Electronic Supplementary Informations

for

Exploration of SMM behavior of Ln_2-complexes derived from thianaphthene-2-carboxylic acid

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Table S1 Selected structural parameters (bond lengths in Å and angles in º) of Ln^{III} center(s) (Ln=Dy for **1** and Ln=Tb for **2**) in **1** and **2** and Y^{III} center(s) in **3**. Symmetry code: A, 2–*x*, 2–*y*, 1–*z* for **1**; A, 1–*x*, 2–*y*, 1–*z* for **2** and A, 1–*x*, 1–*y*, 2–*z* for **3**.

	Dy^{III}	Tb^{III}		Y^{III}		Dy^{III}	Tb^{III}		Y^{III}
Ln1–O1	2.497(5)	2.511(7)	Y1–O1	2.494(4)	O1–Ln1–O2	53.30(17)	53.1(2)	O1–Y1–O2	53.88(13)
Ln1–O2	2.399(5)	2.404(7)	Y1–O2	2.376(4)	O1–Ln1–O3	134.01(17)	133.4(2)	O1–Y1–O3	134.55(14)
Ln1–O3	2.396(5)	2.398(6)	Y1–O3	2.375(4)	O1– Ln1–O4	120.79(17)	120.3(2)	O1– Y1–O4	121.07(13)
Ln1–O4	2.485(5)	2.491(6)	Y1–O4	2.473(4)	O1– Ln1–O5	82.4(2)	82.5(3)	O1– Y1–O5	82.39(15)
Ln1–O5	2.265(6)	2.292(7)	Y1–O5	2.252(4)	O1– Ln1–O6	75.3(2)	75.0(2)	O1– Y1–O6	75.32(15)
Ln1–O6	2.315(6)	2.319(7)	Y1–O6	2.294(4)	O1– Ln1–O7	146.06(18)	145.5(2)	O1– Y1–O7A	146.05(14)
Ln1–O7	2.348(5)	2.362(7)	Y1–O7A	2.335(4)	O1– Ln1–O8	76.94(19)	77.0(2)	O1– Y1–O8	76.71(14)
Ln1–O8	2.355(5)	2.375(7)	Y1–O8	2.345(4)	O2– Ln1–O3	86.03(18)	85.5(2)	O2– Y1–O3	86.10(14)
Ln1···Ln1A	4.551	4.523	Y1···Y1A	4.602	O2– Ln1–O4	74.94(18)	74.6(2)	O2– Y1–O4	74.91(14)
					O2– Ln1–O5	87.1(2)	86.9(3)	O2– Y1–O5	86.79(16)
					O2– Ln1–O6	93.16(19)	92.9(2)	O2– Y1–O6	93.59(16)
					O2– Ln1–O7	149.51(18)	149.2(2)	O2– Y1–O7A	150.25(15)
					O2– Ln1–O8	129.7(2)	129.5(2)	O2– Y1–O8	129.90(15)
					O3– Ln1–O4	53.78(16)	53.6(2)	O3– Y1–O4	54.17(13)
					O3– Ln1–O5	74.13(19)	73.9(2)	O3– Y1–O5	73.88(15)
					O3– Ln1–O6	134.07(18)	134.4(2)	O3– Y1–O6	134.25(15)
					O3– Ln1–O7	79.90(19)	81.0(2)	O3– Y1–O7A	79.40(15)
					O3– Ln1–O8	133.41(19)	134.2(2)	O3– Y1–O8	132.59(14)
					O4– Ln1–O5	125.29(18)	124.9(2)	O4– Y1–O5	125.31(14)
					O4– Ln1–O6	81.64(18)	82.0(2)	O4– Y1–O6	81.56(14)
					O4– Ln1–O7	74.91(18)	75.1(2)	O4– Y1–O7A	75.54(14)
					O4– Ln1–O8	149.6(2)	149.7(3)	O4– Y1–O8	149.81(15)
					O5– Ln1–O6	151.8(2)	151.7(3)	O5– Y1–O6	151.86(16)
					O5– Ln1–O7	114.3(2)	115.4(3)	O5– Y1–O7A	113.38(16)
					O5– Ln1–O8	78.6(2)	79.3(3)	O5– Y1–O8	78.25(15)
					O6– Ln1–O7	78.0(2)	77.4(2)	O6– Y1–O7A	78.77(15)
					O6– Ln1–O8	79.63(19)	79.1(3)	O6– Y1–O8	80.06(15)
					O7– Ln1–O8	77.9(2)	77.9(3)	O7A– Y1–O8	77.53(15)

Table S2 Summary of SHAPE analysis around Ln^{III} center(s) for **1** and **2** and Y^{III} center(s) in **3** (Ln = Dy for **1**, Ln = Tb for **2**).

ML_8		**1**	**2**	**3**
Octagon	D_{8h}	30.016	29.845	30.157
Heptagonal pyramid	C_{7v}	21.366	21.318	21.339
Hexagonal bipyramid	D_{6h}	13.123	13.242	12.963
Cube	Oh	9.958	10.036	9.788
Square antiprism	D_{4d}	2.799	2.846	2.725
Triangular dodecahedron	D_{2d}	3.184	3.282	3.118
Johnson gyrobifastigium J26	D_{2d}	12.451	12.463	12.389
Johnson elongated triangular bipyramid J14	D_{3h}	25.745	25.606	25.886
Biaugmented trigonal prism J50	C_{2v}	2.750	2.782	2.674
Biaugmented trigonal prism	C_{2v}	**2.210**	**2.207**	**2.215**
Snub diphenoid J84	D_{2d}	4.111	4.209	4.013
Triakis tetrahedron	Td	10.660	10.685	10.464
Elongated trigonal bipyramid	D_{3h}	21.570	21.213	21.793

Table S3 Parameters obtained from Cole Cole fitting for **1'**

Temperature (K)	χ_{Iso}	α	τ
1.85	0.99474	0.33093	2.26486×10^{-4}
2	0.92544	0.36166	1.06772×10^{-4}
2.14	0.8818	0.3922	5.51724×10^{-5}
2.29	0.8439	0.40798	3.36914×10^{-5}
2.45	0.79426	0.42295	1.86669×10^{-5}
2.56	0.73978	0.43161	9.58461×10^{-6}
2.71	0.70505	0.43298	5.71799×10^{-6}
2.85	0.67261	0.42897	3.55239×10^{-6}
3	0.64428	0.42721	2.20762×10^{-6}
3.25	0.60038	0.40931	1.13417×10^{-6}

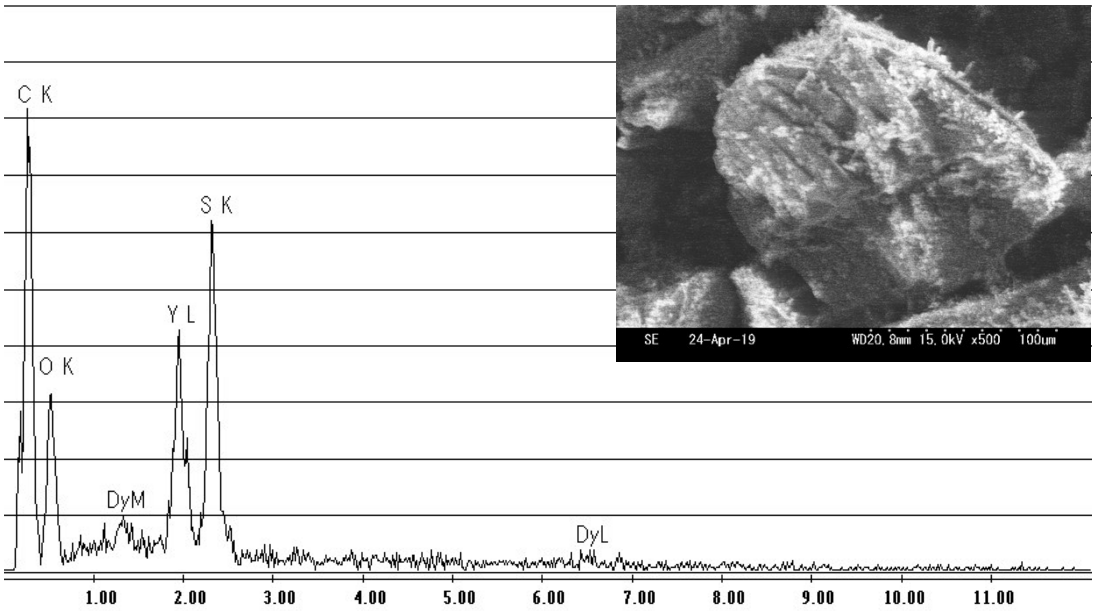


Fig. S1 EDX spectrum for the compound **1'**. Inset shows the SEM image of the same.

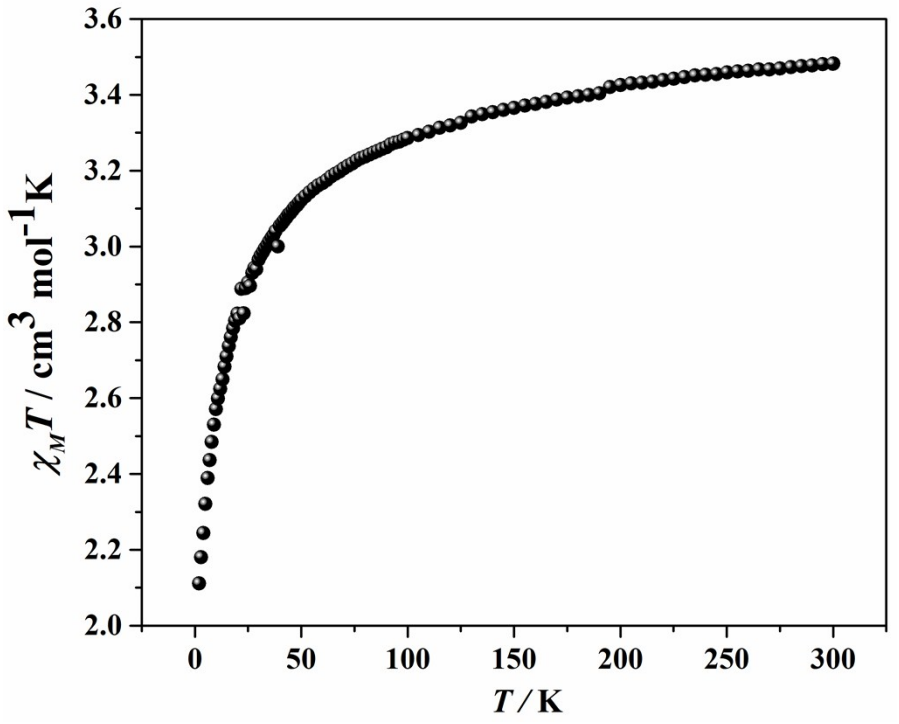


Fig. S2 Temperature dependence of the $\chi_M T$ products in 1000 Oe for **1'**.

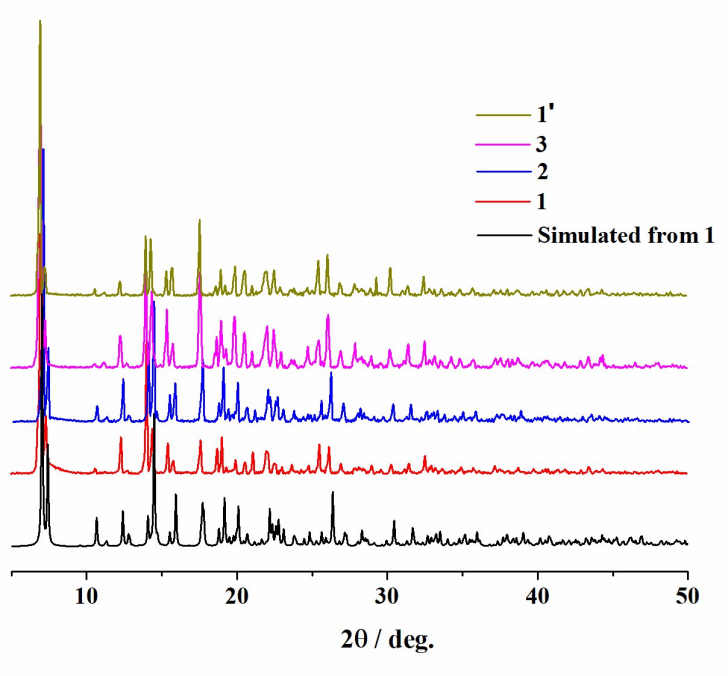
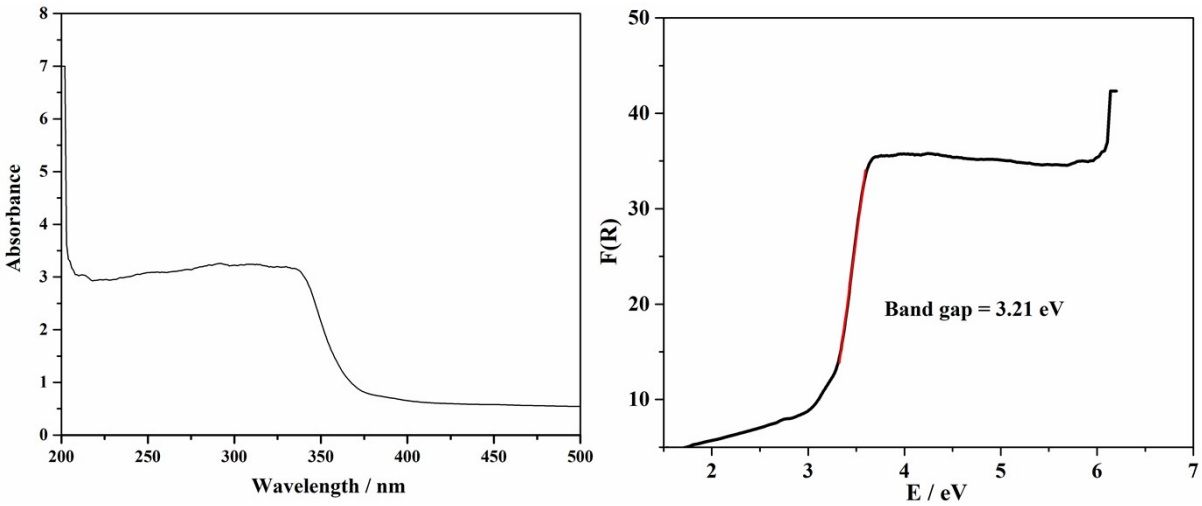


Fig. S3 Simulated and observed PXRD patterns of the complexes.



(a) (b)

Fig. S4 (a) UV-VIS absorption spectra for complex **1** and (b) the band gap estimated using Kubelka-Munk function.[1]

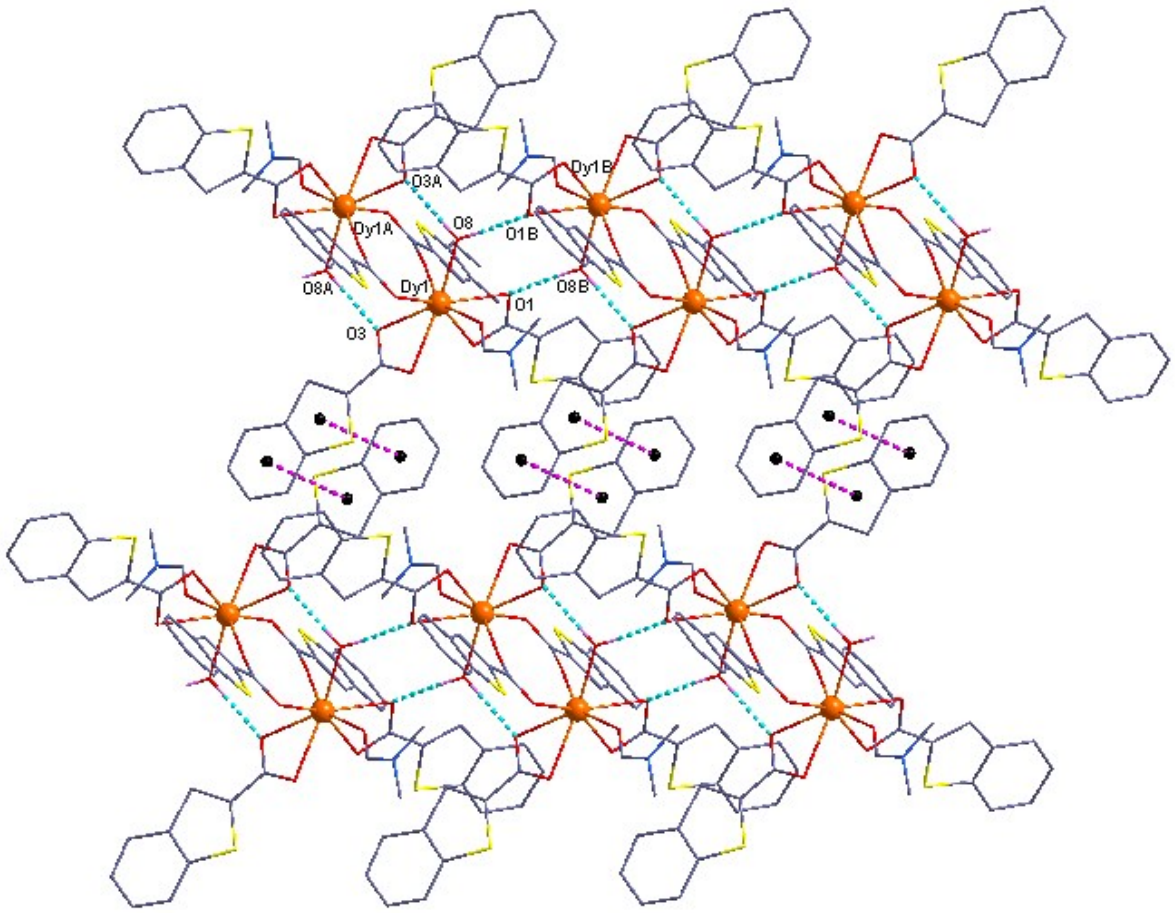
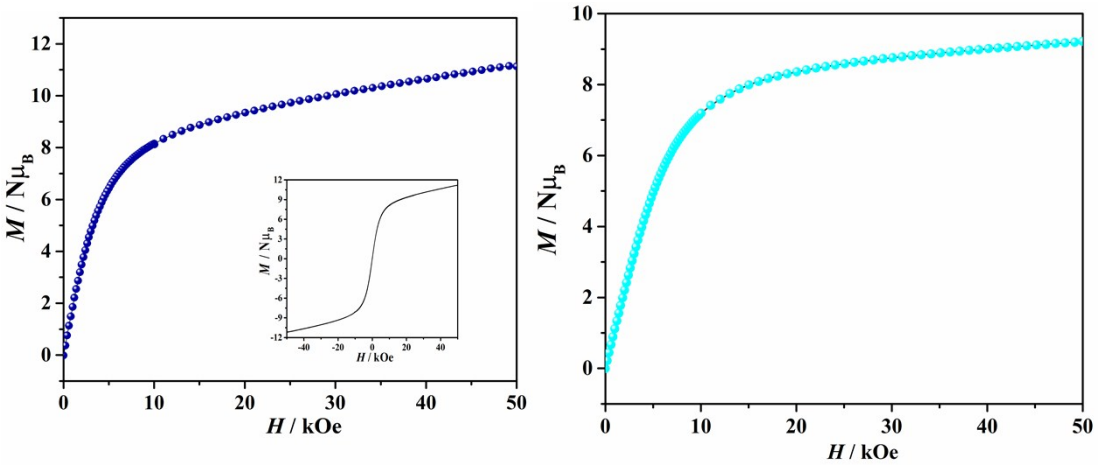


Fig. S5 Perspective view of two dimensional sheet caused by intermolecular π···π stacking interaction and intra- and inter-molecular hydrogen bonding interactions in crystallographic *ac* plane for **1**. Hydrogen atoms, except those of the water molecules, are omitted for clarity. Symmetry codes: A, 2–*x*, 2–*y*, 1–*z*; B, 1–*x*, 2–*y*, 1–*z*.



(a) (b)

Fig. S6 Isothermal magnetization plot for (a) **1** (inset: magnetic hysteresis) and (b) **2**.

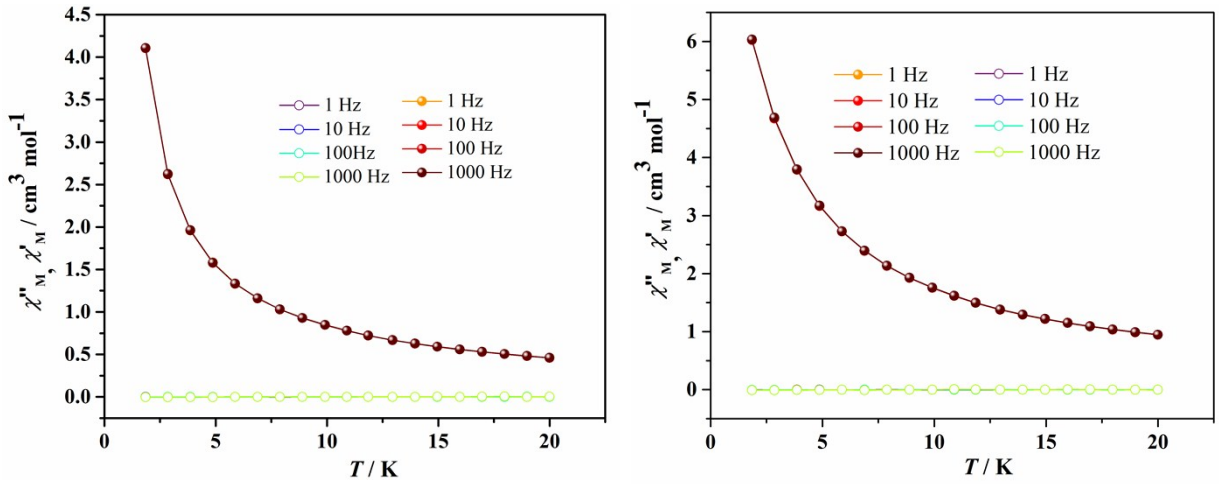


Fig. S7 Frequency and temperature dependency without dc field for (a) **1** and (b) **2**.

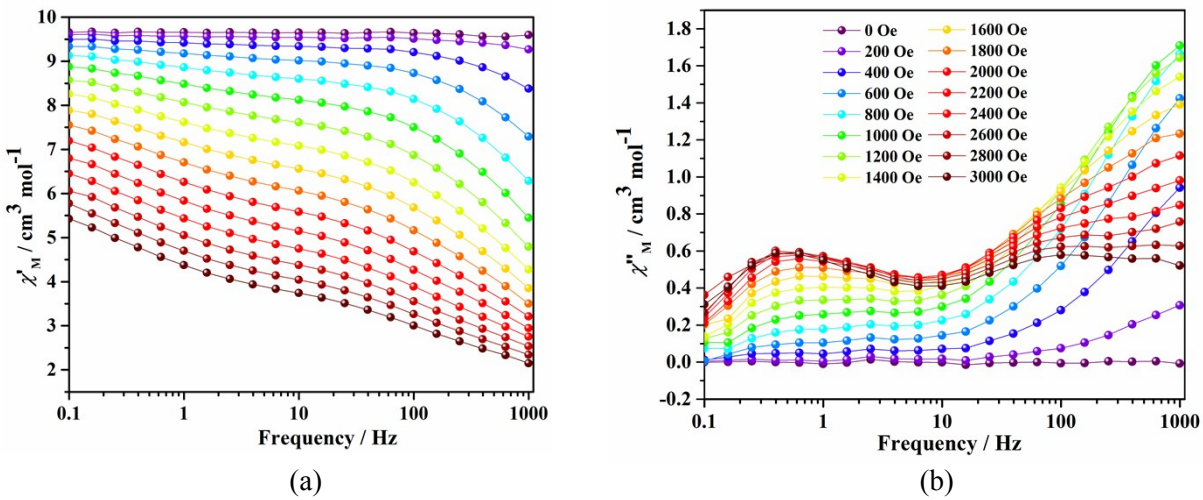


Fig. S8 Frequency dependency of the (a) in phase and (b) out of phase ac susceptibility under indicated dc fields at 1.85 K for **1**. The indication for the fields for both plots are shown only in (b) for clarity.

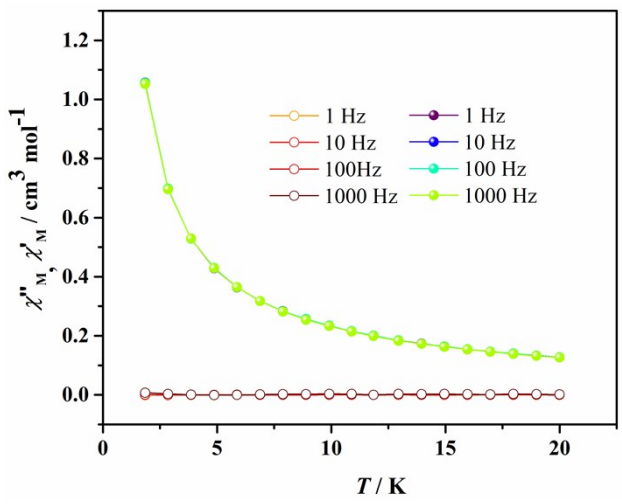
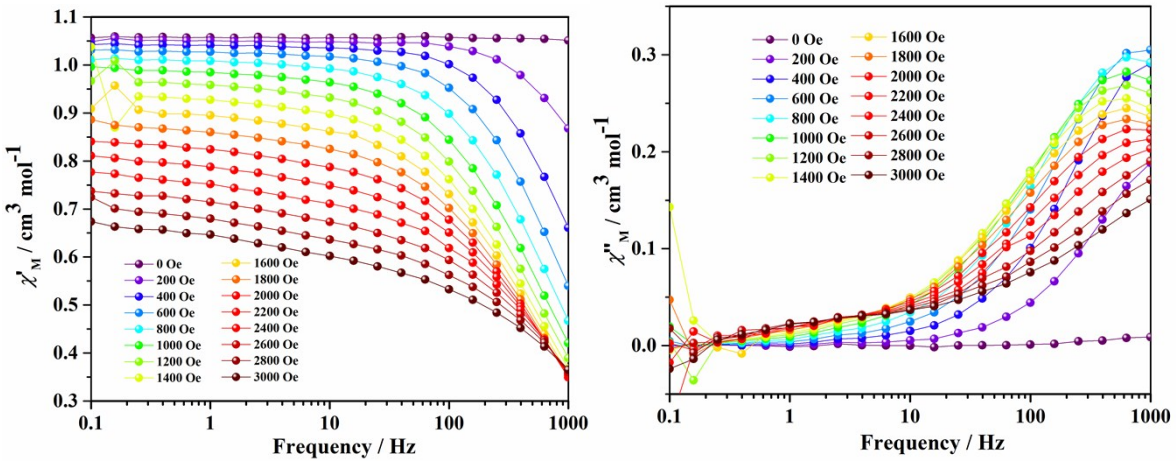


Fig. S9 Frequency and temperature dependency without dc field for **1'**.



(a) (b)

Fig. S10 Frequency dependency of the (a) in phase and (b) out of phase ac susceptibility under indicated dc fields at 1.85K for **1'**.

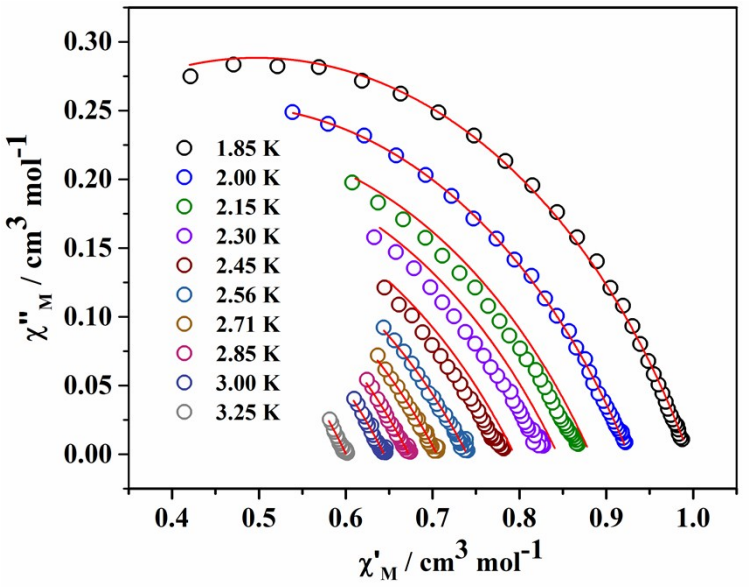


Fig. S11 Cole-Cole plots for **1'** at different temperatures.

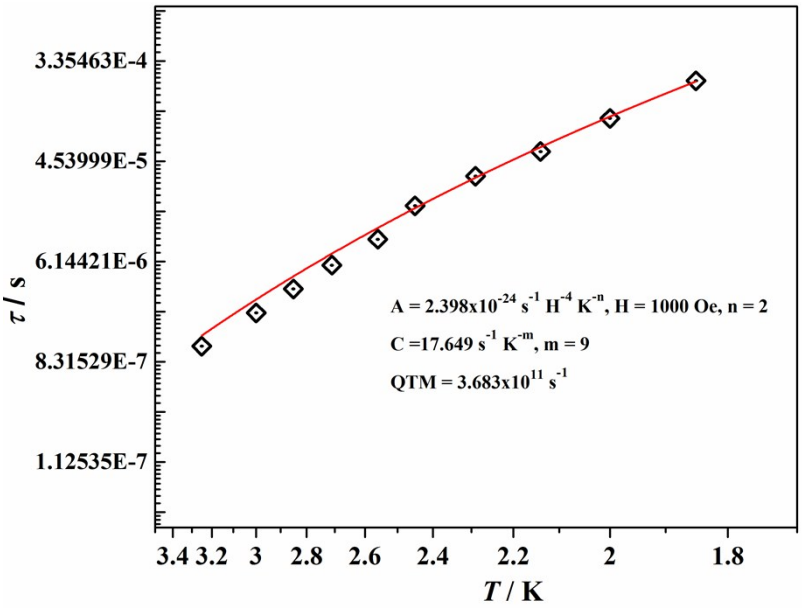


Fig. S12 Temperature dependence of relaxation time for **1'** with quantum tunnelling, direct contributions and Raman process.

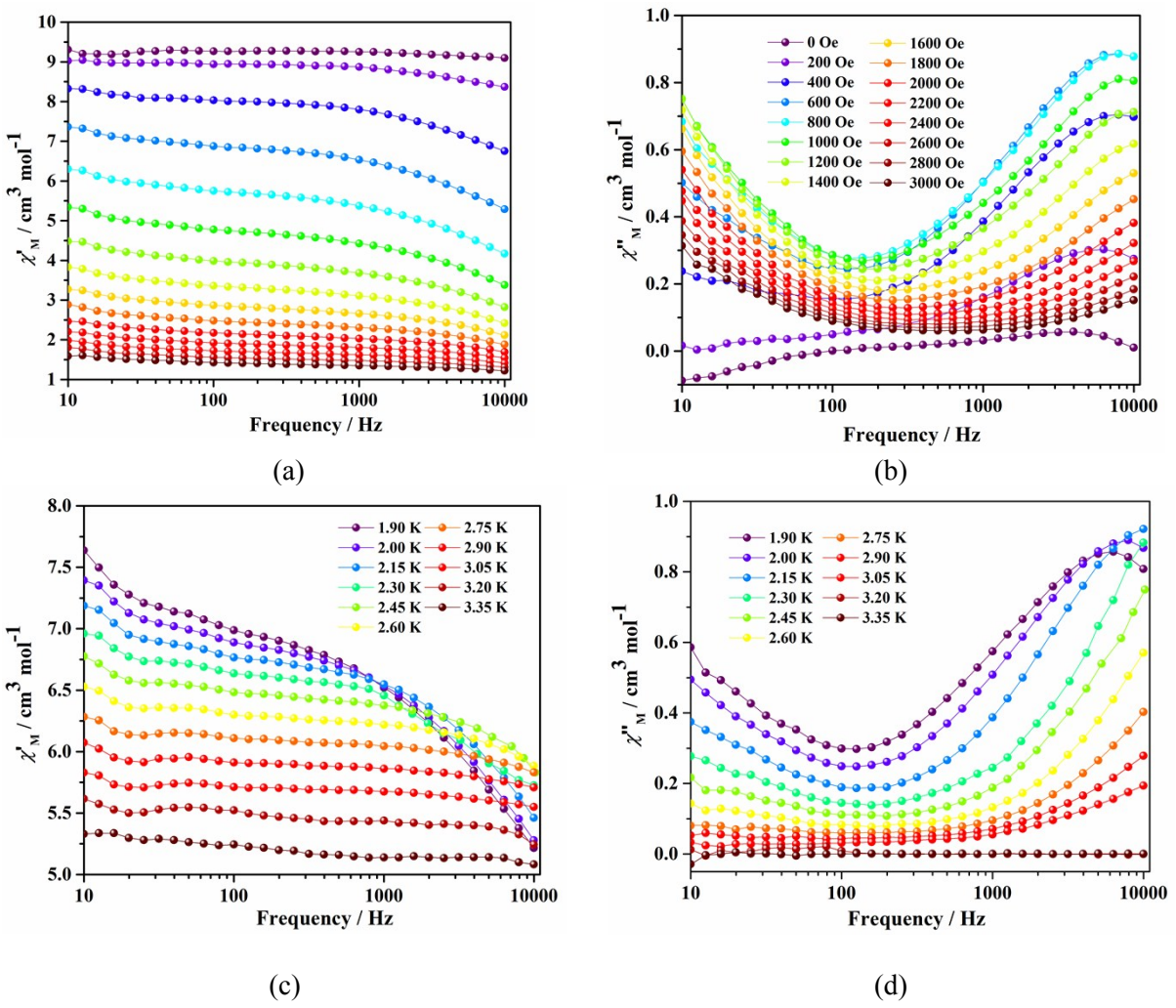
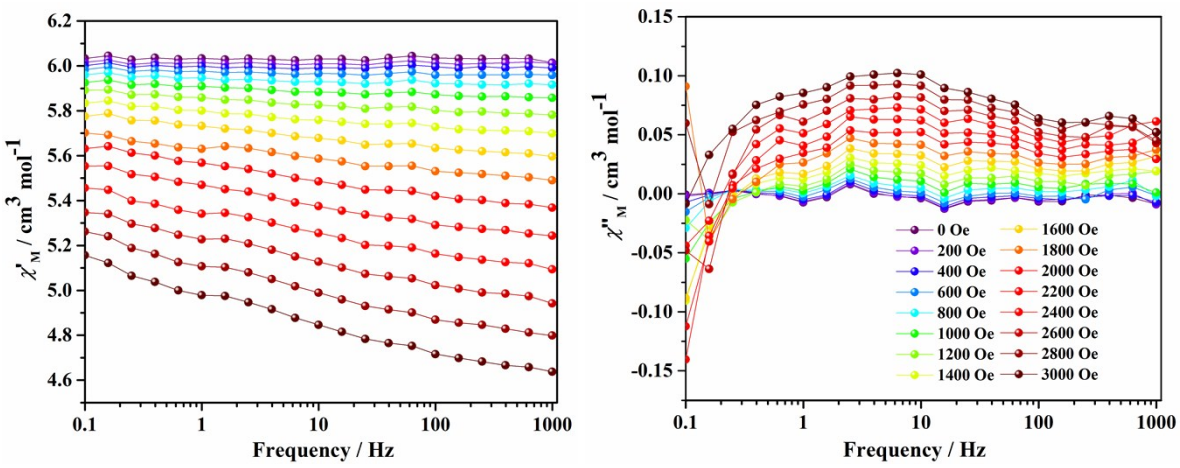


Fig. S13 Frequency dependency of the (a) in phase and (b) out of phase ac susceptibility under indicated dc fields at 1.85 K (the indication for the fields for both plots are shown only in (b) for clarity) and frequency dependency of the (c) in-phase and (d) out-of-phase components of the ac magnetic susceptibility under 600 Oe dc field for **1** in the high frequency region.



(a) (b)

Fig. S14 Frequency dependency of the (a) in phase and (b) out of phase ac susceptibility under indicated dc fields at 1.85 K for **2**. The indication for the fields for both plots are shown only in (b) for clarity.

References:

1 (*a*) T. Okubo, H. Anma, N. Tanaka, K. Himoto, S. Seki, A. Saeki, M. Maekawa and T. Kuroda-Sowa, *Chem. Commun*., 2013, **49**, 4316. (*b*) S. Tominaka, H. Hamoudi,T. Suga, T. D. Bennett, A. B. Cairns and A. K. Cheetham, *Chem. Sci*., 2015, **6**, 1465.