Supporting Information
for

Single-Ion Magnet behaviour in [U(Tp^{Me2})_2I]

by

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EXPERIMENTAL

General Preparative Procedures. All manipulations were carried out using vacuum line techniques and a purified nitrogen-filled glove box. THF and n-hexane were pre-dried using 4 Å molecular sieves, freshly distilled from sodium-benzophenone under an atmosphere of N₂ and degassed with freeze pump-thaw cycles. Benzene-d₆ was pre-dried over Na and distilled from sodium-benzophenone under an atmosphere of Ar. "H NMR spectra were recorded at 296 K on a Varian INOVA-300 spectrometer operating at 300 MHz and referenced internally to the residual proton solvent resonances relative to tetramethylsilane (benzene-d₆, δ 7.16 ppm). CHN elemental analyses were performed in-house using an EA110 CE Instruments automatic analyzer.

Synthesis of [U(TpMe₂)₂I] (1). Compound 1 was prepared according to the method previously reported by Takats and coworkers [1] and crystallized by slow evaporation of a THF solution. The crystals were washing with n-hexane and vacuum dried. The formulation and purity of the compound were checked by "H NMR spectroscopy and CHN elemental analysis. Data are in agreement with those previously reported. Found: C, 37.5; H, 5.0; N, 17.7. C₃₀H₄₆B₃I₂N₁₂U requires C, 37.7; H, 4.6; N, 17.5 %. δH (300.1 MHz; C₆D₆; Me₄Si; 296 K): 7.40 (6H, s, 4-H of TpMe₂), 0.27 (18H, s, CH₃ of TpMe₂), -11.66 (18H, s, CH₃ of TpMe₂).

Magnetic measurements. Magnetic measurements were performed in polycrystalline powder samples imbedded in hexane and sealed in a 4 mm inner diameter quartz tube. Measurements of 1 were taken using a 6.5 T S700X SQUID magnetometer (Cryogenic Ltd.) in the temperature range 1.8-300 K under several applied magnetic fields from 100 G to 1 kG. For compound 2, a ³He insert adapted to the SQUID magnetometer was used to measure below 2 K both temperature dependent and field dependent magnetization curves at fixed temperatures. Above 1.8 K field dependent magnetization up to 5 T at different temperatures and AC susceptibility measurements in 1 were taken using a MagLab 2000 system (Oxford Instruments). The paramagnetic data was obtained after a correction for the core diamagnetism estimated, using Pascal’s constants, as χ₉ = -753.6×10⁻⁶ and -811.4×10⁻⁶ emu/mol for 1 and 2 respectively. Temperature dependence of AC magnetic susceptibility was measured using a 5 Oe oscillating field in the 30-10000 Hz frequency range.
range under zero and 500 Oe static fields. Additional isothermal AC susceptibility measurements, $\chi_{AC} = f(\omega)$, were taken in the 10-10000 Hz frequency range, within 1.7 and 6 K, the temperature range in which the relaxation time reaches a maximum. Cole-Cole plots were fitted using a generalized Debye model [2],

$$\chi(\omega) = \chi_S + (\chi_T + \chi_S)/(1+i\omega\tau)^{1-\alpha}$$

which describes both real and imaginary components of AC susceptibility, $\chi'$ and $\chi''$ in terms of frequency, isothermal susceptibility ($\chi_T$), adiabatic susceptibility ($\chi_S$), relaxation time ($\tau$), and a variable representing the distribution of relaxation times ($\alpha$).

Figure S11. Reduced magnetisation plots (M vs. B/T) for 1 (left) and 2 (right).

**Quantum Chemistry Calculations.** The excited states of the complexes have been calculated with the SO-CASPT2 method using the MOLCAS76 suite of programs [3]. A ANO-RCC basis sets of TZP and DZ qualities were used for the Uranium and the other atoms respectively. The active space consists of 3 electrons in the 7 5f orbitals. First, a CASSCF (Complete Active Space Self Consistent Field) calculation was performed [4], then dynamical correlation was included by the CASPT2 (Complete Active Space Perturbation Theory at the 2nd order) method [5] and finally, the spin-orbit coupling was evaluated by a state interaction between the CASPT2 wave functions by the RASSI (Restricted Active Space
State Interaction) method [6]. g factors were calculated according to reference [7]. Expectation values of J are calculated by diagonalizing the matrix of the $\vec{L} + \vec{S}$ operator in the 10 first states (since there is a large energy gap between the 10th and 11th states).

References:


Table S1. Experimental effective energy barriers, $E_{\text{eff}}$, and blocking temperatures, $T_b$, and calculated (CASPT2) energy gaps, $\Delta E$, g-values, angles between the principal magnetic axes of the ground state and the first excited state, $\theta$ and expectation values of J, L, S, for mononuclear U compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{eff}}$/cm$^{-1}$</th>
<th>$T_b$/K</th>
<th>$\Delta E$/cm$^{-1}$</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$g_3$</th>
<th>$\theta$</th>
<th>J</th>
<th>L</th>
<th>S</th>
</tr>
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<tr>
<td>1</td>
<td>21.0</td>
<td>3.5</td>
<td>146</td>
<td>4.9</td>
<td>1.1</td>
<td>0.5</td>
<td>77</td>
<td>4.3</td>
<td>5.4</td>
<td>1.1</td>
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<tr>
<td>2</td>
<td>18.2</td>
<td>4.5</td>
<td>138</td>
<td>3.4</td>
<td>1.3</td>
<td>0.7</td>
<td>65</td>
<td>4.2</td>
<td>5.5</td>
<td>1.3</td>
</tr>
<tr>
<td>[U(H$_2$Bpz$_2$)$_3$]*</td>
<td>8</td>
<td>~3</td>
<td>28</td>
<td>5.1</td>
<td>1.0</td>
<td>0.4</td>
<td>56</td>
<td>4.2</td>
<td>5.4</td>
<td>1.1</td>
</tr>
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