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Electronic Supplementary Informations

for

Anion-driven structures and SMM behavior of dinuclear terbium and ytterbium complexes

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Table S1 Selected structural parameters (bond lengths in Å and angles in °) for **1**, **3** and **5**. Ln = Tb, Yb and Y for **1**, **3** and **5**, respectively. Symmetry code: A, *2–x, 1–y, 1–z* for **1**, A, *1–x, 2–y, –z* for **3** and A, *2–x, 2–y,–z* for **5**.

	1	**3**	**5**		**1**	**3**		**5**
Ln1–O1	2.350(3)	2.291(3)	2.336(3)	O1–Ln1–O1A	67.42(10)	67.35(12)	O1–Ln1–O1A	67.47(12)
Ln1–O1A	2.372(3)	2.313(3)	2.335(3)	O1–Ln1–O2	148.00(9)	148.05(12)	O1A–Ln1–O2	147.50(11)
Ln1–O2	2.221(3)	2.169(3)	2.200(3)	O1–Ln1–O3	102.96(10)	101.93(12)	O1A–Ln1–O3	102.25(11)
Ln1–O3	2.438(3)	2.387(3)	2.413(3)	O1–Ln1–O4	79.93(9)	79.17(11)	O1A–Ln1–O4	79.13(12)
Ln1–O4	2.527(3)	2.477(3)	2.498(4)	O1–Ln1–O6	75.60(9)	76.04(11)	O1A–Ln1–O6	75.71(10)
Ln1–O6	2.521(3)	2.473(3)	2.497(3)	O1–Ln1–O7	125.91(9)	127.41(11)	O1A–Ln1–O7	126.88(11)
Ln1–O7	2.441(3)	2.385(4)	2.411(3)	O1–Ln1–O9	75.97(9)	76.58(11)	O1A–Ln1–O9	76.45(11)
Ln1–O9	2.514(3)	2.466(3)	2.494(4)	O1–Ln1–O10	119.23(9)	119.84(11)	O1A–Ln1–O10	119.78(12)
Ln1–O10	2.487(3)	2.452(3)	2.465(3)	O1A–Ln1–O2	87.39(9)	88.20(12)	O1–Ln1–O2	87.51(11)
Ln1⋯ Ln1A	3.928(1)	3.831(1)	3.884(2)	O1A–Ln1–O3	132.80(9)	133.01(12)	O1–Ln1–O3	132.77(12)
				O1A–Ln1–O4	81.19(9)	80.54(11)	O1–Ln1–O4	80.86(11)
				O1A–Ln1–O6	139.52(9)	139.93(11)	O1–Ln1–O6	139.65(11)
				O1A–Ln1–O7	151.25(10)	151.13(11)	O1–Ln1–O7	150.96(11)
				O1A–Ln1–O9	85.58(9)	87.06(11)	O1–Ln1–O9	86.32(11)
				O1A–Ln1–O10	79.86(10)	79.67(12)	O1–Ln1–O10	79.68(11)
				O2–Ln1–O3	79.35(10)	79.38(12)	O2–Ln1–O3	79.20(12)
				O2–Ln1–O4	76.84(10)	76.66(12)	O2–Ln1–O4	76.58(12)
				O2–Ln1–O6	132.87(9)	131.72(13)	O2–Ln1–O6	132.68(11)
				O2–Ln1–O7	85.62(10)	83.83(12)	O2–Ln1–O7	84.97(12)
				O2–Ln1–O9	123.20(10)	124.23(12)	O2–Ln1–O9	124.09(12)
				O2–Ln1–O10	72.33(10)	72.45(12)	O2–Ln1–O10	72.62(12)
				O3–Ln1–O4	51.75(9)	52.54(12)	O3–Ln1–O4	52.03(11)
				O3–Ln1–O6	70.42(10)	69.24(11)	O3–Ln1–O6	69.99(12)
				O3–Ln1–O7	72.93(10)	72.55(12)	O3–Ln1–O7	73.02(12)
				O3–Ln1–O9	138.93(10)	136.82(11)	O3–Ln1–O9	138.02(11)
				O3–Ln1–O10	135.57(10)	136.03(13)	O3–Ln1–O10	135.85(12)
				O4–Ln1–O6	108.49(10)	108.60(11)	O4–Ln1–O6	108.35(11)
				O4–Ln1–O7	123.92(10)	123.95(12)	O4–Ln1–O7	124.14(11)
				O4–Ln1–O9	155.51(9)	155.51(12)	O4–Ln1–O9	155.29(11)
				O4–Ln1–O10	144.30(10)	143.57(11)	O4–Ln1–O10	144.01(12)
				O6–Ln1–O7	51.71(9)	52.64(11)	O6–Ln1–O7	52.51(11)
				O6–Ln1–O9	69.64(9)	68.62(11)	O6–Ln1–O9	69.13(11)
				O6–Ln1–O10	105.59(9)	106.25(11)	O6–Ln1–O10	106.10(11)
				O7–Ln1–O9	75.18(10)	74.89(12)	O7–Ln1–O9	74.98(11)
				O7–Ln1–O10	71.44(10)	71.47(12)	O7–Ln1–O10	71.30(11)
				O9–Ln1–O10	50.94(9)	52.05(10)	O9–Ln1–O10	51.60(11)
				Ln1–O1–Ln1A	112.58(10)	112.65(12)	Ln1–O1–Ln1A	112.53(12)

Table S2 Summary of SHAPE analysis around Ln^{III} centre for **1, 3** and **5**. Ln = Tb, Yb and Y for **1**, **3** and **5**, respectively.

ML_9		**1**	**3**	**5**
Enneagon	D_{9h}	35.196	34.999	35.098
Octagonal pyramid	C_{8v}	20.370	20.583	20.428
Heptagonal bipyramid	D_{7h}	17.590	17.592	17.636
Johnson triangular cupola J3	C_{3v}	14.722	14.940	14.822
Capped cube J8	C_{4v}	10.835	10.511	10.744
Spherical-relaxed capped cube	C_{4v}	9.478	9.183	9.380
Capped square antiprism J10	C_{4v}	3.047	2.893	2.916
Spherical capped square antiprism	C_{4v}	**2.163**	**2.035**	**2.037**
Tricapped trigonal prism J51	D_{3h}	4.148	3.884	3.985
Spherical tricapped trigonal prism	D_{3h}	3.208	3.018	3.071
Tridiminished icosahedron J63	C_{3v}	11.174	11.294	11.254
Hula-hoop	C_{2v}	10.770	10.389	10.587
Muffin	C_s	2.338	2.164	2.198

Table S3 Selected structural parameters (bond lengths in Å and angles in °) for **2** and **4**. Ln = Tb and Yb for **2** and **4**, respectively. Symmetry code: A, *–x, 2–y, –z* for **2** and **4**.

Distance (Å)			Angle (°)		
	2	**4**		**2**	**4**
Ln1–O1	2.153(8)	2.079(7)	O1–Ln1–O2	155.7(3)	158.6(2)
Ln1–O2	2.320(8)	2.239(6)	O1–Ln1–O2A	86.4(3)	89.0(2)
Ln1–O2A	2.361(7)	2.305(6)	O1–Ln1–Cl1	89.8(2)	90.1(2)
Ln1–Cl1	2.640(3)	2.585(3)	O1–Ln1–Cl2	108.6(2)	105.7(2)
Ln1–Cl2	2.621(3)	2.560(2)	O1–Ln1–Cl3	87.3(2)	87.4(2)
Ln1–Cl3	2.676(3)	2.638(3)	O2–Ln1–O2A	69.5(3)	69.8(3)
Ln1···Ln1A	3.846(2)	3.728(1)	O2–Ln1–Cl1	93.9(2)	93.57(18)
			O2–Ln1–Cl2	95.09(18)	95.09(17)
			O2–Ln1–Cl3	87.64(19)	88.09(18)
			O2A–Ln1–Cl1	91.35(19)	91.87(18)
			O2A–Ln1–Cl2	163.9(2)	164.15(17)
			O2A–Ln1– Cl3	85.57(19)	86.27(17)
			Cl1–Ln1–Cl2	94.40(10)	93.77(9)
			Cl1–Ln1–Cl3	175.85(9)	176.93(8)
			Cl2–Ln1–Cl3	89.30(10)	88.66(9)
			Ln1–O2–Ln1A	110.5(3)	110.2(3)

Table S4 Summary of SHAPE analysis around Ln^{III} centre for **2** and **4.** Ln = Tb and Yb for **2** and **4**, respectively.

ML_6		**2**	**4**
Hexagon	D_{6h}	33.848	33.344
Pentagonal pyramid	C_{5v}	25.751	25.709
Octahedron	Oh	**2.157**	**2.037**
Trigonal prism	D_{3h}	13.324	13.572
Johnson pentagonal pyramid J2	C_{5v}	28.678	28.557

Table S5 Parameters obtained from Cole Cole fitting for **1'**

Temperature (K)	χ_{Iso}	α	τ
1.85	1.25193	0.19517	1.42446×10^{-4}
2	1.18415	0.18842	1.30246×10^{-4}
2.15	1.12082	0.18155	1.19467×10^{-4}
2.3	1.06912	0.17207	1.10869×10^{-4}
2.45	1.01728	0.16407	1.02246×10^{-4}
2.6	0.9699	0.15711	9.38286×10^{-5}
2.75	0.92568	0.14863	8.72495×10^{-5}
2.9	0.88455	0.13868	8.09657×10^{-5}
3.05	0.84659	0.12834	7.58433×10^{-5}
3.2	0.81273	0.13029	6.9021×10^{-5}
3.35	0.77871	0.1137	6.62752×10^{-5}
3.5	0.74844	0.10461	6.1922×10^{-5}
3.75	0.70301	0.09437	5.45335×10^{-5}
4	0.66217	0.07941	4.86639×10^{-5}
4.25	0.62513	0.07471	4.28836×10^{-5}
4.5	0.59141	0.06766	3.68746×10^{-5}

Table S6 Parameters obtained from Cole Cole fitting for **3**

Temperature (K)	χ_{Iso1}	χ_{Iso2}	α_1	τ_1	τ_2
1.85	1.48405	0.13376	0.20388	5.069×10^{-4}	1.309×10^{-4}
2	1.36203	0.14774	0.20221	4.47×10^{-4}	1.264×10^{-4}
2.15	1.26578	0.14724	0.20138	3.878×10^{-4}	1.234×10^{-4}
2.3	1.19272	0.14635	0.19046	3.455×10^{-4}	1.094×10^{-4}
2.45	1.09734	0.17047	0.17047	3.097×10^{-4}	1.06×10^{-4}
2.6	1.01021	0.19308	0.16976	2.791×10^{-4}	9.929×10^{-5}
2.74	0.98413	0.1593	0.15869	2.367×10^{-4}	8.712×10^{-5}

Table S7 SMM properties of some reported ytterbium-based complexes

Complex*	H (Oe)	U_{eff} (K)	τ_0 (s)	*Ref* in main text
$[Yb_2L_2(acac)_2(H_2O)]\cdot 2CH_2Cl_2$	1600	24.5	$6.8x10^{-7}$	10*b*
$[Yb_2(DBM)_6(L)]$	2000	23	$7.919\ x10^{-7}$	10*a*
$[Yb(dnbz)(acac)_2(H_2O)(EtOH)]_2$	2000	26	$2.8\ x10^{-7}$	10*c*
$[Yb_2L_3(CH_3OH)]\cdot 3CH_3CN$	3000	14.5	$1.6\ x10^{-6}$	10*d*
$[Yb_2L(OAc)_4(CH_3OH)_2]\cdot 2CH_3OH$	3000	9.5	$4.8\ x10^{-6}$	10*d*
$[Yb_2(HL)_4(NO_3)_6]$	3000	3.9 (2.78 cm^{-1})	$5.93\ x10^{-5}$	This work

* Please check the reference for the complete molecular formula.

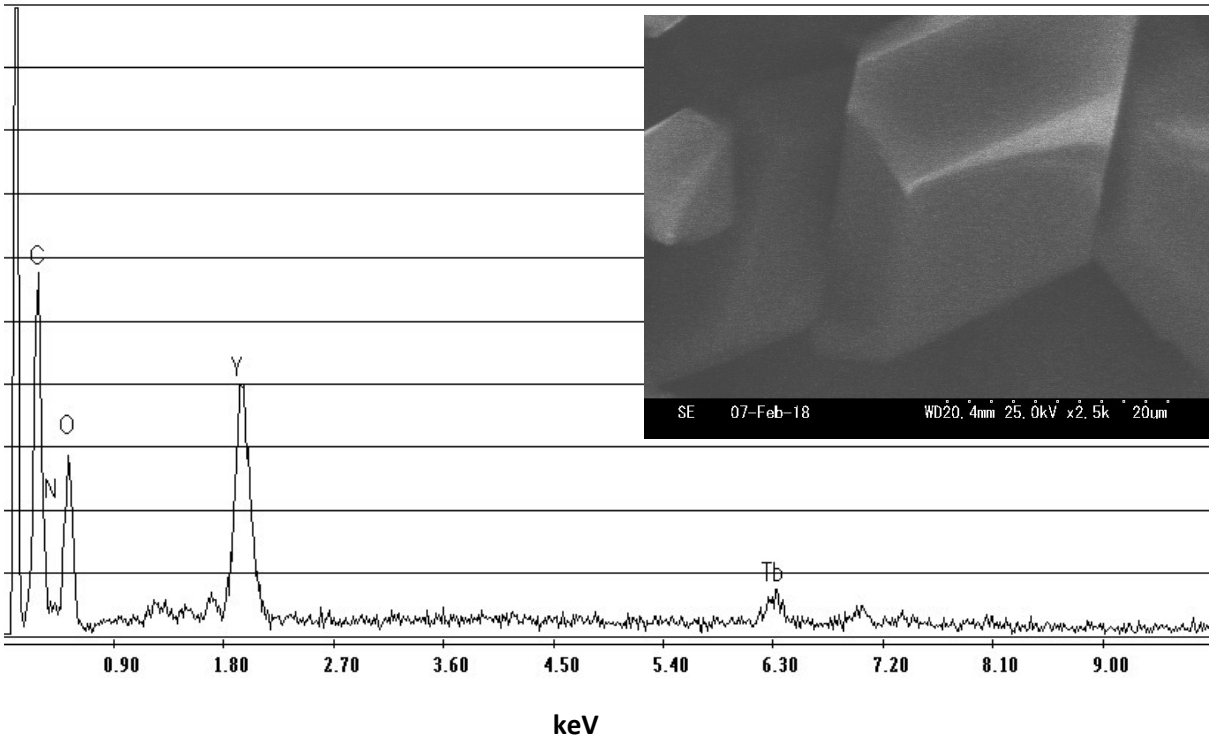


Fig. S1 EDX spectrum for the compound **1'**. Inset shows the SEM image of the same.

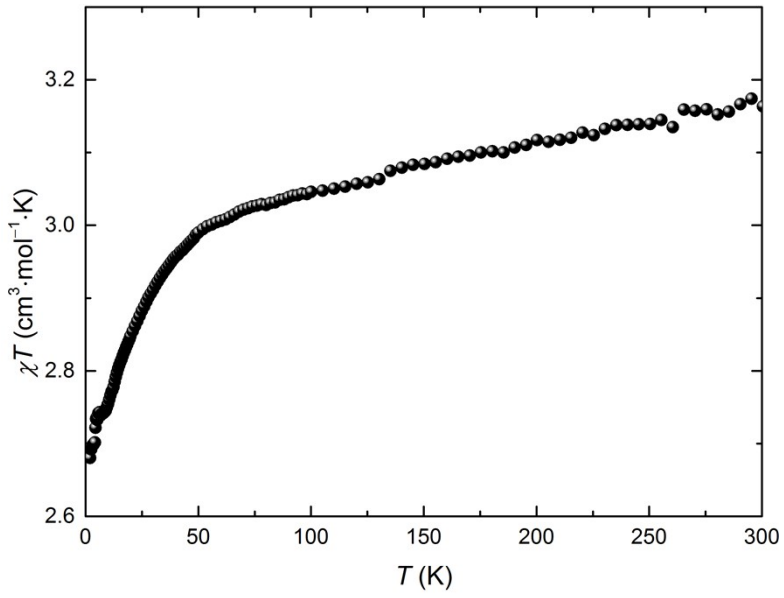


Fig. S2 Temperature dependence of the χT products in 1000 Oe for **1'**.

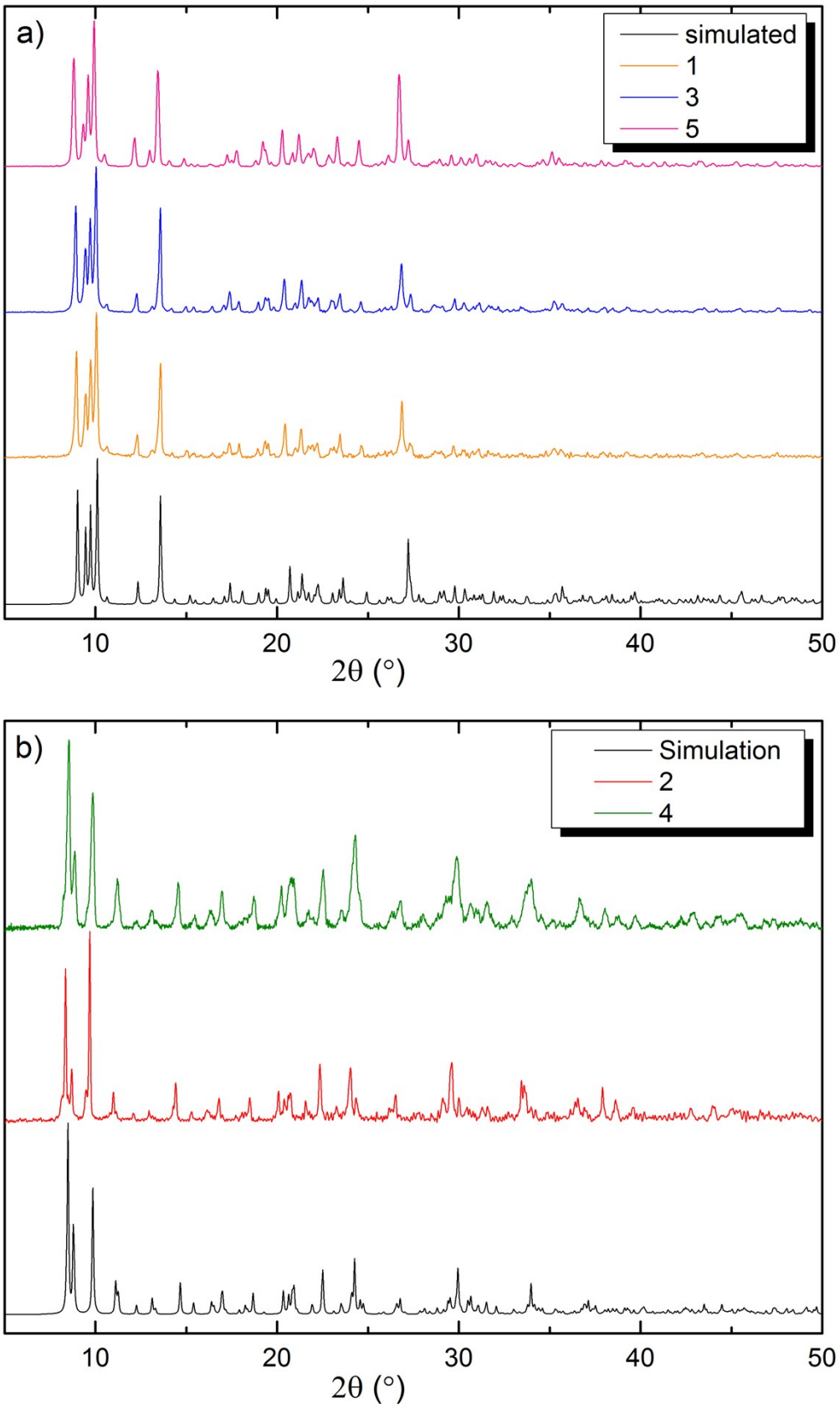
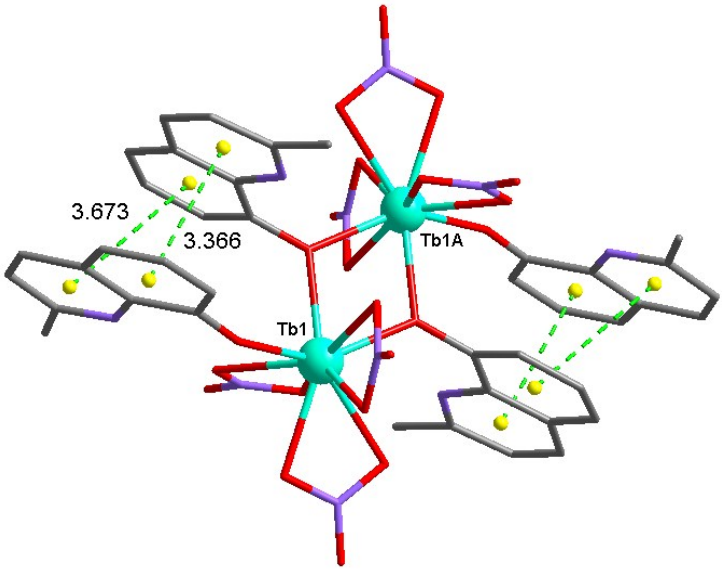
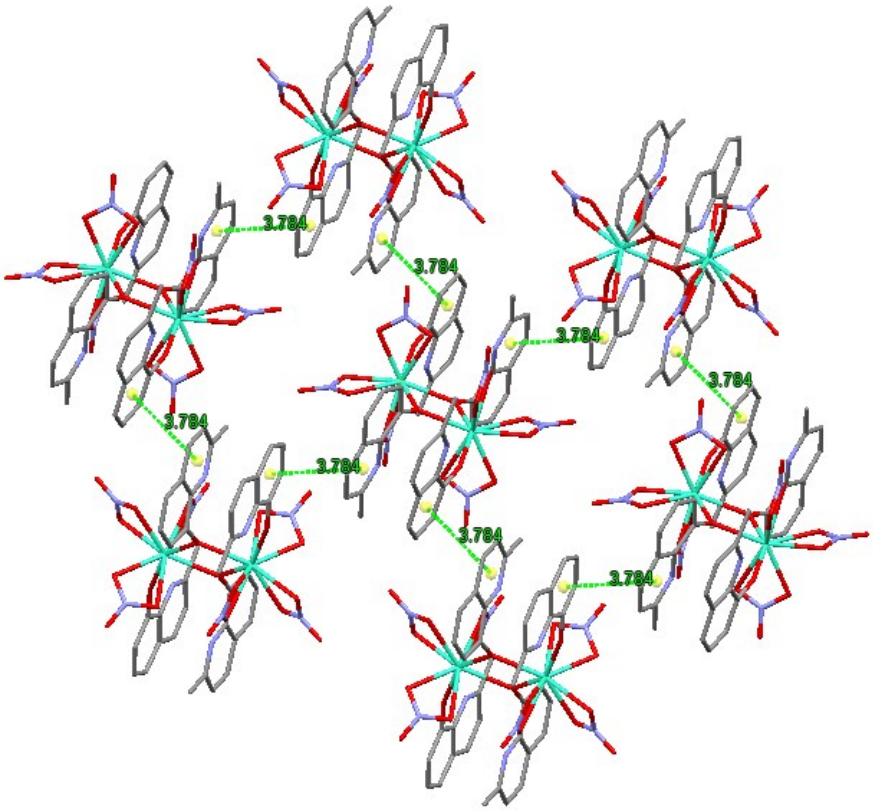


Fig. S3 Simulated and observed PXRD patterns of a) **1**, **3** and **5** and b) **2** and **4**.

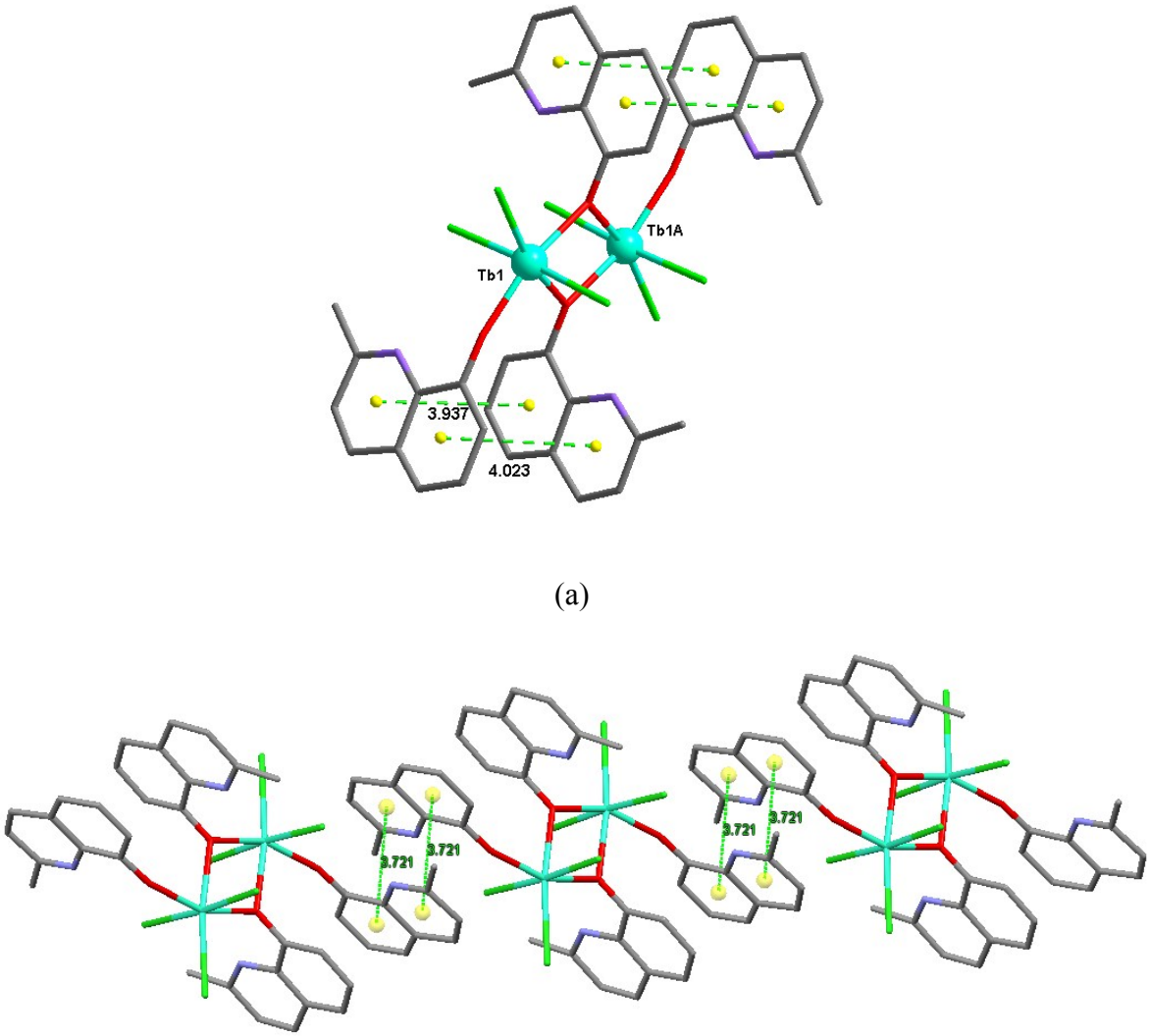


(a)



(b)

Fig. S4 (a) Crystal structure of compound **1** showing intramolecular π···π stacking interaction. (b) Perspective view of two dimensional sheet caused by intermolecular π···π stacking interaction in crystallographic *bc* plane for compound **1**. Hydrogen atoms are omitted for clarity. The distances shown in the figure are in Å. Symmetry code: A, 2–*x*, 1–*y*, 1–*z*.



(a)

(b)

Fig. S5 (a) Crystal structure of compound **2** showing intramolecular π···π stacking interaction. (b) Perspective view of one dimensional chain caused by intermolecular π···π stacking interaction in crystallographic *bc* plane for compound **2**. Solvent ethanol molecules and hydrogen atoms are omitted for clarity. The distances shown in the figure are in Å. Symmetry code: A, –*x*, 2–*y*, –*z*.

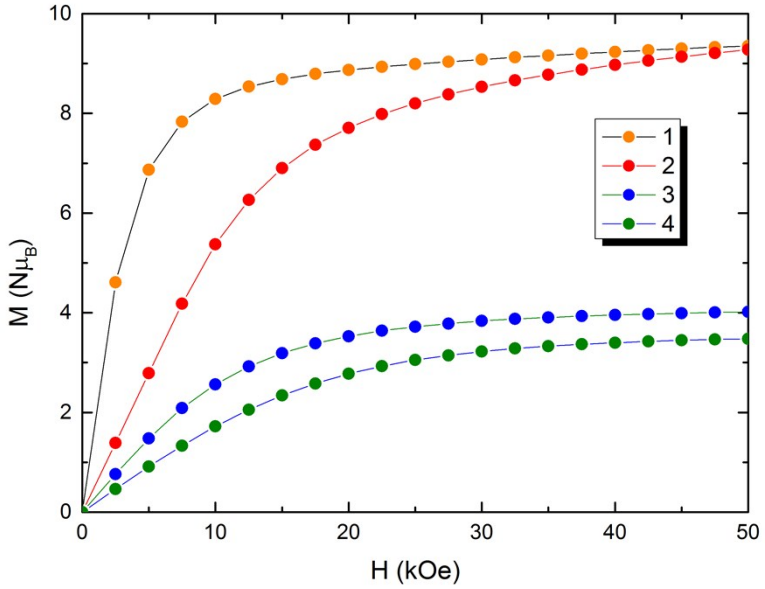


Fig. S6 Magnetization (M) *vs.* Field (H) plots at 1.8 K.

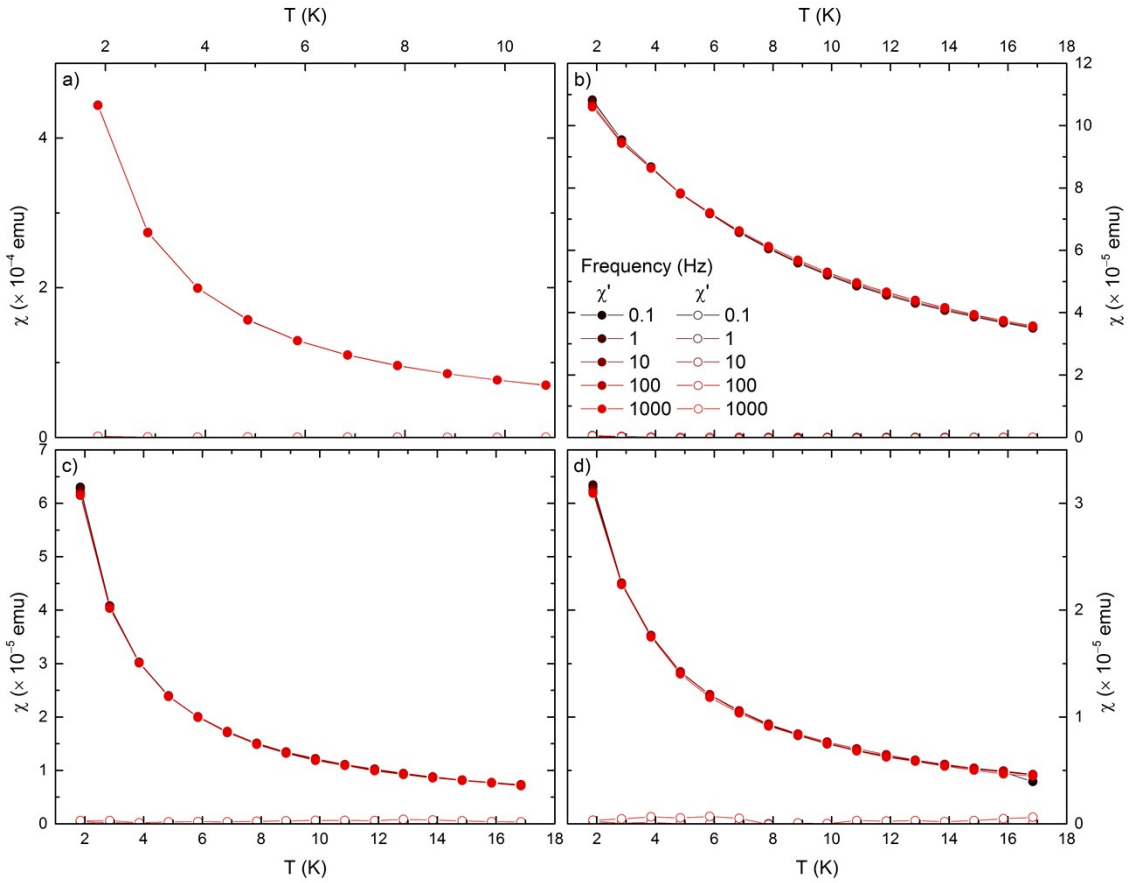


Fig. S7 Frequency and temperature dependency without dc field for a) **1**, b) **2**, c) **3** and d) **4**.

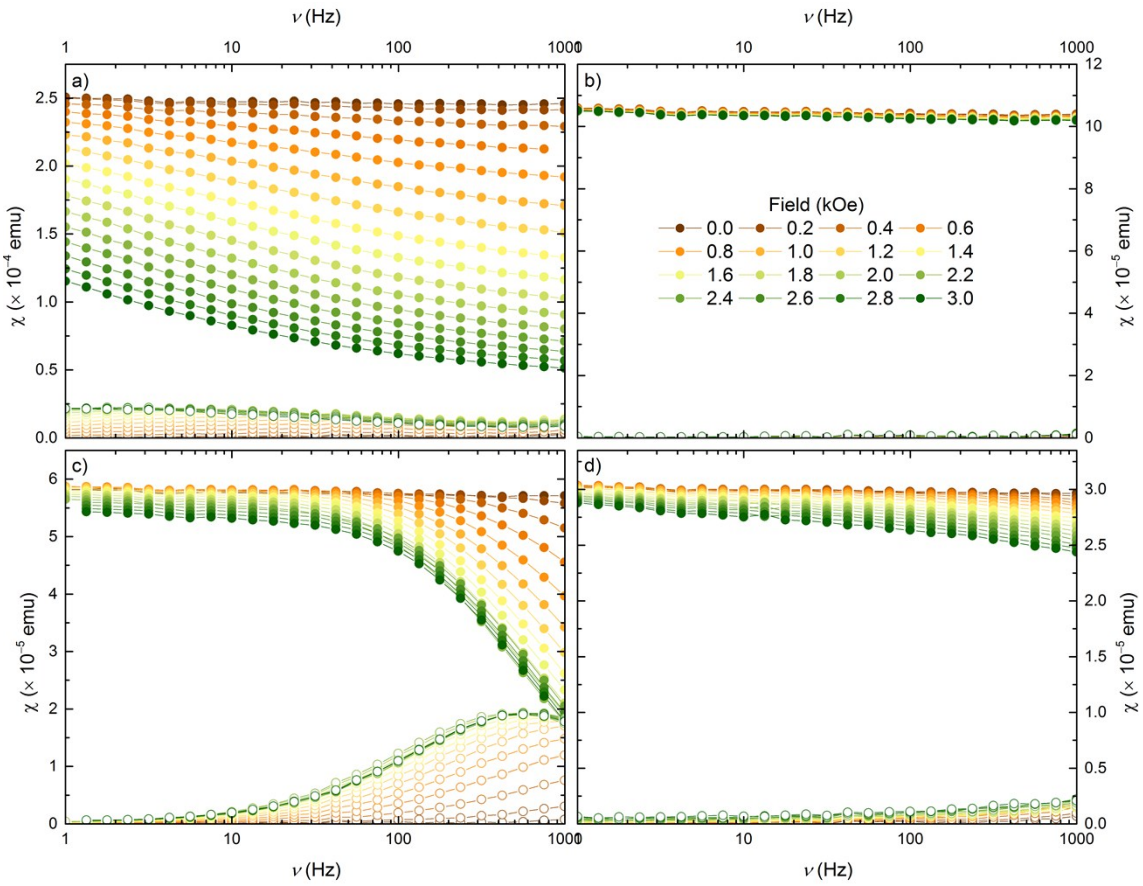


Fig. S8 Frequency dependency of the out-of-phase ac susceptibility under indicated dc fields at 2K for complexes a) **1**, b) **2,** c) **3** and d) **4**.

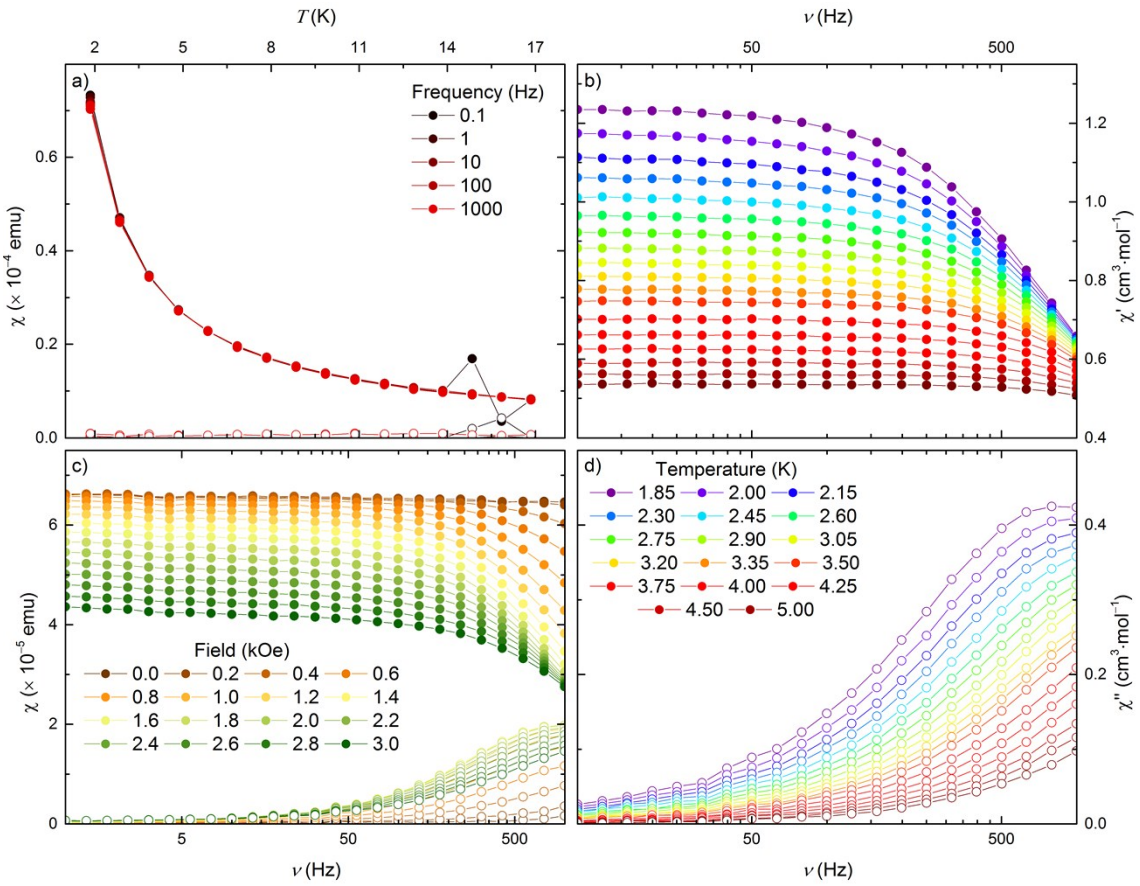


Fig. S9 a) Frequency and temperature dependence without dc field for **1'**. c) Frequency and field dependence at 2K for **1'**. Frequency dependence of the b) in-phase and d) out-of-phase components of the ac magnetic susceptibility for compound **1'** under 1600 Oe dc field.

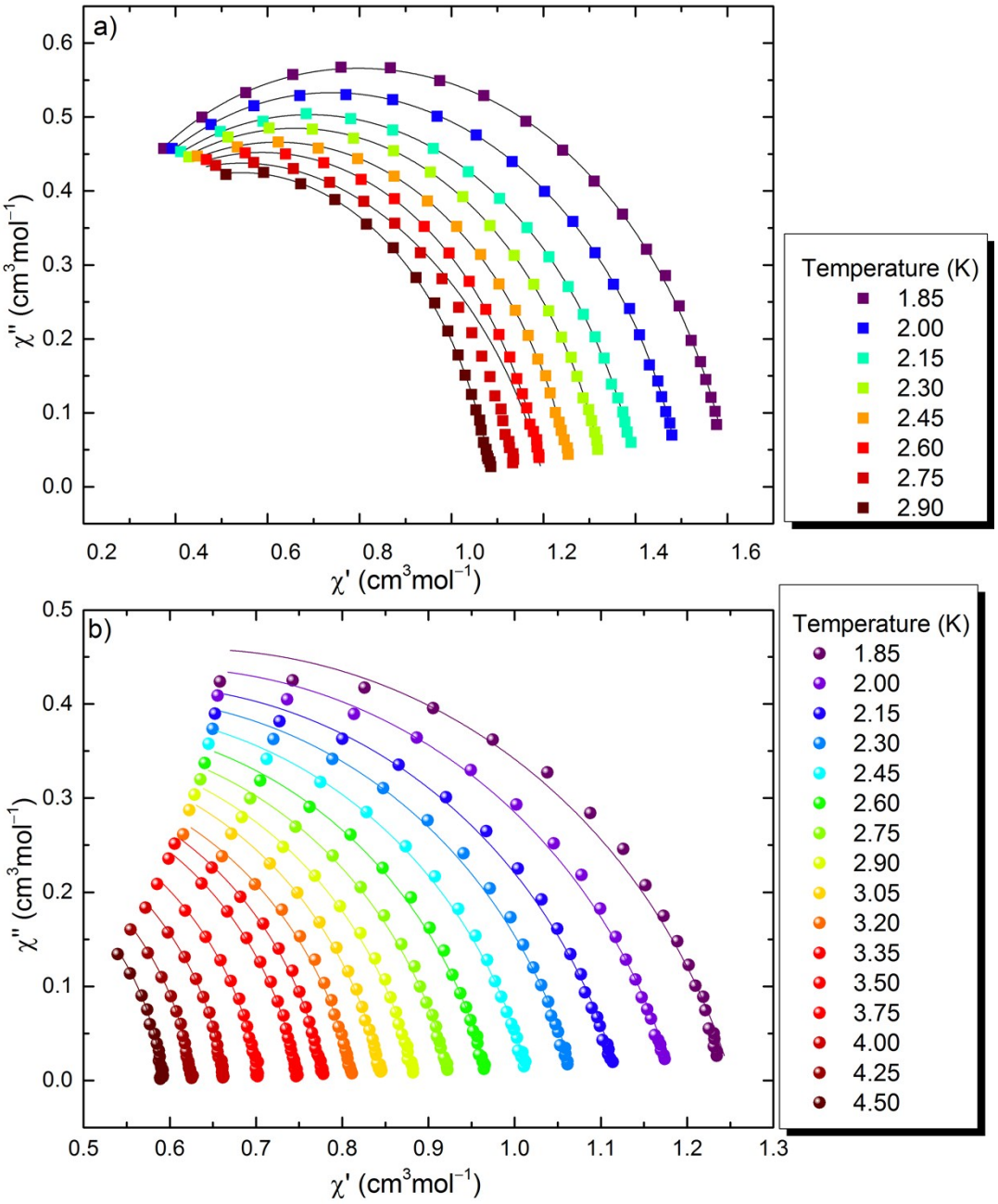


Fig. S10 Cole-Cole plots measured for a) **3** in a 3000 Oe dc field and b) **1'** in a 1600 Oe dc field. The solid lines are best fits to the experimental data.