Supplementary Information (SI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2025

Supporting Information for

Versatility of the Methyl-Bipyrimidine-*N*-oxide Ligand for the Design of Lanthanide Single-Molecule Magnets

Haiet Douib,[a,b] Bertrand Lefeuvre,[a] Jessica Flores Gonzalez,[a] Vincent Dorcet,[a] Fabrice Pointillart*[a]

[a] *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, 35000 Rennes (France)*

E-mail: fabrice.pointillart@univ-rennes.fr

[b] *Laboratoire des Matériaux Organiques et Hétérochimie (LMOH), Département des sciences de la matière, Université Larbi, Tébessi de Tébessa, Tébessa, Algéria.*

Table S1. X-ray crystallographic data for the complexes **1-(±)8**.

Compounds	$[Yb_2(hfac)_6(\mathbf{L})]$ (**1**)	$[Yb_6(hfac)_{14}(OH)_4(\mathbf{L})_2]$ (**2**)	$[Dy(hfac)_3(\mathbf{L})]_2\cdot(C_2H_4Cl_2)$ (**3**)$\cdot(C_2H_4Cl_2)$
Formula	$C_{39}H_{14}F_{36}N_4O_{13}Yb_2$	$C_{88}H_{34}F_{84}N_8O_{34}Yb_6$	$C_{50}H_{26}Cl_2Dy_2F_{36}N_8O_{14}$
M / g.mol^{-1}	1776.62	4381.47	2038.65
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1 (N°2)	$P2_1/c$ (N°14)	$P2_1/n$ (N°14)
Cell parameters	a = 11.6950(9) Å b = 15.9999(12) Å c = 16.7054(13) Å α = 71.873(2)° β = 70.644(3)° γ = 81.626(4)°	a = 24.4464(10) Å b = 18.0114(7) Å c = 32.9488(12) Å β = 110.320(2)°	a = 12.0886(7) Å b = 13.4975(6) Å c = 21.2220(10) Å β = 93.840(3)°
Volume / Å^3	2799.7(4)	13605.0(9)	3454.9 (3)
Cell formula units	2	4	2
T / K	150 (2)	150(2)	150(2)
Diffraction reflection	$2.68 \leq 2\theta \leq 55.01$	$4.30 \leq 2\theta \leq 54.99$	$4.53 \leq 2\theta \leq 54.90$
ρ_{calc}, g.cm^{-3}	2.107	2.139	1.960
μ, mm^{-1}	3.501	4.270	2.386
Number of reflections	60760	94244	28825
Independent reflections	12666	31153	7849
$Fo^2 > 2\sigma(Fo)^2$	9690	14919	5192
Number of variables	840	2033	506
R_{int}, R_1, wR_2	0.0373, 0.0560, 0.1320	0.0933, 0.0669, 0.1413	0.0574, 0.0568, 0.1470
Compounds	$[Dy(hfac)_3(\mathbf{L})]_2[Dy(hfac)_3(H_2O)_2]$ (**4**)	$[Dy_6(hfac)_{14}(OH)_4(\mathbf{L})_2]$ (**5**)	$[Yb(tta)_3(\mathbf{L})]$ (**6**)
Formula	$C_{63}H_{29}Dy_3F_{54}N_8O_{22}$	$C_{88}H_{34}F_{84}N_8O_{34}Dy_6$	$C_{33}H_{20}F_9N_4O_7S_3Yb$
M / g.mol^{-1}	2763.44	4318.23	1024.75
Crystal system	Monoclinic	monoclinic	Orthorhombic
Space group	C2/c (N°15)	$P2_1/n$ (N°14)	Pbcn (N°60)
Cell parameters	a = 21.636(4) Å b = 15.445(2) Å c = 27.323(4) Å β = 99.797(5)°	a = 16.4799(9) Å b = 19.9305(11) Å c = 43.098(2) Å β = 93.330(2)°	a = 33.7474(18) Å b = 10.9749(6) Å c = 20.4309(12) Å
Volume / Å^3	8998(2)	14126.5(13)	7567.1(7)
Cell formula units	4	4	8
T / K	150 (2)	150(2)	150(2)
Diffraction reflection	$4.22 \leq 2\theta \leq 54.97$	$1.89 \leq 2\theta \leq 55.07$	$4.38 \leq 2\theta \leq 54.98$
ρ_{calc}, g.cm^{-3}	2.040	2.030	1.799
μ, mm^{-1}	2.649	3.314	2.734
Number of reflections	10141	110377	35040
Independent reflections	10141	32166	8659
$Fo^2 > 2\sigma(Fo)^2$	6960	17051	4604
Number of variables	678	2083	515
R_{int}, R_1, wR_2	0.0929, 0.0684, 0.1584	0.0790, 0.0853, 0.2202	0.1088, 0.0654, 0.1691
Compounds	$[Dy_2((-)hfc)_6(\mathbf{L})]$ (**(-)7**)	$[Dy_2((+)hfc)_6(\mathbf{L})]$ (**(+)7**)	$[Yb_2((-)hfc)_6(\mathbf{L})]$ (**(-)8**)

Formula	$C_{93}H_{92}Dy_2F_{42}N_4O_{13}$	$C_{93}H_{92}Dy_2F_{42}N_4O_{13}$	$C_{93}H_{92}Yb_2F_{42}N_4O_{13}$
M / g.mol^{-1}	2596.70	2596.70	2611.73
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (N°19)	$P2_12_12_1$ (N°19)	$P2_12_12_1$ (N°19)
Cell parameters	a = 20.373(3) Å	a = 20.3763(6) Å	a = 20.1753(11) Å
	b = 21.863(3) Å	b = 21.8829(6) Å	b = 21.9101(12) Å
	c = 23.974(3) Å	c = 23.9653(8) Å	c = 23.9762(16) Å
Volume / Å^3	10678(2)	10685.9(6)	10598.5(11)
Cell formula units	4	4	4
T / K	150	150	150
Diffraction reflection	$4.00 \leq 2\theta \leq 55.15$	$4.73 \leq 2\theta \leq 55.04$	$4.56 \leq 2\theta \leq 55.02$
ρ_{calc}, g.cm^{-3}	1.615	1.614	1.637
μ, mm^{-1}	1.521	1.519	1.887
Number of reflections	71582	73824	47342
Independent reflections	24154	24497	24066
$Fo^2 > 2\sigma(Fo)^2$	11607	19822	17507
Number of variables	1409	1404	1435
R_{int}, R_1, wR_2	0.1542, 0.0816, 0.1413	0.0416, 0.0386, 0.0793	0.0478, 0.0571, 0.1194

Compounds	$[Yb_2((+)hfc)_6(\mathbf{L})]$ (**(+)8**)
Formula1194b	$C_{93}H_{92}Dy_2F_{42}N_4O_{13}$
M / g.mol^{-1}	2611.73
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (N°19)
Cell parameters	a = 20.1867(3) Å
	b = 21.914(2) Å
	c = 23.957(3) Å
Volume / Å^3	10597.6(19)
Cell formula units	4
T / K	150
Diffraction reflection	$4.56 \leq 2\theta \leq 55.33$
ρ_{calc}, g.cm^{-3}	1.641
μ, mm^{-1}	1.887
Number of reflections	53770
Independent reflections	24285
$Fo^2 > 2\sigma(Fo)^2$	11434
Number of variables	1420
R_{int}, R_1, wR_2	0.1369, 0.0832, 0.1586

Table S2. SHAPE analyses for compounds **1, 3**·($C_2H_4Cl_2$), **4**, **6**, **(-)7**, **(+)7,** (-)**8** and **(+)8**.

		Shape calculations							
Compounds		SAPR-8 (D_{4d})	TDD-8 (D_{2d})	JBTPR-8 (C_{2v})	BTPR-8 (C_{2v})	JCSAPR-9 (C_{4v})	CSAPR-9 (C_{4v})	TCTPR-9 (D_{3h})	MFF-9 (Cs)
(1)	Yb1	2.349	0.472	1.965	1.908	/	/	/	/
	Yb2	1.833	1.144	2.019	1.422	/	/	/	/
(2)	Yb1	1.015	2.364	3.201	2.556	/	/	/	/
	Yb2	2.913	1.167	3.089	2.324	/	/	/	/
	Yb3	1.302	2.438	3.391	2.770	/	/	/	/
	Yb4	4.192	1.715	2.829	2.336	/	/	/	/
	Yb5	0.636	2.207	2.973	2.379	/	/	/	/
	Yb6	0.487	2.126	2.335	1.820	/	/	/	/
(3)·($C_2H_4Cl_2$)	Dy1	/	/	/	/	1.547	0.639	1.310	1.005
(4)	Dy1	/	/	/	/	1.762	0.899	1.299	1.092
	Dy2	0.208	2.547	2.904	2.253	/	/	/	/
(5)	Dy1	1.562	1.576	1.611	1.232	/	/	/	/
	Dy2	0.748	1.534	2.315	1.765	/	/	/	/
	Dy3	1.126	1.450	1.668	1.371	/	/	/	/
	Dy4	0.740	1.472	2.390	2.013	/	/	/	/
	Dy5	2.983	0.732	3.699	2.852	/	/	/	/
	Dy6	2.573	0.967	3.552	2.925	/	/	/	/
(6)	Yb1	0.753	1.687	1.990	2.013	/	/	/	/
(-)7	Dy1	1.815	1.448	0.996	1.064	/	/	/	/
	Dy2	0.537	2.649	2.549	2.063	/	/	/	/
(+)7	Dy1	1.756	1.364	1.059	1.095	/	/	/	/
	Dy2	0.529	2.648	2.625	2.139	/	/	/	/
(-)8	Yb1	1.634	1.599	0.966	1.066	/	/	/	/
	Yb2	0.496	2.701	2.615	2.154	/	/	/	/
(+)8	Yb1	1.730	1.619	0.929	1.064	/	/	/	/
	Yb2	0.446	2.780	2.649	2.187	/	/	/	/

*TDD-8 corresponds to a Triangular dodecahedron geometry, BTPR-8 to a Biaugmented trigonal prism, JBTPR-8 to a Biaugmented trigonal prism J50 and to SAPR-8 to Square antiprism, JCSAPR-9 to a Capped square antiprism, CSAPR-9 to a Spherical capped square antiprism, TCTPR-9 to a Spherical tricapped trigonal prism and MFF-9 to a Muffin prism.

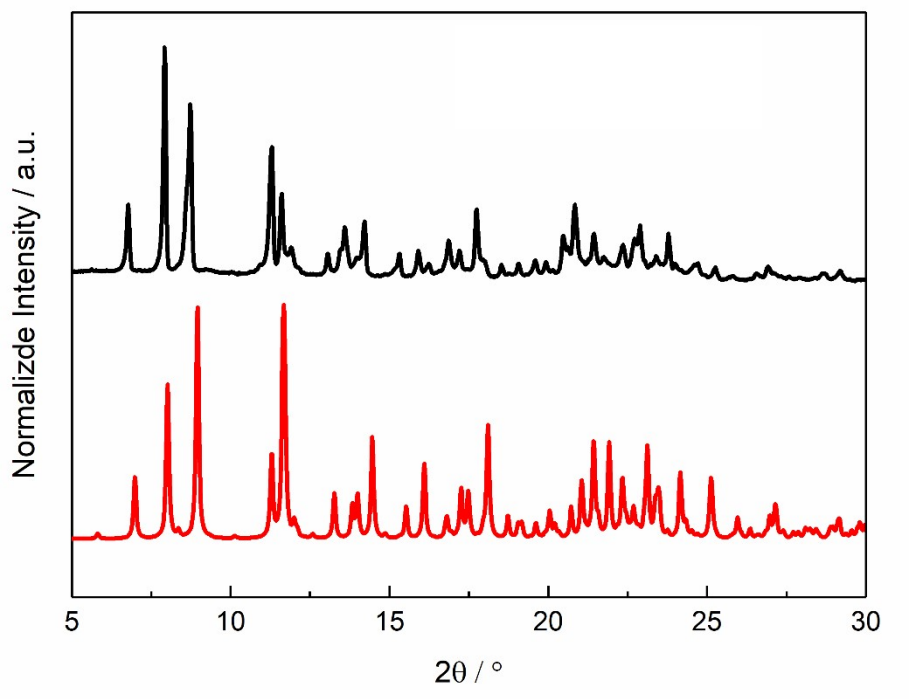

Figure S1. Experimental (black line) and simulated (red line) PXRD of **1**.

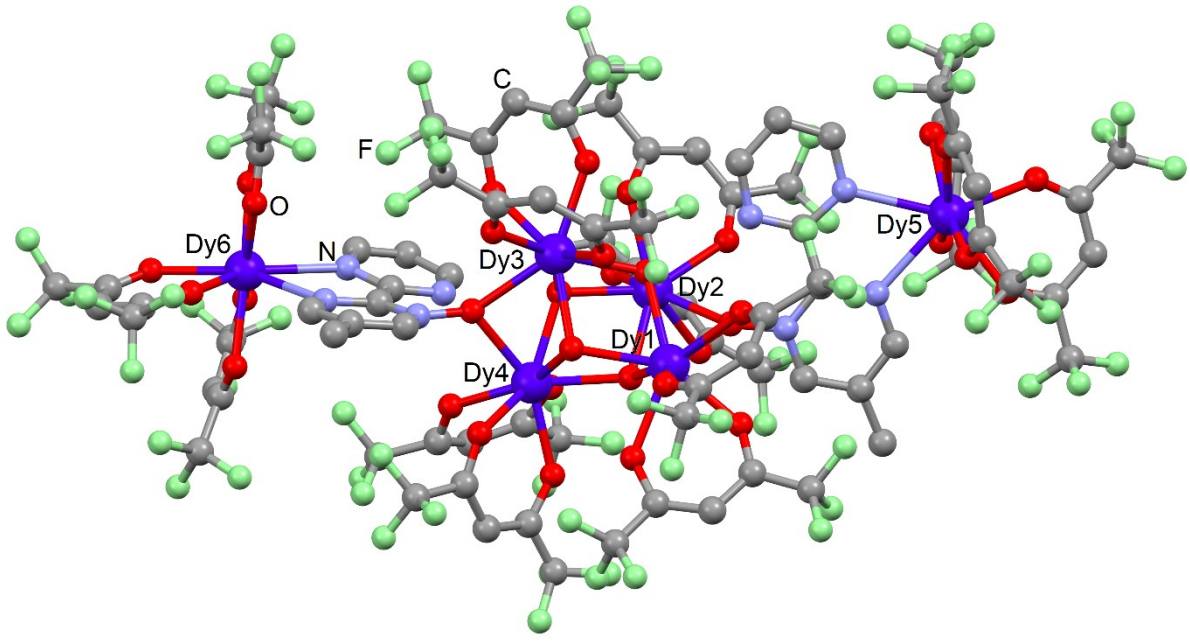

Figure S2. Molecular structure of $[Dy_6(hfac)_{14}(OH)_4(L)_2]$ (**5**) determined from single crystal X-ray diffraction. Hydrogen atoms are omitted for clarity. Dark green, Yb; green, F; red, O; blue, N; and gray, C.

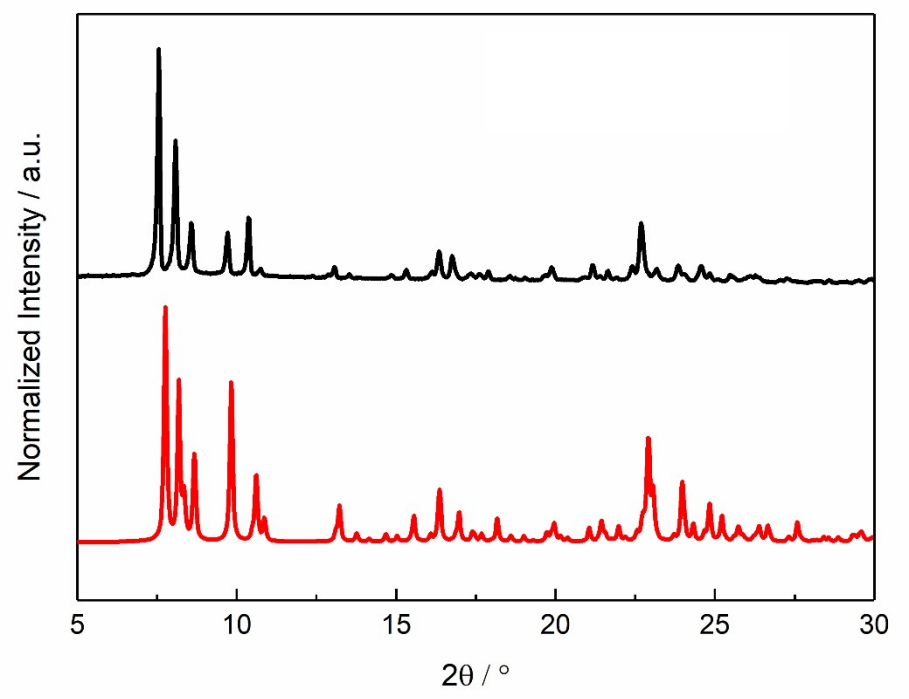

Figure S3. Experimental (black line) and simulated (red line) PXRD of **3**·($C_2H_4Cl_2$).

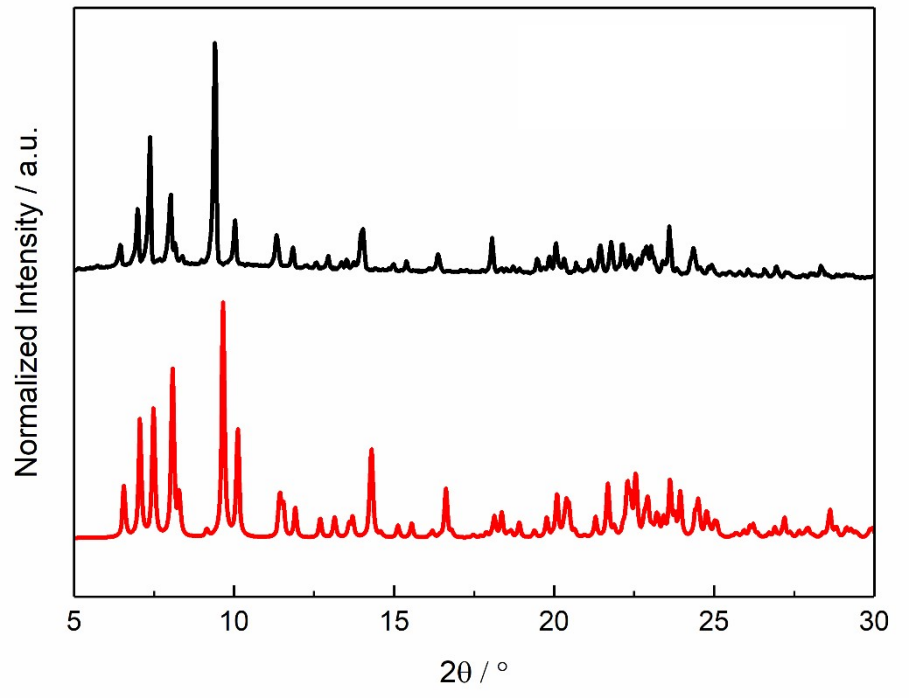

Figure S4. Experimental (black line) and simulated (red line) PXRD of **4**.

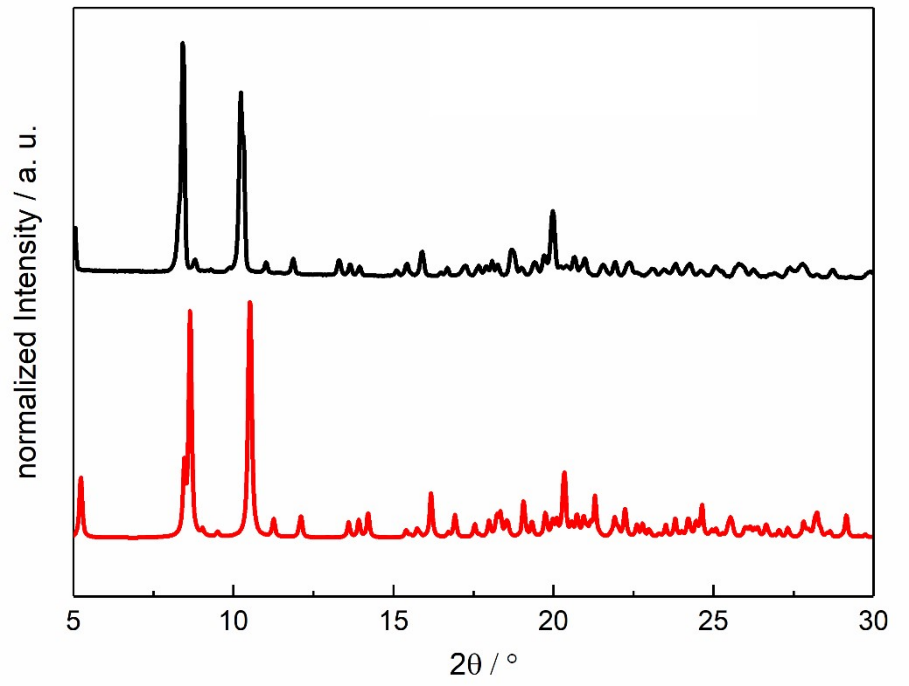

Figure S5. Experimental (black line) and simulated (red line) PXRD of **6**.

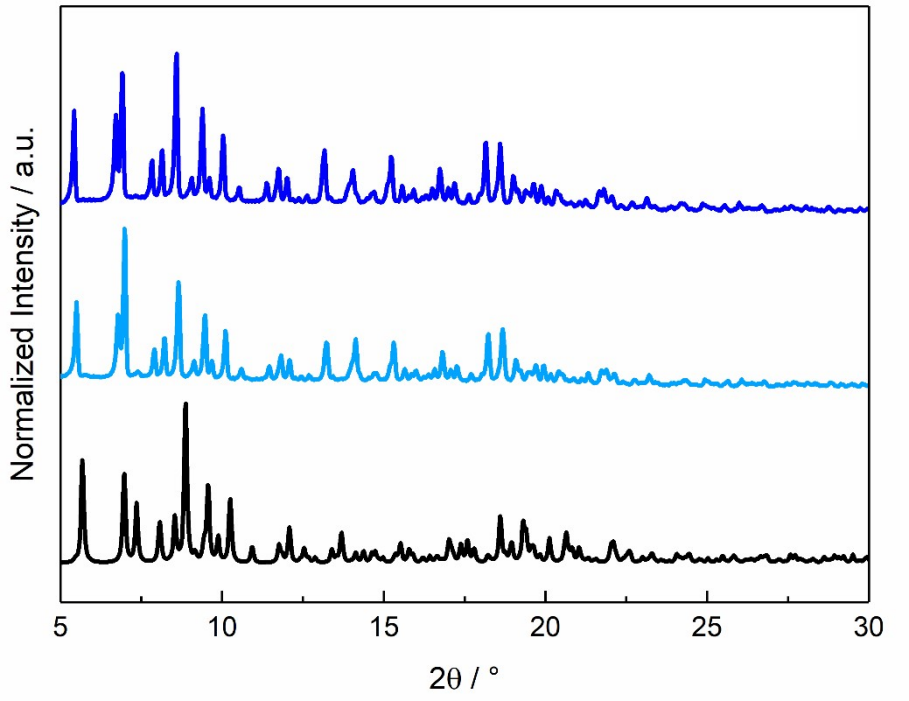

Figure S6. Experimental PXRD of **(-)7** (light blue line) and **(+)7** (dark blue line) and simulated PXRD of (-)**7** (black line).

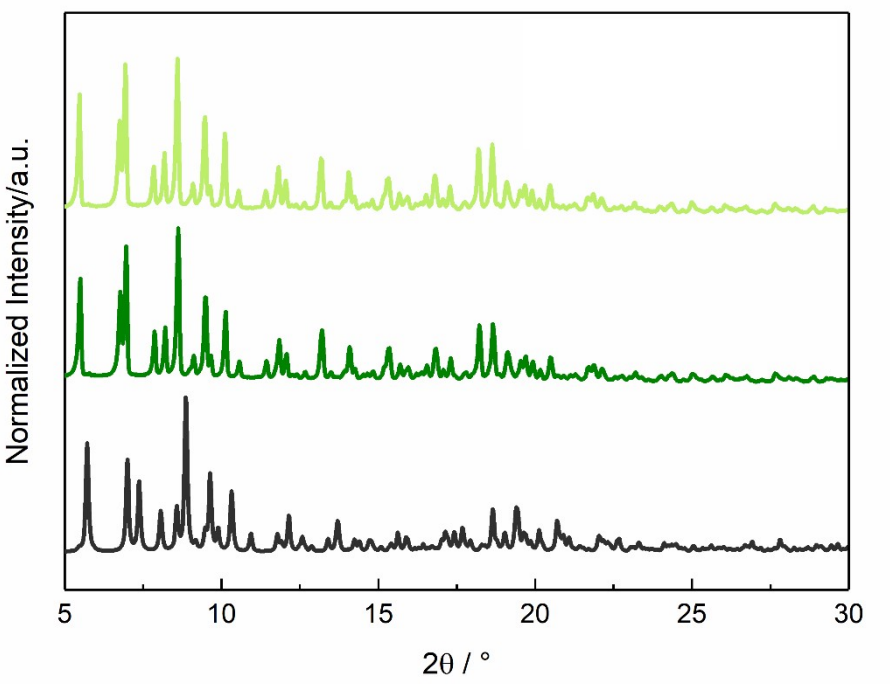

Figure S7. Experimental PXRD of **(-)8** (light green line) and **(+)8** (dark green line) and simulated PXRD of (-)**8** (black line).

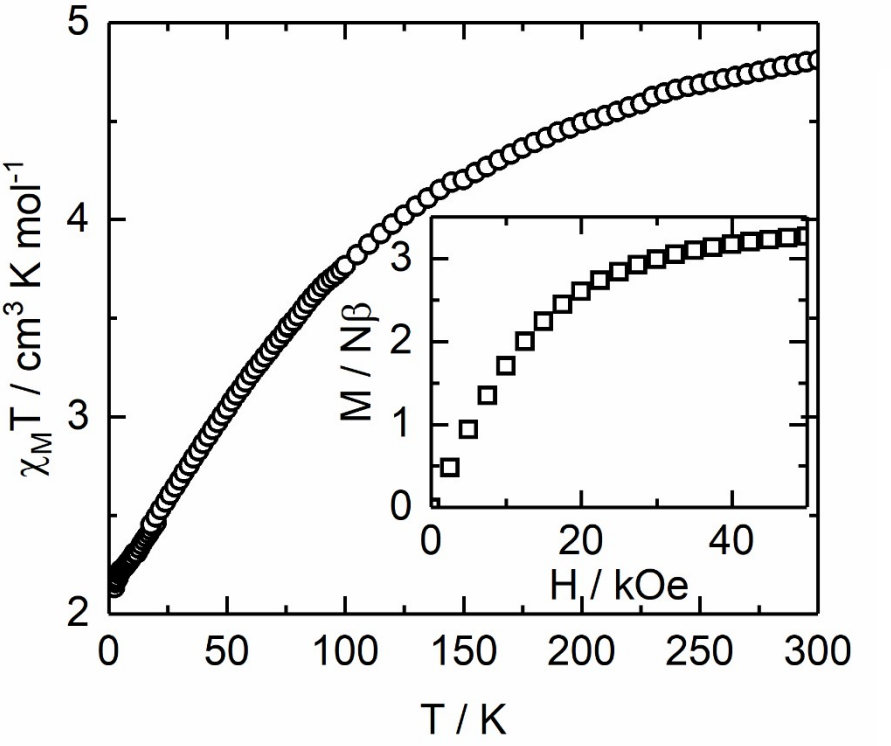

Figure S8. Thermal dependence of the magnetic susceptibility for **1** in the 2-300 K temperature range. In inset, field dependence of the magnetization at 2 K for complex **1** in the 0-50 kOe magnetic field range.

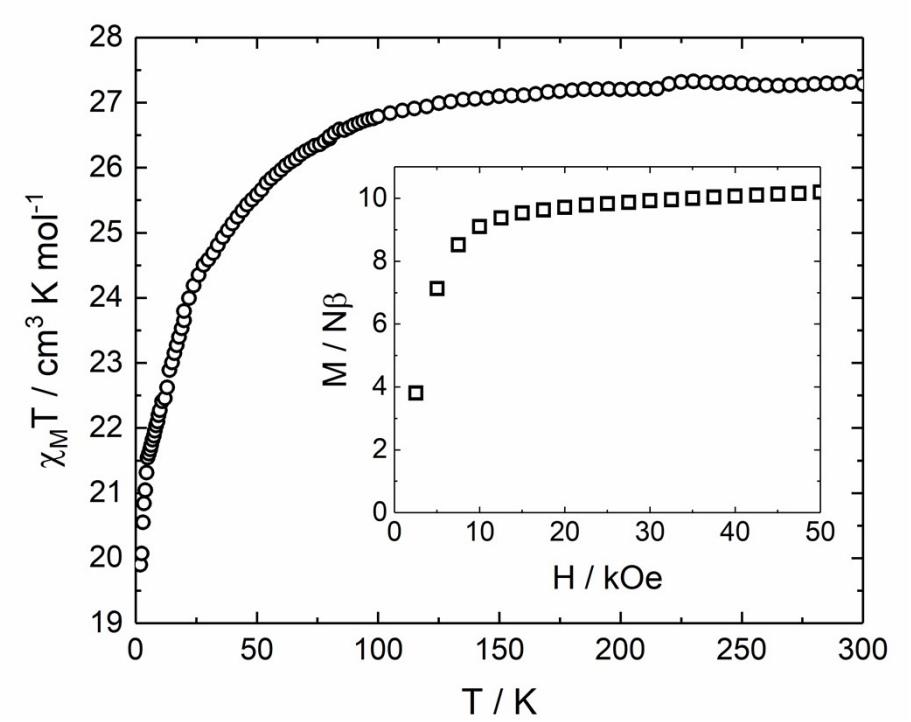

Figure S9. Thermal dependence of the magnetic susceptibility for **3** in the 2-300 K temperature range. In inset, field dependence of the magnetization at 2 K for complex **3** in the 0-50 kOe magnetic field range.

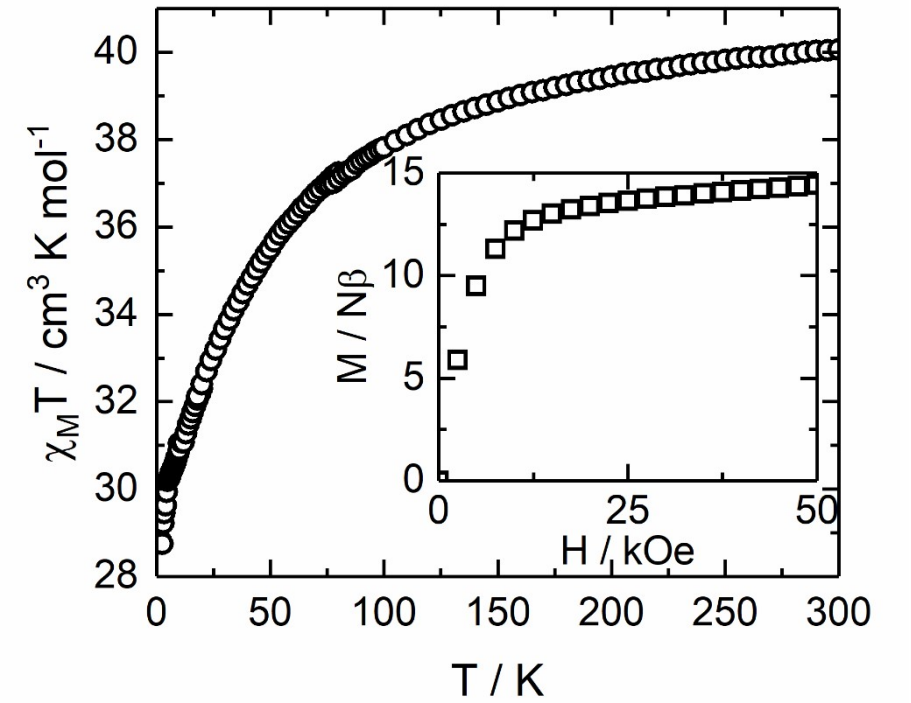

Figure S10. Thermal dependence of the magnetic susceptibility for **4** in the 2-300 K temperature range. In inset, field dependence of the magnetization at 2 K for complex **4** in the 0-50 kOe magnetic field range.

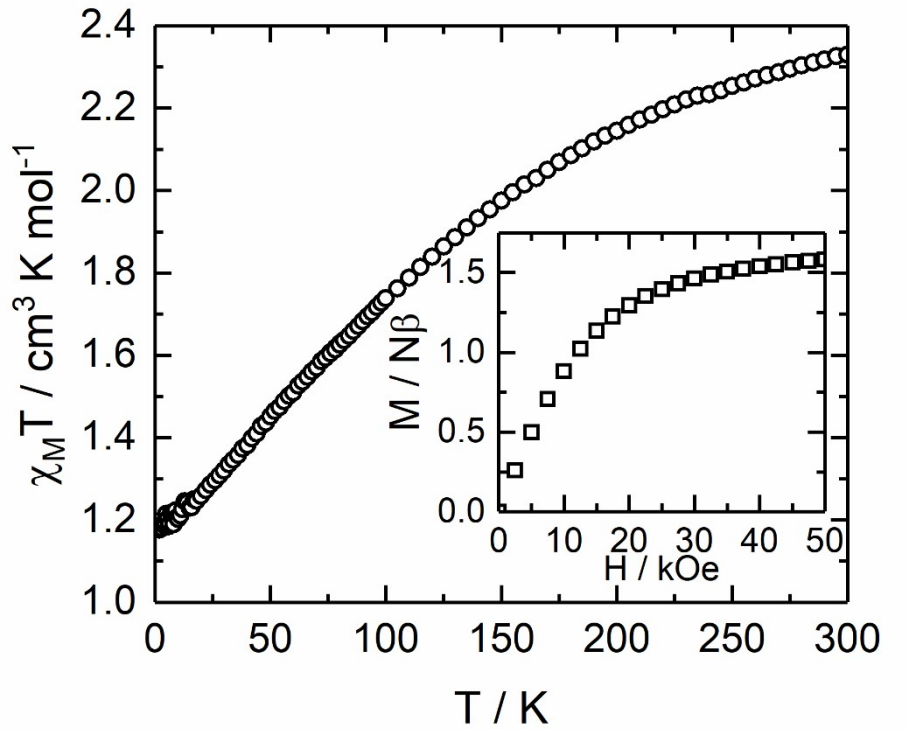

Figure S11. Thermal dependence of the magnetic susceptibility for **6** in the 2-300 K temperature range. In inset, field dependence of the magnetization at 2 K for complex **6** in the 0-50 kOe magnetic field range.

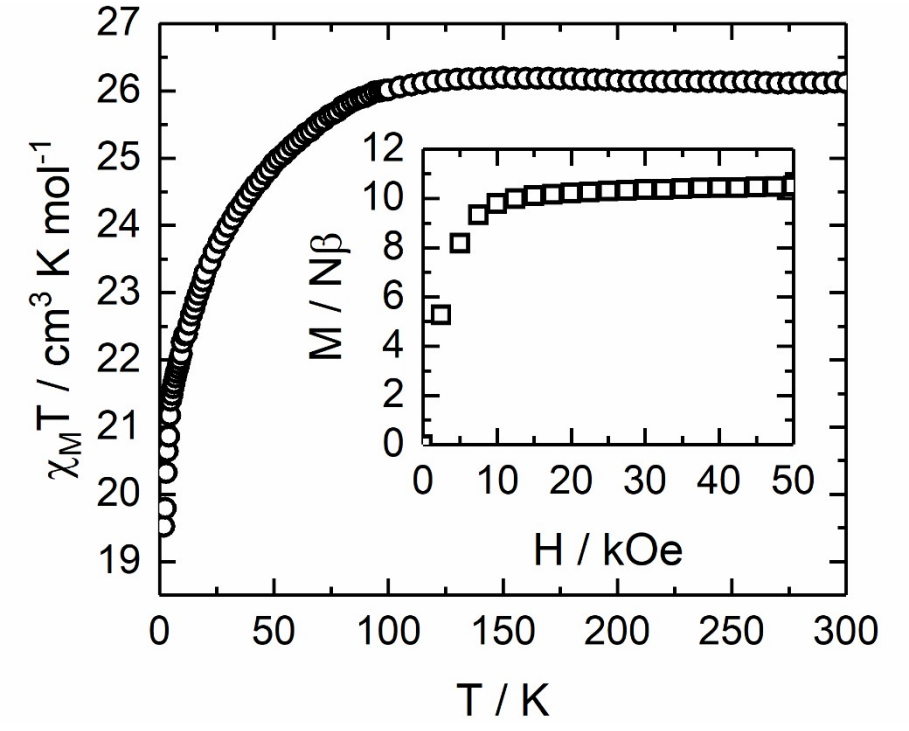

Figure S12. Thermal dependence of the magnetic susceptibility for **(+)7** in the 2-300 K temperature range. In inset, field dependence of the magnetization at 2 K for complex **(+)7** in the 0-50 kOe magnetic field range.

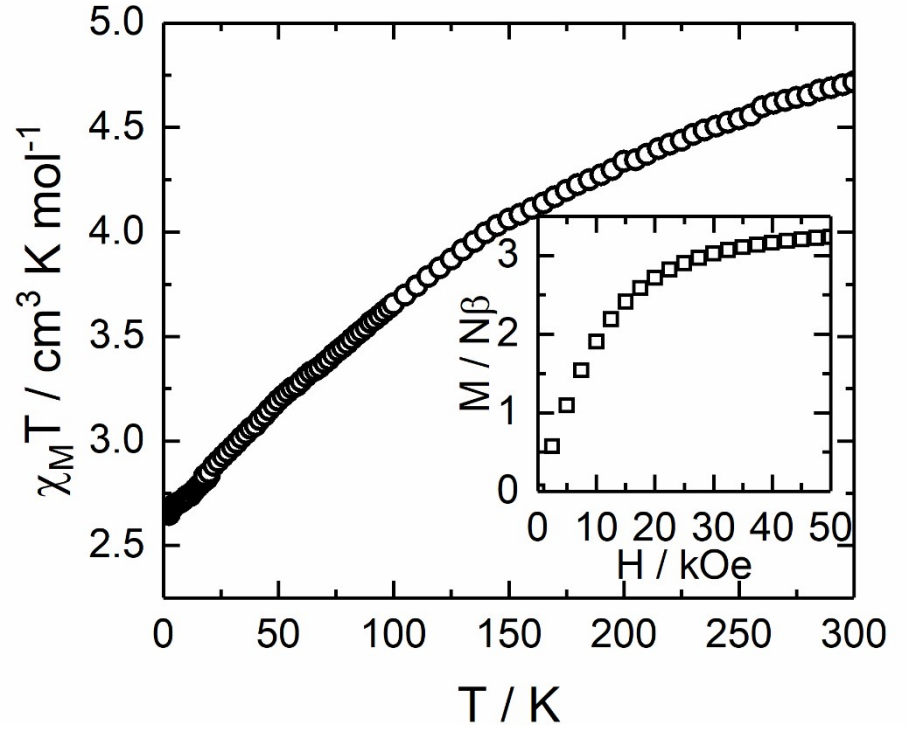

Figure S13. Thermal dependence of the magnetic susceptibility for **(+)8** in the 2-300 K temperature range. In inset, field dependence of the magnetization at 2 K for complex **(+)8** in the 0-50 kOe magnetic field range.

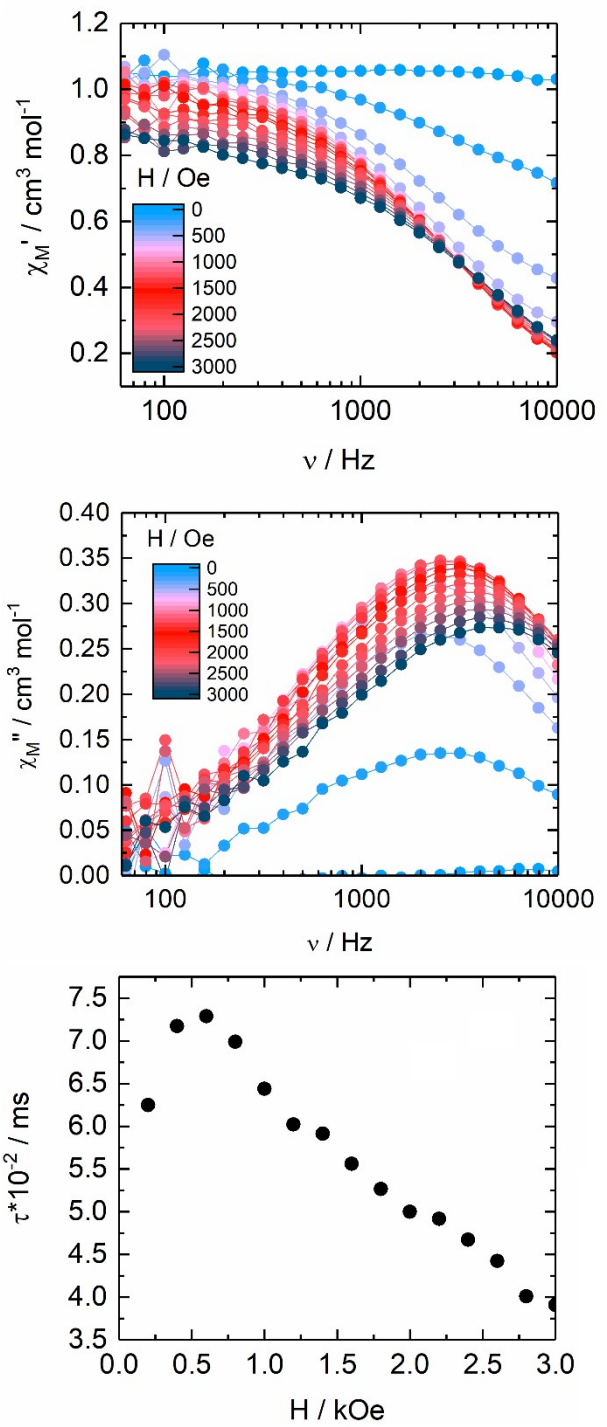

Figure S14. Field dependence of the in-phase (top) and out-of-phase (middle) components of the magnetic susceptibility for **1** at 2 K in the 0-3000 Oe field range. (bottom) Field dependence of the relaxation time at 2 K in the 0-3000 Oe field range for **1**.

Extended Debye model (Eq. S1).

$$\chi_M' = \chi_S + (\chi_T - \chi_S)\frac{1+(\omega\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)}{1+2(\omega\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)+(\omega\tau)^{2-2\alpha}}$$

$$\chi_M'' = (\chi_T - \chi_S)\frac{(\omega\tau)^{1-\alpha}\cos\left(\alpha\frac{\pi}{2}\right)}{1+2(\omega\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)+(\omega\tau)^{2-2\alpha}}$$

With χ_T the isothermal susceptibility, χ_S the adiabatic susceptibility, τ the relaxation time and α an empiric parameter which describe the distribution of the relaxation time. For SMM with only one relaxation time, α is close to zero. The extended Debye model was applied to fit simultaneously the experimental variations of χ_M' and χ_M'' with the frequency ν of the oscillating field ($\omega = 2\pi\nu$). Typically, only the temperatures for which a maximum on the χ'' vs. ν curves, have been considered. The best fitted parameters τ, α, χ_T, χ_S are listed in Tables S3-S14 and S15-S16 with the coefficient of determination R^2.

Table S3. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **1** at 2 K in the field range 200-3000 Oe.

H / Oe	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
200	0.68397	1.05175	0.16568	6.24906E-5	0.99896
400	0.32748	1.06633	0.19864	7.17234E-5	0.99709
600	0.17768	1.05728	0.19007	7.28686E-5	0.99901
800	0.10441	1.04433	0.19235	6.99019E-5	0.99858
1000	0.05026	1.0321	0.21259	6.44052E-5	0.99709
1200	1.94694E-13	1.0398	0.25222	6.02072E-5	0.99792
1400	2E-15	1.03414	0.25239	5.91338E-5	0.99935
1600	2E-15	1.0035	0.24378	5.56248E-5	0.99966
1800	2E-15	0.97881	0.23877	5.26438E-5	0.99921
2000	2E-15	0.95221	0.24159	4.99995E-5	0.99883
2200	2E-15	0.94978	0.25836	4.91571E-5	0.99851
2400	2E-15	0.91783	0.26357	4.67327E-5	0.99509
2600	2E-15	0.8958	0.26392	4.42451E-5	0.99891
2800	2E-15	0.85413	0.25488	4.00885E-5	0.99855
3000	1.06033E-17	0.83863	0.26529	3.91037E-5	0.99908

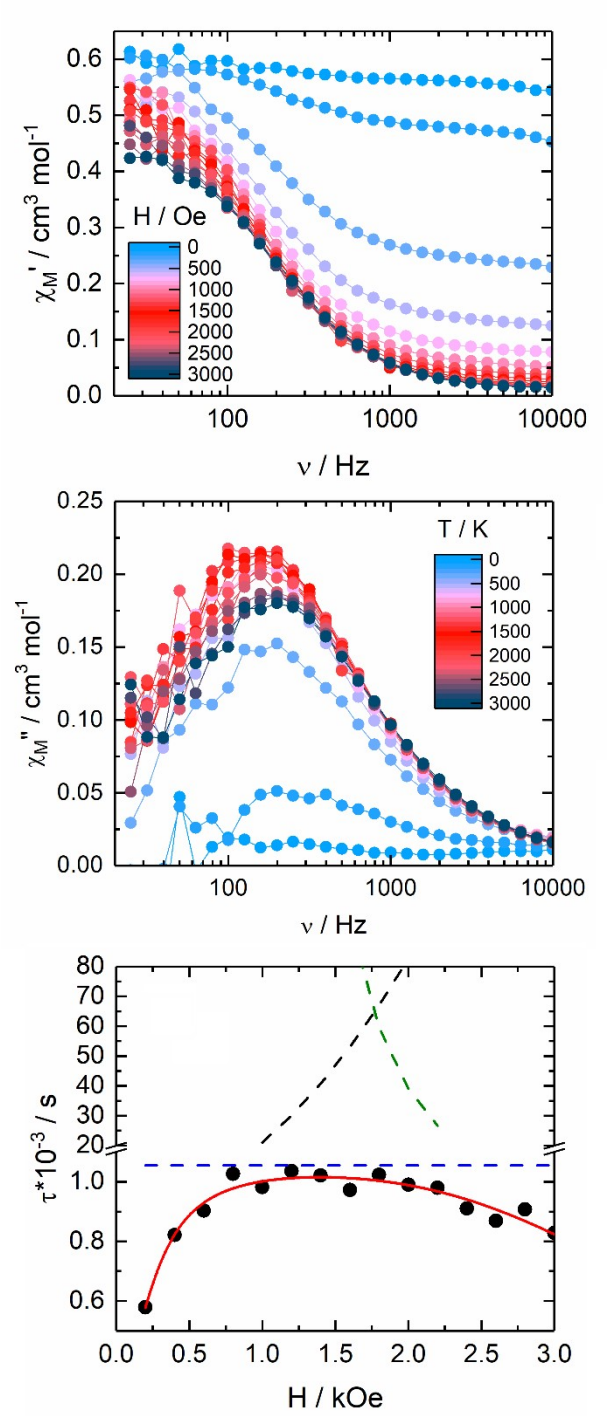

Figure S15. Field dependence of the in-phase (top) and out-of-phase (middle) components of the magnetic susceptibility for **6** at 2 K in the 0-3000 Oe field range. (bottom) Field dependence of the relaxation time (black dots) at 2 K in the 0-3000 Oe field range for **6** with the best fit (full red line) obtained with equation S1. The dashed black, blue and green lines represent the QTM, Raman + Orbach and direct processes contributions, respectively.

Table S4. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **6** at 2 K in the field range 200-3000 Oe.

H / Oe	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
200	0.4741	0.58808	0.08282	5.78515E-4	0.9997
400	0.23553	0.59601	0.11692	8.21375E-4	0.99794
600	0.12554	0.57936	0.12461	9.03251E-4	0.9975
800	0.07426	0.59671	0.15026	0.00103	0.99833
1000	0.04932	0.57257	0.13397	9.81793E-4	0.99659
1200	0.03453	0.58644	0.14276	0.00104	0.99636
1400	0.02491	0.56664	0.14417	0.00102	0.99882
1600	0.02083	0.54518	0.12703	9.72397E-4	0.9959
1800	0.01419	0.55551	0.16627	0.00102	0.9966
2000	0.01502	0.54213	0.14802	9.90101E-4	0.99729
2200	0.01037	0.53085	0.16581	9.79544E-4	0.9975
2400	0.01175	0.50538	0.14643	9.10484E-4	0.99733
2600	0.00969	0.48704	0.15264	8.68897E-4	0.9976
2800	0.00543	0.50444	0.1917	9.07232E-4	0.99485
3000	0.00474	0.47693	0.18534	8.28602E-4	0.9997

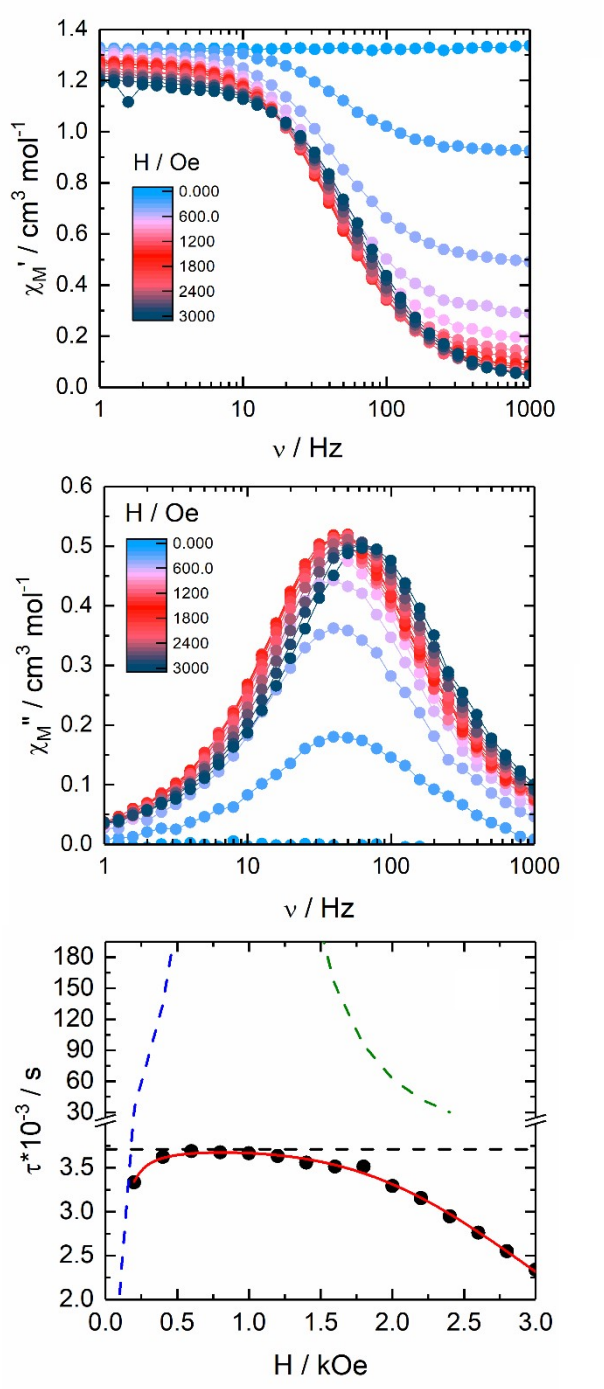

Figure S16. Field dependence of the in-phase (top) and out-of-phase (middle) components of the magnetic susceptibility for **(+)8** at 2 K in the 0-3000 Oe field range. (bottom) Field dependence of the relaxation time (black dots) at 2 K in the 0-3000 Oe field range for **(+)8** with the best fit (full red line) obtained with equation S1. The dashed black, blue and green lines represent the QTM, Raman + Orbach and direct processes contributions, respectively.

Table S5. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **(+)8** at 2 K in the field range 200-3000 Oe.

H / Oe	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
200	2.77979	3.98256	0.05326	0.00333	0.99993
400	1.46976	3.95197	0.08123	0.00362	0.99991
600	0.8467	3.92096	0.09038	0.00369	0.99986
800	0.5482	3.9032	0.09561	0.00368	0.99986
1000	0.38807	3.88068	0.09327	0.00367	0.99985
1200	0.29716	3.8698	0.1003	0.00363	0.9998
1400	0.22536	3.85022	0.10282	0.00356	0.99978
1600	0.19252	3.82962	0.09931	0.00351	0.99985
1800	0.19252	3.82962	0.09931	0.00351	0.99985
2000	0.13471	3.77075	0.09918	0.00329	0.99986
2200	0.11888	3.74266	0.09826	0.00315	0.9999
2400	0.10134	3.70408	0.1012	0.00295	0.99987
2600	0.08861	3.66698	0.10201	0.00276	0.99993
2800	0.07168	3.62557	0.104	0.00255	0.99994
3000	0.0548	3.57308	0.10849	0.00234	0.99593

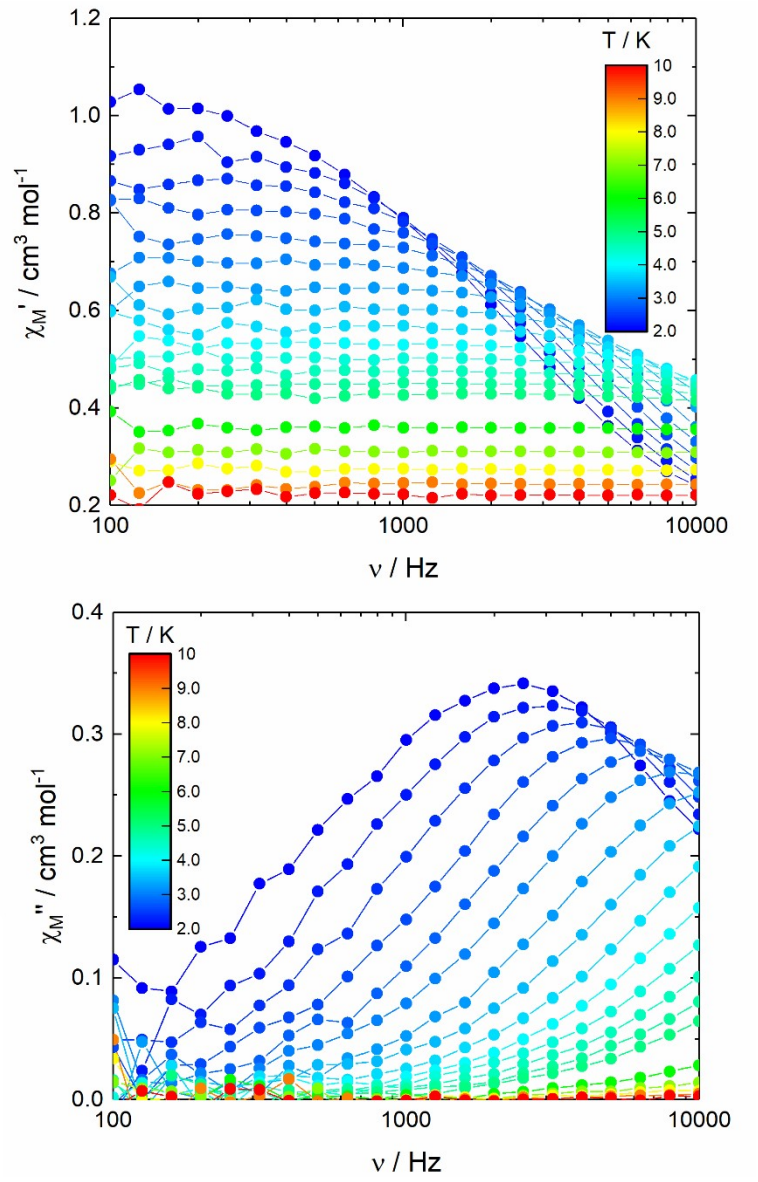

Figure S17. Frequency dependence of χ_M'' (above) and χ_M'' (below) for **1** in the 2–10 K temperature range under an 800 Oe applied magnetic field.

Table S6. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **1** at 800 Oe in the temperature range 2-3.5 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	0.07971	1.07585	0.23194	7.08463E-5	0.99916
2.2	0.11149	0.9539	0.15518	5.39655E-5	0.99793
2.4	0.10404	0.88281	0.13845	4.11735E-5	0.9994
2.6	0.10712	0.82126	0.11379	3.21256E-5	0.99932
2.8	0.10221	0.76375	0.09671	2.47587E-5	0.99809
3	0.10095	0.70496	0.06944	1.93151E-5	0.99778
3.25	0.13096	0.64593	0.0146	1.57058E-5	0.99797
3.5	0.04516	0.61482	0.09323	9.74023E-6	0.99648

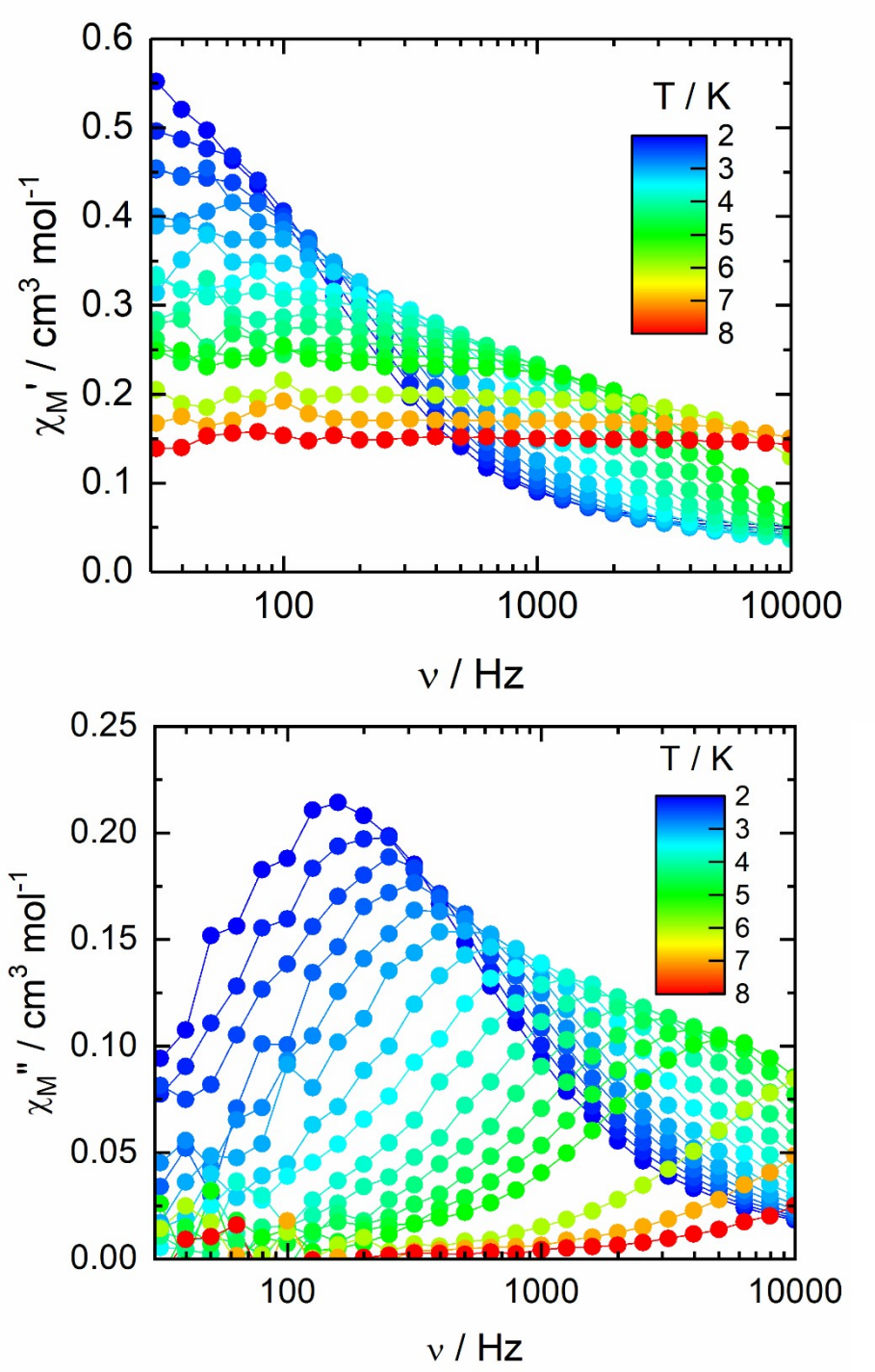

Figure S18. Frequency dependence of χ_M'' (above) and χ_M'' (below) for **6** in the 2–8 K temperature range under an 1000 Oe applied magnetic field.

Table S7. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **6** at 1000 Oe in the temperature range 2-5 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	0.05061	0.5756	0.12951	9.77361E-4	0.99821
2.2	0.04748	0.52603	0.11415	7.69712E-4	0.99925
2.4	0.04213	0.48219	0.11413	6.15859E-4	0.99904
2.6	0.04273	0.45133	0.08622	4.92041E-4	0.99587
2.8	0.03746	0.42005	0.09464	3.96612E-4	0.99846
3	0.03422	0.39547	0.09322	3.16567E-4	0.99887
3.25	0.03361	0.3565	0.05989	2.26732E-4	0.99565
3.5	0.02974	0.33154	0.05951	1.6739E-4	0.99835
3.75	0.02724	0.31588	0.06315	1.26174E-4	0.99814
4.0	0.02674	0.29408	0.04513	9.29877E-5	0.99404
4.25	0.02617	0.27438	0.0278	6.92856E-5	0.99779
4.5	0.02659	0.25559	0.00586	5.21665E-5	0.99571
4.75	0.0212	0.24612	0.02785	3.99174E-5	0.99818
5.0	0.01349	0.23926	0.06284	3.0269E-5	0.99447

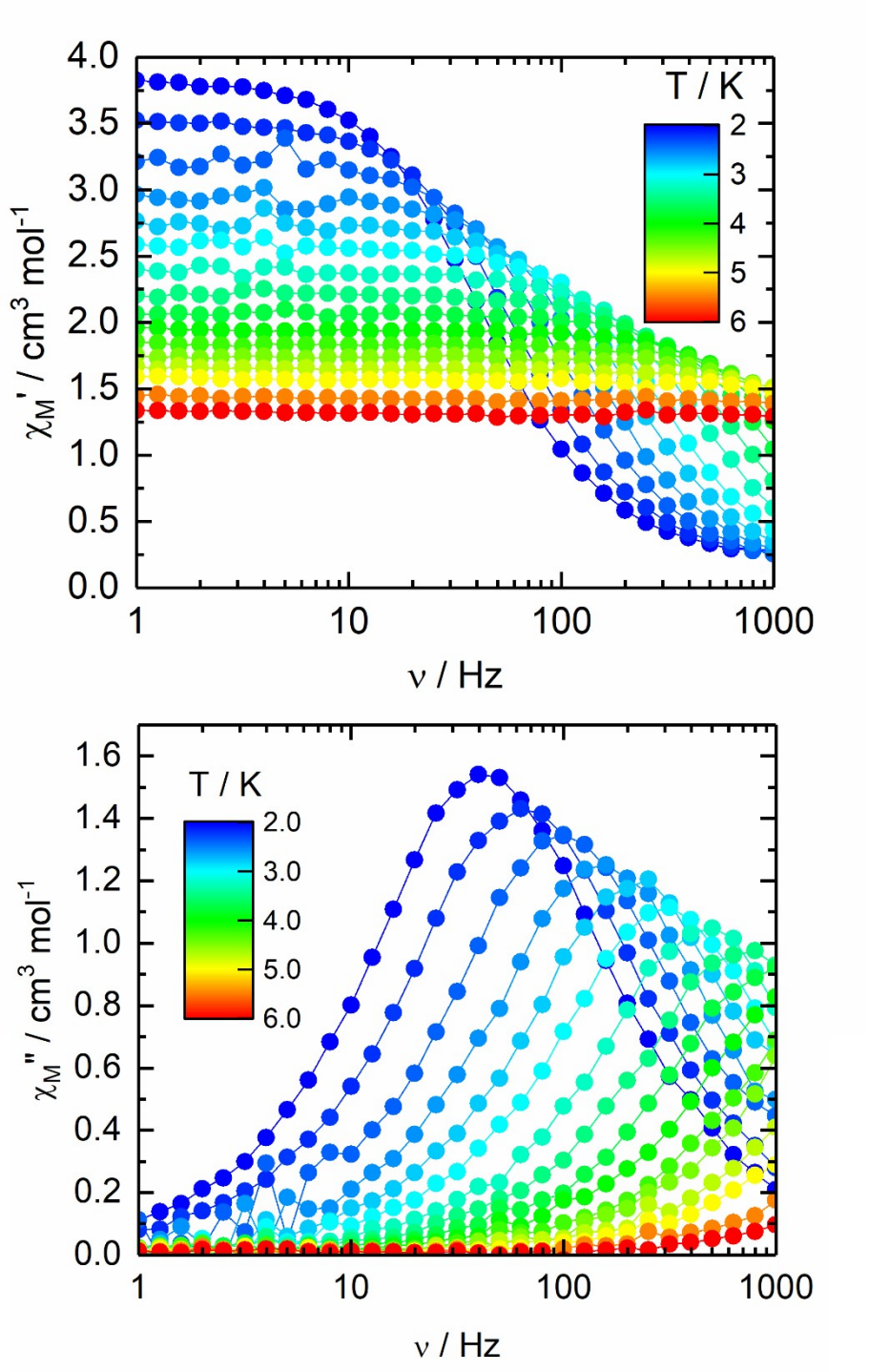

Figure S19. Frequency dependence of χ_M'' (above) and χ_M'' (below) for **(+)8** in the 2–6 K temperature range under an 1400 Oe applied magnetic field.

Table S8. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **(+)8** at 1400 Oe in the temperature range 2-4.0 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	0.23403	3.8511	0.10023	0.0036	0.99988
2.2	0.21225	3.53728	0.09209	0.00244	0.99989
2.4	0.16788	3.24375	0.08562	0.00155	0.99843
2.6	0.17156	2.94676	0.06362	0.00104	0.99918
2.8	0.14126	2.75122	0.06422	7.18357E-4	0.99946
3	0.15748	2.57934	0.05501	5.24459E-4	0.99963
3.25	0.15151	2.38196	0.04614	3.50038E-4	0.99953
3.5	0.0719	2.21141	0.05784	2.29032E-4	0.99976
3.75	0.08518	2.06586	0.04739	1.63283E-4	0.99978
4.0	0.03822	1.94151	0.05238	1.12283E-4	0.99986

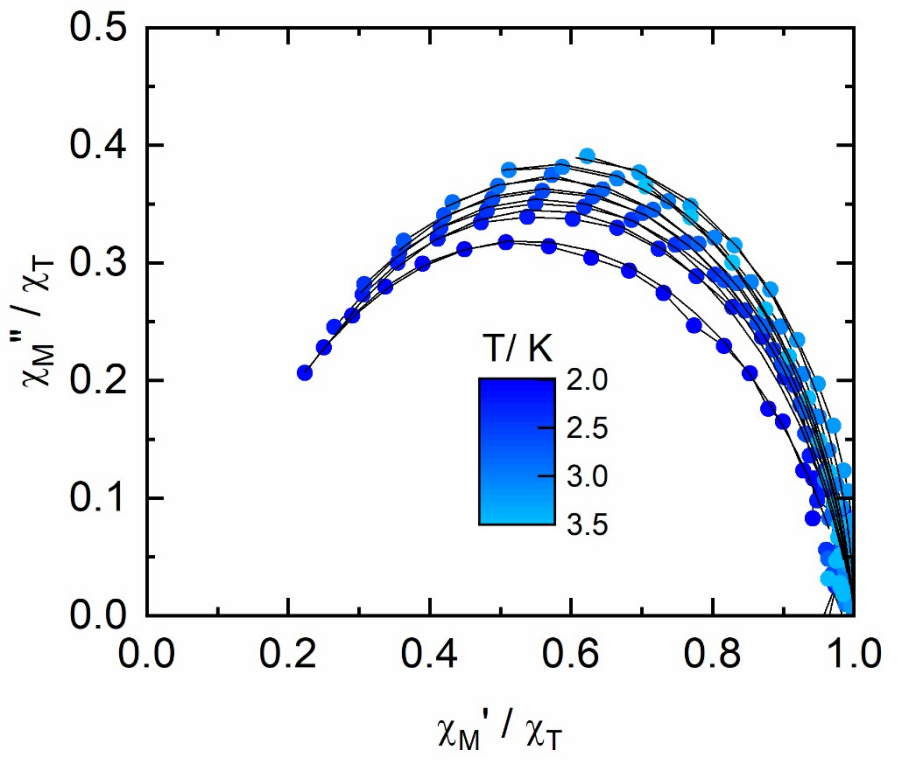

Figure S20. Normalized Argand plot for **1** in the temperature range of 2-3.5 K at 800 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S1).

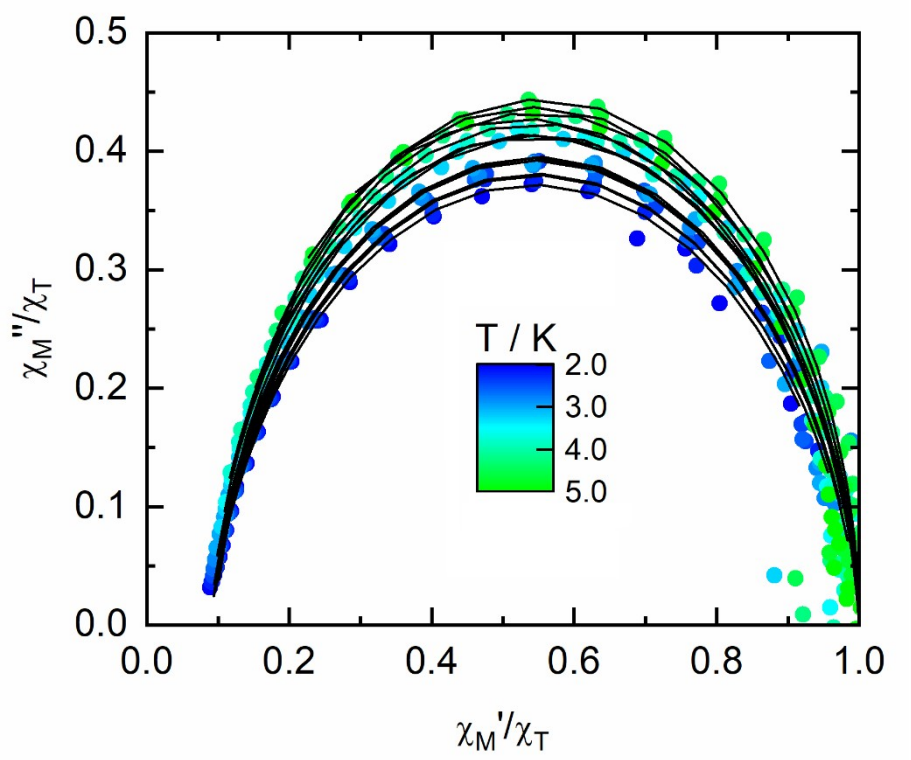

Figure S21. Normalized Argand plot for **6** in the temperature range of 2-5 K at 1000 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S1).

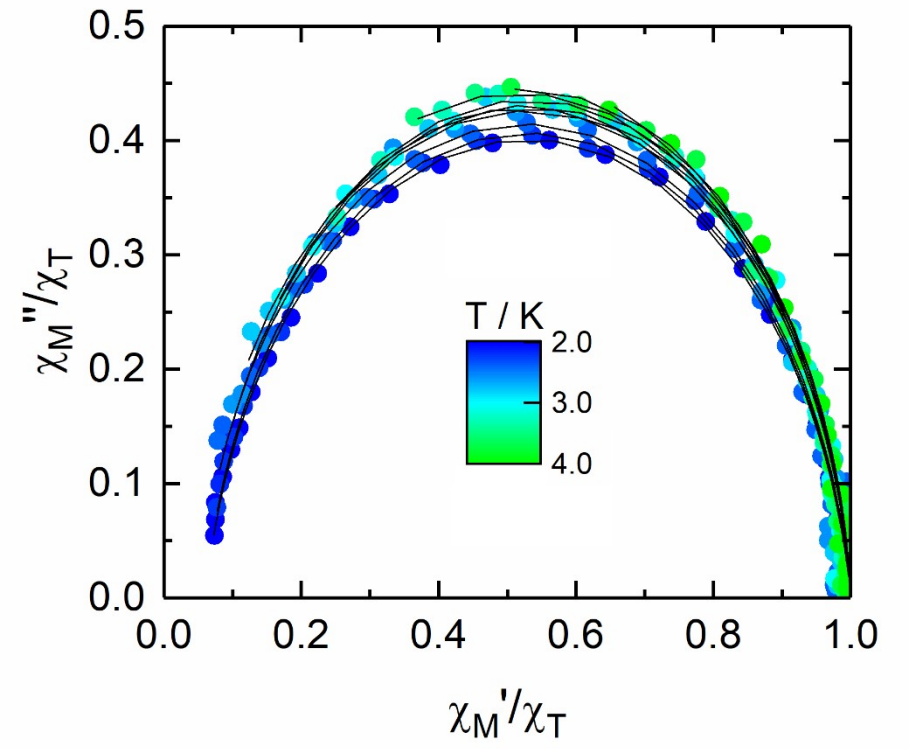

Figure S22. Normalized Argand plot for **(+)8** in the temperature range of 2-4 K at 1400 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S1).

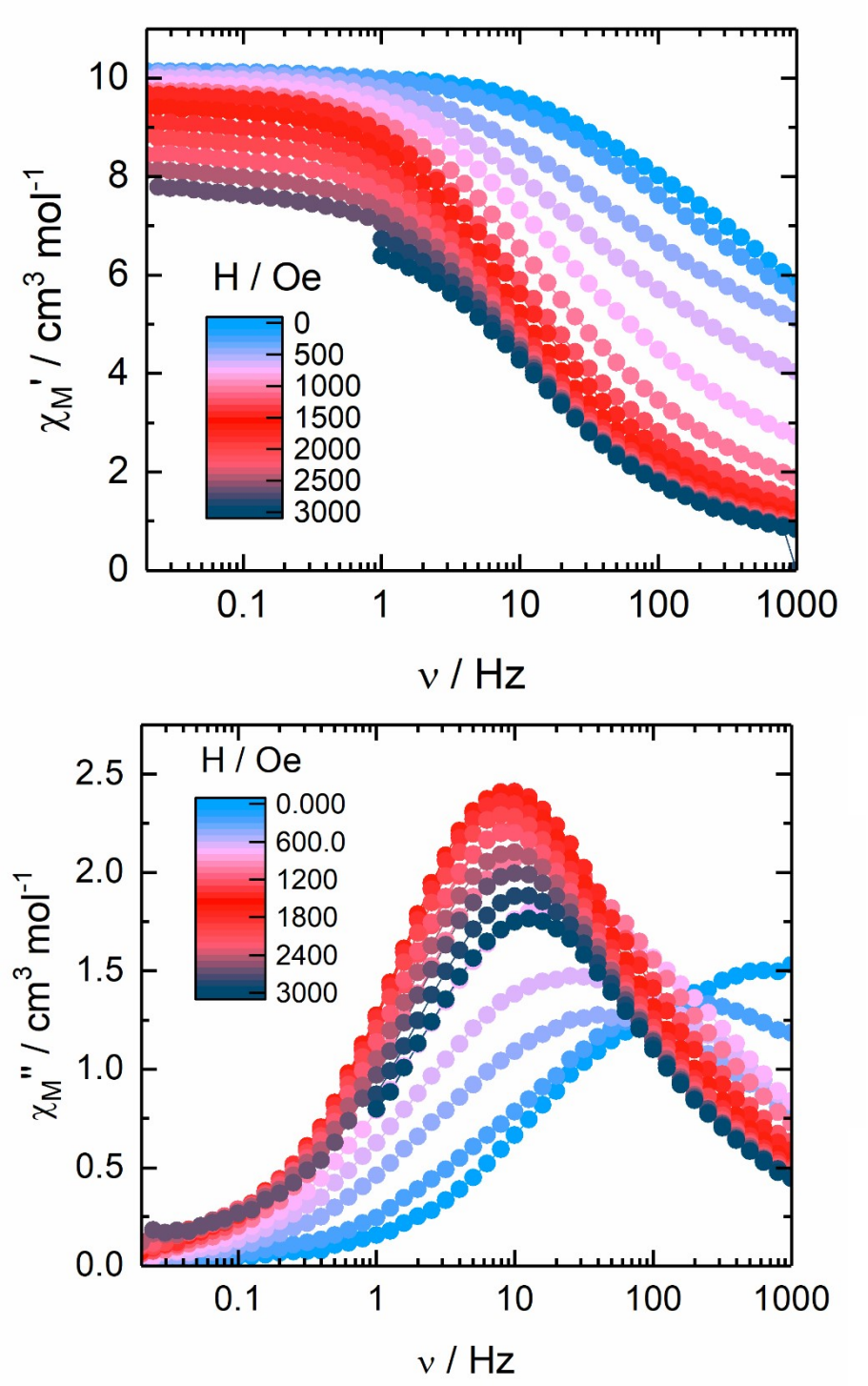

Figure S23. Field dependence of the in-phase (above) and out-of-phase (below) components of the magnetic susceptibility for **3** at 2 K in the 0-3000 Oe field range.

Table S9. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **3** at 2 K in the field range 200-3000 Oe.

H / Oe	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
200	4.02459	10.29403	0.48476	9.6779E-4	0.99997
400	4.16407	10.42626	0.50387	0.0033	0.99996
600	3.96722	10.17942	0.42638	0.0064	0.99991
800	2.02174	10.46153	0.47481	0.00675	0.99985
1000	1.43549	10.4083	0.44387	0.01036	0.99986
1200	1.29125	9.99103	0.39545	0.0132	0.99973
1400	0.89635	10.66581	0.4222	0.0172	0.99958
1600	0.80907	10.28484	0.40821	0.01883	0.99953
1800	0.75315	9.91864	0.40089	0.01943	0.99947
2000	0.71836	9.51761	0.39496	0.01906	0.99944
2200	0.75144	8.82469	0.37008	0.01685	0.99951
2400	0.72564	8.41675	0.36828	0.01574	0.99958
2600	0.69604	8.00763	0.3685	0.01444	0.99962
2800	0.6658	7.58047	0.3705	0.01309	0.9997
3000	0.58827	7.19745	0.38129	0.01169	0.9996

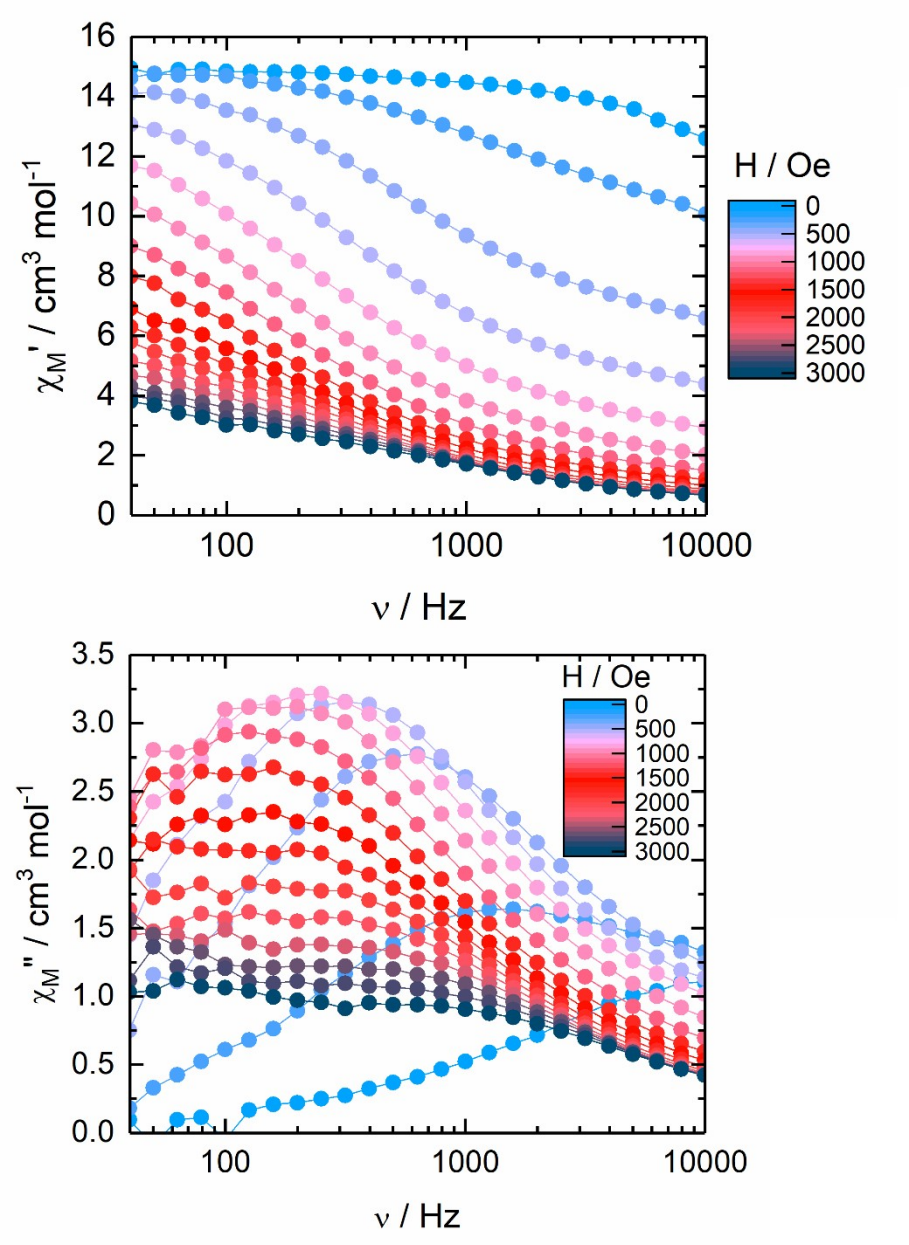

Figure S24. Field dependence of the in-phase (above) and out-of-phase (below) components of the magnetic susceptibility for **4** at 2 K in the 0-3000 Oe field range.

Table S10. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **4** at 2 K in the field range 200-3000 Oe.

H / Oe	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
200	9.7268	14.92592	0.26985	1.10844E-4	0.99986
400	6.2514	14.72951	0.26245	2.63212E-4	0.99981
600	3.91936	14.30666	0.30913	4.5523E-4	0.9995
800	2.6354	13.61636	0.32579	6.88626E-4	0.99956
1000	1.5067	13.23045	0.37728	9.38629E-4	0.99955
1200	0.88445	12.71312	0.41962	0.00128	0.99911
1400	0.72534	11.23113	0.40049	0.0013	0.9993
1600	0.55272	9.73244	0.40354	0.00121	0.99914
1800	0.36654	9.31998	0.43799	0.00138	0.99883
2000	0.34327	7.79878	0.42007	0.00102	0.99882
2200	0.2444	7.18187	0.44436	9.68983E-4	0.99879
2400	0.30769	5.68878	0.39858	5.82439E-4	0.99919
2600	0.26546	5.1701	0.41092	5.03052E-4	0.9993
2800	0.23457	4.65716	0.42043	4.15589E-4	0.99922
3000	0.22531	4.04321	0.416	3.06693E-4	0.99947

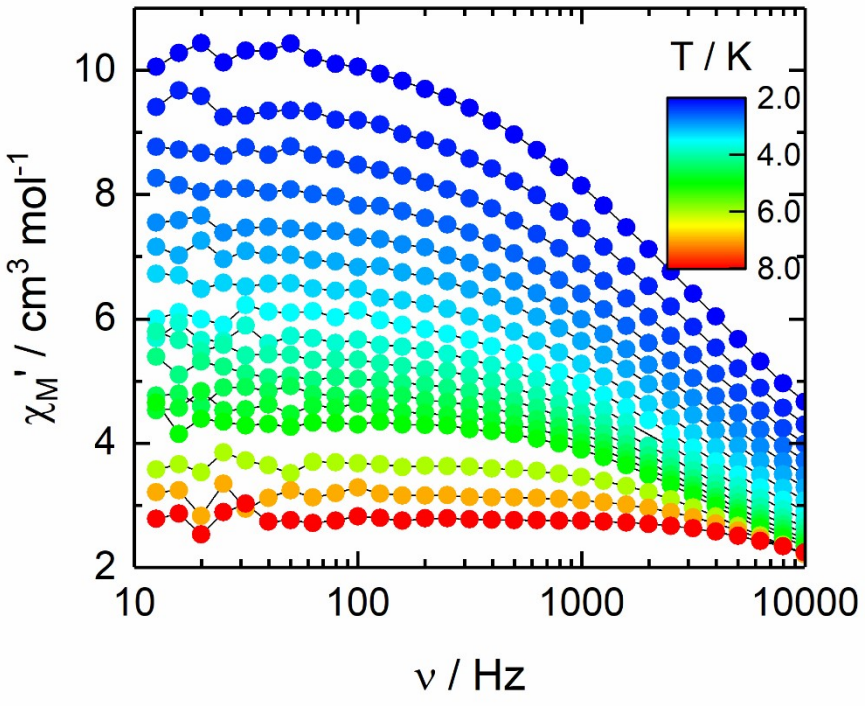

Figure S25. Frequency dependence of χ_M' for **3** in the 2–8 K temperature range in zero applied magnetic field.

Table S11. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **3** at 0 Oe in the temperature range 2-7 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	2.53652	10.51683	0.36037	5.45186E-5	0.99957
2.2	2.27963	9.63337	0.36508	5.34342E-5	0.99967
2.4	2.06032	8.92058	0.37143	5.26489E-5	0.99968
2.6	2.00777	8.27017	0.36134	5.38878E-5	0.99965
2.8	1.91122	7.66697	0.35208	5.27808E-5	0.99967
3	1.68649	7.23375	0.36821	5.03182E-5	0.99976
3.25	1.62099	6.72758	0.36094	5.01667E-5	0.99945
3.5	1.65769	6.20894	0.33141	5.03228E-5	0.99937
3.75	1.57506	5.8264	0.32483	4.81807E-5	0.99933
4.0	1.46856	5.5155	0.32796	4.57328E-5	0.99978
4.25	1.41334	5.20797	0.31883	4.29937E-5	0.99985
4.5	1.54844	4.85732	0.26014	4.30195E-5	0.99858
4.75	1.40686	4.65	0.27434	3.83004E-5	0.99896
5.0	1.38008	4.39887	0.25387	3.49931E-5	0.99902
6.0	1.30099	3.68038	0.19409	2.46417E-5	0.99853
7.0	1.25464	3.16905	0.14778	1.6784E-5	0.9966

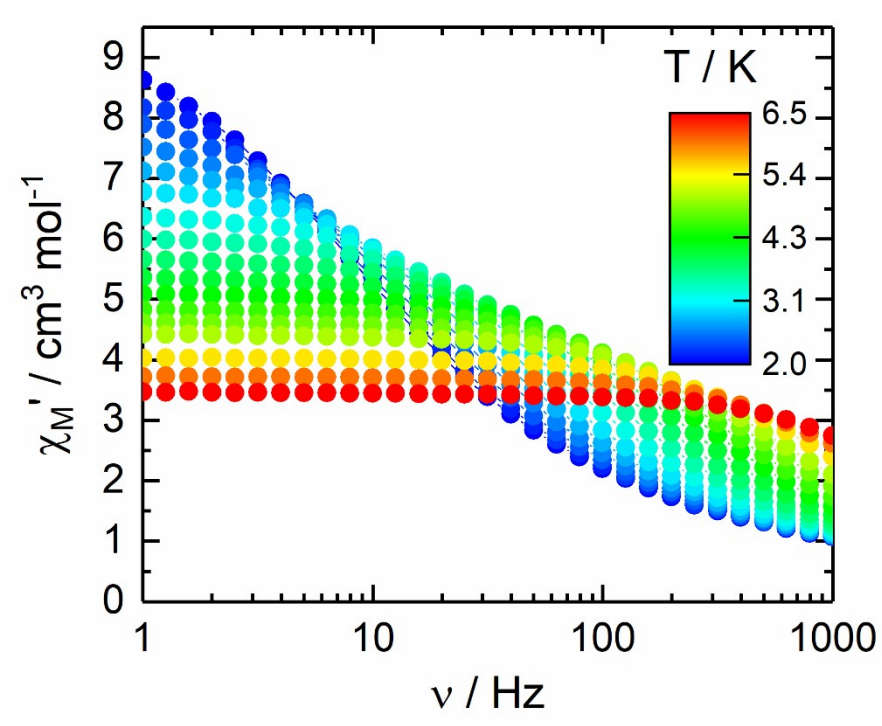

Figure S26. Frequency dependence of χ_M' for **3** in the 2–6.5 K temperature range under 1600 Oe applied magnetic field.

Table S12. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **3** at 1600 Oe in the temperature range 2-6.5 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	0.93945	9.98016	0.01733	0.37615	0.99959
2.2	0.97449	9.23248	0.01335	0.35689	0.9994
2.4	0.88922	8.61643	0.00952	0.35192	0.9996
2.6	0.8237	8.05481	0.00679	0.34417	0.99974
2.8	0.77668	7.49893	0.00469	0.32498	0.99965
3	0.76962	7.04209	0.00338	0.30556	0.99973
3.25	0.75706	6.52739	0.00226	0.28279	0.99979
3.5	0.75059	6.10166	0.00156	0.26366	0.99984
3.75	0.76805	5.72148	0.00111	0.2431	0.99988
4.0	0.7605	5.39735	8.01314E-4	0.23043	0.99987
4.25	0.75862	5.11482	5.8651E-4	0.22127	0.99988
4.5	0.83763	4.85369	4.61041E-4	0.19859	0.99986
4.75	0.82801	4.63013	3.48827E-4	0.19917	0.99991
5.0	0.86523	4.42722	2.75818E-4	0.19085	0.99993
5.5	0.96053	4.03681	1.82293E-4	0.16893	0.99996
6.0	1.03529	3.71904	1.25043E-4	0.15656	0.99997
6.5	0.97833	3.45597	8.01313E-5	0.16045	0.99997

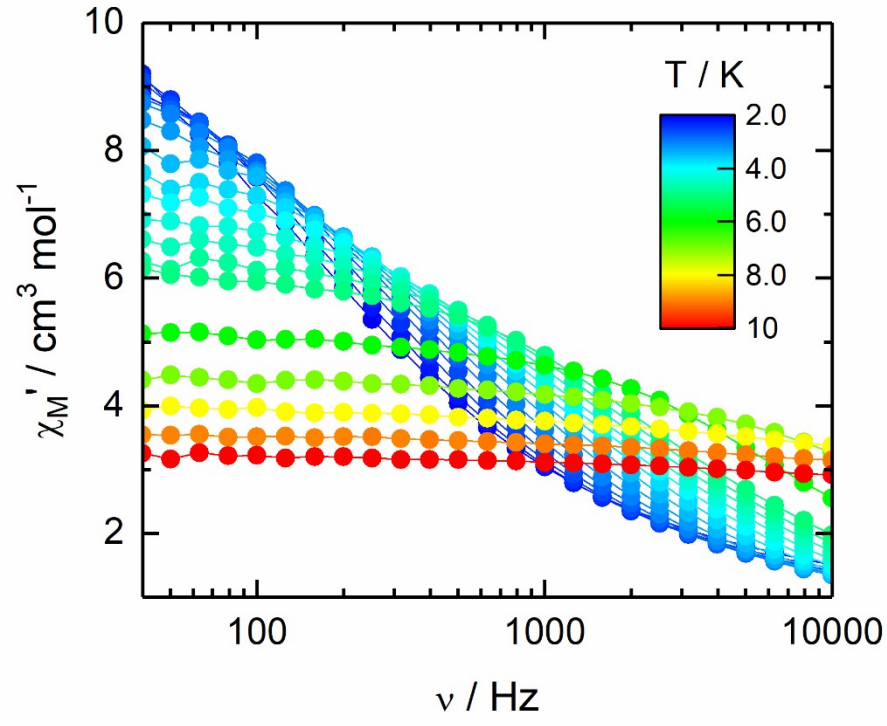

Figure S27. Frequency dependence of χ_M' for **4** in the 2–10 K temperature range under 1200 Oe applied magnetic field.

Table S13. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **4** at 1200 Oe in the temperature range 2-7 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	1.04077	11.99246	0.38216	0.00109	0.99977
2.2	0.98063	11.55443	0.36276	8.79219E-4	0.99967
2.4	0.90242	11.06216	0.35256	7.02584E-4	0.99977
2.6	0.81634	10.69819	0.35036	5.7994E-4	0.99978
2.8	0.76943	10.18129	0.34077	4.62948E-4	0.9997
3	0.66481	9.81977	0.34922	3.82458E-4	0.9998
3.25	0.70474	9.13486	0.32576	2.90312E-4	0.99862
3.5	0.53236	8.84326	0.35183	2.34346E-4	0.99951
3.75	0.56643	8.16919	0.33131	1.75299E-4	0.9994
4.0	0.55568	7.76666	0.32813	1.39542E-4	0.99928
4.25	0.60226	7.33866	0.31783	1.12004E-4	0.9994
4.5	0.71206	6.82522	0.28502	8.73528E-5	0.99903
4.75	0.77757	6.45454	0.26762	7.07328E-5	0.9991
5.0	0.89859	6.10474	0.23963	5.84964E-5	0.99827
5.5	0.71967	5.09403	0.23253	2.19959E-5	0.99989
6.0	1.01093E-13	4.45015	0.33099	5.16517E-6	0.99912
7.0	1.04077	11.99246	0.38216	0.00109	0.99977

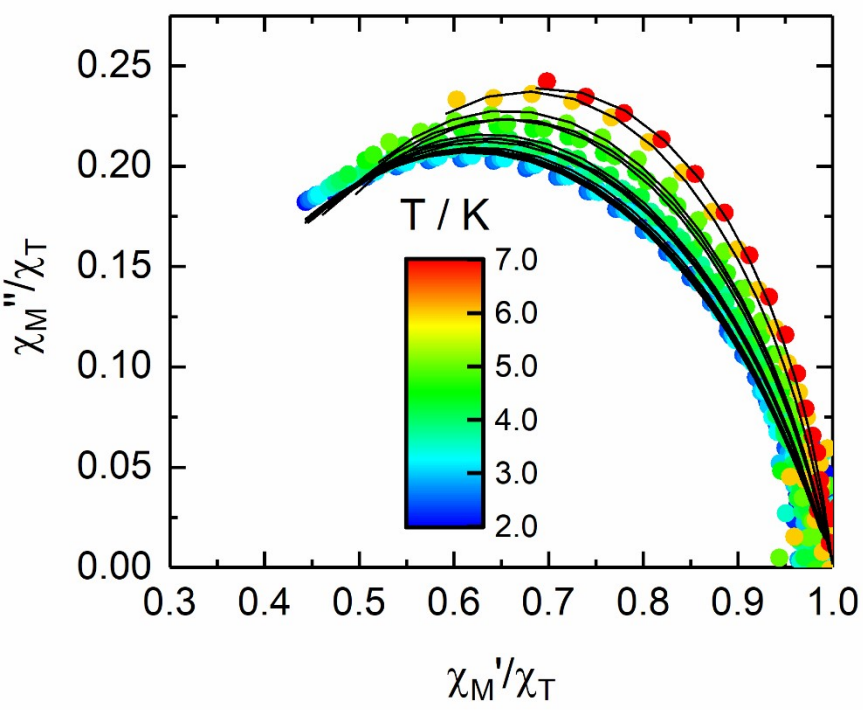

Figure S28. Normalized Argand plot for **3** in the temperature range of 2-7 K at 0 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S1).

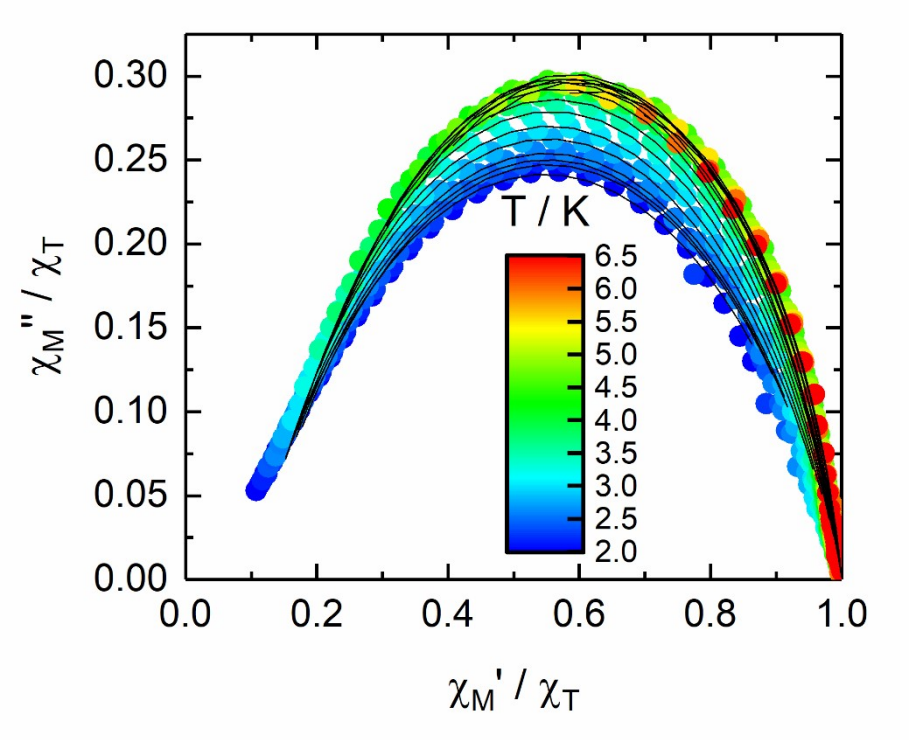

Figure S29. Normalized Argand plot for **3** in the temperature range of 2-6.5 K at 1600 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S1).

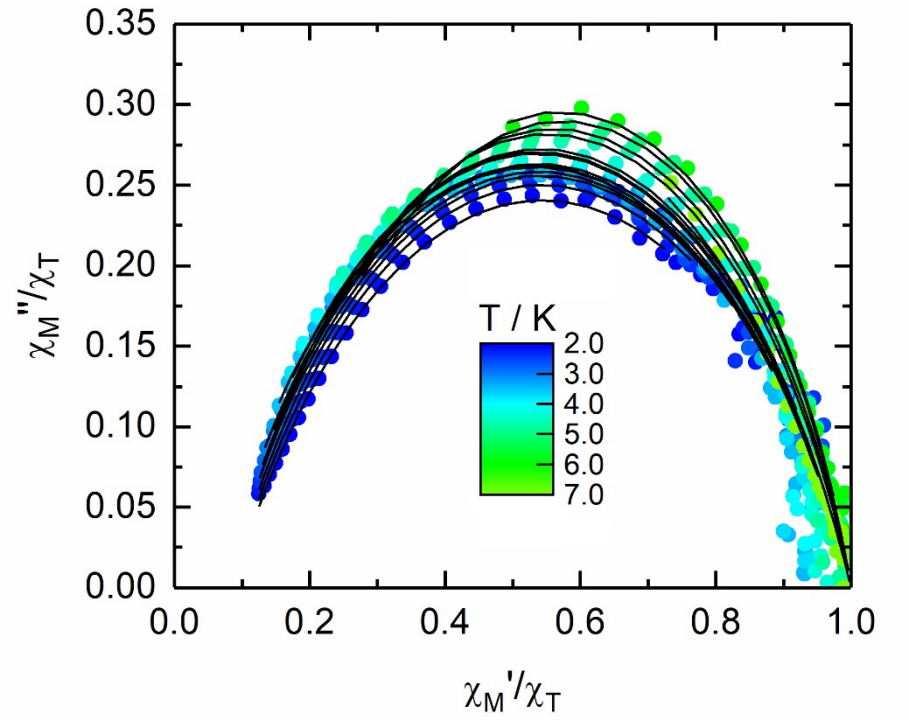

Figure S30. Normalized Argand plot for **4** in the temperature range of 2-7 K at 1200 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S1).

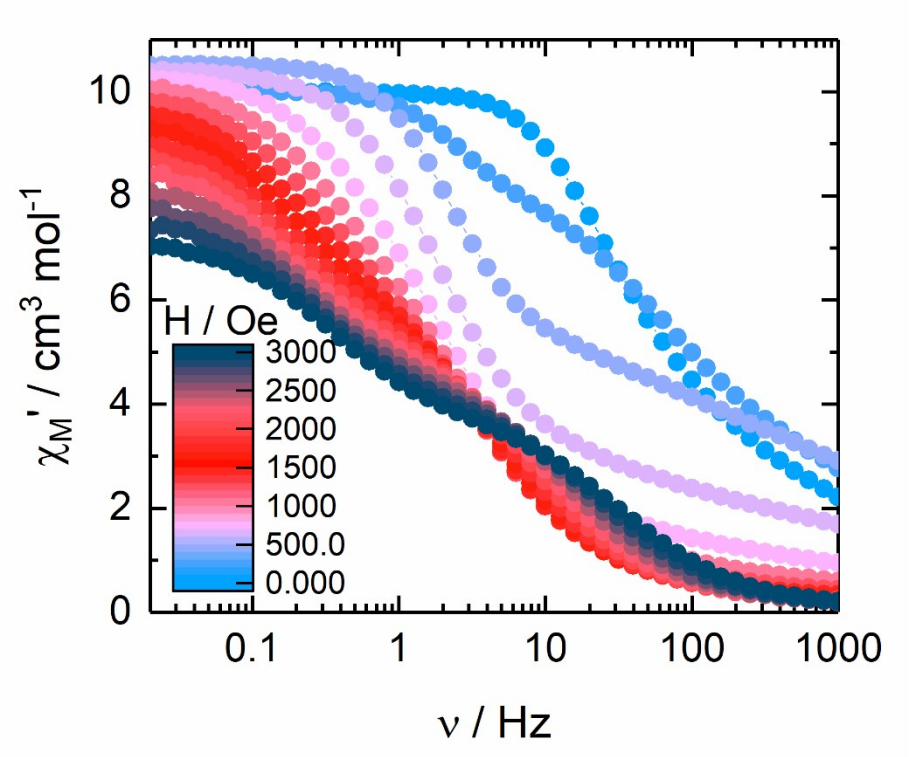

Figure S31. Field dependence of χ_M' in the 0-3000 Oe field range at 2 K for **(+)7**.

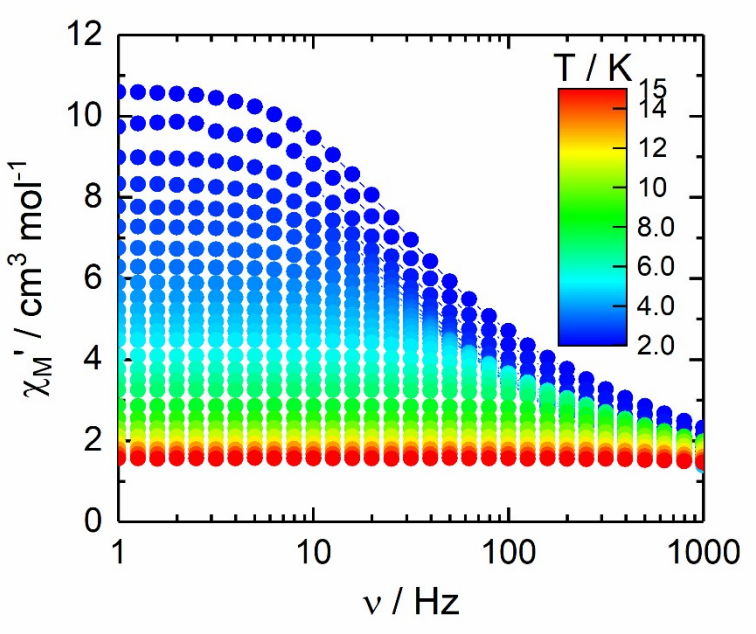

Figure S32. Frequency dependence of χ_M' for **(+)7** in the 2–15 K temperature range under a 0 Oe applied magnetic field.

Table S14. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **(+)7** at 0 Oe in the temperature range 2-10 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	2.00674	11.09146	0.28262	0.00381	0.99728
2.2	1.882	10.25613	0.27356	0.00372	0.99715
2.4	1.73476	9.35672	0.2619	0.00352	0.99718
2.6	1.63679	8.63978	0.24677	0.00328	0.99731
2.8	1.54222	8.02697	0.23274	0.00301	0.99739
3	1.45684	7.49486	0.2186	0.00271	0.99766
3.25	1.35235	6.92151	0.20519	0.00233	0.99796
3.5	1.26247	6.43135	0.19196	0.00197	0.99842
3.75	1.19544	6.00656	0.1812	0.00166	0.99865
4.0	1.10757	5.63908	0.17699	0.00136	0.99892
4.25	1.03026	5.31281	0.1759	0.00111	0.99907
4.5	0.98918	5.02358	0.17061	9.26186E-4	0.99922
4.75	0.92588	4.76907	0.17578	7.52716E-4	0.99926
5.0	0.88853	4.53649	0.17785	6.22221E-4	0.9993
5.5	0.88699	4.136	0.17513	4.46352E-4	0.99939
6.0	0.98407	3.79657	0.16065	3.50453E-4	0.99955
6.5	1.11455	3.50751	0.13999	2.94052E-4	0.99971
7.0	1.20875	3.26407	0.11566	2.57239E-4	0.99982
8.0	1.27698	2.86356	0.08584	1.95438E-4	0.99995
9.0	1.30996	2.55272	0.05722	1.591E-4	0.99999
10	1.26341	2.30827	0.05223	1.29899E-4	0.99999

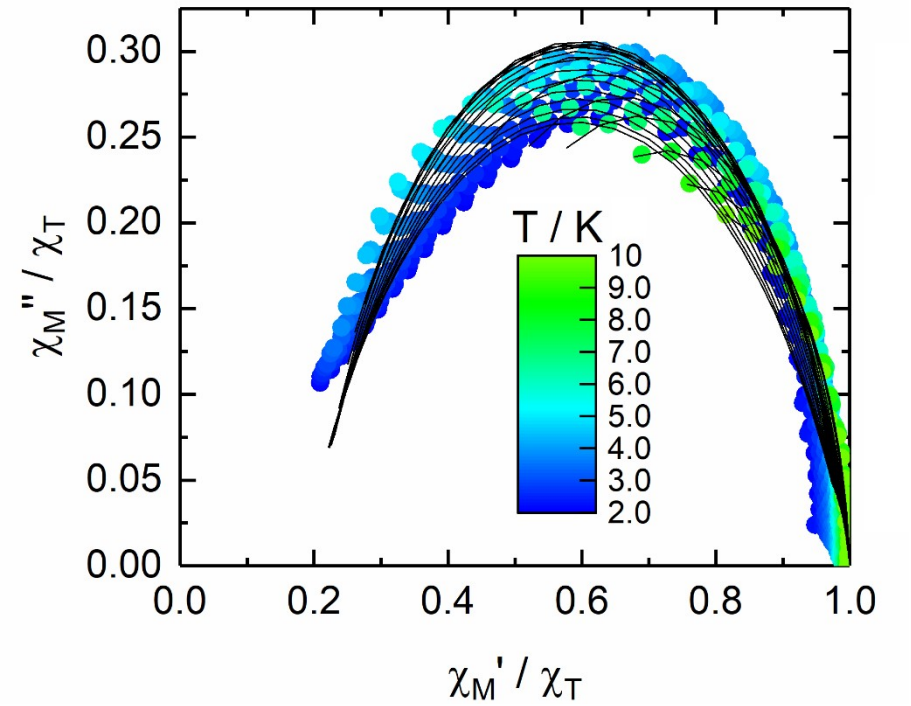

Figure S33. Normalized Argand plot for **(+)7** in the temperature range of 2-10 K at 0 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S1).

Extended Debye model used for two relaxation contributions (Eq. S2).

$$\chi_M' = \chi_S + (\chi_T - \chi_S) \left\{ \frac{\beta\left[1 + (\omega\tau_1)^{1-\alpha_1} \sin\left(\frac{\pi}{2}\alpha_1\right)\right]}{1 + 2(\omega\tau_1)^{1-\alpha_1} \sin\left(\frac{\pi}{2}\alpha_1\right) + (\omega\tau_1)^{2(1-\alpha_1)}} + \frac{(1-\beta)\left[1 + (\omega\tau_2)^{1-\alpha_2} \sin\left(\frac{\pi}{2}\alpha_2\right)\right]}{1 + 2(\omega\tau_2)^{1-\alpha_2} \sin\left(\frac{\pi}{2}\alpha_2\right) + (\omega\tau_2)^{2(1-\alpha_2)}} \right\}$$

$$\chi_M'' = (\chi_T - \chi_S) \left\{ \frac{\beta\left[(\omega\tau_1)^{1-\alpha_1} \cos\left(\frac{\pi}{2}\alpha_1\right)\right]}{1 + 2(\omega\tau_1)^{1-\alpha_1} \sin\left(\frac{\pi}{2}\alpha_1\right) + (\omega\tau_1)^{2(1-\alpha_1)}} + \frac{(1-\beta)\left[(\omega\tau_2)^{1-\alpha_2} \cos\left(\frac{\pi}{2}\alpha_2\right)\right]}{1 + 2(\omega\tau_2)^{1-\alpha_2} \sin\left(\frac{\pi}{2}\alpha_2\right) + (\omega\tau_2)^{2(1-\alpha_2)}} \right\}$$

With χ_T the isothermal susceptibility, χ_S the adiabatic susceptibility, τ the relaxation time and α an empiric parameter which describe the distribution of the relaxation time. For SMM with only one relaxing object α is close to zero. The extended Debye model was applied to fit simultaneously the experimental variations of χ_M' and χ_M'' with the frequency ν of the oscillating field ($\omega = 2\pi\nu$). The best fitted parameters τ_1, α_1, χ_{1T}, χ_{1S}, τ_2, α_2, χ_{2T} and χ_{2S} are listed in Tables S15 and S17 with the coefficient of determination R^2. τ_1, α_1, χ_{1T}, χ_{1S} are parameters for the high frequency contribution while τ_2, α_2, χ_{2T} and χ_{2S} are for the low frequency contribution.

Table S15. Best fitted parameters ($\chi_{T,1}$, $\chi_{S,1}$, τ_1, α_1, ($\chi_{T,2}$, $\chi_{S,2}$, τ_2 and α_2) with the extended Debye model (Eq. S2) for compound **(+)7** at 2 K in the magnetic field range 0-3000 Oe.

H / Oe	$\chi_{T,1}$ / cm^3 mol^{-1}	χ_S / cm^3 mol^{-1}	τ_1 / s	α_1	$\chi_{T,2}$ / cm^3 mol^{-1}	α_2	τ_2 / s	R^2
0	10.25058	2.62489	0.00444	0.20373	--	--	0.00444	0.99898
200	8.84555	1.71235	0.00189	0.40863	2.95727	0	0.05861	0.99982
400	5.77992	1.75969	8.14551E-4	0.51096	6.56501	0.03272	0.07069	0.99995
600	10.54638	2.46393	0.07788	0.20202	--	--	0.07788	0.9995
800	10.57572	1.06119	0.09544	0.31753	--	--	0.09544	0.99941
1000	8.93695	0.62705	0.075	0.31458	1.93279	0.03192	0.70259	0.9998
1200	8.17416	0.4214	0.064	0.30782	2.2197	0.03463	0.90527	0.99988
1400	6.85829	0.32687	0.04355	0.27466	3.21565	0.13117	0.8604	0.99991
1600	6.2318	0.26189	0.03331	0.25869	3.52426	0.15369	0.88891	0.99993
1800	5.73994	0.21797	0.02534	0.2492	3.69562	0.1673	0.87984	0.99995
2000	5.33003	0.18597	0.01924	0.24348	3.78616	0.17808	0.8462	0.99995
2200	5.00715	0.15039	0.01475	0.2462	3.77473	0.18429	0.81069	0.99994
2400	4.70013	0.12765	0.01128	0.24966	3.68251	0.18329	0.72257	0.99996
2600	4.36179	0.11044	0.00852	0.25152	3.66617	0.2002	0.63091	0.99996
2800	4.09285	0.09155	0.0066	0.26011	3.56399	0.20621	0.54903	0.99992
3000	3.82437	0.06875	0.00509	0.27111	3.42734	0.21319	0.46547	0.99996

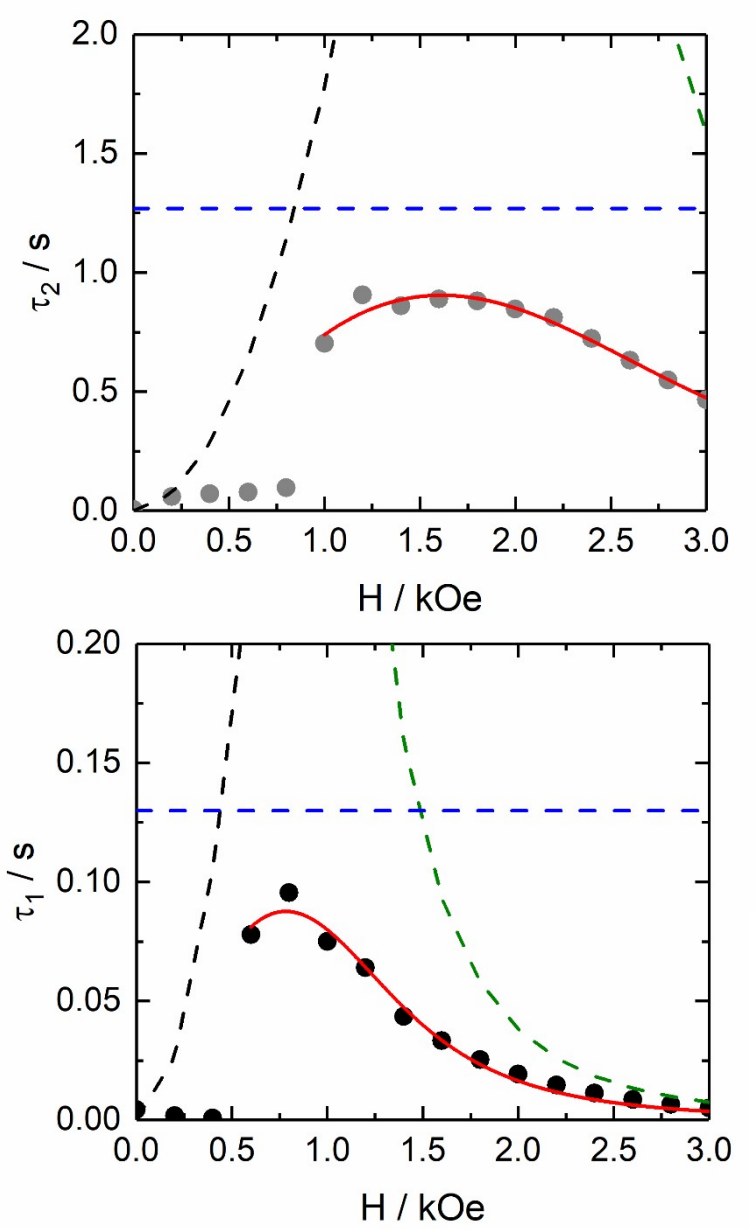

Figure S34. Field dependence of the magnetic relaxation time τ_1 (full black circles) (below) and τ_2 (full grey circles) (above) at 2 K in the field range of 0-3000 Oe for **(+)7** with the corresponding best fit depicted in full red line. The separated thermally activated Orbach + Raman, QTM and direct processes are drawn in dashed blue, black and green lines, respectively.

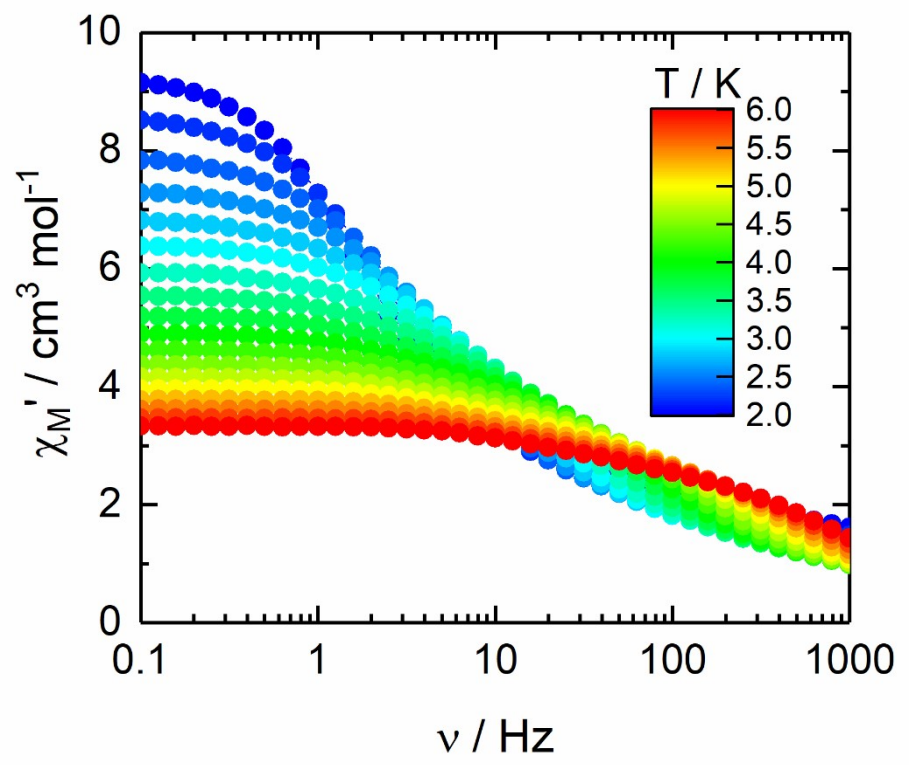

Figure S35. Frequency dependence of χ_M' for **(+)7** in the 2–6 K temperature range under a 600 Oe applied magnetic field.

Table S16. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **(+)7** at 600 Oe in the temperature range 2-6 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	2.41768	9.41438	0.17854	0.084	0.9996
2.2	2.14112	8.68616	0.19079	0.05646	0.99987
2.4	1.82904	7.96291	0.2157	0.03619	0.99996
2.6	1.54334	7.38611	0.24234	0.02393	0.99995
2.8	1.2911	6.90167	0.27291	0.01627	0.99983
3	1.04854	6.48858	0.30633	0.01133	0.99956
3.25	0.89923	6.00575	0.32051	0.00767	0.99965
3.5	0.76265	5.59617	0.33525	0.0053	0.99965
3.75	0.65056	5.23978	0.34954	0.00377	0.99951
4.0	0.51936	4.93258	0.3672	0.00265	0.99943
4.25	0.37522	4.66292	0.38788	0.00184	0.99939
4.5	0.25194	4.42237	0.40474	0.00132	0.99931
4.75	0.06683	4.21783	0.43156	8.89502E-4	0.99935
5.0	0	4.02001	0.44417	6.48964E-4	0.99938
5.25	0	3.83673	0.45161	4.96282E-4	0.99934
5.5	0	3.67339	0.46032	3.87795E-4	0.99929
5.75	0	3.52579	0.47228	3.03295E-4	0.99927
6.0	0	3.3897	0.48194	2.41743E-4	0.9993

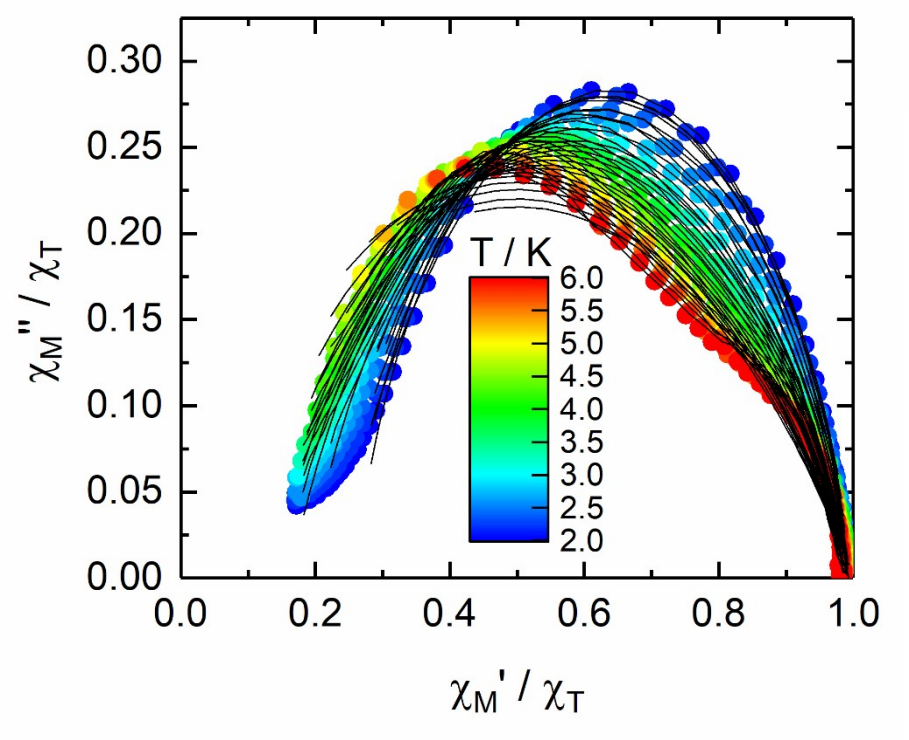

Figure S36. Normalized Argand plot for **(+)7** in the temperature range of 2-6 K at 600 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S1).

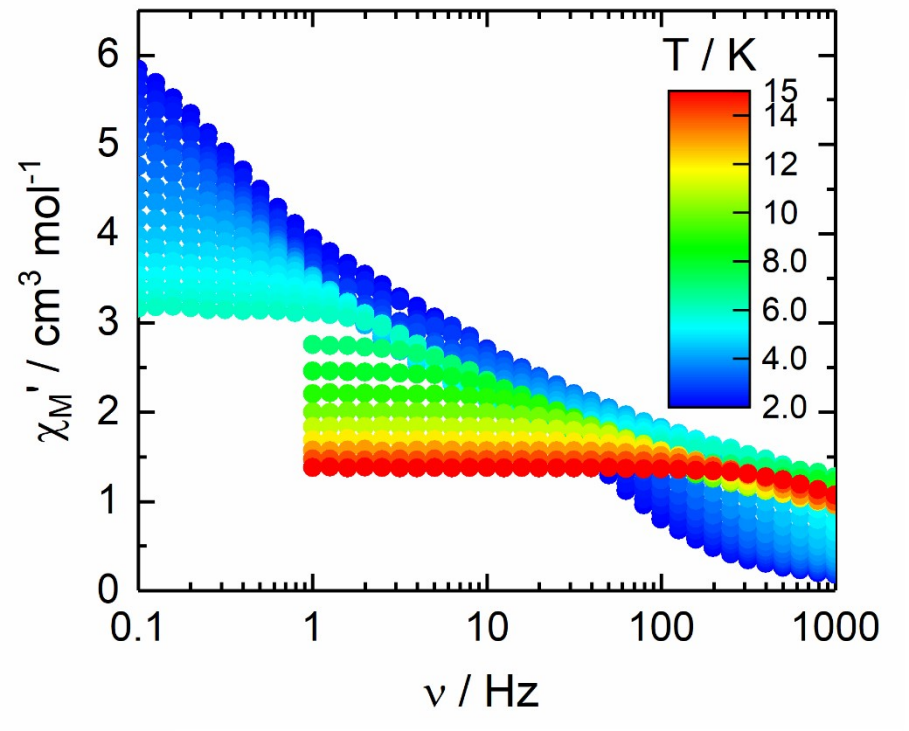

Figure S37. Frequency dependence of χ_M' for **(+)7** in the 2–15 K temperature range under a 3000 Oe applied magnetic field.

Table S17. Best fitted parameters ($\chi_{T,1}$, $\chi_{S,1}$, τ_1, α_1, ($\chi_{T,2}$, $\chi_{S,2}$, τ_2 and α_2) with the extended Debye model (Eq. S2) for compound **(+)7** at 3000 Oe in the temperature range 2-5.5 K.

T / K	$\chi_{T,1}$ / cm^3 mol^{-1}	χ_S / cm^3 mol^{-1}	τ_1 / s	α_1	$\chi_{T,2}$ / cm^3 mol^{-1}	α_2	τ_2 / s	R^2
2	3.22985	0.05858	0.50349	0.23782	3.38866	0.27341	0.00555	0.99998
2.2	3.24412	0.06322	0.46693	0.23882	3.23081	0.25938	0.00456	0.99997
2.4	3.16632	0.10281	0.40263	0.20471	3.06041	0.21527	0.00351	0.99901
2.6	3.04668	0.11168	0.35863	0.19636	2.95332	0.19885	0.00291	0.99948
2.8	2.90383	0.10443	0.32149	0.1951	2.8654	0.19723	0.00243	0.9998
3	2.87293	0.12767	0.27167	0.19591	2.68723	0.1661	0.00194	0.99987
3.25	2.66582	0.1272	0.23339	0.16134	2.60995	0.15931	0.00156	0.99983
3.5	2.5967	0.16225	0.19142	0.15501	2.46392	0.13419	0.00123	0.99991
3.75	2.46852	0.16902	0.15632	0.14036	2.3503	0.1185	9.76437E-4	0.99996
4	2.35827	0.17467	0.12739	0.12614	2.24957	0.10979	7.7019E-4	0.99997
4.25	2.23649	0.16804	0.10247	0.11875	2.15376	0.10584	5.94569E-4	0.99996
4.5	2.15623	0.19182	0.08178	0.10712	2.06287	0.09155	4.79225E-4	0.99996
4.75	2.03731	0.16031	0.0656	0.10191	1.98428	0.09945	3.63016E-4	0.99996
5	1.93754	0.14348	0.0522	0.09394	1.90596	0.09677	2.80718E-4	0.99996
5.5	1.86061	0.14509	0.04136	0.08711	1.83248	0.0996	2.1933E-4	0.99996
5.75	1.81894	0.17382	0.03314	0.07978	1.76597	0.0956	1.76009E-4	0.99996
6	1.67836	0.09583	0.02681	0.07509	1.70413	0.11242	1.29773E-4	0.99996
7	1.5251	0	0.02167	0.07108				0.99995
8	2.78154	1.39961	0.00963	0.07924				0.99994
9	2.47046	1.24989	0.0049	0.07055				0.99993
10	2.21831	1.13295	0.0027	0.06295				0.99995
11	2.0147	1.03947	0.00161	0.06017				0.99994
12	1.84523	0.96653	0.001	0.05495				0.99996
13	1.69017	0.89776	6.13274E-4	0.05041				0.99996
14	1.57202	0.8512	4.01394E-4	0.04369				0.99996
15	1.46922	0.80156	2.54424E-4	0.04934				0.99997

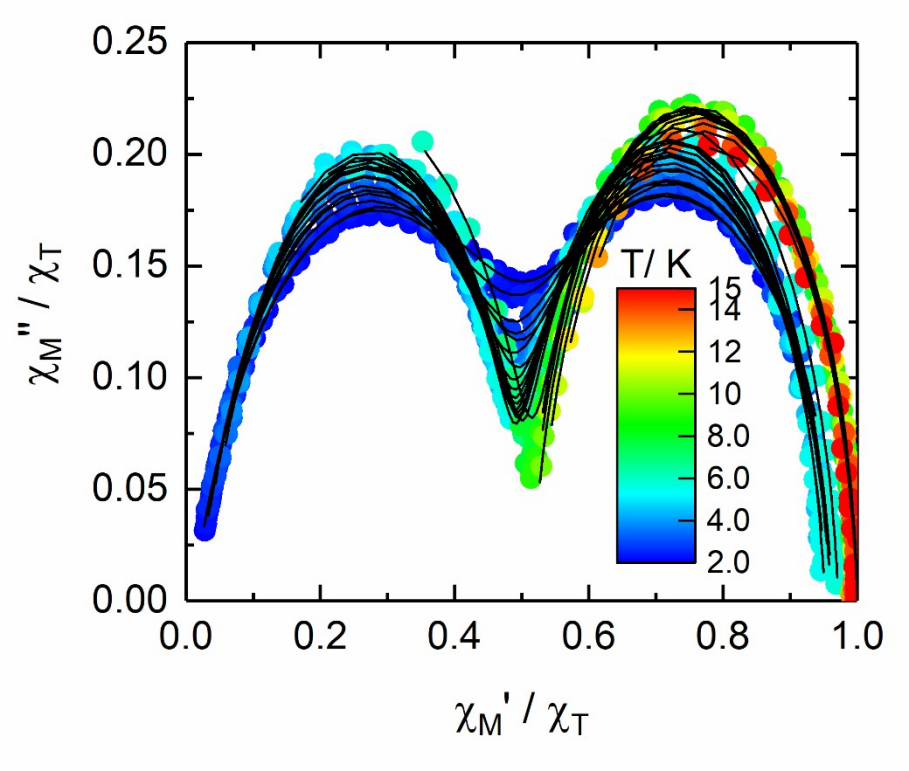

Figure S38. Normalized Argand plot for **(+)7** in the temperature range of 2-15 K at 3000 Oe. Full black lines are the best fits obtained from the extended Debye equation (Eq. S2).