Supporting information to

Spectroscopic Determination of Crystal Field Splittings in Lanthanide Double Deckers

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Contents

1. Syntheses and analytical data

$(NBu_4)^+[DyPc_2]^-$ ·2 dmf (1Dy). Dysprosium acetate hydrate (0.823 g, 2 mmol) and 1,2-dicyanobenzene (2.56 g, 20 mmol) were added to dry 1-pentanol (15 ml) and heated to 100 °C while stirring. Then 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 1 ml) was added to the solution and the reaction mixture heated under reflux (140 °C) for 4 h. During this time, the colour changed from yellow to green and finally to blue as the double decker forms. After 4 h, the reaction mixture was cooled to room temperature, and the solvent removed under reduced pressure. Polymeric impurities were removed by washing with hexane; free phthalocyanine was removed by filtering a N,N-dimethylformamide (dmf) solution of the crude product. The solution was concentrated and 1 mL of hydrazine hydrate was added to obtain the anionic double decker species. The product was further purified by means of column chromatography (alumina) using pure dmf as eluent. After evaporating all the suitable fractions, an excess of NBu_4Br in dmf with added hydrazine hydrate (to prevent oxidation) was added, and the product purified by a second column (alumina/dmf). Finally, the product was recrystallized by slow evaporation of a dmf solution. The crystals were collected by filtration, followed by washing with hexane. Yields of up to 20% were obtained by using this procedure.

$(NBu_4)^+[HoPc_2]^-$ ·2 dmf (1Ho). and **$(NBu_4)^+[ErPc_2]^-$ ·2 dmf (1Er)**. were prepared analogously.

Analytical data:

1Dy:
^{1}H NMR (250 MHz, CD_3CN) δ (ppm): -41.4(bs, H_α), -17.9 (bs, H_β).
IR (KBr) $\tilde{\nu}$ (cm^{-1}): 728, 809, 883, 1060, 1078, 1113, 1159, 1329, 1384, 1481, 1608.
UV/Vis (in DMF): 332, 621, 682 nm.
MALDI-TOF MS m/z: (M-) anal.calcd. for ($[Dy(C_{32}H_{16}N_8)_2]^-$) 1188.23, found 1188.3 (negative ionisation)
Elemental analysis anal. calcd. for ($[Dy(C_{32}H_{16}N_8)_2]^-$ $[NBu_4]^+$ · 2 dmf) C = 65.53 %, H = 5.24 %, N = 16.88 %, found C = 67.07 %, H = 5.19 %, N = 16.00 %.

1Ho:
^{1}H NMR (250 MHz, CD_3CN) δ (ppm):-5.63 (bs, H_α), 0.32 (bs, H_β).
IR (KBr) $\tilde{\nu}$ (cm^{-1}): 434, 497, 562, 626, 727, 740, 773, 809, 883, 948, 1003, 1059, 1077, 1112, 1159, 1281, 1328, 1381, 1404, 1456, 1481, 1585, 1605, 1672.
UV/Vis (in DMF): 334, 625, 692.
MALDI-TOF-MS m/z: (M-) anal.calcd. for ($[Ho(C_{32}H_{16}N_8)_2]^-$) 1189.23, found 1189.72. (negative ionisation).
Elemental analysis anal. calcd. for ($[Ho(C_{32}H_{16}N_8)_2]^-$ $[NBu_4]^+$ · 2 dmf) C = 65.43 %, H = 5.24 %, N = 16.86 %, found C = 66.13 %, H = 5.036 %, N = 16.56 %.

1Er:
^{1}H-NMR (250 MHz, CD_3CN) δ (ppm) = 34.78 (bs, H_α), 21.08 (bs, H_β), 8.02 (bs, 2 H), 1.36 (m), 1.17 (bs), 0.97 (m), -0.16 (bs), -0.50 (bs).
IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 729, 741, 774, 810, 884, 948, 1002, 1060, 1080, 1110, 1160, 1280, 1310, 1330, 1380, 1400, 1450, 1480, 1580, 1605.
UV/Vis (in DMF) λ (nm) = 332, 619, 679.
MALDI-TOF-MS m/z: (M-) anal.calcd. for ($[Er(C_{32}H_{16}N_8)_2]^-$) 1192.32, found 1191.68 (negative ionisation).
Elemental analysis anal. calcd. for ($[Er(C_{32}H_{16}N_8)_2]^-$ $[NBu_4]^+$ · 2 dmf) C = 66.73 %, H = 5.04 %, N = 16.54 %, found C = 64.66 %, H = 4.63 %, N = 16.08 %.

2. Crystallography

Table S 1 Crystal structure and refinement parameters for **1Dy**, **1Ho**, **1Er**.

	$(NBu_4)[DyPc_2]\cdot 2$ dmf (**1Dy**)	$(NBu_4)[HoPc_2]\cdot 2$ dmf (**1Ho**)	(NBu_4) $[ErPc_2]\cdot 2$ dmf (**1Er**)
CCDC number	996593	996594	996595
formula	$C_{86}H_{82}DyN_{19}O_2$	$C_{86}H_{82}HoN_{19}O_2$	$C_{86}H_{82}ErN_{19}O_2$
fw	1576.21	1578.64	1580.97
T (K)	110(2)	110(2)	100(2)
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
a (Å)	11.6002(6)	11.5698(8)	11.5308(9)
b (Å)	15.3265(8)	15.3429(12)	15.2909(12)
c (Å)	22.3436(12)	22.3337(17)	22.2700(18)
α (deg)	92.480(3)	92.514(4)	92.524(4)
β (deg)	95.186(2)	95.132(4)	95.122(4)
γ (deg)	109.408(2)	109.356(4)	109.342(4)
V (Å^3)	3720.0(3)	3714.1(5)	3678.8(5)
Z	2	2	2
ρ_{calc} (Mg/m^3)	1.407	1.412	1.427
μ (mm^{-1})	1.069	1.130	1.206
$R1$ [I>2σ(I)]	0.0286	0.0266	0.0350
$R1$(all data)	0.0358	0.0341	0.0442

Table S 2 Comparison between metal-ligand bond distances and relevant planes between $(NBu_4)[HoPc_2]\cdot 2$ dmf **(1Ho)** and $(NBu_4)[HoPc_2]\cdot H_2O$ (Ref 1)

	$(NBu_4)[HoPc_2]\cdot 2$ dmf (T = 110 K)	$(NBu_4)[HoPc_2]\cdot H_2O$ (T = 296 K)
Ho-N_{iso} (1) (Å)	2.397	2.407
Ho-N_{iso} (2) (Å)	2.401	2.407
Ho-N_{iso} (3) (Å)	2.422	2.407
Ho-N_{iso} (4) (Å)	2.406	2.407
Ho-N_{iso} (5) (Å)	2.402	2.424
Ho-N_{iso} (6) (Å)	2.416	2.424
Ho-N_{iso} (7) (Å)	2.427	2.424
Ho-N_{iso} (8) (Å)	2.430	2.424
average Ho-N_{iso} (Å)	2.413 ± 0.012	2.416 ± 0.009
Angle between two N_4 planes	0.59°	0
Angle between N-Ho-N planes (skew angle)	45.0 ± 1.1	43.0

3. Calculational details

All calculations were done with MOLCAS 7.8 and are of CASSCF/RASSI/SINGLE_ANISO type.

Two basis set approximations have been employed: **1** – small, **2** – large; Table S3 shows the contractions of the employed basis sets for all elements.

Table S 3 Contractions of the employed basis sets.

Basis 1	**Basis 2**
Ln.ANO-RCC...7s6p4d2f1g.	Ln.ANO-RCC...8s7p5d4f2g1h.
N.ANO-RCC...3s2p.	N.ANO-RCC...4s3p1d.
C.ANO-RCC...3s2p.	C.ANO-RCC...4s3p1d. (close)
H.ANO-RCC...2s.	C.ANO-RCC...3s2p. (distant)
	H.ANO-RCC...2s.

The active space of the CASSCF method included the electrons from the last shell spanning the 7 orbitals (4*f* orbitals of the Ln^{3+} ion).

For the Er compound all spin states were allowed to mix by spin orbit coupling, while for Dy and Ho only a limited number of roots were allowed to mix.

On the basis of the resulting spin-orbital multiplets the SINGLE_ANISO program computed local magnetic properties (*g*-tensors, main magnetic axes, local magnetic susceptibility, Crystal-Field parameters for the ground atomic multiplet, etc.)

In order to take into account the effect of neighbouring molecules, five layers of point charges were added to the molecular structure. One point charge was placed at the position of each atom in the crystal, while its value corresponded to the previously calculated Mulliken charge for this specific atom obtained in the corresponding CASSCF calculation. All atoms were considered within 5 crystallographic shells of unit cells, in all directions of the crystal.

An investigation of the influence of small distortions of the molecule on the calculated energy spectrum was performed for **1Dy**, **1Ho**, and **1Er**. As a model distortion, we have used a movement of the entire (Pc) ligands along the line connecting the centers of both Pc ligands towards each other. In other words, the negative distortion corresponds to a small "compression" of the molecule, while the positive distortion is an "expansion" of the molecule along the line connecting the centers of the Pc ligands. Basis 1 (DZP-quality) was employed for these calculations.

4. $(NBu_4)^+[DyPc_2]^-$ ·2 dmf (1Dy)

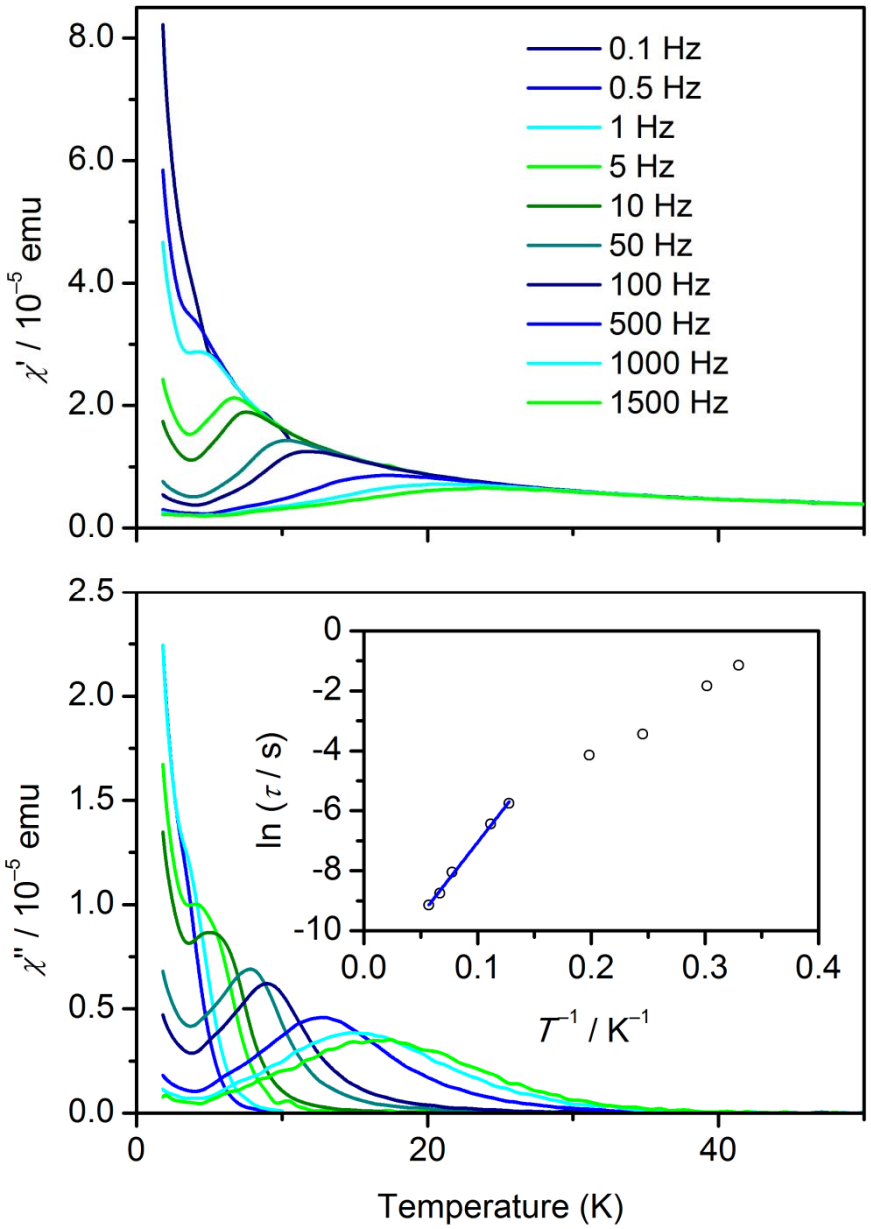

Figure S 1 Real (top) and imaginary (bottom) components of the ac susceptibility of a powder sample of **1Dy** . The inset shows the Arrhenius plot of ln τ vs T^{-1}. The line is the fit of the high-temperature part of the data to the Arrhenius law, giving $\Delta E = 34 \pm 1$ cm^{-1}, and $\tau_0 = (6.6 \pm 0.8) \times 10^{-6}$ s.

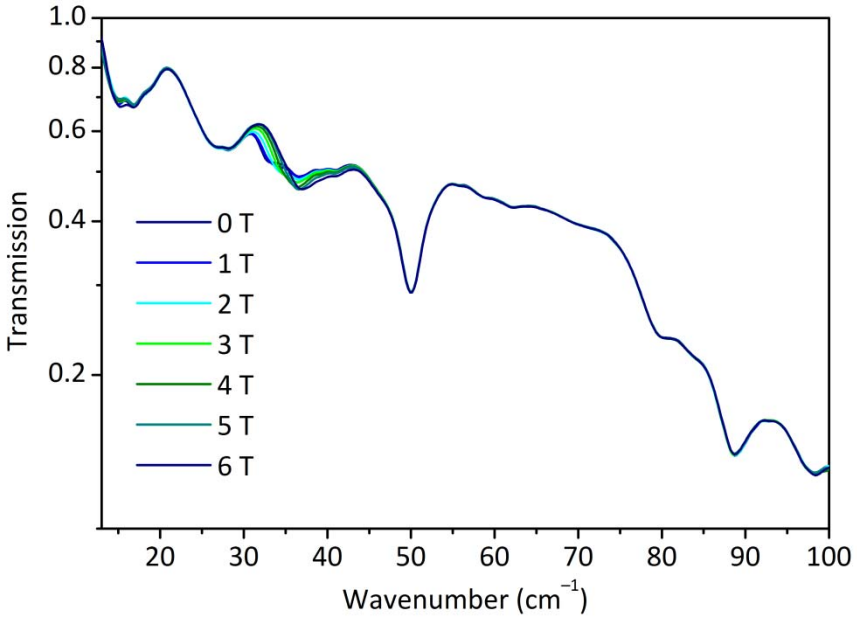

Figure S 2 Far-infrared transmission spectra recorded on a 10 mm pressed powder pellet of **1Dy** at 10 K and different magnetic fields as indicated.

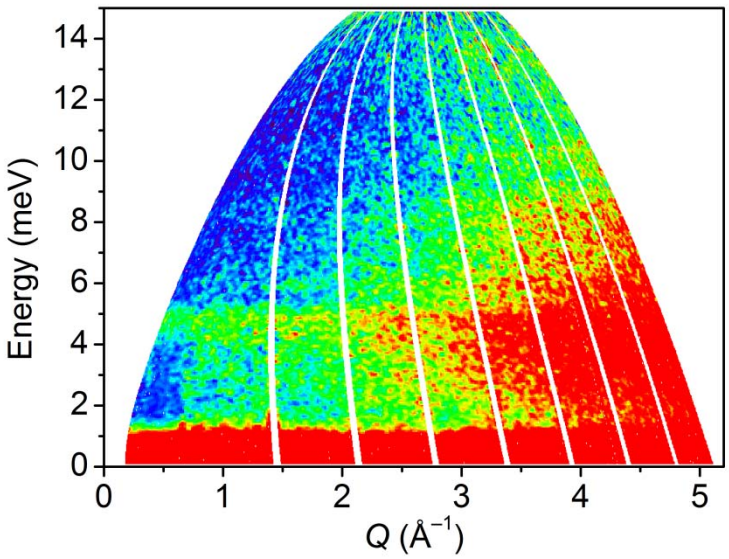

Figure S 3 INS scattering intensity (arb. u.) for **1Dy** as a function of energy transfer and momentum transfer (Q). E_i = 16 meV, T = 5 K.

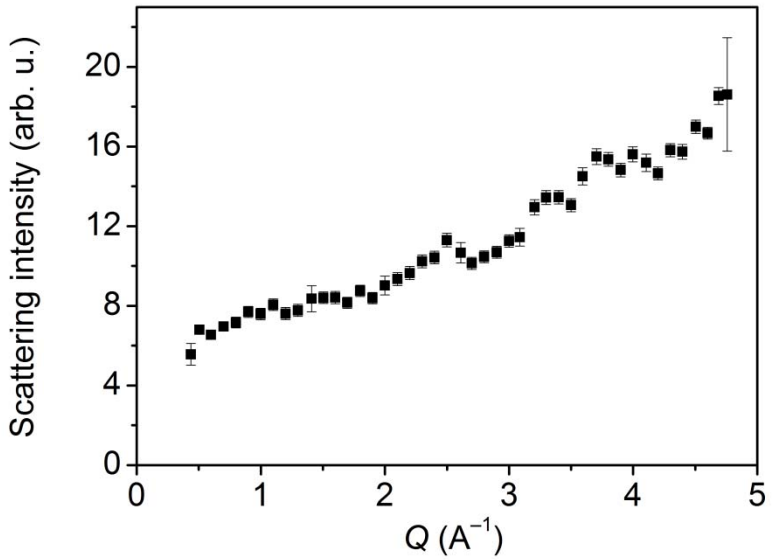

Figure S 4 Q dependence of the 37 cm^{-1} excitation in **1Dy**. E_i = 16 meV. Integration range 4.1 ≤ E ≤ 5.3 meV. T = 5 K.

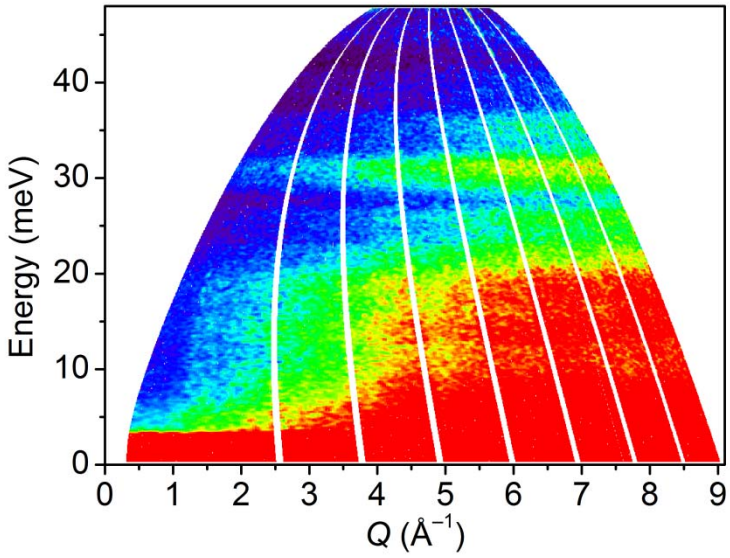

Figure S 5 INS scattering intensity (arb. u.) for **1Dy** as a function of energy transfer and momentum transfer (Q). E_i = 50 meV, T = 5 K.

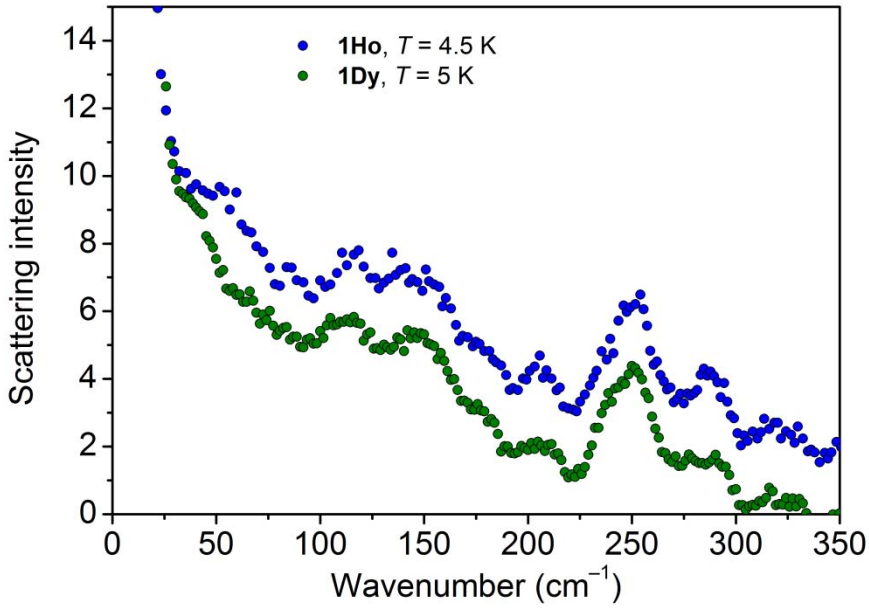

Figure S 6 INS scattering intensity for **1Ho** and **1Dy** at an incident energy of *Ei* = 50 meV and temperatures as indicated.

Table S 4 CASSCF/RASSI calculated **e**nergies of the lowest spin-orbit Kramers doublets (cm^{-1}) of **1Dy**.

experimental geometry		experimental geometry + 5 layers point charges		D_{4h}		D_{4d}	
Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
79.968	57.326	75.600	52.289	106.959	97.582	93.331	65.995
118.414	142.217	124.672	146.276	111.425	131.389	96.012	120.112
218.589	175.085	209.651	166.668	260.347	239.967	250.847	193.985
357.040	297.148	344.992	286.207	389.784	375.711	406.312	327.389
465.600	393.799	451.513	381.259	448.043	379.138	531.995	437.111
536.316	458.281	521.345	445.331	877.716	818.580	615.645	509.923
581.976	495.587	564.917	480.552	927.111	872.383	656.301	549.445
3606.113	3594.576	3609.692	3596.955	3595.717	3589.302	3590.951	3581.149
3691.721	3650.816	3688.760	3647.604	3718.534	3692.449	3697.978	3650.814
3754.821	3697.073	3748.481	3690.678	3805.092	3762.302	3779.775	3711.887
3835.416	3762.103	3825.936	3753.247	3921.245	3866.549	3877.064	3789.742
3925.329	3838.558	3913.147	3827.561	4064.591	4007.044	3980.319	3875.303
4006.584	3910.663	3992.681	3898.304	4205.435	4135.197	4071.660	3952.892
4062.825	3959.304	4047.209	3945.472	4275.398	4192.099	4127.295	4003.196
6121.104	6088.366	6122.418	6088.693	6100.560	6071.526	6111.883	6078.750
6298.522	6238.277	6294.244	6233.990	6334.668	6292.012	6311.966	6243.470
6362.188	6284.537	6354.568	6277.255	6450.501	6392.059	6396.038	6306.237
6413.153	6322.399	6402.890	6312.808	6523.299	6446.640	6460.820	6354.766
6476.173	6374.552	6463.497	6363.135	6629.119	6566.531	6533.466	6411.287
6520.224	6410.231	6505.383	6396.961	6709.684	6615.064	6576.733	6448.315
8110.182	8059.097	8109.510	8057.819	8074.431	8026.456	8108.252	8054.151
8318.076	8238.361	8311.882	8233.158	8361.084	8306.728	8341.061	8252.277
8342.561	8251.079	8333.883	8242.086	8396.988	8308.788	8383.202	8276.805
8383.945	8281.586	8372.897	8271.430	8528.050	8457.357	8433.152	8314.250
8452.771	8337.445	8438.753	8324.839	8649.812	8560.306	8504.984	8371.320
9670.119	9608.062	9668.649	9606.223	9612.792	9554.267	9671.581	9604.739
9873.778	9772.232	9864.777	9763.744	9875.424	9791.797	9909.150	9806.929
9885.697	9792.019	9877.380	9784.127	9985.097	9914.526	9926.556	9808.018
9986.229	9868.325	9972.874	9855.920	10119.802	10044.832	10035.849	9901.701
...	...	...		...	...	...	...

Table S 5 Crystal field splitting parameters (cm^{-1}) from CASSCF/RASSI/single_aniso in terms of Extended Stevens Operators after projection of the calculated levels onto the $^6H_{15/2}$ ground multiplet of **1Dy**. Higher ranks k than 6 were eliminated because they have no physical meaning and were calculated to be $<10^{-6}$ in any case.

k	q	experimental geometry		exp. geometry + 5 layers point charges	
		Basis 1	Basis 2	Basis 1	Basis 2
2	–2	–0.21311561E+00	–0.13449162E+00	–0.18204885E+00	–0.12591492E+00
	–1	–0.10933866E+00	–0.97052119E–01	–0.18481713E+00	0.13186725E+00
	0	–0.32240473E+01	–0.25843094E+01	–0.30933039E+01	–0.24726386E+01
	1	0.17295907E+01	0.12799074E+01	0.16144475E+01	0.12395343E+01
	2	0.30073115E+00	0.21394611E+00	0.27543986E+00	0.17547241E+00
4	**–4**	0.79568793E–03	0.78459153E–03	0.75386675E–03	0.66433518E–03
	–3	0.70000240E–03	0.96182497E–03	0.25639970E–03	0.83098162E–03
	–2	0.56722027E–03	0.46911958E–03	0.55911950E–03	0.49740885E–03
	–1	–0.20134433E–02	–0.20513046E–02	–0.20834048E–02	–0.21429207E–02
	0	0.81887791E–02	0.81169197E–02	0.82148589E–02	0.81432754E–02
	1	–0.18713334E–01	–0.18426059E–01	–0.18796749E–01	–0.18526205E–01
	2	0.87466430E–03	0.10133828E–02	0.86053867E–03	0.98662054E–03
	3	–0.19078817E–02	–0.20494692E–02	–0.22368491E–02	–0.22475409E–02
	4	0.27578917E–02	0.28066733E–02	0.28795553E–02	0.29723590E–02
6	–6	0.29041353E–05	0.26394013E–05	0.25105984E–05	0.21026152E–05
	–5	0.77713354E–04	0.71068483E–04	0.80454352E–04	0.73458212E–04
	–4	–0.12798566E–04	–0.12900733E–04	–0.15445712E–04	–0.15423497E–04
	–3	0.21423672E–05	0.34348601E–05	–0.20580339E–06	0.11650748E–06
	–2	0.17310646E–06	–0.74771031E–06	–0.79746026E–06	–0.23186560E–05
	–1	–0.18856770E–04	–0.19173653E–04	–0.17530800E–04	–0.16013598E–04
	0	0.21028333E–04	0.20447139E–04	0.20928909E–04	0.20356656E–04
	1	–0.99237833E–04	–0.97861202E–04	–0.98558386E–04	–0.96436950E–04
	2	0.26276542E–04	0.27060027E–04	0.25895755E–04	0.26621129E–04
	3	0.77322828E–06	–0.98989939E–07	0.20131451E–05	0.45322572E–06
	4	–0.36760855E–04	–0.37229677E–04	–0.33886012E–04	–0.35097192E–04
	5	0.51778014E–04	0.55590323E–04	0.46379860E–04	0.42599663E–04
	6	–0.10551750E–05	–0.39978972E–07	–0.35914929E–06	0.57027923E–06

Table S 6 Composition of wavefunctions for **1Dy** as derived from CASSCF/RASSI/single_aniso calculations with TZP basis and five layers of point charges to take into account effects of neighbouring molecules.

w.f.	m_J	c_i
1	–7.5	–0.000002
1	–6.5	8.06226E–06
1	–5.5	1.84391E–05
1	–4.5	5.38516E–06
1	–3.5	2.56125E–05
1	–2.5	0.000152003
1	–1.5	0.000313436
1	–0.5	4.31393E–05
1	0.5	–0.000664425
1	1.5	–0.004927297
1	2.5	–0.005302869
1	3.5	–0.008960746
1	4.5	–0.01289247
1	5.5	0.170684531
1	6.5	0.952982973
1	7.5	–0.249783
2	–7.5	–0.24978282
2	–6.5	–0.952982831
2	–5.5	0.170685506
2	–4.5	–0.012892124
2	–3.5	–0.008960249
2	–2.5	–0.005302487
2	–1.5	0.004927485
2	–0.5	–0.000665368
2	0.5	4.272E–05
2	1.5	0.000313409
2	2.5	–0.00015199
2	3.5	2.56125E–05
2	4.5	6.08276E–06
2	5.5	1.83576E–05
2	6.5	–8.48528E–06
2	7.5	0.000002
3	–7.5	–6.67308E–05
3	–6.5	–0.000327808
3	–5.5	–0.001649673
3	–4.5	0.000492391
3	–3.5	0.000180499
3	–2.5	0.000388274
3	–1.5	0.000118849
3	–0.5	–0.000431005
3	0.5	–0.004064376
3	1.5	–0.003255513
3	2.5	–0.006546723
3	3.5	0.037164876
3	4.5	0.274890088
3	5.5	0.943701128
3	6.5	–0.175921232
3	7.5	–0.038219
4	–7.5	0.038219176
4	–6.5	0.175922273
4	–5.5	0.943700655
4	–4.5	–0.274889551
4	–3.5	–0.037165145
4	–2.5	0.006547205
4	–1.5	–0.003256087
4	–0.5	0.004064034
4	0.5	–0.000431668
4	1.5	–0.000118596
4	2.5	0.000388911
4	3.5	–0.000180314
4	4.5	0.00049259
4	5.5	0.001649658
4	6.5	–0.000327452
4	7.5	–0.000066
5	–7.5	0
5	–6.5	8.94427E–06
5	–5.5	0.000041
5	–4.5	0.000145774
5	–3.5	4.66154E–05
5	–2.5	0.000144222
5	–1.5	0.000373202
5	–0.5	–0.000868743
5	0.5	–0.000479138
5	1.5	–0.002669684
5	2.5	–0.014099339
5	3.5	0.038983219
5	4.5	0.053220692
5	5.5	0.06381546
5	6.5	0.243229784
5	7.5	0.965509
6	–7.5	–0.965508661
6	–6.5	0.243230371
6	–5.5	–0.063815083
6	–4.5	0.053220766
6	–3.5	–0.038983342
6	–2.5	0.014099677
6	–1.5	0.002669772
6	–0.5	–0.000479588
6	0.5	0.000868407
6	1.5	0.000373289
6	2.5	–0.000144499
6	3.5	4.66476E–05
6	4.5	–0.000145619
6	5.5	4.08044E–05
6	6.5	–9.21954E–06
6	7.5	0
7	–7.5	0.058329862
7	–6.5	0.038861046
7	–5.5	0.270149336
7	–4.5	0.905104585
7	–3.5	–0.316397177
7	–2.5	0.04932366
7	–1.5	–0.009058296
7	–0.5	–0.015569957
7	0.5	0.004980588
7	1.5	–0.000948005
7	2.5	0.000380402
7	3.5	0.000951412
7	4.5	0.000564512
7	5.5	–0.000176082
7	6.5	4.993E–05
7	7.5	–0.000134
		0
8	–7.5	–0.00013438
8	–6.5	4.92443E–05
8	–5.5	0.000176709
8	–4.5	0.000564939
8	–3.5	0.000950897
8	–2.5	0.000381211
8	–1.5	0.000947469
8	–0.5	–0.004981186
8	0.5	0.015570894
8	1.5	–0.009058499
8	2.5	–0.049323617
8	3.5	–0.316397678
8	4.5	0.90510533
8	5.5	–0.270149433
8	6.5	–0.038860945
8	7.5	–0.058329
9	–7.5	0.023037771
9	–6.5	–0.011445906
9	–5.5	–0.05596827
9	–4.5	–0.310544314
9	–3.5	–0.879052684
9	–2.5	0.346097727
9	–1.5	–0.051421155
9	–0.5	–0.016292823
9	0.5	0.041779262
9	1.5	–0.015258294
9	2.5	0.009322949
9	3.5	0.04526625
9	4.5	–0.014751774
9	5.5	0.002794942
9	6.5	–0.000481274
9	7.5	–0.00109
10	–7.5	0.001090594
10	–6.5	–0.000480953
10	–5.5	–0.002794858
10	–4.5	–0.0147521
10	–3.5	–0.045266081
10	–2.5	0.00932342
10	–1.5	0.01525827
10	–0.5	–0.041779871
10	0.5	0.016292397
10	1.5	0.051421194
10	2.5	–0.346097534
10	3.5	–0.879052877
10	4.5	0.310544289
10	5.5	–0.055969011
10	6.5	0.011445901
10	7.5	0.023038
		0
11	–7.5	–9.90202E–05
11	–6.5	–0.001644902
11	–5.5	0.002338569
11	–4.5	0.012661629
11	–3.5	0.054895813
11	–2.5	0.100056373
11	–1.5	–0.192401176
11	–0.5	0.039232992
11	0.5	0.057829206
11	1.5	0.337779256
11	2.5	0.847977221
11	3.5	–0.326682352
11	4.5	0.070106403
11	5.5	–0.006364052
11	6.5	–0.007971939
11	7.5	0.00226
12	–7.5	0.002259719
12	–6.5	0.007972988
12	–5.5	–0.006364527
12	–4.5	–0.070106404
12	–3.5	–0.326682816
12	–2.5	–0.847976532
12	–1.5	0.33777931
12	–0.5	–0.05782865
12	0.5	0.039233123
12	1.5	0.192401548
12	2.5	0.100056264
12	3.5	–0.05489595
12	4.5	0.012662062
12	5.5	–0.002338155
12	6.5	–0.001644673
12	7.5	0.000099
13	–7.5	0.000773656
13	–6.5	0.001295533
13	–5.5	–0.004290902
13	–4.5	–0.003972599
13	–3.5	–0.081340386
13	–2.5	–0.323246662
13	–1.5	–0.724507438
13	–0.5	0.460091405
13	0.5	0.050725696
13	1.5	0.36095705
13	2.5	–0.127346128
13	3.5	0.054954428
13	4.5	–0.01260528
13	5.5	0.001460918
13	6.5	0.001608518
13	7.5	–0.000397
14	–7.5	–0.000397458
14	–6.5	–0.001607862
14	–5.5	0.00146135
14	–4.5	0.012604973
14	–3.5	0.054953934
14	–2.5	0.127346003
14	–1.5	–0.360957139
14	–0.5	–0.050725883
14	0.5	0.460091396
14	1.5	0.724507282
14	2.5	–0.323246983
14	3.5	0.081340257
14	4.5	–0.003972867
14	5.5	–0.004290861
14	6.5	–0.001295531
14	7.5	–0.000774
15	–7.5	0
15	–6.5	0.001491975
15	–5.5	0.003000654
15	–4.5	0.011240492
15	–3.5	0.046466831
15	–2.5	–0.106334697
15	–1.5	–0.36062636
15	–0.5	–0.359529236
15	0.5	0.805792788
15	1.5	–0.246236551
15	2.5	0.127820646
15	3.5	–0.024432435
15	4.5	0.013769214
15	5.5	0.004851859
15	6.5	–0.000784498
15	7.5	0.000589
16	–7.5	–0.000588412
16	–6.5	–0.000784041
16	–5.5	–0.004852135
16	–4.5	0.013769033
16	–3.5	0.02443305
16	–2.5	–0.127820917
16	–1.5	0.246236461
16	–0.5	–0.805792853
16	0.5	0.359529473
16	1.5	–0.360626662
16	2.5	0.106335315
16	3.5	–0.046466755
16	4.5	0.011240496
16	5.5	0.003000962
16	6.5	–0.001491878
16	7.5	0

Table S 7 CASSCF/RASSI calculated energies of the lowest spin-orbit Kramers doublets (cm^{-1}) of **1Dy**.

small compression of the molecule dist = -0.05 Å Basis 1	original experimental geometry dist = 0.00 Å Basis 1	small expansion of the molecule dist = +0.05 Å Basis 1
0.000	0.000	0.000
0.000	0.000	0.000
70.754	79.968	76.652
70.754	79.968	76.652
160.128	118.414	92.432
160.128	118.414	92.432
205.183	218.589	233.277
205.183	218.589	233.277
337.385	357.040	377.215
337.385	357.040	377.215
435.594	465.600	494.359
435.594	465.600	494.359
495.972	536.316	573.891
495.972	536.316	573.891
538.316	581.976	622.757
538.316	581.976	622.757
g tensors of the ground Kramers Doublets		
0.000197	0.000141	0.000093
0.000236	0.000170	0.000117
17.355955	17.371469	17.430660

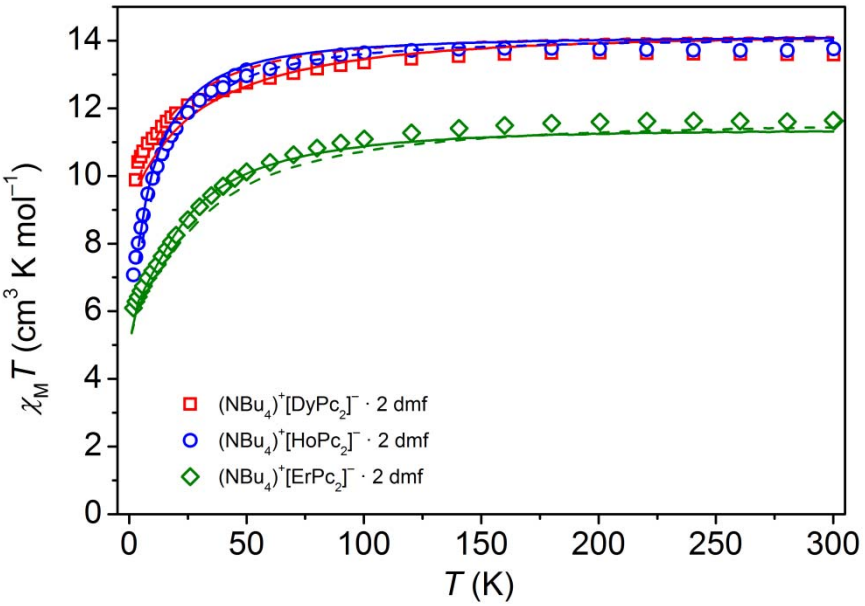

Figure S 7 DC magnetic susceptibility temperature product ($\chi_m T$) as a function of temperature for **1Dy**, **1Ho**, and **1Er** (symbols), measured with a static magnetic field of 1000 Oe, as well as simulations based on crystal field parameters obtained from CASSCF/RASSI calculations projected on an effective angular momentum ground multiplet (solid lines). Dashed lines are obtained after scaling the CASSCF energies by 0.68 (**1Dy**), 1.31 (**1Ho**), 1.27 (**1Er**)

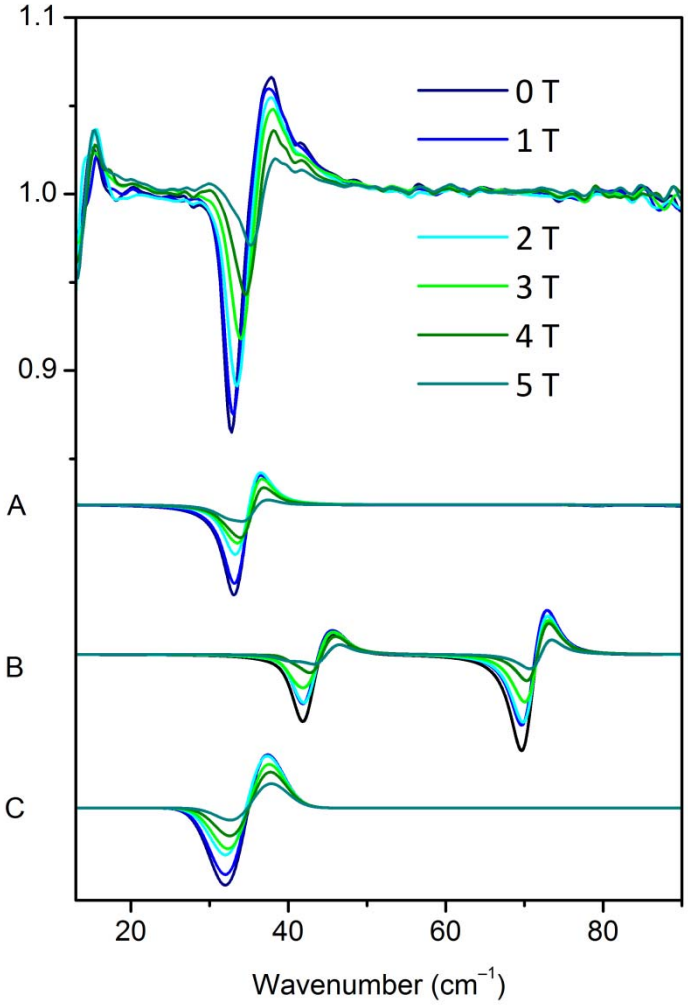

Figure S 8 Experimental FIR data for **1Dy**, as well as simulations based on (A) CF parameters derived from CASSCF calculations, after rescaling of the energies of the states by 0.68; (B) CF parameters reported by Gaita Ariño[2]; (C) CF parameters reported by Ishikawa.[3]

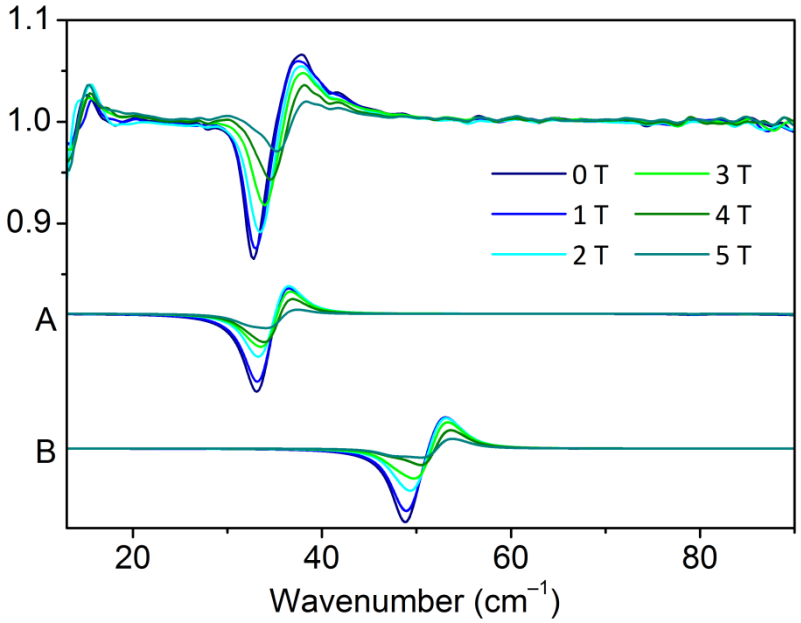

Figure S 9 Experimental FIR data for **1Dy**, as well as simulations based on (A) CF parameters derived from CASSCF calculations, after rescaling of the energies of the states by 0.68; (B) CF parameters derived from CASSCF calculations without any scaling of the energies of the states.

4. $(NBu_4)^+[HoPc_2]^-$ ·2 dmf (1Ho)

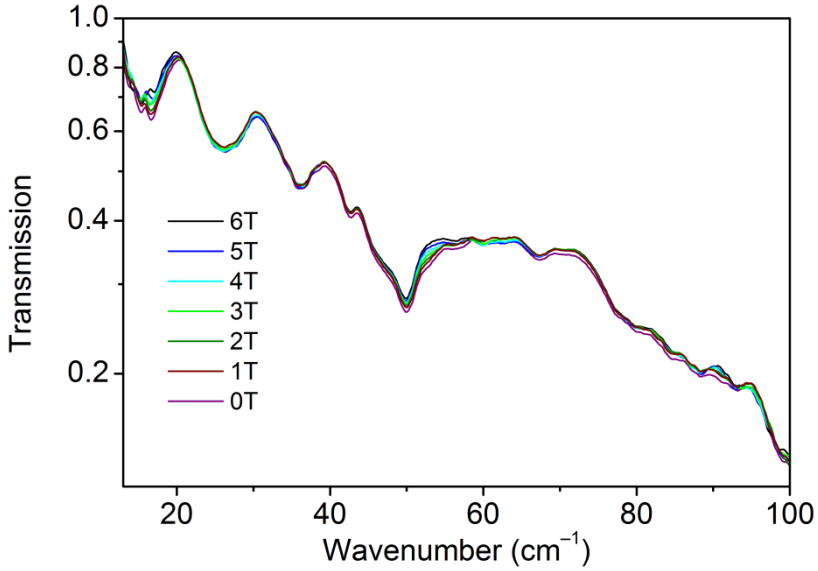

Figure S 10 Far-infrared transmission spectra recorded on a 10 mm pressed powder pellet of **1Ho** at 10 K and different magnetic fields as indicated.

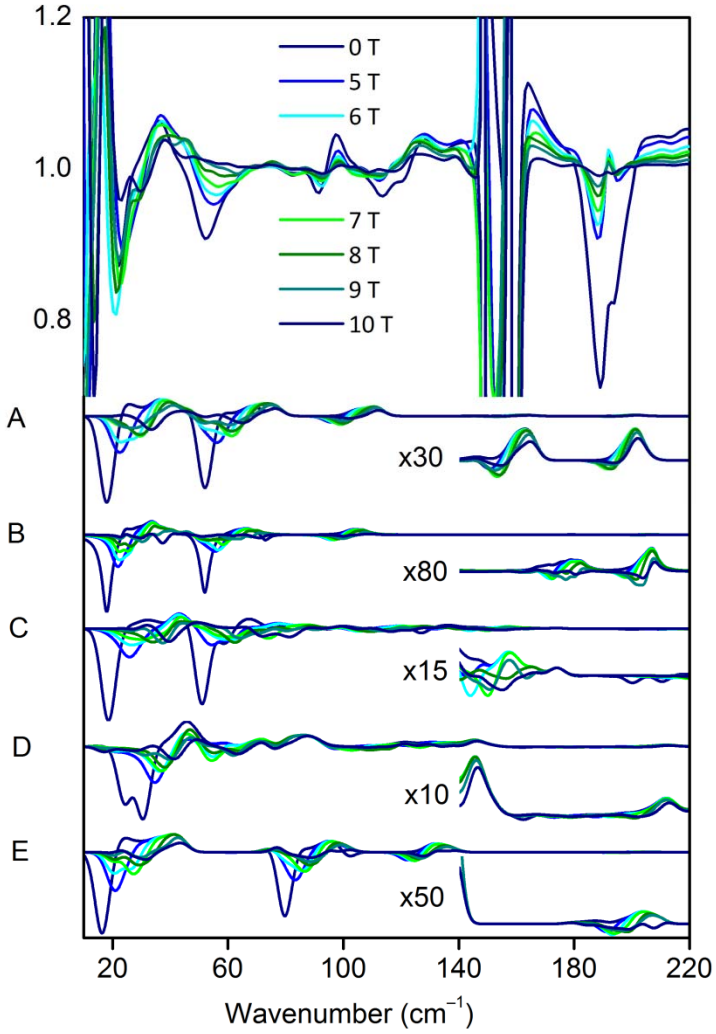

Figure S 11 Experimental FIR spectra recorded on a pressed powder sample of **1Ho** at 10 K and different magnetic fields as indicated, as well as simulations based on CF parameters (A) derived in this work assuming a |±5> ground doublet; (B) derived in this work assuming a |±6> ground doublet; (C) derived from CASSCF calculations, after rescaling of the energies of the states by 1.31; (D) reported by Gaita Ariño[2]; (E) reported by Ishikawa.[3]

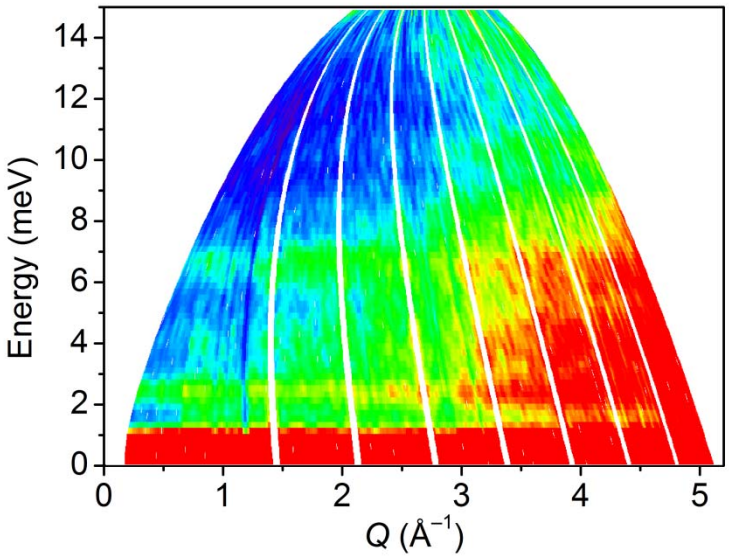

Figure S 12 INS scattering intensity (arb. u.) for **1Ho** as a function of energy transfer and momentum transfer (Q). E_i = 16 meV, T = 4.5 K.

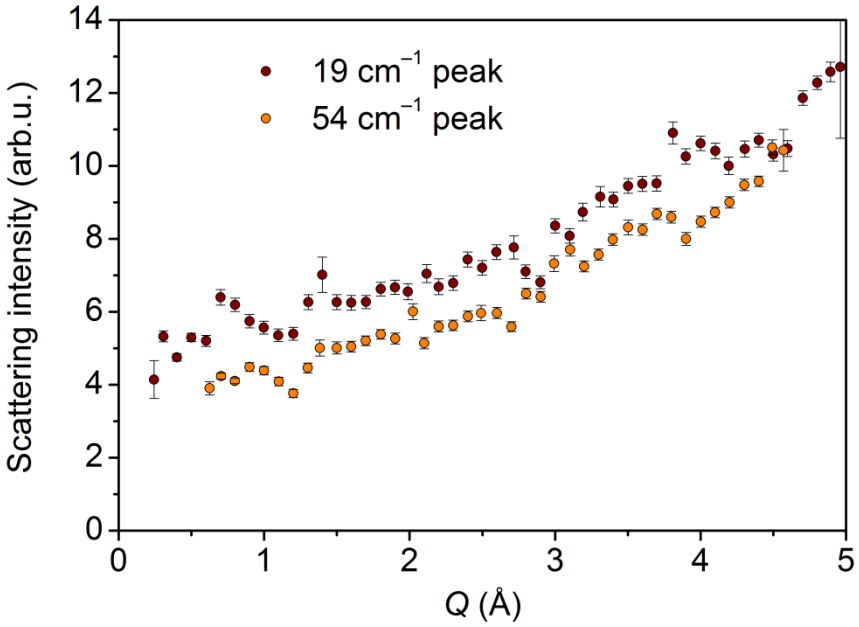

Figure S 13 Q dependence of the 19 and 54 cm^{-1} excitations in **1Ho**. E_i = 16 meV. Integration range $1.9 \leq E \leq 2.9$ meV and $5.7 \leq E \leq 7.5$ meV. T = 5 K.

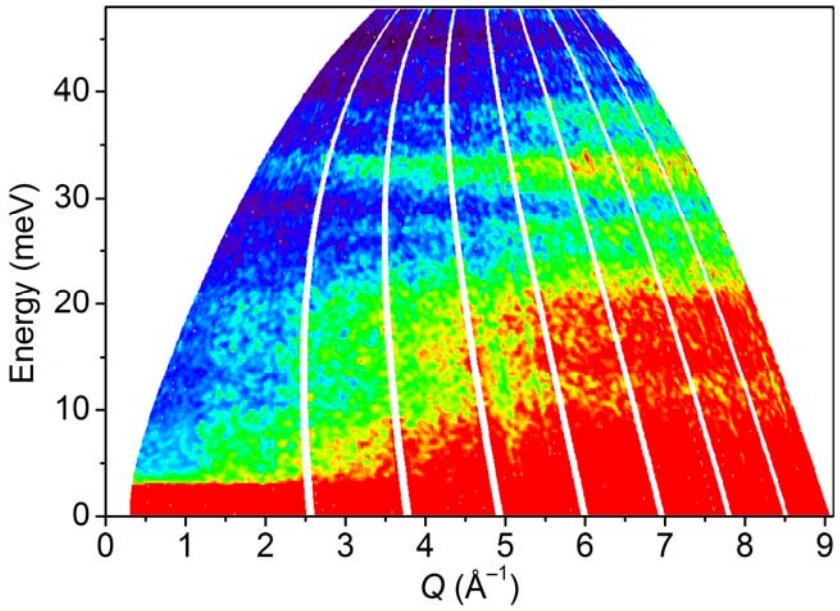

Figure S 14 INS scattering intensity (arb. u.) for **1Ho** as a function of energy transfer and momentum transfer (Q). E_i = 50 meV, T = 4.5 K.

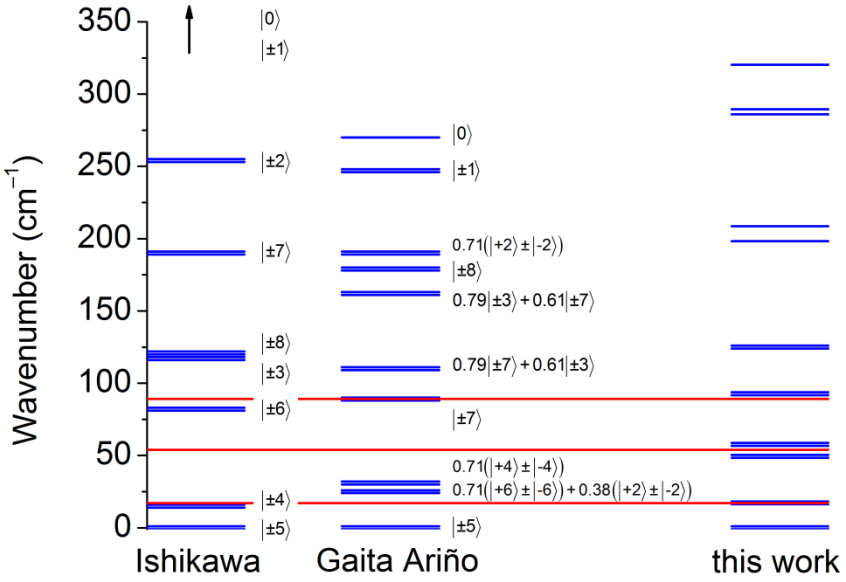

Figure S 15 Energy level diagram for **1Ho**, as derived by Ishikawa et al.,[3] Gaita Ariño et al. [2] and from CASSCF calculations reported here, with values rescaled by 1.31.

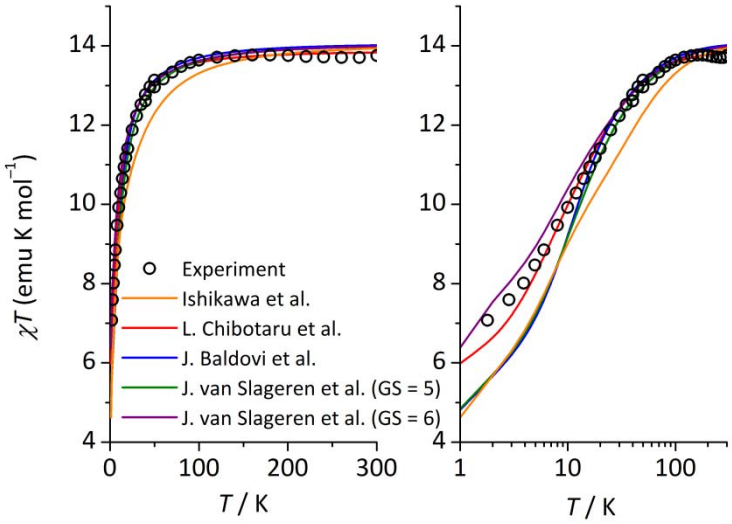

Figure S 16 Magnetic susceptibility curves for **1Ho** and simulations using CF parameters derived in this work, as well as those previously reported.[2, 3]

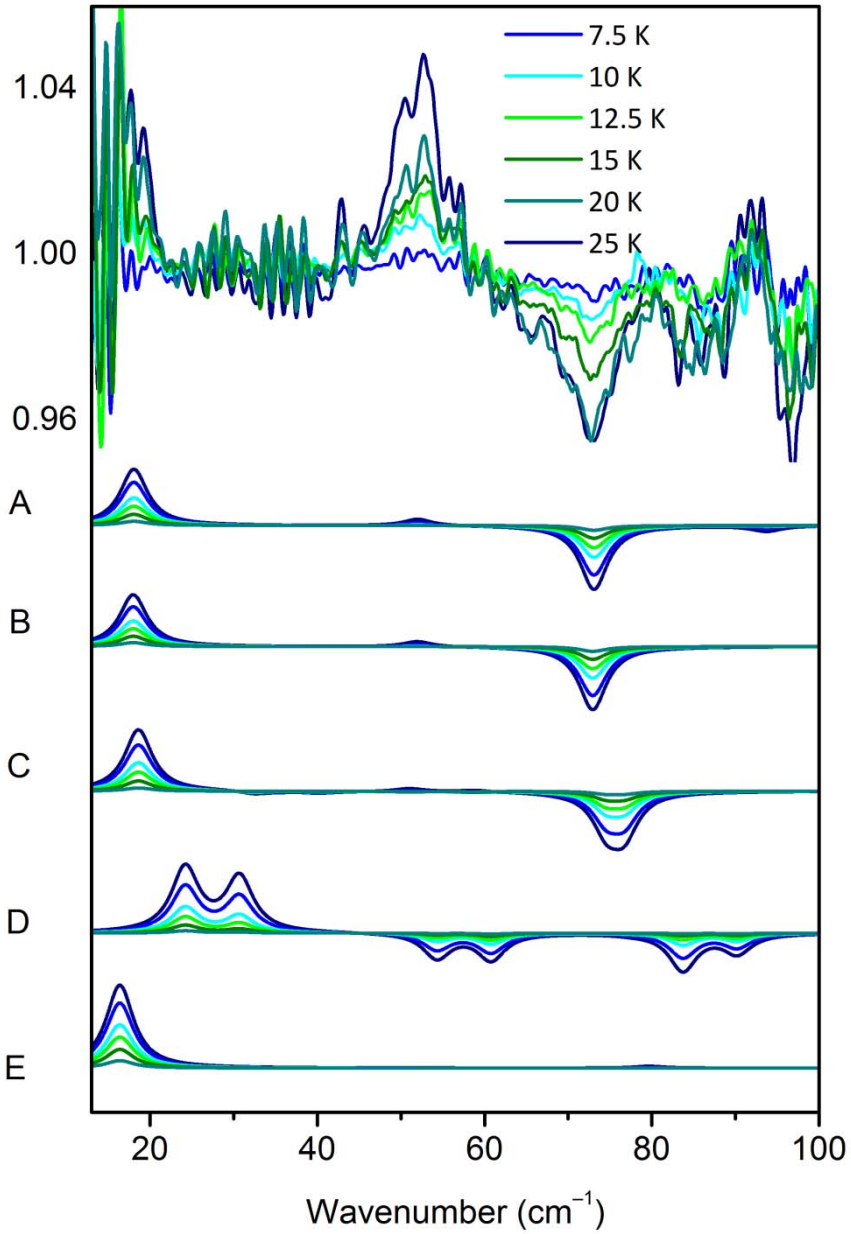

Figure S 17 Experimental FIR data for **1Ho**, as well as simulations based on (A) CF parameters derived in this work, assuming a |±5> ground doublet; (B) CF parameters derived in this work, assuming a |±6> ground doublet; (C) CF parameters derived from CASSCF calculations, after rescaling of the energies of the states by 1.31; (D) CF parameters reported by Gaita Ariño[2]; (E) CF parameters reported by Ishikawa.[3]

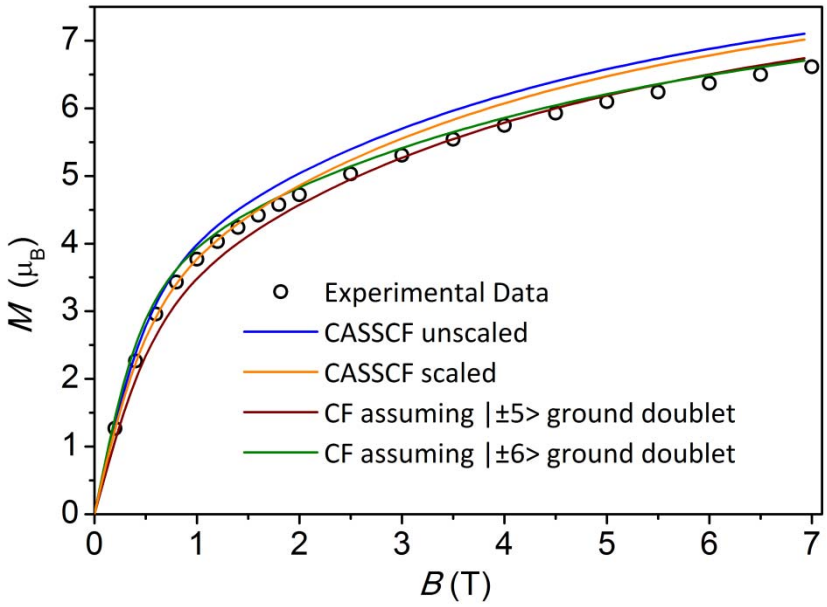

Figure S 18 Magnetization as a function of applied field, recorded at 1.8 K on a powder sample of **1Ho**, as well as fits using several models as described in the text.

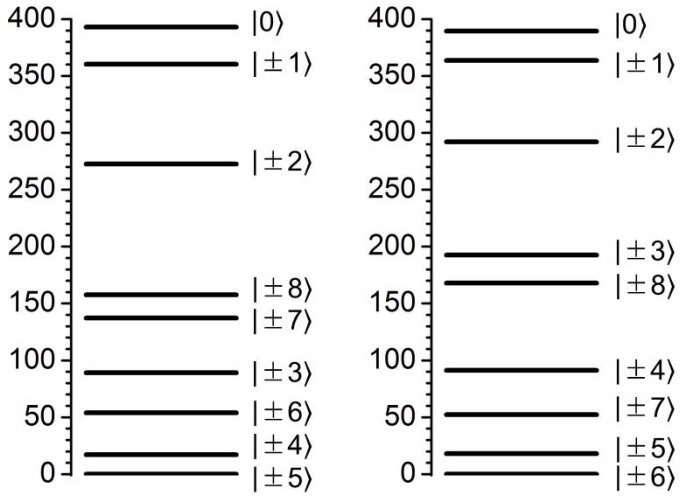

Figure S 19 Energy level diagram for **1Ho**, calculated from the observed transition energies, assuming nonzero values for B_2^0, B_4^0 and B_6^0 only, and assuming a |±5> ground doublet (left) and a |±6> ground doublet (right).

Table S 8 CASSCF/RASSI calculated energies of the lowest spin-orbit microstates (cm^{-1}) of **1Ho**.

experimental geometry		experimental geometry + 5 layers point charges		D_{4h}		D_{4d}	
Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.098	0.104	0.103	0.102	0.753	0.595	0.000	0.000
7.120	12.933	10.255	12.889	15.567	0.607	41.202	12.867
7.247	13.455	10.482	13.428	15.577	0.946	41.203	12.867
25.958	36.730	26.271	37.711	42.548	21.010	41.577	19.898
26.435	36.850	26.648	37.771	85.429	69.377	41.577	19.898
36.902	40.685	36.537	44.053	144.054	124.992	54.433	22.695
36.968	40.784	36.610	44.117	144.070	125.017	54.433	22.695
72.255	70.536	72.665	69.961	345.970	340.367	97.723	57.332
72.993	72.220	73.522	71.590	346.531	341.282	98.097	57.703
94.641	94.848	93.298	95.188	429.647	403.662	164.055	117.599
96.472	95.461	94.748	95.629	430.404	406.731	164.055	117.604
170.186	153.772	166.650	151.318	430.418	406.738	234.082	182.022
177.953	161.972	174.246	159.280	481.561	442.088	234.084	182.027
239.011	220.773	235.232	218.333	525.950	498.565	287.006	230.915
247.307	225.126	242.156	221.072	525.965	498.580	287.010	230.915
269.903	248.087	265.065	244.548	564.225	538.012	306.673	249.104
5154.454	5131.923	5155.528	5132.980	5266.292	5238.572	5146.237	5108.648
5154.462	5131.939	5155.534	5133.004	5266.292	5238.573	5146.237	5108.648
5160.756	5138.170	5163.111	5139.050	5290.321	5249.395	5162.287	5111.122
5160.764	5138.180	5163.121	5139.077	5290.980	5250.286	5162.287	5111.122
5164.108	5150.762	5166.319	5154.276	5326.711	5275.719	5194.182	5132.640
5164.143	5150.771	5166.333	5154.324	5326.711	5275.720	5194.182	5132.640
5192.615	5157.922	5190.991	5157.099	5374.031	5315.139	5241.680	5172.090
5192.910	5158.217	5191.292	5157.359	5397.603	5339.720	5241.855	5172.268
5234.773	5194.907	5232.181	5193.089	5450.153	5387.129	5294.569	5218.763
5235.285	5195.377	5232.646	5193.506	5450.158	5387.133	5294.570	5218.765
5278.386	5234.723	5274.939	5232.057	5491.621	5424.307	5343.162	5262.641
5280.046	5236.226	5276.877	5234.148	5518.863	5450.402	5343.162	5262.643
5309.711	5264.522	5306.396	5262.412	5543.612	5472.356	5378.083	5294.460
5319.022	5270.922	5314.529	5267.333	5543.615	5472.366	5378.086	5294.460
5328.284	5280.365	5324.061	5277.244	5555.924	5483.414	5390.910	5306.178
8832.879	8800.209	8834.175	8801.795	8961.658	8912.002	8845.480	8793.352
8832.919	8800.242	8834.209	8801.819	8962.695	8914.354	8845.480	8793.352
8856.790	8832.917	8860.638	8835.184	8996.292	8936.411	8860.822	8795.926
8856.825	8833.061	8860.673	8835.706	8996.293	8936.411	8860.822	8795.927
8879.351	8837.289	8878.482	8837.890	9058.303	8986.561	8919.606	8842.856
8880.289	8838.088	8879.416	8838.275	9074.986	9003.642	8920.202	8843.443
8932.374	8882.727	8930.033	8881.119	9116.761	9035.001	8981.363	8895.925
8933.174	8883.385	8930.725	8881.661	9116.768	9035.011	8981.364	8895.925
8963.581	8909.543	8960.502	8907.300	9141.598	9058.421	9028.163	8937.018
8969.343	8915.202	8966.178	8913.052	9210.576	9120.466	9028.163	8937.018
8980.844	8924.964	8977.678	8922.979	9233.747	9147.183	9057.634	8963.126
8990.854	8932.468	8986.563	8928.937	9233.748	9147.195	9057.637	8963.127
8993.384	8934.799	8989.252	8931.602	9255.148	9171.213	9068.010	8972.331
…	…	…	…	…	…	…	…

Table S 9 Crystal field splitting parameters (cm^{-1}) from CASSCF/RASSI/single_aniso in terms of Extended Stevens Operators after projection of the calculated levels onto the $^5I_8$ ground multiplet of **1Ho**. Higher ranks *k* than 6 were eliminated because they have no physical meaning and were calculated to be $<10^{-6}$ in any case.

k	q	experimental geometry		exp. geometry + 5 layers point charges	
		Basis 1	Basis 2	Basis 1	Basis 2
2	–2	0.11830886E+00	0.88516474E–01	0.10898734E+00	0.58430556E–01
	–1	0.25117460E–01	0.19090524E–02	–0.98459032E–02	0.79012407E–01
	0	–0.85463946E+00	–0.66409650E+00	–0.81428035E+00	–0.63364079E+00
	1	0.14277878E+01	0.10422576E+01	0.13372271E+01	0.94461867E+00
	2	–0.54092674E–01	–0.41363522E–01	–0.57633606E–01	–0.39171934E–01
4	–4	–0.60651288E–03	–0.57331603E–03	–0.59204026E–03	–0.52556541E–03
	–3	–0.16223914E–02	–0.17758981E–02	–0.15481242E–02	–0.17910355E–02
	–2	0.32168455E–03	0.36834609E–03	0.37048879E–03	0.40448352E–03
	–1	–0.16998146E–02	–0.16410962E–02	–0.17353828E–02	–0.16875991E–02
	0	0.23516537E–02	0.23620851E–02	0.23732073E–02	0.23825861E–02
	1	–0.15764476E–01	–0.15780270E–01	–0.15869269E–01	–0.15866064E–01
	2	0.34115670E–02	0.34258112E–02	0.34469575E–02	0.34509194E–02
	3	–0.21999553E–02	–0.22771549E–02	–0.21636425E–02	–0.23095917E–02
	4	–0.10311522E–02	–0.10130268E–02	–0.11126067E–02	–0.11316176E–02
6	–6	–0.13101913E–04	–0.12382283E–04	–0.12805787E–04	–0.11457569E–04
	–5	0.93079319E–04	0.95208572E–04	0.99707766E–04	0.99862085E–04
	–4	–0.17657458E–04	–0.18254829E–04	–0.18779667E–04	–0.19477255E–04
	–3	–0.12648411E–05	0.34540037E–06	–0.66530583E–05	–0.60284023E–05
	–2	–0.31281907E–04	–0.31346768E–04	–0.30718419E–04	–0.30338496E–04
	–1	0.17716767E–04	0.14957948E–04	0.14868434E–04	0.11288964E–04
	0	–0.11866117E–04	–0.11387323E–04	–0.11737792E–04	–0.11284006E–04
	1	0.24448484E–03	0.23286026E–03	0.24144575E–03	0.23025257E–03
	2	–0.95985318E–04	–0.92301534E–04	–0.94215656E–04	–0.90806723E–04
	3	0.35926641E–04	0.33999545E–04	0.41173004E–04	0.38833531E–04
	4	–0.38252251E–04	–0.38208054E–04	–0.35050453E–04	–0.35556832E–04
	5	0.54384354E–04	0.62780753E–04	0.40528571E–04	0.46756582E–04
	6	–0.70324559E–05	–0.79140370E–05	–0.59789730E–05	–0.63989454E–05

Table S 10 Composition of wavefunctions for **1Ho** as derived from CASSCF/RASSI/single_aniso calculations with TZP basis and five layers of point charges to take into account effects of neighbouring molecules.

w.f.	m_J	c_i
1	–8	0.056413648
1	–7	–0.236187884
1	–6	–0.451259933
1	–5	–0.242464538
1	–4	0.375553514
1	–3	–0.190602549
1	–2	0.032425464
1	–1	0.01358377
1	0	–0.002392097
1	1	–0.013583535
1	2	–0.032424872
1	3	–0.190602668
1	4	–0.37555364
1	5	–0.242464817
1	6	0.451259546
1	7	–0.236188272
1	8	–0.056413
2	–8	–0.056807026
2	–7	0.2368884
2	–6	0.451142271
2	–5	0.243326984
2	–4	–0.373822182
2	–3	0.190045437
2	–2	–0.043252252
2	–1	–0.012648056
2	0	–0.007475961
2	1	–0.012648673
2	2	–0.043251999
2	3	–0.190045422
2	4	–0.373821732
2	5	–0.243328052
2	6	0.451143259
2	7	–0.236888722
2	8	–0.056807
3	–8	–0.153465446
3	–7	0.094690191
3	–6	–0.188890433
3	–5	–0.383741126
3	–4	–0.197058675
3	–3	0.413775884
3	–2	–0.255884761
3	–1	0.091067039
3	0	–0.038272447
3	1	0.091066797
3	2	0.255884644
3	3	0.413775958
3	4	0.197057781
3	5	0.383740329
3	6	–0.18888975
3	7	–0.094690681
3	8	–0.153466
4	–8	–0.156894262
4	–7	0.096360506
4	–6	–0.191422195
4	–5	–0.382709262
4	–4	–0.19865719
4	–3	0.409124017
4	–2	–0.259232826
4	–1	0.091420547
4	0	–0.034169383
4	1	–0.091420873
4	2	–0.25923335
4	3	–0.409124482
4	4	–0.198657129
4	5	–0.38270922
4	6	0.191422352
4	7	0.096359774
4	8	0.156894
5	–8	0.38547256
5	–7	0.247851835
5	–6	0.270098454
5	–5	–0.403366503
5	–4	0.224217585
5	–3	–0.046735371
5	–2	0.018657721
5	–1	–0.038410298
5	0	0.009114955
5	1	–0.038409971
5	2	–0.018657619
5	3	–0.046735356
5	4	–0.224217882
5	5	0.403366631
5	6	0.270098234
5	7	–0.247852094
5	8	0.385472
6	–8	–0.382925539
6	–7	–0.251079502
6	–6	–0.267981212
6	–5	0.407380141
6	–4	–0.221098695
6	–3	0.045224764
6	–2	–0.022969836
6	–1	0.019264096
6	0	–0.038093021
6	1	–0.019263859
6	2	–0.022970104
6	3	–0.045224596
6	4	–0.221098911
6	5	0.407379869
6	6	0.26798186
6	7	–0.251080063
6	8	0.382926
7	–8	–0.484099496
7	–7	0.427412647
7	–6	–0.124851039
7	–5	–0.058538072
7	–4	0.177365884
7	–3	–0.1492859
7	–2	0.091683593
7	–1	0.036206813
7	0	0.03130127
7	1	0.036206705
7	2	0.091683744
7	3	0.149286102
7	4	0.177366064
7	5	–0.058538178
7	6	0.124850609
7	7	0.427413021
7	8	0.4841
8	–8	0.480000347
8	–7	–0.429409951
8	–6	0.125188968
8	–5	0.062459427
8	–4	–0.17810688
8	–3	0.153657345
8	–2	–0.091445918
8	–1	0.043476798
8	0	0.009807816
8	1	0.04347704
8	2	0.091445897
8	3	0.153657538
8	4	0.178106556
8	5	–0.062459203
8	6	0.125188599
8	7	0.429410314
8	8	0.48
9	–8	–0.138772417
9	–7	–0.210746106
9	–6	0.109163238
9	–5	–0.311078067
9	–4	–0.321957195
9	–3	–0.117668805
9	–2	0.361461743
9	–1	–0.281712761
9	0	–0.015693008
9	1	–0.281712557
9	2	–0.361461964
9	3	–0.117668547
9	4	0.321956303
9	5	0.311077851
9	6	0.109163486
9	7	0.210746616
9	8	–0.138773
10	–8	0.146919688
10	–7	0.221939856
10	–6	–0.125526384
10	–5	0.315408836
10	–4	0.316164856
10	–3	0.122717403
10	–2	–0.356717773
10	–1	0.221062826
10	0	–0.213455698
10	1	–0.22106258
10	2	–0.356717554
10	3	–0.122717419
10	4	0.316164968
10	5	0.315409007
10	6	0.125526311
10	7	0.221940359
10	8	–0.14692
11	–8	–0.270987289
11	–7	–0.37965283
11	–6	0.400249511
11	–5	–0.109569424
11	–4	0.236079016
11	–3	0.049496606
11	–2	–0.18319401
11	–1	0.135739912
11	0	–0.010595838
11	1	0.135739837
11	2	0.183193898
11	3	–0.049497174
11	4	–0.236078928
11	5	0.109568875
11	6	0.400249599
11	7	0.37965258
11	8	–0.270988
12	–8	0.266291162
12	–7	0.37299768
12	–6	–0.394948327
12	–5	0.102411999
12	–4	–0.249170263
12	–3	–0.058739173
12	–2	0.193529579
12	–1	–0.121695045
12	0	0.106676311
12	1	0.121695268
12	2	0.193529675
12	3	–0.058739412
12	4	0.249170417
12	5	0.102411884
12	6	0.394947994
12	7	0.372997157
12	8	–0.266291
13	–8	–0.011969369
13	–7	–0.026368656
13	–6	–0.01854692
13	–5	0.129661264
13	–4	0.250526396
13	–3	0.391609515
13	–2	0.07031179
13	–1	–0.483528475
13	0	0.232981441
13	1	0.483528684
13	2	0.070312068
13	3	–0.391610072
13	4	0.250526734
13	5	–0.129661003
13	6	–0.01854774
13	7	0.026368946
13	8	–0.011969
14	–8	0.010137362
14	–7	0.023714394
14	–6	0.012814271
14	–5	–0.124914535
14	–4	–0.25176903
14	–3	–0.400493617
14	–2	–0.095754008
14	–1	0.320764027
14	0	–0.543554515
14	1	0.320764863
14	2	0.09575449
14	3	–0.400493346
14	4	0.251769631
14	5	–0.124913674
14	6	–0.012813868
14	7	0.023714763
14	8	–0.010137
15	–8	0.002591285
15	–7	0.00714072
15	–6	0.006898851
15	–5	–0.016610419
15	–4	–0.107871117
15	–3	–0.26106117
15	–2	–0.339228463
15	–1	–0.282047352
15	0	0.67112394
15	1	–0.282047033
15	2	0.339227909
15	3	–0.261060592
15	4	0.107871155
15	5	–0.01661019
15	6	–0.006898842
15	7	0.007140714
15	8	–0.002592
16	–8	0.002568816
16	–7	0.006861105
16	–6	0.00522883
16	–5	–0.027872183
16	–4	–0.132020346
16	–3	–0.301978065
16	–2	–0.462392521
16	–1	0.332016958
16	0	0.364635868
16	1	–0.332017215
16	2	–0.462392544
16	3	0.301977476
16	4	–0.132020956
16	5	0.027872259
16	6	0.005229338
16	7	–0.006861776
16	8	0.002569
17	–8	0.000966617
17	–7	0.00340939
17	–6	0.006742611
17	–5	0.00860444
17	–4	–0.04392057
17	–3	–0.175871658
17	–2	–0.418143359
17	–1	–0.538530849
17	0	–0.06554569
17	1	0.538531588
17	2	–0.41814337
17	3	0.175872
17	4	–0.043920837
17	5	0.008605028
17	6	0.006743137
17	7	–0.003409113
17	8	0.000966

Table S 11 CASSCF/RASSI calculated energies of the lowest spin-orbit Ising doublets (cm^{-1}) of **1Ho**.

small compression of the molecule dist = -0.05 Å Basis 1	original experimental geometry dist = 0.00 Å Basis 1	small expansion of the molecule dist = +0.05 Å Basis 1
0.000	0.000	0.000
0.134	0.098	0.010
7.587	7.120	14.822
8.218	7.247	14.891
32.122	25.958	30.828
32.255	26.435	30.912
54.524	36.902	44.539
54.585	36.968	45.008
74.776	72.255	57.511
77.388	72.993	57.648
117.254	94.641	109.599
117.456	96.472	111.786
168.001	170.186	182.990
176.186	177.953	190.308
244.760	239.011	244.400
253.836	247.307	252.067
279.558	269.903	271.782
gZ values of the ground Ising Doublets (gX=gY=0)		
13.327114	14.219021	19.162867

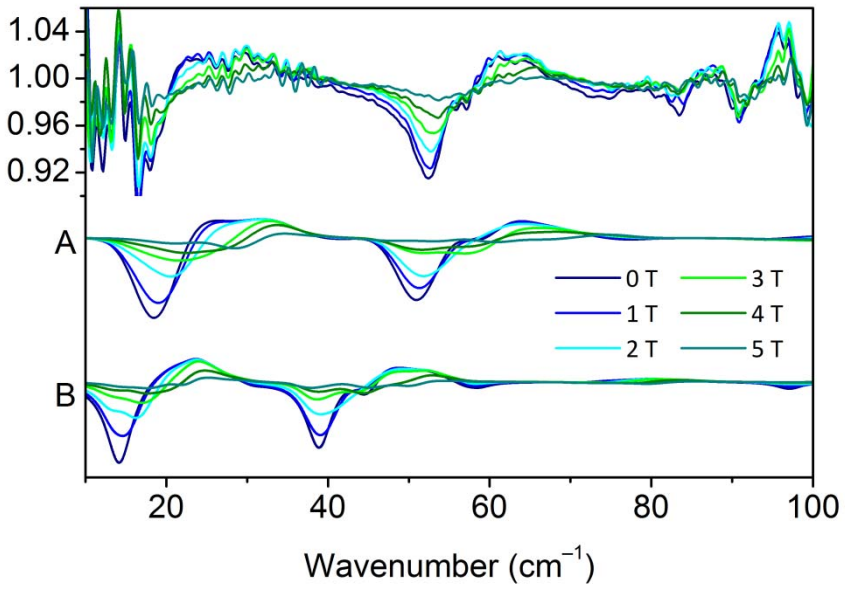

Figure S 20 Experimental FIR data for **1Ho**, as well as simulations based on (A) CF parameters derived from CASSCF calculations, after rescaling of the energies of the states by 1.31; (B) CF parameters derived from CASSCF calculations without any scaling of the energies of the states.

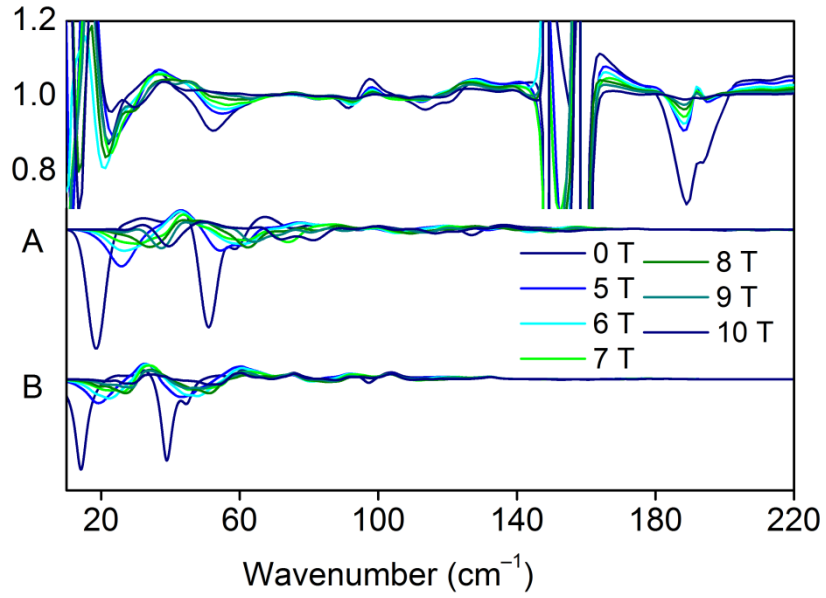

Figure S 21 Experimental FIR data for **1Ho**, as well as simulations based on (A) CF parameters derived from CASSCF calculations, after rescaling of the energies of the states by 1.31; (B) CF parameters derived from CASSCF calculations without any scaling of the energies of the states.

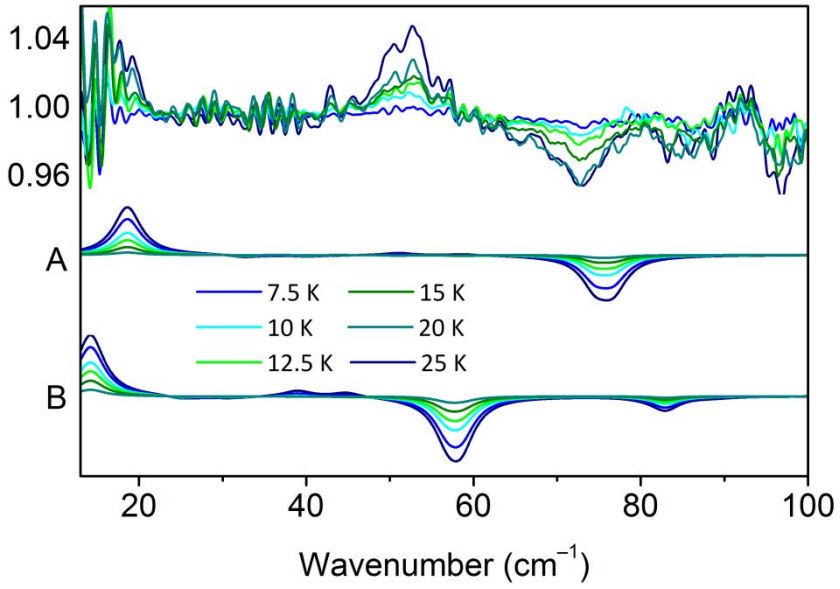

Figure S 22 Experimental FIR data for **1Ho**, as well as simulations based on (A) CF parameters derived from CASSCF calculations, after rescaling of the energies of the states by 1.31; (B) CF parameters derived from CASSCF calculations without any scaling of the energies of the states.

5. $(NBu_4)^+[ErPc_2]^-$ ·2 dmf (1Er)

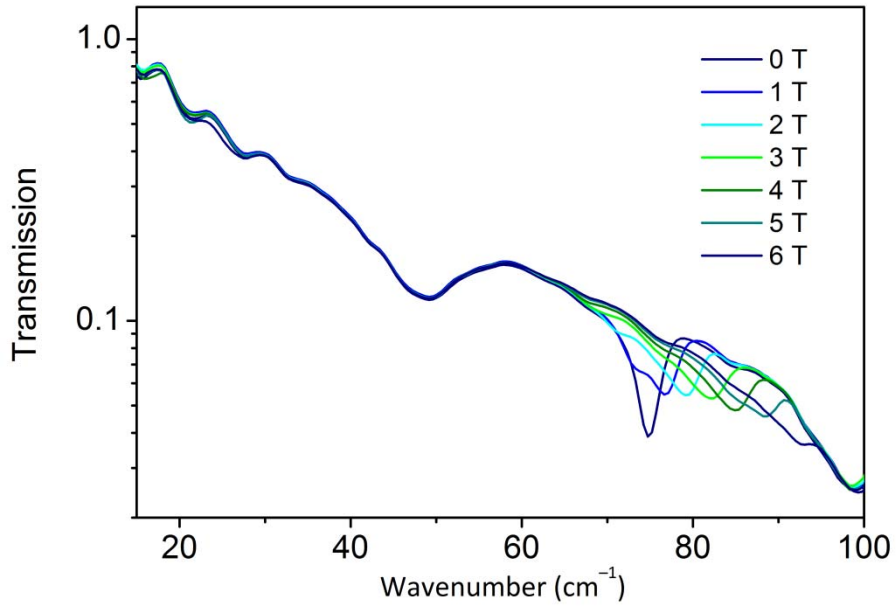

Figure S 23 Far-infrared transmission spectra recorded on a 10 mm pressed powder pellet of **1Er** at 10 K and different magnetic fields as indicated.

Table S 12 CASSCF/RASSI calculated energies of the lowest spin-orbit Kramers doublets (cm^{-1}) of **1Er**.

experimental geometry		experimental geometry + 5 layers point charges		D_{4h}		D_{4d}	
Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
63.467	59.563	62.481	58.713	64.004	73.549	58.439	53.283
164.273	153.642	161.734	151.330	125.112	120.452	154.968	140.197
238.562	204.086	231.760	198.995	221.738	197.287	253.668	228.448
261.312	236.418	256.450	228.555	502.405	495.329	295.041	247.030
290.146	253.963	283.367	248.931	571.058	561.654	315.814	270.420
296.740	262.382	286.729	257.577	638.971	633.236	321.422	281.621
313.608	289.371	308.608	285.912	659.550	639.141	340.384	282.229
6657.670	6610.863	6656.821	6610.131	6718.518	6686.256	6655.212	6605.874
6702.900	6652.717	6701.326	6651.369	6764.922	6722.896	6699.165	6646.002
6776.124	6720.567	6773.462	6718.309	6853.290	6799.840	6773.960	6712.651
6845.539	6782.342	6841.539	6776.956	7011.743	6963.855	6851.318	6780.251
6871.303	6788.458	6863.512	6781.815	7075.268	7021.327	6899.905	6818.119
6877.287	6795.273	6867.461	6789.334	7110.964	7042.745	6915.390	6820.326
6879.959	6808.600	6873.971	6804.541	7113.346	7049.805	6926.613	6824.587
10720.103	10667.702	10718.401	10666.289	10801.477	10761.229	10720.739	10664.297
10756.831	10701.486	10754.458	10699.501	10865.331	10819.244	10758.176	10698.211
10814.945	10754.704	10811.469	10751.826	10974.821	10929.089	10820.501	10753.085
10856.281	10790.054	10851.476	10786.055	11029.360	10977.309	10873.711	10798.248
10874.428	10800.623	10867.984	10794.254	11073.961	11014.854	10906.494	10821.982
10887.226	10804.193	10877.881	10797.973	11084.924	11016.301	10930.373	10831.089
13466.473	13424.130	13464.423	13422.460	13431.104	13391.998	13477.440	13431.904
13578.059	13530.598	13574.593	13527.545	13683.021	13647.414	13578.292	13524.132
13606.087	13551.769	13601.269	13547.971	13792.704	13752.034	13641.505	13578.680
13644.317	13579.233	13635.933	13572.415	13875.269	13840.783	13666.481	13599.937
13663.532	13610.968	13658.925	13607.195	13977.082	13936.809	13678.621	13604.679
18864.196	18949.723	18866.216	18950.967	18950.002	19056.744	18838.342	18929.210
19026.681	19092.671	19024.829	19090.713	19156.383	19240.490	19024.863	19089.207
19065.578	19117.656	19060.530	19113.249	19198.985	19264.913	19089.118	19134.853
19083.256	19126.678	19075.812	19121.249	19279.915	19340.982	19121.059	19151.610

Table S 13 Crystal field splitting parameters (cm^{-1}) from CASSCF/RASSI/single_aniso in terms of Extended Stevens Operators after projection of the calculated levels onto the $^4I_{15/2}$ ground multiplet of **1Er**. Higher ranks k than 6 were eliminated because they have no physical meaning and were calculated to be $<10^{-6}$ in any case.

k	q	experimental geometry		exp. geometry + 5 layers point charges	
		Basis 1	Basis 2	Basis 1	Basis 2
2	–2	–0.55579090E–01	–0.38649979E–01	–0.42846733E–01	–0.25433164E–01
	–1	–0.15443125E+00	–0.11669205E+00	–0.14519575E+00	–0.18796420E+00
	0	0.13477162E+01	0.10701191E+01	0.12833868E+01	0.10194806E+01
	1	–0.10400752E+00	–0.12281218E+00	–0.14236806E+00	0.22688688E–02
	2	–0.14120600E+00	–0.96253442E–01	–0.13159189E+00	–0.81373664E–01
4	–4	–0.13683884E–02	–0.13606033E–02	–0.12333660E–02	–0.11868064E–02
	–3	–0.17716864E–02	–0.18729897E–02	–0.12146165E–02	–0.18481986E–02
	–2	0.19402590E–03	0.13945143E–03	0.16938520E–03	0.96888244E–04
	–1	–0.88746841E–04	–0.89908684E–04	–0.23095470E–04	–0.52422665E–05
	0	–0.58244743E–02	–0.57150182E–02	–0.58488279E–02	–0.57369742E–02
	1	–0.67572315E–04	–0.43190812E–04	–0.99578182E–04	–0.10090279E–03
	2	0.22159306E–03	0.11896292E–03	0.29218911E–03	0.20181864E–03
	3	–0.28694132E–03	–0.42738086E–03	–0.87727134E–03	–0.43844816E–03
	4	0.13579895E–02	0.13525016E–02	0.13951606E–02	0.13881706E–02
6	–6	–0.68081543E–05	–0.53568426E–05	–0.61651084E–05	–0.50364178E–05
	–5	0.65861848E–04	0.60811155E–04	0.64044706E–04	0.63639951E–04
	–4	–0.40963995E–04	–0.42917632E–04	–0.52761018E–04	–0.52905783E–04
	–3	–0.44184070E–04	–0.44941632E–04	–0.48020636E–04	–0.51312723E–04
	–2	0.46262219E–05	0.61825268E–05	0.62627785E–05	0.82161276E–05
	–1	0.10321902E–04	0.10473552E–04	0.13481736E–04	0.13245136E–04
	0	0.50556743E–04	0.48497948E–04	0.49742167E–04	0.47756243E–04
	1	0.47823911E–05	0.46429569E–05	0.35921471E–06	–0.16466693E–05
	2	0.11946243E–04	0.14987857E–04	0.10809201E–04	0.13801864E–04
	3	0.13365714E–04	0.13565609E–04	0.18057814E–04	0.21930716E–04
	4	0.50000338E–04	0.50445120E–04	0.46537295E–04	0.47582936E–04
	5	0.48658826E–04	0.49796626E–04	0.60374088E–04	0.95561905E–04
	6	–0.28185162E–05	–0.40979456E–05	–0.23642468E–05	–0.28750352E–05

Table S 14 Composition of wavefunctions for **1Er** as derived from CASSCF/RASSI/single_aniso calculations with TZP basis and five layers of point charges to take into account effects of neighbouring molecules.

w.f.	m_J	c_i
1	–7.5	9.93277E–05
1	–6.5	–0.001802905
1	–5.5	0.013471974
1	–4.5	0.01373247
1	–3.5	–0.010589421
1	–2.5	–0.015013861
1	–1.5	0.003000433
1	–0.5	–0.993325451
1	0.5	0.107730595
1	1.5	–0.026139617
1	2.5	0.012066834
1	3.5	–0.00543373
1	4.5	–0.01088968
1	5.5	0.000921543
1	6.5	–0.000727842
1	7.5	0.000916
2	–7.5	–0.000916163
2	–6.5	0.000727698
2	–5.5	–0.000920685
2	–4.5	–0.010889415
2	–3.5	0.005433344
2	–2.5	0.012066776
2	–1.5	0.0261401
2	–0.5	0.107730551
2	0.5	0.993325163
2	1.5	0.003001136
2	2.5	0.015014353
2	3.5	–0.010589096
2	4.5	–0.013732929
2	5.5	0.013471697
2	6.5	–0.001802706
2	7.5	0.0001
3	–7.5	4.34166E–05
3	–6.5	0.007157712
3	–5.5	0.005374534
3	–4.5	0.001963923
3	–3.5	–0.009009291
3	–2.5	–0.042863629
3	–1.5	–0.101184868
3	–0.5	–0.02635473
3	0.5	0.002526698
3	1.5	0.991973241
3	2.5	0.00381613
3	3.5	–0.017950396
3	4.5	–0.008101265
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3	6.5	–0.023008849
3	7.5	–0.001038
		0
4	–7.5	0.001037432
4	–6.5	–0.023008476
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4	–4.5	0.008100793
4	–3.5	0.01795046
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4	–1.5	0.991973215
4	–0.5	0.002526915
4	0.5	–0.026354492
4	1.5	–0.101185533
4	2.5	0.042863588
4	3.5	0.009009358
4	4.5	0.001963563
4	5.5	–0.005374552
4	6.5	–0.007157801
4	7.5	0.000044
5	–7.5	0.000154742
5	–6.5	–0.007950367
5	–5.5	–0.004509536
5	–4.5	0.001116756
5	–3.5	0.006042526
5	–2.5	0.021304954
5	–1.5	0.041905126
5	–0.5	–0.012320645
5	0.5	–0.013509456
5	1.5	0.01290064
5	2.5	–0.965671412
5	3.5	0.025960803
5	4.5	–0.028955585
5	5.5	0.020379043
5	6.5	–0.248793386
5	7.5	–0.028652
6	–7.5	–0.028652493
6	–6.5	–0.248792697
6	–5.5	–0.020379079
6	–4.5	0.028955829
6	–3.5	–0.025961105
6	–2.5	0.965671511
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6	2.5	0.021304324
6	3.5	0.006042231
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6	5.5	–0.004508973
6	6.5	–0.007949821
6	7.5	–0.000155
7	–7.5	–0.000281789
7	–6.5	0.024083261
7	–5.5	–0.002719796
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7	–0.5	0.001747176
7	0.5	0.004747822
7	1.5	0.024379923
7	2.5	0.251057411
7	3.5	0.096981529
7	4.5	0.014339649
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7	6.5	–0.959505422
7	7.5	–0.041066
8	–7.5	0.04106605
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8	–5.5	0.060988366
8	–4.5	0.014339114
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9	0.5	–0.005398602
9	1.5	0.007599714
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11	–3.5	–0.806469832
11	–2.5	–0.010447977
11	–1.5	0.023561666
11	–0.5	–0.006703354
11	0.5	–0.003495223
11	1.5	–0.006622453
11	2.5	0.006533699
11	3.5	–0.006997986
11	4.5	0.008776959
11	5.5	–0.012982706
11	6.5	0.003245802
11	7.5	–0.001394
12	–7.5	–0.00139396
12	–6.5	–0.003245939
12	–5.5	0.012982754
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12	–3.5	–0.006998264
12	–2.5	–0.006533599
12	–1.5	–0.006622036
12	–0.5	–0.00349567
12	0.5	0.006702883
12	1.5	–0.023562461
12	2.5	–0.010447873
12	3.5	0.806469819
12	4.5	0.042788416
12	5.5	0.301905661
12	6.5	–0.076991611
12	7.5	0.499585
13	–7.5	0.000702353
13	–6.5	0.002048542
13	–5.5	–0.025896691
13	–4.5	–0.007826391
13	–3.5	0.005451231
13	–2.5	–0.003288442
13	–1.5	–0.003268955
13	–0.5	0.000856237
13	0.5	0.017052093
13	1.5	0.041002813
13	2.5	–0.015059187
13	3.5	0.254593842
13	4.5	0.186603412
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13	6.5	0.039989671
13	7.5	0.155523
14	–7.5	–0.155523257
14	–6.5	0.039990329
14	–5.5	–0.933588039
14	–4.5	0.186603064
14	–3.5	0.254594149
14	–2.5	–0.015059078
14	–1.5	–0.041001952
14	–0.5	–0.017051346
14	0.5	0.00085623
14	1.5	–0.003269474
14	2.5	–0.003288164
14	3.5	0.005451292
14	4.5	–0.007826557
14	5.5	0.025896645
14	6.5	–0.002048703
14	7.5	0.000702
15	–7.5	–0.00731654
15	–6.5	0.000680827
15	–5.5	0.009544028
15	–4.5	–0.047961785
15	–3.5	–0.009899268
15	–2.5	0.000920078
15	–1.5	0.003343512
15	–0.5	0.010044484
15	0.5	–0.0124637
15	1.5	0.010636105
15	2.5	0.029251975
15	3.5	0.08234147
15	4.5	–0.975296255
15	5.5	0.161620711
15	6.5	0.010030421
15	7.5	0.109613
16	–7.5	–0.109613106
16	–6.5	0.010030334
16	–5.5	0.161620303
16	–4.5	–0.975295803
16	–3.5	–0.082341374
16	–2.5	0.029251681
16	–1.5	0.010635553
16	–0.5	–0.012464058
16	0.5	–0.010044002
16	1.5	–0.003342758
16	2.5	–0.000920513
16	3.5	–0.009899029
16	4.5	0.047961652
16	5.5	–0.009544601
16	6.5	–0.000680753
16	7.5	–0.007316

Table S 15 CASSCF/RASSI calculated energies of the lowest spin-orbit Kramers doublets (cm^{-1}) of **1Er**.

small compression of the molecule dist = -0.05 Å Basis 1	original experimental geometry dist = 0.00 Å Basis 1	small expansion of the molecule dist = +0.05 Å Basis 1
0.000	0.000	0.000
0.000	0.000	0.000
70.173	63.467	57.273
70.173	63.467	57.273
177.448	164.273	150.257
177.448	164.273	150.257
212.208	238.562	242.964
212.208	238.562	242.964
272.081	261.312	265.741
272.081	261.312	265.741
281.055	290.146	295.094
281.055	290.146	295.094
292.877	296.740	302.371
292.877	296.740	302.371
323.980	313.608	312.204
323.980	313.608	312.204
g tensors of the ground Kramers Doublets		
10.764110	10.752748	10.766338
8.328855	8.342994	8.330524
1.202465	1.200502	1.197981

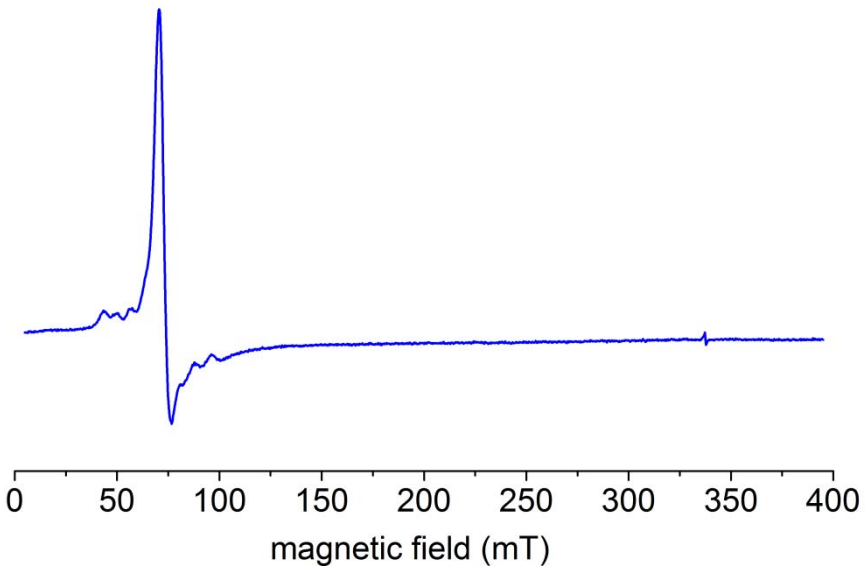

Figure S 24 X-band EPR spectrum recorded on a powder sample of **1Er** at 10 K. The less intense lines left and right of the main resonance line are due to the hyperfine coupling of the electron spin with the erbium nuclear spin.

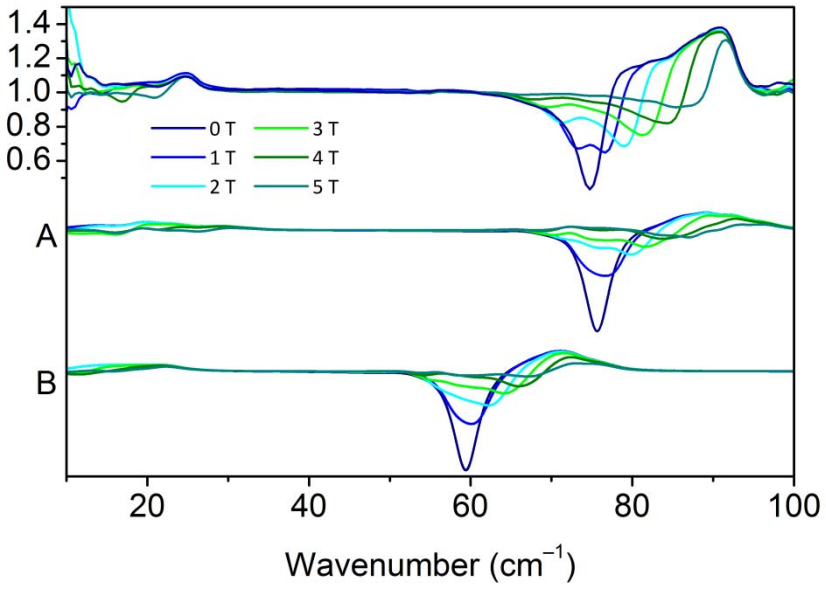

Figure S 25 Experimental FIR data for **1Er**, as well as simulations based on (A) CF parameters derived from CASSCF calculations, after rescaling of the energies of the states by 1.27; (B) CF parameters derived from CASSCF calculations without any scaling of the energies of the states.

References

1. N. Koike, H. Uekusa, Y. Ohashi, C. Harnoode, F. Kitamura, T. Ohsaka and K. Tokuda, *Inorg. Chem.*, 1996, **35**, 5798-5804.
2. J. J. Baldoví, J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado and A. Gaita-Ariño, *Dalton Trans.*, 2012, **41**, 13705-13710.
3. N. Ishikawa, M. Sugita, T. Okubo, N. Tanaka, T. Lino and Y. Kaizu, *Inorg. Chem.*, 2003, **42**, 2440-2446.