Electronic Supporting Information (ESI)

Anisotropy barrier enhancement via ligand substitution in tetranuclear {$Co^{III}_2Ln^{III}_2$} single molecule magnets.

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Experimental

Synthesis of $[Tb^{III}_2Co^{III}_2(OH)_2(bdea)_2(acac)_2(NO_3)_4]$ (2).

$Co(acac)_2{\cdot}2H_2O$ (0.15 g, 0.5 mmol) and $Tb(NO_3)_3{\cdot}6H_2O$ (0.66 g, 1.5 mmol) were dissolved in MeOH (20 mL), followed by the addition of n-butyldiethanolamine (0.08 mL, 0.5 mmol), and triethylamine (0.3 mL, 2.0 mmol) to give a green solution. This was stirred for 2 hours after which the solution turned blue/green. This was subsequently layered with diethylether (Et_2O) and within 2 - 3 days dark green crystals of **2** had appeared, in approximate yield of 65 %. Anal. Calculated (found) for **2**: $Co_2Tb_2C_{26}H_{50}N_6O_{22}$: C, 25.29 (25.43); H, 4.08 (4.02); N, 6.81 (6.54).

Synthesis of $[Dy^{III}_2Co^{III}_2(OH)_2(bdea)_2(acac)_2(NO_3)_4]$ (3).

$Co(acac)_2{\cdot}2H_2O$ (0.15 g, 0.5 mmol) and $Dy(NO_3)_3{\cdot}6H_2O$ (0.66 g, 1.5 mmol) were dissolved in MeOH (20 mL), followed by the addition of n-butyldiethanolamine (0.08 mL, 0.5 mmol), and triethylamine (0.3 mL, 2.0 mmol) to give a green solution. This was stirred for 2 hours after which the solution turned blue/green. This was subsequently layered with diethylether (Et_2O) and within 2 - 3 days dark green crystals of **3** had appeared, in approximate yield of 65 %. Anal. Calculated (found) for **3**: $Co_2Dy_2C_{26}H_{50}N_6O_{22}$: C, 25.15 (25.40); H, 4.16 (4.02); N, 6.77 (6.59).

X-RAY CRYSTALLOGRAPHY. X-ray measurements for **2** and **3** were performed at 123(2) K using a Bruker Smart Apex X8 diffractometer with Mo Kα radiation. The data

collection and integration were performed within SMART and SAINT+ software programs, and corrected for absorption using the Bruker SADABS program. Compounds **2** and **3** were all solved by direct methods (SHELXS-97), and refined (SHELXL-97) by full least matrix least-squares on all F^2 data.[1] Crystallographic data and refinement parameters for **2** and **3** are summarized in Table S1.

Table S1. Crystallographic data for compounds **2** and **3**.

	2	**3**
Formula[a]	$Co_2Tb_2C_{26}H_{50}N_6O_{22}$	$Co_2Dy_2C_{26}H_{50}N_6O_{22}$
M, $gmol^{-1}$	1234.42	1241.58
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	11.3107(5)	11.310(2)
b/Å	11.7100(5)	11.725(2)
c/Å	15.4715(7)	15.497(3)
α/deg	90	90
β/deg	102.871(2)	102.90(3)
γ/deg	90	90
V/$Å^3$	1997.69(15)	2003.2(7)
T/K	123(2)	123(2)
Z	2	2
$\rho_{, calc}$ [g cm^{-3}]	2.052	2.058
λ[b]/ Å	0.71073	0.71073
Data Measured	9293	12647

Ind. reflns	3372	3472
R_{int}	0.0295	0.1015
Reflns with $I > 2\sigma(I)$	3079	3226
Parameters	268	268
Restraints	1	0
$R1^c$ (obs), $wR2^c$ (all)	0.0211, 0.0526	0.1525, 0.0608
goodness of fit	1.026	1.138
Largest residuals/ e Å $^{-3}$	0.576, -0.576	3.141, -3.057

[a] Including solvate molecules. [b] Graphite monochromator.

[c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2. Selected bond lengths (Å) for **2** and **3**.

	2 {Co_2Tb_2}	**3 {Co_2Dy_2}**
Ln1-O2A	2.255(2)[I]	2.227(5)[II]
Ln1-O3	2.238(2)	2.237(5)
Ln1-O1	2.407(2)	2.384(5)
Ln1-O6	2.403(2)	2.389(6)
Ln1-O10	2.397(2)	2.390(5)
Ln1-O1A	2.394(2)[I]	2.399(5)[II]
Ln1-O9	2.466(2)	2.449(5)
Ln1-O7	2.456(2)	2.469(5)
Co1-O2	1.887(2)	1.884(5)
Co1-O5	1.890(2)	1.892(5)
Co1-O3	1.8816(19)	1.895(5)
Co1-O4	1.881(2)	1.909(5)
Co1-O1	1.953(2)	1.950(5)
Co1-N1	1.962(3)	1.975(6)

Symmetry transformation: (I) 2 - x, 1 - y, 1 - z; (II) 1 - x, 1 - y, - z;

Reference

1. G. M. Sheldrick, *Acta Cryst. A*, 2008, **A64**, 112.

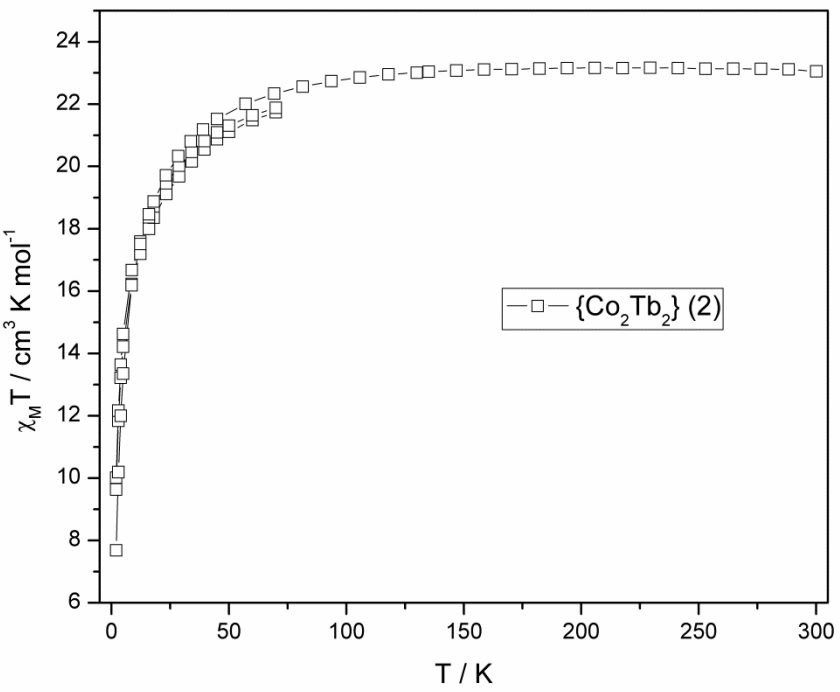


Figure S1. Plot of $\chi_M T$ versus T for **2** measured at 0.01, 0.1 and 1 T. The solid lines just join up the points.

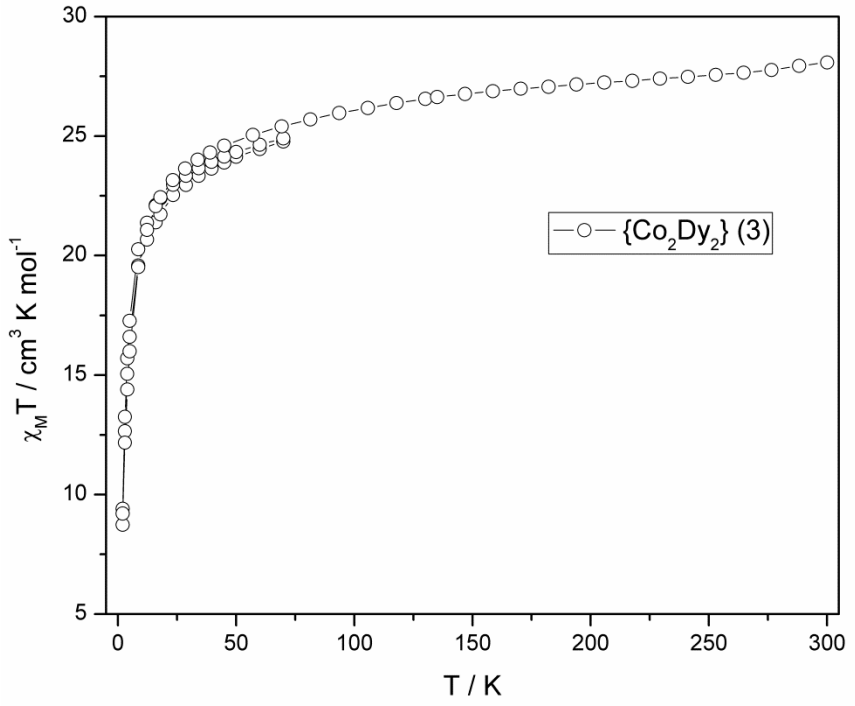


Figure S2. Plot of $\chi_M T$ versus T for **3** measured at 0.01, 0.1 and 1 T. The solid lines just join up the points.

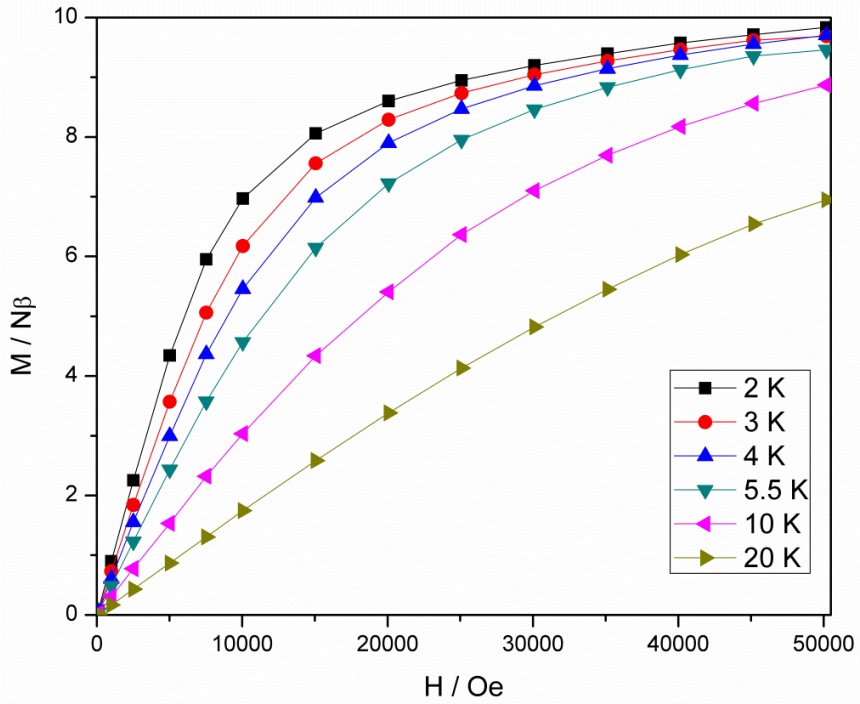


Figure S3. Isothermal *M versus H* plot for compound **2**. The solid lines just join up the points.

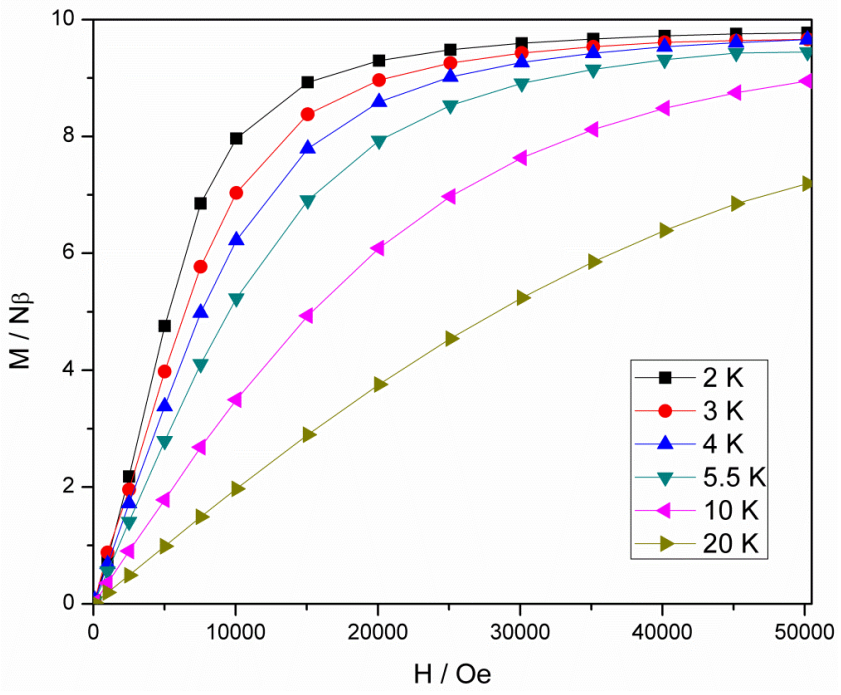
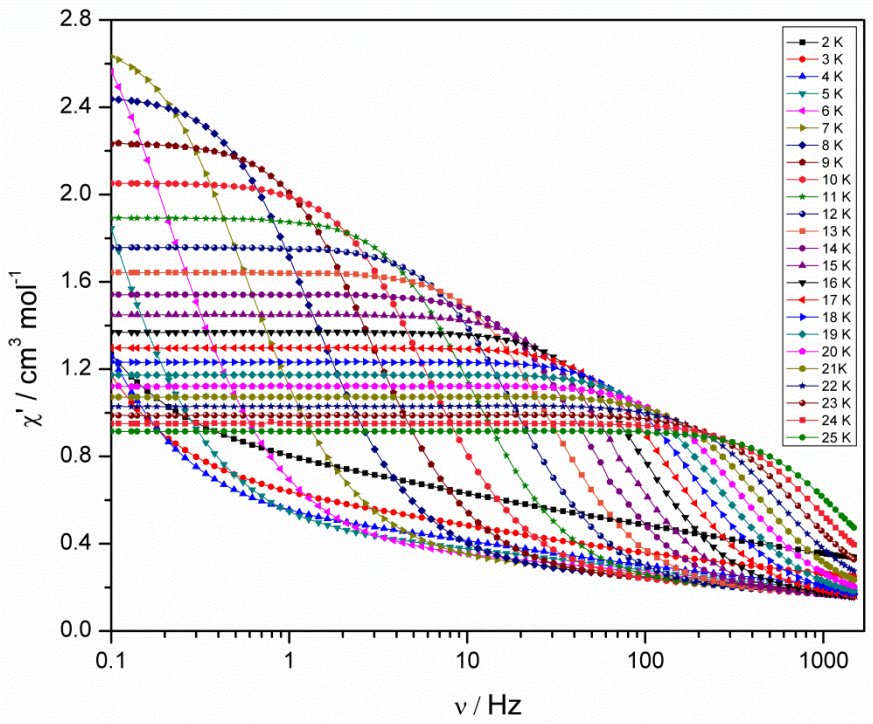


Figure S4. Isothermal *M versus H* plot for compound **3**. The solid lines just join up the points.



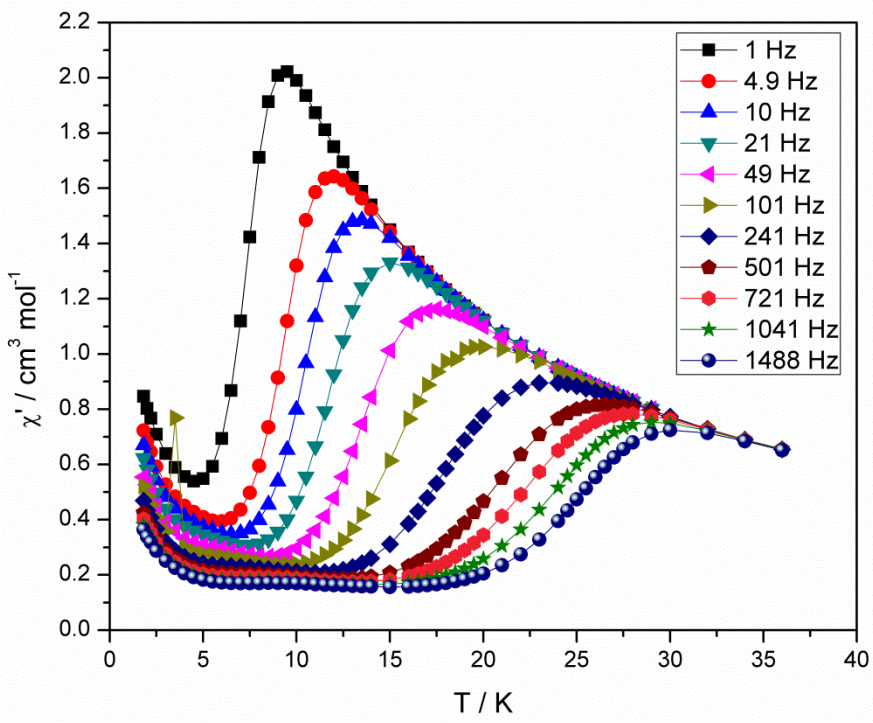


Figure S5. (top) Plot of χ_M' *versus* υ for **3**; (bottom) Plot of χ_M' *versus* T for **3**.

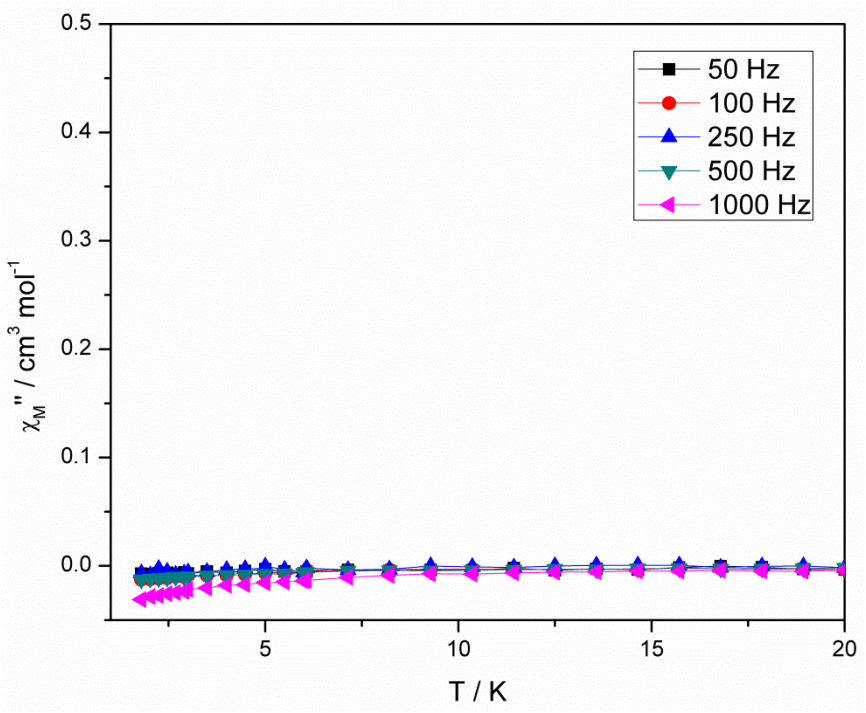


Figure S6. Plot of χ_M'' *versus T* for **2** with H_{DC} = 0 Oe.

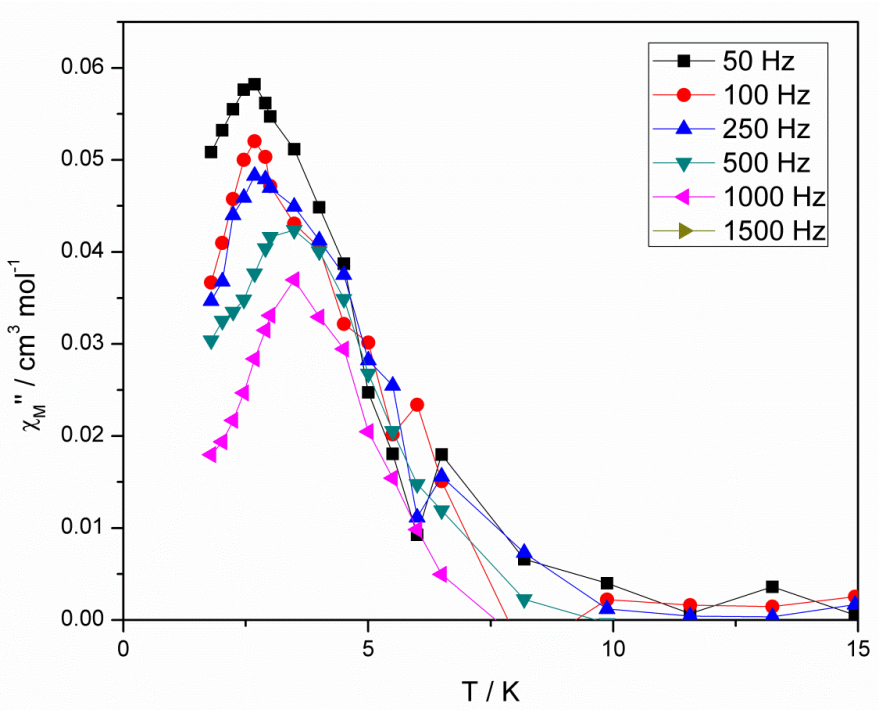


Figure S7. Plot of χ_M'' *versus T* for **2** with H_{DC} = 5000 Oe.