Supporting Information

Centred nine-metal rings of lanthanides

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Experimental Details

All reagents, metal salts and ligands were used as obtained from Aldrich. Analytical data were obtained by the microanalytical service of the University of Manchester.

Preparation of starting materials

$[Gd_2(O_2C^tBu)_6(HO_2C^tBu)_6]$, $[Dy_2(O_2C^tBu)_6(HO_2C^tBu)_6]$ and $[Co_3(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3]\cdot O_2C^tBu$ were prepared as reported.[a,b]

Preparation of compounds 1 and 2

Compound **1** was synthesised by reacting a mixture of dysprosium pivalate $[Dy_2(O_2C^tBu)_6(HO_2C^tBu)_6]$ (0.46 g, 0.30 mmol), $[Co_3(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3]\cdot O_2C^tBu$ (1 g, 0.88 mmol), *tert*-butyl phosphonic acid ($H_2O_3P^tBu$) (0.07 g, 0.507 mmol) and pyridine (C_5H_5N) (0.5 mL, 6.20 mmol) in acetonitrile (CH_3CN) (15 ml) for 7 hrs to form a dark brown solution. The solution was filtered and then allowed to stand undisturbed at room temperature for ten days. Light brown colour crystals of **1** suitable for X-ray were collected. Yield 30 mg (10.56%), based on $[Dy_2(O_2C^tBu)_6(HO_2C^tBu)_6]$ EA for $C_{159}H_{291}Dy_{10}Co_3N_3O_{72}P_6$, found (calc); C 35.57 (35. 46); H 5.48 (5.45); N 0.79 (0.78); Dy 30.21 (30.18); P 3.49 (3.45); Co 3.33 (3.29).

A similar procedure to that used for **1** was used for **2** using $[Gd_2(O_2C^tBu)_6(HO_2C^tBu)_6]$ (0.30 mmol) in place of $[Dy_2(O_2C^tBu)_6(HO_2C^tBu)_6]$. Yield 55 mg (19.24 %), based on $[Gd_2(O_2C^tBu)_6(HO_2C^tBu)_6]$ EA for $C_{159}H_{291}Dy_{10}Co_3N_3O_{72}P_6$, found (calc); C 35.86 (35.81); H 5.54 (5.50); N 0.80 (0.79); Gd. 29.52 (29.49); P 3.51 (3.49); Co 3.35 (3.31).

a. Y. Zheng, M. Evangelisti, F. Tuna and R. E. P. Winpenny, *J. Amer. Chem. Soc.*, 2012, **134**, 1057.
b. G. Aromi, A. S. Batsanov, P. Christian, M. Helliwell, A. Parkin, S. Parsons, A. A. Smith, G. A. Timco, R. E. P. Winpenny, *Chem. Eur. J.* **2003**, *9*, 5142-5161.

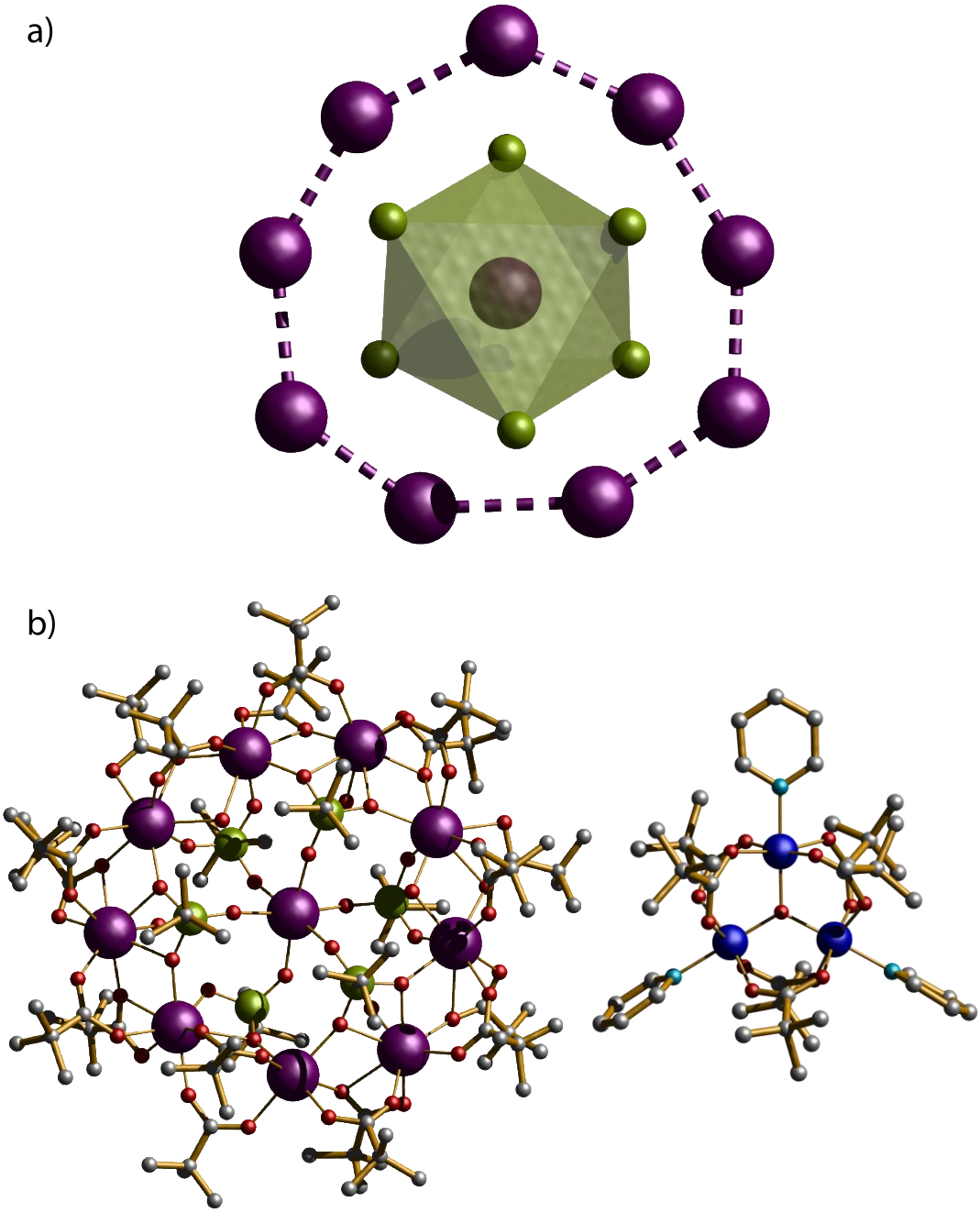

Figure S1. a) Polyhedral representation of central Dy with octahedral environment in $\{Dy_{10}\}$; b) Crystal structure of anion $\{Dy_{10}\}$ and $\{Co_3\}$ cation. Scheme: Dy, purple; P, green; Co, cyan:O, red.

Magnetic measurements

Magnetic measurements were performed on polycrystalline samples, using a Quantum Design MPMS-XL7 SQUID magnetometer armed with a 7 T magnet. Data were corrected for the diamagnetism of the compounds (Pascal constants) and for diamagnetic contribution of eicosane and the sample holder by measurement.

Fits of data for compound **2**

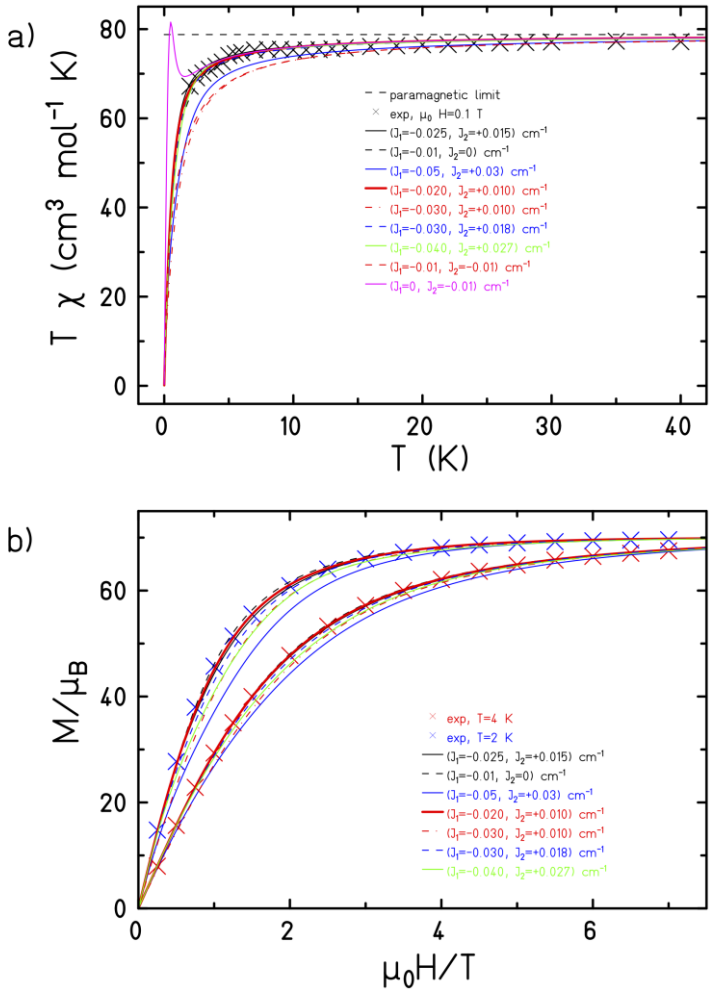

Figure S2. Alternative fits of (a) χT vs T and (b) M vs H for compound **2**. The various exchange value parameter sets used are given in the key.

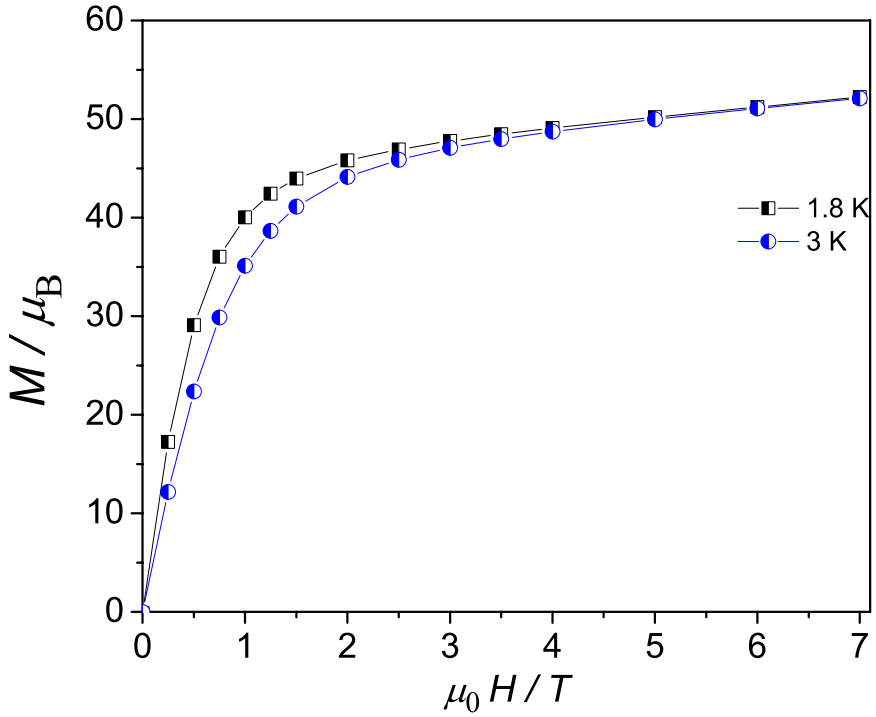

Figure S3. Magnetisation as a function of applied field at different temperatures for **1**.

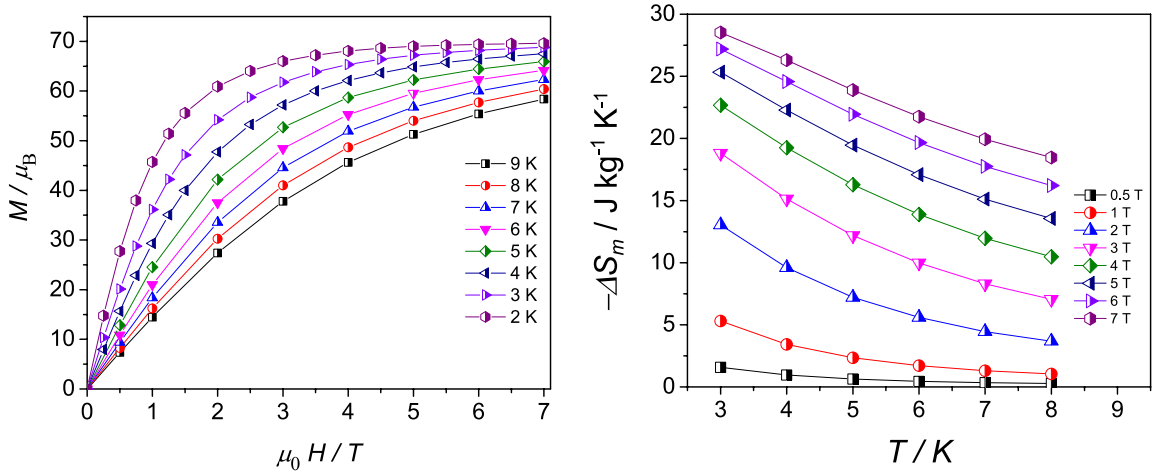

Figure S4. Magnetisation as a function of applied field (*M* vs *H/T*) at different temperatures (left) for **2** and magnetic entropy change (ΔS_m) of **2** at various field and temperatures (right).