Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

Magnetic relaxation and cooling in pentametallic lanthanide square-based pyramids

Robin J. Blagg,[a] Floriana Tuna,[a] Eric J. L. McInnes[a] and Richard E. P. Winpenny*[a]

[a] *School of Chemistry and Photon Science Institute, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom. Tel: +44 (0) 161 275 4654; E-mail: richard.winpenny@manchester.ac.uk*

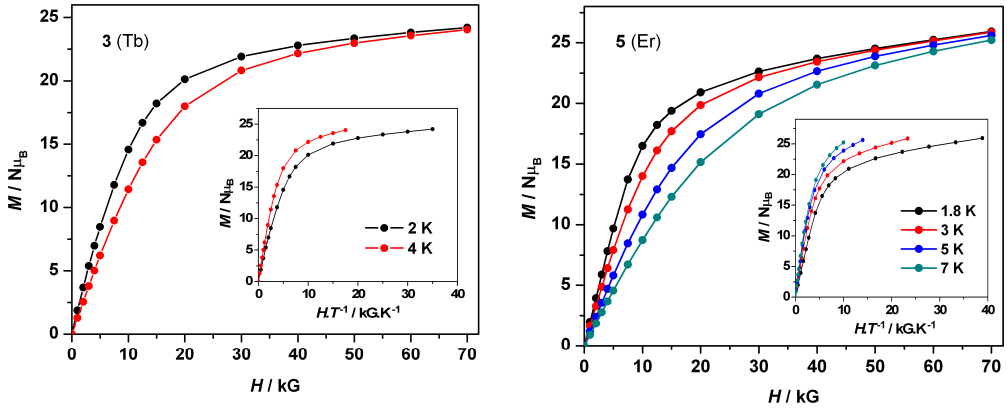

Fig. S1. Left: *M*(*H*) for **3** at 2 and 4 K. Right: *M*(*H*) for **5** at 1.8, 3, 5 and 7 K. Inset: *M*(*H*/*T*) of **3** (left) and **5** (right) at the same temperatures.

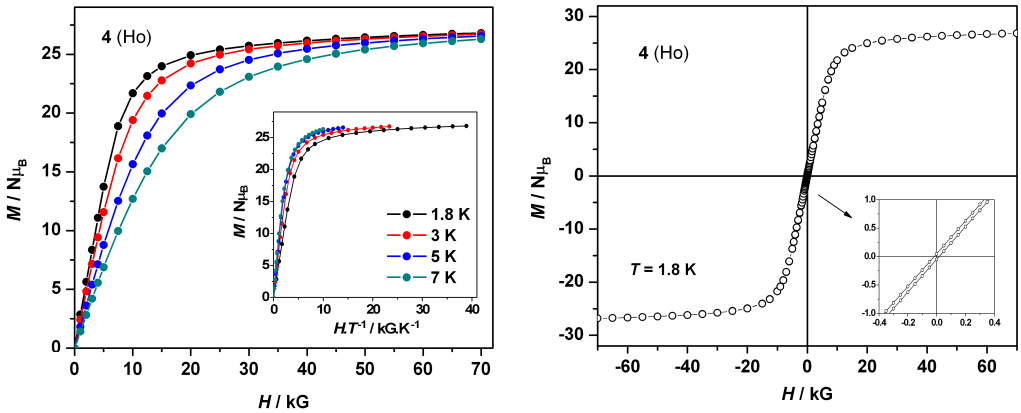

Fig. S2. Left: *M*(*H*) for **4** at 1.8, 3, 5 and 7 K. Inset: *M*(*H*/*T*) of **4** at 1.8, 3, 5 and 7 K. Right: *M*(*H*) for **4** at 1.8 K between -70 and 70 kG.

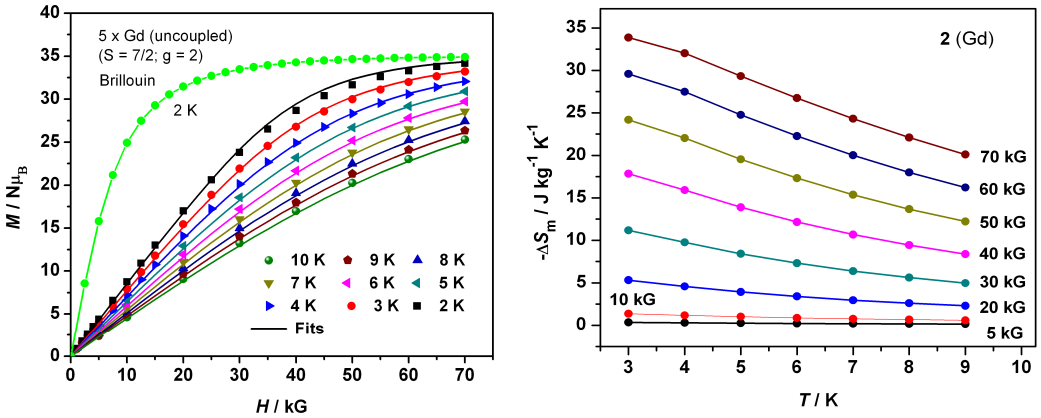

Fig. S3. Left: experimental $M(H)$ for **2** at several temperature between 2 and 10 K, with calculated Brillouin curve (green symbols; $g = 2$; $T = 2$ K) and fits (solid lines; $g = 2$; $J = -0.085$ cm^{-1}) according to eq (1). Right: Calculated $-\Delta S_m(T)$ for **2** at various fields (5 - 70 kG).

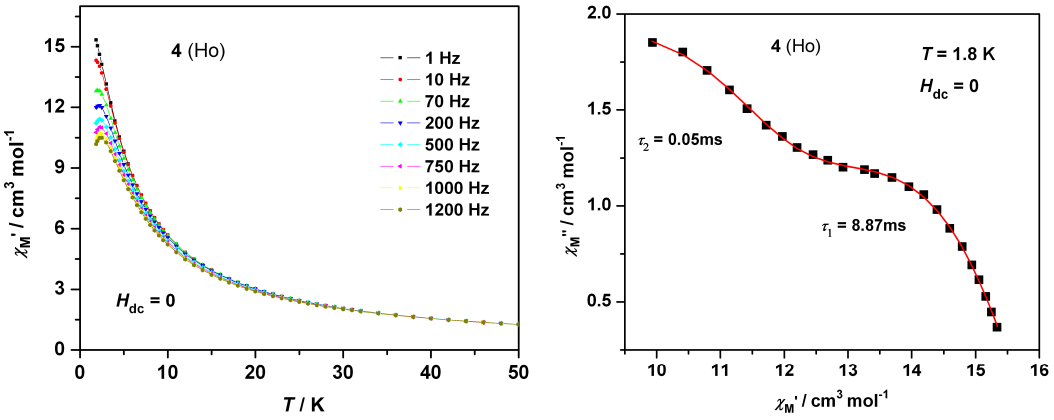

Fig. S4. Left: Temperature dependence of the in-phase (χ_M') ac susceptibility of **4** at zero-dc field and 1.55 G ac field. **Right:** Cole-Cole diagram at 1.8 K and zero-dc field, with the best fit to eq. 2 given as red line.

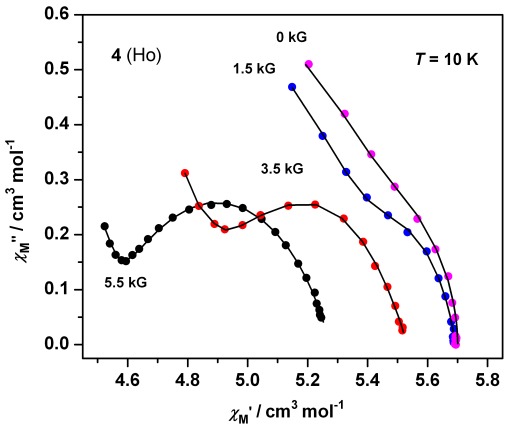

Fig. S5. Cole-Cole diagrams at 10 K for **4** at 0, 1.5, 3.5 and 5.5 kG dc fields. Solid lines represent the best fits to eq. 2.

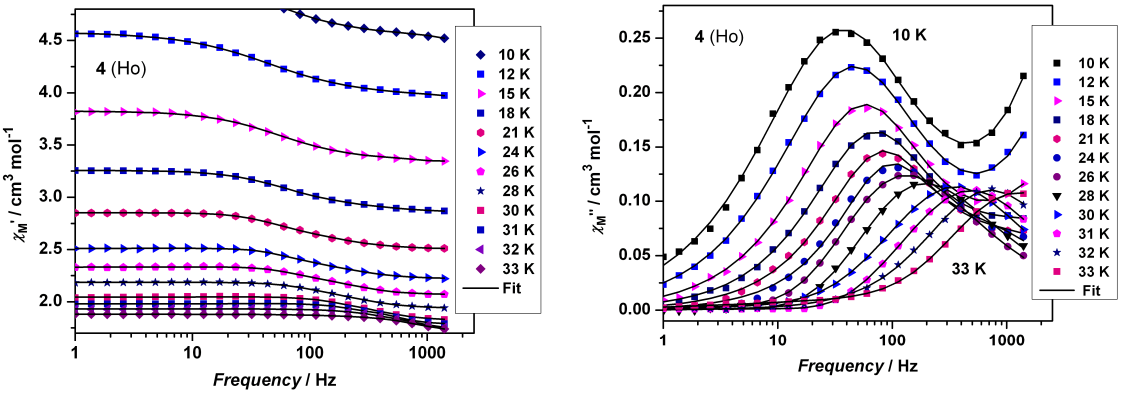

Fig. S6. Frequency dependence (in zero-dc field) of the (left) in-phase (χ_M') and (right) out-of-phase (χ_M'') ac susceptibility of **4** at several temperatures between 10 and 33 K. Solid lines represent the best fits to eq. 2. The results were used to construct the Arrhenius plot in Fig.5.

$$\chi_{ac}(\omega) = \frac{\chi_2 - \chi_1}{1+(i\omega\tau_2)^{(1-\alpha 2)}} + \frac{\chi_1 - \chi_0}{1+(i\omega\tau_1)^{(1-\alpha 1)}} + \chi_0 \qquad \textbf{(2)}$$

$\chi_2 \equiv \chi_T$ = isothermal χ ($\omega \rightarrow 0$)
$\chi_1 \equiv \chi_s$ = adiabatic χ ($\omega \rightarrow \infty$)
ω = angular frequency
τ = relaxation time
α is a measure of the distribution of relaxation times

Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of dry nitrogen. Toluene was dried using an Innovative Technologies solvent purification system, *n*-hexane was dried by heating to reflux over CaH_2, and anhydrous HO^{i}Pr was purchased from Sigma–Aldrich; all solvents were stored over 3 Å molecular sieves and deoxygenated prior to use. Anhydrous $LnCl_3$ (Ln = Sm, Gd, Tb, Ho, Er) was purchased from Strem Chemicals Inc.

Synthesis of $[Gd_5O(O^iPr)_{13}]$ **2**: potassium metal (0.5 g, 12.8 mmol) was dissolved in HO^{i}Pr/toluene (20 cm3) of 1:1 (*v*/*v*) ratio before addition of 1.00 mmol.cm^{-3} H_2O in the same solvent mixture (0.85 cm^3, 0.85 mmol H_2O). $GdCl_3$ (1.12 g, 4.27 mmol) was added after one hour. After stirring for at least 48 h, the reaction mixture was filtered through dry celite and the volatile solvents removed in vacuo. The solid was dissolved in a minimum volume of *n*-hexane, filtered and stored overnight at –20 °C to give crystalline **2** (40%) which was isolated by filtration and dried *in vacuo*.

The compounds $[Ln_5O(O^iPr)_{13}]$ (Ln = Sm **1**, Tb **3**, Ho **4**, Er **5**) were synthesized by an analogous method using the appropriate anhydrous lanthanoid chloride.

Observed and calculated elemental analysis for $C_{39}H_{91}Ln_5O_{14}$

	calculated / %			observed / %		
	C	H	Ln	C	H	Ln
$[Sm_5O(O^iPr)_{13}]$ **1**	30.50	5.97	48.95	30.63	6.12	48.66
$[Gd_5O(O^iPr)_{13}]$ **2**	29.83	5.84	50.07	30.02	5.97	49.89
$[Tb_5O(O^iPr)_{13}]$ **3**	29.67	5.81	50.33	29.66	6.05	50.14
$[Ho_5O(O^iPr)_{13}]$ **4**	29.12	5.70	51.26	29.35	5.94	51.47
$[Er_5O(O^iPr)_{13}]$ **5**	28.91	5.66	51.61	28.99	5.51	51.49