Supporting Information for:

Zero-field slow magnetic relaxation in a uranium(III) complex with a radical ligand

by

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1.	Experimental Details	

General Procedures. All operations were performed in a purified nitrogen glovebox and using vacuum-line techniques. Toluene and THF were pre-dried with 4 Å molecular sieves, refluxed over sodium/benzophenone under an atmosphere of nitrogen, collected by distillation, and degassed through freeze-pump-thaw cycles. Benzene- d_6 was dried over sodium/benzophenone and vacuum distilled. 2,2'-bipyridine was purchased from Merck and sublimed before use. $[U(Tp^{Me2})_2]$ was prepared according to the published procedure.¹ ¹H 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- d_6 , δ 7.16 ppm); NMR tubes with J. Young valves were used to perform the experiments. CHN elemental analyses were carried out inhouse using a CE Instruments EA1110 automatic analyzer.

Synthesis of $[U(Tp^{Me2})_2(bipy)]$ (3). At room temperature, a toluene solution of 2,2'-bipyridine (0.041 g, 0.26 mmol) was added to a toluene solution of $[U(Tp^{Me2})_2]$] (0.251 g, 0.26 mmol), followed by addition of two equivalents of sodium amalgam 0.5% (w/w) (2.392 g, 0.52 mmol of Na). After stirring overnight, the reddish-brown mixture was centrifuged to remove a grey precipitate and the excess of sodium amalgam. The reddish-brown supernatant was evaporated under vacuum leading to a dark brown solid in 76% yield (0.195 g). The solid was dissolved in THF and the resulting solution concentrated to give **3** as a dark brown crystalline solid that was isolated by centrifugation and dried under vacuum. The formulation and purity of compound **3** was confirmed by ¹H NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction analysis.

¹*H NMR* (C₆D₆, 300.1 MHz, 296 K): δ (ppm) 44.19 (2H, bipy), 16.67 (6H, CH₃ of Tp^{Me2}), 12.74 (2H, 4-*H* of Tp^{Me2}), 6.11 (2H, 4-*H* of Tp^{Me2}), -1.54 (6H, CH₃ of Tp^{Me2}), -1.65 (2H, 4-*H* of Tp^{Me2}), -1.70 (6H, CH₃ of Tp^{Me2}), -4.89 (vbr, 2H, B*H* of Tp^{Me2}), -6.28 (6H, CH₃ of Tp^{Me2}), -6.43 (6H, CH₃ of Tp^{Me2}), -14.78 (2H, bipy), -27.00 (6H, CH₃ of Tp^{Me2}), -141.51 (2H, bipy), -268.17 (2H, bipy).

Elemental Analysis for **3**.2THF (C₄₈H₆₈B₂N₁₄O₂U): calcd - C, 50.89; H, 6.05; N, 17.31; found - C, 49.78; H, 6.09; N, 17.16.





2. Single-Crystal X-ray Crystallography

Single crystals of compound **3** were selected and coated with FOMBLIN© protective oil (Aldrich) in a glovebox and rapidly mounted on a loop and placed into the goniometer head of a Bruker APEX II CCD area-detector diffractometer using graphite-monochromated Mo K_a radiation ($\lambda = 0.71069$ Å). X-ray data were collected at 150(2) K. Unit cell parameters were determined using Bruker SMART software and refined using Bruker SAINT on all observed reflections,² and were in agreement with the previously published data.³ The illustration of the molecular structure was prepared with the Mercury 3.1 software using the CIF file available at the Cambridge Structural Database.

3. Magnetic Measurements

To study the magnetic properties of compound **3** different batches were measured as crystalline powder imbedded in oil. Due to their high air sensitivity, the samples were sealed under vacuum inside a quartz tube. Measurements were taken using a 6.5 T S700X SQUID magnetometer (Cryogenic Ltd.) in the temperature range 5 - 300 K at 1 T. A ³He insert was adapted to the SQUID magnetometer to measure below 2 K both temperature dependent and field dependent magnetization curves at fixed temperatures (Figure 4). Above 1.8 K, field dependent magnetization up to 5 T at different temperatures and AC susceptibility measurements were taken using a MagLab 2000 system (Oxford Instruments) (Figure SI2). The paramagnetic data was obtained after the correction for the core diamagnetism estimated using Pascal's constants, giving χ_D = -697.2x10⁻⁶ emu/mol.



Figure SI2 Magnetic field dependence of the magnetization at 10, 5 and 1.8 K for compound **3**.

The temperature dependence of AC magnetic susceptibility was measured using a 5 Oe oscillating field in the 30-10000 Hz frequency range under zero and 500 Oe static fields (Figure 5). Additional isothermal AC susceptibility measurements, $\chi_{AC} = f(\omega)$, were taken in the 10–10000 Hz frequency range, within 1.8 and 6 K, the temperature range in which the relaxation time reaches a maximum. Cole-Cole plots were fitted using a generalized Debye model,⁴ $\chi(\omega) = \chi_S + (\chi_T + \chi_S)/(1 + i\omega\tau)^{1-\alpha}$, which describes both real and imaginary components of AC susceptibility, χ' and χ'' in terms of frequency, isothermal susceptibility (χ_T), adiabatic susceptibility (χ_S), relaxation time (T), and a variable representing the distribution of relaxation times (α) (Figure SI3).



Figure SI3 Cole-Cole plots at several temperatures for complex **3** at 0.05 T. The lines represent the least-squares fit with a generalized Debye model to a distribution of single relaxation modes.

References

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