

Inelastic neutron scattering measurement of the ground state tunnelling gap in Tb and Ho analogues of a Dy field-induced single-molecule magnet

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1. Additional Characterization Details

Table S1. Crystallographic data for compounds **1-RE·MeOH** (RE = Y, Eu, Gd and Ho) and **1-RE** (Tb, Dy and Yb)

	1-Y·MeOH	1-Eu·MeOH	1-Gd·MeOH	1-Tb	1-Dy	1-Ho·MeOH	1-Er	1-Yb
Empirical formula	C ₃₃ H ₂₃ Br ₈ N ₄ O ₆ Y	C ₃₃ H ₂₃ Br ₈ EuN ₄ O ₆	C ₃₄ H ₂₅ Br ₈ GdN ₄ O ₆	C _{32.5} H ₂₀ Br ₈ N ₄ O ₅ Tb ^a	C ₃₃ H ₂₁ Br ₈ DyN ₄ O ₅	C ₃₄ H ₂₅ Br ₈ HoN ₄ O ₆	C ₃₄ H ₂₅ Br ₈ ErN ₄ O ₆	C ₃₃ H ₂₃ Br ₈ N ₄ O ₃ Yb
Formula weight	1313.77	1344.78	1382.11	1344.72	1355.32	1389.79	1392.12	1365.86
Temperature / K	130.00(10)	100(2)	130.01(10)	100(2)	130.00(10)	100.0019(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
<i>a</i> / Å	18.9279(5)	18.802(4)	18.9343(3)	18.230(4)	18.5732(7)	18.765(4)	18.895(4)	17.809(4)
<i>b</i> / Å	11.4544(2)	11.566(2)	11.54153(15)	11.580(2)	11.5300(3)	11.510(2)	11.465(2)	11.515(2)
<i>c</i> / Å	18.0550(4)	18.020(4)	18.0020(2)	18.190(4)	18.0902(5)	18.122(4)	18.094(4)	18.252(4)
<i>α</i> / °	90	90	90	90	90	90	90	90
<i>β</i> / °	94.365(2)	94.39(3)	94.2912(14)	96.08(3)	94.534(3)	94.49(3)	94.32(3)	95.69(3)
<i>γ</i> / °	90	90	90	90	90	90	90	90
<i>V</i> / Å ³	3903.11(16)	3907.2(14)	3922.94(10)	3818.3(13)	3861.9(2)	3902.1(14)	3908.6(14)	3724.5(13)
<i>Z</i>	4	4	4	4	4	4	4	4
$\rho_{\text{calc}} / \text{g} \cdot \text{cm}^{-3}$	2.236	2.286	2.34	2.339	2.331	2.366	2.366	2.436
μ / mm^{-1}	12.123	5.278	20.902	5.878	20.435	10.269	10.375	7.947
<i>F</i> (000)	2496	2520	2596	2512	2532	2608	2612	2548
Crystal size / mm ³	0.611 × 0.389 × 0.09	0.27 × 0.13 × 0.06	0.531 × 0.222 × 0.076	0.04 × 0.03 × 0.01	0.289 × 0.204 × 0.026	0.07 × 0.05 × 0.01	0.08 × 0.05 × 0.01	0.05 × 0.03 × 0.01
Radiation	CuK α (λ = 1.54184)	Synchrotron (λ = 0.9393)	CuK α (λ = 1.54184)	synchrotron (λ = 0.9393)	CuK α (λ = 1.54184)	synchrotron (λ = 0.71092)	Synchrotron (λ = 0.71093)	Synchrotron (λ = 0.9393)
2 θ range for data collection / °	9.032 to 155.364	2.872 to 64.028	8.98 to 154.252	2.97 to 63.606	9.036 to 154.338	2.178 to 64.182	2.162 to 64.142	3.038 to 63.76
Index ranges	-23 ≤ <i>h</i> ≤ 21, -14 ≤ <i>k</i> ≤ 8, -22 ≤ <i>l</i> ≤ 22	-20 ≤ <i>h</i> ≤ 20, -13 ≤ <i>k</i> ≤ 12, -20 ≤ <i>l</i> ≤ 20	-23 ≤ <i>h</i> ≤ 23, -7 ≤ <i>k</i> ≤ 14, -22 ≤ <i>l</i> ≤ 22	-20 ≤ <i>h</i> ≤ 20, -12 ≤ <i>k</i> ≤ 12, -20 ≤ <i>l</i> ≤ 20	-23 ≤ <i>h</i> ≤ 23, -7 ≤ <i>k</i> ≤ 14, -22 ≤ <i>l</i> ≤ 22	-26 ≤ <i>h</i> ≤ 26, -16 ≤ <i>k</i> ≤ 16, -23 ≤ <i>l</i> ≤ 23	-25 ≤ <i>h</i> ≤ 25, -13 ≤ <i>k</i> ≤ 13, -24 ≤ <i>l</i> ≤ 24	-19 ≤ <i>h</i> ≤ 19, -11 ≤ <i>k</i> ≤ 11, -18 ≤ <i>l</i> ≤ 18
Reflections collected	28573	31074	28927	59515	28248	69299	67345	28012
Independent reflections	8162 [R _{int} = 0.0672, R _{sigma} = 0.0501]	4798 [R _{int} = 0.0410, R _{sigma} = 0.0246]	8213 [R _{int} = 0.0545, R _{sigma} = 0.0445]	5076 [R _{int} = 0.1022, R _{sigma} = 0.0462]	8066 [R _{int} = 0.0476, R _{sigma} = 0.0413]	11195 [R _{int} = 0.1128, R _{sigma} = 0.1013]	10648 [R _{int} = 0.1069, R _{sigma} = 0.0650]	4558 [R _{int} = 0.0424, R _{sigma} = 0.0312]
Data/restraints / Parameters	8162/1/483	4798/9/464	8213/3/483	5076/12/467	8066/195/620	11195/531/775	10648/537/658	4558/3/466
Goodness-of-fit on <i>F</i> ²	1.093	1.05	1.022	1.06	1.031	1.029	1.025	1.063
Final <i>R</i> indexes [<i>I</i> □ 2 σ (<i>I</i>)]	R ₁ = 0.0622, wR ₂ = 0.1750	R ₁ = 0.0460, wR ₂ = 0.1214	R ₁ = 0.0540, wR ₂ = 0.1455	R ₁ = 0.0803, wR ₂ = 0.2434	R ₁ = 0.0752, wR ₂ = 0.2116	R ₁ = 0.0655, wR ₂ = 0.1784	R ₁ = 0.0953, wR ₂ = 0.2501	R ₁ = 0.0522, wR ₂ = 0.1304
Final <i>R</i> indexes [all data]	R ₁ = 0.0693, wR ₂ = 0.1860	R ₁ = 0.0492, wR ₂ = 0.1237	R ₁ = 0.0554, wR ₂ = 0.1477	R ₁ = 0.0991, wR ₂ = 0.2664	R ₁ = 0.0823, wR ₂ = 0.2213	R ₁ = 0.0837, wR ₂ = 0.1962	R ₁ = 0.1075, wR ₂ = 0.2629	R ₁ = 0.0534, wR ₂ = 0.1310
Largest diff. peak / hole / e.Å ⁻³	2.13/-1.50	2.83/-1.06	1.96/-1.94	1.70/-1.33	2.66/-1.50	2.71/-2.51	5.61/-5.44	1.64/-1.29

^a The MeOH ligand is disordered with a H₂O ligand for **1-Tb** with a 50 % occupancy.

Table S2. Crystallographic data for compounds **2-RE·MeOH** (RE = Y, Tb, Dy, Ho and Yb).

	2-Y·MeOH	2-Tb·MeOH	2-Dy·MeOH	2-Ho·MeOH	2-Er·MeOH	2-Yb·MeOH
Empirical formula	C ₃₄ H ₂₅ Cl ₈ N ₄ O ₆ Y	C ₃₄ H ₂₅ Cl ₈ N ₄ O ₆ Tb	C ₃₄ H ₂₅ Cl ₈ N ₄ O ₆ Dy	C ₃₄ H ₂₅ Cl ₈ N ₄ O ₆ Ho	C ₃₄ H ₂₅ Cl ₈ ErN ₄ O ₆	C ₃₄ H ₂₅ Cl ₈ N ₄ O ₆ Yb
Formula weight	958.09	1028.10	1031.68	1034.11	1036.44	1042.22
Temperature / K	100.0019(2)	130.01(10)	100(2)	100.0019(2)	100.0019(2)	100.0019(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
<i>a</i> / Å	18.636(4)	18.7014(6)	18.531(4)	18.436(4)	18.598(4)	18.388(4)
<i>b</i> / Å	11.458(2)	11.4698(3)	11.464(2)	11.490(2)	11.467(2)	11.409(2)
<i>c</i> / Å	17.397(4)	17.2942(4)	17.353(4)	17.417(4)	17.364(4)	17.451(4)
α / °	90	90	90	90	90	90
β / °	95.04(3)	94.807(3)	94.89(3)	94.78(3)	94.90(3)	95.13(3)
γ / °	90	90	90	90	90	90
<i>V</i> / Å ³	3700.4(13)	3696.56(17)	3673.1(13)	3676.6(13)	3689.6(13)	3646.3(13)
<i>Z</i>	4	4	4	4	4	4
ρ_{calc} / g.cm ⁻³	1.720	1.847	1.866	1.868	1.866	1.898
μ / mm ⁻¹	2.206	15.172	2.669	2.786	2.906	3.204
F(000)	1920.0	2024.0	2028.0	2032.0	2036	2044.0
Crystal size / mm ³	0.05×0.03×0.01	0.16×0.12×0.03	0.14×0.06×0.01	0.07×0.02×0.01	0.13 × 0.05 × 0.01	0.05×0.03×0.01
Radiation	Synchrotron (λ = 0.71091)	CuK α (λ = 1.54184)	Synchrotron (λ = 0.71079)	Synchrotron (λ = 0.71092)	MoK α (λ = 0.71092)	Synchrotron (λ = 0.71091)
2 θ range for data collection / °	2.194 to 64.016	9.054 to 154.082	2.206 to 62.938	2.218 to 64.084	2.198 to 64.156	2.224 to 64.146
Index ranges	-24 ≤ <i>h</i> ≤ 24, -16 ≤ <i>k</i> ≤ 16, -22 ≤ <i>l</i> ≤ 22	-23 ≤ <i>h</i> ≤ 20, -14 ≤ <i>k</i> ≤ 10, -21 ≤ <i>l</i> ≤ 16	-23 ≤ <i>h</i> ≤ 23, -16 ≤ <i>k</i> ≤ 16, -25 ≤ <i>l</i> ≤ 25	-25 ≤ <i>h</i> ≤ 25, -17 ≤ <i>k</i> ≤ 17, -24 ≤ <i>l</i> ≤ 24	-24 ≤ <i>h</i> ≤ 24, -15 ≤ <i>k</i> ≤ 15, -25 ≤ <i>l</i> ≤ 25	-24 ≤ <i>h</i> ≤ 24, -16 ≤ <i>k</i> ≤ 16, -25 ≤ <i>l</i> ≤ 25
Reflections collected	66691	15255	60136	66252	66349	65410
Independent reflections	10899 [<i>R</i> _{int} = 0.0526, <i>R</i> _{sigma} = 0.0372]	7625 [<i>R</i> _{int} = 0.0304, <i>R</i> _{sigma} = 0.0429]	9721 [<i>R</i> _{int} = 0.0871, <i>R</i> _{sigma} = 0.0567]	10844 [<i>R</i> _{int} = 0.0762, <i>R</i> _{sigma} = 0.0546]	10818 [<i>R</i> _{int} = 0.0592, <i>R</i> _{sigma} = 0.0437]	10658 [<i>R</i> _{int} = 0.0834, <i>R</i> _{sigma} = 0.0847]
Data/restraints / Parameters	10899/3/463	7625/6/494	9721/3/464	10844/0/463	10818/3/464	10658/565/632
Goodness-of-fit on <i>F</i> ²	1.046	1.036	1.037	1.048	1.076	1.039
Final <i>R</i> indexes [<i>I</i> □ 2σ (<i>I</i>)]	<i>R</i> _i = 0.0466, <i>wR</i> ₂ = 0.1310	<i>R</i> _i = 0.0357, <i>swR</i> ₂ = 0.0892	<i>R</i> _i = 0.0471, <i>wR</i> ₂ = 0.1097	<i>R</i> _i = 0.0517, <i>wR</i> ₂ = 0.1389	<i>R</i> _i = 0.0409, <i>wR</i> ₂ = 0.1170	<i>R</i> _i = 0.0615, <i>wR</i> ₂ = 0.1667
Final <i>R</i> indexes [all data]	<i>R</i> _i = 0.0557, <i>wR</i> ₂ = 0.1380	<i>R</i> _i = 0.0428, <i>wR</i> ₂ = 0.0947	<i>R</i> _i = 0.0791, <i>wR</i> ₂ = 0.1224	<i>R</i> _i = 0.0580, <i>wR</i> ₂ = 0.1490	<i>R</i> _i = 0.0426, <i>wR</i> ₂ = 0.1193	<i>R</i> _i = 0.0735, <i>wR</i> ₂ = 0.1801
Largest diff. peak / hole / e.Å ⁻³	0.70/-0.97	0.80/-1.16	1.76/-2.31	3.77/-2.65	2.67/-3.64	3.59/-2.85

Table S3. Crystallographic data for compounds **3-Er**·H₂O, **3-Yb** and **4-Ce**·bpy·acetone

	3-Er ·H ₂ O	3-Yb	4-Ce ·bpy·acetone
Empirical formula	C ₃₈ H ₃₄ Br ₈ N ₅ O ₅ Er	C ₃₈ H ₃₂ Br ₈ N ₅ O ₄ Yb	C ₄₈ H ₂₆ Br ₁₂ N ₆ O ₆ Ce
Formula weight	1447.24	1435.00	1913.85
Temperature / K	130.00(10)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	C2/c
<i>a</i> / Å	16.4700(2)	14.426(3)	35.398(7)
<i>b</i> / Å	18.81704(18)	16.252(3)	13.678(3)
<i>c</i> / Å	16.32332(18)	17.839(4)	26.858(5)
α / °	90	90	90
β / °	116.5022(15)	91.65(3)	116.17(3)
γ / °	90	90	90
<i>V</i> / Å ³	4527.26(10)	4180.7(15)	11671(5)
<i>Z</i>	4	4	8
ρ_{calc} / g.cm ⁻³	2.123	2.280	2.142
μ / mm ⁻¹	12.098	9.930	9.047
F(000)	2740.0	2708.0	7056.0
Crystal size / mm ³	0.163×0.093×0.036	0.02×0.02×0.01	0.18×0.16×0.15
Radiation	CuK α (λ = 1.54184)	Synchrotron (λ = 0.7108)	Synchrotron (λ = 0.71073)
2 θ range for data collection / °	5.996 to 154.72	2.824 to 63.21	3.218 to 45.93
Index ranges	-20 ≤ <i>h</i> ≤ 20, -23 ≤ <i>k</i> ≤ 23, -16 ≤ <i>l</i> ≤ 20	-19 ≤ <i>h</i> ≤ 19, -21 ≤ <i>k</i> ≤ 21, -22 ≤ <i>l</i> ≤ 22	-38 ≤ <i>h</i> ≤ 38, -14 ≤ <i>k</i> ≤ 14, -29 ≤ <i>l</i> ≤ 29
Reflections collected	51619	76064	53988
Independent reflections	9550 [<i>R</i> _{int} = 0.0338, <i>R</i> _{sigma} = 0.0253]	10667 [<i>R</i> _{int} = 0.0399, <i>R</i> _{sigma} = 0.0238]	7890 [<i>R</i> _{int} = 0.1067, <i>R</i> _{sigma} = 0.0557]
Data/restraints / Parameters	9550/0/520	10667/0/509	7890/96/587
Goodness-of-fit on <i>F</i> ²	1.058	1.054	1.046
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0271, <i>wR</i> ₂ = 0.0666	<i>R</i> ₁ = 0.0255, <i>wR</i> ₂ = 0.0646	<i>R</i> ₁ = 0.0937, <i>wR</i> ₂ = 0.2361
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0285, <i>wR</i> ₂ = 0.0676	<i>R</i> ₁ = 0.0269, <i>wR</i> ₂ = 0.0655	<i>R</i> ₁ = 0.1257, <i>wR</i> ₂ = 0.2634
Largest diff. peak / hole / e.Å ⁻³	2.10/-1.19	1.04/-1.55	2.45/-2.02

Supplementary Crystallographic Details

Structure modelling. Several of the crystal structures presented a high degree of disorder and some of the complexes had to be modelled over multiple positions: two positions for **2-Dy** and three positions for **1-Er**, and **2-Yb**. The methanol ligand in the structure of **1-Tb** is only partially occupied, replaced by a water ligand in an occupancy ratio of 1:1. Other crystals measured, however of poorer quality, show a fully occupied methanol ligand. Compound **1-Tb** was therefore formulated as per the rest of the series.

Solvent modelling. As mentioned in the text, co-crystallized solvent molecules were modelled in different ways for each structure depending on the quality of the data. The solvent (MeOH) was located and refined over a unique position for **1-Y**, **1-Gd** and **1-Er** and over two positions for **2-Tb**. In the case of **1-Eu**, **2-Y**, **2-Dy**, **2-Ho**, **2-Er** and **2-Yb** the methanol molecule was disordered over multiple positions and therefore included using the Olex2 solvent mask routine. The structure of **3-Er**·H₂O does not contain any methanol, but a water molecule was refined over a unique position and involved in hydrogen bonding with O1 and O3 of two different catecholate ligands as well as the triethylammonium counterion. Finally, there was a solvent void in **4-Ce**, four voids per unit cell, containing electron density consistent with a molecule of acetone, refinement was carried out using the Olex2 solvent mask routine to account for this diffuse solvent.

Oxidation state of the cerium centre in 4-Ce. Tetravalent cerium was confirmed by bond valence sum (BVS) analysis, following an approach reported by G. J. Palenik using the equations:^{1,2}

$$OS = \sum_j s_{ij} \text{ with } s_{ij} = \exp[(R_0 - R_{ij}) / b]$$

where *OS* is the oxidation state, *s_{ij}* the valence of the individual bonds, *b* a constant fixed at 0.37 and *R_{ij}* the observed bond lengths obtained from the crystal structure. The parameter *R₀*

represents the bond length of unit valence and depends on the coordination number (CN) of the cerium ion and its +III or +IV oxidation state. For 8-coordinate cerium centres, R_0 for oxygen coordination was taken as 2.118 for Ce(III) and 2.070 for Ce(IV). The parameter R_0 for nitrogen coordination was taken as 2.251 for Ce(III) and 2.202 for Ce(IV). The resulting OS of 4.384 (assuming Ce(III)) and 3.848 (assuming Ce(IV)) confirmed the tetravalence of the cerium centre in **4-Ce**.

Charge balance in 4-Ce. This crystal structure contains many co-crystallized 2,2'-bipyridine molecules: one non-coordinating and fully occupied (**bpy1** represented by N3 and N4), half a fully occupied non-coordinating bpy molecule (**bpy2** represented by N5) situated around a centre of symmetry, and a non-coordinating bpy molecule (**bpy3** represented N6 and N7) with a 0.5 occupancy factor, disordered over a centre of symmetry where one of the carbon atoms lies close to the centre of symmetry. This results in a total of two non-coordinating 2,2'-bpy molecules per Ce atom. The atoms of the aromatic rings of the latter two bipyridine ligands (**bpy 2** and **bpy3**) were constrained to ideal geometry. Bond valence sum calculations show the oxidation state to be Ce^{IV} , indicating that there are two hydrogen atoms located on the nitrogen atoms of the non-coordinating 2,2'-bpy ligands for charge balance. One hydrogen atom was placed on N3 of the fully occupied **bpy1**, as this nitrogen appeared to be involved in a hydrogen bond with one of the oxygen atoms (O6) of one of the Br₄Cat ligands. Hydrogen atoms (each 50% occupancy) were placed on nitrogen N6 and N7 of the disordered **bpy3** which was involved in a hydrogen bond with an oxygen atom (O2) of a Br₄Cat ligand of a symmetry related molecule. This totals to a full positive charge completing the charge balance of the asymmetric unit.

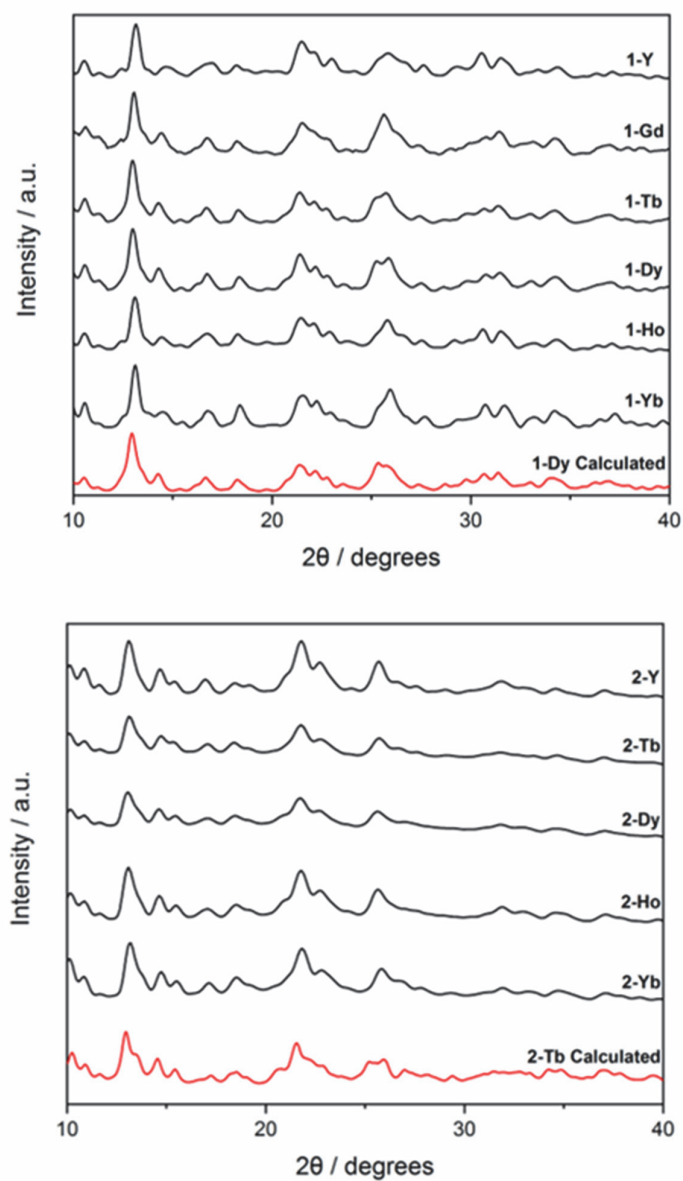


Figure S1. Powder X-ray diffraction data (in black) for the reported **1-RE** and **2-RE·nbpy** compared to the diffractogram calculated from the single crystal structure of **1-Dy** and **2-Tb·MeOH**, respectively (in red).

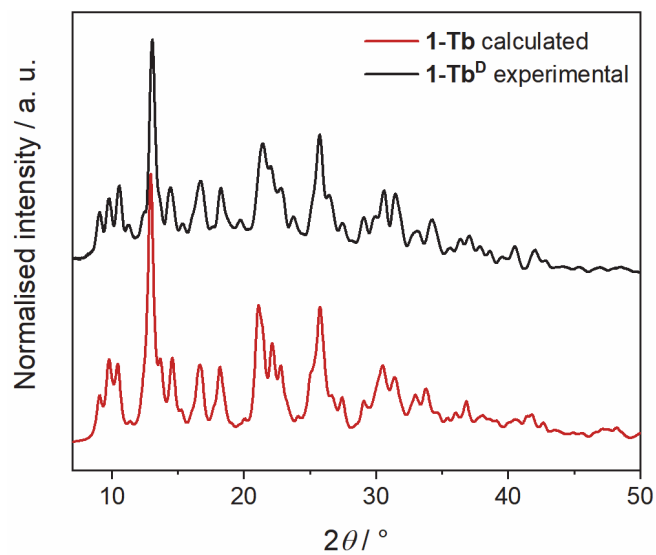


Figure S2. Powder X-ray diffraction data (in black) for **1-Tb^D** compared to the diffractogram calculated from the single crystal structure of **1-Tb** (in red).

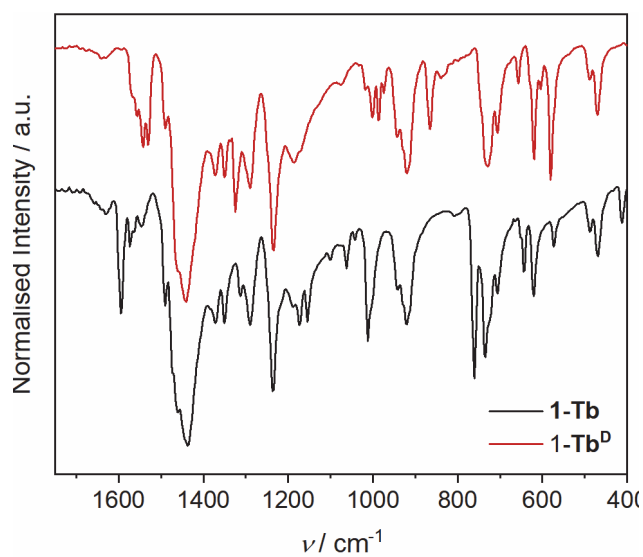


Figure S3. Infra-red spectrum of **1-Tb^D** (in red) compared to the **1-Tb** (in black) non deuterated analogue.

Table S4. Shape parameters for the compounds of the four families **1-RE**, **2-RE**, **3-RE** and **4-Ce**

	OP	HPY	HBPY	CU	SAPR	TDD	JGBF	JETBPY	JBTP	BTPR	JSD	TT	ETBPY
	D _{8h}	C _{7v}	D _{6h}	O _h	D _{4d}	D _{2d}	D _{2d}	D _{3h}	C _{2v}	C _{2v}	D _{2d}	T _d	D _{3h}
1-Y	31.51	21.07	16.72	9.64	0.79	2.42	16.82	27.39	3.54	2.80	5.89	10.43	23.61
1-Eu	31.79	20.70	16.77	9.76	0.96	2.47	16.73	27.04	3.70	2.91	6.03	10.53	23.05
1-Gd	31.68	20.73	16.88	9.89	0.91	2.38	16.86	27.30	3.59	2.81	5.84	10.68	23.22
1-Tb	31.42	21.21	17.31	10.05	0.88	3.05	16.80	26.96	3.02	2.77	5.44	10.72	23.44
1-Dy	31.63	20.87	16.58	9.60	0.85	2.68	16.98	27.08	3.36	2.90	5.79	10.33	23.40
1-Ho	31.50	21.09	16.52	9.48	0.80	2.57	16.97	27.43	3.37	2.81	5.77	10.19	23.44
1-Yb	30.66	21.83	17.10	10.02	0.73	2.46	15.79	26.70	2.55	2.53	4.60	10.63	23.41
2-Y	31.39	21.06	17.13	10.54	0.85	2.35	16.48	27.33	3.32	2.58	5.56	11.24	23.65
2-Tb	31.45	20.98	16.76	10.39	0.97	2.34	16.01	27.28	3.43	2.62	5.46	11.10	23.41
2-Dy	31.42	20.97	17.23	10.62	0.89	2.38	16.58	27.19	3.42	2.66	5.65	11.34	23.55
2-Ho	31.20	21.07	17.15	10.37	0.88	2.39	16.90	27.30	2.20	2.57	5.70	11.13	23.66
2-Yb	31.25	21.00	17.12	10.32	0.76	2.61	17.22	27.20	3.40	2.68	5.82	11.01	23.87
3-Er	32.88	23.89	17.17	10.73	2.73	0.82	12.93	29.79	2.50	2.24	3.19	11.34	24.01
3-Yb	31.85	22.57	15.55	9.20	1.06	2.28	15.01	28.51	3.12	2.30	5.05	10.05	24.37
4-Ce	31.97	23.29	16.03	11.14	2.62	1.04	11.89	28.69	2.82	2.45	3.20	11.63	22.97

* OP = Octagon; HPY = Heptagonal pyramid; HBPY = Hexagonal bipyramide; CU = Cube; SAPR = Square

Antiprism; TDD = Triangular dodecahedron; JGBF = Johnson – Gyrobifastigium (J26); JETBPY = Jonhson –

Biaugmented trigonal prism (J50); BTPR = Biaugmented trigonal prism; JSD = Snub disphenoid (J84); TT =

triaskis tetrahedron ETBPY = Elongated trigonal bipyramid

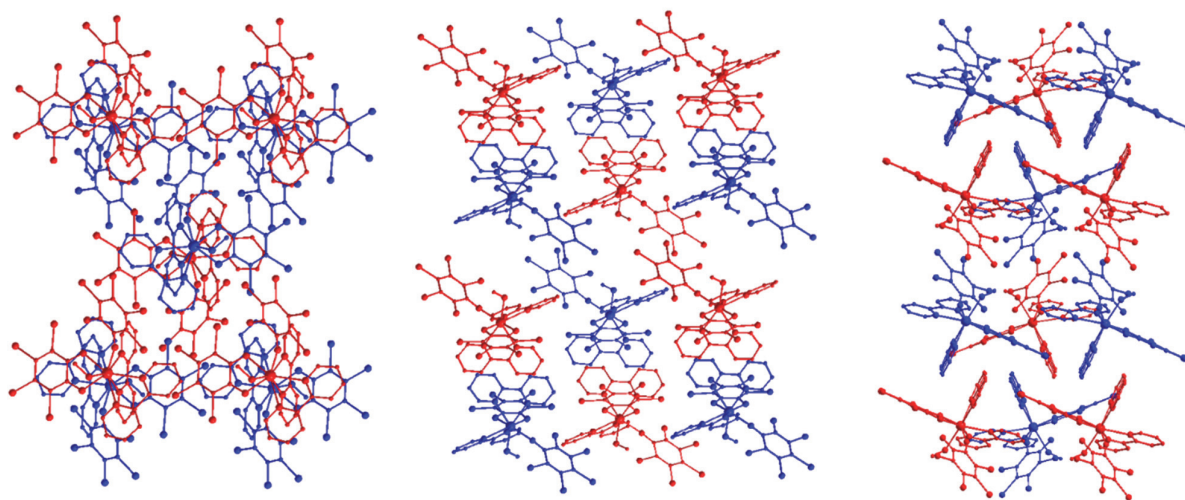


Figure S4. Crystal packing of **1-RE** along the *a* (left), *b* (middle) and *c*-axes (right). Colors indicate different orientations of molecules in the lattice.

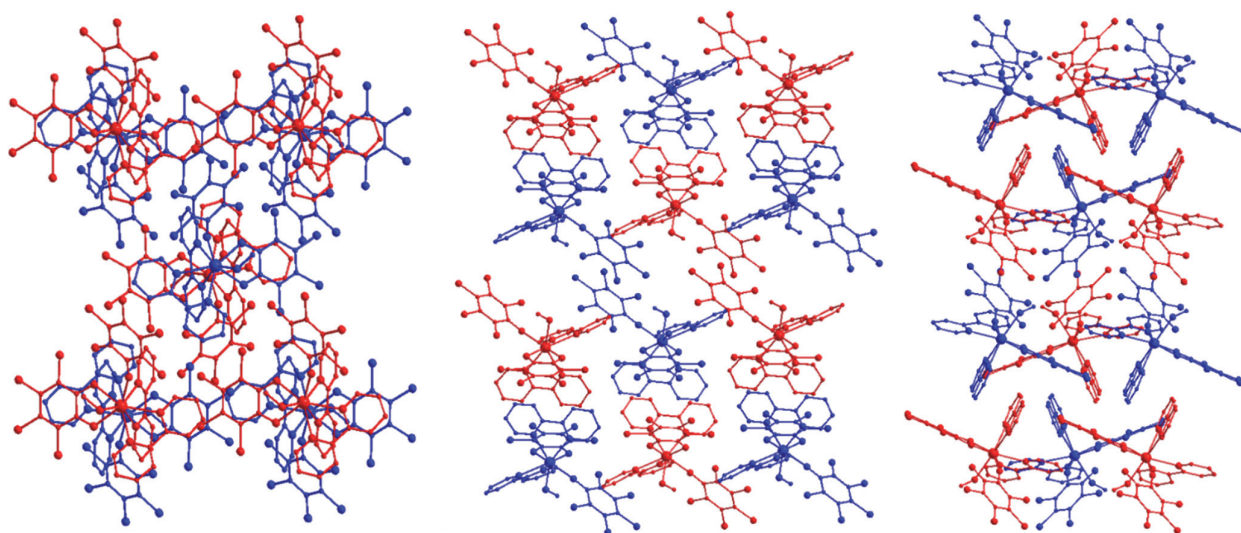


Figure S5. Packing diagram of **2-RE** along the *a* (left), *b* (middle) and *c*-axes (right). Colors indicate different orientations of molecules in the lattice.

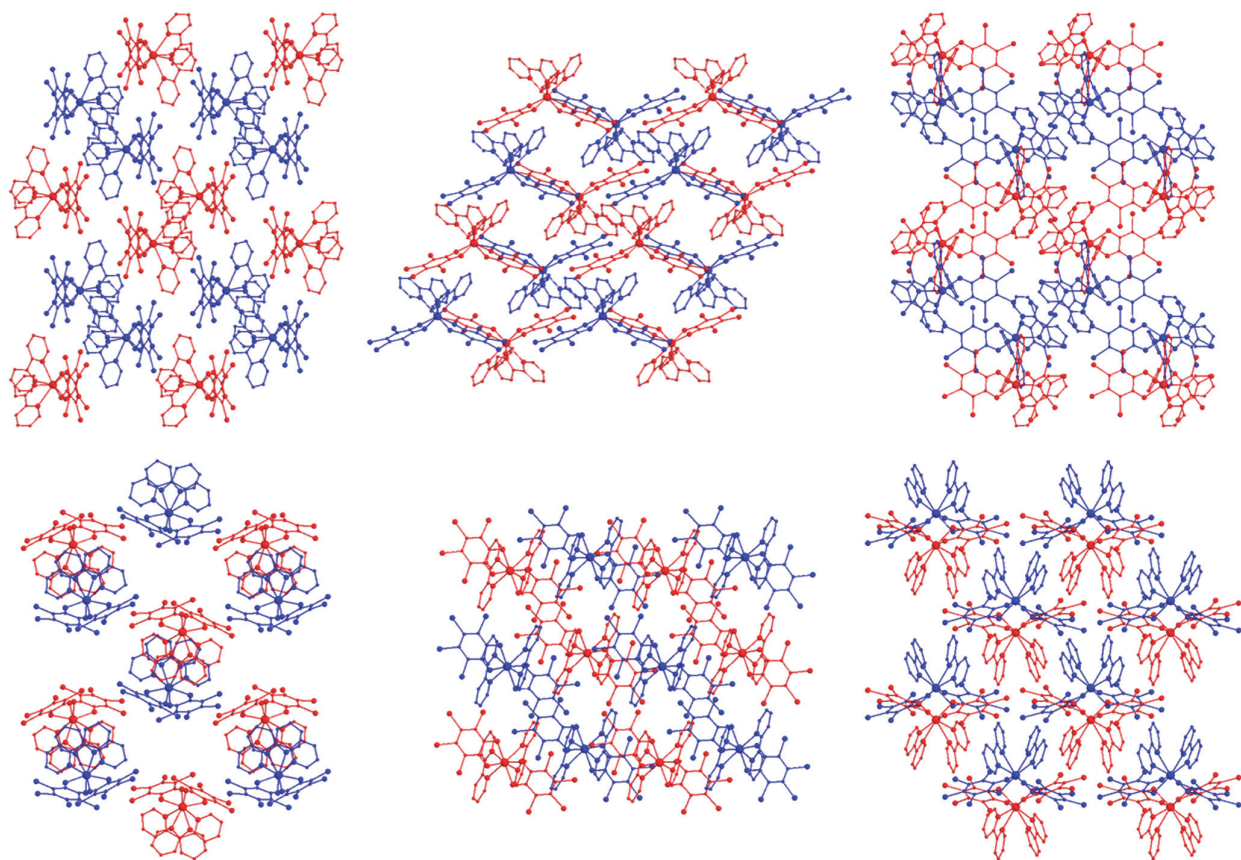


Figure S6. Packing diagrams of **3-Er·H₂O** (top) and **3-Yb** (bottom) along the *a* (left), *b* (middle) and *c*-axes (right).

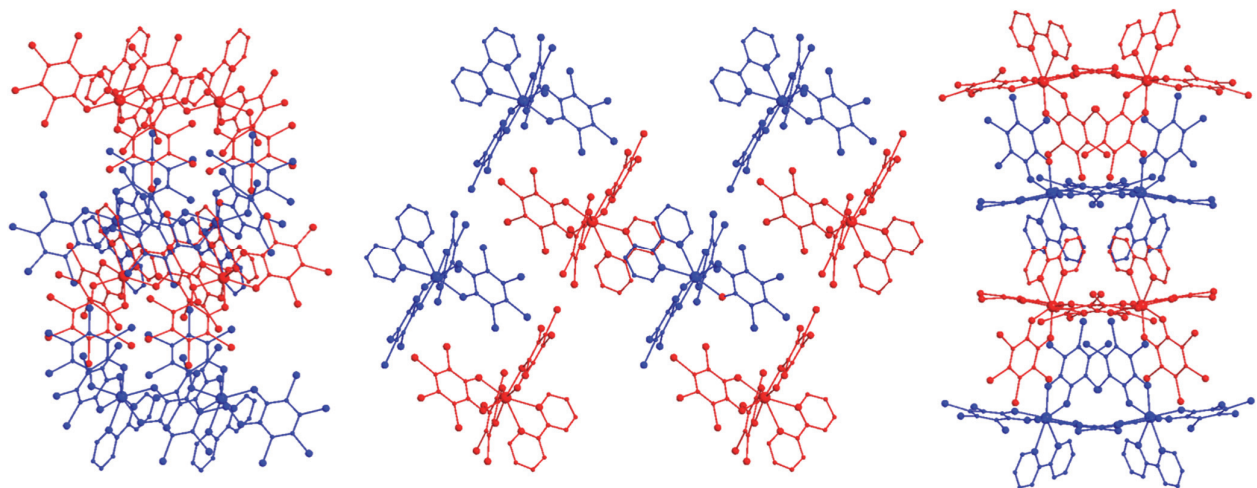


Figure S7. Packing diagrams of **4-Ce·bpy·acetone** along the *a* (left), *b* (middle) and *c*-axes (right).

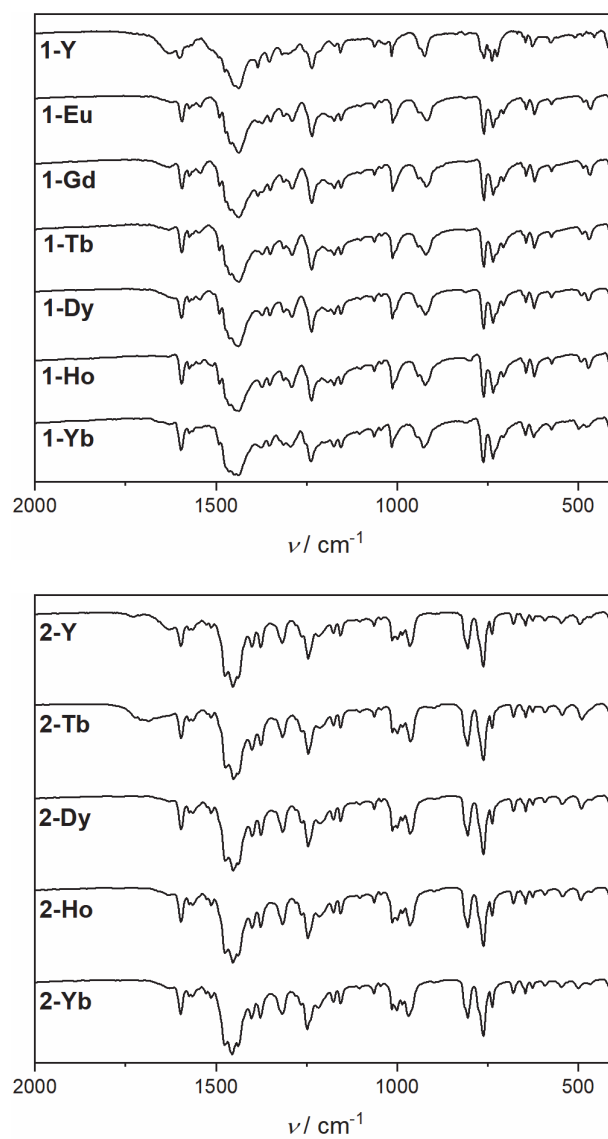


Figure S8. Infrared spectra (KBr disk) of the **1-RE** (top) and **2-RE·nbpy** (bottom) series

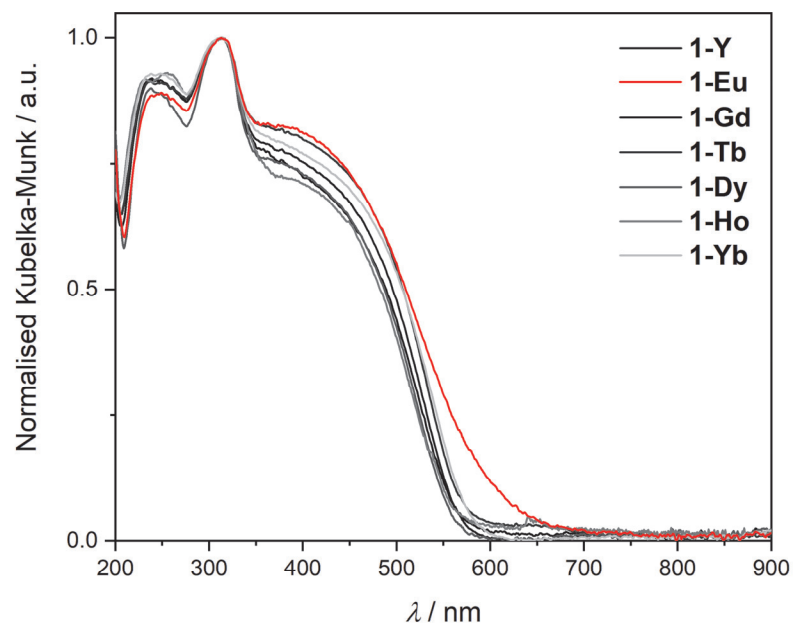


Figure S9. Diffuse reflectance spectra (~5 % in KBr) of the **1-RE** series.

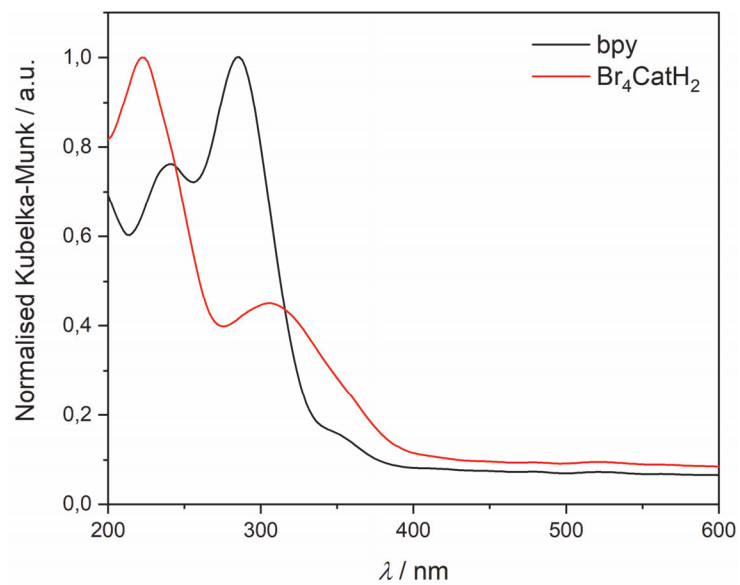


Figure S10. Diffuse reflectance spectra (~5 % in KBr) of the ligands 2,2'-bpy and tetrabromocatechol.

2. Static Magnetic Characterization and Related *Ab Initio* Details

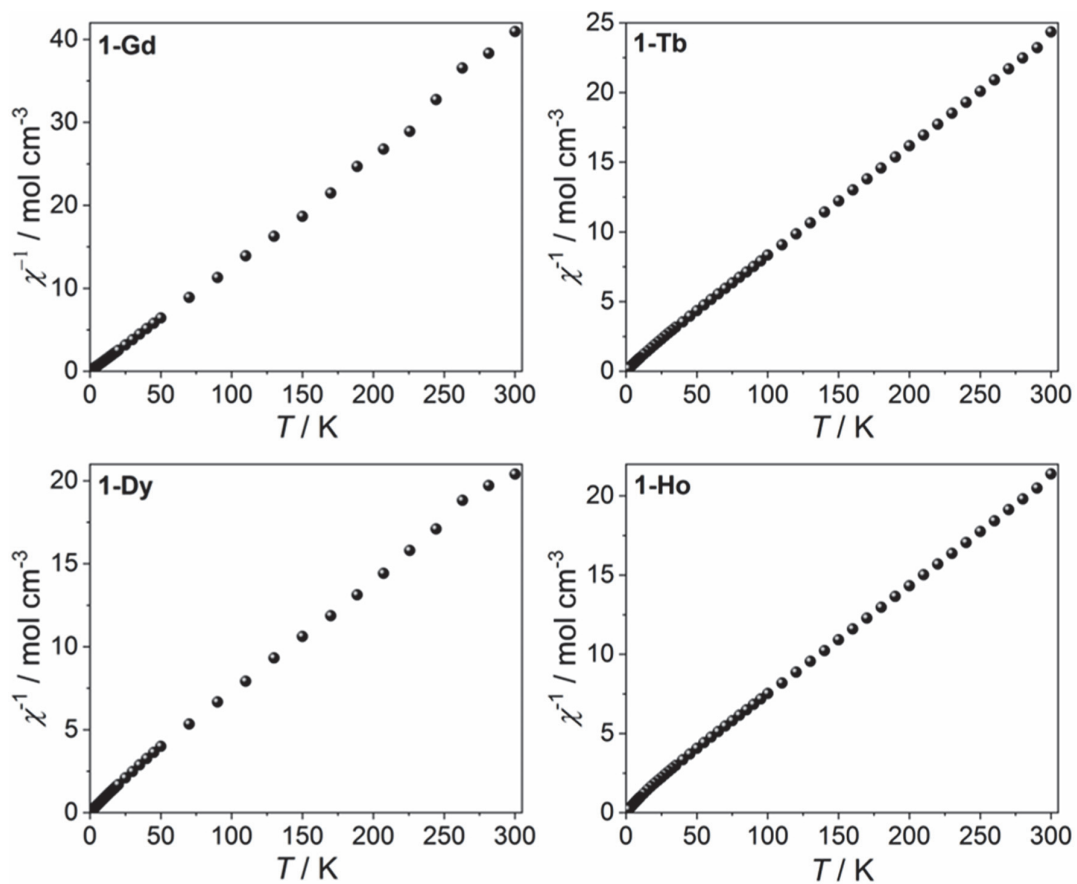


Figure S11. Curie-Weiss plots of magnetic susceptibility data for **1-RE** (RE = Gd, Tb, Dy and Ho).

Table S5. Cartesian atomic coordinates (Å) of **1-Tb-MeOH/H₂O** used as input for CASSCF/RASSI-SO *ab initio* calculations.

1-Tb-MeOH				1-Tb-H₂O			
Tb1	0	0	0	Tb1	0	0	0
O1	0.6886	1.7663	-1.36959	O1	0.6886	1.7663	-1.36959
O2	0.69457	1.75703	1.27844	O2	0.69457	1.75703	1.27844
O3	-1.13583	-0.49759	-1.85254	O3	-1.13583	-0.49759	-1.85254
O4	-2.1136	1.5347	0.10455	O5	-2.11299	1.53459	0.10408
N1	1.9665	-0.98511	-1.33523	N1	1.9665	-0.98511	-1.33523
N2	1.97564	-0.90637	1.33451	N2	1.97564	-0.90637	1.33451
N3	-1.17801	-0.73846	2.13761	N3	-1.17801	-0.73846	2.13761
N4	-0.50845	-2.5322	0.23297	N4	-0.50845	-2.5322	0.23297
Br1	1.75553	3.85614	-3.31836	Br1	1.75553	3.85614	-3.31836
Br2	2.91914	6.53425	-1.68378	Br2	2.91914	6.53425	-1.68378
Br3	2.61496	6.65468	1.58611	Br3	2.61496	6.65468	1.58611
Br4	1.39537	3.98908	3.22232	Br4	1.39537	3.98908	3.22232
Br5	-3.38436	-2.54725	-1.71525	Br5	-3.38436	-2.54725	-1.71525
Br6	-4.95588	-2.70358	-4.59987	Br6	-4.95588	-2.70358	-4.59987
Br7	-4.187	-0.52423	-6.95778	Br7	-4.187	-0.52423	-6.95778
Br8	-1.72548	1.68061	-6.46236	Br8	-1.72548	1.68061	-6.46236
O5	-0.5556	1.42006	-3.75717	O4	-0.5556	1.42006	-3.75717
C1	1.67496	3.94218	-1.42205	C1	1.67496	3.94218	-1.42205
C2	2.15422	5.05154	-0.75281	C2	2.15422	5.05154	-0.75281
C3	2.04071	5.09786	0.60377	C3	2.04071	5.09786	0.60377
C4	1.55808	4.00819	1.31824	C4	1.55808	4.00819	1.31824
C5	-2.91	-1.3823	-3.18379	C5	-2.91	-1.3823	-3.18379
C6	-3.66999	-1.36725	-4.33236	C6	-3.66999	-1.36725	-4.33236
C7	-3.29883	-0.50917	-5.31814	C7	-3.29883	-0.50917	-5.31814
C8	-2.24032	0.43691	-5.14088	C8	-2.24032	0.43691	-5.14088
C9	1.13239	2.84671	-0.77813	C9	1.13239	2.84671	-0.77813
C10	1.10894	2.83745	0.67431	C10	1.10894	2.83745	0.67431
C11	-1.83425	-0.47212	-2.92875	C11	-1.83425	-0.47212	-2.92875
C12	-1.5808	0.49134	-3.95613	C12	-1.5808	0.49134	-3.95613
C13	-3.44428	1.01128	0.08646	C13	1.98078	-0.97585	-2.6502
C14	1.98078	-0.97585	-2.6502	C14	3.09478	-1.48768	-0.73472
C15	3.09478	-1.48768	-0.73472	C15	3.07401	-1.48305	0.72677
C16	3.07401	-1.48305	0.72677	C16	1.98091	-0.84383	2.70556
C17	1.98091	-0.84383	2.70556	C17	-1.48881	0.20184	3.08721
C18	-1.48881	0.20184	3.08721	C18	-1.45157	-2.04584	2.37817
C19	-1.45157	-2.04584	2.37817	C19	-1.11312	-3.00119	1.37431
C20	-1.11312	-3.00119	1.37431	C20	-0.21788	-3.33817	-0.78355
C21	-0.21788	-3.33817	-0.78355	C21	3.0281	-1.45757	-3.44606
C22	3.0281	-1.45757	-3.44606	C22	4.09353	-1.9613	-2.85459
C23	4.09353	-1.9613	-2.85459	C23	4.19511	-1.98331	-1.42928
C24	4.19511	-1.98331	-1.42928	C24	4.13324	-1.97636	1.47921
C25	4.13324	-1.97636	1.47921	C25	4.12756	-1.92425	2.88463
C26	4.12756	-1.92425	2.88463	C26	3.02056	-1.35104	3.47067

C27	3.02056	-1.35104	3.47067	C27	-2.16867	-0.11082	4.18151
C28	-2.16867	-0.11082	4.18151	C28	-2.55475	-1.30356	4.36601
C29	-2.55475	-1.30356	4.36601	C29	-2.04606	-2.44998	3.52674
C30	-2.04606	-2.44998	3.52674	C30	-1.35386	-4.43016	1.39239
C31	-1.35386	-4.43016	1.39239	C31	-1.06633	-5.2176	0.33607
C32	-1.06633	-5.2176	0.33607	C32	-0.51753	-4.69303	-0.76004
C33	-0.51753	-4.69303	-0.76004	H1	-0.8643	2.09747	-3.36917
H1	-0.8643	2.09747	-3.36917	H2	1.22333	-0.61416	-3.09453
H2	-2.14898	2.40204	0.04305	H3	2.97212	-1.42199	-4.3934
H3	-3.42267	0.05561	0.30306	H4	4.79971	-2.31445	-3.38118
H4	-3.83374	1.13594	-0.80378	H5	4.96645	-2.31524	-0.98485
H5	-3.99022	1.48345	0.75052	H6	4.8814	-2.35709	1.03341
H6	1.22333	-0.61416	-3.09453	H7	4.84708	-2.2668	3.40195
H7	2.97212	-1.42199	-4.3934	H8	2.96783	-1.30167	4.41763
H8	4.79971	-2.31445	-3.38118	H9	1.24577	-0.43635	3.1467
H9	4.96645	-2.31524	-0.98485	H10	-1.21038	1.10193	2.95967
H10	4.8814	-2.35709	1.03341	H11	-2.36287	0.55253	4.8275
H11	4.84708	-2.2668	3.40195	H12	-3.19372	-1.48673	5.04961
H12	2.96783	-1.30167	4.41763	H13	-2.11299	-3.36231	3.78125
H13	1.24577	-0.43635	3.1467	H14	-1.72756	-4.81774	2.17358
H14	-1.21038	1.10193	2.95967	H15	-1.25378	-6.14826	0.37408
H15	-2.36287	0.55253	4.8275	H16	-0.33492	-5.23968	-1.51616
H16	-3.19372	-1.48673	5.04961	H17	0.20774	-2.97424	-1.55033
H17	-2.11299	-3.36231	3.78125	H18	-2.23224	2.70519	-0.25001
H18	-1.72756	-4.81774	2.17358	H19	-3.23626	1.26231	0.52442
H19	-1.25378	-6.14826	0.37408				
H20	-0.33492	-5.23968	-1.51616				
H21	0.20774	-2.97424	-1.55033				

Table S6. Cartesian atomic coordinates (Å) of **1-Dy** used as input for CASSCF/RASSI-SO *ab initio* calculations.

Dy1	0	0	0	C19	-1.43779	-1.96448	2.42931
O1	0.63712	1.72512	-1.36857	C20	-1.10283	-3.01025	1.39057
O2	0.70936	1.73435	1.25712	C21	-0.27045	-3.34577	-0.72116
O3	-1.18103	-0.46788	-1.79236	C22	2.8692	-1.45831	-3.51817
O4	-2.04598	1.37346	0.28511	C23	4.00227	-1.96448	-2.93388
N1	1.90238	-0.9948	-1.37398	C24	4.09989	-1.95525	-1.56513
N2	2.00805	-0.91409	1.2986	C25	4.18525	-1.95295	1.41041
N3	-1.09903	-0.70771	2.16241	C26	4.16243	-1.90452	2.79899
N4	-0.5154	-2.49024	0.28331	C27	3.07857	-1.33494	3.42115
Br1	1.63376	3.83442	-3.35948	C28	-2.01484	-0.04704	4.29578
Br2	2.81008	6.51884	-1.75142	C29	-2.40218	-1.30842	4.49595
Br3	2.59326	6.64786	1.52618	C30	-2.03594	-2.35996	3.62493
Br4	1.42533	3.98085	3.18509	C31	-1.45729	-4.33966	1.48074
Br5	-3.41363	-2.54086	-1.70201	C32	-1.18162	-5.18942	0.39331
Br6	-5.12564	-2.60105	-4.51813	C33	-0.60962	-4.67172	-0.70674
Br7	-4.42472	-0.37541	-6.87404	H1	-0.19332	1.23543	-3.08463
Br8	-1.95148	1.7988	-6.35684	H2	-2.7085	0.92351	0.5394
O5	-0.72584	1.47146	-3.69129	H3	1.03863	-0.63762	-3.12259
C1	1.6075	3.94811	-1.47316	H4	2.79194	-1.4303	-4.46439
C2	2.1115	5.05037	-0.77887	H5	4.70549	-2.31574	-3.4675
C3	2.03239	5.10341	0.59349	H6	4.89326	-2.27051	-1.14914
C4	1.54372	3.99192	1.2986	H7	4.93707	-2.31109	0.95183
C5	-3.00625	-1.33724	-3.08717	H8	4.88319	-2.25823	3.30837
C6	-3.76566	-1.29804	-4.23771	H9	3.04076	-1.27735	4.36916
C7	-3.47185	-0.38717	-5.2494	H10	1.31021	-0.44154	3.09379
C8	-2.4169	0.52024	-5.0384	H11	-1.10399	1.12324	2.90355
C9	1.10226	2.82624	-0.76985	H12	-2.17028	0.63133	4.94245
C10	1.1063	2.832	0.63136	H13	-2.94346	-1.50645	5.25066
C11	-1.93088	-0.44021	-2.85273	H14	-2.18685	-3.27244	3.84074
C12	-1.68992	0.53753	-3.83015	H15	-1.88	-4.67623	2.26206
C13	-2.47052	2.3512	-0.63821	H16	-1.39739	-6.11327	0.43607
C14	1.82261	-0.97982	-2.71027	H17	-0.44345	-5.21883	-1.46413
C15	3.04745	-1.48598	-0.77707	H18	0.16816	-3.00945	-1.49387
C16	3.07234	-1.46062	0.68906	H19	-3.19612	2.87902	-0.24567
C17	2.04395	-0.84837	2.64931	H20	-2.79033	1.91261	-1.455
C18	-1.36698	0.22738	3.08212	H21	-1.71893	2.94075	-0.8582

Table S7. Cartesian atomic coordinates (Å) of **1-Ho** used as input for CASSCF/RASSI-SO *ab initio* calculations.

Ho1	0	0	0	C19	-1.39768	-1.98916	2.43101
O1	0.65722	1.72627	-1.37015	C20	-1.10583	-2.97672	1.3669
O2	0.71149	1.73548	1.26031	C21	-0.25113	-3.35079	-0.72338
O3	-1.17093	-0.46984	-1.79471	C22	2.83574	-1.44128	-3.54354
O4	-2.04846	1.35219	0.27569	C23	4.00808	-1.93506	-2.94012
N1	1.90307	-0.98664	-1.36835	C24	4.09556	-1.92585	-1.56888
N2	2.0052	-0.89916	1.32174	C25	4.16993	-1.91895	1.40304
N3	-1.07382	-0.7081	2.17808	C26	4.16734	-1.86255	2.77427
N4	-0.48895	-2.50366	0.27389	C27	3.10702	-1.30892	3.44454
Br1	1.64593	3.83363	-3.3654	C28	-1.97045	-0.04397	4.32437
Br2	2.81958	6.52513	-1.76057	C29	-2.33275	-1.31467	4.54117
Br3	2.59447	6.66222	1.52661	C30	-1.9614	-2.34252	3.65953
Br4	1.41992	3.99305	3.19522	C31	-1.51233	-4.33835	1.45362
Br5	-3.42697	-2.53036	-1.69535	C32	-1.21556	-5.17743	0.39855
Br6	-5.18124	-2.54705	-4.4969	C33	-0.60781	-4.69746	-0.72157
Br7	-4.46931	-0.32873	-6.87444	H1	-0.73918	1.81339	-2.9345
Br8	-1.98299	1.84919	-6.35774	H2	-2.07079	1.68999	1.04518
O5	-0.7092	1.48571	-3.70794	H3	1.01713	-0.64553	-3.10677
C1	1.61265	3.93043	-1.46952	H4	2.74386	-1.42222	-4.48951
C2	2.10537	5.0469	-0.79022	H5	4.72324	-2.26808	-3.46856
C3	2.06167	5.09409	0.6027	H6	4.88755	-2.23628	-1.14584
C4	1.56076	3.99949	1.31812	H7	4.91738	-2.28139	0.94151
C5	-3.01932	-1.30547	-3.08465	H8	4.90598	-2.20886	3.26125
C6	-3.80474	-1.26979	-4.26619	H9	3.0947	-1.25315	4.3934
C7	-3.48511	-0.33057	-5.27791	H10	1.31002	-0.43193	3.11846
C8	-2.45384	0.56376	-5.0286	H11	-1.08204	1.14581	2.92672
C9	1.10463	2.82432	-0.783	H12	-2.13793	0.6327	4.96911
C10	1.10312	2.83353	0.64606	H13	-2.85008	-1.52536	5.30877
C11	-1.93934	-0.42495	-2.88231	H14	-2.09215	-3.25432	3.89202
C12	-1.71289	0.56721	-3.85428	H15	-1.97539	-4.66166	2.21749
C13	-2.4804	2.23156	-0.60414	H16	-1.4371	-6.09981	0.45477
C14	1.81318	-0.97973	-2.70887	H17	-0.43597	-5.25642	-1.47062
C15	3.03842	-1.46545	-0.79564	H18	0.19436	-3.0132	-1.49257
C16	3.06629	-1.44013	0.68941	H19	-2.71641	1.77207	-1.43638
C17	2.04574	-0.8301	2.66949	H20	-1.77743	2.89009	-0.7811
C18	-1.33627	0.24838	3.1067	H21	-3.27244	2.68743	-0.24727

Table S8. CASSCF/RASSI-SO energies (cm⁻¹) for the lowest lying states of **1-Tb-MeOH** and **1-Tb-H₂O**

	1-Tb-MeOH	1-Tb-H₂O
State 1	0.00	0.00
State 2	3.49	1.86
State 3	36.5	44.6
State 4	52.0	55.7
State 5	83.9	98.7
State 6	123.5	134.0
State 7	149.0	165.7
State 8	238.0	251.8
State 9	242.5	259.4
State 10	414.2	432.8
State 11	416.1	434.9
State 12	712.3	738.2
State 13	712.6	738.5

Table S9. CASSCF/RASSI-SO energies (cm⁻¹) for the lowest lying states of **1-Dy**.

Energy	<i>g_x</i>	<i>g_y</i>	<i>g_z</i>	Angle
0.0	0.09	0.20	19.22	--
129.0	0.96	1.52	15.43	28.6
230.7	2.53	3.36	11.74	44.2
329.5	2.31	5.71	9.00	52.2
428.8	0.56	4.16	10.43	81.6
493.9	1.72	2.81	14.01	86.6
580.9	0.16	0.37	17.98	80.0
675.5	0.00	0.00	19.64	65.5

Table S10. CASSCF/RASSI-SO energies (cm⁻¹) for the lowest lying states of **1-Ho**.

State 1	0.0
State 2	0.51
State 3	54.1
State 4	61.7
State 5	105.6
State 6	129.0
State 7	177.6
State 8	190.1
State 9	205.9
State 10	217.6
State 11	227.1
State 12	239.6
State 13	256.3
State 14	300.6
State 15	305.2
State 16	349.1
State 17	349.6

Table S11. Energies (cm⁻¹) and percentage composition of the CASSCF/RASSI wavefunctions corresponding to the lowest energy atomic multiplet $J = 6$ on the basis of total angular momentum eigenstates $|m_J\rangle$ for **1-Tb-MeOH (a)** and **1-Tb-H₂O (b)**. The reference system has the origin on the Tb^{III} ion and is oriented along the main magnetic axes calculated for the ground state pseudo-doublet of Tb.

a)

$ m_J\rangle$	6	5	4	3	2	1	0	-1	-2	-3	-4	-5	-6
Energy													
0.00	44.0	0.0	1.1	2.3	0.4	2.0	0.1	2.0	0.4	2.3	1.1	0.0	44.0
3.49	48.1	0.1	0.6	1.0	0.2	0.1	0.0	0.1	0.2	1.0	0.6	0.1	48.1
36.5	0.1	15.0	4.1	7.0	11.9	4.2	15.3	4.2	11.9	7.0	4.1	15.0	0.1
52.0	3.9	7.1	9.8	7.0	6.4	13.0	5.5	13.0	6.4	7.0	9.8	7.1	3.9
83.9	0.6	37.8	0.7	3.5	3.3	2.9	2.5	2.9	3.3	3.5	0.7	37.8	0.6
123.5	0.4	31.0	4.5	3.3	3.0	6.4	2.9	6.4	3.0	3.3	4.5	31.0	0.4
149.0	1.0	0.4	36.0	0.4	6.8	4.7	1.3	4.7	6.8	0.4	36.0	0.4	1.0
238.0	0.0	3.0	27.9	4.1	5.9	0.2	17.9	0.2	5.9	4.1	27.9	3.0	0.0
242.5	1.4	3.1	4.8	35.4	0.2	5.1	0.1	5.1	0.2	35.4	4.8	3.1	1.4
414.2	0.2	0.7	7.7	7.1	26.5	7.6	0.5	7.6	26.5	7.1	7.7	0.7	0.2
416.1	0.2	1.4	1.3	22.1	13.6	11.0	0.8	11.0	13.6	22.1	1.3	1.4	0.2
712.3	0.0	0.0	0.8	5.8	1.3	40.3	3.3	40.3	1.3	5.8	0.8	0.0	0.0
712.6	0.0	0.3	0.7	1.1	20.4	2.5	49.9	2.5	20.4	1.1	0.7	0.3	0.0

b)

$ m_J\rangle$	6	5	4	3	2	1	0	-1	-2	-3	-4	-5	-6
Energy													
0.00	46.1	0.1	0.8	1.9	0.1	1.1	0.0	1.1	0.1	1.9	0.8	0.1	46.1
1.86	48.1	0.1	0.5	1.1	0.1	0.1	0.1	0.1	0.1	1.1	0.5	0.1	48.1
44.6	0.3	20.9	5.0	5.6	11.1	1.1	11.9	1.1	11.1	5.6	5.0	20.9	0.3
55.7	1.6	18.7	8.2	7.7	4.0	9.4	0.6	9.4	4.0	7.7	8.2	18.7	1.6
98.7	1.6	26.9	5.5	2.7	3.7	8.2	2.8	8.2	3.7	2.7	5.5	26.9	1.6
134.0	1.0	25.3	11.2	2.4	4.7	2.9	5.1	2.9	4.7	2.4	11.2	25.3	1.0
165.7	0.4	2.2	27.2	4.0	5.7	7.1	7.0	7.1	5.7	4.0	27.2	2.2	0.4
251.8	0.1	0.6	29.4	8.2	3.5	3.5	9.3	3.5	3.5	8.2	29.4	0.6	0.1
259.4	0.5	4.0	3.5	29.5	4.2	4.5	7.3	4.5	4.2	29.5	3.5	4.0	0.5
432.8	0.2	0.4	0.2	29.5	3.6	15.6	1.1	15.6	3.6	29.5	0.2	0.4	0.2
434.9	0.0	0.6	7.8	1.7	37.5	2.4	0.0	2.4	37.5	1.7	7.8	0.6	0.0
738.2	0.0	0.1	0.5	0.1	21.3	1.4	53.0	1.4	21.3	0.1	0.5	0.1	0.0
738.5	0.0	0.0	0.2	5.6	0.5	42.7	1.8	42.7	0.5	5.6	0.2	0.0	0.0

Table S12. Energies (cm⁻¹) and percentage composition of the CASSCF/RASSI wavefunctions corresponding to the lowest energy atomic multiplet $J = 15/2$ on the basis of total angular momentum eigenstates $|m_J\rangle$ for **1-Dy**. The reference system has the origin on the Dy(III) ion and is oriented along the main magnetic axes calculated for the ground state Kramers doublet of Dy.

$ m_J\rangle$	15/2	13/2	11/2	9/2	7/2	5/2	3/2	1/2	-1/2	-3/2	-5/2	-7/2	-9/2	-11/2	-13/2	-15/2
Energy																
0.0	89.9	0.5	7.1	1.1	0.5	0.3	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
129.0	0.8	58.9	3.4	15.2	6.3	6.2	3.0	3.5	0.9	0.9	0.1	0.4	0.1	0.1	0.0	0.1
230.7	3.3	24.4	16.1	0.4	12.4	7.9	14.0	4.4	8.3	1.6	2.1	1.8	0.5	1.3	1.3	0.2
329.5	2.2	0.1	42.6	8.8	4.4	3.1	4.2	9.0	5.3	1.8	9.1	1.6	4.2	0.3	3.0	0.3
428.8	0.5	2.5	4.3	30.7	5.9	10.6	0.2	7.1	1.9	20.2	3.9	4.7	0.5	5.9	0.8	0.3
493.9	0.1	0.7	1.3	7.7	23.4	4.5	7.7	3.8	27.1	8.5	7.2	0.6	4.7	1.7	0.6	0.2
580.9	0.0	0.0	0.5	3.9	15.4	26.8	23.4	13.1	3.1	0.5	1.9	3.4	3.5	2.7	1.4	0.4
675.5	1.5	5.7	12.7	18.5	18.7	14.7	10.6	7.4	4.9	3.0	1.5	0.6	0.2	0.0	0.0	0.0

Table S13. Energies (cm⁻¹) and percentage composition of the CASSCF/RASSI wavefunctions corresponding to the lowest energy atomic multiplet $J = 8$ on the basis of total angular momentum eigenstates $|m_J\rangle$ for **1-Ho**. The reference system has the origin on the Ho(III) ion and is oriented along the main magnetic axes calculated for the ground state pseudo-doublet of Ho.

$ m_J\rangle$	8	7	6	5	4	3	2	1	0	-1	-2	-3	-4	-5	-6	-7	-8
Energy																	
0.0	35.3	3.3	4.8	0.8	4.3	0.4	0.9	0.3	0.0	0.3	0.9	0.4	4.3	0.8	4.8	3.3	35.3
0.5	36.2	3.4	4.4	1.1	3.3	0.7	0.1	0.7	0.3	0.7	0.1	0.7	3.3	1.1	4.4	3.4	36.2
54.1	2.1	9.6	1.2	14.7	1.1	15.3	2.1	3.8	0.1	3.8	2.1	15.3	1.1	14.7	1.2	9.6	2.1
61.7	4.2	10.9	2.5	8.3	8.3	3.8	9.9	0.4	3.5	0.4	9.9	3.8	8.3	8.3	2.5	10.9	4.2
105.6	4.1	3.0	5.6	10.2	7.8	7.7	7.2	3.2	2.4	3.2	7.2	7.7	7.8	10.2	5.6	3.0	4.1
129.0	6.0	0.8	11.5	2.7	14.4	2.6	2.3	6.3	6.8	6.3	2.3	2.6	14.4	2.7	11.5	0.8	6.0
177.6	4.1	23.2	0.9	0.7	0.8	1.5	7.3	8.8	5.2	8.8	7.3	1.5	0.8	0.7	0.9	23.2	4.1
190.1	0.7	3.9	12.5	3.5	0.3	10.4	3.8	14.7	0.3	14.7	3.8	10.4	0.3	3.5	12.5	3.9	0.7
205.9	3.7	15.8	4.0	2.9	8.3	4.1	1.0	3.0	14.9	3.0	1.0	4.1	8.3	2.9	4.0	15.8	3.7
217.6	0.4	0.9	15.8	0.2	5.3	1.1	15.0	5.3	12.0	5.3	15.0	1.1	5.3	0.2	15.8	0.9	0.4
227.1	0.9	4.9	4.3	13.9	6.1	3.0	9.3	1.6	11.8	1.6	9.3	3.0	6.1	13.9	4.3	4.9	0.9
239.6	0.9	4.9	5.8	6.3	10.1	6.9	3.8	7.2	8.5	7.2	3.8	6.9	10.1	6.3	5.8	4.9	0.9
256.3	0.5	3.7	3.6	8.2	5.3	17.5	1.4	9.5	0.7	9.5	1.4	17.5	5.3	8.2	3.6	3.7	0.5
300.6	0.8	5.1	8.8	7.6	7.4	2.0	7.7	10.6	0.0	10.6	7.7	2.0	7.4	7.6	8.8	5.1	0.8
305.2	0.0	4.4	7.2	6.8	4.2	11.3	12.5	1.1	4.8	1.1	12.5	11.3	4.2	6.8	7.2	4.4	0.0
349.1	0.1	0.1	4.7	7.9	0.8	10.3	11.1	4.5	20.9	4.5	11.1	10.3	0.8	7.9	4.7	0.1	0.1
349.6	0.1	2.2	2.5	4.2	12.2	1.5	4.5	19.0	7.6	19.0	4.5	1.5	12.2	4.2	2.5	2.2	0.1

Table S14. The effective tensors g^{eff} of the ground KD for **1-Dy** and the lowest-lying states approximated as ground KDs for **1-Tb-MeOH**, **1-Tb-H₂O** and **1-Ho**. Associated main magnetic axes are reported as the components of three unit vectors $\mathbf{xM}$, $\mathbf{yM}$, $\mathbf{zM}$ in the reference frame $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ of the Cartesian coordinates of the atoms, from SA-CASSCF/RASSI-SO/SINGLE_ANISO computations.

Compound	g^{eff}		x	y	z
1-Tb-MeOH	0.0	$\mathbf{xM}$	0.026	0.242	-0.970
	0.0	$\mathbf{yM}$	-0.941	0.333	0.058
	16.94	$\mathbf{zM}$	0.337	0.911	0.237
1-Tb-H₂O	0.0	$\mathbf{xM}$	-0.895	0.399	0.202
	0.0	$\mathbf{yM}$	0.033	-0.392	0.919
	17.32	$\mathbf{zM}$	0.446	0.829	0.337
1-Dy	0.09	$\mathbf{xM}$	0.855	-0.382	-0.351
	0.20	$\mathbf{yM}$	0.026	-0.644	0.764
	19.22	$\mathbf{zM}$	0.518	0.663	0.541
1-Ho	0.0	$\mathbf{xM}$	-0.871	0.479	-0.109
	0.0	$\mathbf{yM}$	-0.306	-0.354	0.884
	17.78	$\mathbf{zM}$	0.385	0.803	0.455

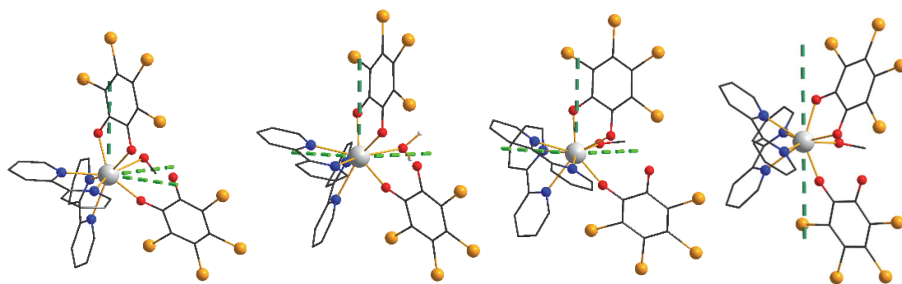


Figure S12. Orientation of the calculated main magnetic axes for the ground pseudo-KD of **1-Tb-MeOH**, **1-Tb-H₂O** and **1-Ho** (RE=, Tb and Ho) from the coordinates given in Table S14. Final figure is electrostatic prediction of Dy easy axis of magnetisation using Magellan treating the each bound oxygen atom with -1 charge and MeOH and bipy as neutral.³

Table S15. CASSCF/RASSI calculated B(k,q) crystal field parameters (cm⁻¹) for **1-Tb-MeOH**, **1-Tb-H₂O**, **1-Dy** and **1-Ho** for the Extended Stevens Operators (ESO), as computed by the SINGLE_ANISO module of Molcas, with k the rank and q the component of the operator. The reference system has the origin on the Ln(III) ion and is oriented along the main axes of the g-tensor calculated for the ground Ising or Kramers doublet.

		1-Tb-MeOH	1-Tb-H₂O	1-Dy	1-Ho
		B(k,q)	B(k,q)	B(k,q)	B(k,q)
<i>k</i>	<i>q</i>				
2	-2	-4.094	1.873	7.024 x 10 ⁻¹	1.084
2	-1	2.005	-1.707	9.386 x 10 ⁻¹	7.983 x 10 ⁻²
2	0	-3.922	-4.294	-2.447	-7.798 x 10 ⁻¹
2	1	1.455	-6.533 x 10 ⁻¹	-1.941	6.358 x 10 ⁻¹
2	2	-6.682	7.550	3.691	7.107 x 10 ⁻¹
4	-4	-4.999 x 10 ⁻³	-7.390 x 10 ⁻³	1.516 x 10 ⁻²	-2.864 x 10 ⁻³
4	-3	-1.649 x 10 ⁻¹	9.757 x 10 ⁻²	-5.854 x 10 ⁻²	-3.961 x 10 ⁻²
4	-2	1.888 x 10 ⁻²	-1.331 x 10 ⁻²	1.419 x 10 ⁻²	9.090 x 10 ⁻³
4	-1	-1.187 x 10 ⁻²	3.004 x 10 ⁻²	-1.906 x 10 ⁻²	-6.942 x 10 ⁻³
4	0	4.930 x 10 ⁻³	6.290 x 10 ⁻³	-4.628 x 10 ⁻³	-1.442 x 10 ⁻³
4	1	-1.783 x 10 ⁻²	2.207 x 10 ⁻²	-1.155 x 10 ⁻²	3.516 x 10 ⁻³
4	2	5.537 x 10 ⁻²	-5.708 x 10 ⁻²	1.452 x 10 ⁻²	2.604 x 10 ⁻³
4	3	1.054 x 10 ⁻¹	1.394 x 10 ⁻¹	-5.049 x 10 ⁻²	6.887 x 10 ⁻³
4	4	-7.968 x 10 ⁻³	5.211 x 10 ⁻³	-1.119 x 10 ⁻²	-5.171 x 10 ⁻³
6	-6	2.951 x 10 ⁻⁴	-3.235 x 10 ⁻⁴	1.787 x 10 ⁻⁵	-4.456 x 10 ⁻⁵
6	-5	7.702 x 10 ⁻⁴	1.820 x 10 ⁻⁴	-6.240 x 10 ⁻⁴	-3.749 x 10 ⁻⁴
6	-4	-1.169 x 10 ⁻⁴	-1.137 x 10 ⁻⁴	1.472 x 10 ⁻⁴	-1.303 x 10 ⁻⁴
6	-3	3.107 x 10 ⁻⁵	-1.180 x 10 ⁻⁴	-1.957 x 10 ⁻⁴	2.429 x 10 ⁻⁴
6	-2	-1.680 x 10 ⁻⁴	4.749 x 10 ⁻⁵	-4.133 x 10 ⁻⁶	-1.117 x 10 ⁻⁶
6	-1	-3.126 x 10 ⁻⁵	-7.519 x 10 ⁻⁵	2.834 x 10 ⁻⁵	-1.742 x 10 ⁻⁴
6	0	-2.605 x 10 ⁻⁵	-2.506 x 10 ⁻⁵	9.373 x 10 ⁻⁶	-1.391 x 10 ⁻⁵
6	1	9.473 x 10 ⁻⁶	-2.803 x 10 ⁻⁴	1.541 x 10 ⁻⁴	-6.234 x 10 ⁻⁵
6	2	-2.757 x 10 ⁻⁴	2.835 x 10 ⁻⁴	7.410 x 10 ⁻⁵	-2.791 x 10 ⁻⁵
6	3	-1.279 x 10 ⁻⁴	7.071 x 10 ⁻⁵	-1.688 x 10 ⁻⁴	1.132 x 10 ⁻⁴
6	4	-9.976 x 10 ⁻⁵	-1.410 x 10 ⁻⁴	3.372 x 10 ⁻⁵	1.284 x 10 ⁻⁴
6	5	-2.569 x 10 ⁻⁴	2.347 x 10 ⁻⁴	4.377 x 10 ⁻⁴	-3.290 x 10 ⁻⁴
6	6	-9.987 x 10 ⁻⁵	-1.143 x 10 ⁻⁴	1.817 x 10 ⁻⁴	2.445 x 10 ⁻⁴

3. Dynamic Magnetic Properties

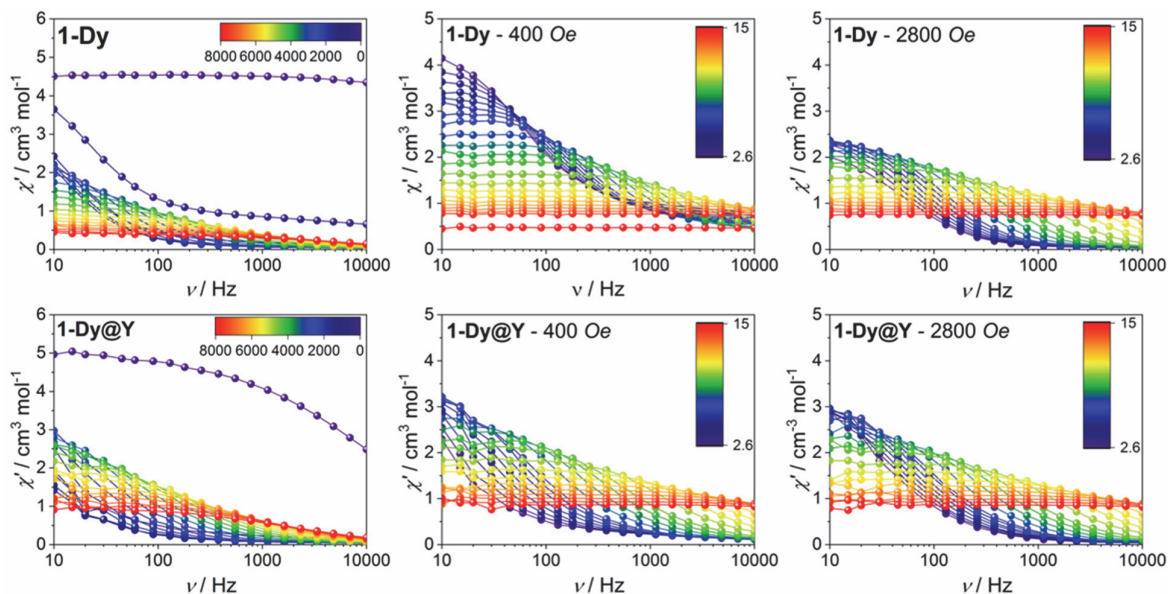


Figure S13. Frequency ($\nu = 1\text{-}10,000$ Hz) dependence of the in-phase ac susceptibility (χ') of **1-Dy** and **1-Dy@Y**; field (0-8000 Oe) scans at 2.6 K (left) and temperature (2.6-15 K) scans in applied dc fields of 400 Oe (middle) and 2800 Oe (right). The solid lines represent fits to the Debye equation, dashed lines are guides to the eye.

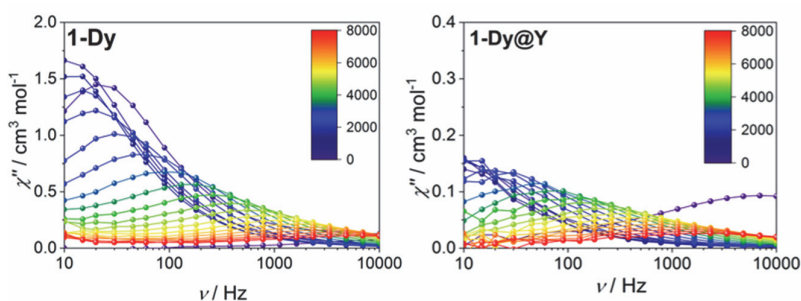


Figure S14. Frequency ($\nu = 1\text{-}10,000$ Hz) dependence of the out-of-phase ac susceptibility (χ'') of **1-Dy** and **1-Dy@Y**; field (0-8000 Oe) scans at 2.6 K.

Table S16. Values of τ and α derived from fitting of the generalized Debye model of the isothermal ac measurements of **1-Dy** and **1-Dy@Y**.

1-Dy					1-Dy@Y			
T / K	400 Oe		2800 Oe		400 Oe		2800 Oe	
	τ / s	α	τ / s	α	τ / s	α	τ / s	α
2.6	0.03771	0.21277	0.02351	0.21735	0.25323	0.3258	0.03959	0.28349
2.8	0.02837	0.19164	0.02042	0.18772	0.12847	0.28437	0.03074	0.25955
3	0.02165	0.17078	0.0178	0.17168	0.09932	0.29818	0.02249	0.20651
3.2	0.01699	0.15983	0.01523	0.15212	0.04767	0.2368	0.02015	0.22365
3.4	0.0134	0.15146	0.01307	0.14418	0.03669	0.24691	0.01784	0.24484
3.6	0.01049	0.13585	0.01099	0.1305	0.02805	0.27209	0.01394	0.21445
3.8	0.00821	0.11865	0.00927	0.12865	0.01849	0.23031	0.00974	0.15802
4	0.00664	0.11616	0.00775	0.12446	0.01282	0.18612	0.00907	0.20629
4.5	0.0039	0.10231	0.00492	1.88452	0.00632	0.16834	0.00529	0.21899
5	0.00242	0.09939	0.00316	0.11303	0.00394	0.19867	0.00328	0.1986
5.5	0.00154	0.10012	0.00205	0.1117	0.00234	0.18863	0.00203	0.17211
6	0.00102	0.09546	0.00136	0.10867	0.00149	0.19039	0.00135	0.18633
7	4.95E-04	0.09002	6.42E-04	0.10741	6.77E-04	0.16123	6.41E-04	0.1801
8	2.65E-04	0.08589	3.31E-04	0.10557	3.53E-04	0.16214	3.41E-04	0.13978
9	1.55E-04	0.07414	1.85E-04	0.09741	1.99E-04	0.14507	1.72E-04	0.20937
10	9.89E-05	0.058	1.10E-04	0.09525	1.20E-04	0.12466	9.92E-05	0.18142
11	6.64E-05	0.04994	6.90E-05	0.08423	6.09E-05	0.16756	4.84E-05	0.20154
12	4.74E-05	0.05047	4.38E-05	0.09018	3.41E-05	0.17871	4.42E-05	0.1496
13	3.60E-05	0.06561	3.39E-05	0.09361	4.72E-05	0.11067	2.31E-05	0.19308
14	4.25E-05	0.05024	2.82E-05	0.11562			5.40E-05	0.08019
15	2.31E-05	0.14704	1.72E-05	0.17405				

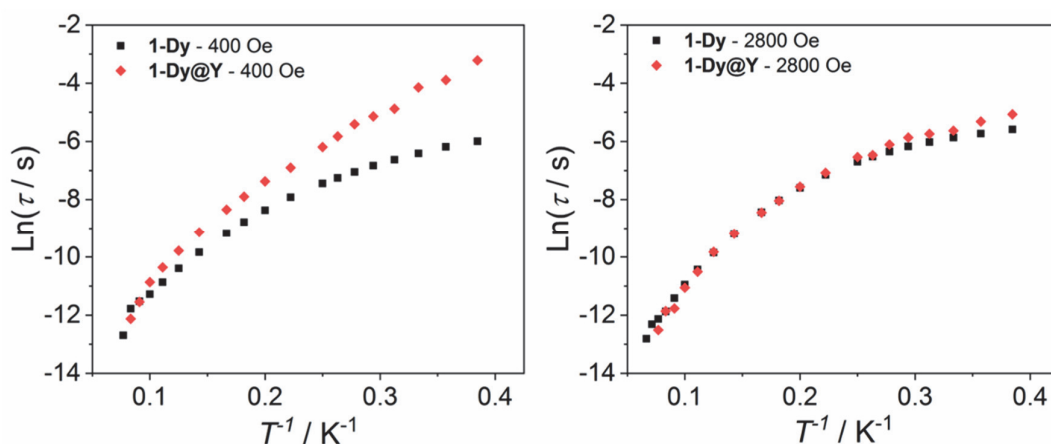


Figure S15. Arrhenius plots of magnetic relaxation time data for **1-Dy** and **1-Dy@Y** as $\ln(\tau)$ versus T^{-1} applied fields of 400 (left) and 2800 Oe (right).

4. Inelastic Neutron Scattering Additional Details

Supplementary INS Data

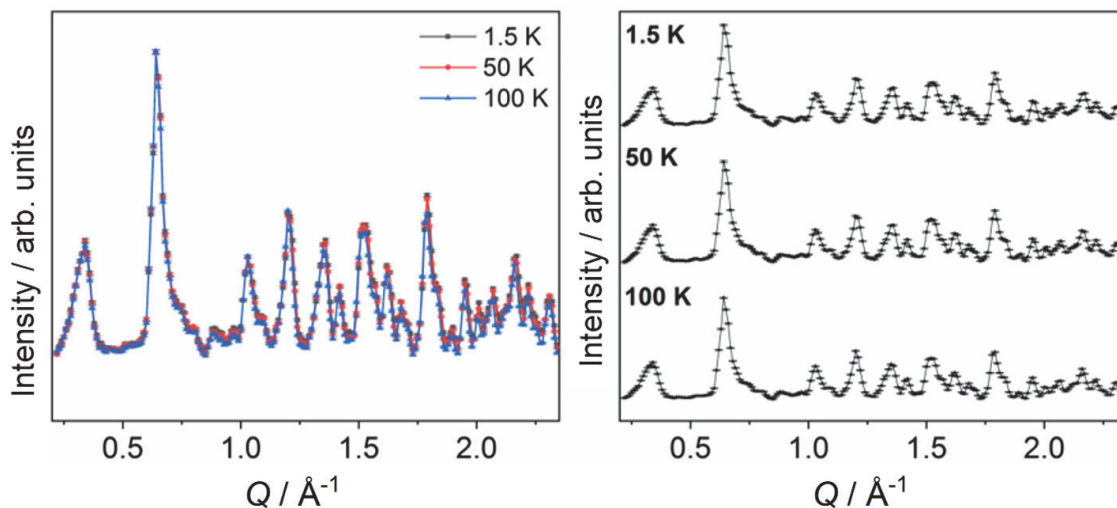


Figure S166. Overlaid (left) and stacked (right) neutron powder patterns for **1-Tb^D** at 1.5, 50 and 100 K.

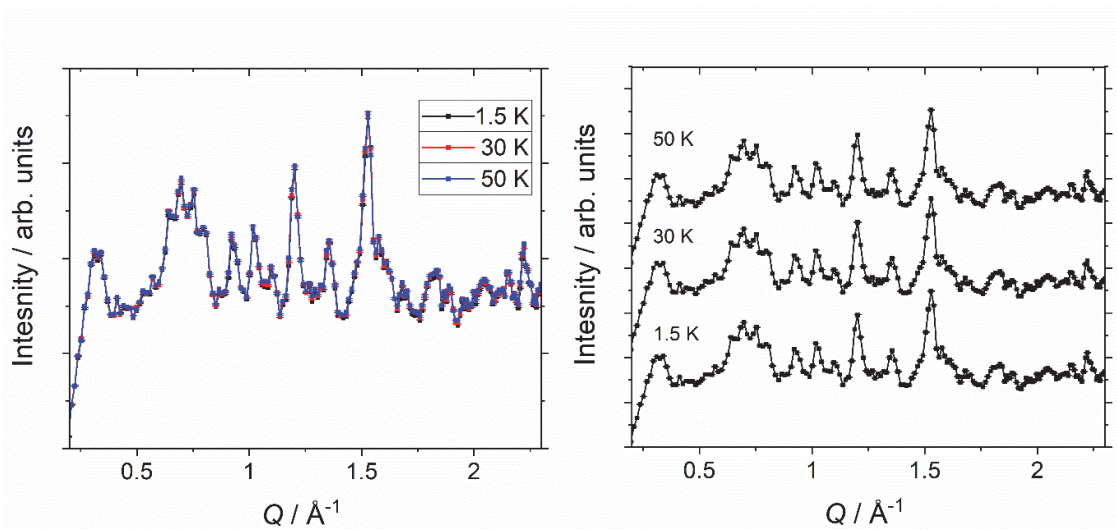


Figure S17. Overlaid (left) and stacked (right) neutron powder patterns for the **1-Ho** sample at 1.5, 30 and 50 K.

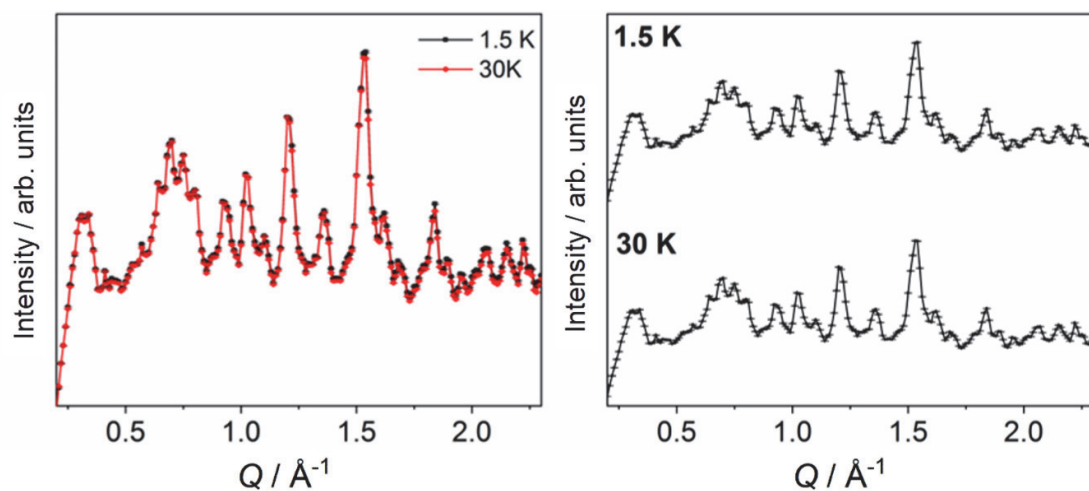


Figure S18. Overlaid (left) and stacked (right) neutron powder patterns for the 1-Y sample at 1.5 and 30 K.

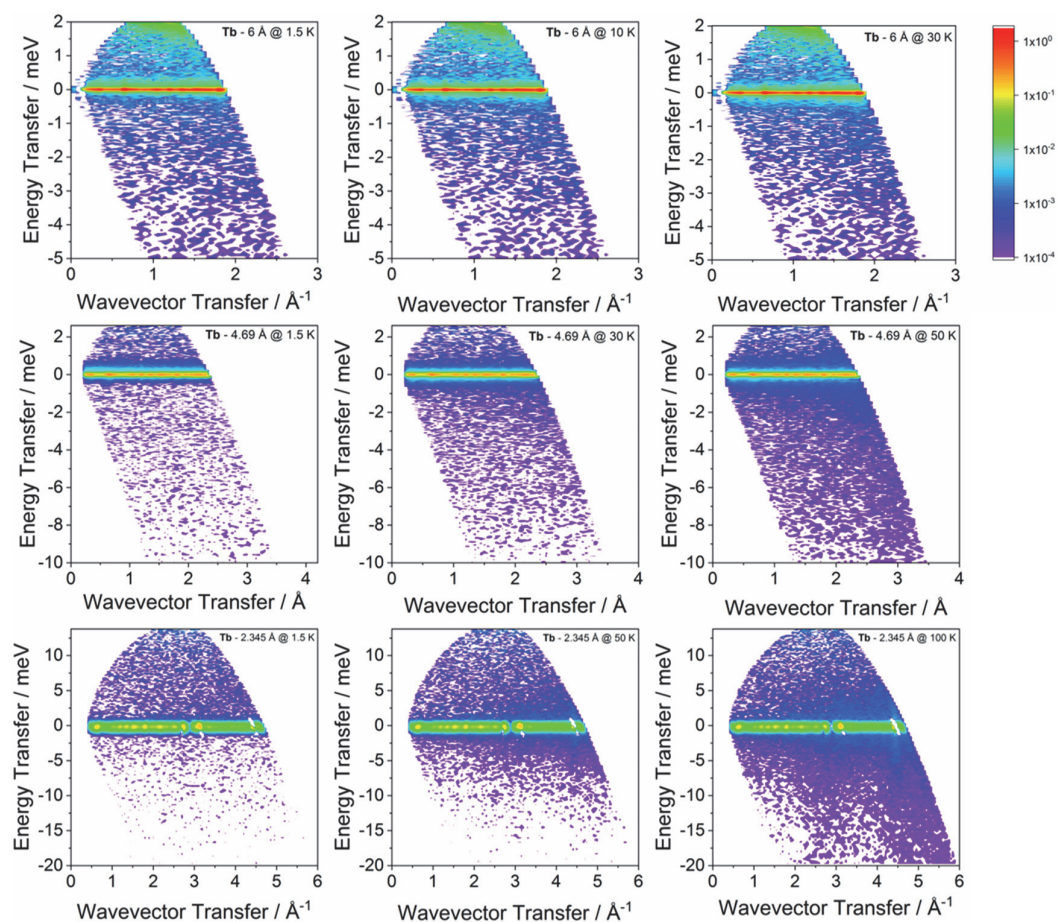


Figure S19. Plots of $S(Q, \omega)$ for 1-Tb^D

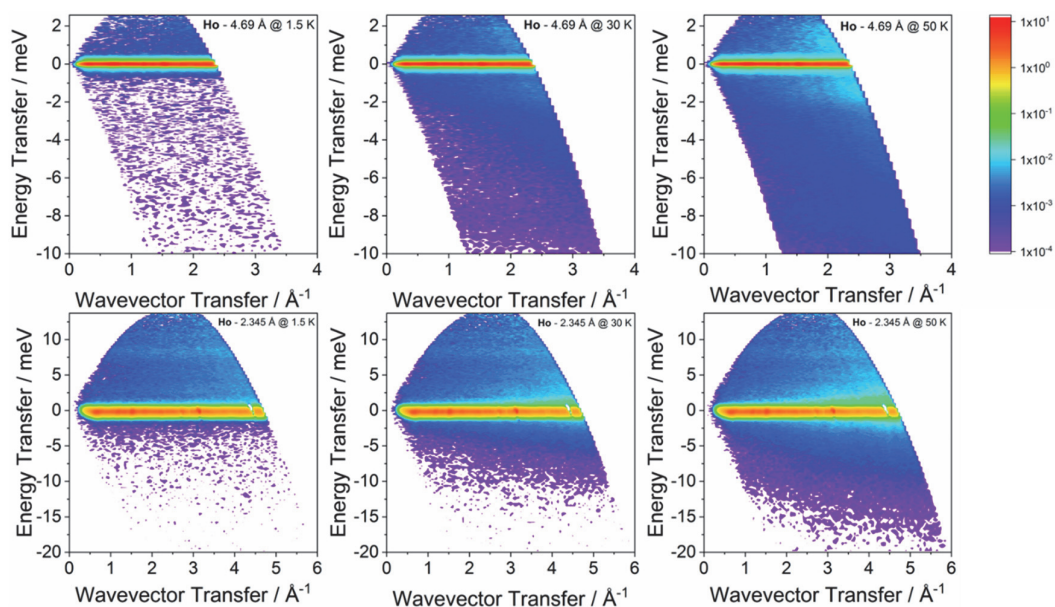


Figure S180. Plots of $S(Q, \omega)$ for 1-Ho

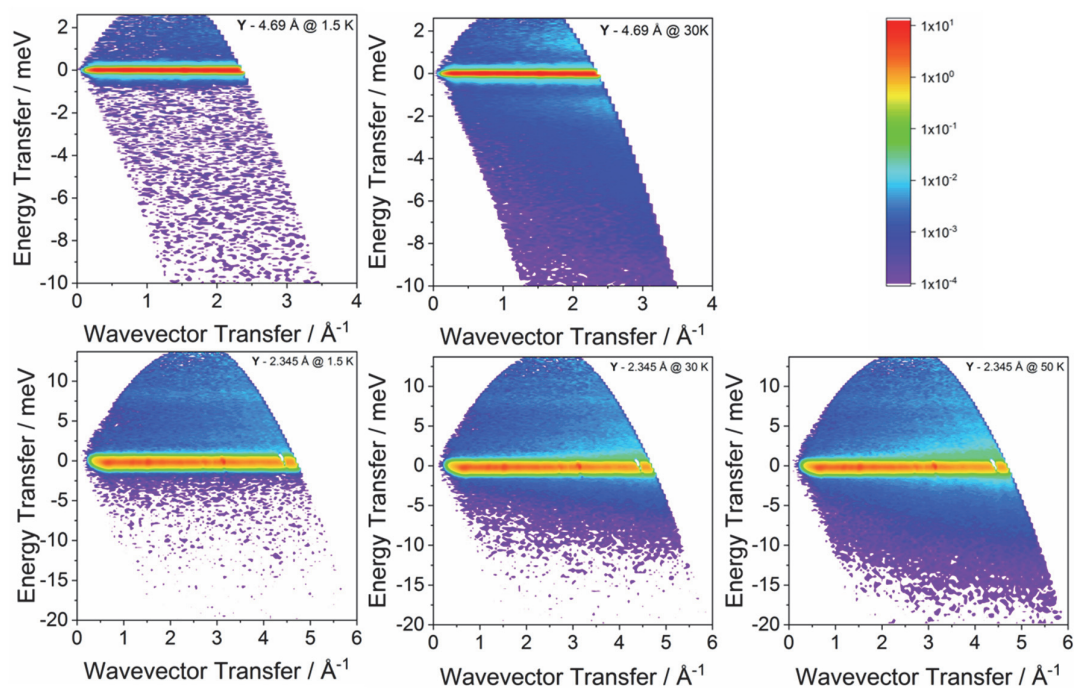


Figure S19. Plots of $S(Q, \omega)$ for 1-Y

Details on the Simulation of INS Spectra

The simulation of the INS spectra has been performed using the program McPhase⁴. This program suite allows, through the Python class CrystalField, to compute the INS crystal field transition intensities for a lanthanoid complex at any chosen temperature when provided with the *ab initio* crystal field parameters. For this purpose, a dedicated Python script has been developed to fetch the crystal field parameters from the output of the SINGLE_ANISO calculation (Table S15), provide them to McPhase and draw the simulated INS spectra at the same neutron wavelengths for which the experimental data has been collected, namely 4.69 Å (for which a peak resolution of 0.147 meV has been used) and 2.345 Å (for which a peak resolution of 0.8 meV has been used), for the same range of temperatures which have been experimentally characterized. The simulated INS transition energies and intensities are reported in Table S17.

Table S17. *Ab initio* predicted INS transitions for **1-Tb** and **1-Ho** at T = 1.5 and 30 K. For each set of data, the first column contains the INS transition energies (in meV) and the second column contains the INS transition intensities (in arbitrary units).

Energy	1-Tb-H ₂ O	Energy	1-Tb-H ₂ O	Energy	1-Tb-MeOH	Energy	1-Tb-MeOH	Energy	1-Ho	Energy	1-Ho
	1.5 K		30 K		1.5 K		30 K		1.5 K		30 K
-0.21	7.52	-6.83	0.15	-0.38	2.22	-6.09	0.15	-0.06	19	-7.67	0.29
0.21	38.34	-5.83	0.36	0.38	42.08	-4.74	0.67	0.06	29.55	-6.8	0.47
5.62	0.27	-1.21	1.04	4.74	8.41	-4.36	0.12	6.74	0.54	-0.93	0.75
5.83	6.08	-0.21	20.11	6.09	0.19	-1.73	1.26	6.8	8.32	-0.06	22.52
6.83	0.78	0.21	21.82	6.47	0.26	-0.38	18	7.67	4.77	0.06	23.02
7.04	0.71	1.21	1.65	10.35	0.25	0.38	20.86	7.72	0.41	0.93	1.08
12.21	0.48	5.38	0.14	10.73	2.1	1.73	2.46	13.11	1.28	6.37	0.44
12.42	1.46	5.62	0.72	14.97	0.11	4.36	0.63	13.17	0.27	6.74	0.64
16.34	0.27	5.83	3.46	15.35	0.8	4.62	0.13	15.99	0.11	6.8	6.49
16.55	0.75	6.83	2.08	18.15	0.55	4.74	4.17	22.07	0.13	7.67	5.65
20.22	0.37	7.04	0.41	29.69	0.15	5.99	0.86	22.13	1.28	7.72	0.32
31.86	0.13	9.51	0.28			6.09	1.55	23.6	0.27	8.32	0.2
		12.21	1.29			6.47	0.13	23.65	0.11	13.11	1.51
		12.42	0.83			8.89	0.31	25.5	0.22	13.17	0.21
		13.18	0.12			10.35	2	25.56	0.44	14.4	0.16
		16.34	0.72			10.73	1.04	28.14	0.12	15.99	0.13
		16.55	0.43			11.68	0.21			16.04	0.55
		20.22	0.21			14.97	0.87			22.07	0.16
						15.35	0.39			22.13	1
						17.77	0.14			23.6	0.32
						18.15	0.27			25.5	0.26
										25.56	0.34
										28.14	0.14

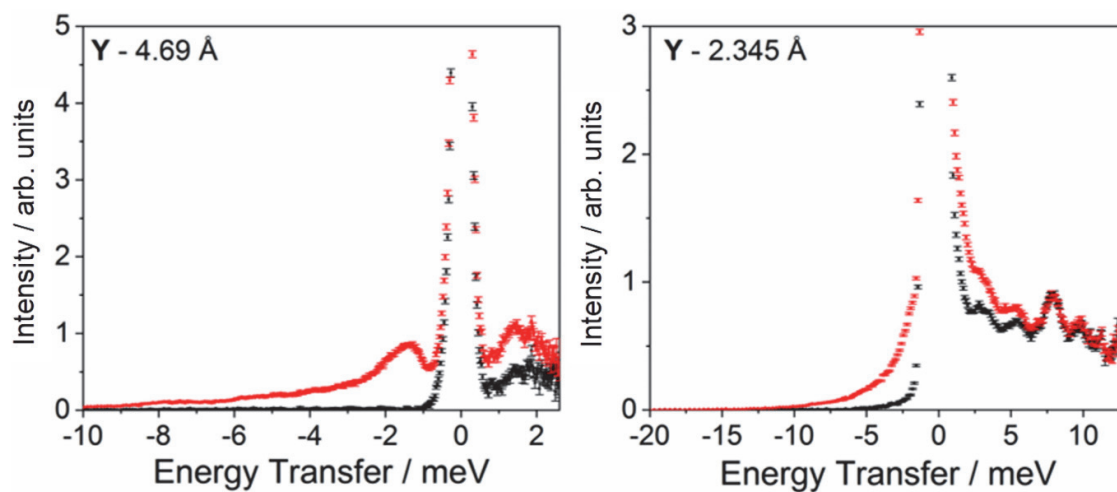


Figure S22. INS spectra of **1-Y** at neutron wavelengths of 4.69 Å (left) and 2.345 Å (right). Measurements were undertaken at 1.5 K (black) and 30 K (red).

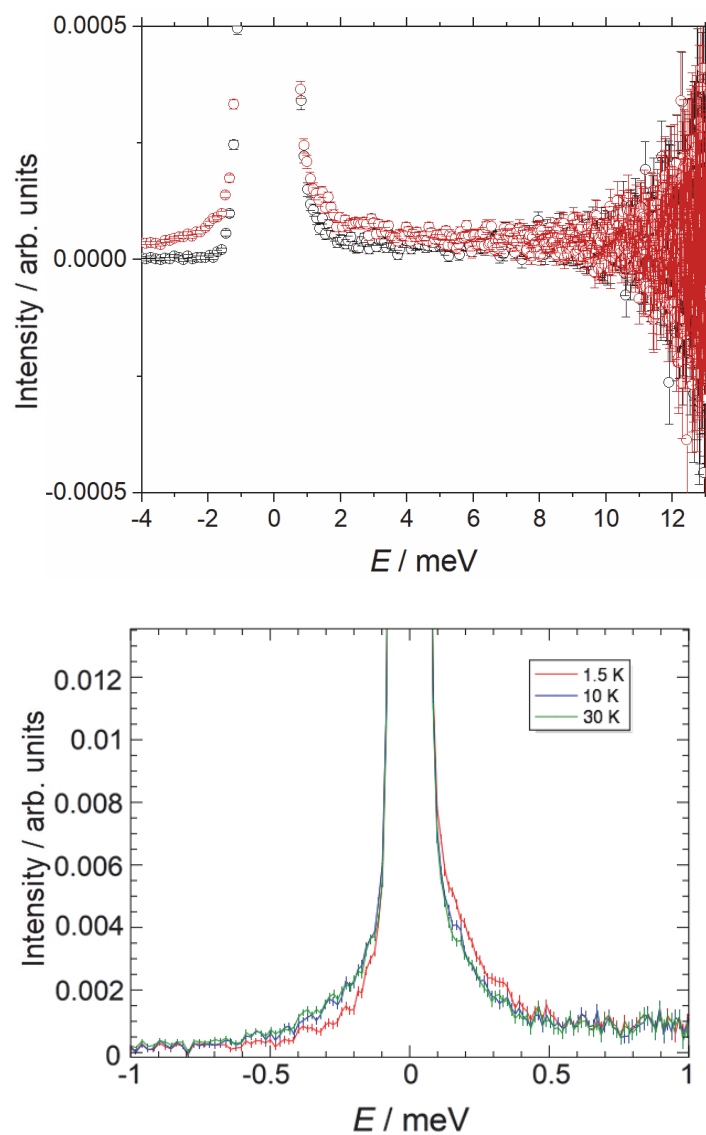


Figure S23. Top) Variable temperature INS spectra of **1-Tb^D** at neutron wavelengths of 2.345 Å at 1.5 K (black points) and 30 K (red points) **Bottom).** INS spectra of **1-Tb^D** at neutron wavelengths of 5.98 Å. Measurements were undertaken at 1.5 K (red), 10 K (blue) and 30 K (green).

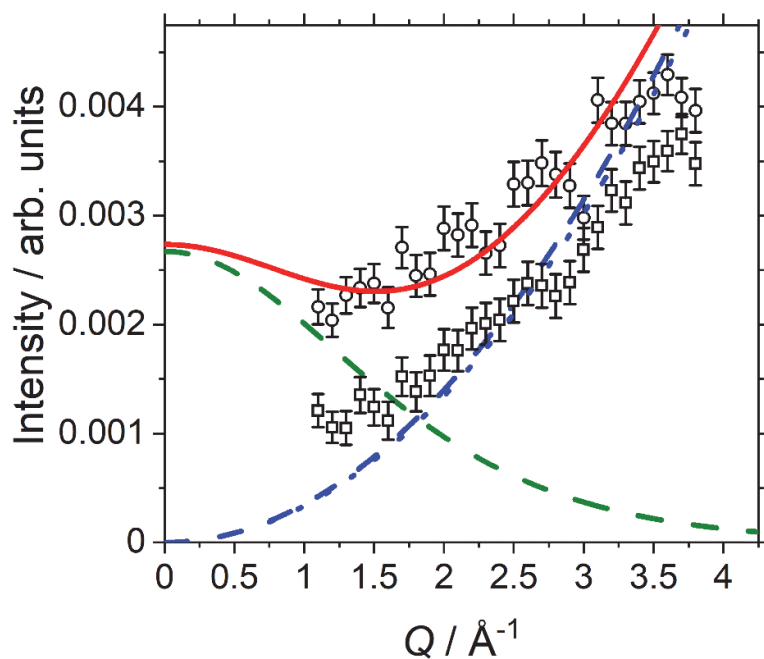


Figure S24. Q -dependence of the **1-Ho** (circles) and **1-Y** (squares) data at $E = 9(1)$ meV. **1-Y** shows a clear phonon-like dependence (dotted blue), while **1-Ho** has increased intensity at low Q and can be modelled (red) by combining the single ion form factor for Ho^{3+} (green dash) and a phonon quadratic dependence (blue dash). Note the quadratic dependence is almost identical for both analogues.

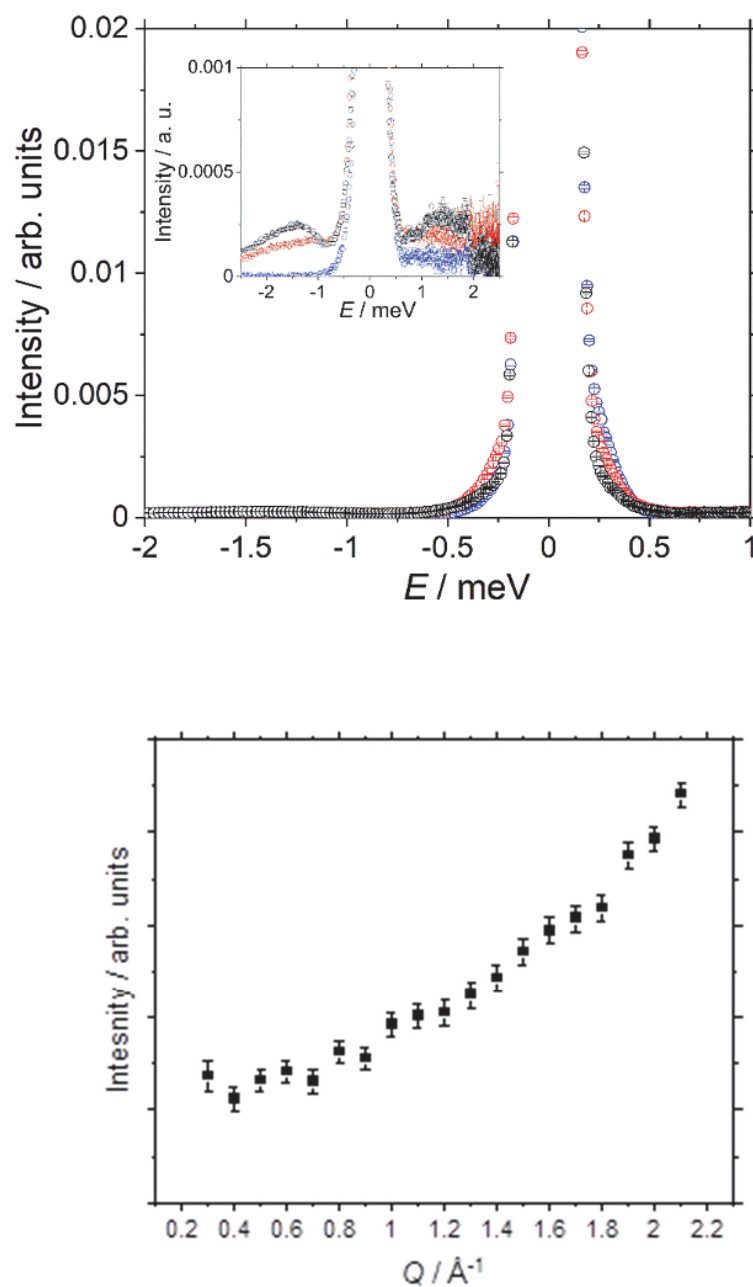


Figure S25. Top) INS spectra of **1-Ho** at neutron wavelengths of 4.69 Å and 1.5 K (blue), 30 K (red) and **1-Y** at 30 K (black). The inset represents a magnification of the base of the peak. **Bottom)** Q dependence of the **1-Ho** data at $E = 1.00(0.25)$ meV. This shows a clear quadratic increase, indicative of a phonon.

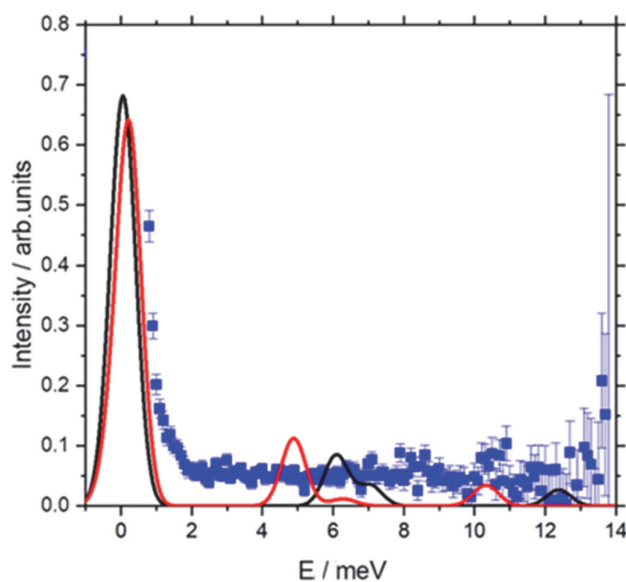


Figure S26. Scaled intensity of the CFP predicted CF transitions for **1-Tb-MeOH** (red) and **1-Tb-H₂O** (black) against the experimental 2.345 Å INS data at 1.5 K (blue).

5. Inelastic Neutron Scattering Fitting Details

The data were processed in the following manner. The data were read in, the data from an empty can were subtracted as a background and the intensity of each detector was normalized to a vanadium standard. The data were then integrated over all Q , to get the spectra $S(\omega)$ shown in Figure S27.

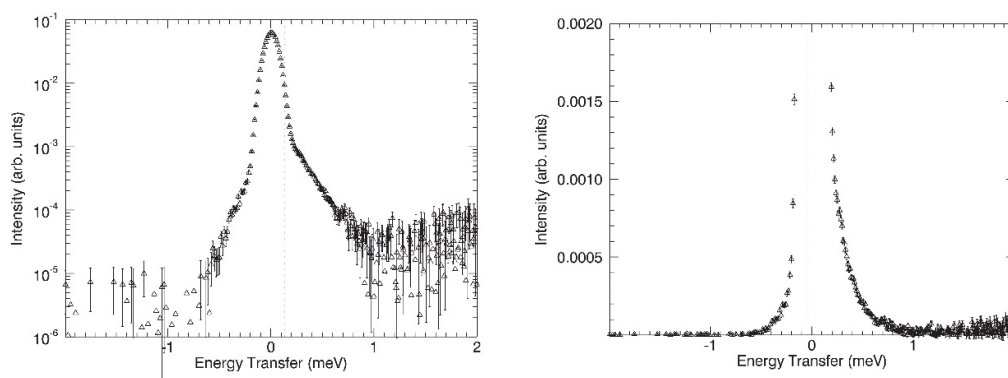


Figure S27. The neutron spectra $S(\omega)$ for sample **1-Tb^D** measured at 1.5 K, left Log scale. Right truncated linear scale.

Data from the vanadium standard, which is the same size and geometry as the sample, were processed in the same way (Figure S28). As the Vanadium approximates a purely incoherent scatterer, the elastic line is not broadened by Bragg reflections or other effects, and this can be used as a measurement of the instrument resolution function.

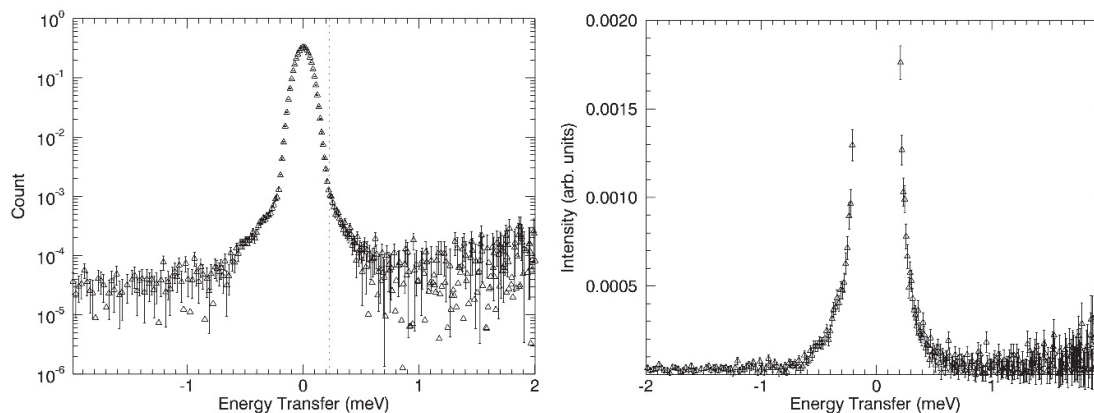


Figure S28. The neutron spectra $S(\omega)$ for the vanadium standard with 4.69 Å neutrons. Left log scale. Right Truncated scale.

The resolution function for a time-of-flight spectrometer such as Pelican is well known and has previously been described.⁵ The resolution as a function of energy transfer is shown in Figure S29.

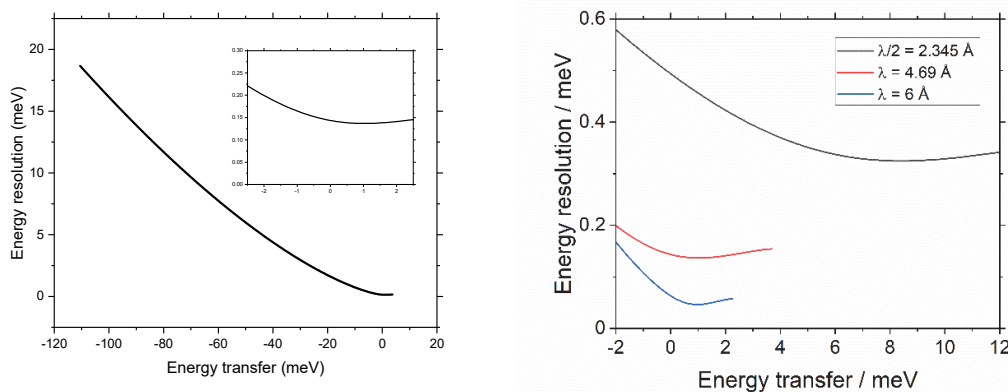


Figure S29. Left) Calculated energy resolution for the time-of-flight spectrometer Pelican when using 4.69 Å neutrons. Inset resolution function in the energy range of interest for **1-Tb^D**. Right) Calculated resolution function for each incident neutron energy.

Initially the following fit was attempted. The data shown in Figure S27 was fit to a Dirac delta function, convoluted with the measured resolution function shown in Figure S30.

$$S_{fit}(\omega) = \delta(\omega_0 = 0) \otimes \mathcal{R}(\omega)$$

Where $\mathcal{R}(\omega)$ is the measured resolution function. In all fitting described in this work, the resolution function used was that measured with the same wavelength as the data.

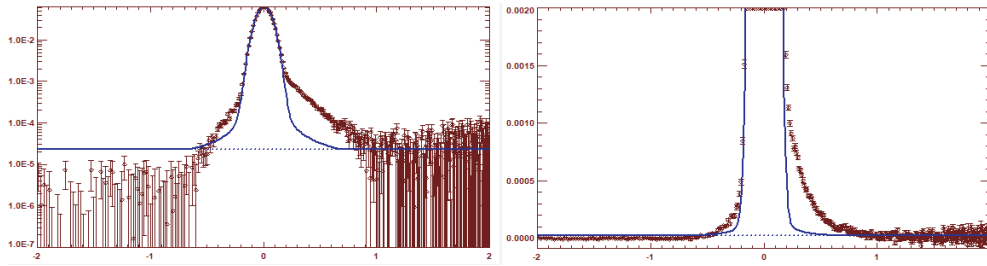


Figure S30. Initial fit of $S(\omega)$ for 1-TbD to the resolution function. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

If the resolution function had described the data, then there would have been no evidence of the inelastic scattering from the sample. In this case, there was clearly an excess of intensity close to the elastic line.

The next step was to see if this was a QENS line broadening (Figure S31). To do this we introduced a second peak function, a Lorentzian. The peak center is constrained to be the same as that of the delta peak. Both the Lorentzian and the delta peak are convoluted with the instrument resolution function.

$$S_{fit}(\omega) = (\mathcal{L}(\omega_0 = 0) + \delta(\omega_0 = 0)) \otimes \mathcal{R}(\omega)$$

Where the Lorentzian peak is described by $\mathcal{L}(\omega_0 = 0)$.

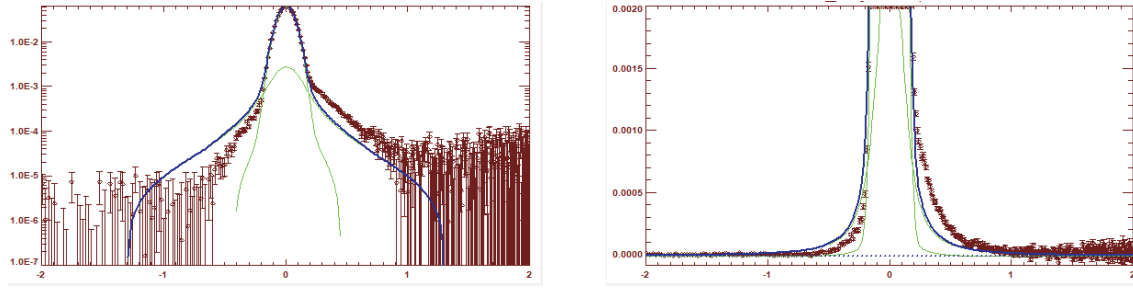


Figure S31. $S(\omega)$ for 1-Tb^{P} fitted with both a Lorentzian peak and a delta peak. Both convoluted with the instrument resolution function. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

This Lorentzian line broadening clearly does not describe the data. However, it is noted that this data was acquired at low temperature so detailed balance should apply. That is:

$$S(Q, -\omega) = S(Q, \omega) \exp(-\hbar\omega/k_b T)$$

This provides a constraint on the intensity of the data collected on the neutron energy loss (positive values) and neutron energy gain (negative values). A fit to the Lorentzian and delta function convoluted with the resolution function was performed with the constraint of detailed balance (Figure S32).

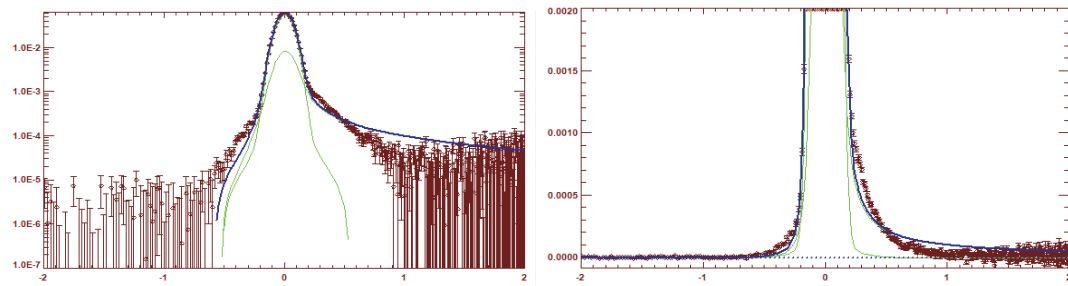


Figure S32. $S(\omega)$ for 1-Tb^{P} fitted with both a Lorentzian peak and a delta peak constrained to obey detailed balance. Both convoluted with the instrument resolution function. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

Introducing detailed balance has the effect of introducing the required asymmetry, however the intensity is not described properly. This led us to believe that there was a low energy excitation. Long lived excitations would demonstrate resolution limited peaks, this would be described by a Dirac delta function, convoluted with the resolution. So initially we modelled this with two delta functions without detailed balance (Figure S33), that is:

$$S_{fit}(\omega) = (\delta(\omega_0 = \omega) + \delta(\omega_0 = 0)) \otimes \mathcal{R}(\omega)$$

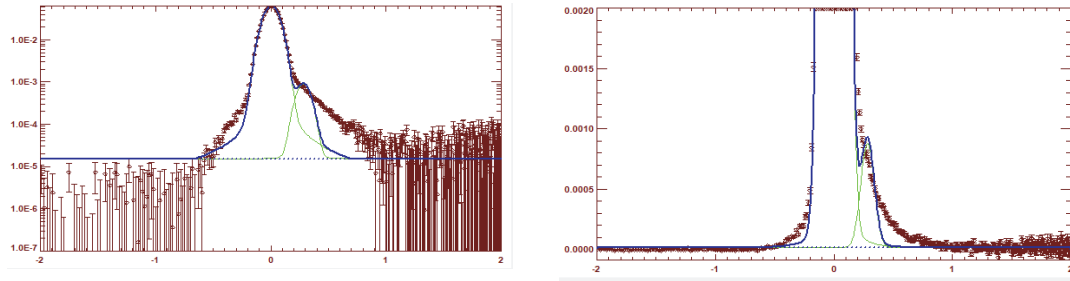


Figure S33. $S(\omega)$ for 1-Tb^{P} fitted with two delta peaks. Both convoluted with the instrument resolution function. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

This describes the intensity on the neutron energy loss (positive energy) side. However, there is clearly still a peak broadening. The second delta peak was changed to a Lorentzian, to reflect the finite lifetime of the excitation (Figure S34). This is written as:

$$S_{fit}(\omega) = (\mathcal{L}(\omega_0 = \omega) + \delta(\omega_0 = 0)) \otimes \mathcal{R}(\omega)$$

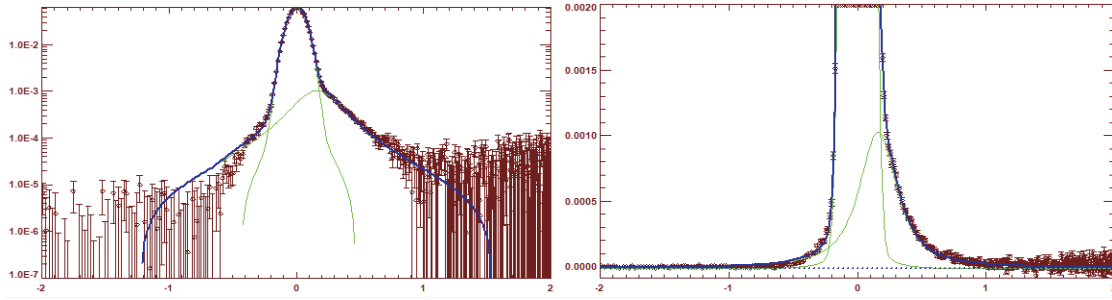


Figure S34. $S(\omega)$ for 1-Tb^{P} fitted with a delta peak and a Lorentzian peak, both convoluted with the instrument resolution function. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

This describes the data quite effectively. However, this was not constrained with detailed balance. The final step was to repeat this with detailed balance (Figure S35).

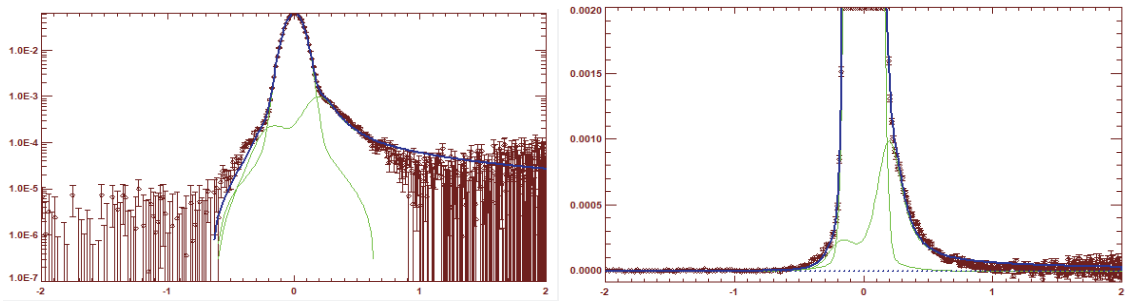


Figure S35. $S(\omega)$ for 1-Tb^{P} fitted with a delta peak and a Lorentzian peak, both convoluted with the instrument resolution function and constrained to obey detailed balance. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

On fitting to this model, the data are now well described. It should be noted that although we observe and model a peak on both the neutron energy gain and neutron energy loss side, the model is restricted to two peaks, a delta peak to describe the elastic line and a single Lorentzian that is then replicated on the neutron energy gain side due to the constraint of detailed balance.

To check that this is not an artefact at low energies, the above fit of a delta peak and a single Lorentzian constrained to obey detailed balance was then repeated with the 30 K data (Figure S36).

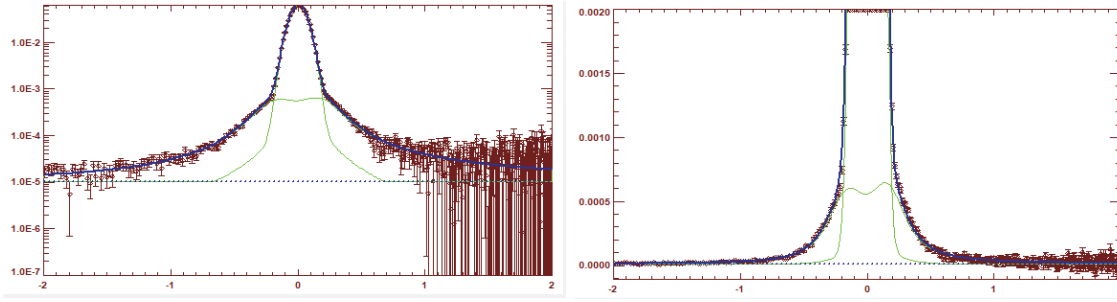


Figure S36. $S(\omega)$ for **1-Tb^P** at 30 K fitted with a delta peak and a Lorentzian peak, both convoluted with the instrument resolution function and constrained to obey detailed balance. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

This fit to the 30 K data demonstrates that the peak has the expected temperature dependence, thus serves as a check that the intensity close to the elastic line is not spurious.

In the case of **1-Tb^P**, the determined energy of the excitation is 0.216(0.014) meV (1.7(1) cm⁻¹). Given the energy resolution of the 4.69 Å configuration of the Pelican spectrometer has a resolution of approximately 0.147 meV at the elastic line, the configuration was changed to 5.98 Å which is known to have a 0.071 meV resolution at the elastic line. A resolution comparison is shown in figure S37.

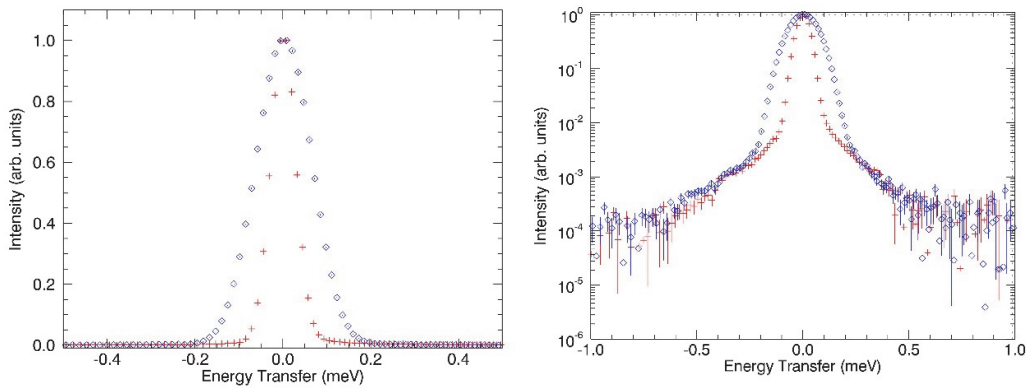


Figure S37. Left) Comparison of $S(\omega)$ for the vanadium standard measured with 4.69 Å neutrons (blue) and 5.98 Å neutrons (red). Note that the error bars are smaller than the datapoints. Right) Same data plotted on a log scale and over a wider energy range, to emphasise the non-uniform nature of the resolution function. These functions were used for the fitting described in the text for 4.69 Å and 5.98 Å neutrons respectively.

A drawback of the 5.98 Å configuration of Pelican is that it has approximately 1/3 the flux of the 4.69 Å configuration, thus long counting times are required. Once we had collected data at 1.5 K with 5.98 Å neutrons, we initially fit the spectra to the same model as the 4.69 Å data (Figure S38). That is one Lorentzian and a delta peak.

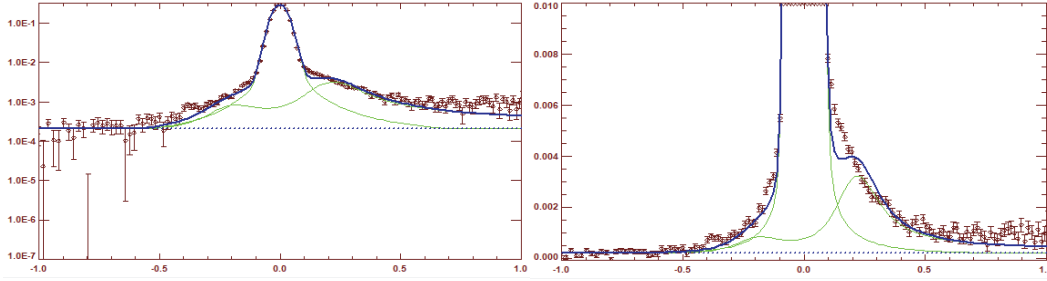


Figure S38. $S(\omega)$ for 1-Tb^{P} measured with 5.98 Å neutrons, fitted with a delta peak and a Lorentzian peak, both convoluted with the instrument resolution function and constrained to obey detailed balance. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

While the initial aim had been to measure an excitation clearly separated from the elastic line, it is clear that this is not the case and that the model of one excitation described by a Lorentzian does not give a good description of the data. Inspection of the high-resolution data indicates that there may be an additional shoulder. To account for this, an additional Lorentzian term was introduced to describe a second excitation, (Figure S39). This is written as:

$$S_{fit}(\omega) = (\mathcal{L}_1(\omega_0 = \omega) + \mathcal{L}_1(\omega_0 = \omega') + \delta(\omega_0 = 0)) \otimes \mathcal{R}(\omega)$$

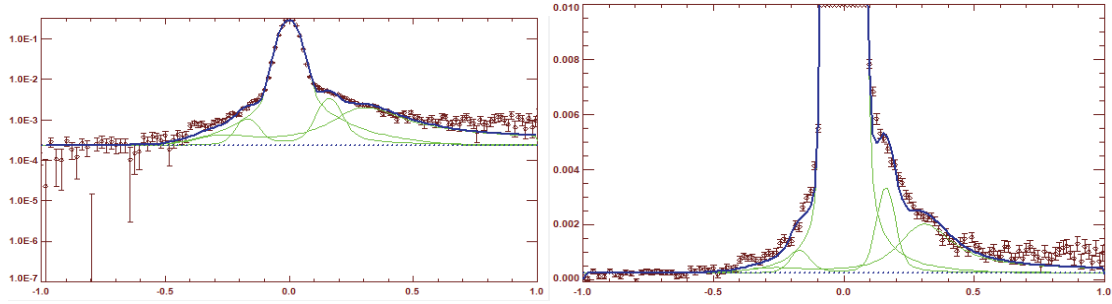


Figure S39. $S(\omega)$ for 1-Tb^{P} measured with $5.98 \text{ \AA}$ neutrons, fitted with a delta peak and two Lorentzian peak, both convoluted with the instrument resolution function and constrained to obey detailed balance. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

Introduction of the second Lorentzian describes the data well. The fit widths are very different between the two excitations. This is likely an artefact of the fitting process, to account for this and to avoid over parameterisation, the fits were repeated with the FWHM of the two Lorentzian components constrained to be the same (Figure S40).

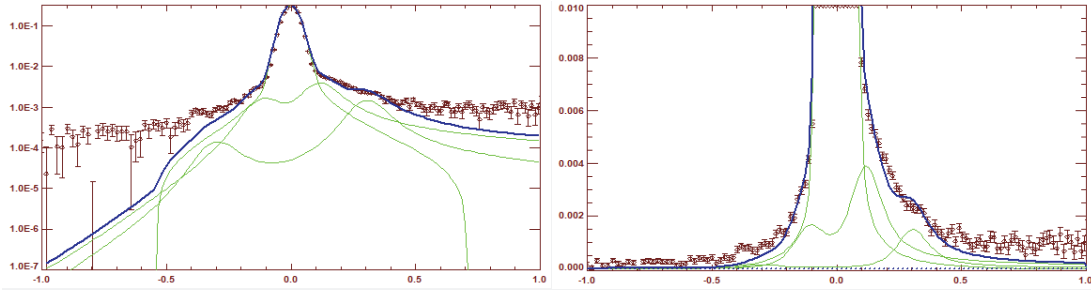


Figure S40. $S(\omega)$ for 1-Tb^{P} measured with $6 \text{ \AA}$ neutrons, fitted with a delta peak and two Lorentzian peaks constrained to have the same FWHM, both convoluted with the instrument resolution function and constrained to obey detailed balance. Left log scale. Right truncated linear scale. For both figures the x-axis is energy in units of meV and the y-axis is intensity in arbitrary units.

This gives a good and reliable fit to the data. Again, note that as detailed balance is applied, to the fit, although two Lorentzian functions are included in the fit, the results is the prediction of two peaks on the neutron energy loss side of the spectrum and again two peaks on the neutron energy gain side – however the peak centered at -0.304 meV has very little intensity at 1.5 K .

All fits shown above were performed using the `str_fit` package that is part of the freely available LAMP software. This IDL based software used a DR.gradient-expansion technique that is included in IDL (COOLfit based upon numerical recipes). A Levenberg marquadt technique is also available in the same package (Minpack based on minpack1).

6. Notes on the Observed Phonon Spectra

The reported data for **1-Tb^D**, **1-Y** and **1-Ho** show very different spectra when comparing the data obtained with 2.345 Å neutrons. Most of these differences can be put down to the difference in neutron scattering cross sections of H and D. The relevant scattering cross sections are shown in Table S18.⁶

Table S18. Neutron scattering cross section comparison for H and D.

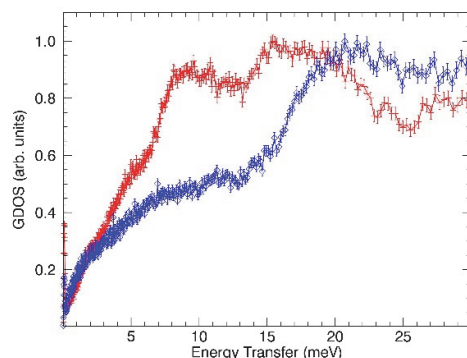
	Coherent cross section / barn	Incoherent cross section / barn	Total cross section / barn
H	1.76	80.27	82.03
D	5.59	2.05	7.64

Phonons and vibrations measured with inelastic neutron scattering are inherently a coherent phenomenon.⁷ However, incoherent scatterers such as hydrogen also give rise to strong contributions to the phonon density of states. Reflecting this, the analysis of phonon density of states is often done with the incoherent approximation.⁸ As such, the structure factors of **1-Tb^D** and **1-Ho** will be significantly different.

While no vibrational modes are observed for **1-Tb^D** when integrated overall all Q , in the range 1-12 meV, it is possible to measure the vibrational spectra over an extended energy range by looking at a generalized density of states (gdos) determined at elevated temperature using the neutron energy gain portion of the spectrum. The generalized density of states is given by:

$$g(Q, \omega) = \frac{\hbar\omega}{Q^2} S(Q, \omega) (1 - e^{-\frac{\hbar\omega}{kT}})$$

The data for **1-Tb^D** and **1-Ho** were processed in this way and integrated over all Q . This allows us to compare the vibrational spectra, shown in Figures S41 and S42.



Figures S41. Red, generalized density of state (GDOS) for **1-Ho** measured at 100 K. Blue generalized density of states for **1-Tb^D** measured at 100 K. The data is normalized to maximum intensity.

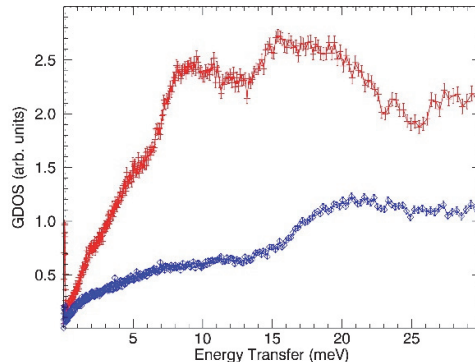


Figure S42. As Figure S41, with no normalization

The data are clearly different both in the intensity of the scattering and the peak positions. The intensity difference is due to the difference in scattering lengths of hydrogen and deuterium. While the observation of and the shifting of certain modes is due to the contribution of H to the scattering cross section and the difference in mass of hydrogen and deuterium. Analysis of these changes in vibrational spectra are beyond the scope of this paper, however it is noted that

in the case of magneto-elastic coupling of single ion magnets, such changes in the spectrum are discussed in reference 9 in the context of vibrational spectra of molecules with different levels of deuteration. A comparison of the raw data collected for both the **1-Tb^D** sample, and the empty sample can (before and after background correction) is shown in Figure S43.

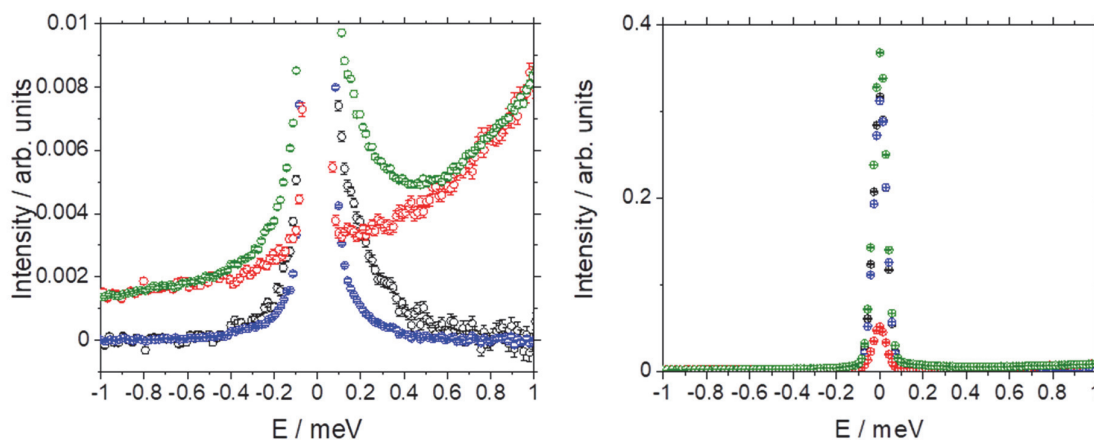


Figure S43. Comparison of presented data at 1.5 K with 6 Å neutrons for **1-Tb^D** after background correction (**black**) with uncorrected data (**green**), empty sample can (**red**) and vanadium standard with background correction and scaled to match intensity of **1-Tb^D** data.

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