# Supporting Informations

# Evidencing under-barrier magnetic relaxation in a Yb(III) SMM: a joint luminescence/polarised neutron diffraction/SQUID study

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## S1 Experimental details

#### S1.1 Materials and methods

All reagents were purchased from commercial sources and used without any further purification.

#### S1.2 Synthesis

234 mg of Yb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.5 mmol) were dissolved in 10 mL of methanol and added dropwise to a stirred solution of 252 mg of KTp (1 mmol) in 10 mL of methanol. A precipitate appeared by the end of the addition. The resulting suspension was stirred at room temperature for 5 to 10 minutes and then evaporated to dryness under reduced pressure. The resulting solid was extracted with  $3\times10$  mL of dichloromethane. The solution was then layered with heptane (approximatively 3 mL) and left to evaporate slowly at room temperature. Single crystals are obtained within 5 to 10 days. ESI mass spectrum in CH<sub>2</sub>Cl<sub>2</sub> revealed a unique peak in the positive (+m/z) region, at +600.1 u, consistent with a [YbTp<sub>2</sub>]<sup>+</sup> ion.

All subsequent measurements on powder were performed on ground single crystals.

#### S1.3 X-Ray diffraction

Single crystal X-ray diffraction experiments were performed on a 4-circles XCalibur apparatus (Oxford Diffraction), at room temperature, under a Mo K $\alpha$  radiation (0.7107 Å). Data reduction and absorption corrections were computed using CrysAlis. Structure solution was achieved by use of the charge flipping method implemented in Superflip (in the Crystals suite). H atoms were obtained by difference Fourier density mapping. All atoms but H were refined anisotropically by least squares on F using Crystals.

Powder X-Ray diffraction (pXRD) diagram was measured at room temperature on a PANalytical diffractometer (Cu K $\alpha$ ,  $\lambda = 1.5406$ Å) with a unidimensional CCD detector, over the range 2-50° with a step of 0.017°/s. The uniqueness of the crystalline phase was confirmed by comparisons between the experimental and calculated patterns (using pXRD simulator from the Mercury software and the single crystal XRD structure). A slight preferential orientation is observed, as could be inferred from the shape of the crystals (platelets).

#### S1.4 Polarised Neutron Diffraction

Polarised Neutron Diffraction (PND) experiments were performed on the 2-axes diffractometers 5c1 (0.84 Å) and 6T2 (1.40 Å) at the LLB-Orphée neutron facility. The diffracted intensities were measured on a 2-dimensional <sup>3</sup>He detector, for an incident neutron beam with vertical polarisation, with alternate up and down direction. A single crystal of **1** was wrapped in an Al foil, mounted in an Al vial and fixed using glass wool. Collections were performed applying the static (vertical) magnetic field roughly parallel to each crystallographic axis. More precise orientations were deduced by neutron diffraction experiments while cooling down the sample from room temperature to 2 K. The magnitude of the magnetic field to be applied for each direction was deduced from the single-crystal SQUID measurements with the following two constraints:

- the magnetisation must be linear with the field;
- it must also be the highest possible in this field range.

The precise magnitudes and relative orientation of the field are gathered in Table S1 in E.S.I.

For each collection, a first correction was applied in order to remove the contributions from the Al sample holder (strong relative intensities). The remaining peaks were then used for the data treatment. First, a precise indexation was performed. Then, equivalent reflections were merged. Flipping ratios  $\mathscr{R}$  were thus computed, and were selected only those with  $|1 - \mathscr{R}| > 2\sigma$ . Then, the susceptibility tensor  $\overline{\chi}$  was refined stepwise (all the components being refined since the Yb(III) ions are not located in special positions). In this approach, the diagonal components of the tensor were computed for each separated collection. Then,

doublets of collections were treated simultaneously, in order to access the off-diagonal terms in the end of a self-consistent convergence procedure. Then, all the collections were treated together, which permitted to compute the whole susceptibility tensor in an orthornormal  $(\vec{i}, \vec{j}, \vec{k})$  frame, related to the monoclinic crystallographic frame by:  $\vec{i} \parallel \vec{a}^*, \vec{j} \parallel \vec{b}, \vec{k} \parallel \vec{c}$ . Diagonalisation of this tensor afforded the eigenvalues and eigenvectors (magnetic principal axes), gathered in Table S3.

Finally, the error bars on the eigenvalues were computed using a home-made program based on a discretisation algorithm (see paragraph S4.2 in ESI for more information).

#### S1.5 Angular-resolved SQUID magnetometry

Single crystal SQUID measurements were performed on a Quantum Design MPMS-XL5 SQUID magnetometer, equipped with a rotating sample holder. Single crystals of **1** were glued on this sample holder prior to the measurements, setting the  $\vec{b}$  or  $\vec{c}$  axis vertical as a starting point. Absolute orientation of the crystals were determined by prior X-Ray diffraction, through faces indexation.

#### S1.6 Luminescence measurements

The luminescence spectra were measured using a Horiba-Jobin Yvon Fluorolog-3 spectrofluorimeter, equipped with a three slit double grating excitation and emission monochromator with dispersions of 2.1 nm/mm (1200 grooves/mm). The steady-state luminescence was excited by unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90°. Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating). Near infra-red spectra were recorded using a liquid nitrogen cooled, solid indium/gallium/arsenic detector (850-1600 nm) and a RG830 filter to cut any visible emission. For low temperature measurements, the quartz tube containing the sample was sealed and set into an Oxford Instrument helium-cooled cryostat (Optistat CF2) insert directly in the sample chamber of the spectrofluorimeter.

For luminescence lifetimes, the sample was excited using a pulsed Nd:YAG laser (SpectraPhysics), operating at 10 Hz. Light emitted at right angles to the excitation beam was focused onto the slits of a monochromator (PTI120), which was used to select the appropriate wavelength. The growth and decay of the luminescence at selected wavelengths was detected using a Ge photodiode (Edinburgh Instruments, EI-P) and recorded using a digital oscilloscope (Tektronix TDS320) before being transferred for analysis. Luminescence lifetimes were obtained by iterative reconvolution of the detector response (obtained by using a scatterer) with exponential components for growth and decay of the metal-centred luminescence.

#### S1.7 Computational details

Ab initio calculations were carried out using the SA-CASSCF/MS-CASPT2/RASSI-SO approach, as implemented in the MOLCAS 8.0 quantum chemistry suite.<sup>1</sup> The relativistic effects are treated in two steps, based on the Douglas-Kroll-Hess Hamiltonian. First, the scalar terms are used to determine the spin-free wave functions and energies, in the State Averaged Complete Active Space Self Consistent Field (SA-CASSCF) method.<sup>2</sup> 7 roots are considered at this level (13 4*f* electrons spanning the 7 4*f* orbitals). Prior to the incorporation of spin-orbit coupling, the effects of dynamic correlation are treated by the means of multistate CASPT2 (MS-CASPT2) calculations on top of the spin-free wavefunctions.<sup>3,4</sup> The core orbitals are kept frozen in this calculation in order to alleviate the computational effort. Then, spin-orbit coupling is added within the Restricted Active Space State Interaction (RASSI-SO) method, which uses the spin-free wavefunctions as basis states.<sup>5,6</sup> Finally, the magnetic properties, Transition Dipole Moment (TDM) and Landé tensors for the lowest 4 Kramers doublets are calculated using the SINGLE ANISO<sup>7</sup> routine.

The calculations were performed on the room temperature X-ray structure. All atoms were represented by ANO-type basis sets from the ANO-RCC library.<sup>8,9</sup> The following contractions were used: [8s7p4d3f2g1h] for Yb, [4s3p2d] for the coordinating atoms (N, O), [3s2p1d] for the non-coordinating C, N, B and O atoms, and [2s] for all the H atoms.

# S2 X-Ray diffraction

## S2.1 Single crystal XRD details

Table S1: Cell and refinement parameters for the single crystal X-Ray study of **1**.  $N_{IR}/N_{RR}$ : number of independent reflections/number of refined reflections.

Formula	$C_{18}H_{20}B_2Yb_1N_{13}O_3$
FW (g/mol)	661.10
a (Å	15.7662(4)
b (Å)	9.1066(2)
c (Å)	17.4455(5)
α, γ (°)	90
β (°)	104.876(3)
V (Å <sup>3</sup> )	2420.8(2)
Z	4
Space group	$P2_{1}/c$
$\mu ({ m cm}^{-1})$	3.914
F <sub>000</sub>	1292
N <sub>IR</sub> /N <sub>RR</sub>	5924/5046
R (F, I> $3\sigma(I)$ )	2.21%
$R_w$ (F, I>3 $\sigma$ (I))	2.57%
GooF	1.0746
CCDC num.	1450925

### S2.2 Powder XRD



Figure S1: Experimental (black) and calculated (red) powder X-Ray diffraction patterns for complex 1 at room temperature, under a Cu K $\alpha$  radiation (1.5406Å).

## S2.3 Crystal packing



Figure S2: Crystal packing of **1** in the unit cell, viewed along the  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  axes. Colour scheme: Yb, green; N, lavender; O, red; C, grey; B, pink; H, white.  $\vec{a}$  axis is depicted in red,  $\vec{b}$  in green and  $\vec{c}$  in blue.

#### S2.4 Shape analysis

\_\_\_\_\_ SHAPE v2.1 Continuous Shape Measures calculation (c) 2013 Electronic Structure Group, Universitat de Barcelona Contact: llunell@ub.edu \_\_\_\_\_ Yb1 OP-8 1 D8h Octagon 2 C7v Heptagonal pyramid 3 D6h Hexagonal bipyramid HPY-8 HBPY-8 CU-8 4 Oh Cube 4 On Cube
5 D4d Square antiprism
6 D2d Triangular dodecahedron
7 D2d Johnson gyrobifastigium J26
8 D3h Johnson elongated triangular bipyramid J14
9 C2v Biaugmented trigonal prism J50
10 C2v Biaugmented trigonal prism
11 D2d Snub diphenoid J84
12 Td Triakis tetrahedron
12 D2h Elemented trigonal bipyramid SAPR-8 TDD-8 JGBF-8 JETBPY-8 JBTPR-8 BTPR-8 JSD-8 TT-8 13 D3h Elongated trigonal bipyramid ETBPY-8 Structure [ML8 ] OP-8 [ML8] OP-8 HPY-8 HBPY-8 CU-8 , 27.164, 22.744, 12.441, 9.885, CU-8 SAPR-8 Yb1 1.955, JGBF-8 JETBPY-8 JBTPR-8 BTPR-8 JSD-8 TT-8 4.001, 10.570, TDD-8 2.595, 12.414, 28.707, 2.251, 1.516,

ETBPY-8 23.574

# S3 Luminescence decay at room temperature



Figure S3: Luminescence decay of 1, measured after an irradiation at 300 nm. The red solid line is the best monoexponential fit with  $\tau = 10.4 \ \mu s$ .

## S4 Single crystal magnetisation at 2K



Figure S4: Magnetic moment as a function of field and orientation, for a single crystal of **1** rotating along the  $\vec{b}$  axis (left), with  $\vec{c^*}$  initially making a -20° angle with  $\vec{H}$ , and rotating along the  $\vec{c^*}$  axis (right), with  $\vec{b}$  initially making a -10° angle with  $\vec{H}$ . H ranges from 0 T (red) to 2 T (pink)

From these measurements,  $\vec{a}$  appears to be the easy axis of magnetisation (2.38  $\mu_B$  at 2 T), while  $\vec{b}$  and  $\vec{c}^*$  appear to be hard axes (respectively, 0.40  $\mu_B$  and 0.68  $\mu_B$  at 2 T).

## S5 Polarised neutron diffraction

#### **S5.1** Refinement details

Note: all the refinements were performed using the routines from the Cambridge Crystallographic Subroutines Library.

The precise magnitudes and relative orientation of the field are gathered in Table S2. The components of the field are given in an orthonormal basis set  $(\vec{i}, \vec{j}, \vec{k})$  related to the monoclinic crystallographic basis set by:  $\vec{i} \parallel \vec{a}^*, \vec{j} \parallel \vec{b}, \vec{k} \parallel \vec{c}$ .

Table S2: Field magnitude, orientations and number of relevant reflections used in the PND experiments.

λ (Å)	Field magnitude (T)	Field orientation in the lattice	Type of axis	No. of equiv. reflns. ( $ 1 - \Re  > 2\sigma$ )
0.84	0.67	(-0.973 ; -0.009 ; 0.232) ( 0.051 : 0.002 : 0.116)	easy	29
1.40	1.50	(0.095; 0.074; 0.993)	mean	43

The deduced susceptibility tensor in the  $(\vec{i}, \vec{j}, \vec{k})$  frame is

$$\bar{\bar{\chi}} = \begin{pmatrix} 1.97(10) & -0.91(5) & -0.33(6) \\ & 0.43(1) & 0.14(3) \\ & & 0.36(2) \end{pmatrix}$$

Diagonalisation of this tensor affords the eigenvalues and eigenvectors (magnetic principal axes), gathered in table Table S3.

Table S3: Eigenvalues (in  $\mu_B/T$ ) and components of the corresponding eigenvectors of the local susceptibility tensor in the orthonormal  $(\vec{i}, \vec{j}, \vec{k})$  basis.

Magnetic axes	Eigenvalues ( $\mu_B/T$ )	Component along $\vec{i}$	Component along $\vec{j}$	Component along $\vec{k}$
1	2.454(1)	0.895	-0.414	-0.166
2	0.2992(2)	-0.133	0.107	-0.985
3	0.007(2)	0.425	0.904	0.040



Figure S5: Susceptibility tensor of 1 deduced from the PND experiments, represented as an ellipsoid on the Yb atoms in the lattice, viewed along the  $\vec{b}$  (left) and  $\vec{c}$  axes. For the sake of simplicity, only the coordinating atoms are represented.

#### S5.2 Error bars calculation

In order to evaluate the error on the diagonal components of  $\bar{\chi}$ , starting from the susceptibility tensor we deduced from the PND analysis, we developed a Fortran 90 program. The program uses a discretisation algorithm: for each component  $\chi_{uv} \pm \delta_{uv}$  of the non-diagonalised tensor, user defines a number of equally separated values comprised between  $\chi_{uv} - \delta_{uv}$  and  $\chi_{uv} + \delta_{uv}$ . For each of these values, the obtained matrix is diagonalised – note that a symmetry constraint on the tensor is imposed in the procedure, to ensure the matrix indeed remains diagonalisable –. This procedure is thus performed independently for all 6 components of the tensor, yielding a total number of diagonalisations of  $N^6$  (if N is the user-defined number of test values).

At the end of the procedure, the standard deviation of the eigenvalues is calculated and used as an error bar.

## S6 Comparison of the SQUID, ab initio and PND data



Figure S6: Comparison between the PND susceptibility tensor of **1** (green ellipsoid) and the *ab initio* easy axis (red arrow).



Figure S7: Comparison between the experimental (•) and calculated single-crystal magnetisation curves, from PND (–) and ab initio (–) data, for a rotation around the  $\vec{b}$  axis, with  $\vec{c}$  initially vertical. Curves for the PND and *ab initio* data were computed using our home-made program "CalcM".<sup>10</sup>.

# S7 AC SQUID data



Figure S8: In-phase and out-of-phase magnetic susceptibilities of **1**, under a static field of 0.2 T, for frequences ranging between 1 Hz (brown) to 1400 Hz (gray), between 2 and 6K.

## S8 AC SQUID data analysis



Figure S9: Arrhenius plot v = f(1/T) for the maxima of the out-of-phase component of susceptibility of 1, measured under a static field of 0.2 T. The red line corresponds to the best linear interpolation at lower 1/T values.



Figure S10: v = f(T) (left) and  $\log v = f(\log T)$  plots for the maxima of the out-of-phase component of susceptibility of **1**, measured under a static field of 0.2 T. The orange and green lines correspond to the best fits  $v_1 = 13(2)T + 0.00636(5)T^9$  and  $v_2 = 39(5) + 0.00643(5)T^9$ .

As one can see from figures Figure S11, Figure S12 and Figure S13, no deviations are observed at 1000Hz. Only small changes are seen at 400Hz, at high fields, and become more marked at 100Hz. This is in total compliance with the proposed mechanisms, since only the direct relaxation, acting at a lower T than the Raman one, is field dependent.



Figure S11:  $\chi'' = f(T)$  curves for **1** at 100Hz, as a function of the static field.



Figure S12:  $\chi'' = f(T)$  curves for **1** at 400Hz, as a function of the static field.



Figure S13:  $\chi'' = f(T)$  curves for **1** at 1000Hz, as a function of the static field.

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