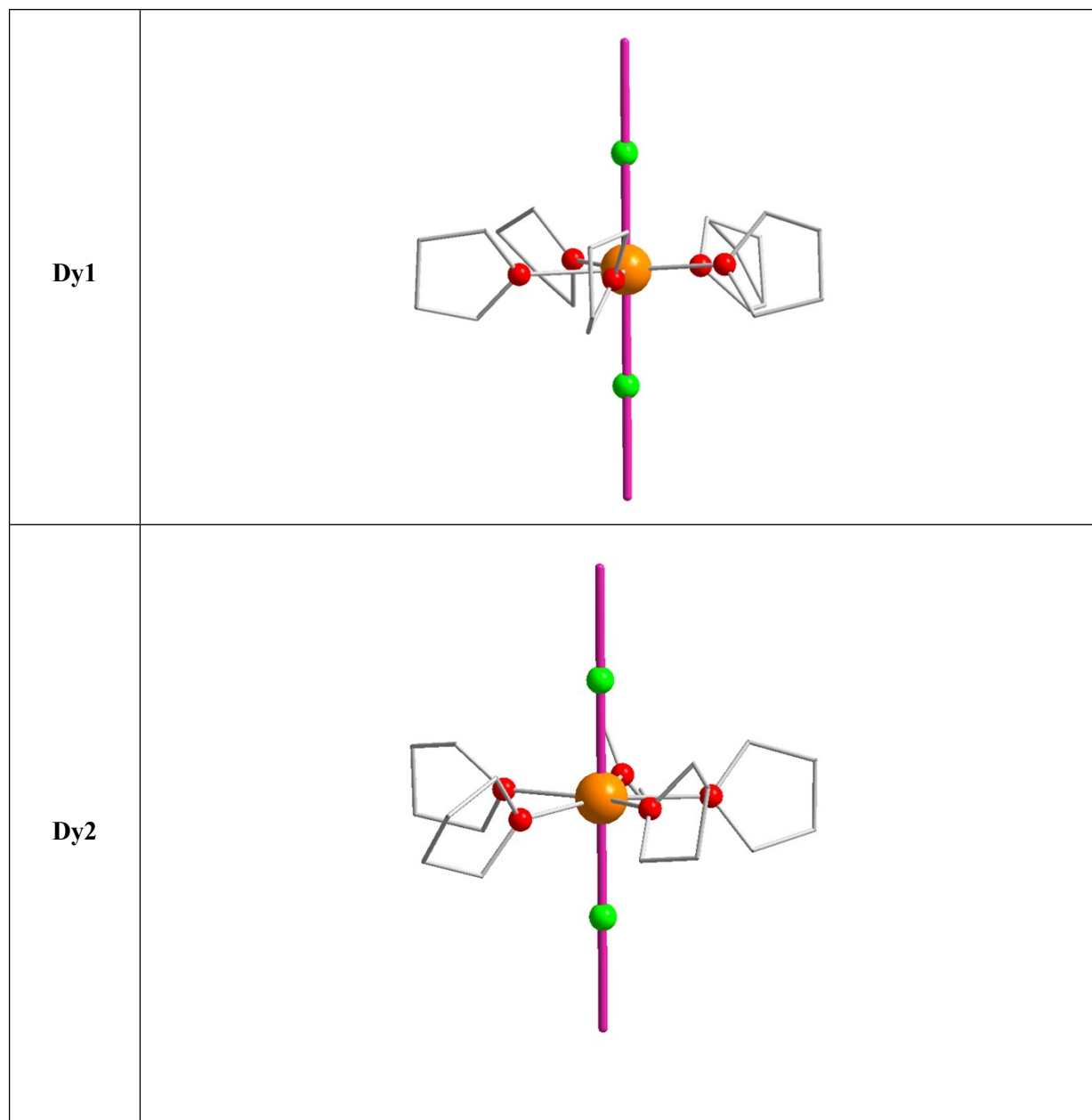


Figure S8: Orientation of the anisotropic axis (purple) in **1** obtained from the MAGELLAN software.

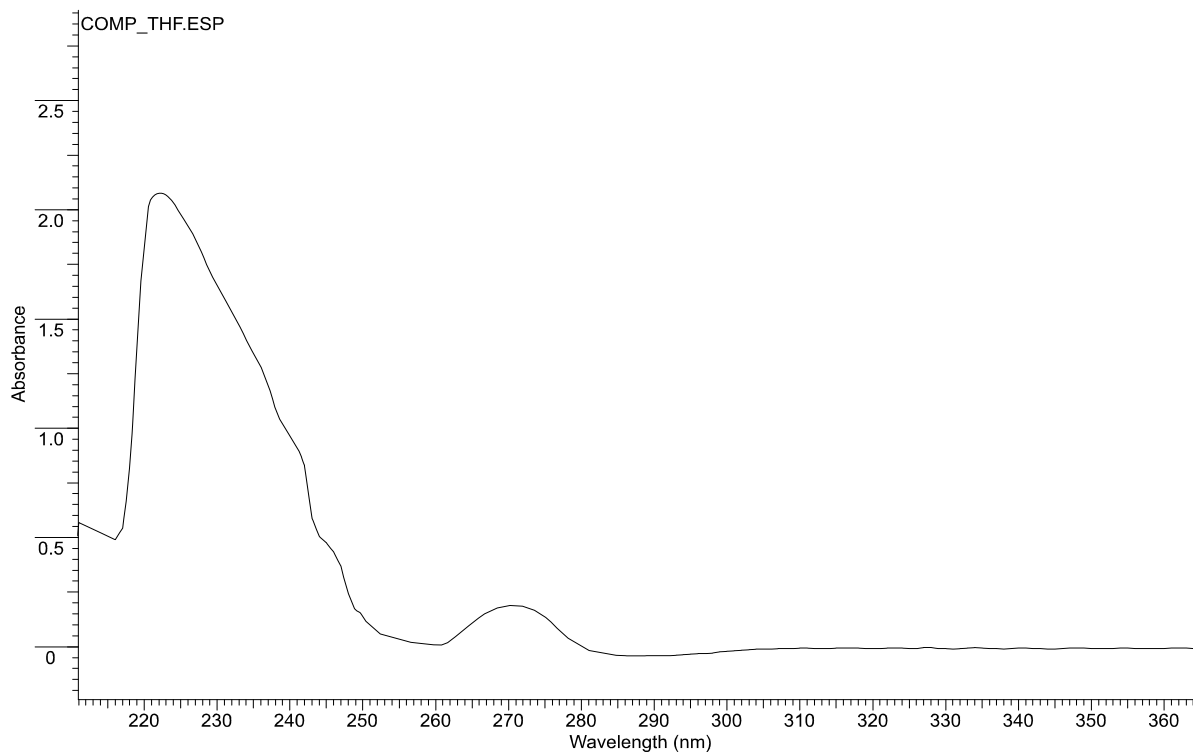


Figure S9: Absorption spectrum of **1** in THF.

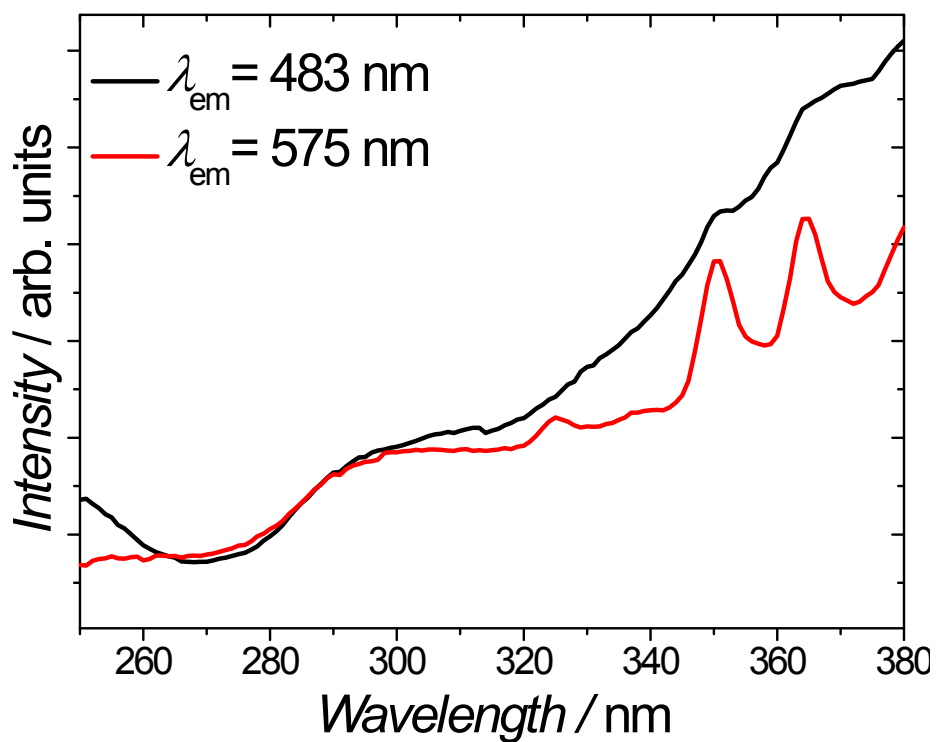


Figure S10: Room temperature excitation spectrum for **1** acquired at different emission wavelengths.

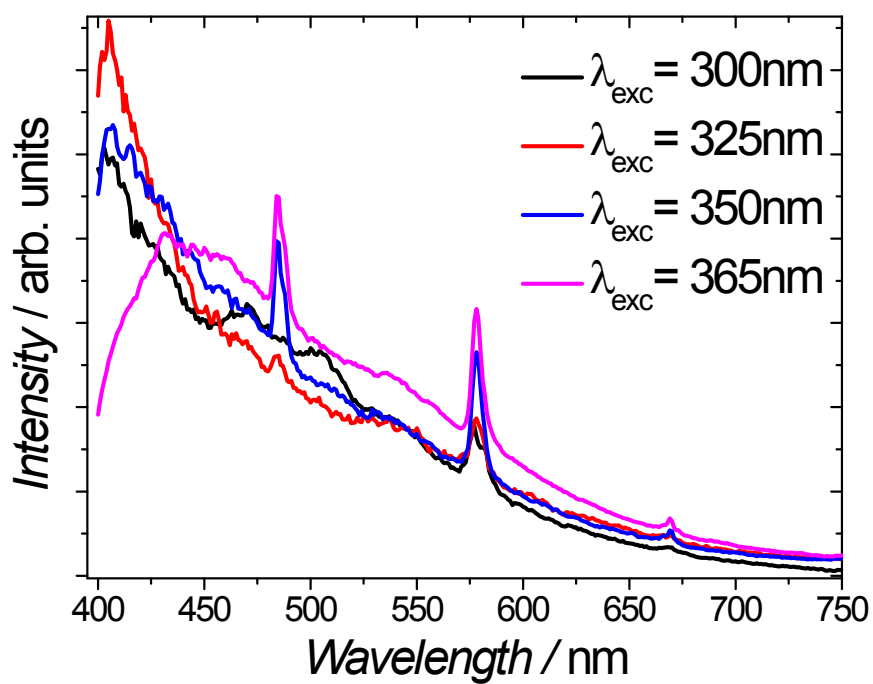


Figure S11: Low temperature (77 K) excitation spectra for **1** acquired at different excitation wavelengths.

Table S1: SHAPE analysis for **1**.

	HP	HPY	PBPY	COC	CTPR	JPBPY	JETPY
Dy1	34.478	26.321	0.219	7.256	5.527	4.991	23.915
Dy2	34.847	26.312	0.244	7.304	5.585	5.142	24.375

HP: Heptagon
 HPY: Hexagonal pyramid
 PBPY: Pentagonal Bipyramid
 COC: Capped Octahedron
 CTPR: Capped trigonal prism
 JPBPY: Johnson pentagonal bipyramid J13
 JETPY: Johnson elongated triangular pyramid J7

Table S2: Fitting of the Cole-Cole plots with a generalized Debye model for temperature ranging from 1.8 to 7.2 K under a zero dc field for **1**.

T (K)	χ_s (cm ³ . mol ⁻¹)	χ_T (cm ³ . mol ⁻¹)	α
1.8	1.74634	7.15696	0.26688
2.22	1.42134	5.87117	0.25043
2.64	1.19728	4.93623	0.24359
3.06	1.03659	4.27193	0.23411
3.48	0.92375	3.78996	0.2275
3.9	0.83877	3.40241	0.23299
4.32	0.74318	3.07156	0.20394
4.74	0.67181	2.8441	0.1817
5.16	0.57872	2.66723	0.11696
5.58	0.48971	2.56247	0.00905
5.98	0.4397	2.39287	0.00903
6.2	0.42526	2.31818	4.64529E-5
6.38	0.32319	2.21484	0.04235
6.5	0.41384	2.21309	3.51806E-14
6.78	0.24311	2.08388	0.04459
7.2	0.43152	1.99703	0.00937

Table S3: Fit parameters of the field dependence of the relaxation time at 6 K for **1**.

<i>Compound</i>	<i>D (s⁻¹K⁻¹Oe⁻⁴)</i>	<i>B₁ (s⁻¹)</i>	<i>B₂ (Oe⁻²)</i>	<i>K</i>
1 (6 K)	1.16 × 10 ⁻¹⁴	93218	2.09 × 10 ⁻³	226.22

Table S4. Fitting of the Cole-Cole plots with a generalized Debye model for temperature ranging from 4.5 to 7.0 K under a 1000 Oe dc field for **1**.

<i>T</i> (K)	<i>χ_S</i> (cm ³ . mol ⁻¹)	<i>χ_T</i> (cm ³ . mol ⁻¹)	<i>α</i>
4.50	0.47122	3.13444	0.05289
4.75	0.42955	2.93622	0.03255
5.00	0.4032	2.78395	0.03079
5.25	0.38574	2.65712	0.03649
5.50	0.35361	2.55904	0.01565
5.75	0.33963	2.4536	0.01536
6.00	0.32793	2.36935	1.02555E-5
6.25	0.30033	2.23252	0.05523
6.50	0.25249	2.14083	0.06483
6.75	0.16797	2.04945	0.07991
7.00	0.40735	2.03833	1.40246E-5

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