Electronic supplementary information

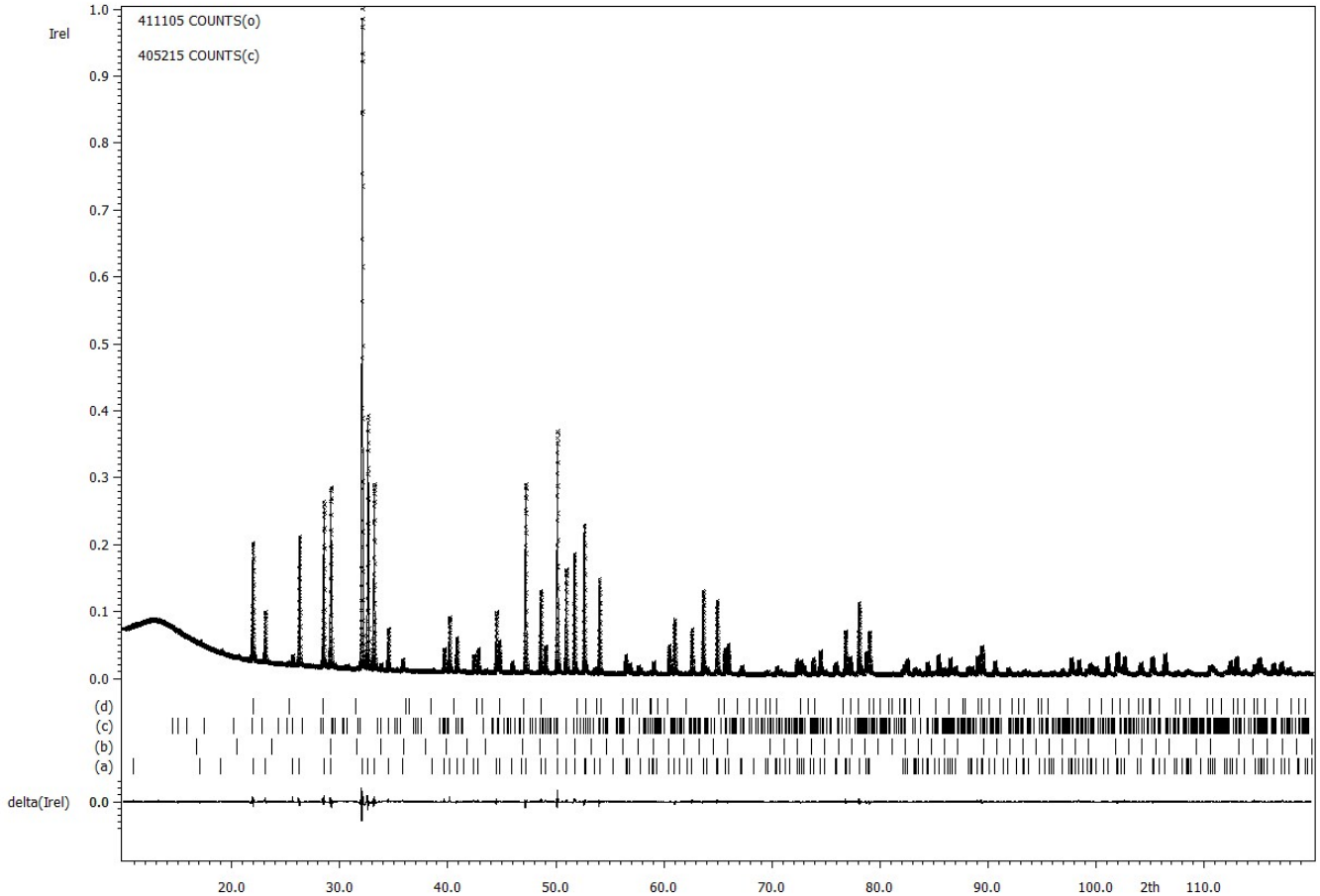


Figure S1. X-ray powder diffraction pattern of $Y_{7.75}Dy_{0.25}Ca_2(SiO_4)_6O_2$ (**1**). Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are shown as strokes underneath. (a) the main apatite phase, (b) Y_2O_3 (1.2 wt. %), Y_2SiO_5 (1.4 wt. %), cristobalite SiO_2 (2.4 wt. %).

Table S1. Crystal structure refinement data for **1**.

Temperature (K)	293 K
Wavelength (Å)	1.5406
Formula (refined)	$Y_{7.51}Dy_{0.24}Ca_{2.25}(SiO_4)_6O_2[H_\delta]$
Number of reflections	283
Number of data points	16749
Space group	$P6_3/m$
a (Å)	9.3474(2)
c (Å)	6.7830(1)
V (Å^3)	513.25(2)
Z	1
2θ range (deg.)	10 – 120
R_{wp}	0.032
R_{all}	0.014
ΔF_{max}, ΔF_{min} (e Å^{-3})	0.31, -0.42

Table S2. Atomic parameters and thermal displacement parameters (Å^2) in **1**.

Atom	Y1[a], Ca1	Y2[a], Ca2	Si	O1	O2	O3	O4
Site	4f	6h	6h	6h	6h	12i	4e
SOF	0.564(8), 0.436(8)	0.916(10), 0.084(10)	1	1	1	1	1
x	1/3	0.00315(20)	0.3995(3)	0.3183(8)	0.6002(8)	0.3392(5)	0
y	2/3	0.23722(13)	0.3721(3)	0.4896(8)	0.4751(8)	0.2491(5)	0
z	0.0021(4)	1/4	1/4	1/4	1/4	0.0597(5)	0.25
U_{iso}	0.0117(9)	0.0088(8)	0.0096(12)	0.010(2)	0.007(2)	0.0106(17)	0.014(3)

[a] Y1, Y2 was refined as a mixture $Y_{0.96875}Dy_{0.03125}$.

Table S3. Selected interatomic distances (Å) and angles (degrees) in the crystal structure of **1**.

Y1,Ca1-O1	2.314(6)	3x	Si-O1	1.621(10)	
Y1,Ca1-O2	2.420(6)	3x	Si-O2	1.627(7)	
Y1,Ca1-O3	2.784(5)	3x	Si-O3	1.631(4)	2x
Y2,Ca2-O1	2.692(5)		O1-Si-O2	113.6(4)	
Y2,Ca2-O2	2.368(11)		O1-Si-O3	111.4(3)	2x
Y2,Ca2-O3	2.282(4)	2x	O2-Si-O3	107.7(3)	2x
Y2,Ca2-O3	2.423(4)	2x	O3-Si-O3	104.7(3)	
Y2,Ca2-O4	2.2026(15)				

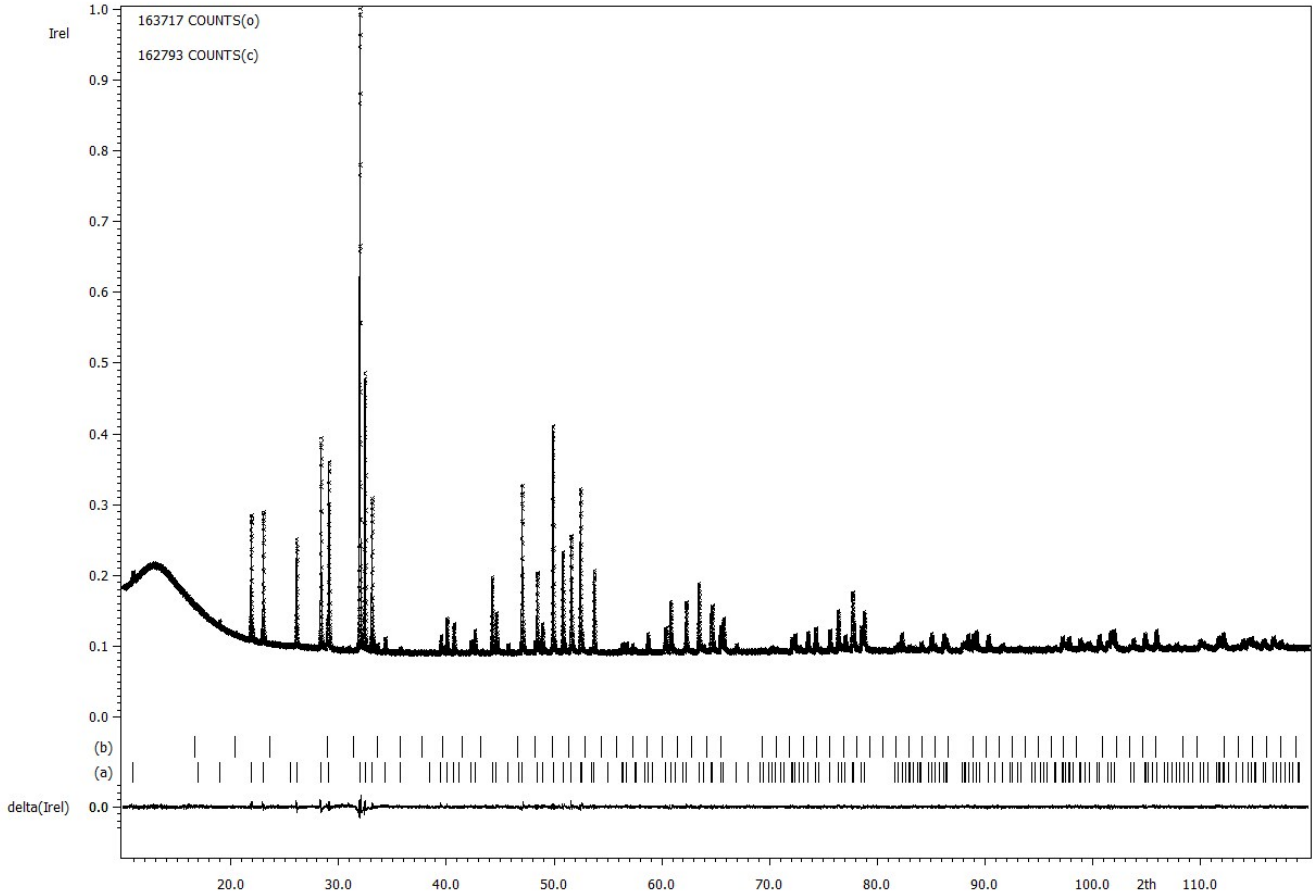


Figure S2. X-ray powder diffraction pattern of $Dy_8Ca_2(SiO_4)_6O_2$ (**2**). Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are shown as strokes underneath. (a) the main apatite phase, (b) Dy_2O_3 (1.1 wt. %).

Table S4. Crystal structure refinement data for **2**.

Temperature (K)	293 K
Wavelength (Å)	1.5406
Formula (refined)	$Dy_{8.04}Ca_{1.96}(SiO_4)_6O_2$
Number of reflections	283
Number of data points	16749
Space group	$P6_3/m$
a (Å)	9.3654(2)
c (Å)	6.8188(1)
V (Å^3)	517.95(2)
Z	1
2θ range (deg.)	10 – 120
R_{wp}	0.011
R_{all}	0.020
ΔF_{max}, ΔF_{min} (e Å^{-3})	0.48, -0.63

Table S5. Atomic parameters and thermal displacement parameters (Å^2) in **2**.

Atom	Dy1, Ca1	Dy2, Ca2	Si	O1	O2	O3	O4
Site	4f	6h	6h	6h	6h	12i	4e
SOF	0.594(7), 0.406(7)	0.944(10), 0.056(10)	1	1	1	1	1
x	1/3	0.0054(3)	0.3994(6)	0.3176(11)	0.6018(11)	0.3377(7)	0
y	2/3	0.23865(16)	0.3716(6)	0.4889(11)	0.4747(10)	0.2487(7)	0
z	-0.0002(7)	1/4	1/4	1/4	1/4	0.0609(7)	0.25
U_{iso}	0.0101(9)	0.0069(6)	0.0078(18)	0.009(4)	0.003(3)	0.006(3)	0.008(4)

Table S6. Selected interatomic distances (Å) and angles (degrees) in the crystal structure of **2**.

Dy1,Ca1-O1	2.336(9)	3x	Si-O1	1.623(15)	
Dy1,Ca1-O2	2.414(9)	3x	Si-O2	1.642(10)	
Dy1,Ca1-O3	2.802	3x	Si-O3	1.630(6)	2x
Dy2,Ca2-O1	2.682(8)		O1-Si-O2	113.5(6)	
Dy2,Ca2-O2	2.372(15)		O1-Si-O3	110.9(4)	2x
Dy2,Ca2-O3	2.289(5)	2x	O2-Si-O3	108.2(4)	2x
Dy2,Ca2-O3	2.440(6)	2x	O3-Si-O3	104.6(4)	
Dy2,Ca2-O4	2.2103(19)				

Table S7. Crystal field parameters (in Wybourne notation) derived in the program CONCORD for Dy^{3+} using experimental atomic coordinates of the coordination polyhedrons of Dy1 and Dy2 sites (from Table S5). Partial charges on the silicate oxygen atoms and on the intrachannel oxygen atom are -0.5 and -1.0 respectively (adjusted to fit the $\chi T(T)$ dependence for **2**).

Parameter	Value (cm^{-1})		
	Dy1 ($a \rightarrow x$, $c \rightarrow z$)	Dy2 ($a \rightarrow x$, $c \rightarrow z$)	Dy2 (z axis along easy magnetization axis)
B_{20}	701.38363	-426.97211	993.34326
B_{22}		-450.63672	56.914996
B_{40}	-157.63795	157.89317	294.91316
B_{42}		10.477190	-48.373936
B_{43}	-54.565652		
B_{44}		-131.48428	8.6605777
B_{60}	-19.835861	-17.388239	41.718889
B_{62}		-22.479997	-8.5295564
B_{63}	-9.0345006		
B_{64}		5.9183550	6.4517547
B_{66}	1.9031082	14.562523	5.9352741
B_{21}			
B_{41}			
B_{61}			
B_{65}			
B_{21}'			-84.160426
B_{22}'		-457.67948	
B_{41}'			126.32885
B_{42}'		161.23726	
B_{43}'	72.107571		-47.108550
B_{44}'		90.664794	
B_{61}'			-0.83957308
B_{62}'		-12.005122	
B_{63}'	20.817456		3.5214506
B_{64}'		-8.0281853	
B_{65}'			-10.676067
B_{66}'	7.5849117	-5.8940102	

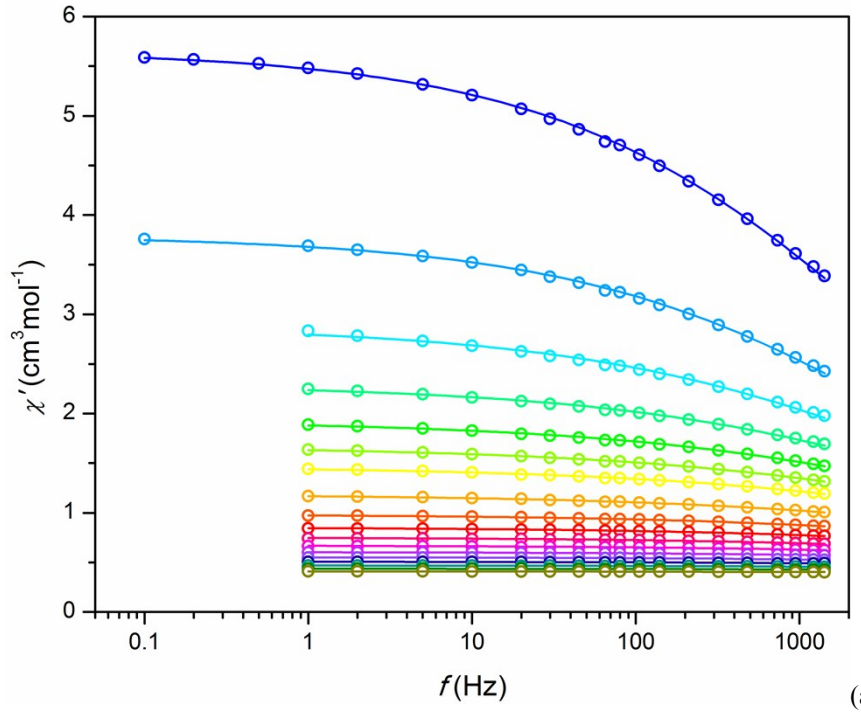
Table S8. Modeling with the program PHI using crystal field parameters listed in Table S7. The KDs of the ground multiplet $^6H_{15/2}$ are shown only.

Dy1

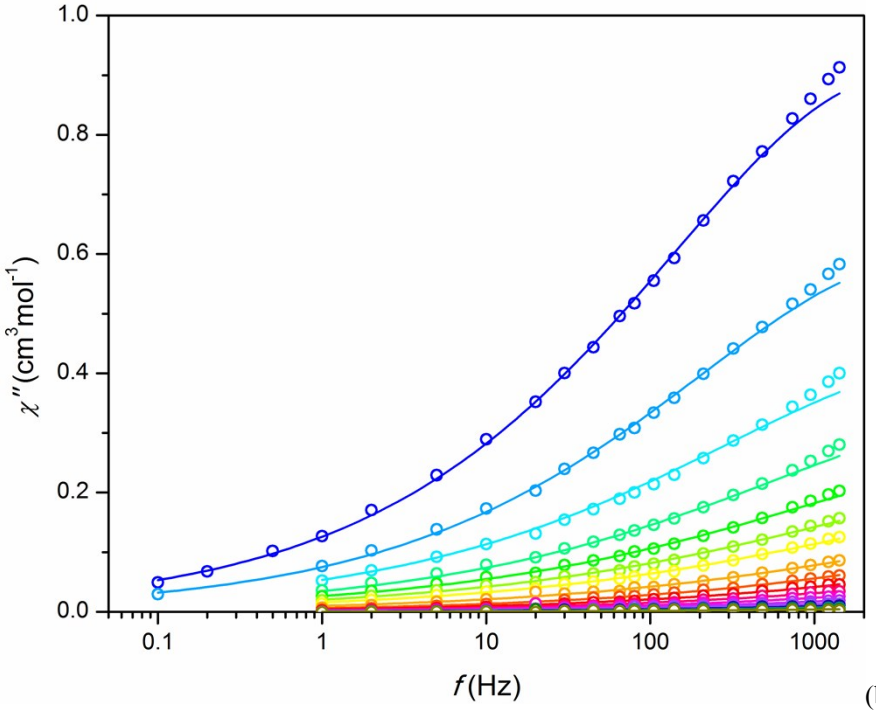
Energy (cm^{-1})	M_J (%)	g_z	g_x	g_y	Probability $M_J \rightarrow -M_J$
0	15/2 (99.97)	19.9976	0	0	
64.0008	13/2 (99.85)	17.2988	0.0001	0.0001	0.4501E-08
135.343	11/2 (99.64)	14.5908	0.0001	0.0001	0.1192E-05
204.748	9/2 (99.35)	11.8897	0	0	0.1182E-04
266.071	7/2 (98.99)	9.2065	0.0890	0.0890	0.2549E-02
315.214	5/2 (98.23)	6.5484	0.1024	0.1024	0.5682E-01
349.429	3/2 (94.50)	4.0055	0	0	0.2511E+00
366.971	1/2 (96.25)	10.6436	1.3030	10.6436	0.1819E+02

Dy2

Energy (cm^{-1})	M_J (%)	g_z	g_x	g_y	Probability $M_J \rightarrow -M_J$
0	15/2 (100)	19.9994	0	0	
167.926	13/2 (99.87)	17.2872	0	0	0.7178E-03
298.260	11/2 (99.78)	14.6456	0.0009	0.0010	0.2984E-06
392.941	9/2 (98.49)	12.0443	0.0035	0.0059	0.2841E+00
456.651	7/2 (94.07)	9.1918	0.9112	1.2725	0.1201E+00
493.969	5/2 (68.07) 1/2 (22.07)	7.3280	4.3505	6.9856	0.8801E+01
526.148	3/2 (56.56) -1/2 (14.91) -5/2 (24.58)	14.0515	0.9259	2.0046	0.1735E+02
564.749	1/2 (62.31) -3/2 (30.75)	18.9301	0.0319	0.0653	0.3064E+02

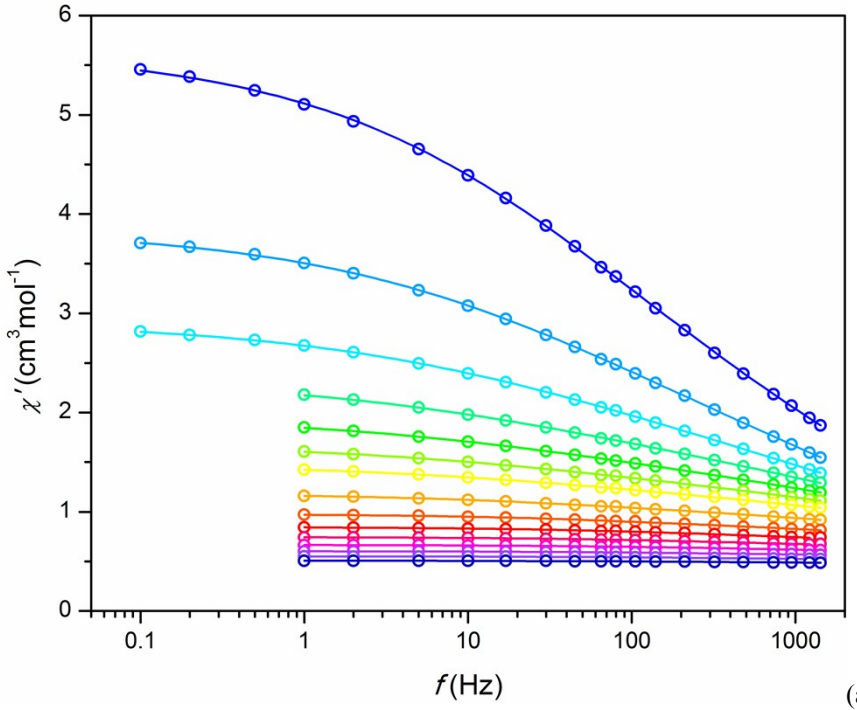


(a)

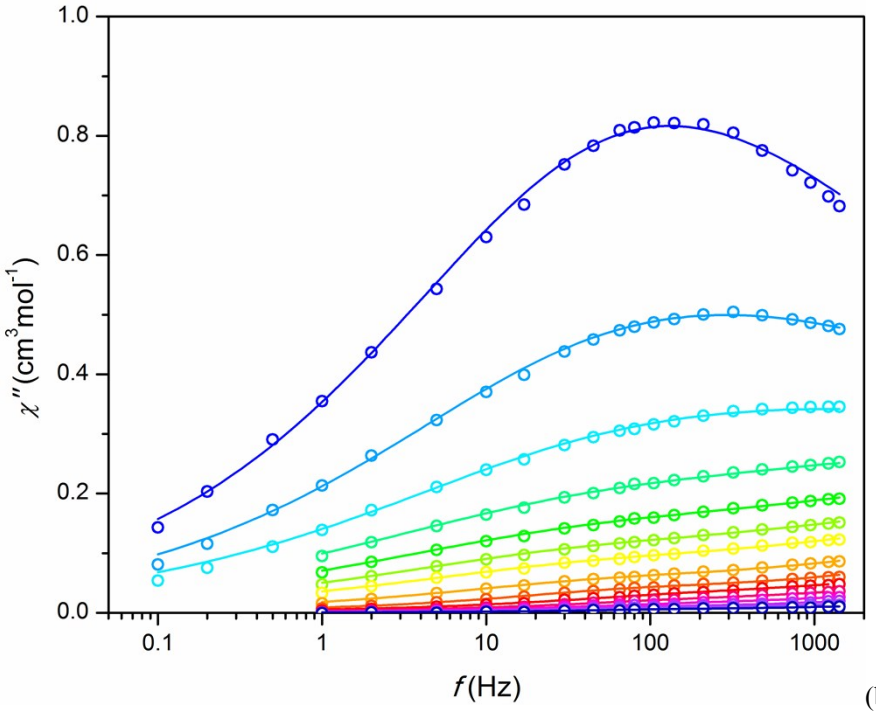


(b)

Figure S3. Frequency dependence of ac susceptibility per mol of Dy for **1** at different temperatures under a zero field. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''. Symbols – experimental points, lines – fitting. Color designation: blue – green – red – navy – dark-yellow, T = 2 – 8 K (step 1 K), T = 10 – 30 K (step 2 K), respectively.

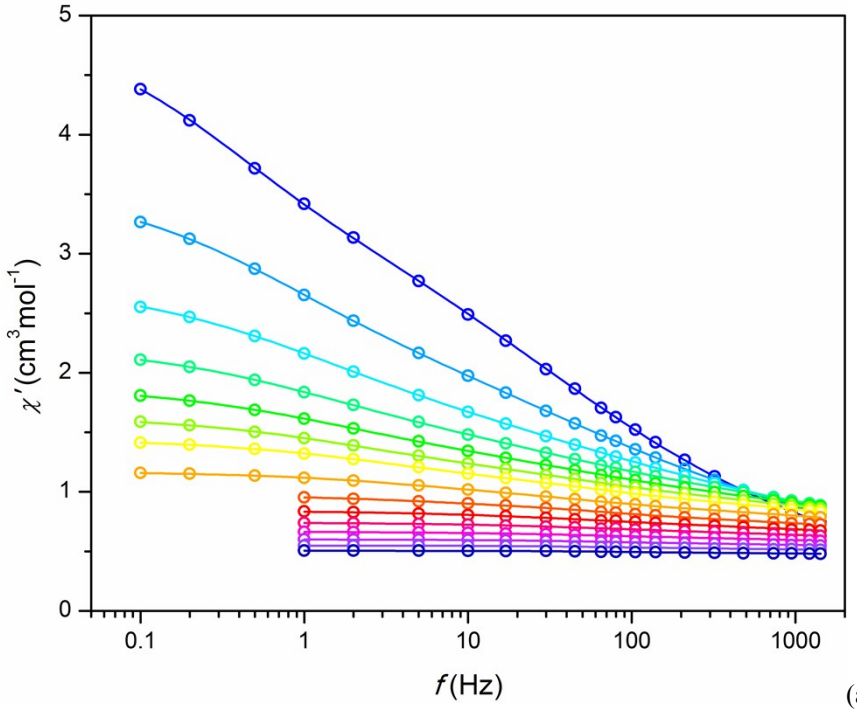


(a)

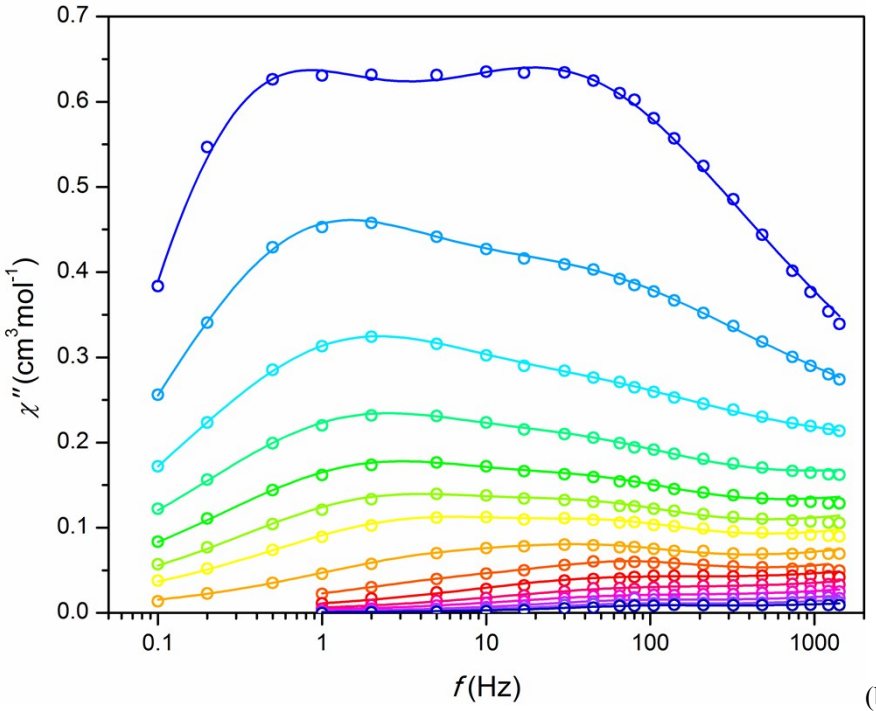


(b)

Figure S4. Frequency dependence of ac susceptibility per mol of Dy for **1** at different temperatures under a field of 0.4 kOe. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''. Symbols – experimental points, lines – fitting. Color designation: blue – green – red – navy, T = 2 – 8 K (step 1 K), T = 10 – 24 K (step 2 K), respectively.



(a)



(b)

Figure S5. Frequency dependence of ac susceptibility per mol of Dy for **1** at different temperatures under a field of 1.5 kOe. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''. Symbols – experimental points, lines – fitting. Color designation: blue – green – red – navy, T = 2 – 8 K (step 1 K), T = 10 – 24 K (step 2 K), respectively.

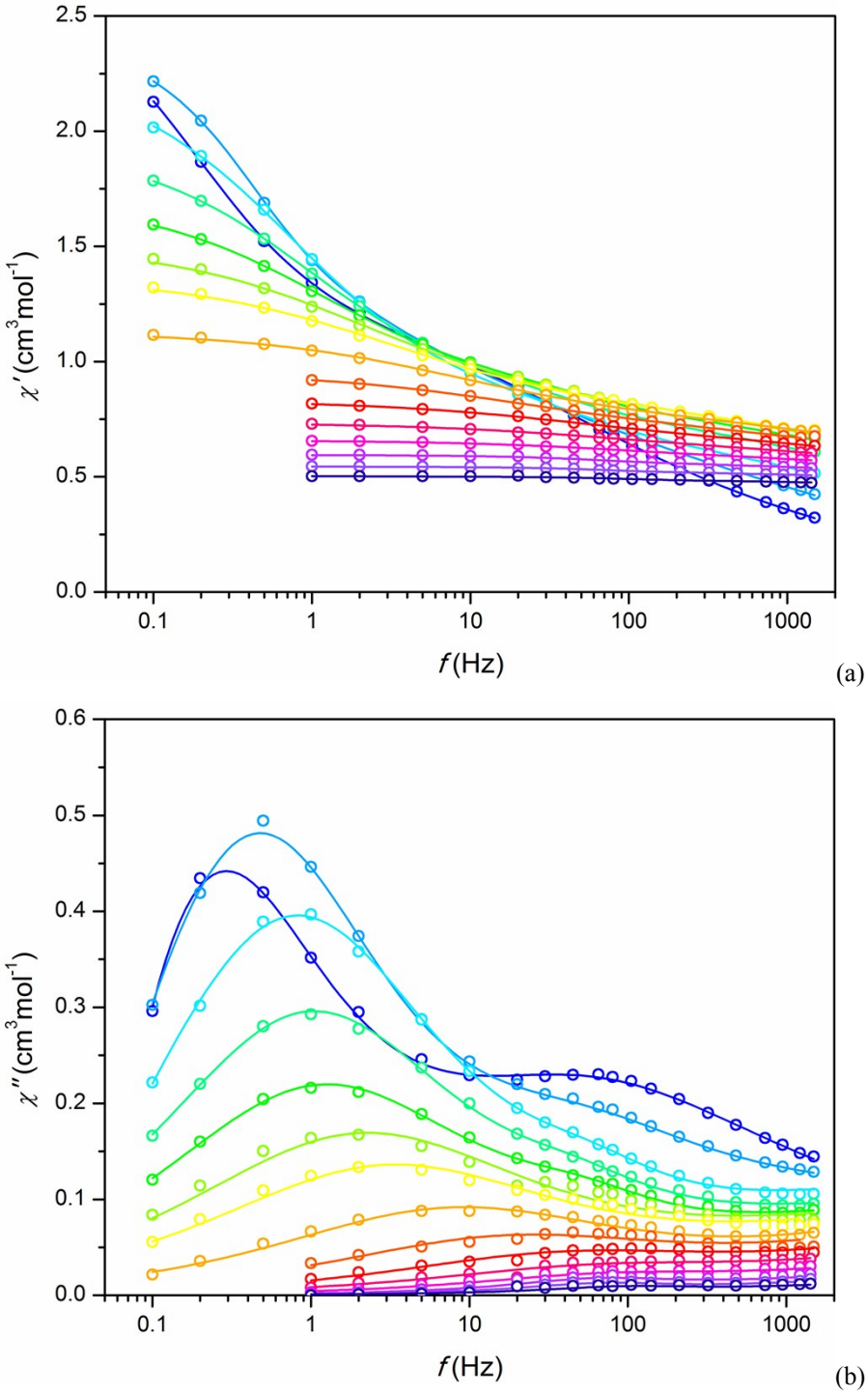
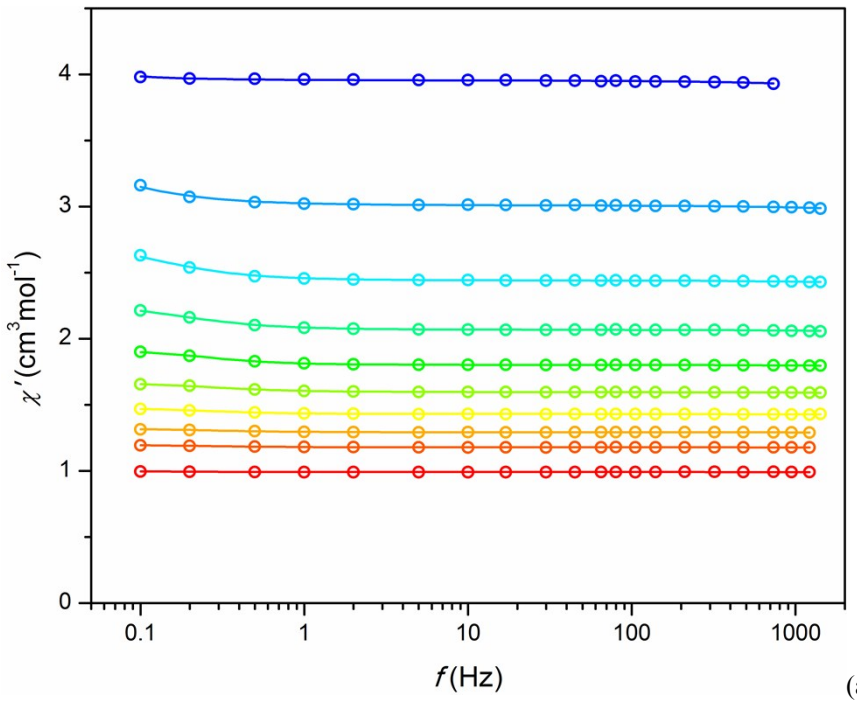
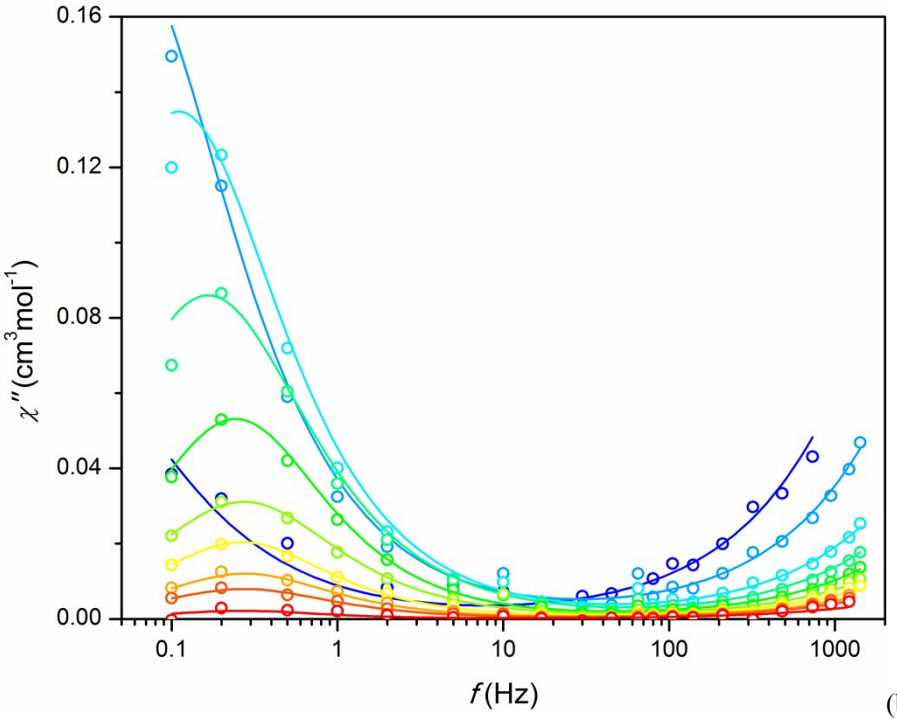


Figure S6. Frequency dependence of ac susceptibility per mol of Dy for **1** at different temperatures under a field of 4 kOe. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''. Symbols – experimental points, lines – fitting. Color designation: blue – green – red – navy, T = 2 – 8 K (step 1 K), T = 10 – 24 K (step 2 K), respectively.



(a)



(b)

Figure S7. Frequency dependence of ac susceptibility per mol of Dy for **2** at different temperatures under a field of 1.5 kOe. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''. Symbols – experimental points, lines – fitting. Color designation: blue – green – red, T = 2 – 10 K (step 1 K), and T = 12 K, respectively. Values of χ_0 (derived from dc magnetization measurements as differential susceptibilities) taken for the fitting: 4.310, 3.336, 2.658, 2.184 for T = 2, 3, 4, 5 K, respectively.

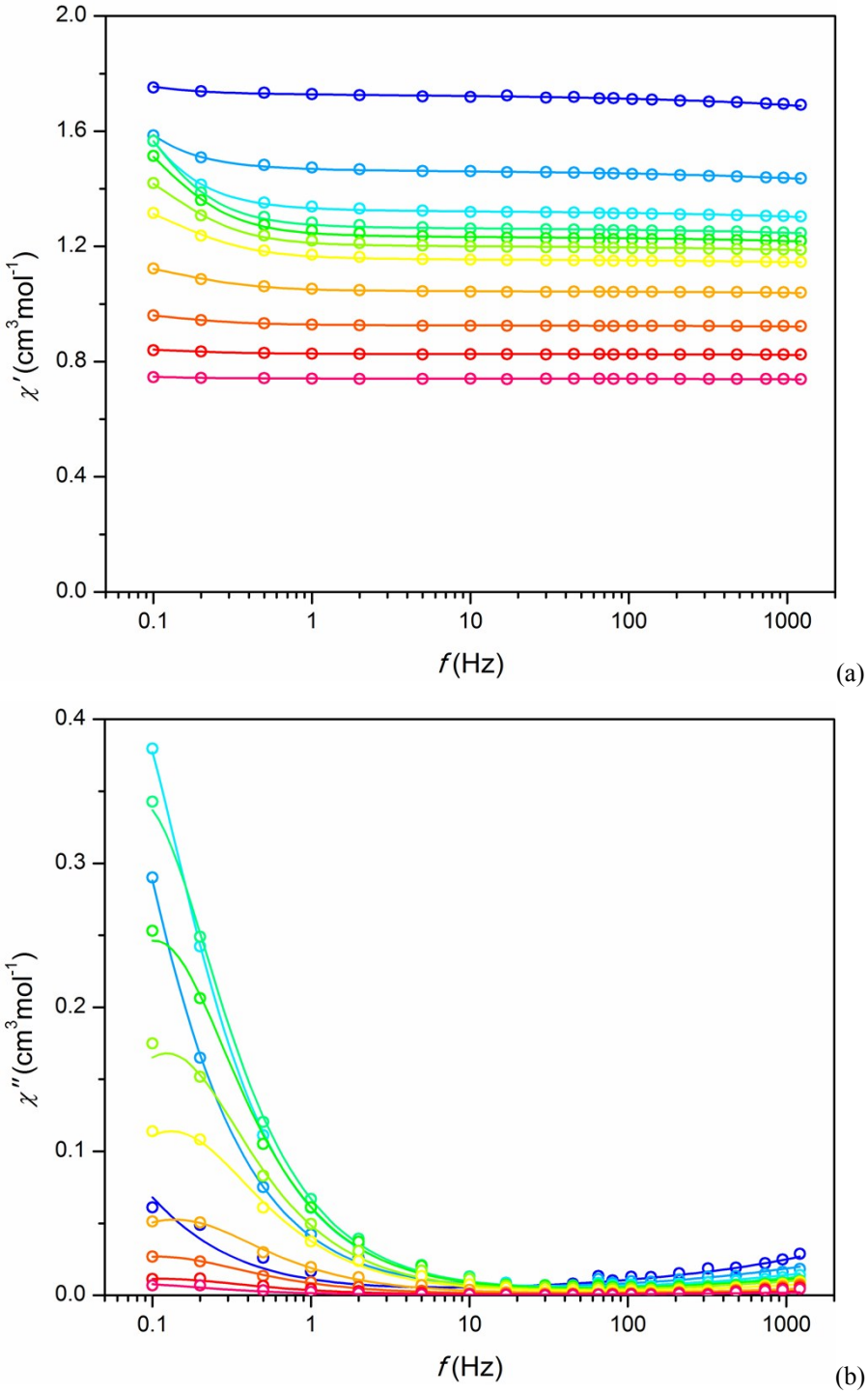


Figure S8. Frequency dependence of ac susceptibility per mol of Dy for **2** at different temperatures under a field of 4 kOe. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''. Symbols – experimental points, lines – fitting. Color designation: blue – green – carmine-red, T = 2 – 8 K (step 1 K), T = 10 – 16 K (step 2 K), respectively. Values of χ_0 (derived from dc magnetization measurements as differential susceptibilities) taken for the fitting: 2.560, 2.465, 2.202, 1.922, 1.695, 1.500, 1.353, 1.117, for T = 2, 3, 4, 5, 6, 7, 8, 10 K, respectively.

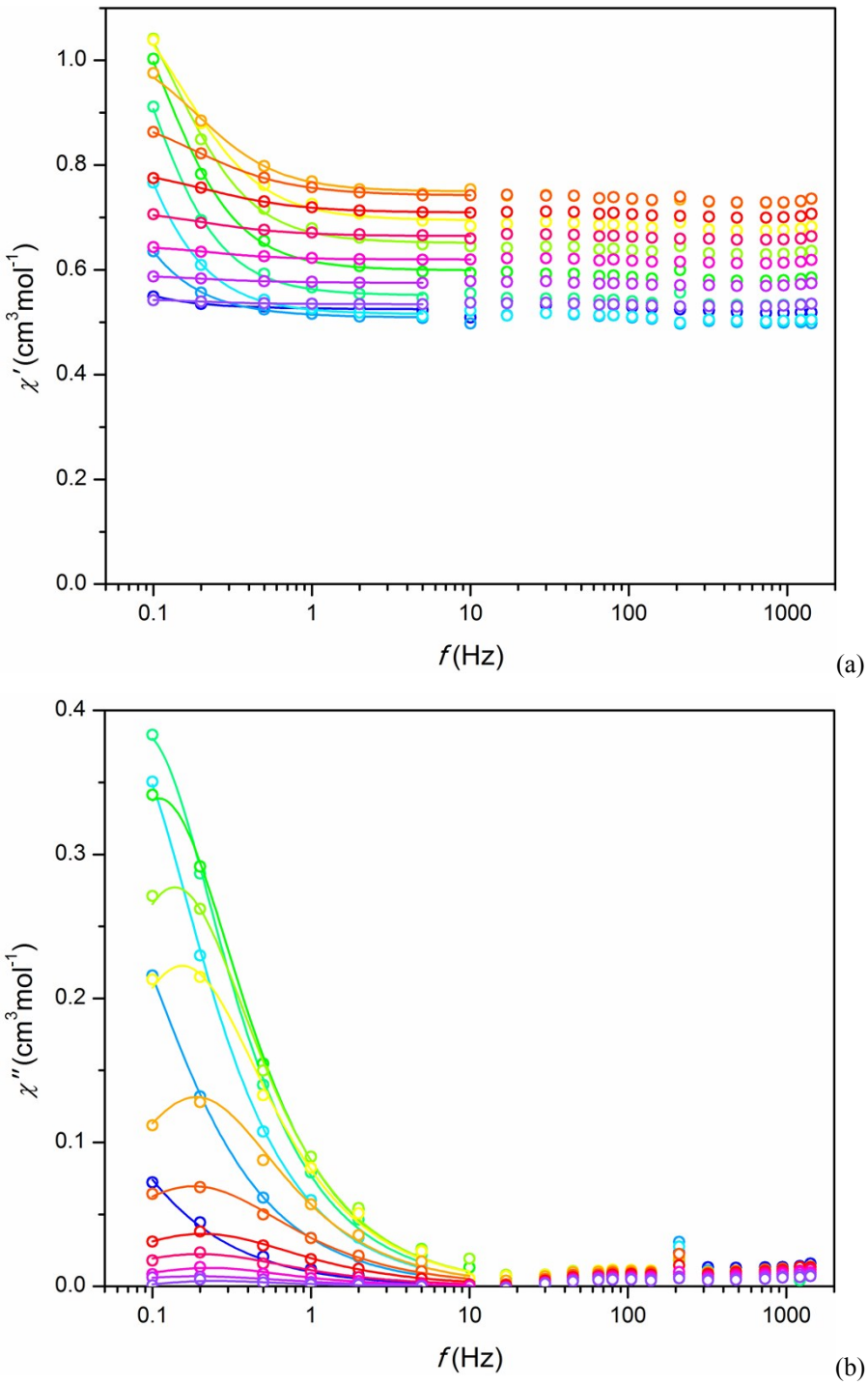


Figure S9. Frequency dependence of ac susceptibility per mol of Dy for **2** at different temperatures under a field of 8 kOe. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''. Symbols – experimental points, lines – fitting. Color designation: blue – green – red – violet, T = 2 – 8 K (step 1 K), T = 10 - 22 K (step 2 K), respectively. Values of χ_0 (derived from dc magnetization measurements as differential susceptibilities) taken for the fitting: 0.906, 1.170, 1.303, 1.314, 1.277, 1.199, 1.140, 0.998, 0.875, 0.778, 0.696, for T = 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16 K, respectively.