Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

for

Structural isomerism-tuned magnetisation relaxation dynamics in lanthanide coordination complexes

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Mass spectra

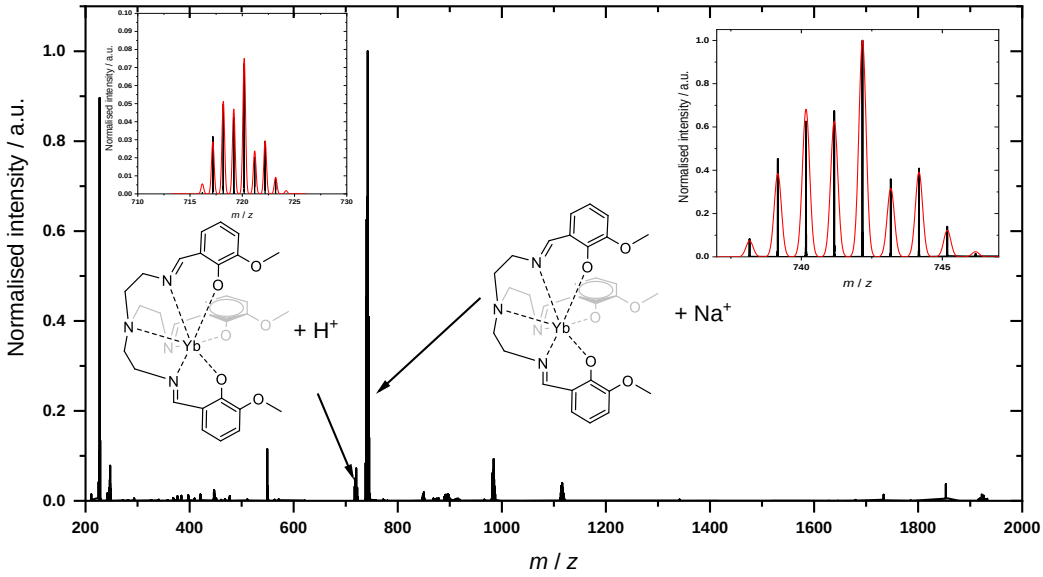

Figure S1. MALDI positive-ion mode mass spectrum of Yb(trenovan). The experiment is in black and the simulated isotope pattern is in red.

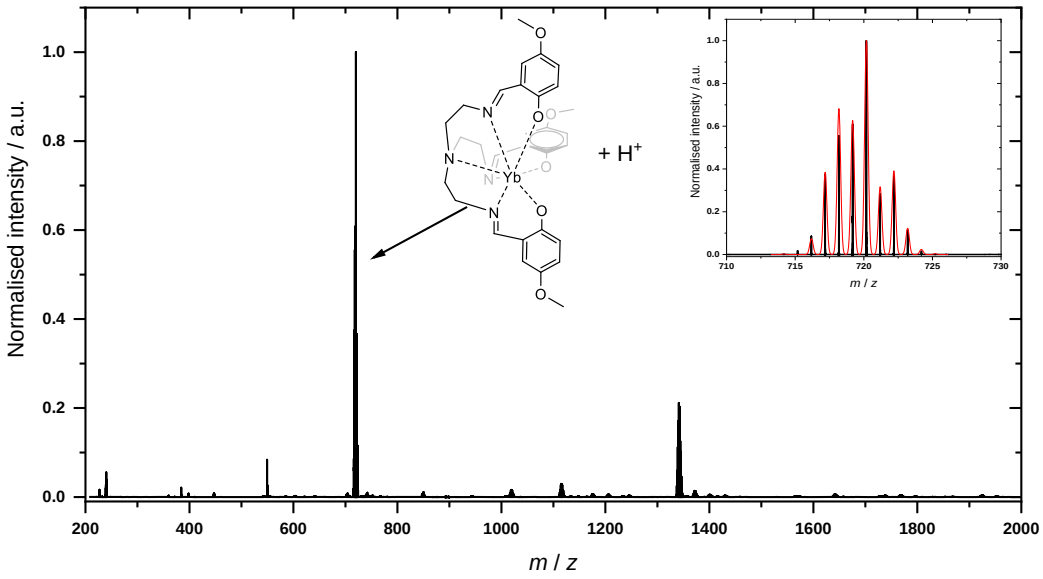

Figure S2. MALDI positive-ion mode mass spectrum of Yb(trenpvan). The experiment is in black and the simulated isotope pattern is in red.

Infrared spectroscopy

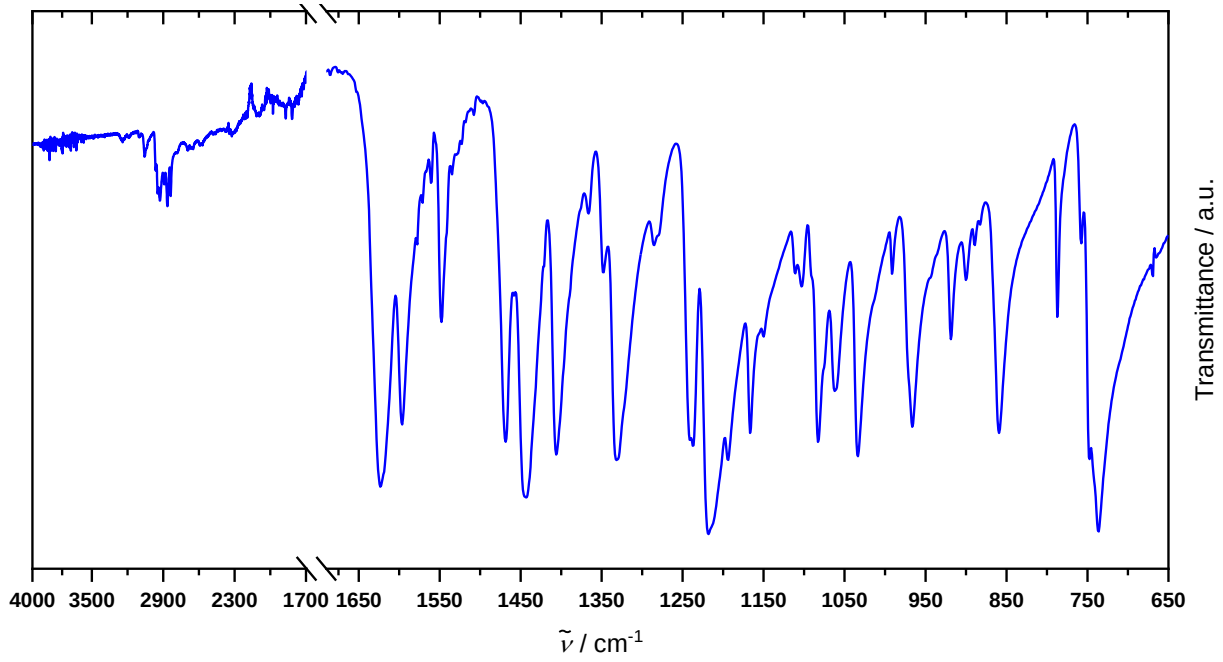

Figure S3. IR spectrum of Yb(trenovan)

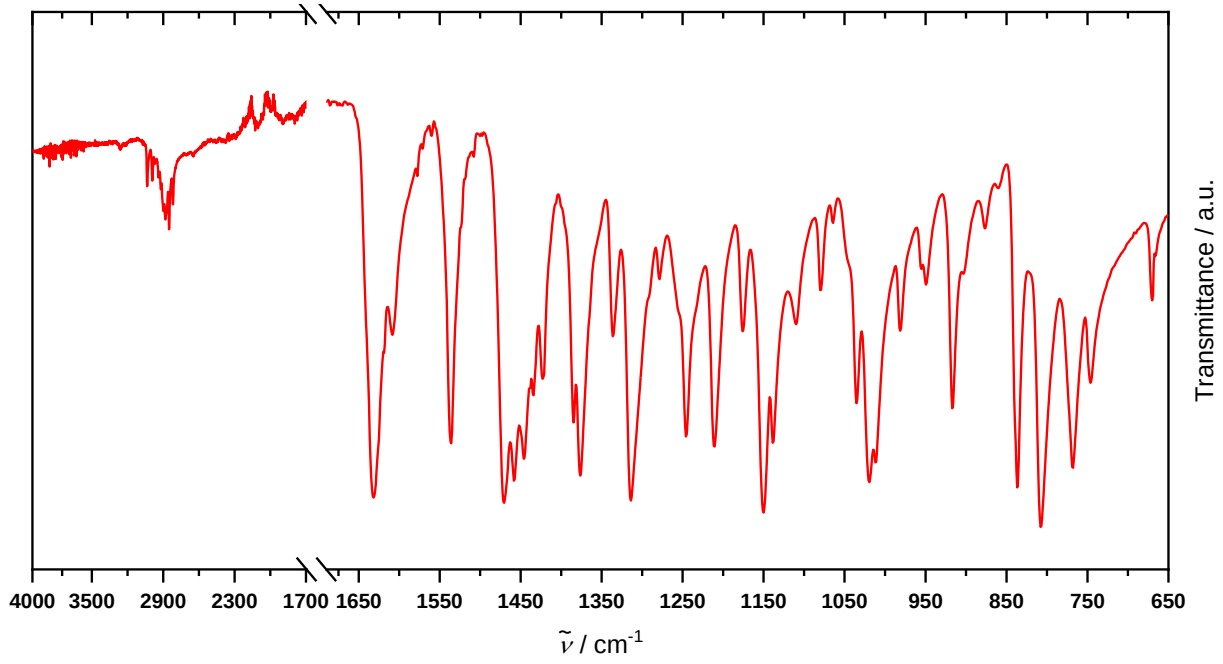

Figure S4. IR spectrum of Yb(trenpvan)

Powder X-ray diffraction

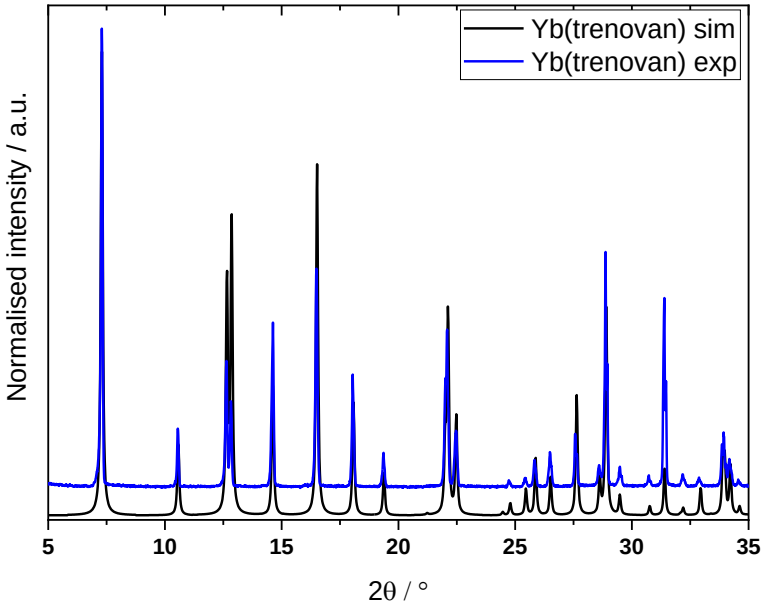

Figure S5. PXRD of Yb(trenovan) in blue and the simulated PXRD in black. The simulated spectrum is based on a crystal structure collected at room temperature.

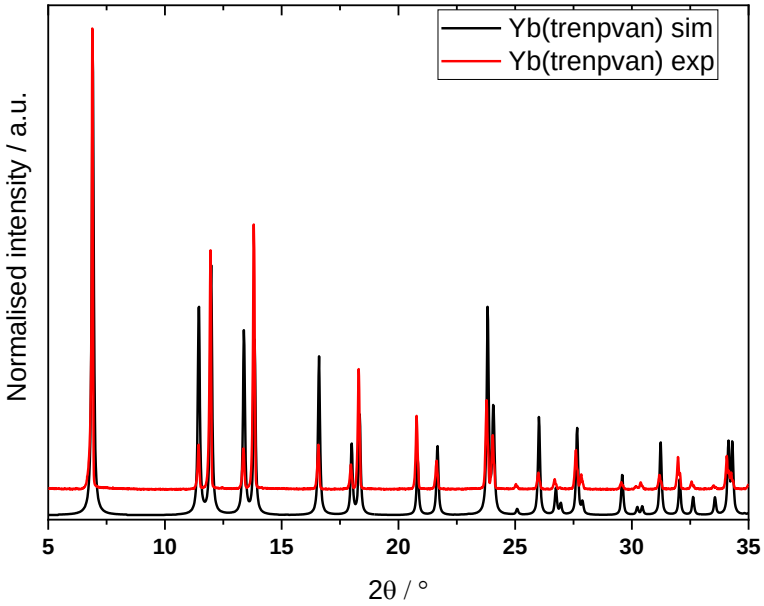

Figure S6. PXRD of Yb(trenpvan) in red and the simulated PXRD in black. The simulated spectrum is based on a crystal structure collected at room temperature.

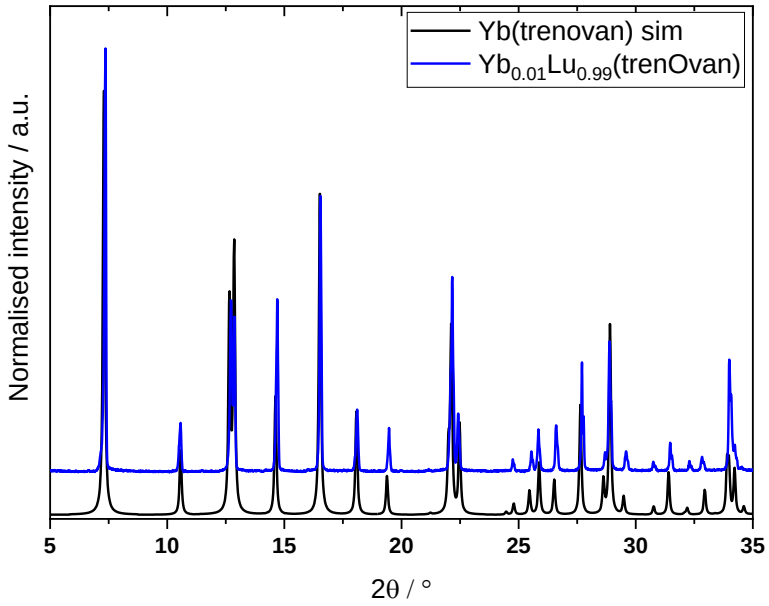

Figure S7. PXRD of $Yb_{0.01}Lu_{0.99}$(trenovan) in blue and the simulated PXRD in black. The simulated spectrum is based on a crystal structure of Yb(trenovan) collected at room temperature.

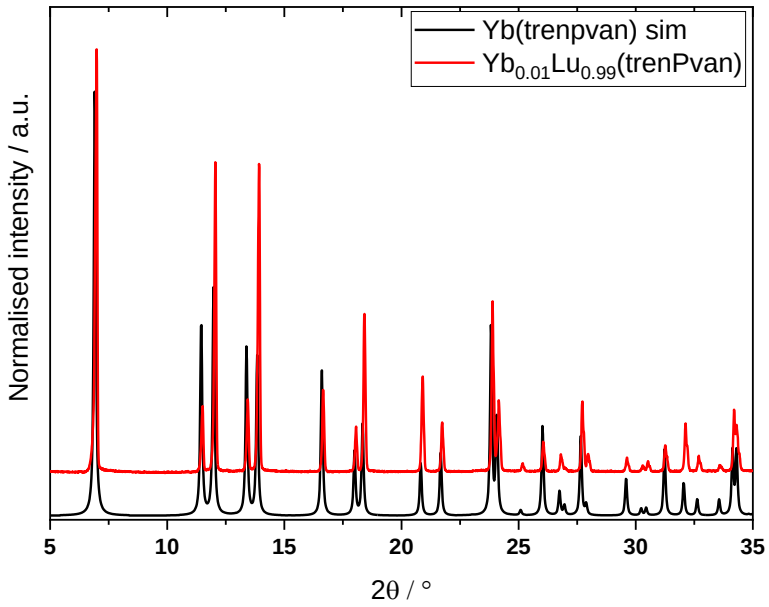

Figure S8. PXRD of $Yb_{0.01}Lu_{0.99}$(trenpvan) in red and the simulated PXRD in black. The simulated spectrum is based on a crystal structure of Yb(trenpvan) collected at room temperature.

Crystallographic data

Table S1. Crystallographic data of Yb(trenOvan) and Yb(trenPvan)

Identification code	Yb(trenovan)	Yb(trenpvan)
Empirical formula	$C_{30}H_{33}N_4O_6Yb$	
Formula weight	718.65	
Temperature/K	120	
Crystal system	trigonal	
Space group	$P\bar{3}$	
a/Å	13.9911(5)	14.7420(5)
b/Å	13.9911(5)	14.7420(5)
c/Å	8.1853(3)	7.5448(4)
α/°	90	
β/°	90	
γ/°	120	
Volume/Å^3	1387.61(11)	1420.01(12)
Z	2	
ρ_{calc}g/cm^3	1.720	1.681
μ/mm^{-1}	3.422	3.343
F(000)	718.0	718.0
Crystal size/mm^3	0.417 × 0.271 × 0.258	0.422 × 0.247 × 0.136
Radiation	MoKα (λ = 0.71073)	
2Θ range for data collection/°	4.976 to 56.538	5.526 to 55.72
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -10 ≤ l ≤ 10	-18 ≤ h ≤ 19, -19 ≤ k ≤ 19, -9 ≤ l ≤ 9
Reflections collected	21437	19885
Independent reflections	2298 [R_{int} = 0.0364, R_{sigma} = 0.0181]	2254 [R_{int} = 0.0535, R_{sigma} = 0.0253]
Data/restraints/parameters	2298/0/125	2254/0/125
Goodness-of-fit on F^2	1.149	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0161, wR_2 = 0.0365	R_1 = 0.0167, wR_2 = 0.0405
Final R indexes [all data]	R_1 = 0.0189, wR_2 = 0.0376	R_1 = 0.0186, wR_2 = 0.0413
Largest diff. peak/hole / e Å^{-3}	0.80/-0.77	0.53/-1.12

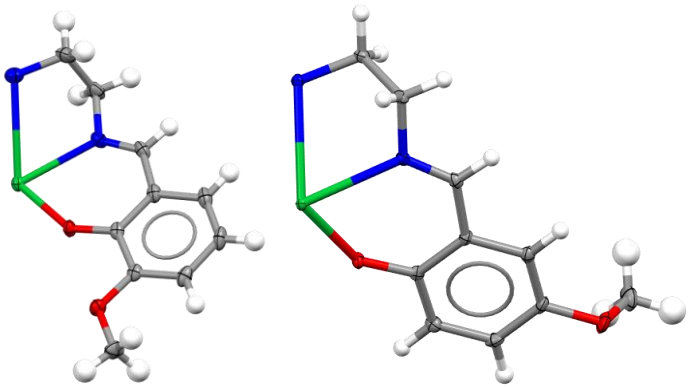

Figure S9. Asymmetric unit of Yb(trenovan) (left) and Yb(trenpvan) (right). Thermal ellipsoids are set to 50 % probability. Colour code: C, grey; H, white; N, blue; O, red; Yb, green.

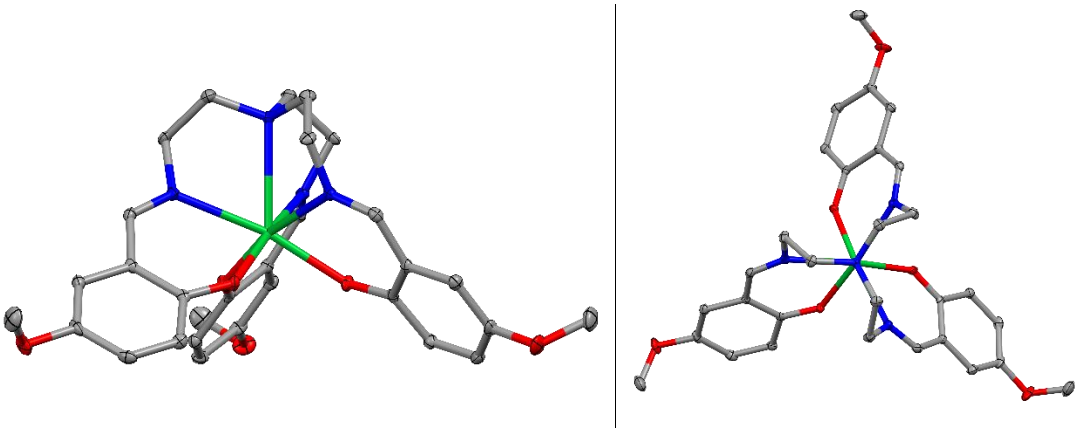

Figure S10. Left: Crystal structure obtained at 120 K of Yb(trenpvan) seen from the side (left) and from the top along the threefold axis (right). Hydrogens have been omitted for clarity and thermal ellipsoids have been set to 50 %. Colour scheme: C, grey; O, red; N, blue and Yb, green.

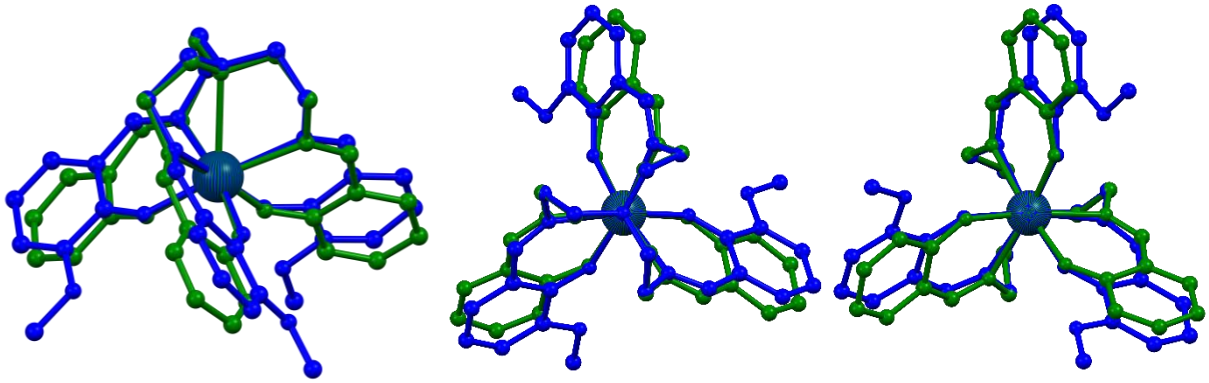

Figure S11. Overlay of the crystal structures of Yb(trensal) in green and Yb(trenovan) in blue viewed from the side (left), top (middle) and bottom (right). The crystal structure of Yb(trensal) was obtained from literature.[1]

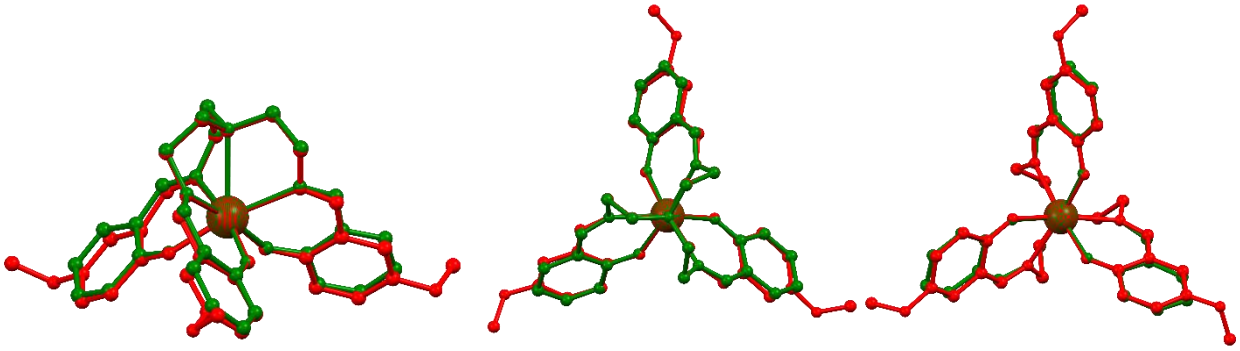

Figure S12. Overlay of the crystal structures of Yb(trensal) in green and Yb(trenpvan) in red viewed from the side (left), top (middle) and bottom (right). The crystal structure of Yb(trensal) was obtained from literature.[1]

Structural analysis with SHAPE program

Table S2. Results of the continuous shape measures performed with the SHAPE program.[2]

	HP-7	HPY-7	PBPY-7	COC-7	CTPR-7	JPBPY-7	JETPY-7
Yb(trensal)	36.445	19.408	8.598	0.882	2.612	12.312	16.724
Yb(trenovan)	36.169	20.153	8.872	1.356	2.986	12.46	15.043
Yb(trenpvan)	36.768	18.68	8.559	0.707	2.484	12.284	17.723

Where the symmetries given in the top row are: HP-7, Heptagon; HPY-7, Hexagonal pyramid; PBPY-7, Pentagonal bipyramid; COC-7, Capped octahedron; CTPR-7, Capped trigonal prism; JPBPY-7, Johnson pentagonal bipyramid J13; and JETPY-7, Johnson elongated triangular pyramid 37.

Static magnetic properties

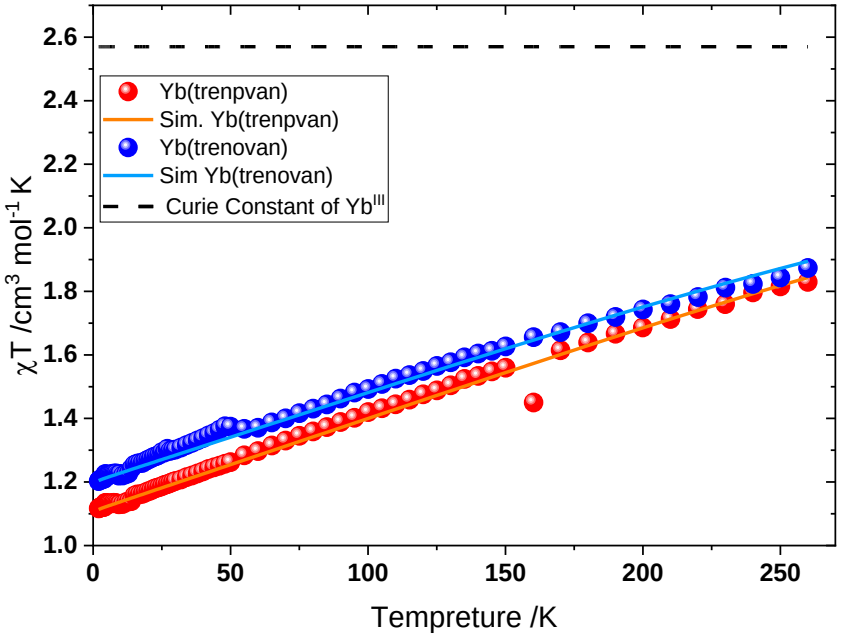

Figure S13. χT product of Yb(trenovan) and Yb(trenpvan). Experiment in scatter and the best fit (solid lines) obtained as described in the main text.

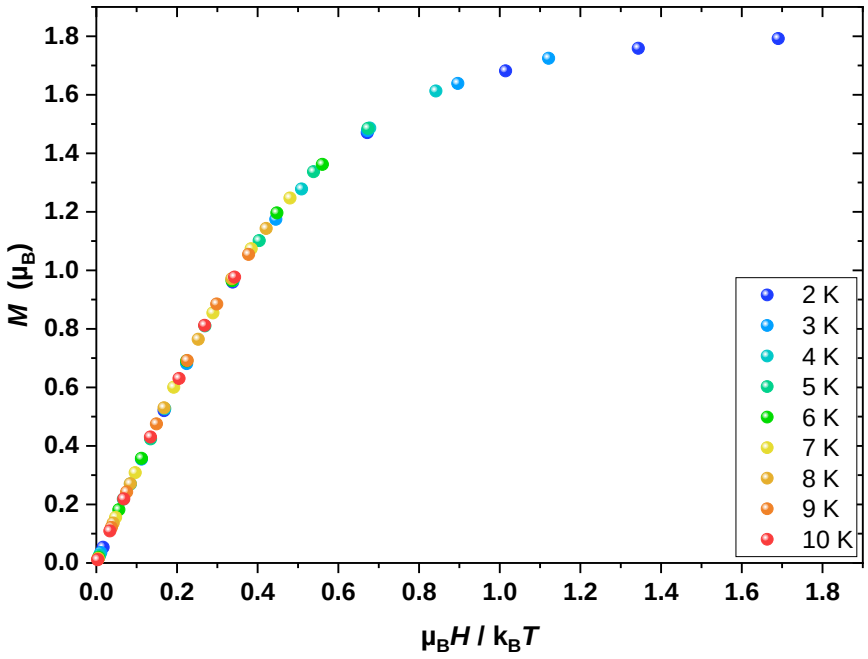

Figure S14. Temperature dependence of the reduced magnetisation of Yb(trenovan).

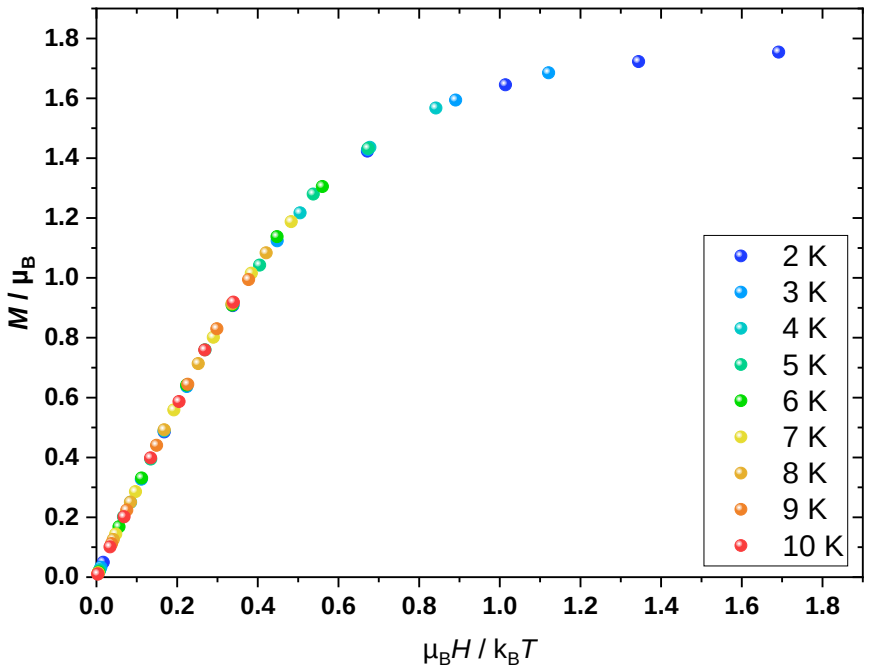

Figure S15. Temperature dependence of the reduced magnetisation of Yb(trenpvan).

Ac susceptibility

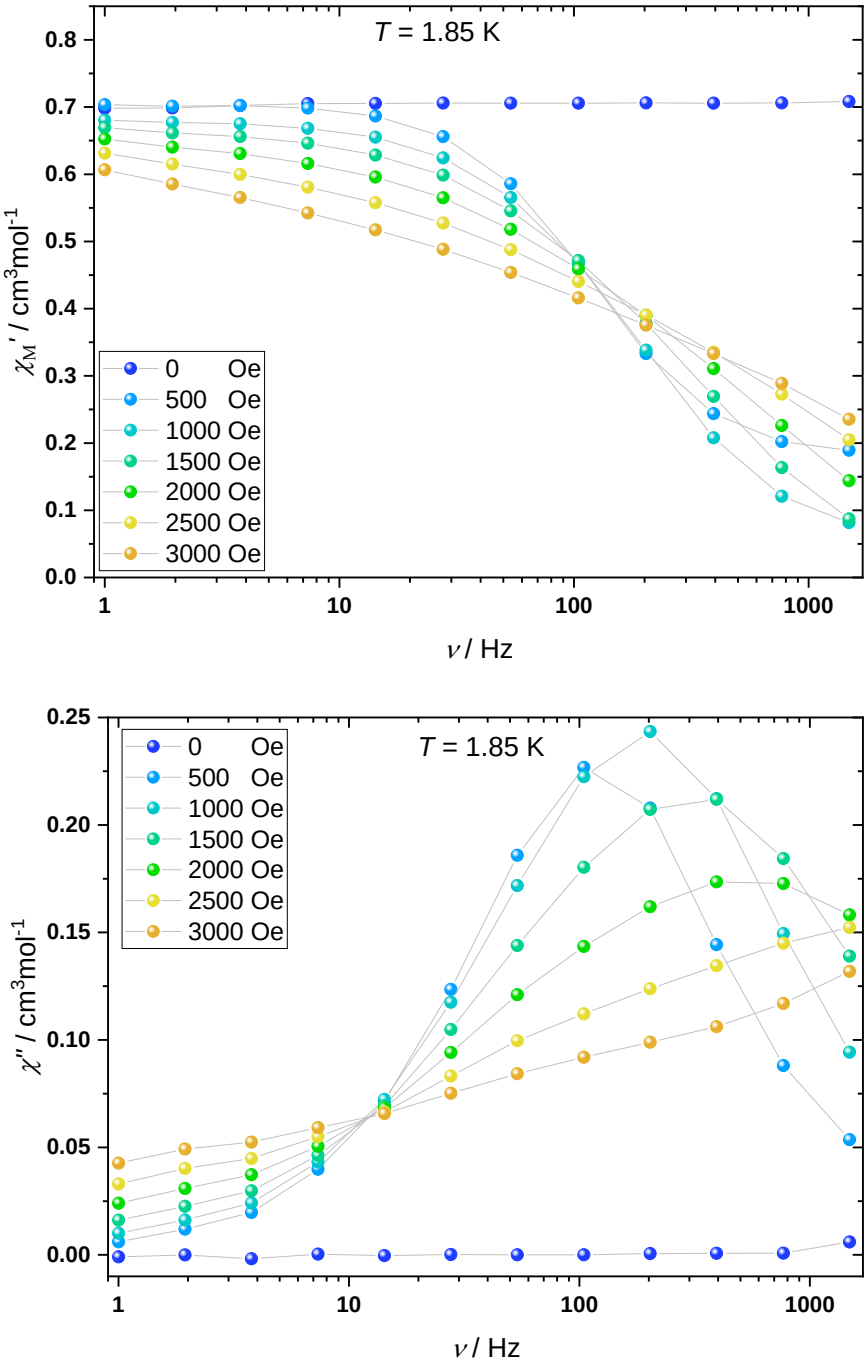

Figure S16. Magnetic field dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibility of Yb(trenovan). Solid lines are guidelines for the eye.

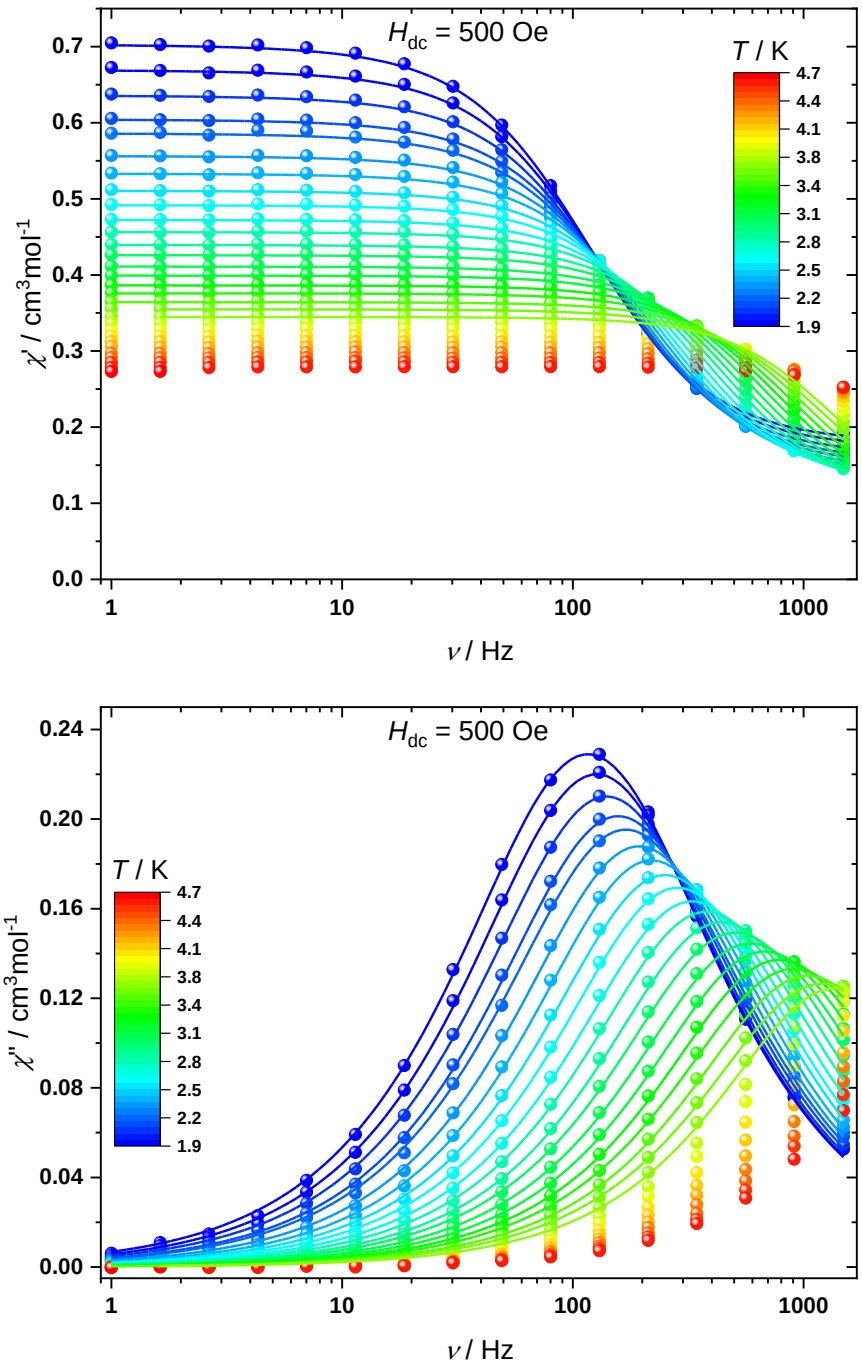

Figure S17. Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibility (scatter) of Yb(trenovan) with the best fit (solid lines) obtained for a generalized Debye model as described in the main text. For the fitting parameters used in the generalized Debye model please see Table S3. The data could be fitted up to 3.7 K.

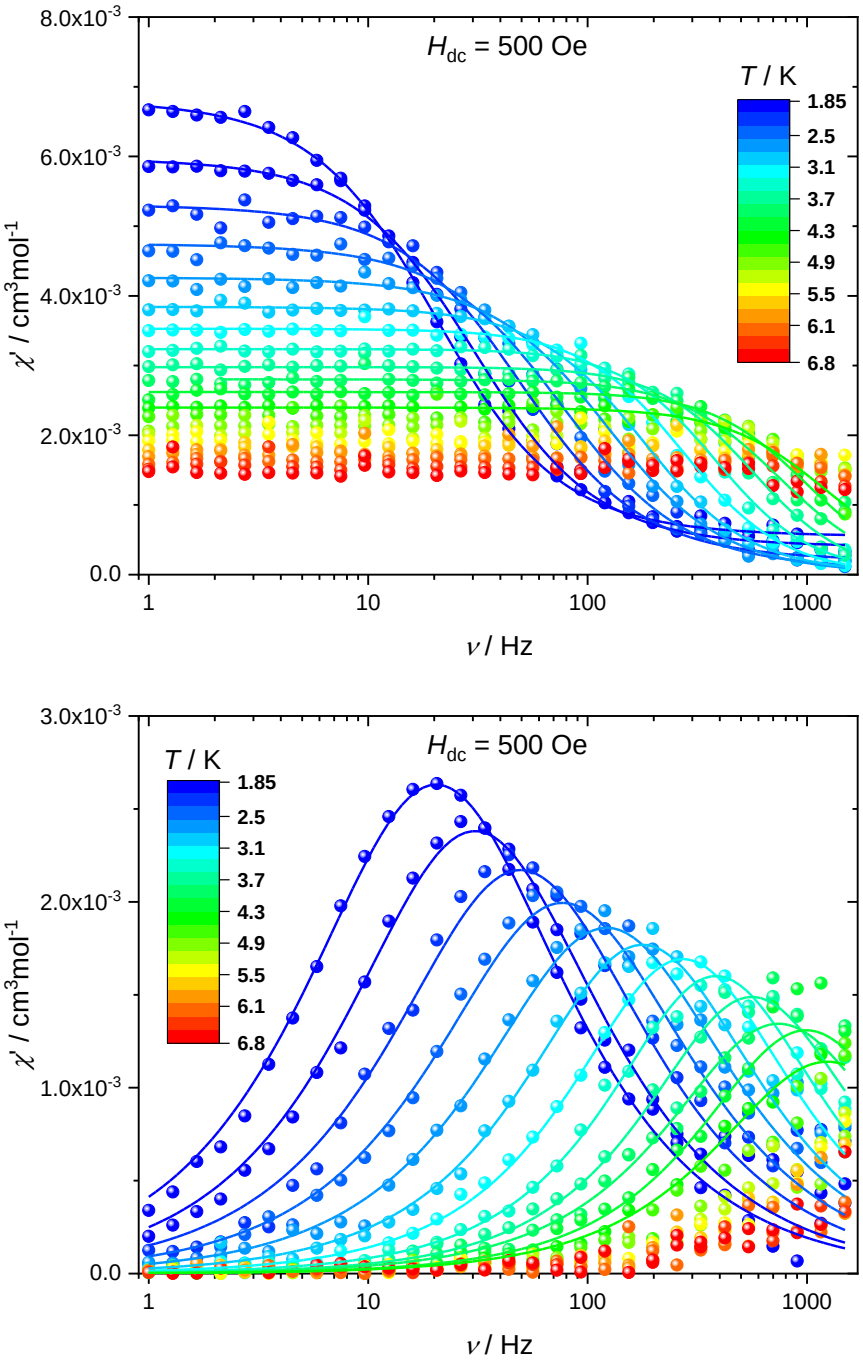

Figure S18. Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibility (scatter) for $Yb_{0.01}Lu_{0.99}$(trenovan) with the best fit (solid lines) obtained for a generalized Debye model as described in the main text. For the fitting parameters used in the generalized Debye model please see Table S4. The data could be fitted up to 4.55 K.

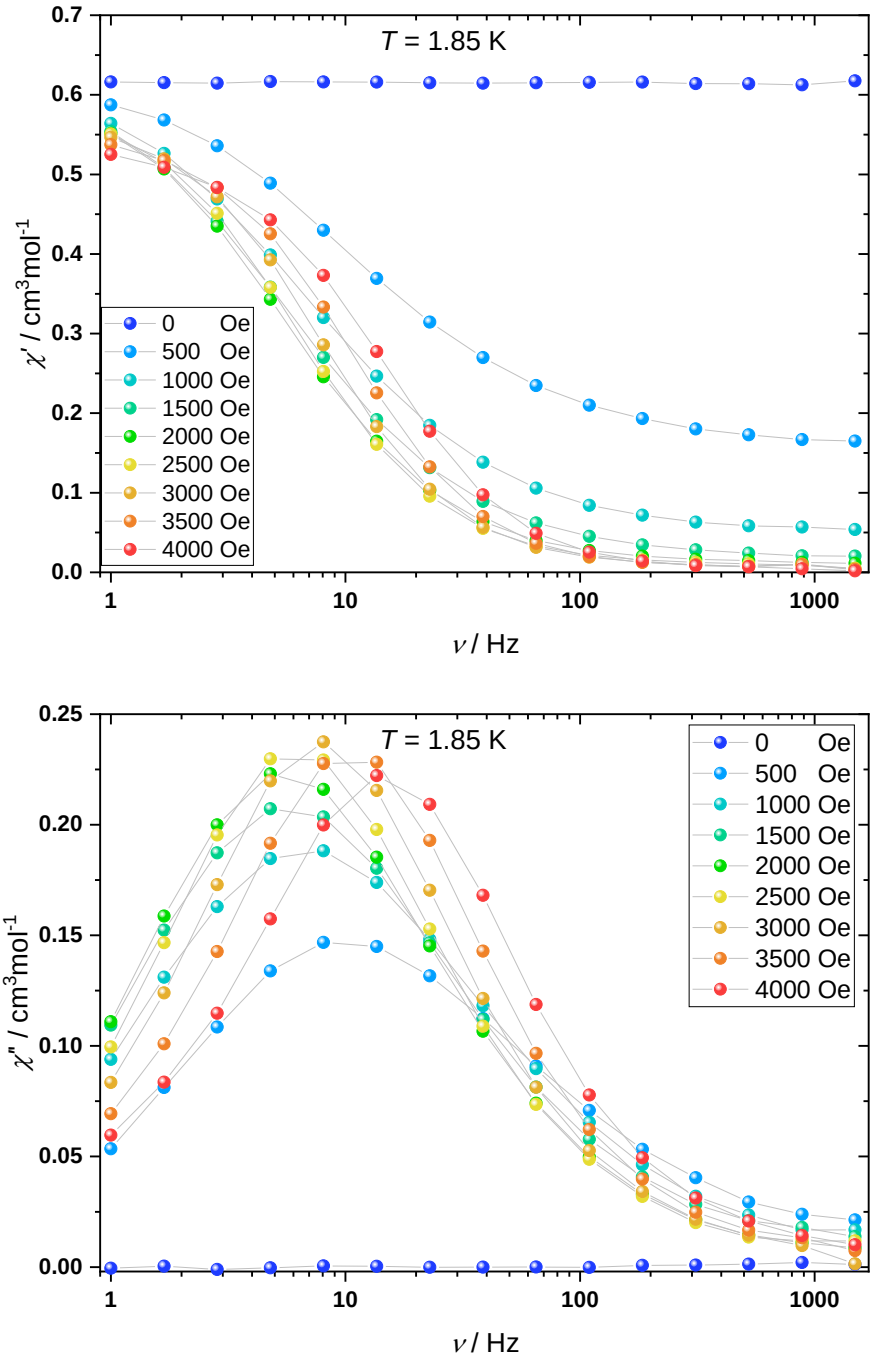

Figure S19. Magnetic field dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibility of Yb(trenpvan). Solid lines are guidelines for the eye.

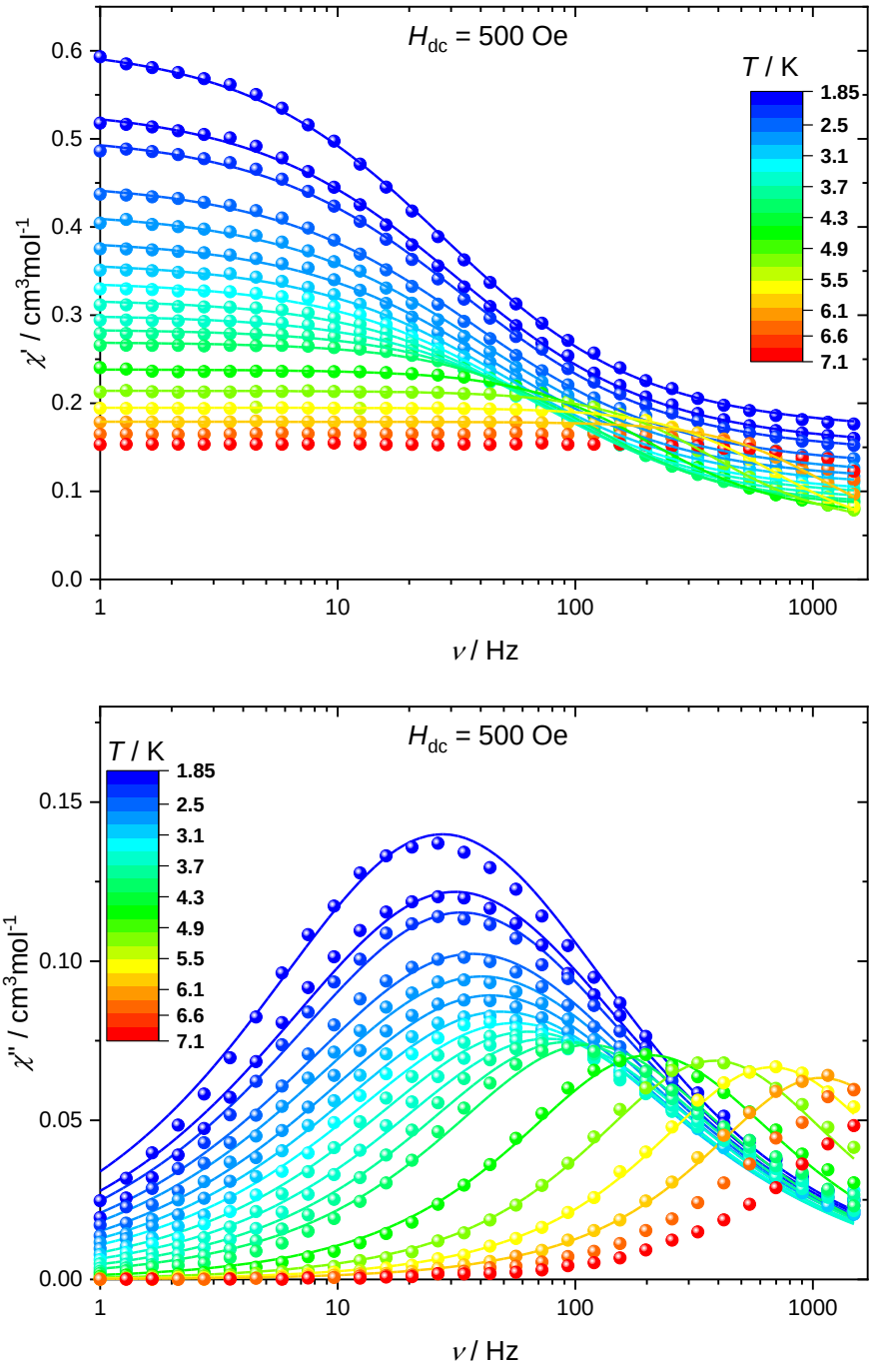

Figure S20. Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibility (scatter) for Yb(trenpvan) with the best fit (solid lines) obtained for a generalized Debye model as described in the main text. For the fitting parameters used in the generalized Debye model please see Table S5. The data could be fitted up to 6.05 K.

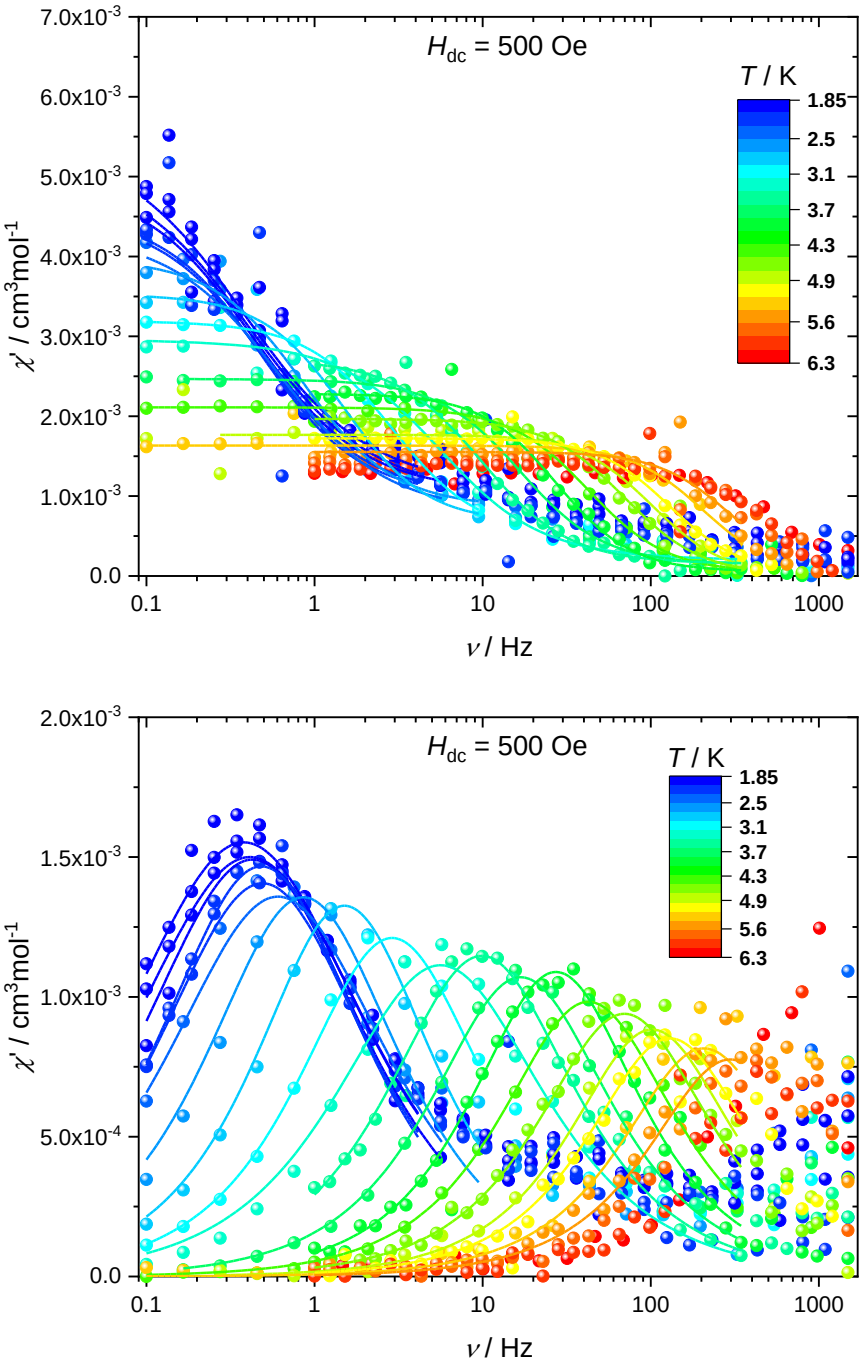

Figure S21. Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibility (scatter) for $Yb_{0.01}Lu_{0.99}$(trenpvan) with the best fit (solid lines) obtained for a generalized Debye model as described in the main text. For the fitting parameters used in the generalized Debye model please see Table S6. The data could be fitted up to 5.55 K.

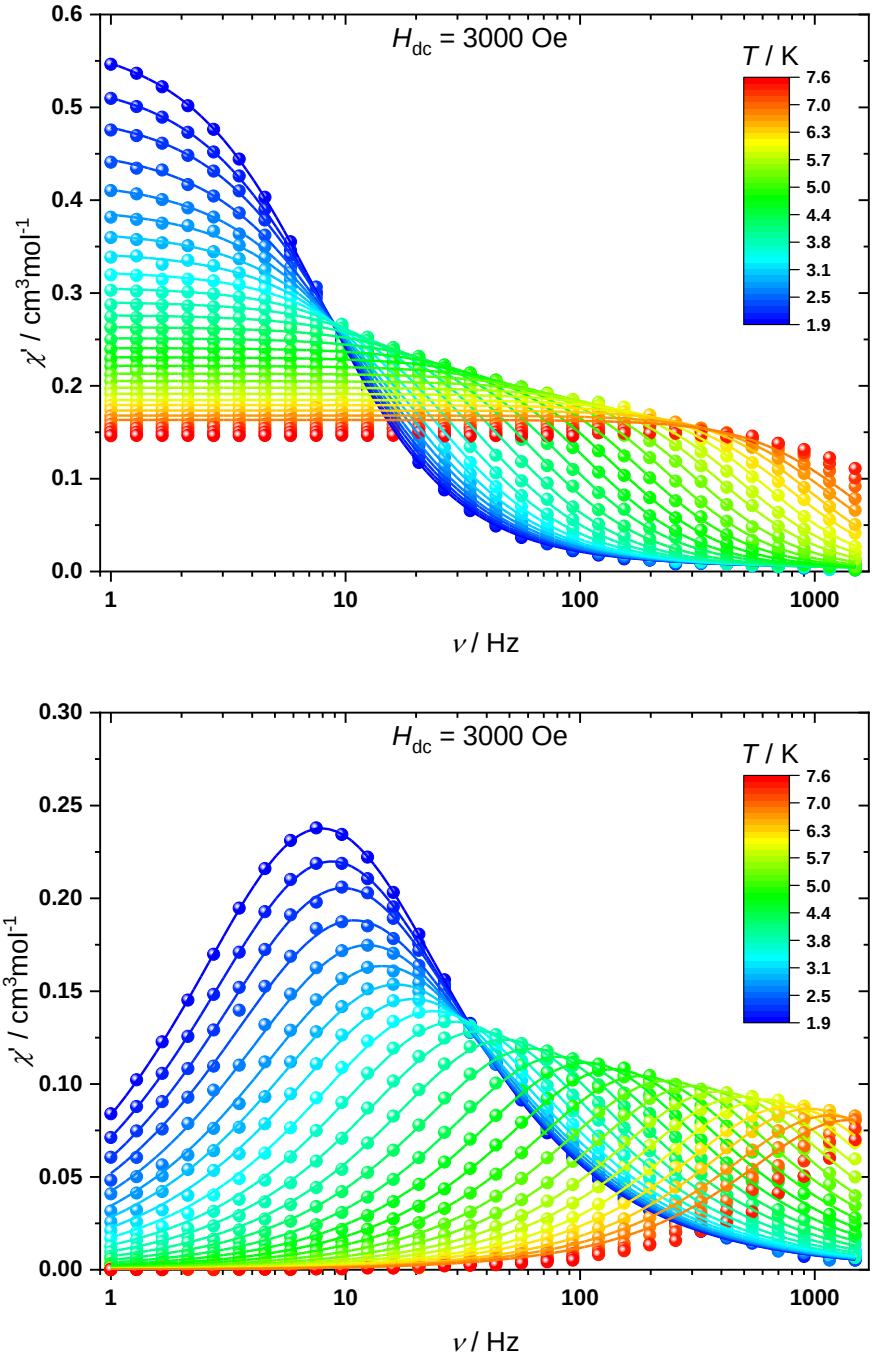

Figure S22. Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibility (scatter) for Yb(trenpvan) with the best fit (solid lines) obtained for a generalized Debye model as described in the main text. For the fitting parameters used in the generalized Debye model please see Table S7. The data could be fitted up to 6.8 K.

Table S3. Best fit parameters (τ and α) with uncertainties for the generalized Debye model fitted to the temperature dependence of the ac magnetic susceptibility of Yb(trenovan) with an applied magnetic field of 500 Oe.

Temperature / K	τ / ms	τ (uncertainty) / ms	α	α (uncertainty)
1.84	1.37	0.00531	0.087	0.002
1.90	1.26	0.00570	0.079	0.003
2.00	1.14	0.00455	0.076	0.002
2.10	1.01	0.00513	0.071	0.003
2.20	0.939	0.00616	0.073	0.004
2.30	0.822	0.00423	0.063	0.003
2.40	0.725	0.00373	0.057	0.003
2.50	0.635	0.00333	0.055	0.003
2.60	0.560	0.00305	0.051	0.003
2.70	0.485	0.00316	0.050	0.004
2.80	0.420	0.00285	0.048	0.004
2.90	0.362	0.00284	0.045	0.004
3.00	0.314	0.00252	0.048	0.004
3.10	0.272	0.00218	0.044	0.004
3.20	0.235	0.00200	0.042	0.004
3.30	0.202	0.00192	0.040	0.005
3.40	0.176	0.00173	0.045	0.004
3.50	0.153	0.00190	0.038	0.005
3.60	0.132	0.00162	0.045	0.005
3.70	0.116	0.00172	0.033	0.005

Table S4. Best fit parameters (τ and α) with uncertainties for the generalized Debye model fitted to the temperature dependence of the ac magnetic susceptibility of $Yb_{0.01}Lu_{0.99}$(trenovan) with an applied magnetic field of 500 Oe.

Temperature / K	τ / ms	τ (uncertainty) / ms	α	α (uncertainty)
1.84	7.80	0.124	0.1119	0.0088
2.05	5.19	0.120	0.1009	0.0131
2.30	3.22	0.106	0.1039	0.0184
2.55	2.07	0.053	0.1014	0.0145
2.80	1.30	0.036	0.0864	0.0159
3.05	0.895	0.015	0.0508	0.0102
3.30	0.586	0.016	0.0265	0.0169
3.55	0.414	0.008	0.0000	0.0122
3.80	0.284	0.009	0.0000	0.0187
4.05	0.215	0.013	0.0261	0.0300
4.30	0.161	0.009	0.0000	0.0254
4.55	0.129	0.007	0.0316	0.0203

Table S5. Best fit parameters (τ and α) with uncertainties for the generalized Debye model fitted to the temperature dependence of the ac magnetic susceptibility of Yb(trenpvan) with an applied magnetic field of 500 Oe.

Temperature / K	τ / ms	τ (uncertainty) / ms	α	α (uncertainty)
1.85	5.77	0.079	0.2818	0.0057
2.05	5.10	0.078	0.2870	0.0064
2.25	4.80	0.072	0.2818	0.0063
2.45	4.31	0.072	0.2870	0.0070
2.65	3.95	0.070	0.2854	0.0074
2.85	3.623	0.064	0.2716	0.0076
3.05	3.281	0.060	0.2625	0.0079
3.25	2.872	0.069	0.2565	0.0105
3.45	2.512	0.049	0.2314	0.0088
3.65	2.093	0.044	0.2141	0.0099
3.85	1.718	0.034	0.1877	0.0097
4.05	1.402	0.023	0.1556	0.0082
4.55	0.774	0.009	0.1050	0.0064
5.05	0.412	0.004	0.0678	0.0058
5.55	0.237	0.003	0.0450	0.0051
6.05	0.147	0.002	0.0241	0.0047

Table S6. Best fit parameters (τ and α) with uncertainties for the generalized Debye model fitted to the temperature dependence of the ac magnetic susceptibility of $Yb_{0.01}Lu_{0.99}$(trenpvan) with an applied magnetic field of 500 Oe.

Temperature / K	τ / ms	τ (uncertainty) / ms	α	α (uncertainty)
1.85	419	33.3	0.2247	0.0409
1.95	386	29.6	0.2199	0.0409
2.05	372	59.3	0.1767	0.0877
2.15	324	5.95	0.1502	0.0113
2.25	329	71.7	0.1269	0.1382
2.30	263	12.8	0.1692	0.0285
2.55	186	14.1	0.0936	0.0478
2.80	106	6.79	0.0504	0.0425
3.05	55.0	1.11	0.0701	0.0119
3.30	28.4	2.15	0.1380	0.0393
3.80	9.46	0.228	0.0529	0.0144
4.30	3.74	0.076	0.0337	0.0123
4.80	1.57	0.143	0.0000	0.0562
5.30	0.769	0.070	0.0000	0.0447
3.55	16.1	0.503	0.0724	0.0193
4.05	5.83	0.181	0.0142	0.0207
4.55	2.29	0.092	0.0294	0.0253
5.05	1.22	0.057	0.0000	0.0276
5.55	0.536	0.111	0.0000	0.0820

Table S7. Best fit parameters (τ and α) with uncertainties for the generalized Debye model fitted to the temperature dependence of the ac magnetic susceptibility of Yb(trenpvan) with an applied magnetic field of 3000 Oe.

Temperature / K	τ / ms	τ (uncertainty) / ms	α	α (uncertainty)
1.84	20.1	0.043	0.117	0.001
2.00	18.2	0.059	0.117	0.002
2.18	16.3	0.078	0.114	0.003
2.40	14.6	0.078	0.122	0.003
2.60	12.8	0.069	0.115	0.003
2.80	11.1	0.061	0.110	0.003
3.00	9.67	0.048	0.107	0.003
3.20	8.19	0.046	0.101	0.003
3.40	6.73	0.044	0.089	0.004
3.60	5.45	0.031	0.079	0.003
3.80	4.30	0.029	0.071	0.004
4.00	3.33	0.019	0.064	0.003
4.20	2.56	0.016	0.059	0.004
4.40	1.96	0.011	0.052	0.003
4.60	1.50	0.0077	0.044	0.003
4.80	1.15	0.0071	0.038	0.004
5.00	0.884	0.0044	0.036	0.003
5.20	0.680	0.0039	0.028	0.004
5.40	0.524	0.0027	0.023	0.003
5.60	0.409	0.0022	0.020	0.003
5.80	0.326	0.0022	0.017	0.004
6.00	0.259	0.0020	0.005	0.004
6.20	0.207	0.0019	0.014	0.005
6.40	0.168	0.0018	0.000	0.005
6.60	0.137	0.0016	0.008	0.005
6.80	0.113	0.0017	0.008	0.005

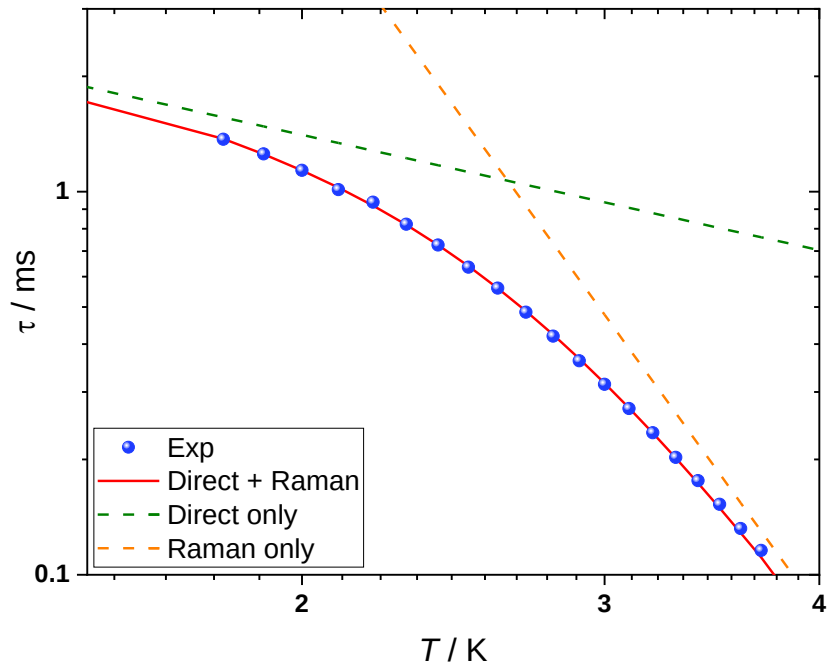

Figure S23. The temperature dependence of the spin lattice relaxation (τ) in Yb(trenovan) (scatter), the best fit as described in the main text (solid line) and the two relaxation components of the fit (dashed lines). The relaxation times were obtained with an applied static magnetic field of 500 Oe.

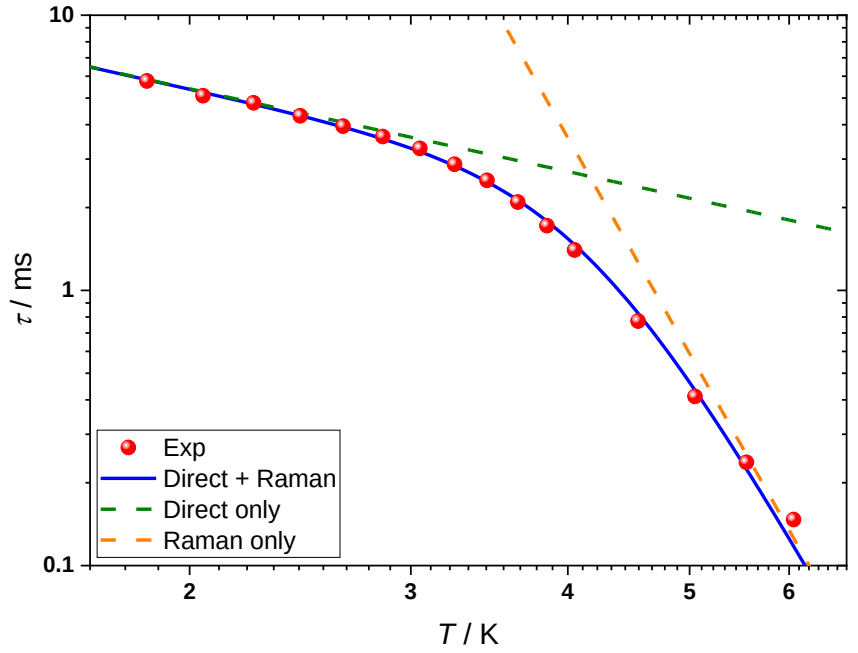

Figure S24. The temperature dependence of the spin lattice relaxation (τ) in Yb(trenpvan) (scatter), the best fit as described in the main text (solid line) and the two relaxation components of the fit (dashed lines). The relaxation times were obtained with an applied static magnetic field of 500 Oe.

Eigenvector composition and Eigenvalues

Table S8. Stevens parameters in cm^{-1} for Yb(trensal), Yb(trenovan) and Yb(trenpvan)

	Yb(trensal)	Yb(trenovan)	Yb(trenpvan)
$B_2^0\ /\mathrm{cm}^{-1}$	-11.13	-11.3	−9.49
$B_4^0\ /\mathrm{cm}^{-1}$	$-1.53\cdot\ 10^{-1}$	$-1.58\ \cdot\ 10^{-3}$	$-6.67\cdot\ 10^{-3}$
$B_4^3\ /\mathrm{cm}^{-1}$	8.92	9.26	7.45
$B_4^{-3}\ /\mathrm{cm}^{-1}$	0 (fixed)	0 $(fixed)$	0 $(fixed)$
$B_6^0\ /\mathrm{cm}^{-1}$	$7.1\cdot\ 10^{-3}$	$1.28\cdot\ 10^{-2}$	$1.11\cdot\ 10^{-2}$
$B_6^3\ /\mathrm{cm}^{-1}$	$-6.0\cdot\ 10^{-2}$	$2.76\cdot\ 10^{-1}$	$2.88\cdot\ 10^{-1}$
$B_6^{-3}\ /\mathrm{cm}^{-1}$	$7\cdot\ 10^{-2}$	$4.38\cdot\ 10^{-2}$	$8.95\cdot\ 10^{-2}$
$B_6^6\ /\mathrm{cm}^{-1}$	$3.4\cdot\ 10^{-2}$	$7.13\cdot\ 10^{-2}$	$1.87\cdot\ 10^{-1}$
$B_6^{-6}\ /\mathrm{cm}^{-1}$	$1.01\cdot\ 10^{-1}$	$8.12\cdot\ 10^{-2}$	$1.41\cdot\ 10^{-1}$

Table S9. Eigenvector composition and eigenvalues in cm^{-1} of Yb(trenovan) obtained by the simultaneous fit to the luminescence spectrum, single crystal EPR spectra, χT curve and VTVB measurements as described in the main text.

	0	**0**	**479**	**479**	**819**	**819**	**989**	**989**
$\|\mathbf{7/2}\rangle$	0	0.617	0.0555	0	0	0	0	0.327
$\|\mathbf{5/2}\rangle$	0.0689	0	0	0.912	0	0	0.0189	0
$\|\mathbf{3/2}\rangle$	0	0	0	0	0	1	0	0
$\|\mathbf{1/2}\rangle$	0	0.314	0.0320	0	0	0	0	0.654
$\|\mathbf{-1/2}\rangle$	0.314	0	0	0.0320	0	0	0.654	0
$\|\mathbf{-3/2}\rangle$	0	0	0	0	1	0	0	0
$\|\mathbf{-5/2}\rangle$	0	0.0689	0.912	0	0	0	0	0.0189
$\|\mathbf{-7/2}\rangle$	0.617	0	0	0.055	0	0	0.327	0

Table S10. Eigenvector composition and eigenvalues in cm^{-1} of Yb(trenpvan) obtained by the simultaneous fit to the luminescence spectrum, single crystal EPR spectra, χT curve and VTVB measurements as described in the main text.

	0	**0**	**496**	**496**	**762**	**762**	**941**	**941**
$\|\mathbf{7/2}\rangle$	0	0.597	0.0398	0	0	0	0	0.363
$\|\mathbf{5/2}\rangle$	0.155	0	0	0.760	0	0	0.0849	0
$\|\mathbf{3/2}\rangle$	0	0	0	0	0	1	0	0
$\|\mathbf{1/2}\rangle$	0	0.248	0.201	0	0	0	0	0.552
$\|\mathbf{-1/2}\rangle$	0.248	0	0	0.201	0	0	0.552	0
$\|\mathbf{-3/2}\rangle$	0	0	0	0	1	0	0	0
$\|\mathbf{-5/2}\rangle$	0	0.155	0.760	0	0	0	0	0.0849
$\|\mathbf{-7/2}\rangle$	0.597	0	0	0.0398	0	0	0.363	0

Table S11. Eigenvector composition and eigenvalues in cm^{-1} of Yb(trensal) from literature.[3]

	0	**0**	**464**	**464**	**737**	**737**	**913**	**913**
$\|7/2\rangle$	0	0.583	0.314	0	0	0	0.103	0
$\|5/2\rangle$	0.119	0	0	0.523	0	0	0	0.358
$\|3/2\rangle$	0	0	0	0	0	1	0	0
$\|1/2\rangle$	0	0.298	0.163	0	0	0	0.539	0
$\|-1/2\rangle$	0.298	0	0	0.163	0	0	0	0.539
$\|-3/2\rangle$	0	0	0	0	1	0	0	0
$\|-5/2\rangle$	0	0.119	0.523	0	0	0	0.358	0
$\|-7/2\rangle$	0.583	0	0	0.314	0	0	0	0103

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