

Electronic supplementary Information (ESI)

Enhancing the Magnetic Blocking Temperature and Magnetic Coercivity of $\{\text{Cr}^{\text{III}}_2\text{Ln}^{\text{III}}_2\}$ Single-Molecule Magnets via Bridging Ligand Modification

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Experimental details

General Information. All reactions were carried out under aerobic conditions. Chemicals and solvents were obtained from commercial sources and used without further purification. Elemental analyses (CHN) were carried out by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

*Synthesis of $[\text{Cr}^{\text{III}}_2\text{Tb}^{\text{III}}_2(\text{OMe})_{0.8}(\text{OH})_{1.2}(2\text{-Cl-4,5-F-benz})_4(\text{mdea})_2(\text{NO}_3)_2] \cdot 1.2\text{MeOH}$ (**4**).*

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.13 g, 0.5 mmol) and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.22 g, 0.5 mmol) were dissolved in MeCN (20 mL), followed by the addition of N-methyldiethanolamine (0.06 mL, 0.5 mmol), 2-chloro-4,5-fluorobenzoic acid (0.19 g, 1.0 mmol) and triethylamine (0.28 mL, 2.0 mmol) resulting in a green/blue solution. The solution quickly turned deep purple and was stirred for 2 hours after which the solvent was removed to give a purple oil. This was re-dissolved in MeOH and layered with diethylether (Et_2O). Within 5 – 7 days magenta crystals of **4** had appeared, in approximate yield of 42 %. Anal. Calculated (found) for **4**: $\text{Cr}_2\text{Tb}_2\text{C}_{40}\text{H}_{38.4}\text{O}_{21.2}\text{N}_4\text{Cl}_4\text{F}_8$: C, 29.54 (29.49); H, 4.36 (4.37); N, 3.44 (3.09).

*Synthesis of $[\text{Cr}^{\text{III}}_2\text{Dy}^{\text{III}}_2(\text{OMe})_{1.4}(\text{OH})_{0.6}(2\text{-Cl-4,5-F-benz})_4(\text{mdea})_2(\text{NO}_3)_2] \cdot 0.6\text{MeOH}$ (**5**).*

The synthesis for **4** was followed but $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.22 g, 0.5 mmol) was used in place of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Magenta crystals of **5** appeared within 5 – 7 days, in approximate yield of

49 %. Anal. Calculated (found) for **5**: Cr₂Dy₂C₄₀H_{37.20}O_{20.6}N₄Cl₄F₈: C, 29.42 (29.21); H, 2.36 (2.42); N, 3.44 (3.22).

Synthesis of [Cr^{III}₂Ho^{III}₂(OMe)_{1.16}(OH)_{0.84}(2-Cl-4,5-F-benz)₄(mdea)₂(NO₃)₂]·0.84MeOH (6).****

The synthesis for **4** was followed but Ho(NO₃)₃·6H₂O (0.22 g, 0.5 mmol) was used in place of Tb(NO₃)₃·6H₂O. Magenta crystals of **6** appeared within 5 – 7 days, in approximate yield of 39 %. Anal. Calculated (found) for **6**: Cr₂Ho₂C₄₀H_{37.67}O_{20.83}N₄Cl₄F₈: C, 29.32 (29.40); H, 2.34 (2.41); N, 3.42 (3.32).

Synthesis of [Cr^{III}₂Dy^{III}₂(OMe)(OH)(4-*t*Bubenz)₄(mdea)₂(NO₃)₂]·MeOH·2Et₂O (7).****

CrCl₃·6H₂O (0.13 g, 0.5 mmol) and Dy(NO₃)₃·6H₂O (0.22 g, 0.5 mmol) were dissolved in MeCN (20 mL), followed by the addition of *tert*-butyldiethanolamine (0.08 g, 0.5 mmol), 4-*tert*-butylbenzoic acid (0.18 g, 1.0 mmol) and triethylamine (0.28 mL, 2.0 mmol) resulting in a green/blue solution. The solution quickly turned deep purple and was stirred for 2 hours after which the solvent was removed to give a purple oil. This was re-dissolved in MeOH and layered with diethylether (Et₂O). Within 5 – 7 days red/pink crystals of **7** had appeared, in approximate yield of 32 %. Anal. Calculated (found) for **7**: Cr₂Dy₂C₇₀H₁₁₄O₂₃N₄: C, 46.48 (46.21); H, 6.35 (6.39); N, 3.10 (3.29).

X-ray Crystallography. X-ray crystallographic measurements for **4** were performed using a Bruker Smart Apex X8 diffractometer with Mo K α radiation. The data collection and integration were performed within SMART and SAINT+ software programs, and corrected for absorption using the Bruker SADABS program. X-ray diffraction measurements for **5** – **7** were performed at 100(2) K at the Australian synchrotron MX1 beam-line. The data collection and integration were performed within Blu-Ice¹ and XDS² software programs. Compounds **4** – **7** were all solved by direct methods (SHELXS-97), and refined (SHELXL-97) by full least matrix least-squares on all F^2 data.³ Crystallographic data and refinement parameters for **4** – **7** are summarized in Table S1. Crystallographic details are available in the Supporting Information (ESI) in CIF format. CCDC numbers 1495740 (**4**), 1495741 (**5**), 1495742 (**6**), 1495743 (**7**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for complexes **4** – **7**.

	4	5	6	7
Formula ^a	Cr ₂ Tb ₂ C ₄₀ H _{38.4} O _{21.2} N ₄ Cl ₄ F ₈	Cr ₂ Dy ₂ C ₄₀ H _{37.20} O _{20.6} N ₄ Cl ₄ F ₈	Cr ₂ Ho ₂ C ₄₀ H _{37.67} O _{20.83} N ₄ Cl ₄ F ₈	Cr ₂ Dy ₂ C ₇₀ H ₁₁₄ O ₂₃ N ₄
M, gmol ⁻¹	1629.98	1626.33	1635.34	1808.64
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a/[Å]	9.6481(6)	9.5430(19)	9.6670(19)	11.164(2)
b/[Å]	11.3861(7)	11.414(2)	11.331(2)	11.907(2)
c/[Å]	13.3598(8)	13.306(3)	13.316(3)	16.534(3)
α/[°]	67.617(5)	67.56(3)	67.54(3)	70.77(3)
β/[°]	78.339(5)	77.95(3)	78.27(3)	73.76(3)
γ/[°]	87.410(5)	87.25(3)	87.69(3)	82.43(3)
V/[Å ³]	1328.23(14)	1309.2(5)	1318.7(5)	1990.5(7)
T/K	123(2)	100(2)	100(2)	100(2)
Z	1	1	1	1
ρ _{calc} [g cm ⁻³]	2.036	2.062	2.058	1.508
λ/[Å]	0.71073	0.71079	0.71079	0.71079
Data	18565	16519	27401	32265
Measured				
Ind. Reflns	6101	4234	5907	8352
R _{int}	0.0427	0.0318	0.0391	0.0344
Reflns with I > 2σ(I)	5374	4040	5734	8051
Parameters	384	383	384	512
Restraints	0	0	0	66
R ₁ ^b (obs), wR ₂ ^b (all)	0.0284, 0.0645	0.0310, 0.0826	0.0315, 0.0819	0.0432, 0.1177
goodness of fit	1.091	1.068	1.059	1.059
Largest residuals/[e Å ⁻³]	0.991, -0.899	0.919, -1.435	1.106, -1.734	2.369, -1.463

^aIncludes solvate molecules.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

Magnetic Measurements. The magnetic susceptibility measurements were carried out on a Quantum Design SQUID magnetometer MPMS-XL 7 operating between 1.8 and 300 K for dc-applied fields ranging from 0 – 5 T. Microcrystalline samples were dispersed in Vaseline in order to avoid torquing of the crystallites. The sample mulls were contained in a calibrated gelatine capsule held at the centre of a drinking straw that was fixed at the end of the sample rod. Alternating current (ac) susceptibility measurements were carried out under an oscillating ac field of 3.5 Oe and frequencies ranging from 0.1 to 1500 Hz.

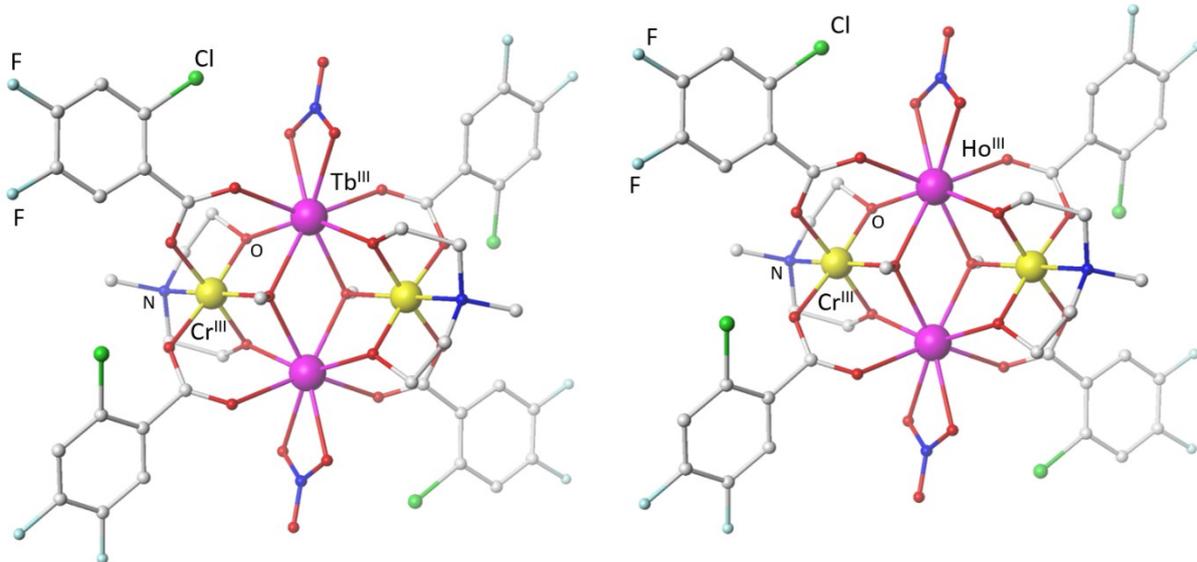
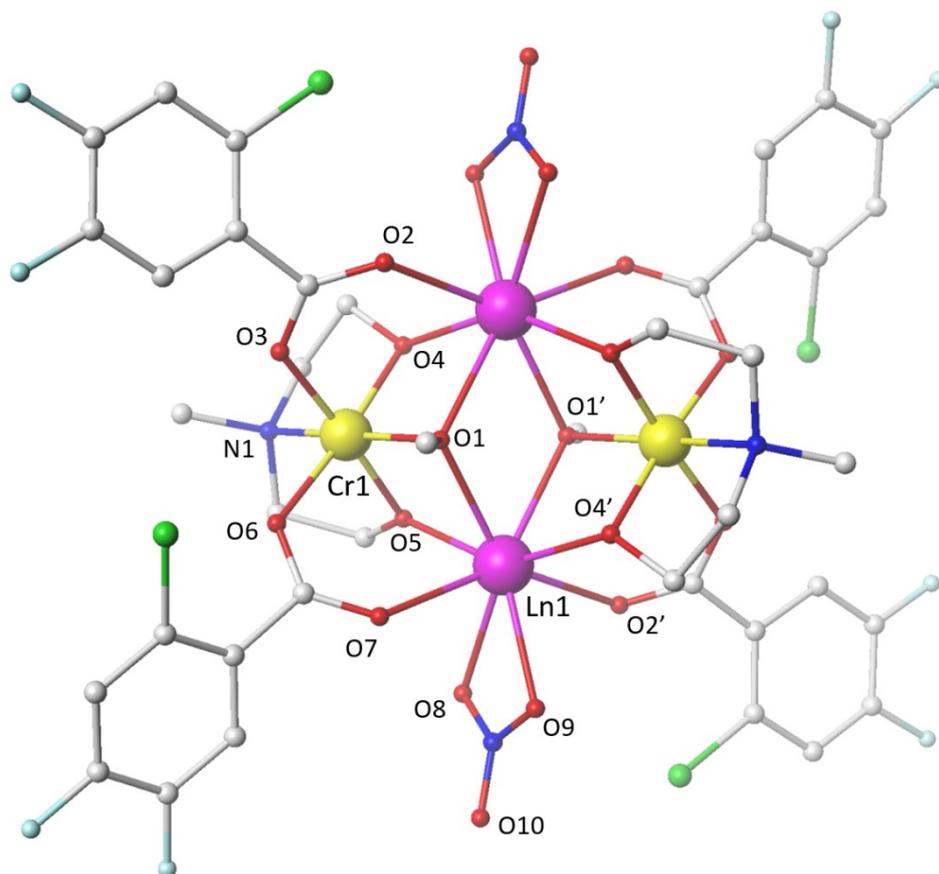


Fig. S1. Molecular structure of **4** (left) and **6** (right), the H-atoms are omitted for clarity. Colour scheme; Cr^{III}, yellow; Ln^{III}, purple; O, red; N, blue; C, light grey.

Table S2. Selected bond lengths (Å) and angles (°) for **4** – **7**, using the labelling scheme shown below. The first coordination sphere for **7** is identical to that shown below.



Atom	4 {Cr ₂ Tb ₂ }	5 {Cr ₂ Dy ₂ }	6 {Cr ₂ Ho ₂ }	7 {Cr ₂ Dy ₂ }
Cr1-O4	1.952(2)	1.953(3)	1.953(3)	1.955(3)
Cr1-O5	1.954(2)	1.954(3)	1.949(3)	1.951(3)
Cr1-O1	1.967(2)	1.968(3)	1.972(3)	1.970(3)
Cr1-O3	1.983(2)	1.972(3)	1.977(3)	1.979(3)
Cr1-O6	1.993(2)	1.989(3)	1.993(3)	1.982(3)
Cr1-N1	2.074(3)	2.082(4)	2.083(3)	2.176(4)
Ln1-O5	2.260(2)	2.241(3)	2.236(3)	2.243(3)
Ln1-O4'	2.265(2)	2.242(3)	2.238(3)	2.249(3)
Ln1-O2'	2.388(2)	2.387(3)	2.365(3)	2.365(3)
Ln1-O7	2.391(2)	2.384(3)	2.365(3)	2.356(3)
Ln1-O1	2.429(2)	2.432(3)	2.418(3)	2.423(3)
Ln1-O1'	2.449(2)	2.449(3)	2.428(3)	2.425(3)
Ln-O8	2.460(2)	2.442(3)	2.428(3)	2.437(4)
Ln-O9	2.463(2)	2.439(3)	2.424(3)	2.445(3)
Ln1-O1-Ln1'	95.65(9)	95.00(11)	95.44(10)	97.23(11)
Cr1-O1-Ln1	96.73(8)	95.88(12)	95.81(11)	97.26(13)
Cr1-O4-Ln1'	102.23(9)	102.34(12)	102.36(11)	103.72(13)

Cr1-O5-Ln1	102.84(9)	102.78(13)	102.61(11)	104.06(14)
Ln1-O1-Ln1'	113.79(9)	113.88(12)	114.17(10)	113.59(12)

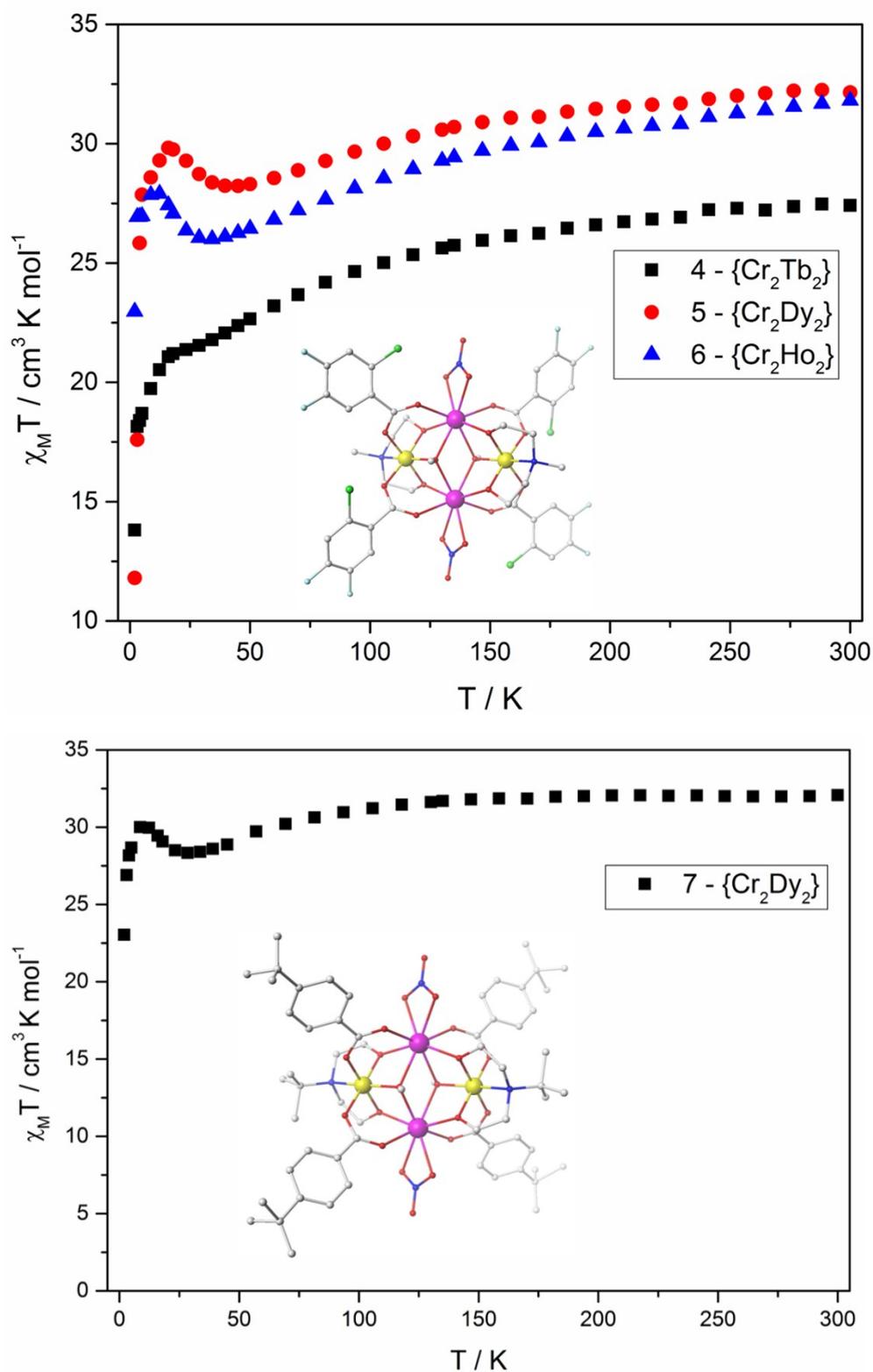


Fig. S2. Plots of $\chi_M T$ versus T for 4 – 6 (top) and 7 (bottom), using an applied magnetic field of 0.1 T.

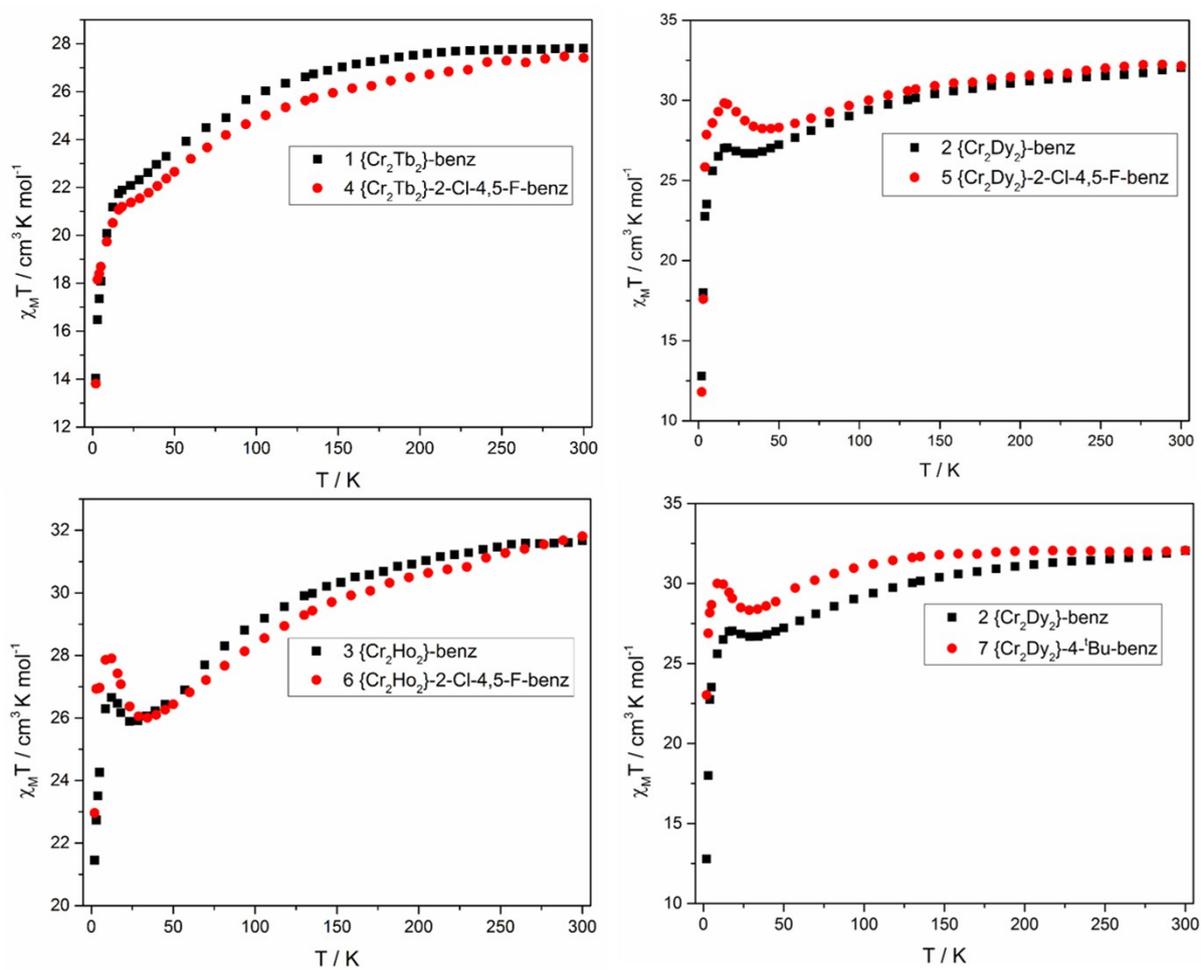


Fig. S3. Plots of $\chi_M T$ versus T for **1** and **4** (top left), **2** and **5** (top right), **3** and **6** (bottom left) and **2** and **7** (bottom right) using an applied magnetic field of 0.1 T.

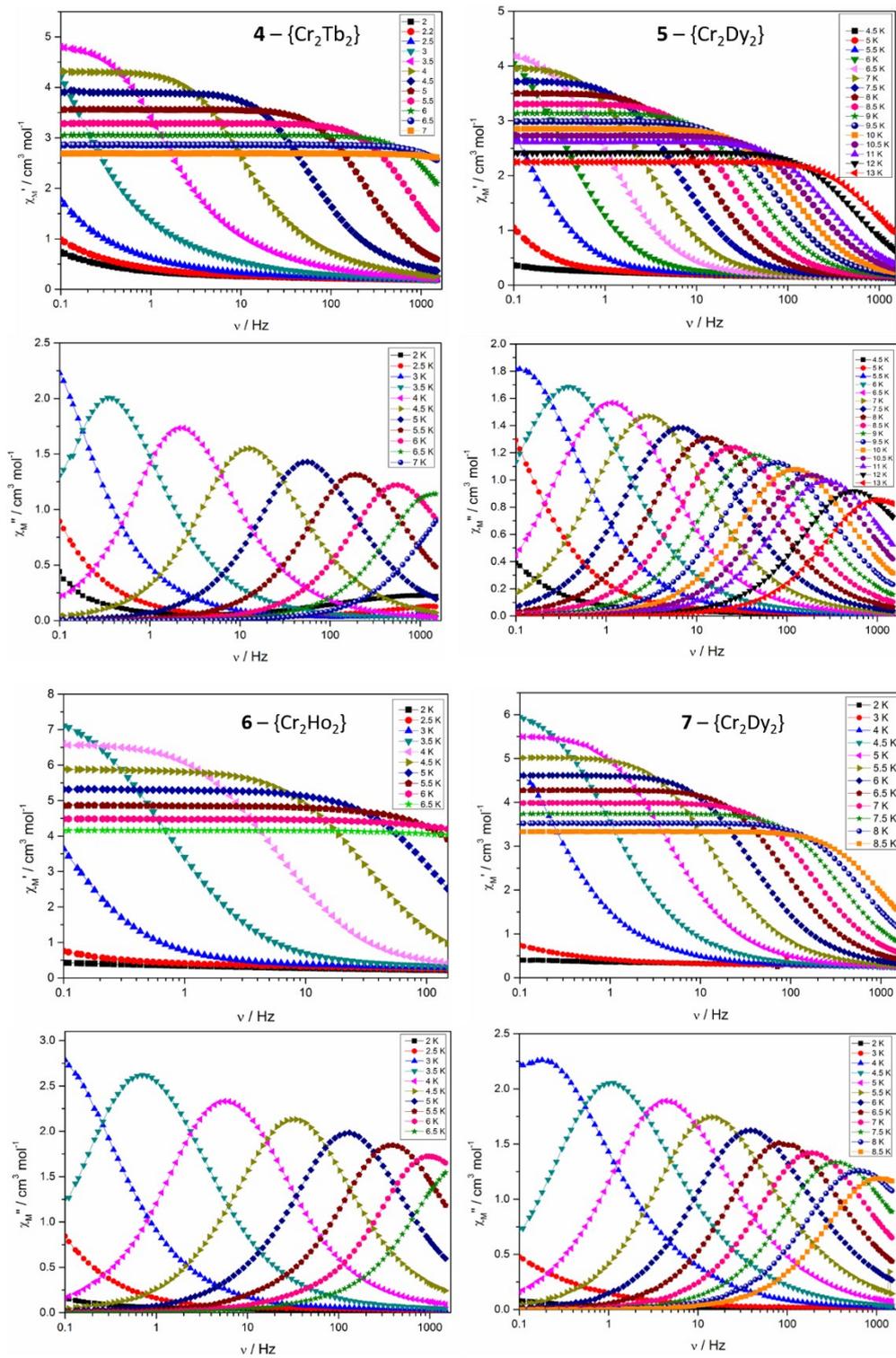


Fig. S4. Alternating current magnetic susceptibility measurements. In-phase (χ_M') and out of phase (χ_M'') signals for **4** (top left), **5** (top right), **6** (bottom left) and **7** (bottom right).

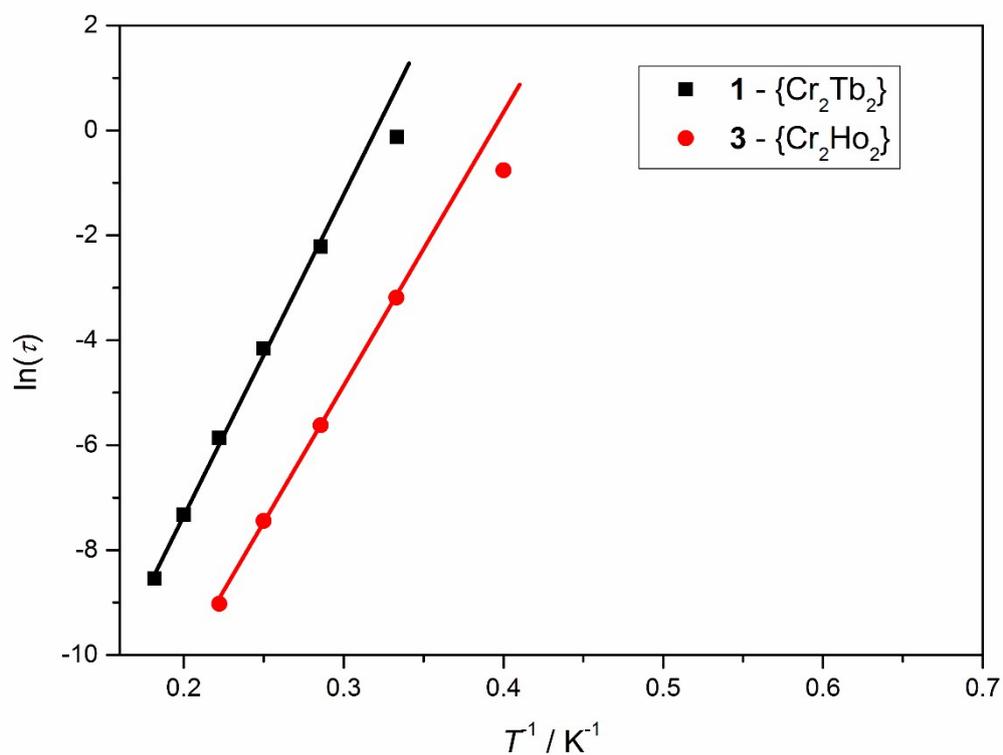


Fig. S5. Relaxation data for **1** and **3** plotted as $\ln(\tau)$ versus T^{-1} . At the lowest temperatures the data begins to deviate from linearity.

References

1. T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis, P. Kuhn, Blu-Ice and the Distributed Control System: software for data acquisition and instrument control at macromolecular crystallography beamlines., *J. Synchrotron Rad.*, **2002**, 9, 401-406.
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3. G. M. Sheldrick, *Acta Cryst. A*, **2008**, A64, 112.