Supplementary Information (SI)

Heterometallic tetranuclear $[Ln^{III}_2Co^{III}_2]$ complexes including suppression of quantum tunneling of magnetization in the $[Dy^{III}_2Co^{III}_2]$ single molecule magnet.

Stuart K. Langley,[a] Nicholas F. Chilton,[a] Liviu Ungur,[b] Boujemaa Moubaraki,[a] Liviu F. Chibotaru*[b] and Keith S. Murray*[a]

[a] ***School of Chemistry, Monash University, Clayton, Victoria 3800, Australia***
email: keith.murray@monash.edu
[b] **Division of Quantum and Physical Chemistry and INPAC -Institute of Nanoscale Physics and Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium. email: Liviu.Chibotaru@chem.kuleuven.be**

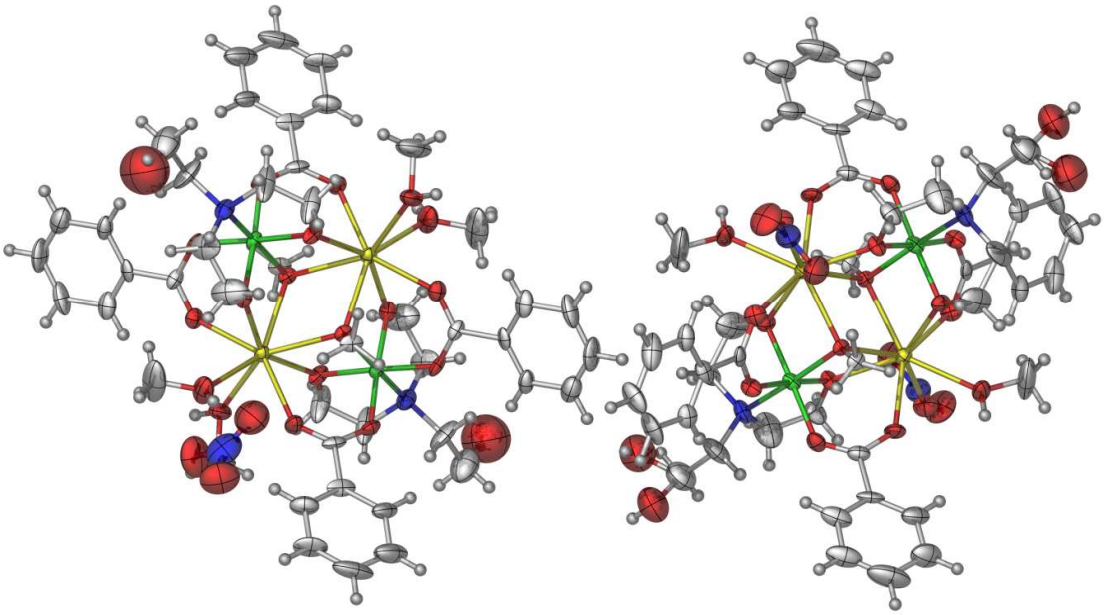


Figure S1. Thermal ellipsoid plot at the 50% probability level for **1**. Colour scheme; Gd^{III}, yellow; Co, green; O, red; N, blue; C and H, grey.

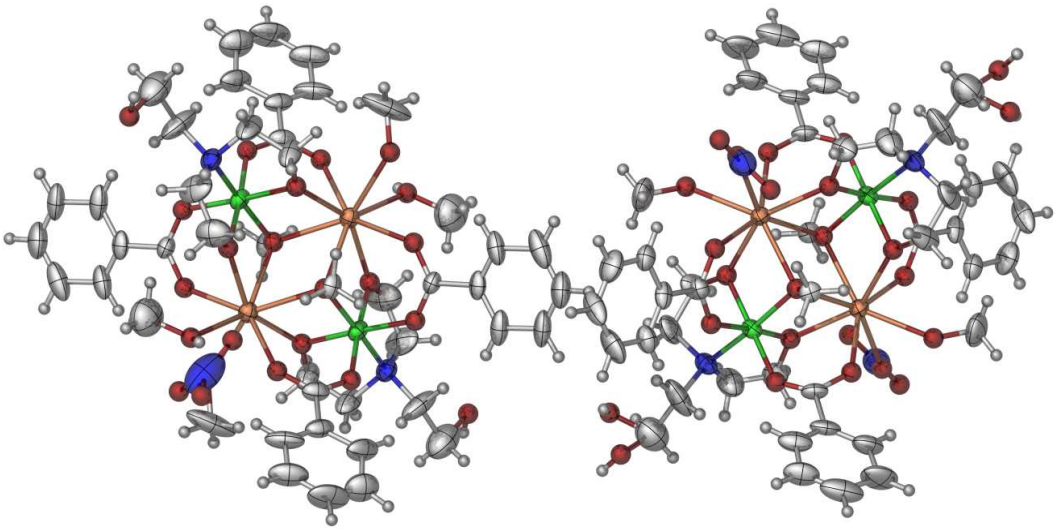


Figure S2. Thermal ellipsoid plot at the 50% probability level for **3**. Colour scheme; Tb^{III}, yellow; Co, green; O, red; N, blue; C and H, grey.

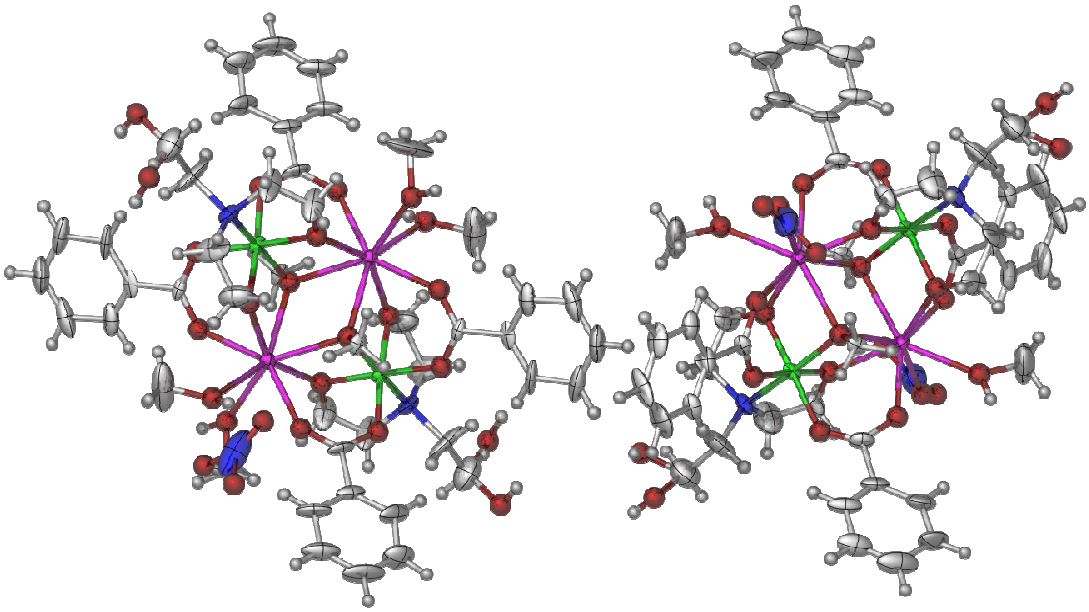


Figure S3. Thermal ellipsoid plot at the 50% probability level for **3**. Colour scheme; Dy^{III}, purple; Co, green; O, red; N, blue; C and H, grey.

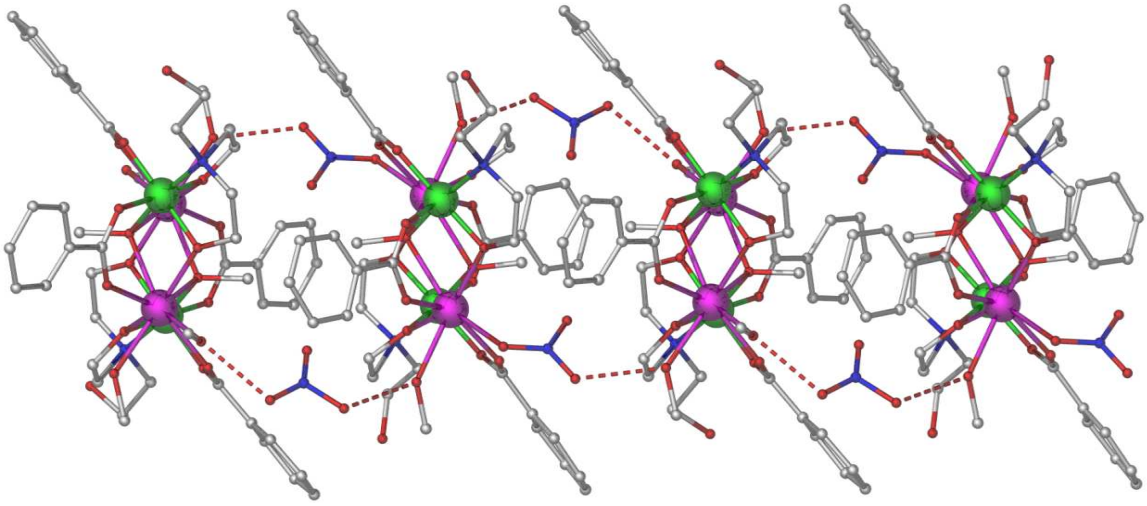


Figure S4. 1-D H-bonded chains via the nitrate and MeOH molecules. H-bonds are indicated by the dashed red lines.

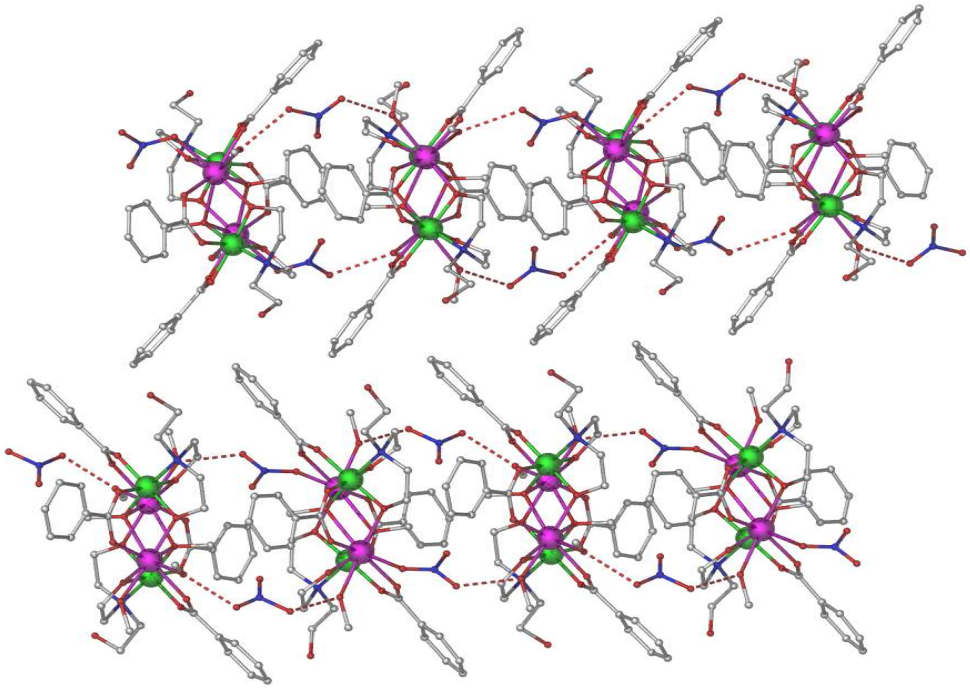


Figure S5. Aromatic C-H···π interactions between the 1-D H-bonded chains, shown along the c-axis.

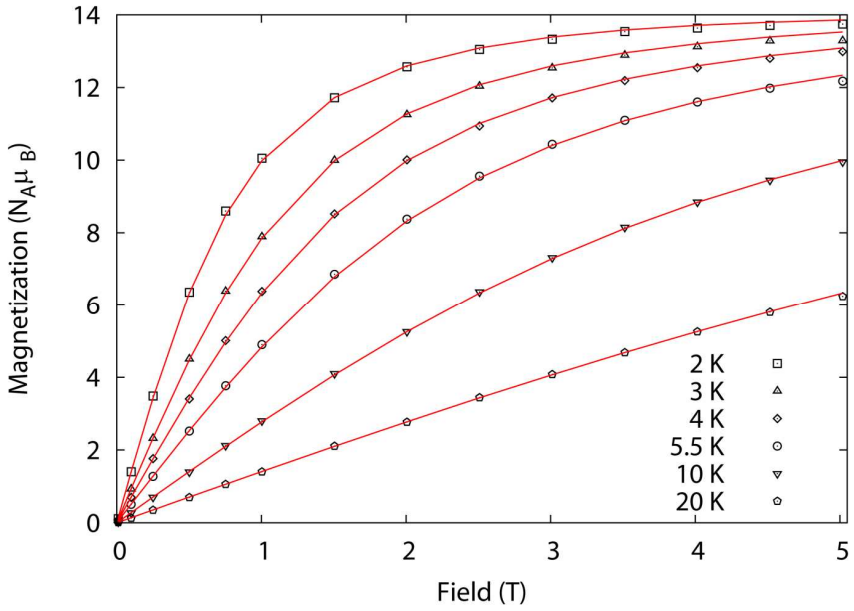


Figure S6. Isothermal *M vs H* plot for compound **1** at temperatures; 2 (top), 3, 4, 5.5, 10 and 20 (bottom) K. The red lines are fits to the data using the parameters mentioned in the script.

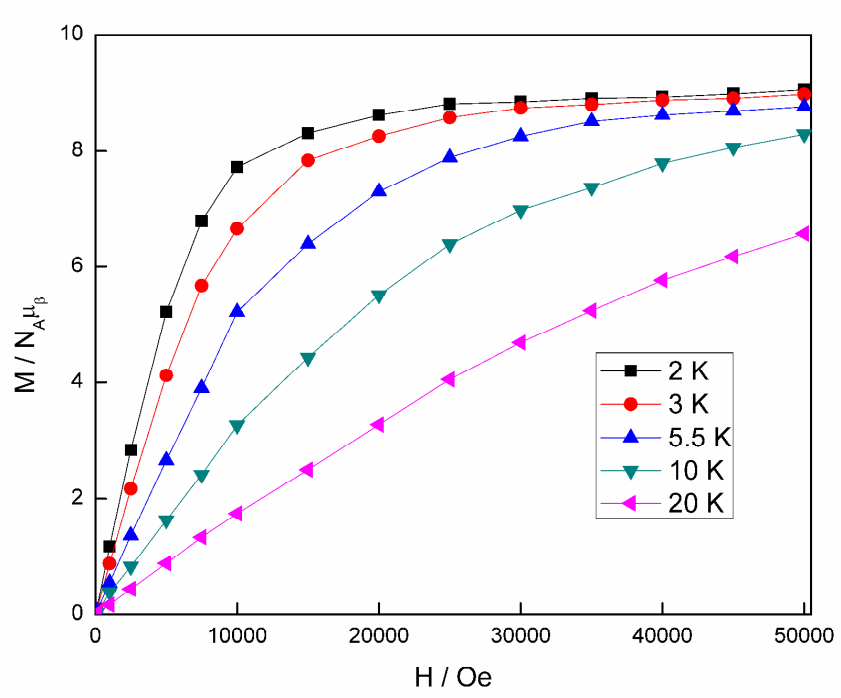


Figure S7. Isothermal *M vs H* plot for compound **2** at temperatures; 2 (top), 3, 4, 5.5, 10 and 20 (bottom) K. The solid lines just join the points.

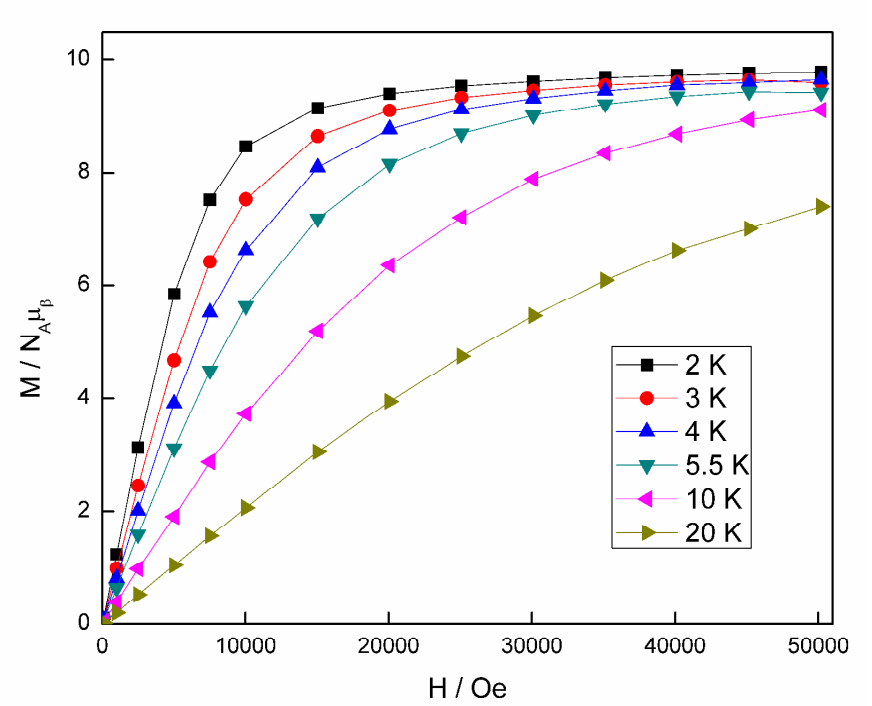


Figure S8. Isothermal *M vs H* plot for compound **3** at temperatures; 2 (top), 3, 5.5, 10 and 20 (bottom) K. The solid lines just join the points.

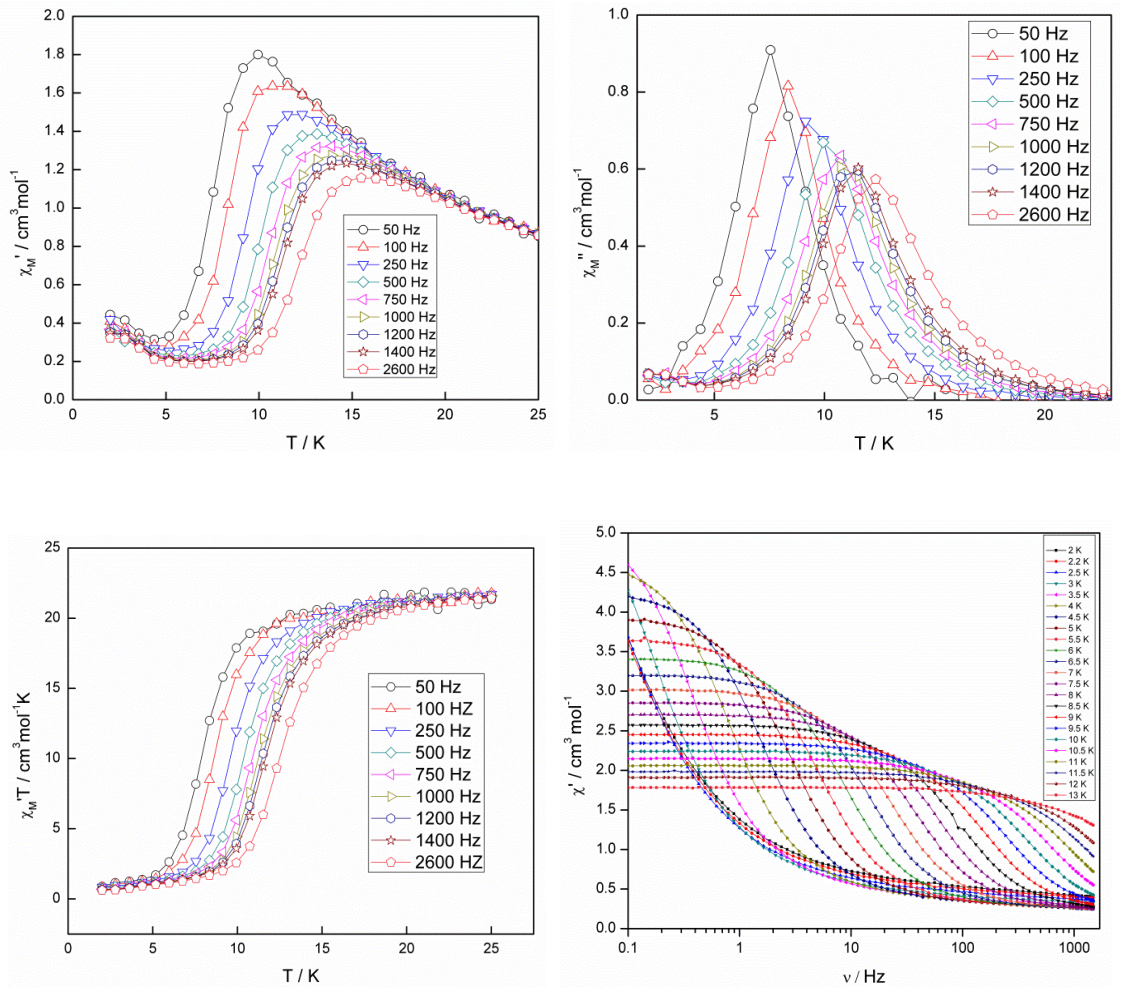


Figure S9. AC susceptibility data for **3** plotted as χ_M' *vs T* (top left), χ_M' *vs T* (top right), $\chi_M'T$ *vs T* (bottom left) and χ_M' *vs freq* (bottom left).

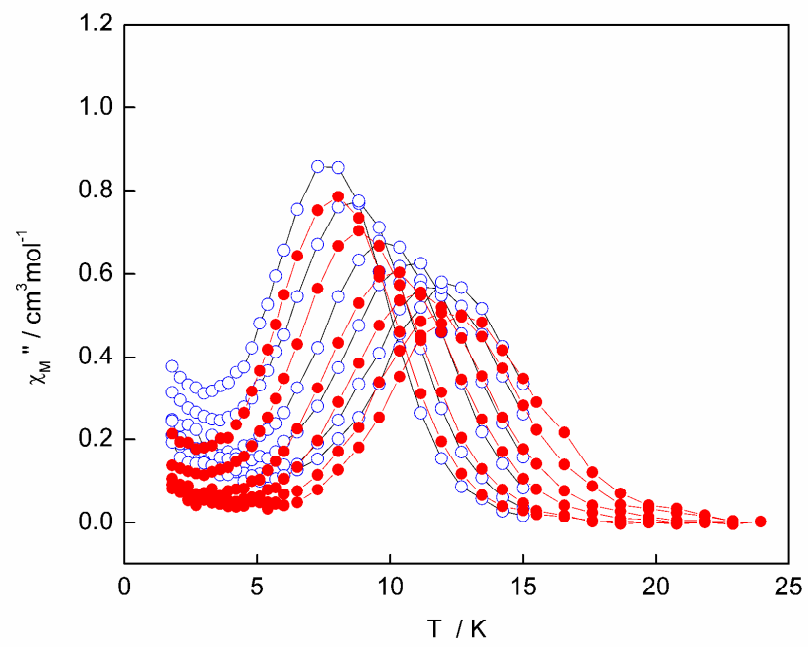


Figure S10. Comparison of the AC susceptibility data for **3** under a zero (red circles) and applied DC field of 1000 Oe (blue open circles), plotted as χ_M'' *vs T*.

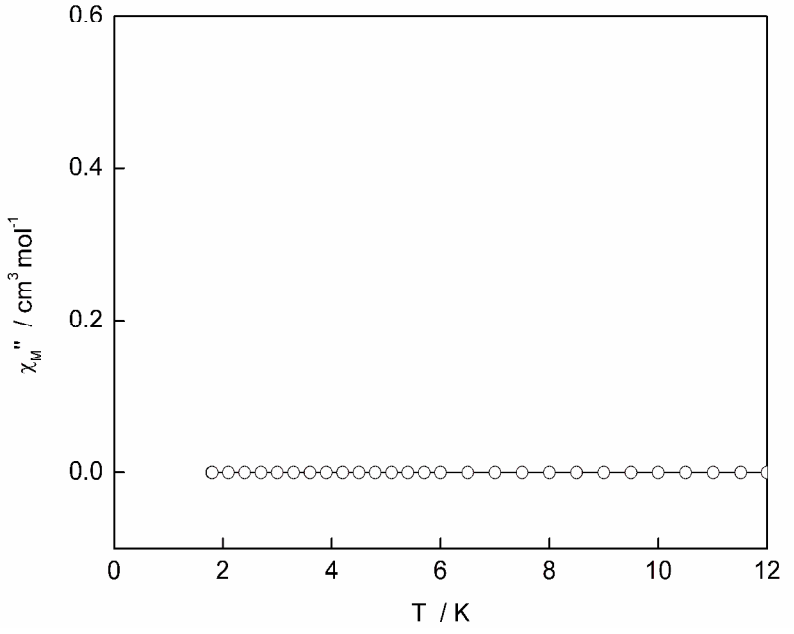


Figure S11. AC susceptibility data for **2** plotted as χ_M'' *vs T*.

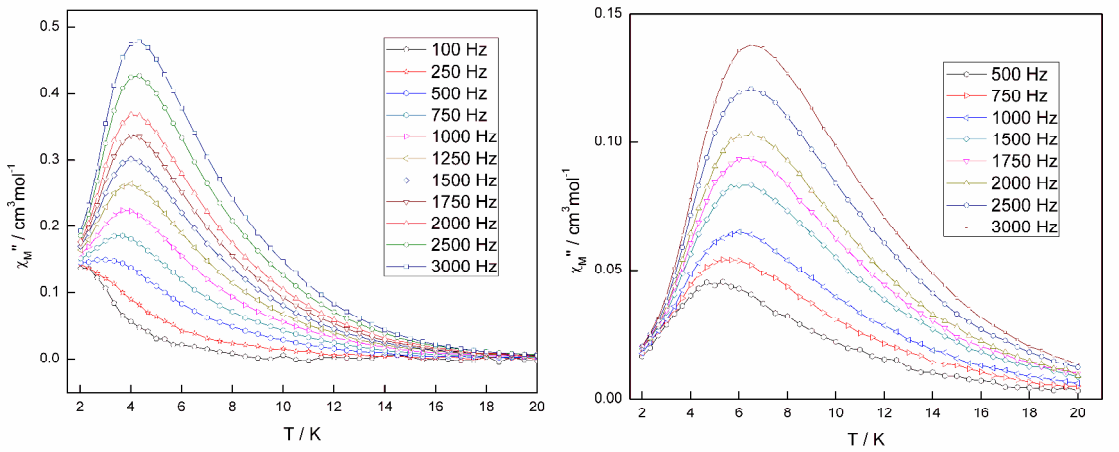


Figure S12. AC susceptibility data for **2** under a applied DC field of 1 T (left) and 1.75 T (right) plotted as χ_M'' *vs T*.

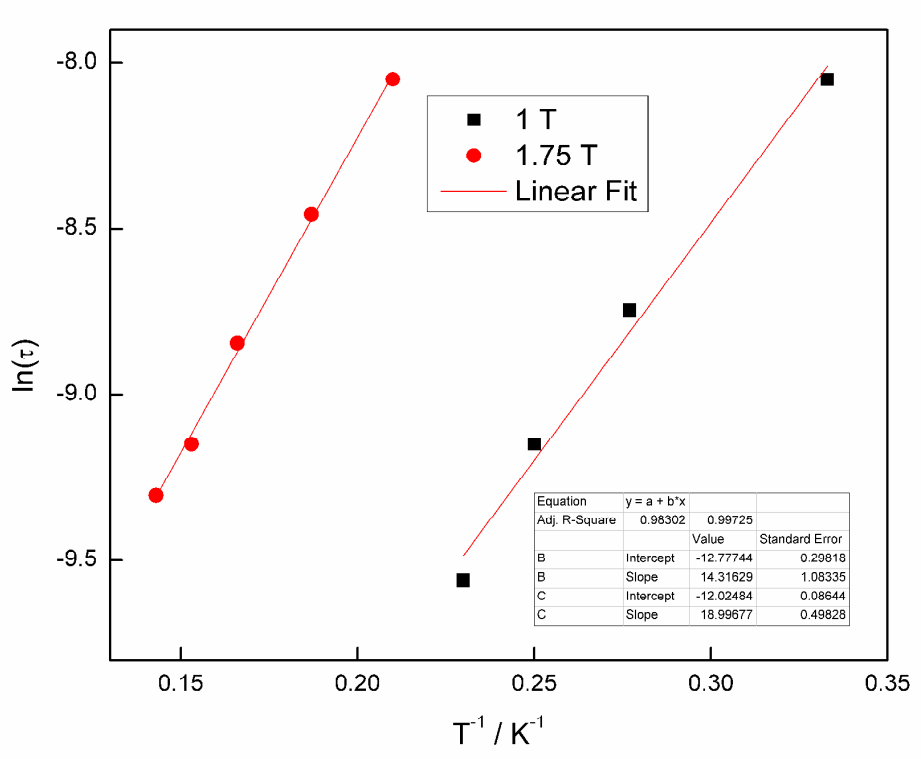


Figure S13. Temperature dependence of the relaxation time for **2** at 1 and 1.75 T, with two linear Arrhenius fits.

Table S1. Contractions of the employed basis sets in computational approximations **λ** and **θ**.

Basis λ	**Basis θ**
Dy.ANO-RCC...7s6p4d3f1g.	Dy.ANO-RCC...8s7p5d4f2g1h.
Lu.ANO-RCC...7s6p4d3f1g.	Lu.ANO-RCC...7s6p4d3f1g.
Co.ANO-RCC...5s4p2d1f.	Co.ANO-RCC...5s4p2d1f.
O.ANO-RCC...3s2p1d. (close)	O.ANO-RCC...4s3p2d. (close)
O.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)	O.ANO-RCC...3s2p. (distant)
N.ANO-RCC...3s2p1d. (close)	N.ANO-RCC...4s3p2d. (close)
N.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)	N.ANO-RCC...3s2p. (distant)
C.ANO-DK3.Tsuchiya.12s8p.2s1p.	C.ANO-RCC...3s2p.
H.ANO-DK3.Tsuchiya.6s.1s.	H.ANO-RCC...2s.

Table S2. Energies of the lowest Kramers doublets (cm^{-1}) (molecule 1).

Aλ	**Aθ**	**Bλ**	**Bθ**
0	0	0	0
91.168	102.93	90.96	102.608
190.425	214.88	189.937	214.728
261.566	298.374	260.84	297.419
325.581	370.009	324.691	367.808
377.24	406.936	376.416	403.613
490.428	504.759	489.678	502.437
690.116	734.554	689.504	734.189
3577.67	3580.834	3577.56	3580.537
3678.7	3692.227	3678.33	3691.966
3769.82	3797.231	3769.18	3795.869
3842.01	3875.907	3841.22	3874.103
3912.31	3944.481	3911.52	3942.392
3972.78	3998.649	3972.06	3996.772
4065.23	4097.132	4064.66	4096.408
6139.26	6145.304	6139.04	6144.975
6224.8	6241.787	6224.31	6240.854
6323.95	6349.649	6323.25	6348.08
6410.2	6441.608	6409.4	6439.671
6453.75	6487.522	6453.07	6486.383
6537.05	6558.708	6536.49	6557.506
8120.87	8130.777	8120.53	8130.257
8199.73	8219.003	8199.14	8217.771
8322.81	8349.597	8322.02	8347.658
8381.1	8412.579	8380.47	8411.626
8466.83	8487.547	8466.25	8486.284

9648.24	9660.208	9647.84	9659.498
9773.83	9795.312	9773.13	9793.825
9896.4	9925.048	9895.73	9923.628
9986.78	10009.4	9986.17	10008.27
…	…	…	…

Table S3. Energies (cm^{-1}) and *g* tensors of the lowest Kramers doublets (KD) (molecule 1).

KD		Aλ		Aθ		Bλ		Bθ	
		E	***g***	**E**	***g***	**E**	***g***	**E**	***g***
1	g_X	0	0.0339	0	0.0216	0	0.0342	0	0.0217
	g_Y		0.0569		0.0331		0.0574		0.033
	g_Z		19.636		19.6957		19.6349		19.6972
2	g_X	91.168	0.2097	102.93	0.1542	90.96	0.2111	102.608	0.1552
	g_Y		0.2427		0.1687		0.2446		0.1698
	g_Z		16.7262		16.8427		16.7244		16.8491
3	g_X	190.425	0.7543	214.88	0.3096	189.937	0.7617	214.728	0.3119
	g_Y		1.2089		0.505		1.224		0.5072
	g_Z		14.5772		14.8105		14.5722		14.8172
4	g_X	261.566	2.2728	298.374	1.2894	260.84	2.2827	297.419	1.2415
	g_Y		4.1054		2.1934		4.1281		2.1411
	g_Z		10.4371		11.5965		10.4197		11.6299
5	g_X	325.581	2.8007	370.009	1.3878	324.691	2.7981	367.808	1.28
	g_Y		4.1689		3.3887		4.1588		3.236
	g_Z		11.7779		10.9704		11.7843		11.0556
6	g_X	377.24	1.7752	406.936	3.0735	376.416	1.7634	403.613	3.0744
	g_Y		2.2311		4.6248		2.2186		4.7985
	g_Z		14.7835		12.904		14.7862		12.6138
7	g_X	490.428	0.3171	504.759	0.4068	489.678	0.3154	502.437	0.401
	g_Y		0.4294		0.705		0.4265		0.6968
	g_Z		17.4166		17.3512		17.4186		17.3389
8	g_X	690.116	0.0182	734.554	0.0149	689.504	0.0181	734.189	0.0144
	g_Y		0.0357		0.0282		0.0353		0.0272
	g_Z		19.2622		19.3644		19.2631		19.3685

Table S4. Energies of the lowest Kramers doublets (cm^{-1}), (molecule 2).

Aλ	Aθ	Bλ	Bθ
0	0	0	0
83.692	94.489	84.058	94.528
186.129	208.872	187.447	209.62
271.868	290.392	271.701	288.822
334.461	344.972	332.485	338.817
368.97	380.544	366.686	375.385
426.724	442.522	424.828	438.701
705.078	746.598	704.777	745.924
3572.18	3573.96	3572.13	3573.66
3675.53	3690.6	3676.76	3691.24
3775.16	3783.28	3774.43	3780.8
3842.3	3852.96	3840.89	3849.18
3897.66	3905.43	3895.37	3900.01
3950	3971.22	3948.98	3968.67
4060.77	4098.02	4060.67	4097.38
6131.37	6135.88	6131.72	6135.82
6224.16	6233.69	6224.19	6232.44
6319.19	6327.29	6318.03	6324.11
6401.89	6408.26	6399.83	6403.45
6465.77	6483.18	6464.54	6480.56
6507.49	6540.36	6507.78	6539.85
8113.1	8118.7	8113.29	8118.21
8196.34	8205.43	8195.85	8203.37
8313.48	8318.42	8311.81	8314.03
8393.54	8407.76	8392.16	8405.04
8440.29	8467.35	8440.45	8466.54
9640.05	9646.08	9640.02	9645.13
9771.41	9777.95	9770.64	9775.1
9895.76	9902.39	9893.8	9898.45
9969.16	9997.09	9969.31	9996.35
…	…	…	…

Table S5. Energies (cm^{-1}) and *g* tensors of the lowest Kramers doublets (KD), (molecule 2).

KD		Aλ		Aθ		Bλ		Bθ	
		E	***g***	**E**	***g***	**E**	**g**	***E***	**g**
1	g_X	0	0.0317	0	0.0212	0	0.0313	0	0.0208
	g_Y		0.0517		0.0303		0.0504		0.0291
	g_Z		19.6438		19.7124		19.6513		19.7167
2	g_X	83.692	0.1944	94.489	0.1746	84.058	0.1964	94.528	0.1778
	g_Y		0.2078		0.1869		0.2104		0.1914
	g_Z		16.7947		16.9536		16.8202		16.9736
3	g_X	186.129	0.1676	208.872	0.1114	187.447	0.1732	209.62	0.1371
	g_Y		0.3513		0.2479		0.3506		0.2592
	g_Z		14.9559		14.9115		14.9772		14.9017
4	g_X	271.868	1.0226	290.392	0.3259	271.701	1.0072	288.822	0.3615
	g_Y		1.5846		0.7062		1.5757		0.8019
	g_Z		11.8617		12.0253		11.8659		12.0482
5	g_X	334.461	2.4883	344.972	2.4975	332.485	2.517	338.817	2.5727
	g_Y		5.3086		5.0287		5.2378		4.8776
	g_Z		12.5342		12.7501		12.7851		13.2309
6	g_X	368.97	0.7788	380.544	1.874	366.686	0.6689	375.385	1.9929
	g_Y		3.1502		2.9879		2.9366		2.7861
	g_Z		9.341		8.828		9.2623		8.8247
7	g_X	426.724	1.0899	442.522	0.9198	424.828	1.0893	438.701	0.8864
	g_Y		3.4655		2.6769		3.3943		2.486
	g_Z		14.691		15.1327		14.7522		15.2449
8	g_X	705.078	0.011	746.598	0.0069	704.777	0.0106	745.924	0.0065
	g_Y		0.0186		0.0113		0.0178		0.0106
	g_Z		19.4886		19.5369		19.4933		19.5408

Table S6. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational approximations (degrees) (molecule 1).

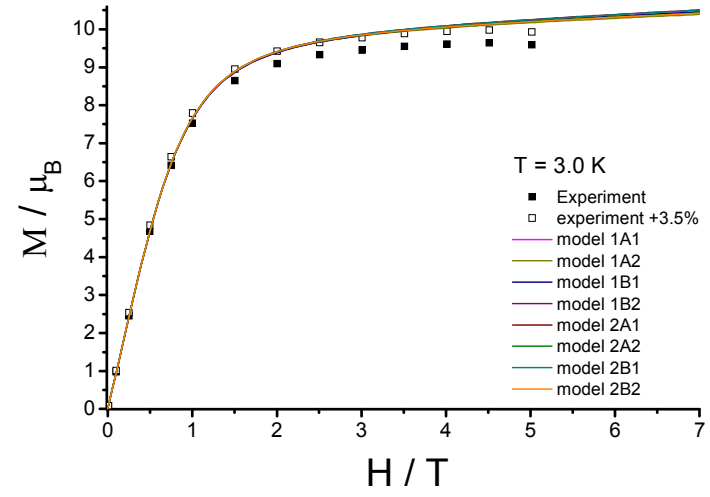
	Aλ	**Aθ**	**Bλ**	**Bθ**
Aλ	0	4.001	0.052	3.812
Aθ	4.001	0	4.053	0.198
Bλ	0.052	4.053	0	3.864
Bθ	3.812	0.198	3.864	0

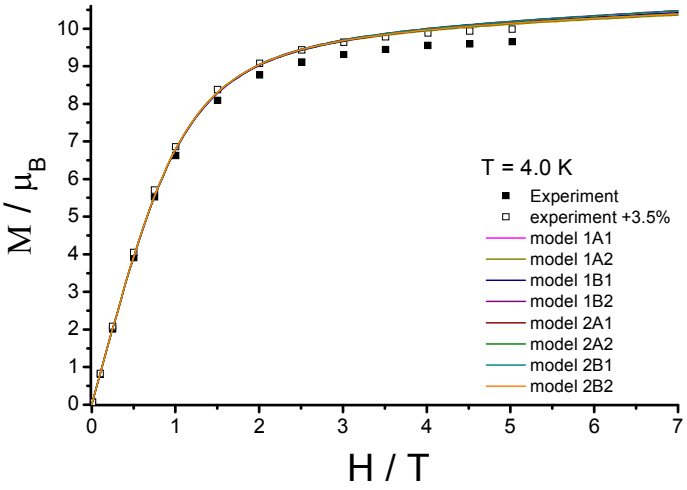
Table S7. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational approximations (degrees) (molecule 2).

	Aλ	**Aθ**	**Bλ**	**Bθ**
Aλ	0	2.586	0.816	3.285
Aθ	2.586	0	1.803	0.716
Bλ	0.816	1.803	0	2.487
Bθ	3.285	0.716	2.487	0

Table S8. Angles between the main magnetic axes of the lowest Kramers doublet of molecule 1 and molecule 2 (degrees).

	Aλ	**Aθ**	**Bλ**	**Bθ**
Angle	80.067	83.175	79.829	82.918





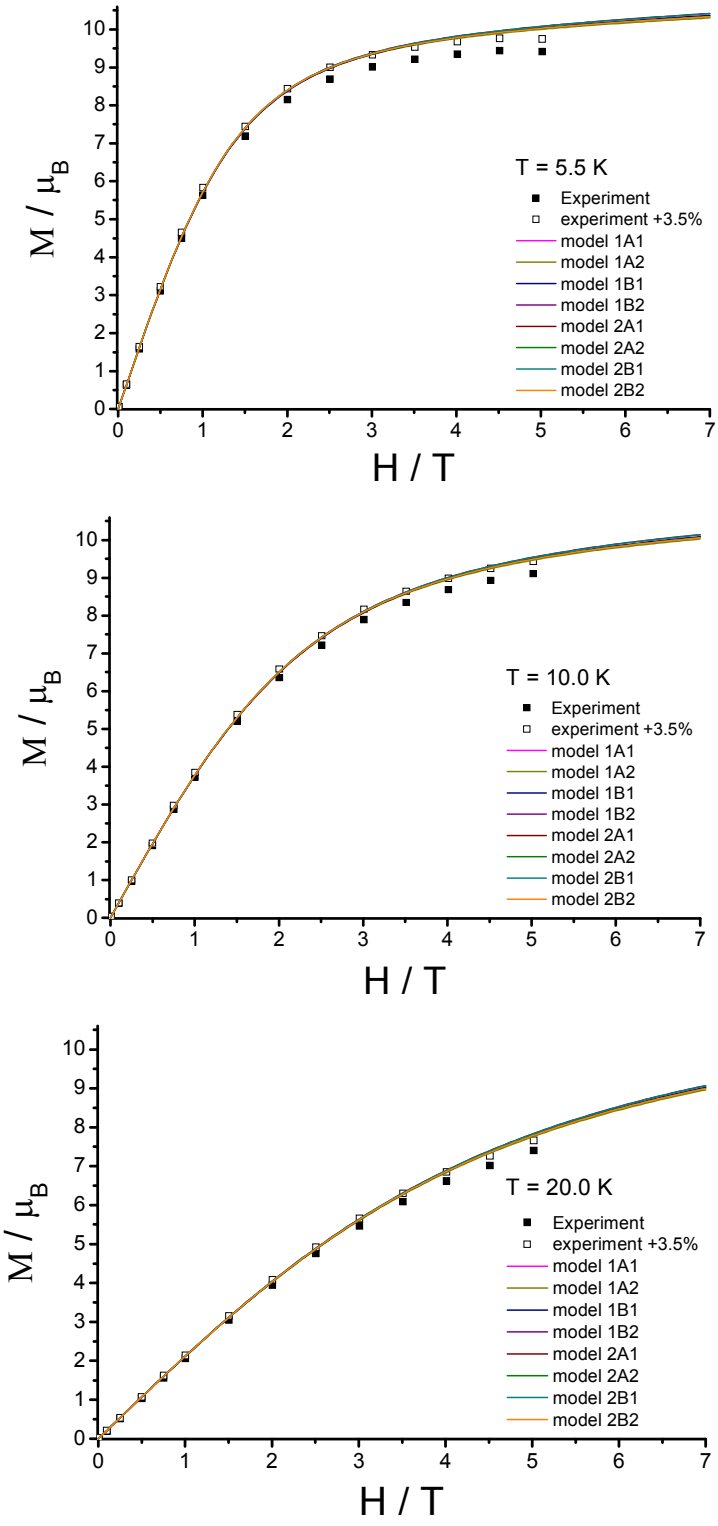


Figure S14. Measured and calculated molar magnetization of Co_2Dy_2 at the temperatures indicated on the plots. A good agreement is achieved if one up-scales the experiment with about 3.5%.

Table S9. Energies (cm^{-1}) and the corresponding tunnelling gaps and g_Z values of the lowest four exchange doublet states of the complex **3** (molecule 1).

Aλ			**Aθ**		
Energy	**Δ_{tun}**	**g_Z**	**Energy**	**Δ_{tun}**	**g_Z**
0			0	1.30E-06	
4.797E-06	4.80E-06	0	1.298E-06		0
1.4408634			1.4521225	7.01E-06	
1.440883	1.95E-05	39.27094	1.4521295		39.39075
91.142406			102.90716	3.66E-05	
91.142508	1.01E-04	0	102.9072		0
91.39598			103.1576	3.45E-05	
91.396076	9.61E-05	0	103.15763		0
Bλ			**Bθ**		
Energy	**Δ_{tun}**	**g_Z**	**Energy**	**Δ_{tun}**	**g_Z**
0			0	1.26E-06	
4.882E-06	4.88E-06	0	1.264E-06		0
1.4406749			1.452928	6.99E-06	
1.4406948	1.99E-05	39.26891	1.452935		39.39381
90.934482			102.58406	3.65E-05	
90.934585	1.03E-04	0	102.5841		0
91.188039			102.83426	3.41E-05	
91.188136	9.76E-05	0	102.8343		0

Table S10. Energies (cm^{-1}) and the corresponding tunnelling gaps and g_Z values of the lowest four exchange doublet states of the complex **3** (molecule 2).

Aλ			**Aθ**		
Energy	**Δ_{tun}**	**g_Z**	**Energy**	**Δ_{tun}**	**g_Z**
0			0		
4.258E-06	4.26E-06	0	8.873E-07	8.87E-07	0
1.4507979			1.4639575		
1.4508144	1.65E-05	39.28653	1.4639638	6.32E-06	39.42413
83.669694			94.467099		
83.66978	8.56E-05	0	94.467134	3.52E-05	0
83.922945			94.713364		
83.923027	8.28E-05	0	94.713392	2.86E-05	0
Bλ			**Bθ**		
Energy	**Δ_{tun}**	**g_Z**	**Energy**	**Δ_{tun}**	**g_Z**
0			0		
3.909E-06	3.91E-06	0	7.397E-07	7.40E-07	0
1.4529247	1.59E-05	39.30167	1.4650446	5.94E-06	39.43291

1.4529406			1.4650505		
84.036379			94.507111		
84.036463	8.33E-05	0	94.507145	3.39E-05	0
84.288235			94.751889		
84.288315	7.94E-05	0	94.751915	2.64E-05	0

Experimental information for dilution studies

It was found that the yttrium analog is isostructural to compounds 1 – 3.

Synthesis of $[Y^{III}_2Co^{III}_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_4](NO_3)_2{\cdot}H_2O$ (4a) and $[Y^{III}_2Co^{III}_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_2(NO_3)_2]{\cdot}MeOH{\cdot}H_2O$ (4b). The same procedure was used to synthesize **1 - 3** except that $Y(NO_3)_3{\cdot}6H_2O$ was used in place of $Ln(NO_3)_3{\cdot}6H_2O$, giving blue/purple needle like crystals. Yield of 70 %. Anal. Calculated (found) for **4**: $Co_2Y_2C_{45.5}H_{68}O_{26.5}N_4$ (average of the two molecules found in the ASU) : C, 39.26 (39.20); H, 4.98 (4.72); N, 4.07 (4.34). Selected IR data ATR (cm^{-1}): 3487w, 1594s, 1554s, 1483s, 1388s, 1285m, 1219w, 1176w, 1122w, 1088w, 1068w, 1022w, 944w, 921w, 846w, 812w, 742w, 716w, 687w, 641w, 610w.

Crystal data for **4** $Co_2Y_2C_{45.5}H_{68}O_{26.5}N_4$ (1390 g mol^{-1}); tetragonal, a = 40.969(6), b = 40.969(6), c = 16.039(3) A˚, $a = b = c = 90$, V = 26921(8) A˚ ^{3}, T = 150(2) K, $I4_1/a$, Z = 16, λ(synchrotron) = 0.71090, 14736 unique reflections (R_{int} = 0.0701), reflections with $I \geq 2\sigma(I)$ 13758, 758 parameters, final wR_2 = 0.3463, S = 1.699 (all data), R_1 [$I \geq 2\sigma(I)$] = 0.1207.

Doping of compound **4** with $Dy(NO_3)_3{\cdot}6H_2O$ (0.023 g) for **5%**, resulted in very similar looking crystals. Yields = 55-70%. CCDC number 903131.

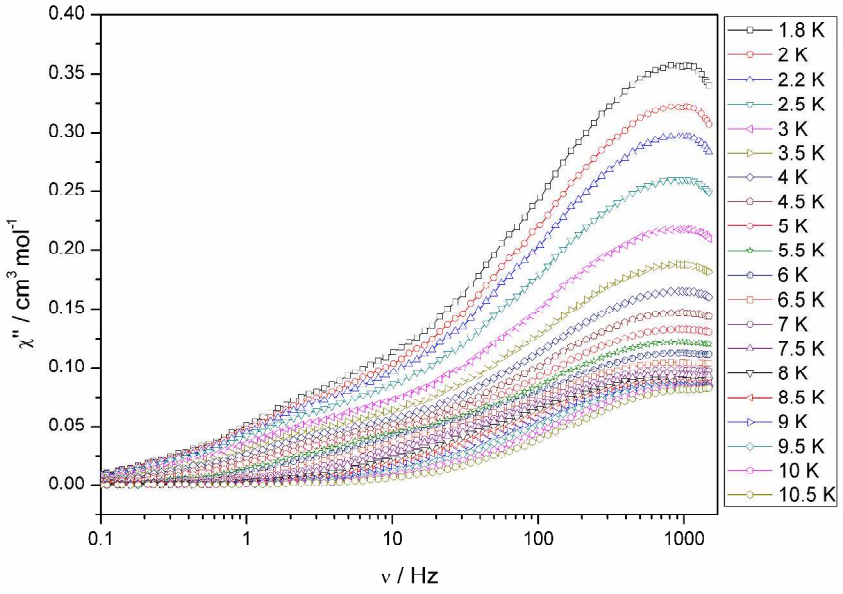


Figure S15. Frequency dependence of the out-of-phase AC susceptibility, χ_M'', of the 5 % Dy diluted sample, under zero applied DC field.