Chemical Communications

Supplementary Information for:

Single-molecule magnetism in cyclopentadienyl-dysprosium chlorides

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General experimental considerations

All synthetic manipulations were performed using standard Schlenk techniques. Toluene was degassed and dried by refluxing over sodium-potassium alloy under nitrogen.

X-ray diffraction data on **1a**, **1b** and **2** were collected on an OXFORD Diffraction XCaliber2 CCD diffractometer using $Mo_{K\alpha}$ radiation.

SQUID measurements were carried out on polycrystalline samples of **1** and **2** by enclosing the sample in O-ring-sealed Kel-F capsules. The capsules were transferred to sample holders in a glovebox, transported to the SQUID magnetometer in a sealed Schlenk tube, and then rapidly transferred to the helium-purged sample space of the magnetometer. Corrections for diamagnetism were made using Pascal's constants.

Synthesis of 1a and 1b. A freshly prepared solution of sodium cyclopentadienide (37 mmol) in thf (60 mL) was added to a stirred suspension of anhydrous dysprosium(III) chloride (5.00 g, 18 mmol) in thf (100 mL) at 0°C. The mixture was refluxed for 16 hours and the solvent then evaporated under reduced pressure, producing a pale yellow solid. Sublimation of the yellow solid (10^{-3} mbar/180°C) resulted in the formation of yellow single-crystals of $[Cp_2Dy(\mu\text{-Cl})]_2$ (**1a**) and $[Cp_2Dy(\mu\text{-Cl})]_\infty$ (**1b**), suitable for X-ray diffraction. Total yield of $[Cp_2Dy(\mu\text{-Cl})]_n$ (3.27 g, 54%). Elemental analysis calculated (%) for $C_{10}H_{10}ClDy$: C 36.60, H 3.07; found C 37.12, H 2.99.

Synthesis of 2. A mixed polymorph sample of **1a**/**1b** (1.50g, 2 mmol) was transferred to a Soxhlet apparatus and repeatedly extracted with hot thf for 6 hours. Slow cooling of the resulting yellow solution produced large yellow crystals of $[Cp_2Dy(thf)(\mu\text{-Cl})]_2$ (**2**) (1.27 g, 70%). Elemental analysis calculated (%) for $C_{14}H_{18}OClDy$: C 42.01, H 4.53; found C 41.93, H 4.40.

Table S1. Crystal data and structure refinement for $[Cp_2Dy(\mu\text{-}Cl)]_2$ (**1a**)

Empirical formula	$C_{20}H_{20}Cl_2Dy_2$	
Formula weight	656.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.8935(6) Å	α = 90°.
	b = 7.7893(3) Å	β = 111.968(6)°.
	c = 12.4090(7) Å	γ = 90°.
Volume	976.49(10) Å^3	
Z	2	
Density (calculated)	2.232 Mg/m^3	
Absorption coefficient	7.865 mm^{-1}	
F(000)	612	
Crystal size	0.2 × 0.2 × 0.2 mm^3	
Theta range for data collection	3.16 to 28.53°.	
Index ranges	-13<=h<=14, -9<=k<=10, -16<=l<=14	
Reflections collected	6469	
Independent reflections	2485 [R(int) = 0.0461]	
Completeness to theta = 28.53°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2218 / 0 / 149	
Goodness-of-fit on F^2	0.962	
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0771	
R indices (all data)	R1 = 0.0469, wR2 = 0.0810	
Largest diff. peak and hole	2.340 and -2.520 e.Å^{-3}	

Table S2. Crystal data and structure refinement for $[Cp_2Dy(\mu\text{-}Cl)]_\infty$ (**1b**)

Empirical formula	$C_{10}H_{10}ClDy$	
Formula weight	328.13	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.6550(4) Å	α = 90°.
	b = 8.3541(5) Å	β = 90°.
	c = 17.7593(12) Å	γ = 90°.
Volume	987.36(10) Å^3	
Z	4	
Density (calculated)	2.207 Mg/m^3	
Absorption coefficient	7.778 mm^{-1}	
F(000)	612.0	
Crystal size	0.1 × 0.1 × 0.01 mm^3	
Theta range for data collection	3.27 to 28.55°.	
Index ranges	-4<=h<=8, -2<=k<=10, -14<=l<=23	
Reflections collected	2727	
Independent reflections	2018 [R(int) = 0.0538]	
Completeness to theta = 28.55°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2018 / 60 / 109	
Goodness-of-fit on F^2	0.906	
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0457	
R indices (all data)	R1 = 0.0405, wR2 = 0.0469	
Absolute structure parameter	-0.06(2)	
Largest diff. peak and hole	1.171 and -1.389 e.Å^{-3}	

Table S3. Crystal data and structure refinement for $[Cp_2Dy(thf)(\mu\text{-}Cl)]_2$ (**2**)

Empirical formula	$C_{28}H_{36}Cl_2Dy_2O_2$	
Formula weight	800.47	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.9778(7) Å	α = 90°.
	b = 21.270(3) Å	β = 108.500(11)°.
	c = 8.3900(9) Å	γ = 90°.
Volume	1350.1(2) Å^3	
Z	2	
Density (calculated)	1.969 Mg/m^3	
Absorption coefficient	5.713 mm^{-1}	
F(000)	772	
Crystal size	0.1 × 0.1 × 0.05 mm^3	
Theta range for data collection	3.20 to 27.50°.	
Index ranges	-10<=h<=10, -24<=k<=27, -10<=l<=4	
Reflections collected	5221	
Independent reflections	2965 [R(int) = 0.0511]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.732 and 0.570	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2965 / 90 / 152	
Goodness-of-fit on F^2	1.132	
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1139	
R indices (all data)	R1 = 0.0907, wR2 = 0.1214	
Largest diff. peak and hole	3.620 and -1.720 e.Å^{-3}	

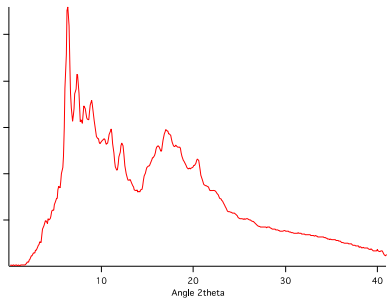

Fig. S1. Powder X-ray diffraction pattern of a mixed polymorph sample of **1a**/**1b**.

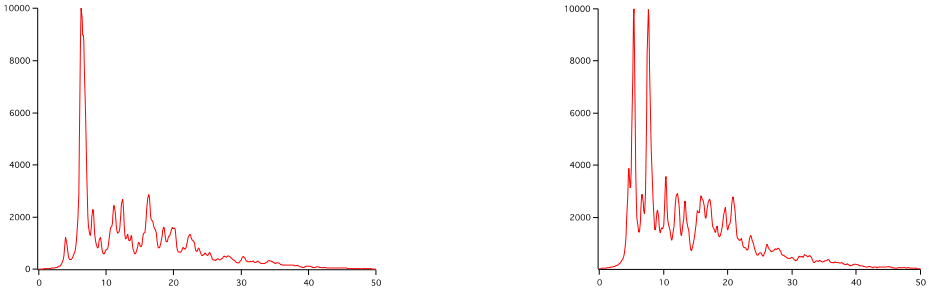

Fig. S2. Powder patterns of **1a** (left) and **1b** (right) calculated based on single-crystal diffraction data using the Mercury software. **1a** has a large single peak at 6.3°, and **1b** has large peaks at 5.4 and 7.6°.

Isolated 2θpeaks are present in each compound that show little overlap, allowing the determination of a mixing ratio. The experimental powder patterns shows significant peaks at 6.3° and one at 7.3°, althoughno peak was observed at 5.4° due to the beam stop obscuring the diffraction. Matching the intensities of the 6.3 and 7.3° peaksin the experimental powder pattern with the calculated intensities for the 6.3 and 7.6° peaks yielded an approximate mixing ratio of 3:1 for **1a**:**1b**.

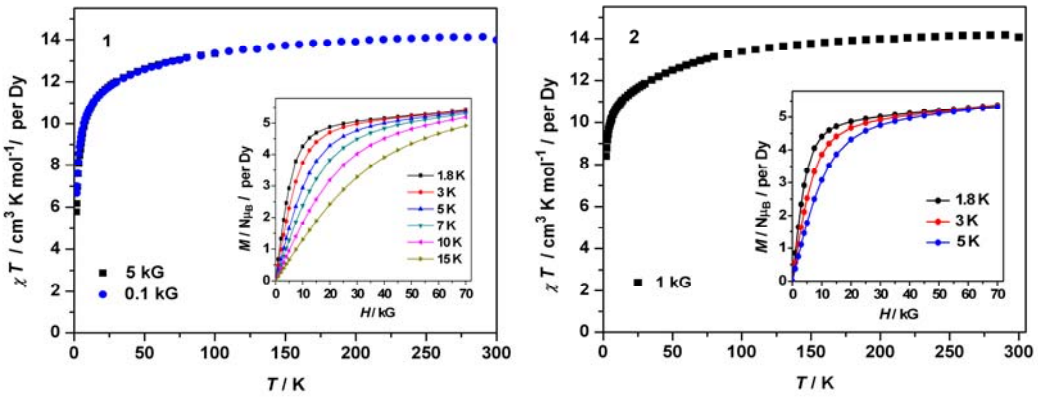

Fig. S3.Plots of χT vs. T for (left) **1** at H = 0.1 and 5 kG, and (right) **2**at H = 1 kG. Inset: Plots of M vs. H for (left) **1** and (right) **2,** at temperatures between 1.8 and 15 K.

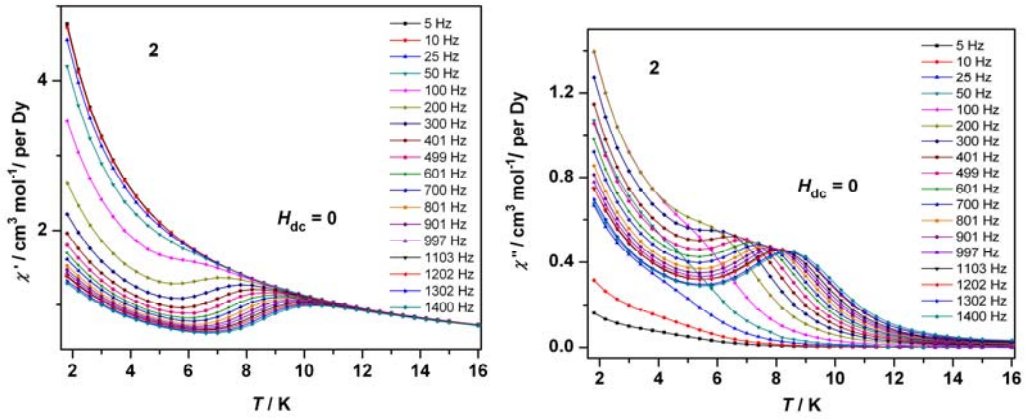

Fig.S4. Temperature dependence of the (left) in-phase (χ') and (right) out-of-phase (χ'') ac susceptibility of **2** at zero-d.c. field and 1.55 G a.c. field oscillating at the indicated frequencies.

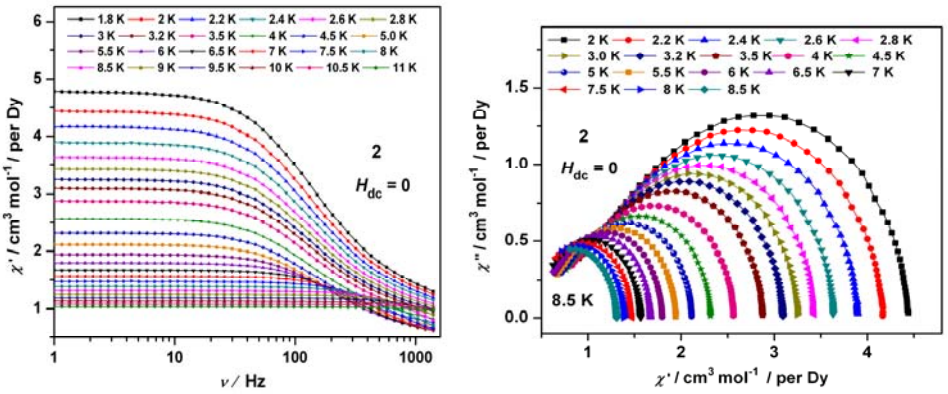

Fig. S5.Left: Frequency dependence (in zero-d.c. field) of the in-phase (χ')a.c. susceptibility of **2** at several temperatures between 1.8 and 11 K.**Right:** Cole-Cole diagrams for **2** at different temperatures between 2 and 8.5 K.

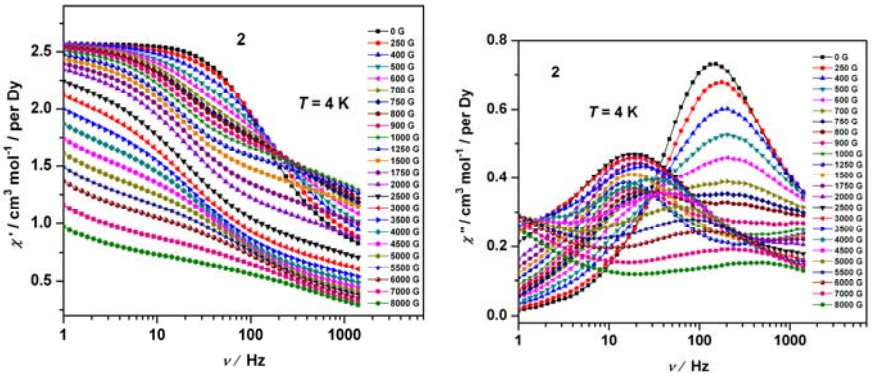

Fig. S6. Frequency dependence at 4 K of the in-phase (χ') (left) and out-of-phase (χ_M'') (right) a.c. susceptibility of **2** under several d.c.-fields from 0 to 8000 G.

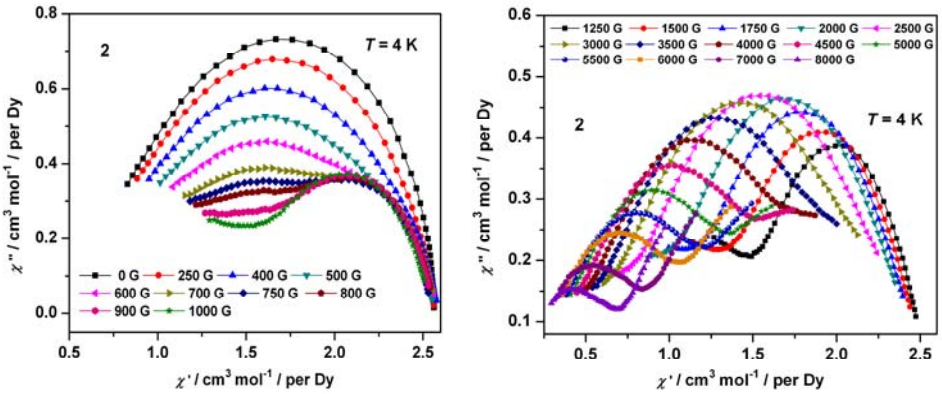

Fig. S7. Argand plots for **2** at 4 K in several d.c.-fields.

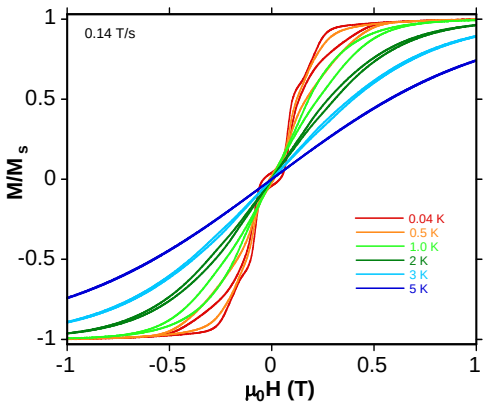

Fig. S8. Field dependence of the magnetization for **2** at the field sweep rate of 0.14 T/sand temperatures between 0.04 and 5 K.

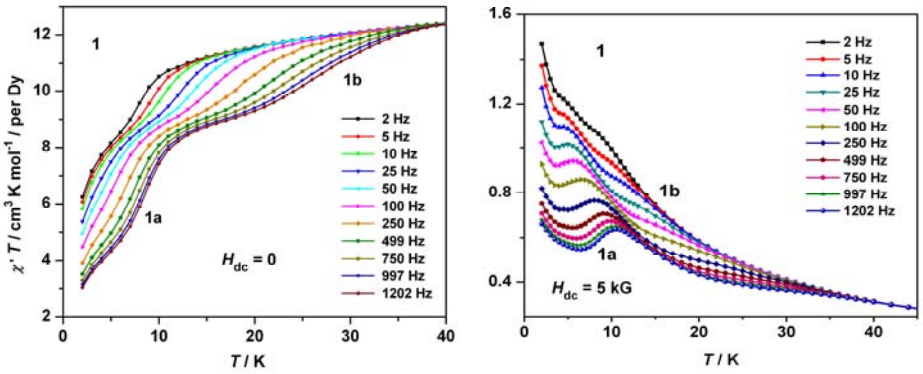

Fig. S9. Plots of (left)χ'*Tvs. T* in zero-d.c. field and (right) χ'*vs. T* in 5kG dc field, for **1a/1b**, at several frequencies between 2 and 1202 Hz.

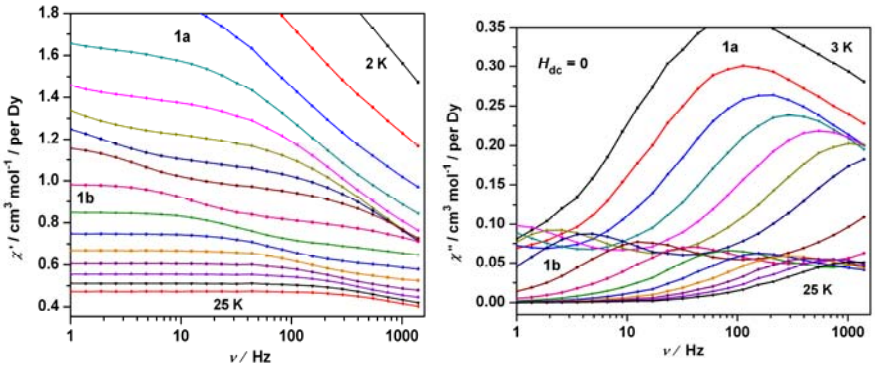

Fig. S10. Frequency dependence of the (left) in-phase (χ') and (right) out-of-phase (χ'') ac susceptibility of **1a/1b** at temperatures between 2 and 25 K.

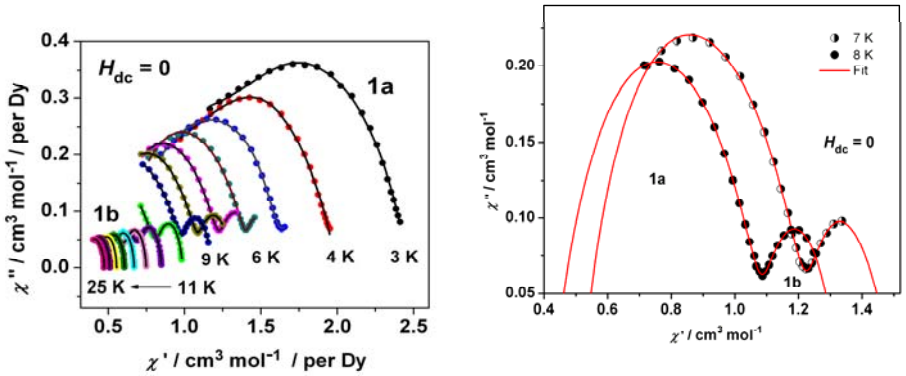

Fig. S11.Left: Cole-Cole plots for **1a/1b** at temperatures between 3 and 25 K and zero d.c.-field. **Right:** Fits of Cole-Cole plots at 7 and 8 K as a sum of two modified Debye processes, withτ_{1a} (ms)/τ_{1b} (ms)/α_{1a} /α_{1b} = 0.27 / 163.7/ 0.33 / 0.11 at 7 K and 0.15 / 78.6 / 0.33 / 0.12 at 8 K.