Electronic Supplementary Information (ESI):

Approaching the 1000 K Energy Barrier in High Coordinate Lanthanide Single-Ion Magnets: Increasing U_{eff} in the [Dy(Tp^{2-py})F]⁺ moiety with Tetrahydrofuran

Jarrod R. Thomas, ^a Marcus J. Giansiracusa ^{b*} and Scott A. Sulway ^{a*}

^a School of Chemistry, The University of New South Wales (UNSW), Kensington, Sydney,
2052, Australia.

^b School of Chemistry, University of Melbourne, Parkville, Victoria, 3010, Australia.

* Corresponding author email: <u>s.sulway@unsw.edu.au</u>, <u>marcus.giansiracusa@unimelb.edu.au</u>

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1. Experimental Information

Starting materials of DyCl₃·6H₂O, YCl₃·6H₂O, AgF, KPF₆ and all spectroscopic grade solvents were used as purchased from commercially available sources, without purification. 3-(2'-pyridyl)-pyrazole and potassium hydrotris(3-(2'-pyridyl)-pyrazol-1-yl)borate (KTp^{2-py}) were prepared from literature procedure and characterised via recently developed spectroscopic techniques.^{1,2} [Ln(Tp^{2-py})F(Solv)₂](PF₆) (Ln = Dy, Y; Solv = pyridine, 1,4-dioxane) were prepared via literate procedures.³ ¹H (400 MHz), ¹¹B (128 MHz), ¹⁹F (377 MHz) and ³¹P (162 MHz) NMR Data was collected on a 400 MHz Brucker Advanced III at 298K fitted with BBFO temperature probes. Deuterated solvents were purchased through Sigma-Aldrich, dried over 3 Å sieves and degassed. ATR-Fourier transform Infrared (ATR-FTIR) spectra were collected on Thermo-Scientific Nicolet iS50 using microcrystalline powders in ambient conditions. Elemental Analysis was carried out at the Mark Wainwright Analytical Centre (MWAC) XRF lab using a Elementar varioMACRO cube (CHN).

Synthesis of $[Dy(Tp^{2-py})F(THF)_2](PF_6)$ (1-THF). $[Dy(Tp^{2-py})F(Solv)_2](PF_6)$ (Solv = 1,4-diox or pyridine) was dissolved in a 1:1 mixture of THF:MeCN, where very large, colourless, block crystals of $[Dy(Tp^{2-py})F(THF)_2](PF_6)$ (1-THF) were grown from a vapour diffusion of this solution with diethyl ether in quantitative yields. Elemental analysis calculated for C₃₂H₃₅BDyF₇N₉O₂P (%): 42.01 C, 3.86 H, 13.78 N; found: 42.27 C, 3.52 H, 14.52 N. FTIR (ATR, microcrystalline): $\hat{\nu}$ = 3683 (w), 3145 (w), 2957 (w), 2876 (w), 2492 (w, ν_{B-H} stretch), 1605 (s), 1570 (w), 1524 (w), 1493 (s), 1457 (w), 1434 (s), 1388 (s), 1362 (s), 1267 (w), 1288 (w), 1246 (w), 1191 (s), 1158 (w), 1141 (w), 1096 (s), 1076 (w), 1051 (s), 1040 (s), 1018 (w), 1005 (w), 969 (w), 961 (w), 883 (w), 834 (s), 798 (w), 772 (s), 728 (s), 713 (w), 685 (s), 635 (w) cm⁻¹.

Synthesis of [Y(Tp^{2-py})F(THF)₂](**PF**₆)·(**MeCN**)_{0.5} (2-THF). Procedure is the same as for 1-THF with large, colourless, block crystals of 2-THF grown from a vapour diffusion of a saturated THF:MeCN (1:1) solution with diethyl ether. NMR: ¹H (d_4 -methanol, 400 MHz, 298 K) δ = 9.30 (d, 3H, ³ J_{HH} = 5.16 Hz, pyH), 7.94 (td, 3H, ³ J_{HH} = 7.69 Hz, ⁴ J_{HH} = 1.70 Hz, pyH), 7.89 (d, 3H, ³ J_{HH} = 2.31 Hz, pzH), 7.84 (dt, 3H, ³ J_{HH} = 7.89 Hz, ⁴ J_{HH} = 0.98 Hz, pyH), 7.48 (ddd, 3H, ³ J_{HH} = 7.49 Hz, ³ J_{HH} = 5.30 Hz, ⁴ J_{HH} = 1.25 Hz, pyH), 6.75 (d, 3H, ³ J_{HH} = 2.32 Hz, pzH), 3.72 (m, 8H, THF), 2.02 (s, 1.5H, MeCN), 1.86 (m, 8H,

THF) ppm; ¹¹B (128 MHz) δ = -3.49 (br, $\nu_{1/2}$ = 260 Hz, borate) ppm; ¹⁹F (377 MHz) δ = -38.35 (*d*, 1F, ¹J_{FY} = 69.4 Hz, Y-F), -74.92 (*d*, 6F, ¹J_{FP} = 707 Hz, PF₆) ppm; ³¹P (162 MHz) δ = -144.59 (*sept*, ¹J_{PF} = 707 Hz, PF₆) ppm. Elemental analysis calculated for C₃₃H_{36.5}BYF₇N_{9.5}O₂P (%): 45.99 C, 4.27 H, 15.44 N; found: 44.62 C, 3.76 H, 15.39 N. FTIR (ATR, microcrystalline): $\hat{\nu}$ = 3682 (w), 3146 (w), 2958 (w), 2877 (w), 2493 (w, ν_{B-H} stretch), 1605 (s), 1570 (w), 1523 (w), 1494 (s), 1457 (w), 1434 (s), 1388 (s), 1362 (s), 1267 (w), 1289 (w), 1246 (w), 1191 (s), 1158 (w), 1142 (w), 1096 (s), 1075 (w), 1051 (s), 1039 (s), 1018 (w), 1005 (w), 969 (w), 961 (w), 881 (w), 835 (s), 798 (w), 772 (s), 731 (s), 713 (w), 685 (s), 634 (w) cm⁻¹.

2. Single Crystal X-ray Diffraction Collection, Refinement Details and Data

Single crystal X-ray diffraction data for **1-THF** and **2-THF** were collected on or a Brucker D8 QUEST diffractometer at 100 K, fitted with a CCD area detector employing a mirrormonochromatic MoK_{α} radiation source (λ = 0.71073 Å). Integration and scaling data of collections were analysed using either APEX3 (1-THF) or APEX4 (2-THF) software. All data was collected with exposures times of 5 seconds with 0.8° frame sweeps on ω and ϕ scans. Multiscan absorptions corrections were used for both compounds. Data was solved in the respective APEX software by intrinsic phasing methods using SHELXL.⁴ Refinement of crystal data was carried out using least-square refinement methods employed by SHELXT,⁵ with all non-hydrogen atoms having anisotropic displacement parameters. Hydrogen atoms were fixed using the riding model besides that of borohydride hydrogen atoms (on the scorpionate ligands) which were placed based on residual electron density with bond distance and angles allowed to refine until convergence. Olex2-1.3⁶ was employed for refining data and molecular graphics using postscript image exports. The following disorder was observed; Only one THF molecule in 2-THF was disordered with the central carbon atom of the lattice solvent of MeCN lying on the mirror plane of the monoclinic space group. All supplementary crystal data sets can be found on the Cambridge Crystal Data Centre under the codes CCDC 2325964 and 2325965.

	1-THF	2-THF
Systematic Name	[Dy(Tp ^{2-PY})F(THF) ₂](PF ₆)	[Y(Tp ^{2-PY})F(THF) ₂](PF ₆)·(MeCN) _{0.5}
Formula	$C_{32}H_{35}BF_7N_9O_2PDy$	C ₃₃ H _{36.5} BF ₇ N _{9.5} O ₂ PY
MW/ g mol⁻¹	914.97	861.90
Crystal syst	monoclinic	monoclinic
Space Group	C2/c	C2/c
<i>a</i> /Å	31.5818(13)	31.635(2)
<i>b</i> /Å	12.2694(5)	12.2783(7)
<i>c</i> /Å	22.8942(9)	22.9447(14)
α /°	90	90
β/°	125.2830(10)	125.349(2)
γ / °	90	90
V/Å ³	7241.7(5)	7269.1(2)
Ζ	8	8
ho /g cm ⁻³	1.678	1.575
F(000)	3640	3512
μ /mm ⁻¹	2.188	1.731
Reflections Collected	92218	113873
R_{int} (R_{σ})	0.0506(0.0237)	0.0638(0.0322)
Data/Restraints/Parameters	8994/0/481	10604/2/510
	$R_1 = 0.0354$	$R_1 = 0.0360$
R indexes $(I \ge 2\sigma(I))$	wR ₂ = 0.0742	$wR_2 = 0.0838$
	$R_1 = 0.0459$	$R_1 = 0.0464$
R Indexes (all data)	$wR_2 = 0.0827$	$wR_2 = 0.0879$
Diff. peak/hole / <i>e</i> Å ⁻³	1.79/-1.43	0.68/-0.74
Goodness-of-fit on F ²	1.112	1.111

Table S1. Crystallographic data for compounds 1-THF and 2-THF.



Figure S1. Solid state structure of **1-THF**, shown with 50% ellipsoids. Dysprosium(III) = turquoise, phosphorus = purple, fluorine = light green, oxygen = red, nitrogen = blue, carbon = grey, boron = orange, hydrogen atoms have been omitted for clarity.



Figure S2. Solid state structure of **2-THF**, shown with 50% ellipsoids. Yttrium(III) = dark blue, phosphorus = purple, fluorine = light green, oxygen = red, nitrogen = blue, carbon = grey, boron = orange, hydrogen atoms and lattice solvent of MeCN have been omitted for clarity.

3. Spectroscopic Analysis



Figure S3. ATR-FTIR for compounds **1-THF** and **2-THF** collected as microcrystalline powders. The transmittance of **2-THF** has been offset by 10 units.



Figure S4. ¹H NMR spectrum of **2-THF** in d_4 -methanol. Deuterated solvent peaks (Δ) and residual diethyl ether (σ) peaks have been annotated.



Figure S5. ¹¹B NMR spectrum of **2-THF** in d_4 -methanol.



Figure S6. ¹⁹F NMR spectrum of **2-THF** in d_4 -methanol.



Figure S7. ³¹P NMR spectrum of **2-THF** in d_4 -methanol.

4. Static and Dynamic Magnetometry Studies

Magnetic measurements were carried out using a Quantum design PPMS (10-10,000 Hz) magnetometer and Quantum design SQUID MPMS (0.1 – 1000 Hz). Crystalline samples of approximate mass of 20 mg were crushed into a microcrystalline state and placed into a gelatine capsule before being loaded with eicosane of mass ~20 mg. Capsules were then heated with a low powered heat gun to melt the eicosane to prevent sample moving. Capsules were then mounted in a drinking straw by wedging the capsule with a small piece of the drinking straw then mounted on the end of the sample rod. Static DC measurements were collected solely on the MPMS using the VSM module. AC magnetic data was collected with ACMS module fitted with an oscillating magnetic field of H_{ac} = 5 Oe for all data collected. In phase (χ') an out-of-phase (χ'') magnetic susceptibility were initially collected in zero applied fields (H_{dc} = 0 Oe) between 2-60 K on the PPMS. Once temperature dependence was determined, zero-applied field χ' and χ'' were measured between 0.1-10,000 Hz, where the χ'' was fitted to the generalised Debye model using the below equation (equation S1), where χ_T is the isothermal susceptibility, χ_S adiabatic susceptibility, ω is the angular frequency of the oscillating field, τ is the magnetic relaxation times and α is the distribution parameter.

$$\chi''(\omega) = (\chi_T - \chi_S) \frac{\cos(\pi \alpha/2)(\omega \tau)^{1-\alpha}}{1+2\sin(\pi \alpha/2)(\omega \tau)^{1-\alpha} + (\omega \tau)^{2-2\alpha}}$$
(S1)



Figure S8. Temperature dependency of $\chi_m T$ with an applied magnetic field of H_{dc} = 1000 Oe for **1-THF**. Solid points are experimental data and dashed line is *ab initio* data.



Figure S9. Zero field cooled (ZFC) and field cooled (FC) magnetic susceptibility for 1-THF employing an applied magnetic field of H_{dc} = 1000 Oe. Peak in the ZFC indicates a magnetic blocking temperature of T_{B} = 4.5 K.



Figure S10. Magnetisation curves for **1-THF** at T = 2, 4 and 6 K. Solid points are experimental data and dashed line is *ab initio* data.



Figure S11. Initial zero applied magnetic field In-phase (χ' , Top) and out-of-phase (χ'' , bottom) magnetic susceptibilities for **1-THF** employing an oscillating field of H_{ac} = 5 Oe between frequencies of ν = 50-1500 Hz. Peaks in the χ'' (bottom insert) are seen at 48 K when the oscillating frequency is 1500 Hz.



Figure S12. Refined zero applied magnetic field χ' (top, insert depicts zoomed in region between 10 and 10,000 Hz) and χ'' (bottom) between 2 K (blue) and 56 K (red) collected at 2 K increments between 0.1 and 10,000 Hz for **1-THF**. Solid lines are guides for the eye and dashed lines are fits to the generalised Debye equations (equations S1).

Т/К	α	τ/s	$\chi_{\rm s}$ /cm ³ mol ⁻¹	χ_T /cm ³ mol ⁻¹	R ²
2	0.278447	0.150835	0.390855	5.598872	0.988593
4	0.258549	0.118045	0.758140	3.364757	0.989196
6	0.244619	0.098608	0.422033	2.158095	0.989236
8	0.231987	0.085138	1.437240	2.738235	0.990033
10	0.211507	0.072847	1.180029	2.215286	0.989749
12	0.155886	0.079794	1.671106	2.412844	0.989920
14	0.140548	0.062643	1.450014	2.081126	0.992410
16	0.118807	0.048453	1.635684	2.183871	0.993345
18	0.108133	0.036443	1.716499	2.198077	0.996431
20	0.092219	0.027490	1.657884	2.088539	0.997519
22	0.084238	0.020525	1.799192	2.187641	0.998165
24	0.075407	0.015309	1.829169	2.18439	0.998284
26	0.069321	0.01151	2.332643	2.660619	0.998582
28	0.049808	0.00845	1.783671	2.082735	0.998114
30	0.055394	0.006465	2.239528	2.521249	0.998442
32	0.044972	0.004826	2.019375	2.28040	0.997921
34	0.058758	0.003703	1.880886	2.129993	0.99819
36	0.045530	0.002738	1.885218	2.116352	0.99639
38	0.045444	0.001938	2.088161	2.307237	0.999298
40	0.038064	0.001243	1.892323	2.102746	0.997476
42	0.035589	0.000746	0.793590	0.993519	0.998262
44	0.030569	0.000408	1.908015	2.099562	0.998392
46	0.024209	0.000206	1.934048	2.116028	0.997252
48	0.029891	0.000102	1.912086	2.087787	0.998338
50	0.021625	5.10E-05	1.916206	2.083742	0.999375
52	0.020850	2.62E-05	1.91923	2.079913	0.999148
54	0.005559	1.44E-05	0.924822	1.075178	0.997059
56	0.013313	7.87E-06	0.302336	0.447664	0.997569

Table S2. Fitted parameters to the generalised Debye equation for **1-THF** extracted from χ'' between 2 K and 56 K with residual sum of squares values (R^2) per fit.

5. Ab initio Methods and Results

Complete-active space self-consistent field spin–orbit (CASSCF-SO) calculations were investigated using single-crystal X-ray diffraction (**1-THF**), performed using OpenMolcas⁷ on the Spartan computational platform. Calculations were performed using the atomic coordinates as determined from single crystal XRD data with relativistic corrected ANO-RCC basis sets of triple- ζ plus polarization for dysprosium ions, double- ζ plus polarization (DZP) for coordinating atoms, and double- ζ (DZ) for all remaining atoms. The active space in **1-THF** was the seven 4f orbitals including 9 electrons for Dy(III). State-averaging at the CASSCF level was performed for 21 sextets, 224 quartets, and 490 doublets for Dy(III). The restricted active space state interaction with the spin–orbit (RASSI-SO) method for Dy(III) was restricted to 21 sextets, 128 quartets, and 130 doublets.

Energy /cm ⁻¹	g ×	gγ	g z	angle /°	Wavefunction composition	<j<sub>z></j<sub>
0	0.0006	0.0007	19.80	-	99% ±15/2>	7.47
284	0.029	0.033	16.99	3.53	98% ±13/2>	6.45
450	0.115	0.151	14.45	10.53	93% ±11/2>	5.41
538	1.72	2.23	11.16	17.90	$74\% \pm 9/2> +9\% \pm 7/2> +6\% \pm 3/2>$	4.06
581	4.14	5.99	9.84	62.33	$55\% \pm 7/2 > + 18\% \pm 1/2 > + 9\% \pm 9/2 > +9\% \mp 5/2 >$	2.35
639	0.45	3.22	13.19	81.60	$51\% \pm 5/2 > +10\% \pm 3/2 > +$ $9\% \pm 1/2 > +9\% \pm 7/2 > +$ $7\% \mp 7/2 > +5\% \mp 3/2 > +$ $5\% \mp 5/2 >$	1.36
686	1.10	3.44	13.58	82.27	$54\% \pm 3/2 > + 11\% \mp 1/2 > + 10\% \pm 5/2 > + 8\% \mp 5/2 > + 6\% \pm 7/2 > $	1.08
743	0.50	1.31	17.88	84.92	$\begin{array}{l} 36\% \pm 1/2 > + 19\% \mp 1/2 > + \\ 10\% \pm 7/2 > + 10\% \mp 3/2 > + \\ 8\% \pm 3/2 > + 8\% \pm 5/2 > \end{array}$	0.63

Table S3. Electronic structure of **1-THF**, where calculations are performed on the cation from **1-THF** only. Wavefunction compositions under 5% are not shown.



Figure S13. Direction of g_z vector (easy axis) in the ground state in **1-THF**.

		1 TUE		
	2.460	1-105		
Dy	2.460			
N _{pz}	-0.348	-0.356	-0.352	
N _{py}	-0.335	-0.338	-0.330	
0	-0.524	-0.526		
F	-0.901			

Table S4. LoProp Chargers for metal centre and coordinating atoms (N_{pz} , N_{py} , O, F) in 1-THF.

Energy /cm ⁻¹	g _x	gγ	g z	angle /°	Wavefunction composition	<j<sub>z></j<sub>
0	0.0007	0.0009	19.80		99% ±15/2>	7.47
291	0.033	0.038	16.98	3.44	98% ±13/2>	6.45
459	0.123	0.172	14.45	10.26	94% ±11/2>	5.41
548	1.73	2.24	11.09	15.92	$75\% \pm 9/2 > +9\% \pm 7/2 > + 6\% \pm 3/2 >$	4.07
591	4.46	6.12	9.76	65.02	$56\% \pm 7/2> + 17\% \pm 1/2> + 10\% \mp 5/2> + 8\% \pm 9/2>$	2.29
649	0.47	2.96	13.91	83.05	$52\% \pm 5/2 > +10\% \pm 1/2 > + 8\% \pm 3/2 > +8\% \mp 7/2 > + 7\% \pm 7/2 > +6\% \mp 3/2 > + $	1.23
697	1.01	3.01	14.19	82.83	$54\% \pm 3/2> + 12\% \mp 1/2> + 9\% \pm 5/2> + 8\% \mp 5/2> + 6\% \pm 7/2>$	1.02
756	0.47	1.24	18.04	83.76	$\begin{array}{l} 35\% \pm 1/2 > + \ 19\% \mp 1/2 > + \\ 10\% \pm 3/2 > + \ 10\% \pm 7/2 > + \\ 9\% \pm 5/2 > + 8\% \mp 3/2 > \end{array}$	0.76

Table S5. Electronic structure of **1-THF**, where calculations are performed on the asymmetric unit, *i.e.* one ion pair, from **1-THF**. Wavefunction compositions under 5% are not shown.



Figure S14. Direction of g_z vector (easy axis) in the ground state in **1-THF** from ion-pair calculations.



Figure S15. *Ab initio* calculated relaxation pathway for **1-THF** calculated using ion-pair. The opacity of the red arrows indicates the transition probability.

		1-THF		
Dy	2.459			
N _{pz}	-0.355	-0.346	-0.358	
N _{py}	-0.324	-0.338	-0.338	
0	-0.520	-0.521		
F	-0.897			

Table S6. LoProp Chargers for metal centre and coordinating atoms (N_{pz} , N_{py} , O, F) in **1-THF**, from ion-pair calculations.

6. Alternate Raman Modelling

As shown from recent theoretical studies, the Raman relaxation exhibits a power law dependence due to the summation over several pairs of phonons, see equation 5 in the work of Sessoli & Lunghi *et al.*⁸ As an approximation, a single exponential energy barrier can be applied to predict the phonon of major contribution to the Raman regime as demonstrated in equation S2 below:

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{U_{eff}}{k_B T}\right) + \tau_{Raman}^{-1} \exp\left(-\frac{E_{Raman}}{k_B T}\right) + \tau_{QTM}^{-1}$$
(S2)

Where τ_{Raman} is the pre-exponential factor for the two-phonon Raman process and E_{Raman} is the energy of the phonon of major contribution to the Raman relaxation. When fitting the relaxation data in this way, an E_{Raman} barrier of 83 cm⁻¹ is determined, indicating a phonon of 83 cm⁻¹ as the major contribution to the Raman regime.



Figure S16. Relaxation time data fitted using equation S2 to extract the energy of the phonon of major contribution to the Raman regime.

Table S7.	Fitting	parameters	for	equation	S2
Table 57.	TILLING	parameters	101	cquation	52

τ_0	2.6(9) x 10 ⁻¹³ s
U _{eff}	661(8) cm ⁻¹
τ_{Raman}	1.0(3) x 10 ⁻⁴ s
E _{Raman}	83(6) cm ⁻¹
τ _{QTM}	0.100(8) s

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