

Electronic Supporting Information

3d – 4f Clusters with Large Spin Ground States and SMM Behaviour

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Experimental details:

TPA was synthesized by literature procedure.¹ All other reagents were used as obtained from Aldrich.

General synthetic procedure: A 1:2:1 ratio mixture of $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Dy}$, Gd or Y), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and TPA in MeCN (15 mL) was stirred for 10 min. The base [LiOMe (for **1**) or a mixture of $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$ and Et_3N in 4:2 ratios (for **2** and **3**)] was added to the above reaction mixture and stirred for 12 h at room temperature. Then the reaction mixture was filtered and on slow evaporation affords the corresponding products as crystals. Specific details of each reaction are given below.

1: $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.40 g, 0.92 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.33 g, 1.80 mmol), TPA (0.30 g, 0.92 mmol) and LiOMe (0.14 g, 3.60 mmol). Blue needle-like crystals were obtained after 4 weeks in 15 % yield. Elemental analysis: calcd. (%): C 36.64, H 3.50, N 0.16, P 4.29; found: C 34.04, H 4.02, N 0.72, P 4.28.

2: $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.41 g, 0.92 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.33 g, 1.80 mmol), TPA (0.30 g, 0.92 mmol), $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$ (0.66 g, 3.60 mmol) and Et_3N (0.25 mL, 1.80 mmol). Tiny blue needle-like crystals were obtained after 8 weeks in less than 5 % yield. There is a K^+ ion in the asymmetric unit found by single crystal X-ray analysis. It is due to the slight impurity of the ligand, TPA. On the other hand, similar reaction condition with pure TPA, no cage **2** was identified. Alternatively, in a deliberate way, KOMe (0.06 g, 0.92 mmol) was used in the above reaction. This time the crystals of **2** obtained in 3 weeks with 9.6 % yield. Elemental analysis: calcd. (%): C 37.52, H 3.73, N 0.46, P 4.08; found: C 37.96, H 3.90, N 1.11, P 4.00.

3: $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.45 g, 1.20 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.44 g, 2.40 mmol), TPA (0.40 g, 1.20 mmol), $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$ (0.89 g, 4.90 mmol) and Et_3N (0.34 mL, 2.40 mmol). Blue crystals were obtained after 2 weeks in 45 % yield. Elemental analysis: calcd. (%): C 41.99, H 3.91, N 0.86, P 4.57; found: C 38.50, H 4.30, N 1.11, P 3.81.

Single crystal X-ray analysis: Data were collected on Bruker SMART APEX CCD diffractometer ($\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$). In all cases the selected crystals were mounted on a Hamilton cryo-loop using Flombin oil and placed in the cold flow (100 K) produced with an Oxford Cryo-cooling device. Complete hemispheres or spheres of data were

collected using ω -scans (0.3°, up to 30 seconds/frame). Integrated intensities were obtained with SAINT² and when they were corrected for absorption SADABS was used.³ Structure solution and refinement was performed with the SHELXTL-package.² The structures were solved by direct methods and completed by iterative cycles of DF syntheses and full-matrix least-squares refinement against F^2 .⁴ Non-hydrogen atoms were refined with anisotropic displacement parameters. Details of the data collection and refinement parameters are given in Table S1. CCDC 655327 (**1**), 655328 (**2**) and 655329 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Figures 1 and 2 (main text) and S1 and S2 (ESI) and its bonding parameters were obtained from DIAMOND 3.2c software package.

Table S1. Crystal data collection and refinement parameters for **1-3**.

Compound	1	2	3
Empirical formula	C ₂₈₅ H _{277.5} N _{11.5} O ₁₂₉ P ₁₂ Cu ₂₄ Dy ₈	C ₂₉₅ H _{309.5} N _{12.50} O ₁₂₃ P ₁₂ Cu ₂₄ Gd ₈ K ₂	C ₃₀₆ H ₃₃₁ N ₁₆ O ₁₁₈ P ₁₂ Cu ₁₆ Y ₁₂
Formula weight (g)	9124.29	9230.85	8576.07
Temperature (K)	100(2)	100(2)	100(2)
Crystal system, Space group	Triclinic, P-1	Monoclinic, P2(1)/n	Triclinic, P-1
Unit cell dimensions			
a (Å):	20.990(4)	23.7646(13)	18.5780(9)
b (Å):	22.894(5)	23.5840(13)	19.6247(9)
c (Å):	23.495(5)	35.765(2)	31.1426(16)
α (°):	101.46(3)	90	104.9180(10)
β (°):	114.81(3)	93.4730(10)	99.2180(10)
γ (°):	106.89(3)	90	107.5860(10)
Volume (Å ³), Z	9114(3), 1	20008.1(19), 2	10103.7(9), 1
F(000)	4504	9154	4335
Crystal size (mm)	0.20 x 0.10 x 0.05	0.2 x 0.1 x 0.05	0.15 x 0.10 x 0.10
θ collection range (°)	1.71 to 25.03	1.63 to 25.03	1.53 to 23.33
Limiting indices			
	-20 ≤ h ≤ 24	-27 ≤ h ≤ 28	-20 ≤ h ≤ 19
	-26 ≤ k ≤ 27	-28 ≤ k ≤ 27	-19 ≤ k ≤ 21
	-27 ≤ l ≤ 24	-38 ≤ l ≤ 42	-29 ≤ l ≤ 34
Reflections collected / unique	47422 / 31559	103776 / 35258	45930 / 28879

	[R(int) = 0.0512]	[R(int) = 0.0560]	[R(int) = 0.0672]
Completeness to θ (%)	98.0	99.7	98.6
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical
Data / Restraints / Parameters	31559 / 1122 / 2034	35258 / 1125 / 1789	28879 / 134 / 2106
Goodness-of-fit on F^2	1.307	1.055	1.017
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0589, wR2 = 0.1211	R1 = 0.0642, wR2 = 0.1784	R1 = 0.0625, wR2 = 0.1876
R indices (all data)	R1 = 0.1160, wR2 = 0.1335	R1 = 0.1085, wR2 = 0.2088	R1 = 0.1210, wR2 = 0.2036
Largest diff. Peak and hole (e. Å ⁻³)	1.567 and -1.109	1.917 and -1.384	1.248 and -0.742

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|; \quad wR = \{[\sum w(|F_o|^2 - |F_c|^2)^2] / [\sum w|F_o|^2]\}^{1/2}$$

Instrumentation: Elemental analysis was performed by School of Chemistry, The University of Manchester micro-analytical laboratory using a Carlo Erba EA1108 elemental analyzer. Magnetic measurements in the temperature range 1.8 K - 300 K were performed on polycrystalline samples (less than 11 mg weight) either constrained in eicosane or finely powdered, using a Qunatum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. Data were corrected for the diamagnetism of the compounds by using Pascal constants and for the diamagnetic contributions of the sample holder and eicosane by measurements. Field and time dependences of the magnetization below 1 K were performed on single crystals using an array of micro-SQUIDs.

References:

1. D. R. Boyd and G. Chignell, *J. Chem. Soc., Trans.*, 1923, **123**, 813.
2. SAINT+ and SHELXTL-PC Package. Bruker Analytical X-ray Systems: Madison, WI, 1998.
3. Area-detector absorption correction; Siemens Industrial Automation Inc., Madison, WI, 1996.
4. G. M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis, University of Göttingen, 1998.

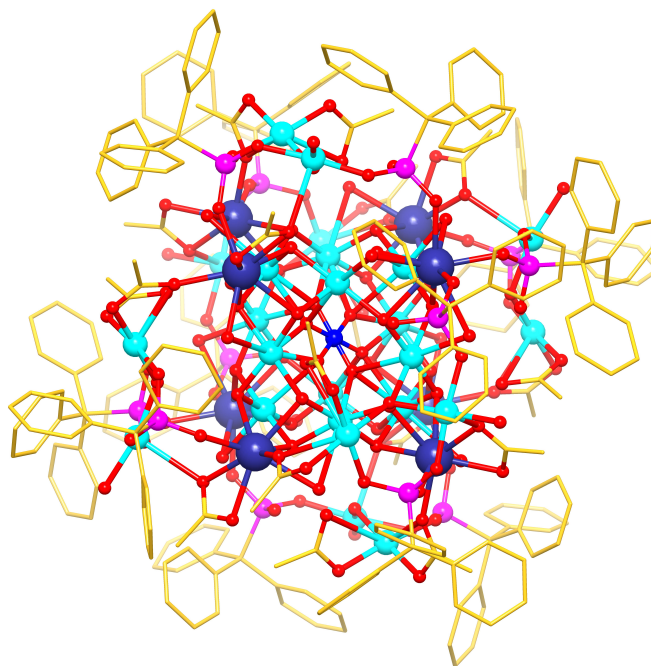


Figure S1. Molecular structure of **1**.

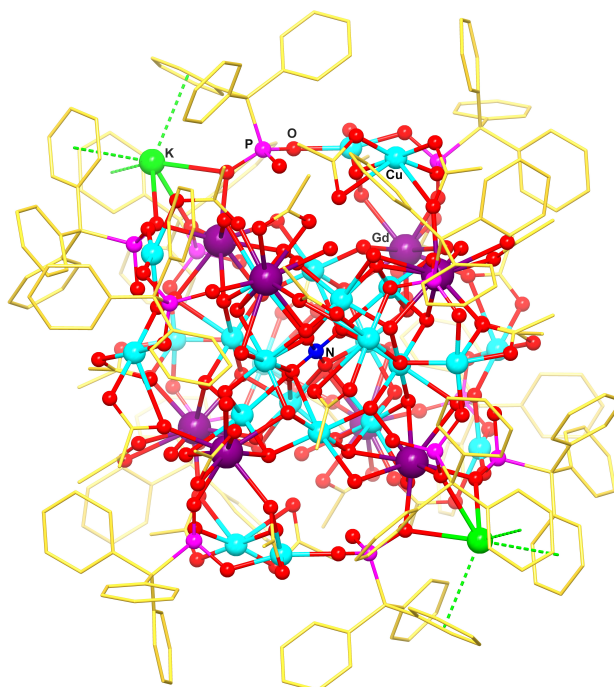


Figure S2. Molecular structure of **2**.

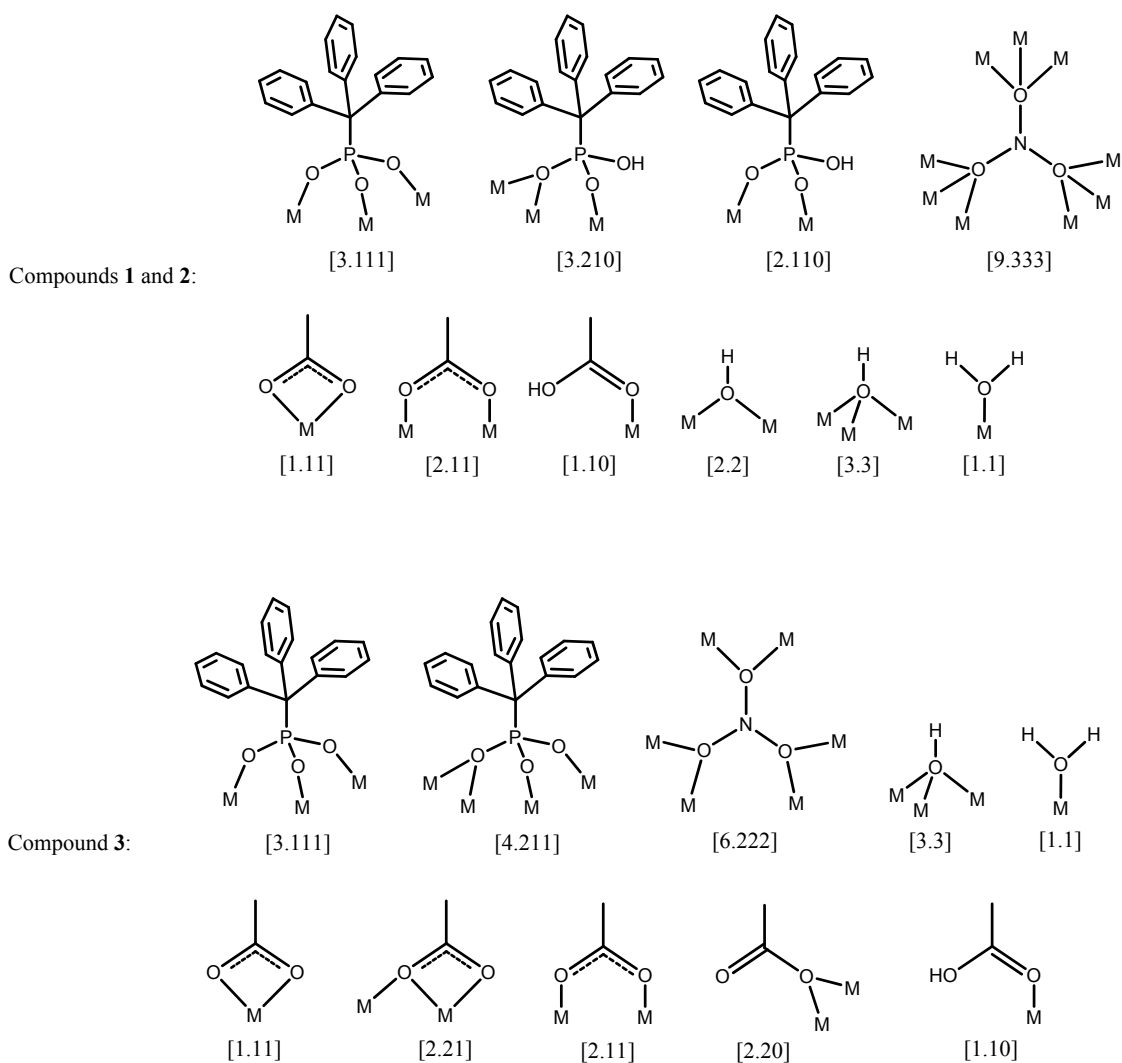


Figure S3. Binding modes for the ligands in the compounds **1-3** (described in terms of Harris notation, see ref. 6 in main text).

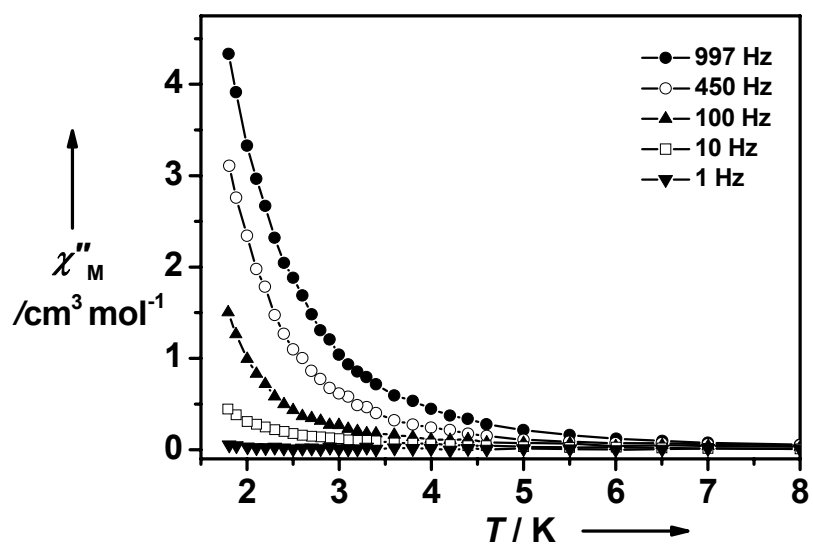


Figure S4

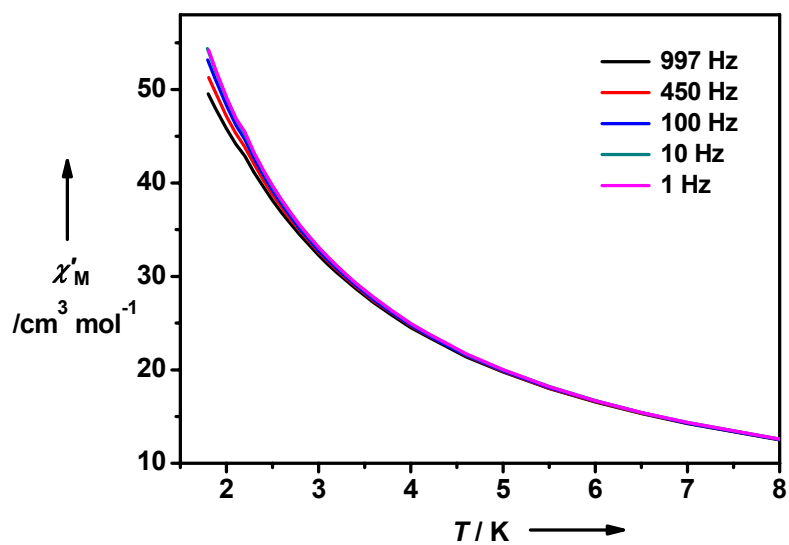


Figure S5

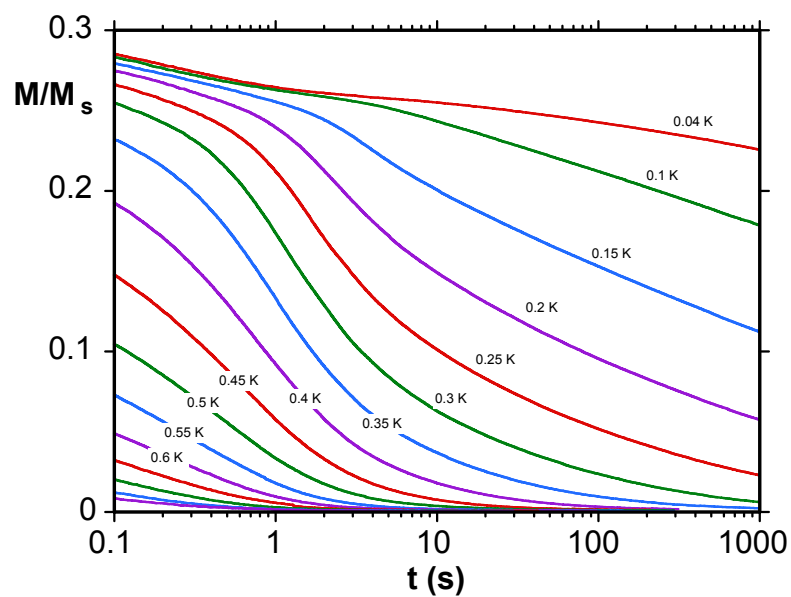


Figure S6

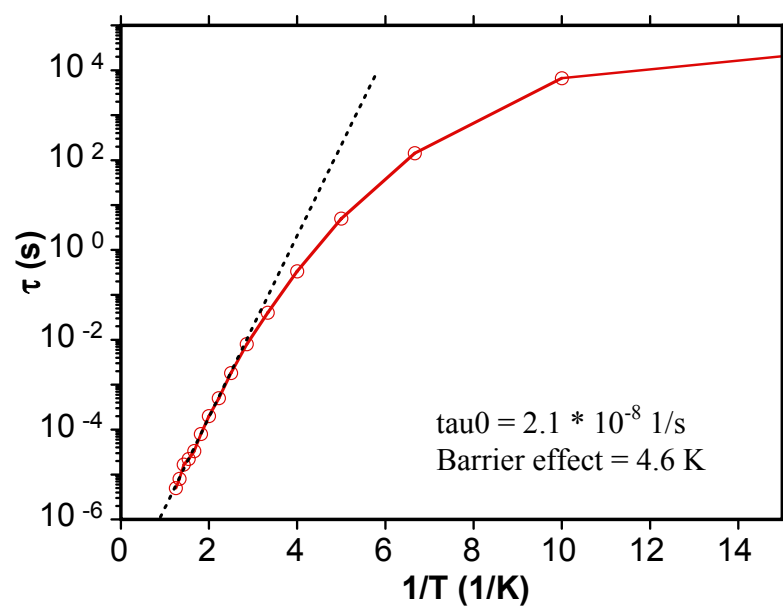


Figure S7

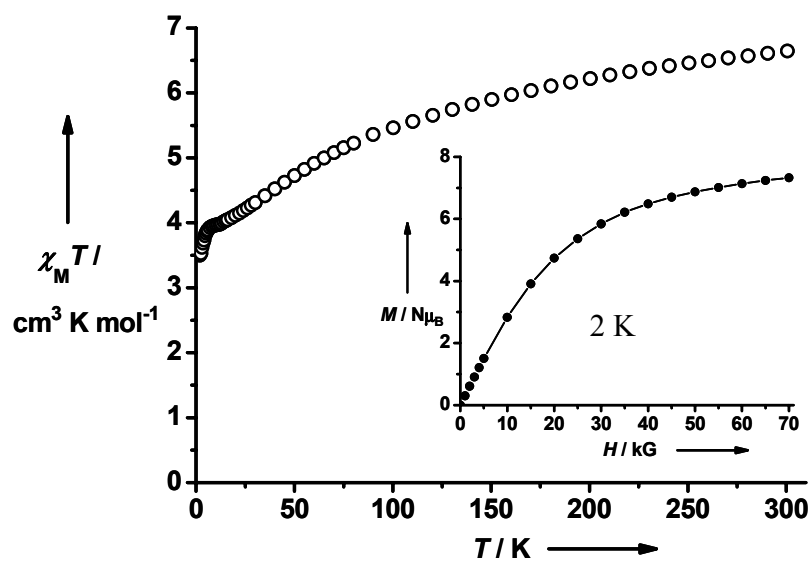


Figure S8