Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Ligand field variations: Tuning the toroidal moment of Dy_6 rings

Amer Baniodeh, Nicola Magnani, Stefan Bräse, Christopher E. Anson and Annie K. Powell

Synthesis

$[Dy_6(Me\text{-}teaH)_6(NO_3)_6]\cdot 6MeCN$ (2)

A solution of (0.228 g, 0.5 mmol) $Ln(NO_3)_3\cdot 6H_2O$ and (0.326 g, 2 mmol) 1-[N,N-Bis(2-hydroxyethyl)amino]-2-propanol (Me-teaH_3) in MeCN/ MeOH (18/14 mL) was stirred at 60°C for 10 min. Triethylamine (0.3 mL) was then added to the clear colorless solution. The reaction mixture was then refluxed for further 20 min. The clear solution was left undisturbed in air. After 1 day, well formed colorless block-like crystals were collected. *Anal.* Calc. (%): C, 20.83; H, 4.247; N, 6.94; found: C, 20.96; H, 4.00; N, 6.91. Selected IR bands (KBr, cm^{-1}): 3371(br), 2970(m), 2934 (w), 2863(s), 1637(w), 1474(m), 1385 (s), 1288(m), 1166(w), 1090(s), 1011(m), 817(m), 646(w), 561(m), 453(m), 400(w). Yield 77%.

$[Dy_6(apdeaH_2)_6(NO_3)_6]\cdot 2THF$ (3)

A solution of (0.46 g, 1mmol) $Dy(NO_3)_3\cdot 6H_2O$ and (0.336 g, 2 mmol) of 3-(n)-amniopropyldiethanolamine (apdeaH_4) in CH_3CN/ THF (40/10 mL) was stirred at r.t. for 10 min, after which triethylamine (0.2 mL) was added to it. The reaction mixture was later heated at 80°C for 10 min. The clear colorless solution was left undisturbed in air. After 1 day, well formed colorless crystals were collected. *Anal.* Calc. C, 24.49; H, 4.60; N, 10.28; found: C, 25.00; H, 4.66; N, 10.57. IR (KBr, cm^{-1}): (3344-3285) (br, w), 2947 (w), 2914 (w), 2886 (w), 2852 (m), 2712 (w), 2491 (w), 2319 (w), 1768 (w), 1740 (w), 1600 (w), 1487 (vs), 1385 (s), 1367 (s), 1304 (s), 1288 (s), 1243 (w), 1125 (w), 1092 (s), 1057 (m), 1036 (m), 1010 (m), 911 (m), 928 (m), 886 (m), 820 (w), 742 and 734 (w), 583 (m) and 568 (w), 494 (w), 386 (m), 386 (m). Yield 83%.

Table S1. Crystallographic data of **2** and **3**.

Compound	Dy_6 (**2**)	Dy_6 (**3**)
Formula	$C_{54}H_{108}Dy_6N_{18}O_{36}$	$C_{50}H_{112}Dy_6N_{18}O_{32}$
FW (g mol^{-1})	2560.58	2452.58
Crystal system	Trigonal	Trigonal
Colour	Colourless	Colourless
Space group	$R\bar{3}$	$R\bar{3}$
a (Å)	17.5124(14)	15.778(1)
c (Å)	24.2551(19)	26.4045(19)
V (Å^3)	6442.1(9)	5692.62(65)
Z	3	3
T (K)	100(2)	200(2)
F(000)	3726	3570
ρ_{calc} (g cm^{-3})	1.980	2.146
μ (mm^{-1})	5.244	5.925
R(int)	0.0296	0.0343
Data with I > 2σ(I)	3003	2174
S (all data)	1.167	1.011
R_1 (I > 2 σ(I))	0.0182	0.0238

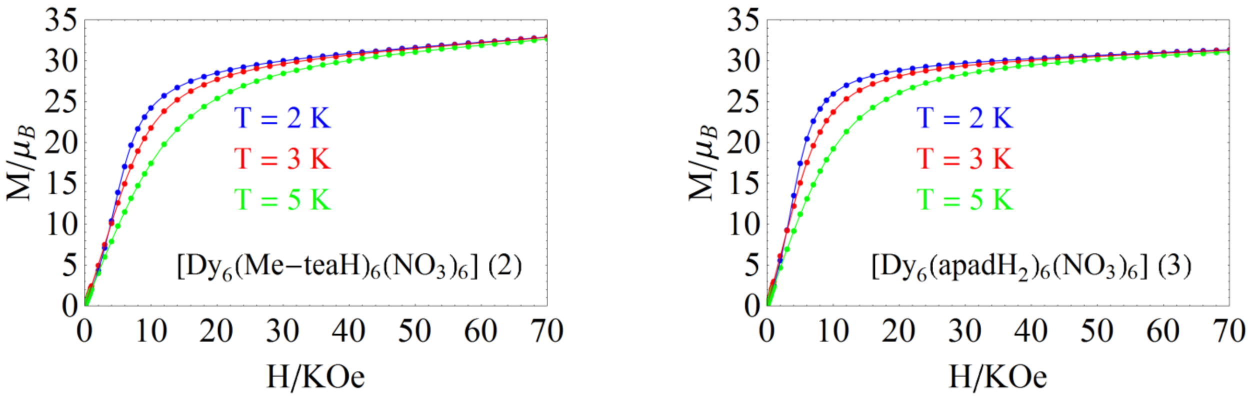

Figure S1. Magnetization curves measured at different temperatures for compounds **2** (left) and **3** (right).

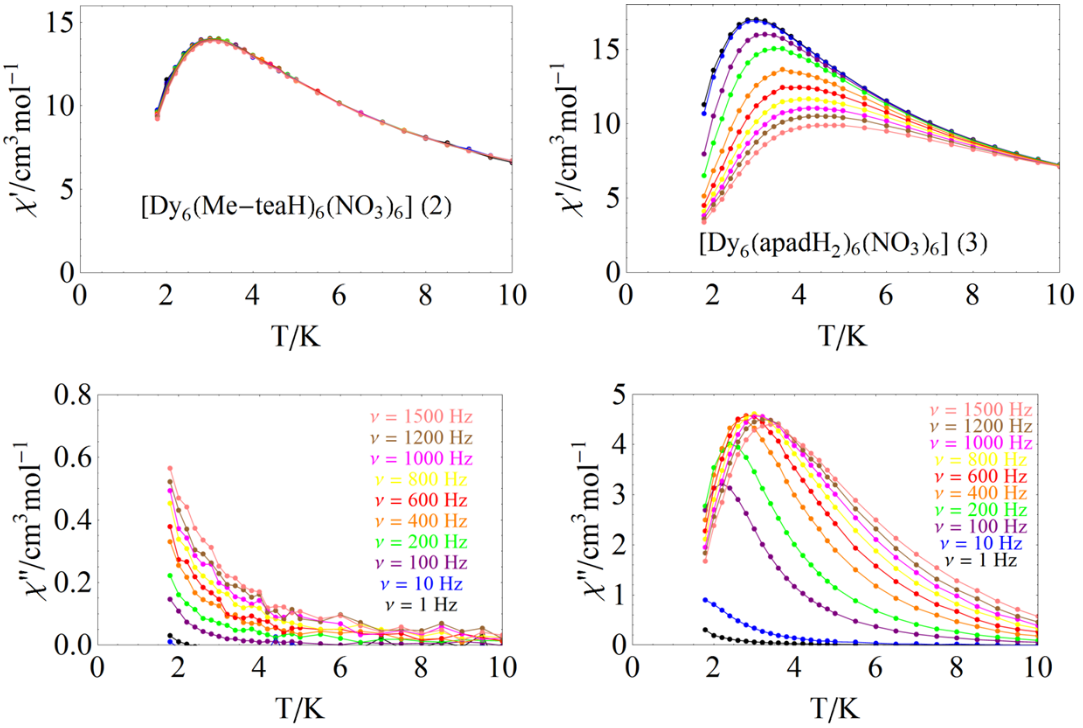

Figure S2. *ac* susceptibility measurements for **2** (left) and **3** (right) under zero *dc* magnetic field. The real and imaginary parts of the generalised dynamic susceptibility are plotted as a function of temperature for different driving field frequencies.

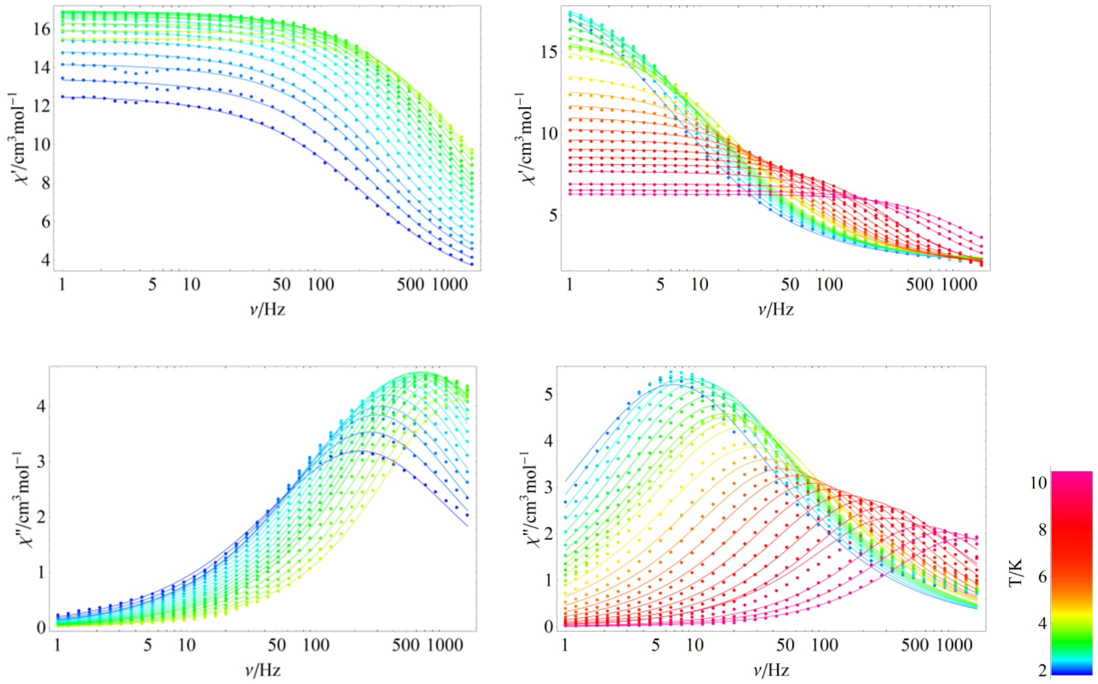

Figure S3. *ac* susceptibility measurements for **3** (right), under zero (left) and 2 kOe (right) applied *dc* magnetic field.

The real and imaginary parts of the generalized dynamic susceptibility are plotted as a function of the driving field frequency for different temperatures (see colour scale). Lines are fits of the data with the equations describing the simultaneous presence of several relaxation processes:

$$\chi^{'}(\omega) = \chi_S + \frac{(\chi_T - \chi_S)\left[1 + (\omega t)^{1-\alpha}\sin\frac{\alpha\pi}{2}\right]}{1 + 2(\omega t)^{1-\alpha}\sin\frac{\alpha\pi}{2} + (\omega t)^{2(1-\alpha)}}, \chi^{''}(\omega) = \frac{(\chi_T - \chi_S)(\omega t)^{1-\alpha}\cos\frac{\alpha\pi}{2}}{1 + 2(\omega t)^{1-\alpha}\sin\frac{\alpha\pi}{2} + (\omega t)^{2(1-\alpha)}}$$

In these equations, χ_S is the adiabatic susceptibility, χ_T the isothermal susceptibility, $\omega = 2\pi\nu$ is the angular frequency, τ is the relaxation time and α is an exponent which gauges the width of the distribution ($\alpha = 0$ for a single relaxation process). The parameters obtained for each curve are given in Table S2.

Table S2. Values of the parameters obtained by fitting the ac susceptibility curves for **3**. See caption of Fig. S3 for details.

H (Oe)	T (K)	χ_S (cm^{3}mol^{-1})	χ_T (cm^{3}mol^{-1})	τ (ms)	α
0	1.9	2.30	12.6	0.72	0.291
0	2.0	2.51	13.4	0.61	0.268
0	2.1	2.85	14.2	0.54	0.242
0	2.2	2.85	14.9	0.50	0.252
0	2.3	3.05	15.5	0.44	0.243
0	2.4	3.21	16.0	0.39	0.237
0	2.5	3.40	16.3	0.35	0.230
0	2.6	3.54	16.6	0.32	0.226
0	2.7	3.68	16.8	0.29	0.221
0	2.8	3.82	16.9	0.27	0.217
0	2.9	3.96	16.9	0.25	0.213
0	3.0	4.09	17.0	0.23	0.207
0	3.1	4.21	16.9	0.21	0.203
0	3.2	4.34	16.8	0.20	0.197
0	3.4	4.58	16.6	0.17	0.187
0	3.6	4.63	16.3	0.15	0.183
0	3.8	4.78	15.9	0.14	0.174
0	4.0	4.78	15.5	0.13	0.169
2000	2.1	2.07	15.5	23.3	0.319
2000	2.3	2.14	15.3	19.7	0.302
2000	2.5	2.18	19.3	16.8	0.290
2000	2.7	2.19	18.8	14.7	0.281

2000	2.9	2.19	18.3	13.0	0.275
2000	3.1	2.17	17.6	11.6	0.273
2000	3.3	2.14	17.0	10.4	0.273
2000	3.5	2.11	16.4	9.4	0.274
2000	3.7	2.13	16.2	8.7	0.269
2000	3.9	2.15	16.1	7.6	0.276
2000	4.1	2.13	15.6	6.9	0.275
2000	4.5	2.00	10.0	5.7	0.271
2000	5.0	2.00	8.9	4.4	0.256
2000	5.5	2.01	7.9	3.4	0.234
2000	6.0	1.99	7.1	2.6	0.209
2000	6.5	1.91	6.5	1.9	0.194
2000	7.0	1.88	5.9	1.5	0.172
2000	7.5	1.81	5.5	1.1	0.157
2000	8.0	1.65	5.3	0.77	0.150
2000	8.5	1.67	4.8	0.55	0.142
2000	9.0	1.47	4.8	0.50	0.179
2000	9.5	1.59	3.7	0.28	0.131
2000	10.0	1.53	3.5	0.19	0.130
2000	10.5	1.61	3.1	0.13	0.130