Supporting Information For:

Bilayered lanthanide squarate hydrates (Ln = Eu to Lu) and magnetization reversal barriers 21 K for Ln = Tm and 57 K for Yb

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Contents

Table S1. Selected crystallographic data of **Eu-sq** – **Lu-sq**.

Compound	**Eu-sq**	**Gd-sq**	**Tb-sq**[S1]	**Dy-sq**	**Ho-sq**
Chemical formula	$C_{12}H_{16}Eu_2O_{20}$	$C_{12}H_{16}Gd_2O_{20}$	$C_{12}H_{16}O_{20}Tb_2$	$C_{12}H_{16}Dy_2O_{20}$	$C_{12}H_{16}Ho_2O_{20}$
Formula weight	784.17	794.75	798.09	805.25	810.11
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pc*	*Pc*	*Pc*	*Pc*	*Pc*
a / Å	11.9363(9)	11.9359(7)	11.9331(8)	11.9063(8)	11.9195(7)
b / Å	8.2215(5)	8.1994(4)	8.1820(6)	8.1711(5)	8.1486(5)
c / Å	10.1229(7)	10.0894(5)	10.0563(7)	10.0452(6)	10.0126(6)
β / deg	96.017(7)	95.928(5)	96.103(6)	95.934(6)	95.907(6)
V / Å ^{3}	987.93(12)	982.14(9)	976.29(11)	972.04(11)	967.33(10)
Z	2	2	2	2	2
d / g cm^{-3}	2.636	2.687	2.715	2.751	2.781
μ / mm^{-1}	6.397	6.801	7.292	7.736	8.228
No. of unique refls.	3858	3976	4200	3920	3550
R_{int}	0.0279	0.0307	0.0261	0.0345	0.0233
$R(F)$ ($I > 2\sigma(I)$) [a)]	0.0377	0.0234	0.0247	0.0305	0.0195
$R_w(F^2)$ (all data) [b)]	0.1112	0.0565	0.0603	0.0848	0.0496
GOF (S)	1.059	1.035	1.020	1.025	1.007
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e Å^{-3}	1.489, –0.600	0.700, –0.752	0.597, –0.642	1.362, –1.237	0.743, –0.835
T / K	296	295	296	296	295
CCDC	2218673	2218674	2108278	2218675	2218676

a) $R(F) = \Sigma||F_O| - |F_C||/|F_O|$

b) $R_w(F^2) = \{\Sigma(w(F_O^2 - F_C^2)^2)/\Sigma w(F_O^2)^2\}^{1/2}$

Table S1. (Continued) Selected crystallographic data of **Eu-sq** – **Lu-sq**.

Compound	**Er-sq**	**Tm-sq**	**Yb-sq**	**Lu-sq**
Chemical formula	$C_{12}H_{16}Er_2O_{20}$	$C_{12}H_{16}O_{20}Tm_2$	$C_{12}H_{16}O_{20}Yb_2$	$C_{12}H_{16}Lu_2O_{20}$
Formula weight	814.77	818.12	826.33	830.19
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pc*	*Pc*	*Pc*	*Pc*
a / Å	11.9232(4)	11.9240(4)	11.9168(4)	11.9151(5)
b / Å	8.1407(2)	8.1318(2)	8.1217(2)	8.1066(3)
c / Å	10.0025(3)	9.9899(4)	9.9844(3)	9.9577(4)
β / deg	95.988(3)	95.876(3)	95.823(3)	95.748(4)
V / Å ^{3}	965.59(5)	963.56(6)	961.35(5)	956.99(7)
Z	2	2	2	2
d / g cm^{-3}	2.802	2.820	2.855	2.881
μ / mm^{-1}	8.740	9.257	9.777	10.365
No. of unique refls.	3455	3610	4622	4006
R_{int}	0.0218	0.0133	0.0317	0.0231
$R(F)$ ($I > 2\sigma(I)$) [a)]	0.0215	0.0182	0.0230	0.0281
$R_w(F^2)$ (all data) [b)]	0.0537	0.0546	0.0607	0.0847
GOF (S)	1.055	1.062	1.036	1.016
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e Å^{-3}	0.677, –0.796	0.873, –1.334	0.885, –1.251	1.052, –1.277
T / K	298	296	298	298
CCDC	2218677	2218678	2218679	2218680

a) $R(F) = \Sigma||F_O| - |F_C||/|F_O|$

b) $R_w(F^2) = \{\Sigma(w(F_O^2 - F_C^2)^2)/\Sigma w(F_O^2)^2\}^{1/2}$

Table S2. Selected geometric data of **Eu-sq** – **Lu-sq**.

Compound	**Eu-sq**	**Gd-sq**	**Tb-sq**[S1]	**Dy-sq**	**Ho-sq**	**Er-sq**	**Tm-sq**	**Yb-sq**	**Lu-sq**
Distance, *d* / Å									
RE1-O1	2.39(1)	2.379(3)	2.375(7)	2.356(8)	2.348(5)	2.343(6)	2.337(3)	2.336(6)	2.324(8)
RE1-O3	2.43(1)	2.422(4)	2.420(7)	2.404(8)	2.396(5)	2.399(6)	2.392(3)	2.381(6)	2.376(8)
RE1-O4	2.46(1)	2.441(3)	2.438(8)	2.43(1)	2.409(6)	2.406(7)	2.400(3)	2.396(7)	2.410(9)
RE1-O5	2.40(1)	2.422(4)	2.417(9)	2.40(1)	2.398(6)	2.394(7)	2.382(4)	2.373(7)	2.37(1)
RE1-O13	2.40(1)	2.394(4)	2.379(6)	2.362(9)	2.354(5)	2.337(6)	2.334(3)	2.331(5)	2.301(8)
RE1-O14	2.43(1)	2.405(3)	2.39(1)	2.39(1)	2.369(7)	2.364(8)	2.339(3)	2.334(8)	2.30(1)
RE1-O15	2.39(1)	2.352(4)	2.343(9)	2.33(1)	2.295(6)	2.291(7)	2.283(4)	2.280(7)	2.27(1)
RE1-O16	2.39(1)	2.367(4)	2.336(7)	2.332(8)	2.314(5)	2.309(6)	2.293(3)	2.287(6)	2.276(8)
RE2-O8	2.35(1)	2.321(4)	2.310(7)	2.295(8)	2.293(5)	2.280(6)	2.271(3)	2.259(5)	2.255(8)
RE2-O9	2.479(9)	2.459(4)	2.449(7)	2.451(8)	2.426(5)	2.416(6)	2.419(3)	2.420(5)	2.406(7)
RE2-O10	2.43(1)	2.431(3)	2.418(7)	2.411(9)	2.402(5)	2.415(6)	2.397(3)	2.395(6)	2.370(9)
RE2-O11	2.41(1)	2.400(4)	2.389(7)	2.384(9)	2.368(5)	2.369(6)	2.354(3)	2.349(5)	2.353(7)
RE2-O17	2.45(1)	2.423(3)	2.41(1)	2.40(1)	2.383(7)	2.364(8)	2.363(3)	2.358(8)	2.36(1)
RE2-O18	2.42(1)	2.386(4)	2.385(9)	2.38(1)	2.351(7)	2.343(7)	2.337(4)	2.327(7)	2.32(1)
RE2-O19	2.38(1)	2.389(4)	2.387(7)	2.350(9)	2.345(5)	2.340(7)	2.327(3)	2.315(6)	2.297(8)
RE2-O20	2.34(1)	2.357(4)	2.331(9)	2.32(1)	2.328(6)	2.327(7)	2.302(4)	2.289(7)	2.28(1)
C1-O1	1.26(2)	1.243(7)	1.25(1)	1.27(1)	1.245(8)	1.25(1)	1.260(6)	1.254(9)	1.25(1)
C2-O2	1.25(2)	1.247(7)	1.26(1)	1.25(2)	1.24(1)	1.25(1)	1.246(6)	1.25(1)	1.26(2)
C3-O3	1.26(2)	1.263(7)	1.25(1)	1.26(1)	1.263(8)	1.27(1)	1.274(6)	1.27(1)	1.25(1)
C4-O4	1.26(2)	1.264(7)	1.27(1)	1.28(2)	1.25(1)	1.27(1)	1.272(6)	1.29(1)	1.26(2)
C5-O5	1.28(1)	1.273(6)	1.27(1)	1.28(1)	1.272(7)	1.273(9)	1.278(5)	1.274(8)	1.29(1)
C6-O6	1.19(2)	1.228(6)	1.23(1)	1.23(1)	1.236(9)	1.25(1)	1.234(6)	1.25(1)	1.24(1)
C7-O7	1.23(2)	1.267(6)	1.25(1)	1.26(1)	1.255(7)	1.27(1)	1.258(6)	1.242(9)	1.27(1)
C8-O8	1.27(2)	1.247(6)	1.25(1)	1.25(1)	1.241(8)	1.26(1)	1.252(5)	1.247(9)	1.23(1)
C9-O9	1.25(2)	1.263(7)	1.26(1)	1.26(1)	1.261(8)	1.26(1)	1.255(6)	1.252(9)	1.26(1)
C10-O10	1.28(2)	1.257(7)	1.25(1)	1.24(2)	1.27(1)	1.25(1)	1.252(6)	1.25(1)	1.26(1)
C11-O11	1.23(2)	1.248(7)	1.23(1)	1.22(1)	1.248(8)	1.24(1)	1.244(6)	1.241(9)	1.24(1)
C12-O12	1.24(2)	1.233(7)	1.25(1)	1.23(2)	1.26(1)	1.26(1)	1.256(6)	1.25(1)	1.25(2)
C1-C2	1.47(2)	1.467(9)	1.46(1)	1.46(1)	1.48(1)	1.46(1)	1.485(7)	1.48(1)	1.48(1)
C2-C3	1.44(2)	1.451(8)	1.44(2)	1.44(2)	1.47(1)	1.47(1)	1.454(7)	1.45(1)	1.46(2)
C3-C4	1.45(2)	1.453(9)	1.46(1)	1.46(1)	1.45(1)	1.44(1)	1.450(7)	1.45(1)	1.46(1)
C4-C1	1.46(2)	1.473(8)	1.45(2)	1.45(2)	1.49(1)	1.46(1)	1.453(7)	1.45(1)	1.47(2)
C5-C6	1.48(2)	1.462(6)	1.46(1)	1.46(1)	1.455(8)	1.45(1)	1.450(6)	1.453(9)	1.45(1)
C6-C7	1.52(2)	1.463(7)	1.47(1)	1.47(1)	1.47(1)	1.46(1)	1.476(7)	1.47(1)	1.46(2)
C7-C8	1.45(2)	1.448(6)	1.47(1)	1.47(1)	1.464(8)	1.45(1)	1.473(6)	1.466(9)	1.46(1)
C8-C5	1.47(2)	1.465(7)	1.45(1)	1.45(1)	1.462(9)	1.45(1)	1.454(6)	1.466(9)	1.46(1)
C9-C10	1.45(2)	1.460(9)	1.46(1)	1.46(1)	1.46(1)	1.47(1)	1.470(7)	1.47(1)	1.47(1)
C10-C11	1.46(2)	1.456(8)	1.49(2)	1.49(2)	1.45(1)	1.49(1)	1.490(7)	1.49(1)	1.48(2)
C11-C12	1.45(2)	1.473(9)	1.46(1)	1.46(1)	1.46(1)	1.47(1)	1.462(7)	1.47(1)	1.47(2)
C12-C9	1.48(2)	1.473(8)	1.47(2)	1.47(2)	1.45(1)	1.45(2)	1.474(7)	1.48(1)	1.48(2)

Compound	**Eu-sq**	**Gd-sq**	**Tb-sq**[S1]	**Dy-sq**	**Ho-sq**	**Er-sq**	**Tm-sq**	**Yb-sq**	**Lu-sq**
angle θ / °									
C2-C1-C4	89(1)	89.0(5)	89.2(8)	88(1)	88.9(6)	89.9(8)	89.3(4)	89.1(7)	88.6(9)
C1-C2-C3	90(1)	89.7(5)	89.5(9)	90(1)	89.7(6)	89.3(8)	89.1(4)	89.8(7)	89.5(9)
C2-C3-C4	89(1)	89.6(5)	89.7(8)	90(1)	89.0(6)	89.8(8)	89.3(4)	89.9(7)	89.8(9)
C1-C4-C3	90(1)	90.0(5)	89.7(8)	89(1)	90.0(6)	89.8(8)	89.5(4)	89.1(6)	89.4(9)
C6-C5-C8	89(1)	89.1(4)	88.8(6)	89.0(7)	88.7(5)	89.4(6)	88.1(3)	89.4(5)	88.2(7)
C5-C6-C7	87(1)	88.4(4)	88.9(6)	88.2(8)	88.7(5)	88.7(6)	88.7(4)	89.6(5)	88.5(8)
C6-C7-C8	90(1)	88.5(4)	89.8(6)	89.4(8)	89.3(5)	89.4(6)	89.9(4)	89.8(5)	88.9(8)
C5-C8-C7	89.7(9)	88.8(4)	89.1(6)	89.6(7)	88.6(4)	89.4(6)	88.6(3)	89.4(5)	87.9(7)
C10-C9-C12	89(1)	89.8(4)	89.8(9)	89(1)	89.0(6)	89.6(8)	89.9(4)	89.8(7)	90.0(9)
C9-C10-C11	89(1)	89.3(5)	89.7(8)	89(1)	89.1(6)	89.7(8)	89.7(4)	89.9(6)	89.8(8)
C10-C11-C12	90(1)	89.9(4)	89.5(8)	89(1)	89.2(6)	88.9(8)	89.6(4)	89.3(6)	89.9(9)
C9-C12-C11	90(1)	89.5(4)	89.6(9)	90(1)	89.4(6)	89.1(8)	89.4(4)	89.7(7)	89.9(9)
torsion ϕ / °									
O1-C1-C2-O2	9(3)	-8(1)	7(2)	-3(3)	6(2)	-4.9(8)	7(1)	-8(2)	-6(2)
O2-C2-C3-O3	-10(4)	8(1)	-9(2)	8(3)	-6(2)	5.0(8)	-6(1)	10(2)	8(3)
O3-C3-C4-O4	9(4)	-7(1)	6(2)	-10(3)	7(2)	-4.9(8)	6(1)	-9(2)	-7(2)
O4-C4-C1-O1	6(3)	-7(1)	6(2)	-6(3)	6(2)	-5.0(8)	8(1)	-8(2)	-6(2)
O5-C5-C6-O6	8(3)	-10(1)	8(2)	-10(2)	9(1)	-6.2(6)	9.9(9)	-11(1)	-11(2)
O6-C6-C7-O7	-9(3)	11(1)	-9(2)	11(2)	-11(1)	6.2(6)	-10(1)	12(2)	13(2)
O7-C7-C8-O8	6(3)	-8(1)	10(2)	-7(2)	8(1)	-6.2(6)	9.0(9)	-9(1)	-10(2)
O8-C8-C5-O5	6(3)	-8(1)	9(2)	-6(2)	6(1)	-6.2(6)	9.0(8)	-8(1)	-8(2)
O9-C9-C10-O10	-5(3)	6(1)	-5(2)	4(3)	-5(2)	3.1(8)	-7(1)	5(2)	6(2)
O10-C10-C11-O11	5(3)	-7(1)	6(2)	-7(3)	5(2)	-3.1(8)	6(1)	-5(2)	-7(2)
O11-C11-C12-O12	-3(3)	3(1)	-4(2)	6(3)	-4(2)	3.1(8)	-2(1)	2(2)	5(2)
O12-C12-C9-O9	-4(3)	4(1)	-3(2)	4(3)	-5(2)	3.2(8)	-4(1)	2(2)	4(2)
C4-C1-C2-C3	3(1)	-4.2(5)	4.3(8)	-4(1)	4.9(6)	-7(2)	4.9(4)	-4.1(7)	-4.8(9)
C1-C2-C3-C4	-3(1)	4.3(5)	-4.3(8)	4(1)	-5.1(6)	8(2)	-4.9(4)	4.0(7)	4.9(9)
C2-C3-C4-C1	3(1)	-4.2(5)	4.3(8)	-4(1)	5.0(6)	-6(2)	5.0(4)	-4.1(7)	-4.9(9)
C3-C4-C1-C2	3(1)	-4.2(5)	4.3(8)	-4(1)	5.0(6)	-6(2)	4.9(4)	-4.1(7)	-4.8(9)
C8-C5-C6-C7	6(1)	-5.3(4)	5.7(6)	-6.2(8)	6.2(5)	-9(2)	6.3(3)	-6.1(5)	-5.9(7)
C5-C6-C7-C8	-6(1)	5.4(4)	-5.7(6)	6.3(8)	-6.2(5)	11(2)	-6.2(3)	6.1(5)	5.9(7)
C6-C7-C8-C5	6(1)	-5.4(4)	5.7(6)	-6.3(8)	6.1(5)	-10(2)	6.2(3)	-6.1(5)	-5.8(7)
C7-C8-C5-C6	6(1)	-5.4(4)	5.7(6)	-6.4(8)	6.2(5)	-8(2)	6.3(3)	-6.1(5)	-5.9(7)
C12-C9-C10-C11	-4(1)	3.1(4)	-3.8(8)	3(1)	-3.9(6)	8(2)	-4.1(4)	5.0(6)	4.3(9)
C9-C10-C11-C12	4(1)	-3.1(4)	3.8(8)	-3(1)	3.9(6)	-8(2)	4.1(4)	-5.0(6)	-4.4(9)
C10-C11-C12-C9	-4(1)	3.0(4)	-3.8(8)	3(1)	-3.9(6)	4(2)	-4.1(4)	5.0(6)	4.4(9)
C11-C12-C9-C10	-4(1)	3.0(4)	-3.9(9)	3(1)	-3.9(6)	4(2)	-4.1(4)	5.0(6)	4.4(9)

Compound	**Eu-sq**	**Gd-sq**	**Tb-sq**[S1]	**Dy-sq**	**Ho-sq**	**Er-sq**	**Tm-sq**	**Yb-sq**	**Lu-sq**
Interatomic distance, *d* / Å[a)]									
RE1 - - - RE1[i]	6.4701(6)	6.4454(3)	6.4246(5)	6.4190(5)	6.3984(4)	6.3923(3)	6.3841(2)	6.3785(3)	6.3670(4)
RE1 - - - RE1[ii]	6.5715(6)	6.5563(3)	6.5405(5)	6.5306(5)	6.5117(4)	6.5050(3)	6.4978(2)	6.4928(3)	6.4739(4)
RE2 - - - RE2[iii]	6.5039(6)	6.4859(3)	6.4671(5)	6.4595(5)	6.4386(4)	6.4306(3)	6.4226(2)	6.4177(3)	6.4023(4)
RE2 - - - RE2[iv]	6.5371(6)	6.5151(3)	6.4973(5)	6.4894(5)	6.4709(4)	6.4660(3)	6.4586(2)	6.4539(3)	6.4381(4)
RE1 - - - RE2	6.5620(8)	6.5497(4)	6.5479(6)	6.5229(7)	6.5214(5)	6.5203(4)	6.5133(3)	6.5059(4)	6.4973(5)
RE1 - - - RE1[v]	8.2215(5)	8.1994(4)	8.1820(6)	8.1711(5)	8.1486(5)	8.1407(2)	8.1318(2)	8.1217(2)	8.1066(3)
RE2 - - - RE2[v]	8.2215(5)	8.1994(4)	8.1820(6)	8.1711(5)	8.1486(5)	8.1407(2)	8.1318(2)	8.1217(2)	8.1066(3)

a) Symmetry operation codes of i,ii, iii, iv, and v are (x, 2–y, –1/2+z), (x, 1–y, –1/2+z), (x,1–y, 1/2+z), (x, 2–y, 1/2+z), and (x, 1+y, z), respectively.

Table S3. Continuous shape measures[S2] of the coordination structures in **Eu-sq** – **Lu-sq**.

OP-8	D_{8h}	Octagon
HPY-8	C_{7v}	Heptagonal pyramid
HBPY-8	D_{6h}	Hexagonal bipyramid
CU-8	O_h	Cube
SAPR-8	D_{4d}	Square antiprism
TDD-8	D_{2d}	Triangular dodecahedron
JGBF-8	D_{2d}	Johnson gyrobifastigium J26
JETBPY-8	D_{3h}	Johnson elongated triangular bipyramid J14
JBTPR-8	C_{2v}	Biaugmented trigonal prism J50
BTPR-8	C_{2v}	Biaugmented trigonal prism
JSD-8	D_{2d}	Snub diphenoid J84
TT-8	T_d	Triakis tetrahedron
ETBPY-8	D_{3h}	Elongated trigonal bipyramid

Structure	OP	HPY	HBPY	CU	SAPR	TDD	JGBF	JETBPY	JBTPR	BTPR	JSD	TT	ETBPY
Eu-sq (Eu1)	29.550	23.545	16.294	9.562	0.405	1.570	15.729	27.481	2.257	1.653	4.231	10.398	23.101
Eu-sq (Eu2)	28.642	23.246	17.009	9.619	0.294	1.619	15.769	27.814	2.320	1.874	4.009	10.378	23.771
Gd-sq (Gd1)	29.421	23.360	16.222	9.558	0.375	1.572	15.806	27.486	2.220	1.691	4.128	10.343	23.211
Gd-sq (Gd2)	28.681	23.114	17.142	9.749	0.290	1.633	15.737	27.886	2.322	1.831	4.057	10.543	23.844
Tb-sq (Tb1)	29.365	23.277	16.372	9.683	0.367	1.597	15.834	27.468	2.176	1.698	4.046	10.411	23.301
Tb-sq (Tb2)	28.502	23.193	17.194	9.808	0.292	1.617	15.621	27.727	2.273	1.791	3.990	10.590	23.683
Dy-sq (Dy1)	29.506	23.225	16.383	9.707	0.373	1.629	15.949	27.309	2.245	1.784	4.117	10.465	23.143
Dy-sq (Dy2)	28.723	23.215	17.095	9.723	0.329	1.565	15.465	27.713	2.204	1.755	3.863	10.450	23.785
Ho-sq (Ho1)	29.790	23.190	16.312	9.637	0.434	1.537	15.713	27.404	2.248	1.809	3.973	10.354	23.241
Ho-sq (Ho2)	28.696	23.101	17.155	9.890	0.325	1.560	15.531	27.638	2.225	1.730	3.913	10.687	23.676
Er-sq (Er1)	29.497	23.187	16.384	9.695	0.421	1.500	15.616	27.265	2.222	1.809	3.865	10.399	23.220
Er-sq (Er2)	28.915	23.119	17.111	9.891	0.337	1.579	15.483	27.809	2.240	1.763	3.894	10.655	23.898
Tm-sq (Tm1)	29.621	23.136	16.507	9.800	0.422	1.538	15.525	27.285	2.218	1.813	3.857	10.482	23.285
Tm-sq (Tm2)	28.835	23.166	17.159	9.841	0.329	1.582	15.590	27.621	2.198	1.736	3.885	10.598	23.733
Yb-sq (Yb1)	29.672	23.026	16.480	9.755	0.437	1.496	15.576	27.332	2.238	1.818	3.834	10.449	23.313
Yb-sq (Yb2)	28.870	23.175	17.116	9.986	0.342	1.615	15.441	27.547	2.160	1.711	3.847	10.715	23.764
Lu-sq (Lu1)	30.040	23.067	16.478	9.700	0.492	1.491	15.346	27.257	2.220	1.898	3.733	10.321	23.368
Lu-sq (Lu2)	28.754	23.165	17.219	9.953	0.348	1.558	15.529	27.654	2.131	1.698	3.797	10.703	23.794

Table S4. Geometry for the basal planes (#1 and #2 for Yb1; #3 and #4 for Yb2) in **Yb-sq**.

---------- Plane number 1 ----------

Atoms Defining Plane		Distance	esd
O1	[1; 0; 0; 0]	-0.0673	-
O14	[1; 0; 0; 0]	0.0690	-
O15	[1; 0; 0; 0]	0.0673	-
O3	[1; 0;-1; 0]	-0.0690	-

Least-squares plane
9.22415x + 0.39552y + 5.48608z = 9.96507
(0.00028) (0.00029) (0.00031) (0.00013)

Additional Atoms		Distance	esd
Yb1	[1; 0; 0; 0]	-1.2422	-

Mean deviation from plane is 0.0681 angstrom
Weight scheem: Sigma Weights
Chi-squared: 1856811.720

---------- Plane number 2 ----------

Atoms Defining Plane		Distance	esd
O5	[1; 0; 0; 0]	0.0707	-
O13	[1; 0; 0; 0]	-0.0705	-
O16	[1; 0; 0; 0]	-0.0661	-
O4	[2; 0; 1;-1]	0.0659	-

Least-squares plane
8.78371x + 0.52524y + 5.93517z = 7.27892
(0.00028) (0.00030) (0.00028) (0.00014)

Additional Atoms		Distance	esd
Yb1	[1; 0; 0; 0]	1.2919	-

Mean deviation from plane is 0.0683 angstrom
Weight scheem: Sigma Weights
Chi-squared: 1868905.142

---------- Plane number 3 ----------

Atoms Defining Plane		Distance	esd
O8	[1; 0; 0; 0]	0.0487	-
O18	[1; 0; 0; 0]	-0.0504	-
O19	[1; 0; 0; 0]	0.0489	-
O10	[2; 0; 1; 0]	-0.0472	-

Least-squares plane
9.21990x - 0.01681y + 5.50936z = 6.62986
(0.00026) (0.00030) (0.00029) (0.00014)

Additional Atoms		Distance	esd
Yb2	[1; 0; 0; 0]	-1.2139	-

Mean deviation from plane is 0.0488 angstrom
Weight scheem: Sigma Weights
Chi-squared: 952359.026

---------- Plane number 4 ----------

Atoms Defining Plane		Distance	esd
O9	[1; 0; 0; 0]	0.0751	-
O17	[1; 0; 0; 0]	-0.0749	-
O20	[1; 0; 0; 0]	-0.0730	-
O11	[1; 0;-1; 0]	0.0728	-

Least-squares plane

9.31815x + 0.05167y + 5.39937z = 4.10940

(0.00027) (0.00029) (0.00031) (0.00014)

Additional Atoms		Distance	esd
Yb2	[1; 0; 0; 0]	1.2876	-

Mean deviation from plane is 0.0740 angstrom

Weight scheem: Sigma Weights

Chi-squared: 2188483.073

Dihedral angles between least-squares planes

---

plane	plane	angle	esd
1	2	3.311	-
1	3	2.912	-
1	4	2.509	-
2	3	4.905	-
2	4	5.078	-
3	4	0.895	-

(Note) Symmetry code: [sym. equiv.; x-shift; y-shift; z-shift]

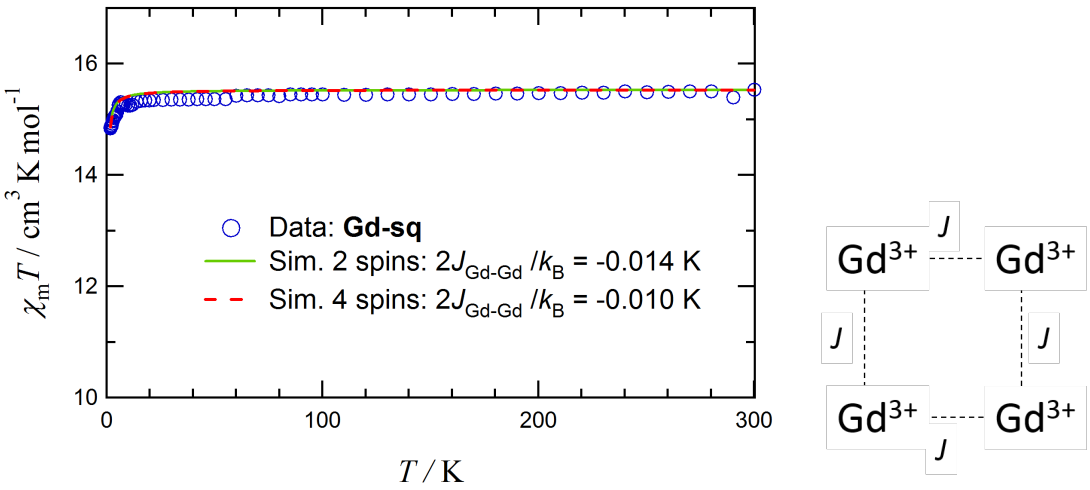
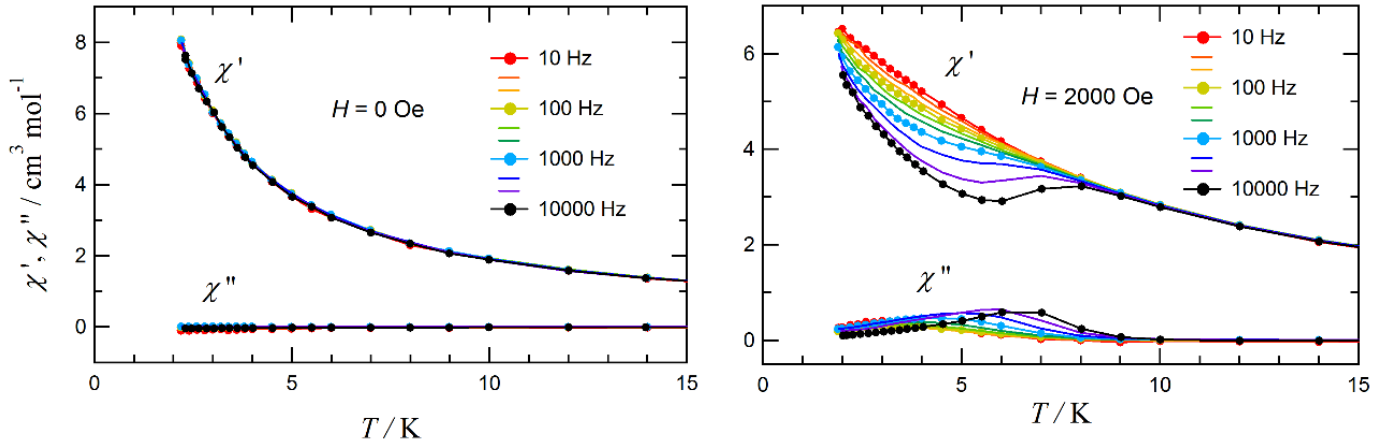
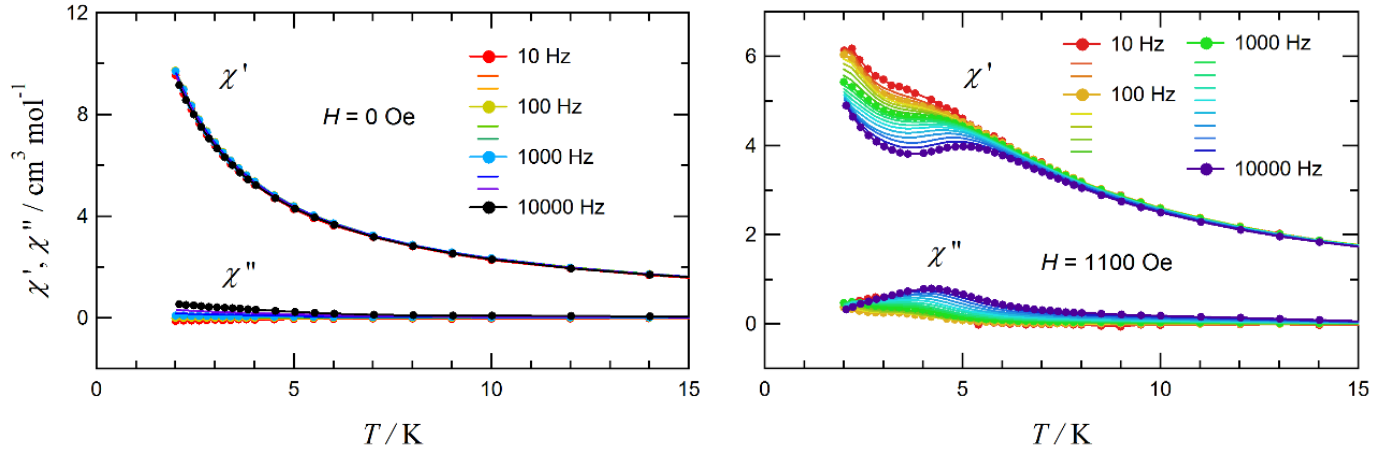


Figure S1. Simulation of the $\chi_m T$ vs T plot for **Gd-sq**. A solid line implies the simulation curve of a dinuclear model $H = -2J_{Gd\text{-}Gd}\, S_1 \bullet S_2$ with $2J/k_B = -0.014$ K and a broken line the simulation curve of a square model $H = -2J_{Gd\text{-}Gd}\,(S_1 \bullet S_2 + S_2 \bullet S_3 + S_3 \bullet S_4 + S_4 \bullet S_1)$ (the right panel) with $2J/k_B = -0.010$ K. Calculation was performed on a Magpack software.[S3]

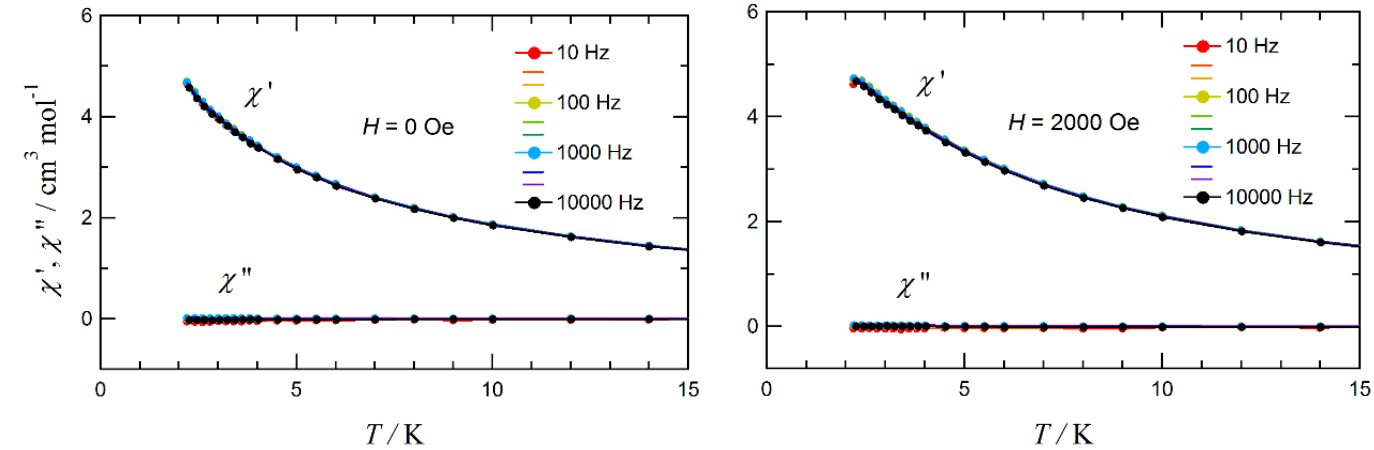
(a)


χ', χ'' / cm3 mol-1
χ'
χ''
H = 0 Oe
H = 2000 Oe
10 Hz
100 Hz
1000 Hz
10000 Hz
T / K

(b)


χ', χ'' / cm3 mol-1
χ'
χ''
H = 0 Oe
H = 1100 Oe
10 Hz
100 Hz
1000 Hz
10000 Hz
T / K

(c)


χ', χ'' / cm3 mol-1
χ'
χ''
H = 0 Oe
H = 2000 Oe
10 Hz
100 Hz
1000 Hz
10000 Hz
T / K

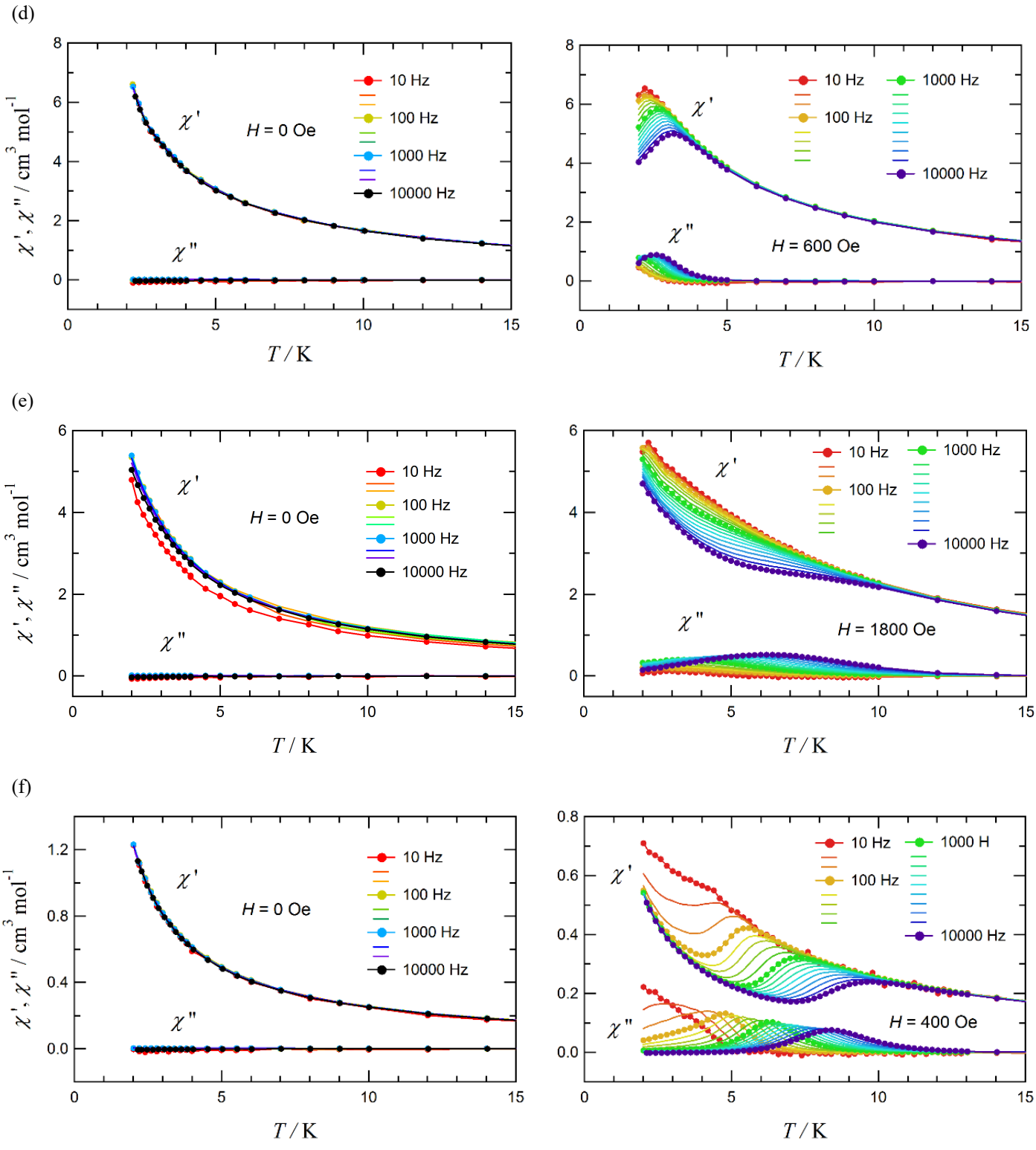


Figure S2. AC magnetic susceptibilities as a function of temperature for **Tb-sq** (a),[S1] **Dy-sq** (b), **Ho-sq** (c), **Er-sq** (d), **Tm-sq** (e), and **Yb-sq** (f). Left panels show the results without any bias field, and right panels with (optimized) applied DC fields, 2000, 1100, 1000, 600, 1800, and 400 Oe, respectively. The applied DC fields were optimized as shown in Figure S3.

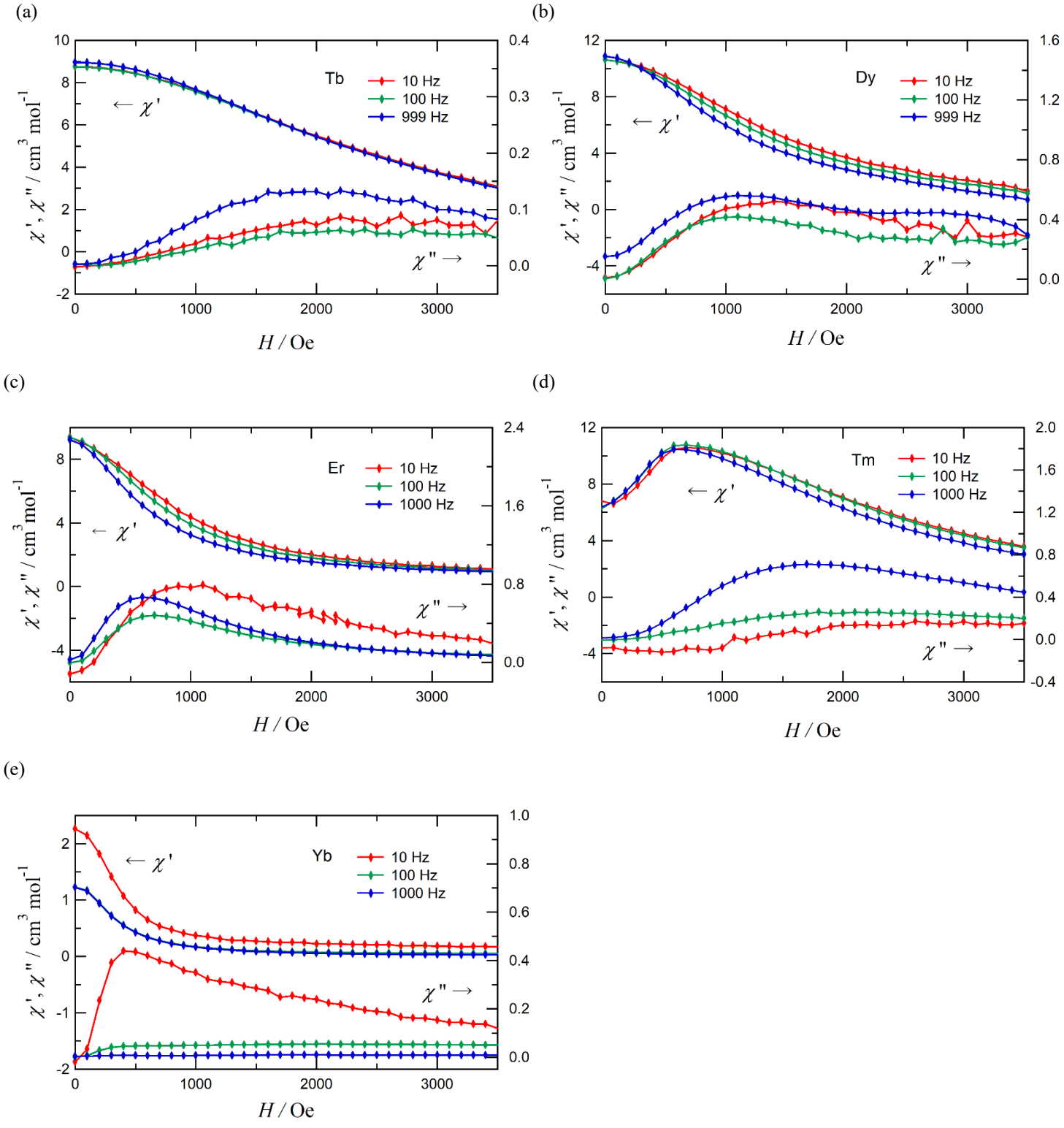


Figure S3. AC magnetic susceptibilities as a variation of a DC bias field for **Tb-sq** (a), **Dy-sq** (b), **Er-sq** (c), **Tm-sq** (d), and **Yb-sq** (e), measured at 2.0 K.

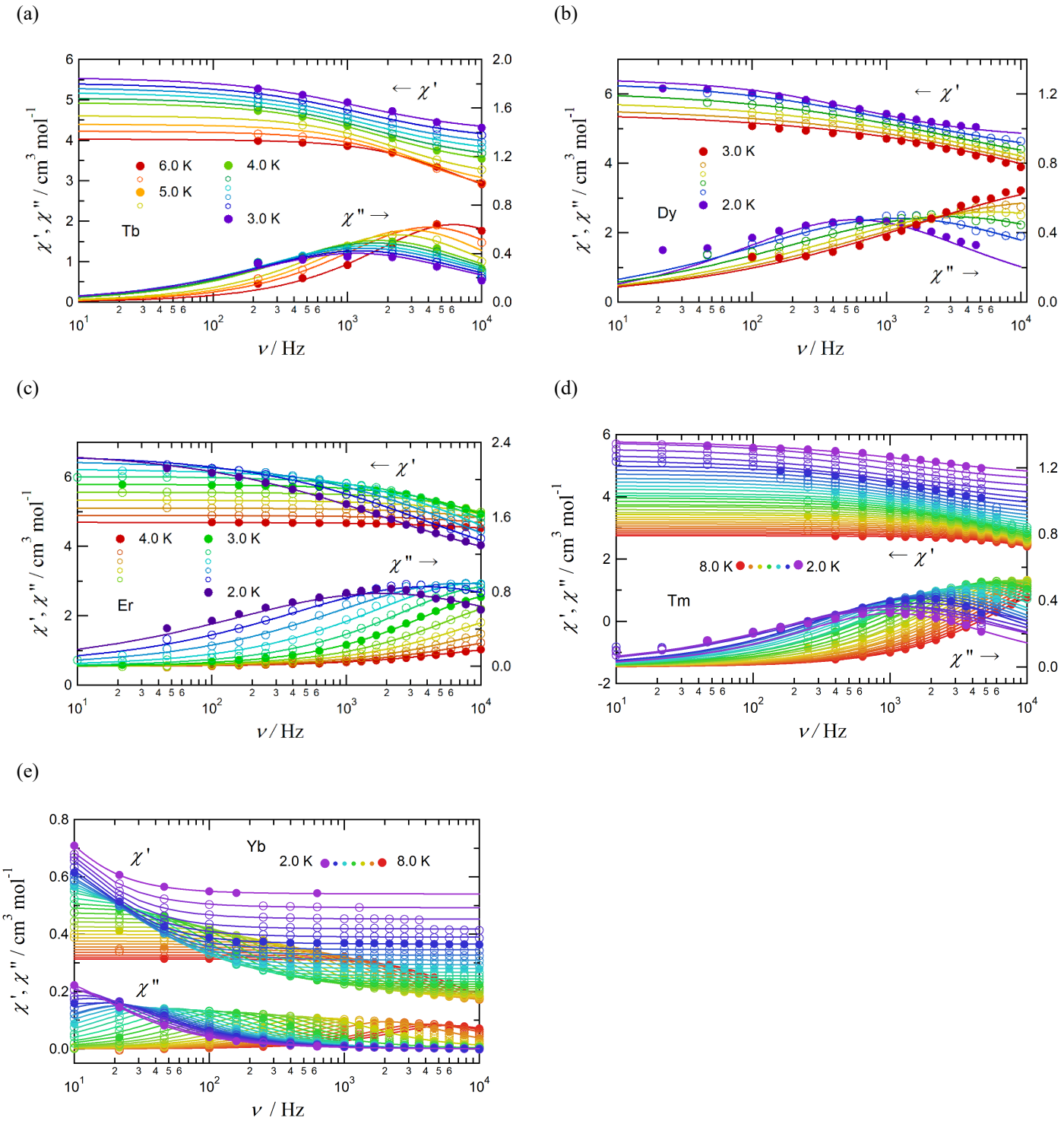


Figure S4. AC magnetic susceptibilities as a function of frequency for **Tb-sq** (a), **Dy-sq** (b), **Er-sq** (c), **Tm-sq** (d), and **Yb-sq** (e). The data were given from Figure S2. Solid lines are drawn according to the generalized Debye model. The optimized parameters are listed in Tables S5a – S5e.

Table S5a. Parameters for the generalized Debye model analysis on **Tb-sq.**

Temp.	χ_T	χ_S	α	τ / 10^{-5}
3.0	5.56(9)	4.16(7)	0.34(7)	13.7(20)
3.2	5.42(7)	3.96(6)	0.34(5)	12.8(15)
3.4	5.31(7)	3.76(6)	0.34(5)	12.0(12)
3.6	5.20(6)	3.60(6)	0.33(4)	11.2(10)
3.8	5.06(6)	3.45(6)	0.31(4)	10.1(9)
4.0	4.94(5)	3.31(5)	0.29(4)	9.2(7)
4.5	4.61(4)	3.03(5)	0.22(3)	6.8(4)
5.0	4.40(3)	2.78(4)	0.20(3)	5.4(2)
5.5	4.22(2)	2.52(5)	0.20(3)	3.9(2)
6.0	4.03(2)	2.32(7)	0.18(3)	2.6(2)

Table S5b. Parameters for the generalized Debye model analysis on **Dy-sq.**

Temp.	χ_T	χ_S	α	τ / 10^{-4}
2.0*	6.46(4)	4.70(4)	0.370(6)	27.1(15)
2.2	6.39(17)	4.1(2)	0.50(2)	12.8(7)
2.4	6.10(19)	3.5(5)	0.54(2)	5.5(6)
2.6	5.82(13)	3.0(4)	0.56(1)	2.6(3)
2.8	5.61(17)	2.2(11)	0.59(2)	1.0(2)
3.0	5.47(4)	1.3(5)	0.60(2)	0.4(2)

*Parameters χ_T, χ_S, and α were given from the Cole-Cole plot.

Table S5c. Parameters for the generalized Debye model analysis on **Er-sq.**

Temp.	χ_T	χ_S	α	τ / 10^{-5}
2.0	6.77(6)	2.95(10)	0.21(2)	8.6(6)
2.2	6.66(3)	2.81(10)	0.47(1)	4.1(3)
2.4	6.45(2)	2.93(12)	0.41(2)	2.5(2)
2.6	6.23(2)	3.03(19)	0.35(2)	1.6(2)
2.8	6.022(9)	3.34(10)	0.28(1)	1.32(10)
3.0	5.793(4)	3.58(6)	0.226(8)	1.08(5)
3.2	5.563(3)	3.63(6)	0.211(9)	0.78(5)
3.4	5.335(4)	3.65(11)	0.23(2)	0.57(8)
3.6	5.109(5)	3.82(17)	0.23(3)	0.52(16)
3.8	4.894(5)	3.88(19)	0.25(5)	0.44(2)
4.0	4.694(2)	4.07(6)	0.25(3)	0.61(10)

Table S5d. Parameters for the generalized Debye model analysis on **Tm-sq.**

Temp.	χ_T	χ_S	α	τ / 10^{-5}
2.0*	5.75(2)	4.77(2)	0.26(3)	15(3)
2.2	5.76(2)	4.41(4)	0.40(2)	15.7(13)
2.4	5.544(15)	4.18(3)	0.37(2)	14.7(9)
2.6	5.35(2)	3.90(5)	0.41(2)	13.0(10)
2.8	5.07(3)	3.81(3)	0.29(3)	10.7(5)
3.0	5.01(2)	3.62(3)	0.32(2)	10.3(5)
3.2	4.88(2)	3.43(4)	0.33(2)	9.3(4)
3.4	4.75(2)	3.28(3)	0.32(2)	8.4(3)
3.6	4.61(2)	3.14(3)	0.31(2)	7.4(3)
3.8	4.49(1)	2.98(3)	0.315(13)	6.4(2)
4.0	4.365(14)	2.87(2)	0.300(13)	5.7(2)
4.2	4.254(12)	2.72(2)	0.294(11)	4.81(11)
4.4	4.124(11)	2.614(16)	0.275(10)	4.22(8)
4.6	4.045(11)	2.48(2)	0.286(11)	3.75(9)
4.8	3.968(11)	2.35(3)	0.295(12)	3.29(11)
5.0	3.862(10)	2.27(3)	0.275(11)	2.96(9)
5.2	3.747(6)	2.242(13)	0.237(7)	2.76(4)
5.4	3.694(9)	2.09(3)	0.269(12)	2.35(10)
5.6	3.591(7)	2.04(3)	0.247(10)	2.16(7)
5.8	3.498(5)	2.01(2)	0.222(7)	2.02(4)
6.0	3.434(6)	1.90(3)	0.240(11)	1.74(7)
6.2	3.342(4)	1.89(2)	0.206(6)	1.66(3)
6.4	3.271(4)	1.82(3)	0.205(9)	1.50(5)
6.6	3.195(2)	1.804(13)	0.187(5)	1.42(2)
6.8	3.131(3)	1.73(3)	0.194(8)	1.26(4)
7.0	3.057(2)	1.740(11)	0.166(4)	1.25(7)
7.2	2.991(2)	1.687(12)	0.162(4)	1.13(2)
7.4	2.931(2)	1.64(2)	0.164(6)	1.03(3)
7.6	2.8655(11)	1.637(12)	0.146(4)	0.99(2)
7.8	2.8056(12)	1.618(14)	0.135(4)	0.93(2)
8.0	2.7497(11)	1.58(2)	0.136(4)	0.85(2)

*Parameters χ_T, χ_S, and α were given from the Cole-Cole plot.

Table S5e. Parameters for the generalized Debye model analysis on **Yb-sq.**

Temp.	χ_T	χ_S	α	τ / 10^{-4}
2.0	1.115(9)	0.5404(6)	0.095(5)	278(6)
2.2	1.013(21)	0.492(1)	0.113(15)	229(14)
2.4	0.948(8)	0.4527(5)	0.109(6)	187(4)
2.6	0.850(7)	0.4182(6)	0.097(8)	139(3)
2.8	0.807(6)	0.3896(5)	0.110(8)	125(3)
3.0	0.758(6)	0.3655(6)	0.102(8)	106(2)
3.2	0.719(4)	0.3457(6)	0.097(7)	89(2)
3.4	0.673(4)	0.3269(6)	0.085(8)	73(1)
3.6	0.662(3)	0.3093(5)	0.098(5)	67.3(9)
3.8	0.631(2)	0.2934(5)	0.090(5)	56.3(7)
4.0	0.604(2)	0.2796(4)	0.075(4)	46.0(4)
4.2	0.582(2)	0.2666(4)	0.070(4)	36.9((3)
4.4	0.600(2)	0.2547(5)	0.052(5)	28.9(3)
4.6	0.5335(9)	0.2439(3)	0.040(3)	21.84(13)
4.8	0.510(2)	0.2343(6)	0.023(6)	16.1(2)
5.0	0.4944(11)	0.2254(4)	0.025(4)	12.16(9)
5.2	0.475(2)	0.2176(9)	0.012(8)	8.85(12)
5.4	0.4572(12)	0.2097(6)	0.011(6)	6.53(6)
5.6	0.4430(10)	0.2021(7)	0.016(5)	4.89(4)
5.8	0.4259(6)	0.1954(5)	0.010(3)	3.62(2)
6.0	0.4116(6)	0.1894(5)	0.008(4)	2.724(15)
6.2	0.3993(5)	0.1835(5)	0.009(4)	2.075(11)
6.4	0.3872(5)	0.1780(6)	0.010(4)	1.596(9)
6.6	0.3756(4)	0.1732(4)	0.007(3)	1.235(5)
6.8	0.3655(3)	0.1688(3)	0.006(2)	0.970(3)
7.0	0.3552(3)	0.1648(3)	0.003(2)	0.767(2)
7.2	0.3462(6)	0.1604(11)	0.008(6)	0.615(5)
7.4	0.3365(4)	0.1563(8)	0.010(4)	0.495(3)
7.6	0.3274(2)	0.1536(4)	0.004(2)	0.4015(13)
7.8	0.3200(2)	0.1502(6)	0.007(2)	0.3277(15)
8.0	0.3128(2)	0.1474(9)	0.010(4)	0.271(2)

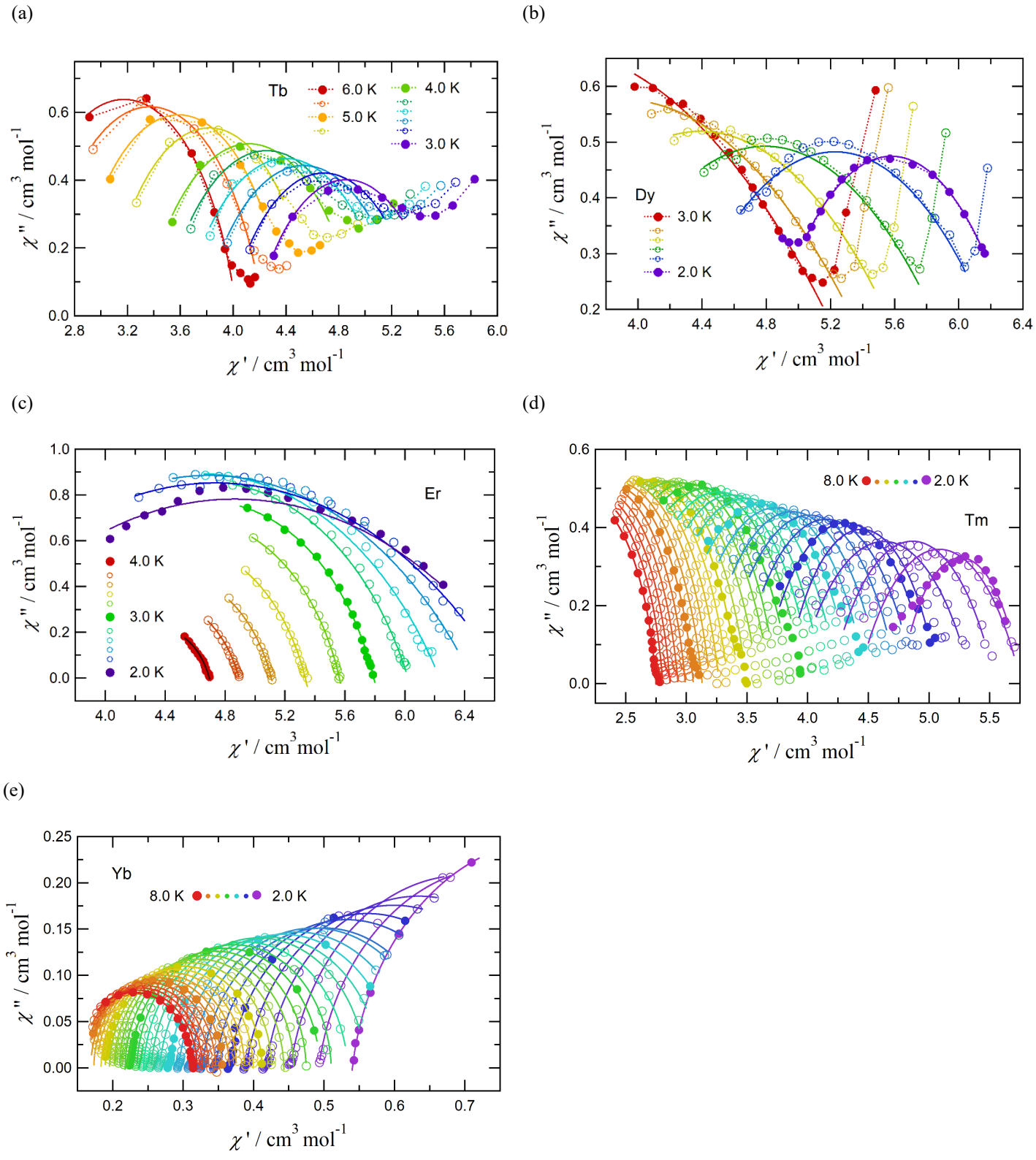


Figure S5. Cole-Cole plots for **Tb-sq** (a),[S1] **Dy-sq** (b), **Er-sq** (c), **Tm-sq** (d), and **Yb-sq** (e). The data were given from Figure S2. For solid lines, see the main text. Dotted lines are drawn for a guide to the eye. The α values are calculated in Figure S4 and listed in Tables S5a – S5e.

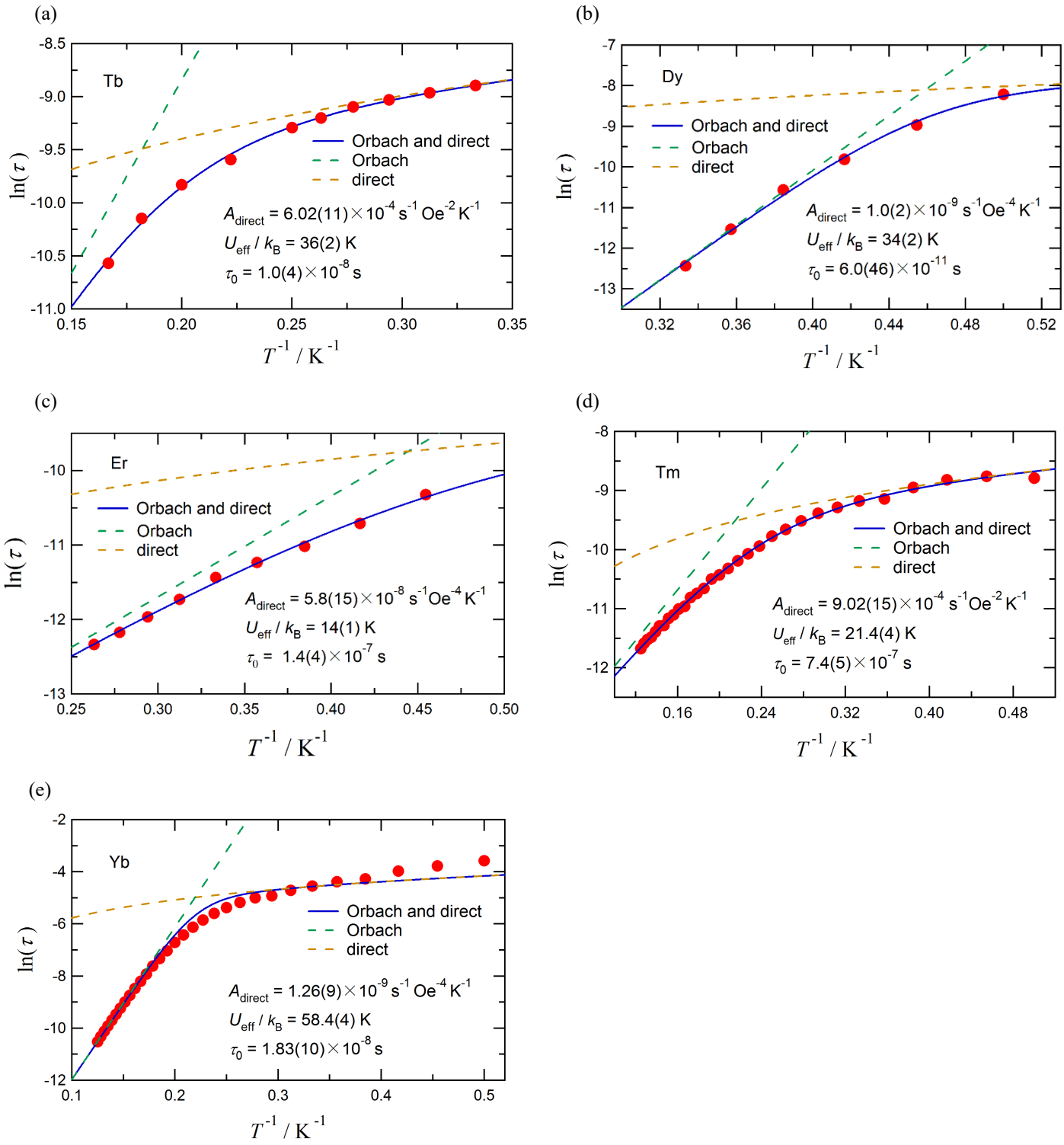


Figure S6. Arrhenius plots for **Tb-sq** (a),[S1] **Dy-sq** (b), **Er-sq** (c), **Tm-sq** (d), and **Yb-sq**. The data were given from Figure S2. Solid lines are drawn as calculation based on the sum of the Orbach and direct terms ($\tau^{-1} = {\tau_0}^{-1} \exp(-U_{\mathrm{eff}}/k_B T) + A_{\mathrm{direct}} H^{n_{\mathrm{direct}}} T$). The optimized parameters are indicated in the figures. For the result of **Tb-sq**, the parameters U_{eff} and τ_0 were different from those of the reference, in which only the Orbach relaxation was applied to the fitting.[S1] For the result of **Yb-sq**, a more satisfactory fit is given by introducing the Raman term (see the main text).

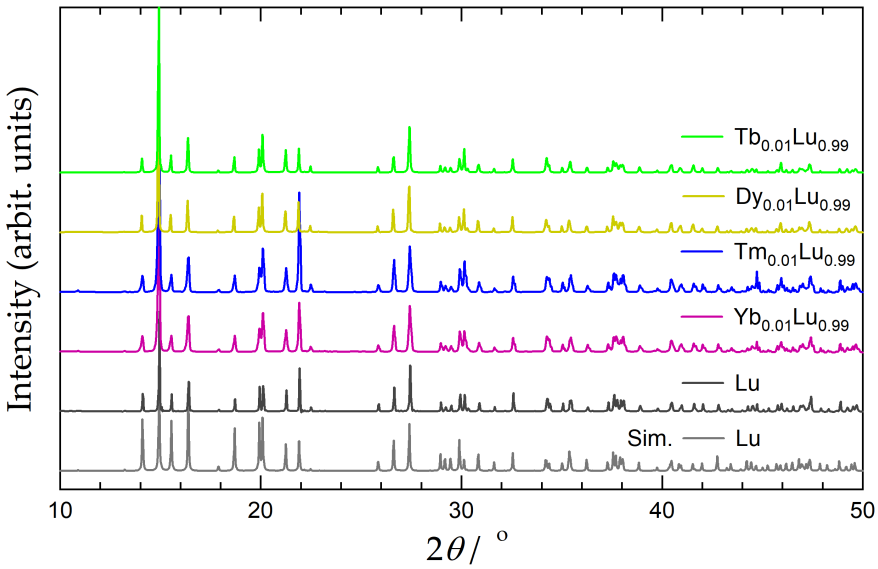


Figure S7. Powder X-ray diffraction patterns for 1% diluted samples **Tb/Lu-sq**, **Dy/Lu-sq**, **Tm/Lu-sq**, and **Yb/Lu-sq**, together with experimental and calculated profiles of **Lu-sq**.

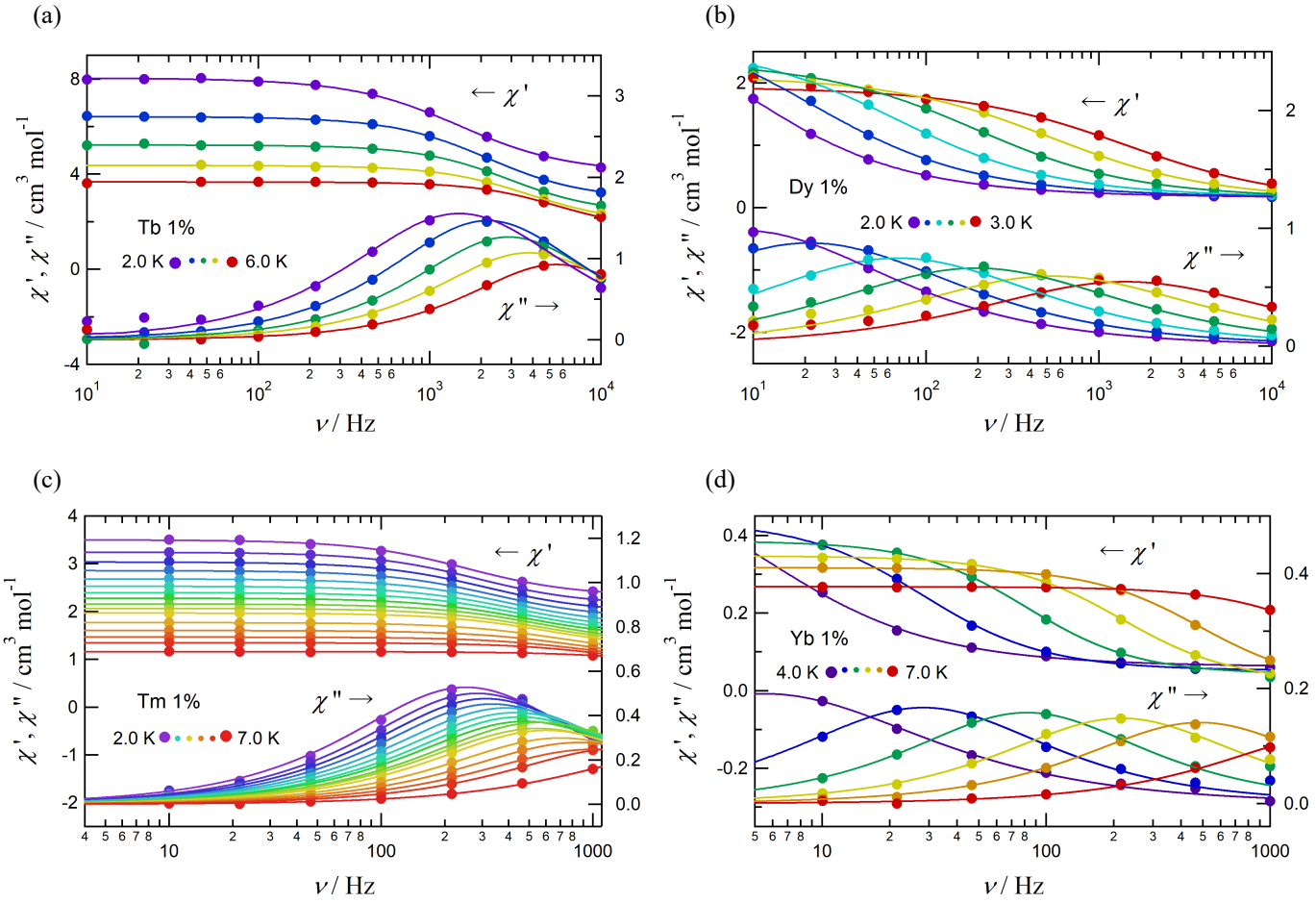


Figure S8. AC magnetic susceptibilities as a function of frequency for 1% diluted samples **Tb/Lu-sq** (a), **Dy/Lu-sq** (b), **Tm/Lu-sq** (c), and **Yb/Lu-sq** (d). Solid lines are drawn according to the generalized Debye model. The optimized parameters are listed in Tables S6.

Table S6. Parameters for the generalized Debye model analysis for **Tb/Lu-sq** (a), **Dy/Lu-sq** (b), **Tm/Lu-sq** (c), and **Yb/Lu-sq** (d).

(a)

Temp.	χ_T	χ_S	α	τ / 10^{-5}
2.0	8.05(4)	4.02(8)	0.16(2)	10.7(5)
3.0	6.422(14)	2.92(4)	0.113(10)	7.29(15)
4.0	5.227(13)	2.34(4)	0.084(12)	5.50(13)
5.0	4.366(8)	1.92(3)	0.084(9)	4.19(7)
6.0	3.671(16)	1.67(7)	0.05(3)	2.89(15)

(b)

Temp.	χ_T	χ_S	α	τ / 10^{-3}
2.0	3.47(6)	0.164(5)	0.320(7)	17.7(8)
2.2	3.18(7)	0.158(12)	0.333(12)	7.5(4)
2.4	2.65(3)	0.158(13)	0.313(11)	2.31(8)
2.6	2.36(2)	0.143(13)	0.315(10)	0.81(2)
2.8	2.12(3)	0.11(2)	0.321(15)	0.298(11)
3.0	19.4(3)	0.07(4)	0.33(2)	0.112(5)

(c)

Temp.	χ_T	χ_S	α	τ / 10^{-4}
2.0	3.502(10)	2.310(18)	0.078(16)	6.33(17)
2.2	3.243(6)	2.134(12)	0.066(11)	5.60(10)
2.4	3.038(6)	1.976(13)	0.069(12)	5.10(10)
2.6	2.858(6)	1.857(15)	0.064(14)	4.77(11)
2.8	2.685(3)	1.700(9)	0.080(8)	4.09(6)
3.0	2.532(4)	1.590(13)	0.083(11)	3.71(8)
3.2	2.3973(18)	1.519(6)	0.069(5)	3.52(3)
3.4	2.281(4)	1.440(12)	0.747(11)	3.33(7)
3.6	2.160(3)	1.324(13)	0.079(11)	2.84(6)
3.8	2.067(3)	1.297(9)	0.0742(9)	2.89(5)
4.0	1.9688(18)	1.229(7)	0.065(7)	2.65(4)
4.5	1.7687(15)	1.101(7)	0.069(7)	2.27(4)
5.0	1.6038(15)	0.975(9)	0.077(8)	1.84(4)
5.5	1.4660(17)	0.913(12)	0.070(12)	1.61(5)
6.0	1.3465(17)	0.789(20)	0.063(15)	1.17(6)
7.0	1.1615(14)	0.61(6)	0.091(22)	0.53(8)

(d)

Temp.	χ_T	χ_S	α	τ / 10^{-3}
4.0	0.61(5)	0.061(4)	0.23(3)	28.4(5)
4.5	0.439(6)	0.051(3)	0.095(15)	5.63(15)
5.0	0.3864(14)	0.0416(16)	0.055(6)	1.939(17)
5.5	0.347(2)	0.021(4)	0.061(13)	0.733(15)
6.0	0.3170(12)	0.013(4)	0.049(10)	0.328(6)
7.0	0.2682(10)	0.002(23)	0.066(26)	0.07(10)

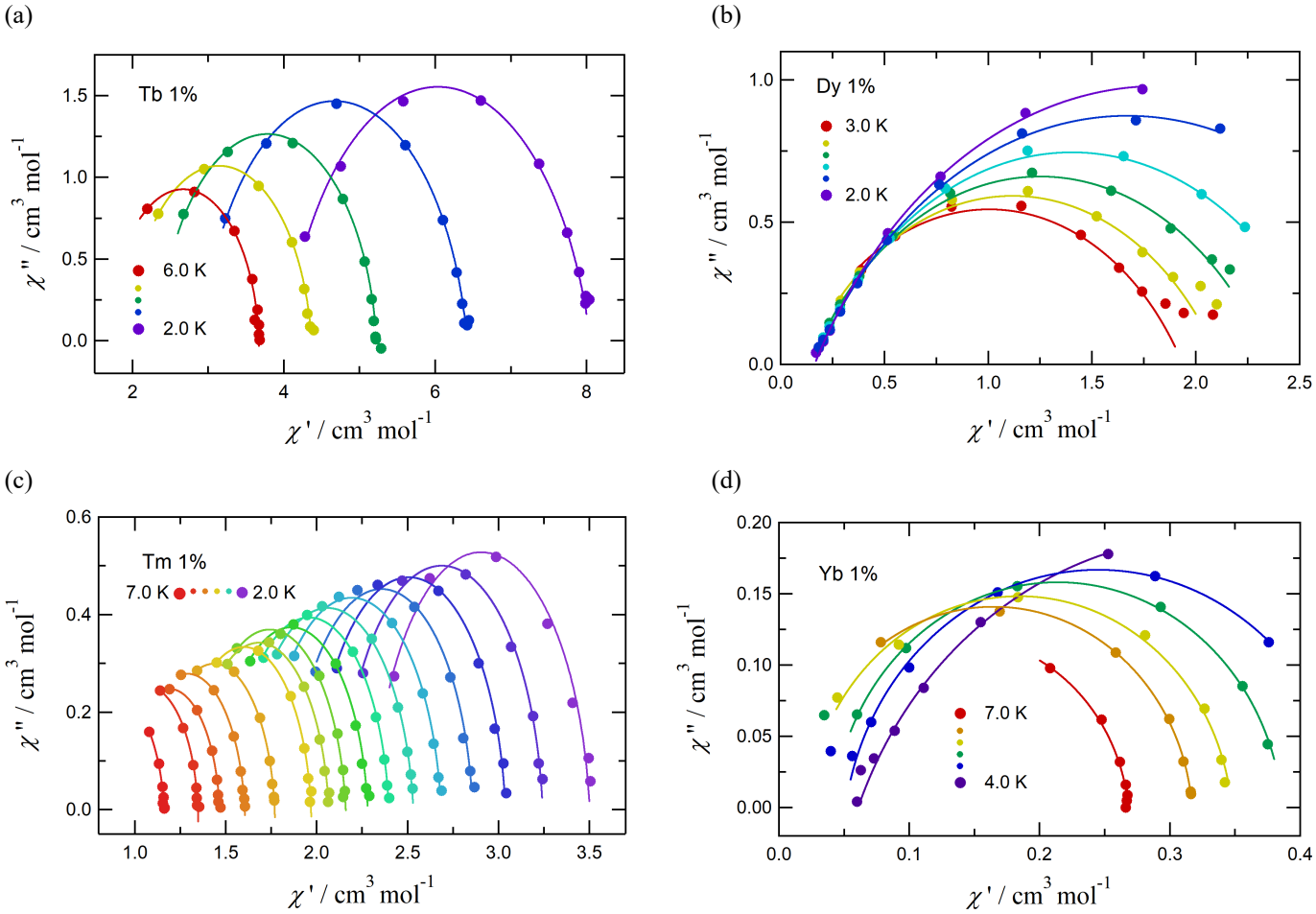


Figure S9. Cole-Cole plots for 1% diluted samples **Tb/Lu-sq** (a), **Dy/Lu-sq** (b), **Tm/Lu-sq** (c), and **Yb/Lu-sq** (d). The data were given from Figure S8. Solid lines are drawn as calculation according to the generalized Debye model (eqn (1) in the main text). The optimized parameters are listed in Tables S6a – S6d.

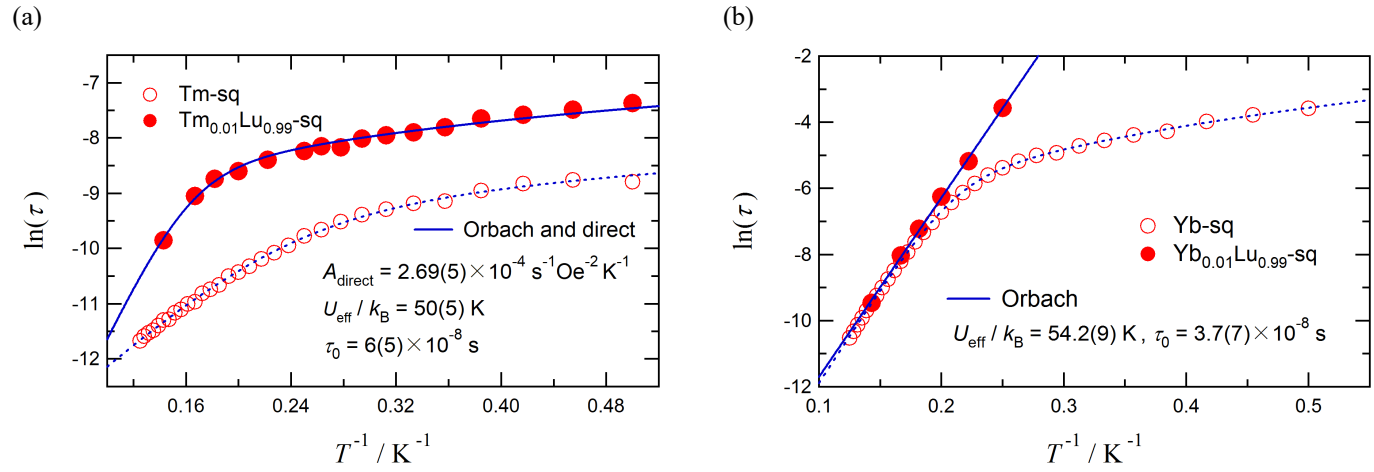
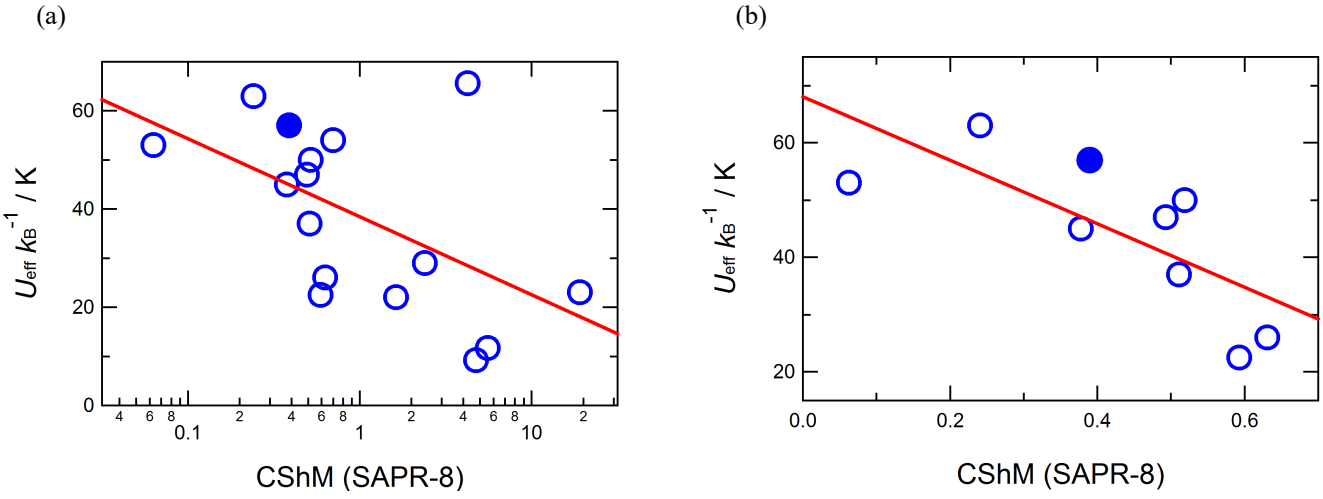


Figure S10. Arrhenius plots for 1% diluted samples **Tm/Lu-sq** (a) and **Yb/Lu-sq** (b). The data were given from Figure S8. The data of undiluted samples are superposed. Solid lines are drawn as calculation based on the equations $\tau^{-1} = {\tau_0}^{-1} \exp(-U_{\mathrm{eff}}/k_{\mathrm{B}}T) + A_{\mathrm{direct}}H^{n_{\mathrm{direct}}}T$ for (a) and $\tau^{-1} = {\tau_0}^{-1} \exp(-U_{\mathrm{eff}}/k_{\mathrm{B}}T)$ for (b). The optimized parameters are indicated in the figures, though the accuracy is limited because of the unsatisfactory signal/noise ratio from diluted samples.



OP	HPY	HBPY	CU	**SAPR**	TDD	JGBF	JETBPY	JBTPR	BTPR	JSD	TT	ETBPY	U_{eff}	Ref.
29.437	23.848	17.595	10.441	**0.241**	2.391	16.597	28.864	2.146	1.648	4.767	11.096	24.734	63	S4
28.882	24.055	16.938	10.697	**0.631**	1.364	14.624	28.377	1.427	1.174	3.349	11.311	24.860	26	S5
29.686	23.225	16.375	10.253	**0.702**	1.354	14.148	27.493	2.303	1.743	3.487	10.843	23.768	54	S6
29.593	23.596	16.486	10.554	**0.519**	1.754	15.187	28.307	1.870	1.104	4.006	11.260	24.294	50	S7
30.679	22.023	15.544	9.055	**0.493**	2.484	16.544	28.633	3.174	2.543	5.566	9.872	24.174	47	S7
32.154	22.075	14.197	10.313	**1.629**	1.757	13.775	25.639	2.608	1.868	4.498	10.994	21.932	22	S7
29.786	22.679	16.048	9.962	**0.511**	2.781	16.232	28.123	2.935	2.568	5.350	10.794	24.090	37	S7
27.734	23.998	17.236	9.766	**0.063**	2.453	16.856	28.668	2.802	2.250	5.187	10.582	24.054	53	S8
28.763	23.650	16.887	10.640	**0.378**	1.909	15.488	28.258	1.882	1.374	4.282	11.397	24.073	45	S9
33.097	23.344	16.970	9.449	**0.593**	2.596	17.541	30.395	3.376	2.792	5.822	10.270	25.874	22.5	S10
33.588	23.818	15.353	13.146	**4.257**	1.740	10.569	28.210	4.001	3.637	3.172	13.387	23.021	65.58	S11
25.485	20.766	13.810	13.926	**5.576**	5.635	9.780	24.467	4.444	3.087	6.623	14.514	18.516	11.7	S12
31.240	24.550	16.635	12.283	**2.393**	2.099	13.726	27.476	1.068	0.475	3.706	12.825	23.600	29	S13
28.703	24.705	13.056	11.906	**4.749**	2.780	9.630	25.324	3.742	3.523	2.314	12.734	22.931	9.2	S14
31.620	22.026	0.584	9.205	**19.158**	16.418	10.710	25.863	18.583	18.226	18.850	10.061	23.148	23	S15
29.271	23.1005	16.798	9.8705	**0.3895**	1.5555	15.5085	27.4395	2.199	1.7645	3.8405	10.582	23.5385	57.0	this work

Figure S11. (a) Correlation between U_{eff} and CShM (in a log scale) referred to SAPR-8. (b) A magnification plot in a small CShM region (in a linear scale) for emphasis on the data from SAPR-8 structures. Literature data[S4-S15] are shown with open circles. The **Yb-sq** data as an averaged value is shown with a filled circle. For the polyhedron symbols, see Figure S3.

Table S7. Cartesian coordinates of the model Tm and Yb complexes used for CASSCF/NEVPT2 calculations.

Tm1 complex				Tm2 complex			
Atom	*x* / Å	*y* / Å	*z* / Å	Atom	*x* / Å	*y* / Å	*z* / Å
Tm	0.000000	0.000000	0.000000	Tm	0.000000	0.000000	0.000000
O	-3.376474	-5.486653	0.397431	O	-4.420741	-3.304922	-0.755092
C	-1.185330	-3.044439	0.939071	C	-1.483678	2.685034	-1.206934
C	-1.084083	-4.522874	0.870723	C	-3.968785	1.196051	2.140460
C	-2.526454	-4.591668	0.707364	O	-3.815443	3.551984	-0.990849
C	-2.631780	-3.160283	0.897316	O	-4.885588	0.340639	2.222214
C	-1.293662	2.834478	-1.464532	C	-1.160740	-3.753454	-1.242042
O	-0.313228	-2.134269	0.899617	C	-1.993354	-2.575984	-0.954881
O	-0.157321	-5.356099	0.856417	C	-3.192719	-3.457059	-0.867044
O	-0.181846	1.922010	1.413425	C	-2.332885	-4.625735	-1.052900
O	-3.569548	-2.296808	0.920905	O	0.030239	-3.939316	-1.594395
O	-1.191821	1.566942	-1.341363	O	-1.790760	-1.345276	-0.855274
O	-3.564405	3.681160	-2.190802	O	-2.522655	-5.866086	-1.119657
O	-1.083452	-1.070400	-1.767814	C	3.103519	-2.548499	0.695794
H	-1.319116	-1.850798	-1.525717	O	-1.434395	1.451943	-0.996496
H	-0.526364	-1.203068	-2.395860	O	-1.748194	0.235684	1.558177
O	-2.115154	0.039956	1.000932	O	2.186716	-3.403911	0.777547
H	-2.797301	-0.506210	0.821740	O	1.013610	-1.445925	-1.517539
H	-2.407344	0.746836	0.845926	H	0.803133	-2.231570	-1.719945
O	1.641131	-0.240111	1.567691	H	1.737316	-1.307486	-1.926652
H	1.954223	-0.958329	1.882844	O	0.054909	-1.873467	1.337568
H	2.028144	0.363344	2.009812	H	0.557730	-2.462683	0.982522
O	1.544680	1.440892	-0.891029	H	-0.711807	-2.243434	1.362684
O	1.625616	-1.406569	-1.065816	C	-1.609597	4.758827	-1.399210
C	2.009298	4.364224	1.955065	C	-2.572498	3.673238	-1.138755
C	2.110546	2.885789	1.886716	C	-3.929623	2.668209	2.182754
C	0.668175	2.816995	1.723357	C	-2.470811	2.632444	2.001843
C	0.562849	4.248380	1.913310	C	-2.534363	1.149994	1.857666
C	-0.373659	3.936609	-1.251525	O	-1.656106	5.993161	-1.416199
C	-1.503726	4.868299	-1.420109	O	-4.798099	3.572759	2.251087
C	-2.381078	3.744805	-1.787179	O	-1.558157	3.487199	1.956406
O	2.881401	5.274394	1.915611	C	-0.585059	3.753581	-1.614319
O	3.037308	2.052564	1.872410	C	3.142680	-1.076341	0.738087
O	-0.374920	5.111855	1.936899	C	4.601493	-1.112105	0.557176
O	0.836922	4.049586	-1.032985	C	4.537941	-2.594555	0.413000
O	-1.725040	6.095931	-1.260637	O	0.611978	3.798243	-2.058500
H	2.388199	1.349096	-0.843302	O	2.274205	-0.171791	0.806420
H	1.424806	2.281053	-0.945637	O	5.514147	-0.257350	0.511739
C	3.807294	-2.623910	-1.112064	O	0.576685	1.879030	1.310608
C	4.942324	-1.704901	-0.851637	H	-0.129035	2.231292	1.638998
C	4.010454	-0.589790	-0.852640	H	1.032908	1.655389	2.004428
C	2.894348	-1.502506	-0.984148	O	1.318916	1.278293	-1.444865
O	3.762539	-3.840025	-1.443108	H	2.032511	1.052385	-1.828774
O	6.180882	-1.815040	-0.766782	H	1.173724	2.060432	-1.720367
O	4.093905	0.680035	-0.865699	O	5.324110	-3.508865	0.113511
H	-2.918632	-6.346857	0.319149	H	-3.475637	-6.049707	-0.989947
H	3.765395	4.863376	1.842996	H	-2.566293	6.299197	-1.235068
H	-0.993099	6.499500	-0.750901	H	-4.405565	4.427701	1.988190
H	6.584942	-0.932151	-0.645340	H	6.226377	-3.151340	-0.010031

Yb1 complex				Yb2 complex			
Atom	*x* / Å	*y* / Å	*z* / Å	Atom	*x* / Å	*y* / Å	*z* / Å
Yb	0.000000	0.000000	0.000000	Yb	0.000003	0.000000	-0.000001
O	-2.394538	-3.392190	0.893208	O	-6.078218	-1.879715	-0.469572
O	1.794396	-5.777112	-1.744725	O	2.400831	-2.893175	2.198809
O	-0.611392	-3.635176	-1.809832	O	-1.525161	-1.652827	-0.894092
O	3.969603	-3.333355	-1.777879	O	-3.671912	-4.085899	-0.734070
O	2.281704	-3.400307	1.154217	O	1.142494	-1.641197	-1.249982
O	5.521057	-2.983779	1.446991	H	1.863819	-1.308737	-1.584016
H	-0.708777	-2.622609	0.945290	H	0.696663	-1.894332	-1.950934
H	0.619049	-2.568462	1.012154	O	0.054203	-1.825489	1.442629
C	1.758869	-4.525206	-1.808922	H	-0.618473	-2.161913	1.816104
C	0.637643	-3.565547	-1.780499	H	0.704884	-2.105553	1.898042
C	1.584215	-2.472488	-1.638120	C	3.162771	-1.950259	1.807566
C	2.683907	-3.410777	-1.768851	C	-2.773630	-1.744458	-0.891227
C	3.057244	-2.441285	1.358409	C	-3.747621	-2.840837	-0.784132
C	4.506607	-2.276939	1.569360	C	-4.858113	-1.849428	-0.696418
C	4.292957	-0.865406	1.902014	O	5.583536	-2.541051	1.734125
O	-5.412793	0.001183	1.335439	O	5.923907	1.418671	-1.913603
O	-5.622559	-3.151963	0.708051	O	3.777150	-1.014403	-1.753581
C	-4.565205	-0.876293	1.045125	C	4.598291	-1.773908	1.673271
C	-4.685649	-2.329734	0.817302	C	4.384876	-0.343787	1.388037
C	-3.237448	-2.446211	0.831242	C	4.675422	1.327039	-1.910737
C	-3.124913	-1.004252	0.953268	C	3.701440	0.230664	-1.803643
O	-1.302082	1.689163	-0.951887	C	2.590939	1.222070	-1.715926
O	-3.707871	3.831099	-1.016995	O	-3.137394	2.471402	1.420515
O	1.523573	-1.239807	-1.344804	O	0.052364	2.238750	0.850160
O	0.873124	4.132919	-0.985042	O	-2.977327	5.675926	0.947829
O	1.913645	-0.194285	1.389736	C	-2.221165	3.272348	1.127112
O	5.051461	0.035490	2.312496	C	-0.771231	3.175439	0.902457
O	-0.063299	1.559209	1.732250	C	-0.680943	4.661972	0.825829
H	-0.798279	2.004623	1.705703	C	-2.149662	4.738721	0.923669
H	-0.096258	1.151611	2.488423	O	1.965235	0.165344	1.100688
O	1.515094	1.466860	-1.000948	O	1.370851	1.191782	-1.489083
H	2.331088	1.404384	-0.628465	O	-3.966302	0.479124	-1.010766
H	1.307920	2.331450	-0.850261	O	-1.836170	0.143217	1.403296
O	-1.281087	-1.036463	-1.575821	H	-2.362094	0.758556	1.620858
H	-1.913982	-0.691479	-2.013373	H	-2.171646	-0.551730	1.743473
H	-1.058099	-1.707566	-2.030890	O	-1.396286	1.131453	-1.418010
O	-0.065022	-2.084510	0.938004	H	-2.198186	1.125447	-1.109723
C	-1.337610	2.941069	-1.016085	H	-1.194610	1.967508	-1.437114
C	-2.458836	3.900728	-0.987662	C	-3.886534	-0.766443	-0.932568
C	-1.512264	4.993787	-0.845282	O	0.224929	5.508287	0.761703
C	-0.412571	4.055498	-0.976013	O	5.095512	0.669747	1.281087
C	2.879678	-1.011053	1.539423	O	3.482760	3.550620	-2.030276
O	-2.159393	-0.154818	1.026219	C	2.936361	-0.568121	1.373420
O	-1.572906	6.226468	-0.551967	C	3.562528	2.305057	-1.952078
H	-6.476697	-2.682290	0.803279	H	6.406841	-2.035783	1.589207
H	5.302753	-3.801313	0.953736	H	-3.879409	5.319754	1.073436
H	0.882180	-6.120270	-1.666489	H	6.320867	0.575785	-1.618464
H	-2.511819	6.495045	-0.500293	H	-6.379092	-2.805426	-0.367724

Table S8. Calculated excitation energies of each m_J state. The active space for the CASSCF/NEVPT2 calculation is "12 electrons,7 orbitals (CAS(12,7))" and "15 electrons, 8 orbitals (CAS(15,8))" for the Tm (a) and Yb complexes (b), respectively, as explained in Figure S11. For Tm complexes, the tendency of energy levels obtained from CASSCF/NEVPT2 are comparable and the value of energy calculated with CASSCF are 10 - 20% smaller than NEVPT2 (c). We note that NEVPT2 cannot estimate the excitation energies of Yb complexes (d).

(a)

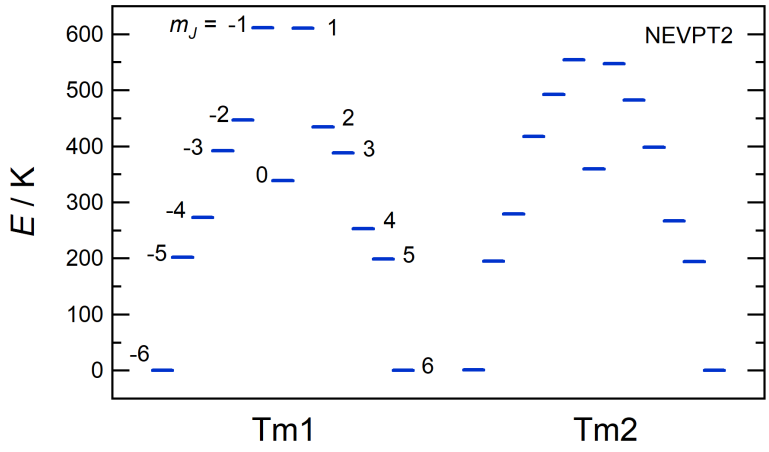
CASSCF	Tm1	Tm2
m_J	Energy / cm^{-1}	
6	0	0
-6	0.20	0.37
5	131.32	107.92
-5	132.17	108.19
4	190.76	191.50
-4	199.82	197.61
0	234.11	238.97
3	263.68	263.31
-3	266.81	267.14
2	287.13	305.81
-2	294.61	310.68
1	363.86	337.24
-1	364.03	342.58

(b)

CASSCF	Yb1	Yb2
m_J	Energy / cm^{-1}	
7/2	0	0
-7/2	0	0
5/2	170.09	152.20
-5/2	170.09	152.20
3/2	236.45	238.31
-3/2	236.45	238.31
1/2	333.16	311.15
-1/2	333.16	311.15

(c)

NEVPT2	Tm1	Tm2
m_J	Energy / cm^{-1}	
6	0	0
-6	0.22	0.51
5	138.28	135.09
-5	140.42	135.31
4	175.67	185.39
-4	189.73	193.69
0	235.23	249.42
3	269.56	276.74
-3	272.25	289.90
2	301.51	335.16
-2	310.26	341.89
1	424.16	380.19
-1	424.74	384.86



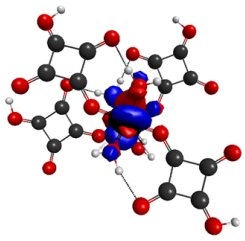
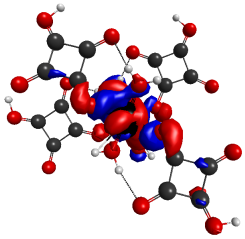
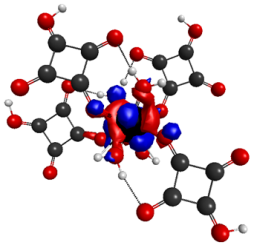
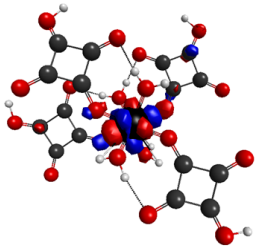
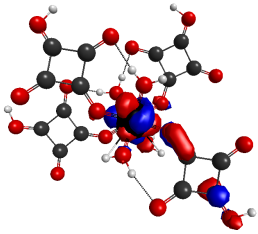
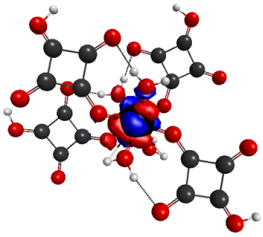
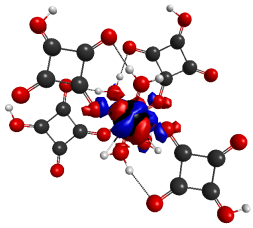
(d)

NEVPT2	Yb1	Yb2
m_J	Energy / cm^{-1}	
7/2	0	0
-7/2	0	0
5/2	47415.59	52246.01
-5/2	47415.59	52246.01
3/2	47700.67	52511.71
-3/2	47700.67	52511.71
1/2	47755	52604.47
-1/2	47755	52604.47

Table S9. Calculated *g*-values of each Kramers Doublet (KD). The active spaces for the Tm and Yb complexes are (12,7) and (15,8), respectively, as explained in Figure S12. We note that the CASSCF result of $m_J = \pm 7/2$ suggests that larger active space is necessary for the calculation of the higher KDs on the Yb complex (See Figure S12).

	Tm1 complex			Tm2 complex		
KD	g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}
$m_J = \pm 6$	0.00	0.00	13.86	0.00	0.00	13.85
±5	0.00	0.00	13.19	0.00	0.00	13.82
±4	0.00	0.00	10.12	0.00	0.00	10.82
±3	0.00	0.00	8.66	0.00	0.00	7.64
±2	0.00	0.00	5.17	0.00	0.00	2.25
±1	0.00	0.00	3.09	0.00	0.00	2.97

	Yb1 complex			Yb2 complex		
KD	g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}
$m_J = \pm 7/2$	0.45	0.53	7.14	0.08	0.24	7.05
±5/2	0.41	0.58	7.80	1.09	1.35	7.05
±3/2	1.24	2.33	4.22	0.64	1.28	4.67
±1/2	1.01	2.10	6.66	1.11	2.50	6.30

(a) Tm1 complex			
163		164	
165		166	
167		168	
169			

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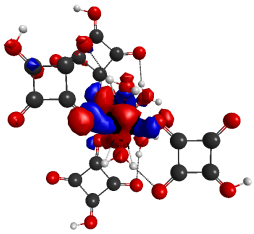
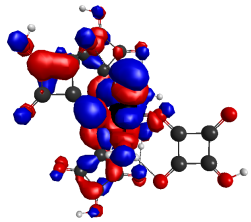
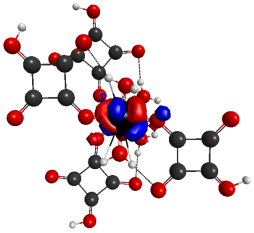
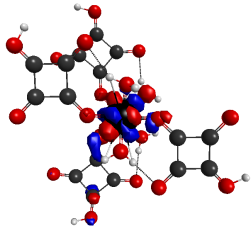
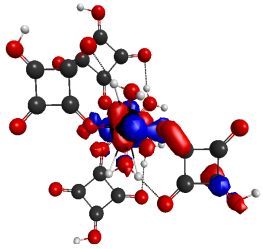
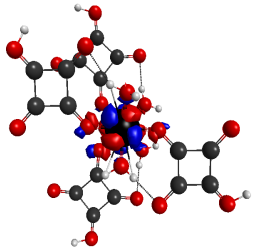
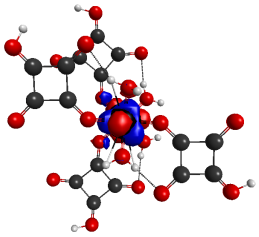
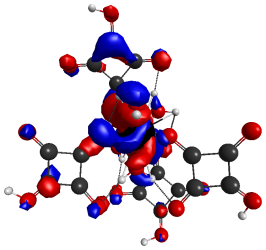
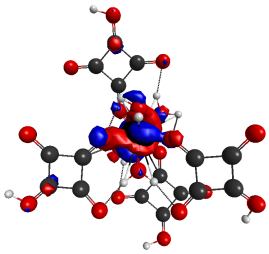
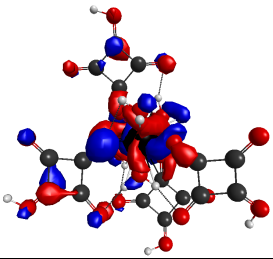
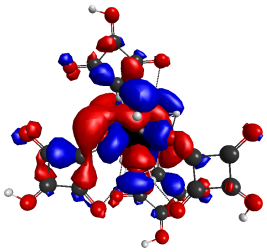
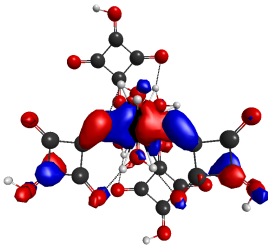
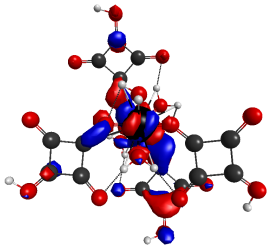
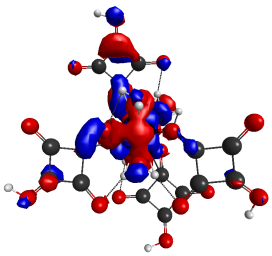
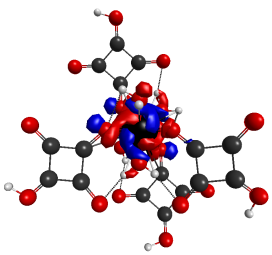
163		164	
165		166	

167		168	
169			

(c) Yb1 complex			
162		163	
164		165	
166		167	
168		169	

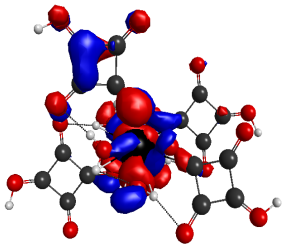
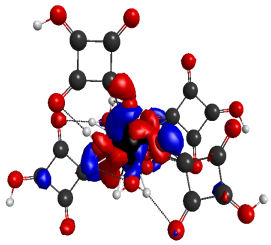
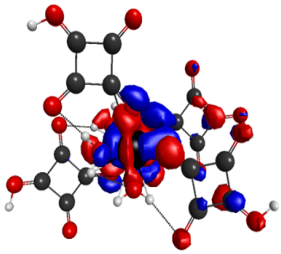
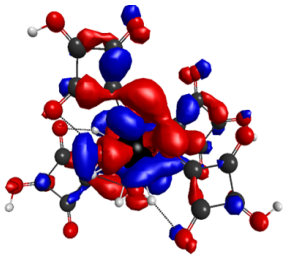
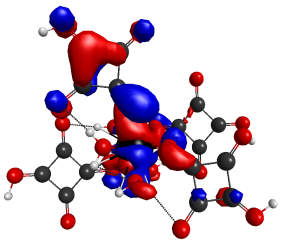
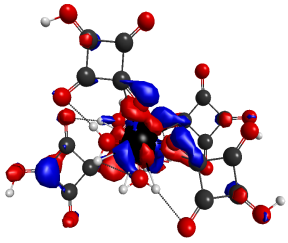
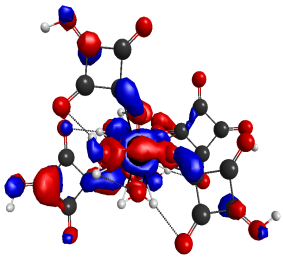
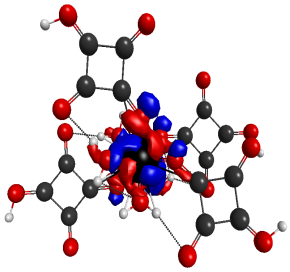
(d) Yb2 complex			
162		163	
164		165	
166		167	
168		169	

Figure S12. (a) Seven natural orbitals used for the CASSCF/NEVPT2 calculation of the Tm1 complex. (b) Seven natural orbitals used for the CASSCF/NEVPT2 calculation of the Tm2 complex. (c) Eight natural orbitals used for the CASSCF/NEVPT2 calculation of the Yb1 complex. Orbital #165 is strongly hybridized with ligand orbitals. (d) Eight natural orbitals used for the CASSCF/NEVPT2 calculation of the Yb2 complex. Orbital #165 is strongly hybridized with ligand orbitals.

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