

# The First Structural and Spectroscopic Study of a Paramagnetic 5f DO3A Complex

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## Supplementary Information:

### Experimental

#### General Methods

Cyclen was purchased from Strem Chemicals, while other reagents, solvents and starting materials were obtained from the Aldrich Chemical Company. All chemicals were used as supplied. Tris ethyl 1,4,7,10-tetraazacyclododecane-1,4,7-triacetate hydrobromide salt<sup>1</sup> and  $\text{UCl}_4$ <sup>2</sup> were prepared according to literature procedures. Uranium stocks was obtained from the Centre for Radiochemistry Research (CRR) isotopes store at The University of Manchester. *Caution! Natural uranium was used during the course of these experiments. As well as the radiological hazards, uranium is a toxic metal and care should be taken with all manipulations. Experiments using uranium materials were carried out using pre-set radiological safety precautions in accordance with the local rules of The University of Manchester.*

All spectroscopic grade solvents used in the preparation and manipulation of the U(IV) complex were dried over molecular sieves and thoroughly degassed before use. DMF was dried by passage over activated alumina columns and thoroughly degassed before use. All manipulations of  $\text{UCl}_4$  were conducted in an argon atmosphere System Two glove box (Innovative Technology) equipped with gas purification system, solvent removal system (carbon inline filter) and  $\text{O}_2$  and  $\text{H}_2\text{O}$  analysers ( $\text{O}_2 < 0.2$  ppm and  $\text{H}_2\text{O} < 0.54$  ppm).

All NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating frequency 400  $\text{MHz}$  ( $^1\text{H}$ ), 101  $\text{MHz}$  ( $^{13}\text{C}$ ), variable temperature unit at 300 K, unless otherwise stated. Chemical shifts are reported in parts per million and referenced to residual proton resonances in  $d_6$ -dmsO,  $d_4$ -MeOH or  $\text{D}_2\text{O}$  and

calibrated externally to TMS.

Mass Spectra were obtained using positive Electrospray in acetonitrile or methanol solutions on a Micromass Platform II spectrometer, or by MALDI using methanol solutions with an ALPHA maxtrix on a Micromass TOF Spec 2E spectrometer.

Elemental analyses were performed using a Carlo ERBA Instruments CHNS-O EA1108 elemental analyzer (C, H, N and S analysis) and a Fisons Horizon Elemental Analysis ICP-OED spectrometer for metals and halogens.

UV-vis absorption spectra were recorded in MeOH on a T60U spectrometer (PG Instruments Ltd.) and UV-vis-nIR spectra were recorded on a double-beam Cary Varian 500 scan UV-vis-nIR spectrophotometer over the range 300–1300 nm using fused silica cells with a path length of 1 cm.

Steady state emission spectra were recorded in Young's tap appended quartz cuvettes on an Edinburgh Instrument FP920 Phosphorescence Lifetime Spectrometer equipped with a 5 watt microsecond pulsed xenon flashlamp (with single 300 mm focal length excitation and emission monochromators in Czerny Turner configuration) and a red sensitive photomultiplier in peltier (air cooled) housing, (Hamamatsu R928P). Lifetime data were recorded following 405 nm excitation with an EPL 405 picosecond pulsed diode laser (Edinburgh Instruments), using time correlated single photon counting (PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fit on the data obtained, and quality of fit judged by minimization of reduced chi-squared and residuals squared. Where the decay profiles are reported as monoexponential, fitting to a double exponential decay yielded no improvement in fit as judged by minimisation of residual squared and reduced chi squared.

X-ray diffraction data for  $[\text{U}(\text{DO3A})(\text{dmsO})_2]\text{Br}$  were collected at 100 K with a Bruker AXS SMART diffractometer using graphite-monochromated Mo-K $\alpha$  radiation. The structure was solved by direct methods using SIR-92<sup>3</sup> running in WIN-GX.<sup>4</sup> The structure was completed by iterative cycles of  $\Delta F$ -syntheses and a full matrix least squares refinement. All non-H atoms were refined anisotropically and difference Fourier syntheses were employed in positioning idealised hydrogen atoms and were allowed to ride on their parent C or N-atoms. All refinements were against  $F^2$  and used SHEL-XL-97.<sup>5</sup> A large amount of highly disordered solvent was present in the unit cell which could not be modeled by parts or by

partial occupancies and no suitable model could be found. *SQUEEZE*<sup>6</sup> was therefore applied to complete the refinement.

## Synthetic Procedures

### Preparation of K<sub>3</sub>DO3A

To a stirred solution of Et<sub>3</sub>DO3A.HBr in DCM (1.5 g, 2.94 mM, 100 mL) at RT was added 1.25 g of 90 % KOTMS (9.77 mM) added in solid in portions. The resultant slurry was stirred at room temperature for 1 week. After this time, the precipitated solid was isolated by filtration, washed with 5 x 10 mL DCM and dried under vacuum suction. The solids were then dissolved in minimal MeOH (20 mL), filtered through a pad of celite and recrystallised by layering with Et<sub>2</sub>O (25 mL). After diffusion was complete (~ 1 week), the precipitated solids were isolated by filtration, washed with 5 x 10 mL Et<sub>2</sub>O and dried under vacuum suction to yield 1.02 g of K<sub>3</sub>DO3A as a white powder (38 % yield). Since the KOTMS reagent is only of 90 % purity, residual KBr salts are associated with the product.

MALDI MS (alpha/CH<sub>3</sub>OH/H<sub>2</sub>O): m/z: 347 (100 %) [M-3K +4H]<sup>+</sup>, 385 (92 %) [M-2K + 3H]<sup>+</sup>, 423 (61 %) [M- K + 2H]<sup>+</sup>, 461 (42 %), [M + H]<sup>+</sup>, 921 (6 %) [2M + H]<sup>+</sup>, 946 (7 %) [2M + Na]<sup>+</sup>.

NMR/D<sub>2</sub>O δ<sub>H</sub>: 3.81 (br, 2H, CH<sub>2</sub> arm), 3.44 (br, 4H, CH<sub>2</sub> arm), 3.37 (br, 4H, CH<sub>2</sub> ring) 3.22 (br, 4H, CH<sub>2</sub> ring) 3.15 (br, 8H, CH<sub>2</sub> ring). δ<sub>C</sub>: 178.98m 162.71 (quaternary C, CO), 57.05, 55.53, 52.35, 49.56, 49.34, 43.61 (CH<sub>2</sub>).

Anal. Calcd. For C<sub>14</sub>H<sub>23</sub>N<sub>4</sub>O<sub>6</sub>K<sub>3</sub>.4.75KBr.3H<sub>2</sub>O: C, 15.57 H, 2.70 N, 5.19 K, 28.06 Br 35.14. Found: C, 15.26 H, 2.40 N, 4.65, K, 28.06 Br, 31.10.

### Preparation of [U(DO3A)]Br

Under argon, in the glove box, 58 mg (0.54 mmol) of K<sub>3</sub>DO3A was dissolved in 4 mL degassed methanol pre-dried over 4Å molecular sieves. This solution was then added dropwise by pipette to a methanol solution of UCl<sub>4</sub> (20 mg, 0.54 mmol). The resultant mint green solution was stirred for 24 hours. After this time, the precipitated salts were allowed to settle and the solution filtered and stored in the glove box. Green needles for a structural analysis were grown by layering a 1:1 v:v DMSO/MeOH

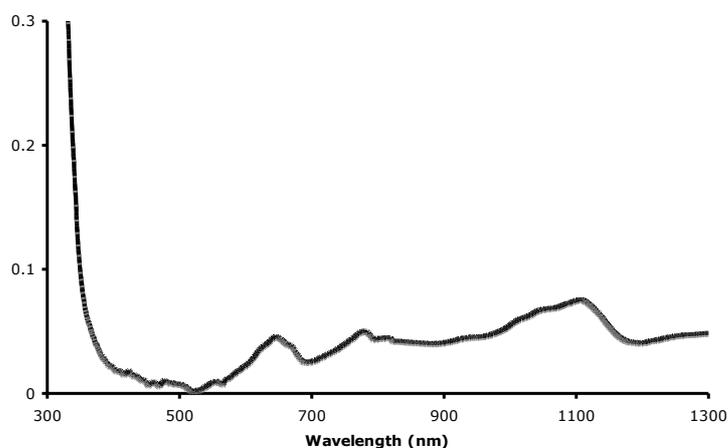
solution of the complex with Et<sub>2</sub>O. These were isolated by filtration, washed with Et<sub>2</sub>O and dried under vacuum suction (15 mg, 42 % yield).

UV-vis-nIR (MeOH)  $\lambda_{\text{max}}$  = 220 nm, 245 nm, 261 nm, 322 nm, 643 nm, 1042 nm, 1103 nm.

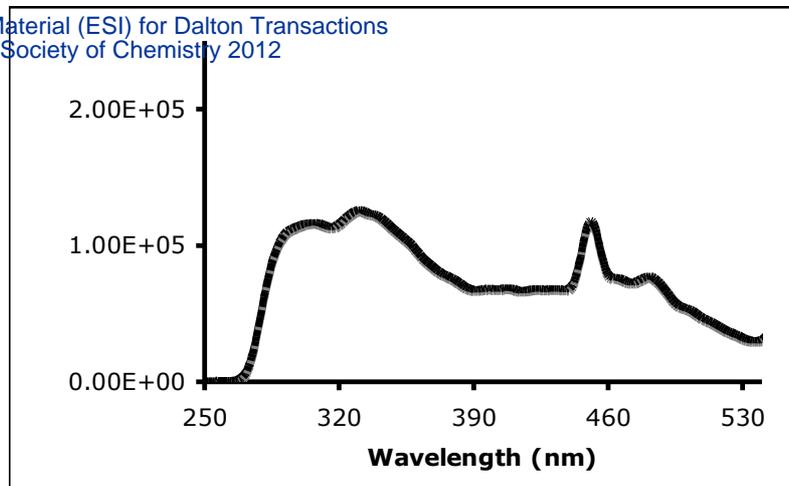
NMR/1:1 v:v *d*<sub>6</sub>-DMSO:*d*<sub>4</sub>-MeOH  $\delta_{\text{H}}$ : 76.73 (br, 2H, CH<sub>2</sub>), 54.85, 52.77, 52.01 (br, overlapping signals, 4H, CH<sub>2</sub>), 30.89 (br, 1H, CH<sub>2</sub>) 18.79, 15.98 (br, overlapping signals, 2H, CH<sub>2</sub>) 8.52, 7.51 (br, overlapping signals, 2H, CH<sub>2</sub>), -8.45, -9.18, -11.55 (br, overlapping signals, 3H, CH<sub>2</sub>), -29.34, -31.40, -32.95, -36.26 (br, overlapping signals, 4H, CH<sub>2</sub>), -45.45 (br, 1H, CH<sub>2</sub>), -50.96 (br, 1H, CH<sub>2</sub>), -64.66 (br, 1H, CH<sub>2</sub>), -69.56 (br, 1H, CH<sub>2</sub>).

Crystal data: *M* = 817.57, monoclinic, *a* = 9.0832(7), *b* = 23.8096(18), *c* = 14.3980(11) Å,  $\beta$  = 99.664(1)° *V* = 3069.6(4) Å<sup>3</sup>, *T* = 100(2) K, *P*2<sub>1</sub>/*n*, *Z* = 4, 5587 unique reflections, *R*<sub>1</sub> (all) = 0.0565, *wR*<sub>2</sub> = 0.1263.

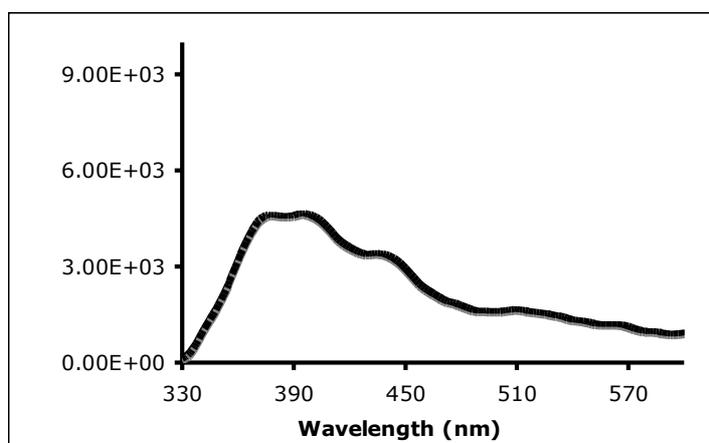
CCDC reference number xxxxx.



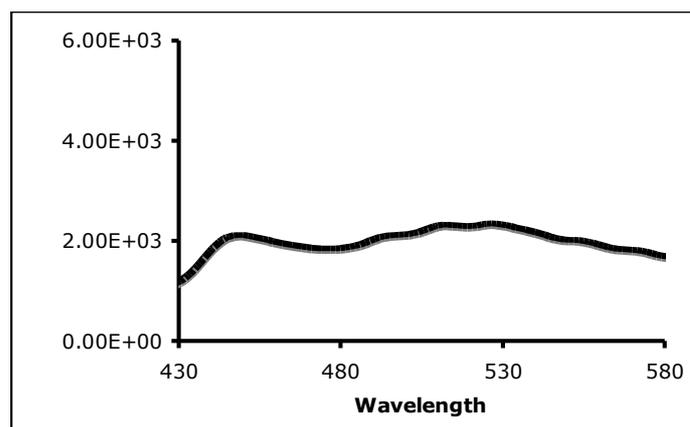
**Figure S1.** UV-vis-nIR absorption spectrum of [U(DO3A)]Br in MeOH at 10<sup>-2</sup> M



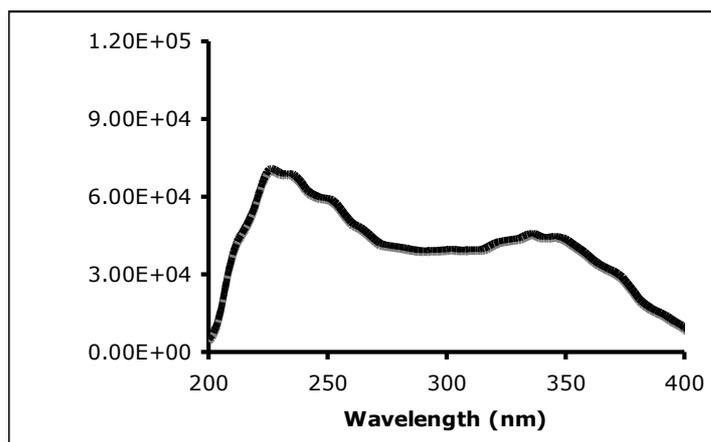
**Figure S2.** Emission spectrum of [U(DO3A)]Br in MeOH following excitation at 250 nm; the peak at ca. 450 nm is due to scattered light at half the frequency of the excitation source



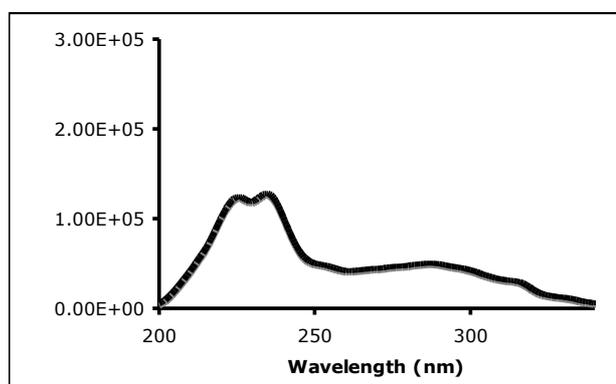
**Figure S3.** Emission spectrum of [U(DO3A)]Br in MeOH following excitation at 310 nm with a 340 nm bandpass filter



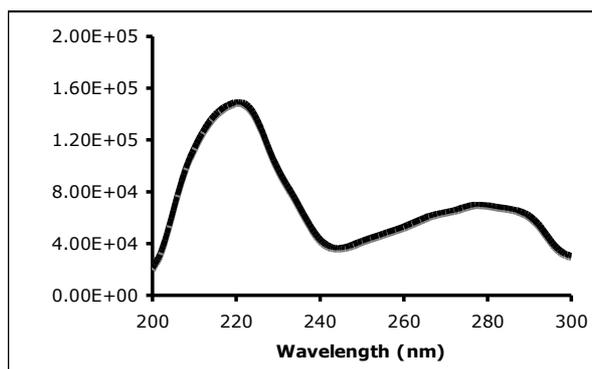
**Figure S4.** Emission spectrum of [U(DO3A)]Br in MeOH following excitation at 405 nm



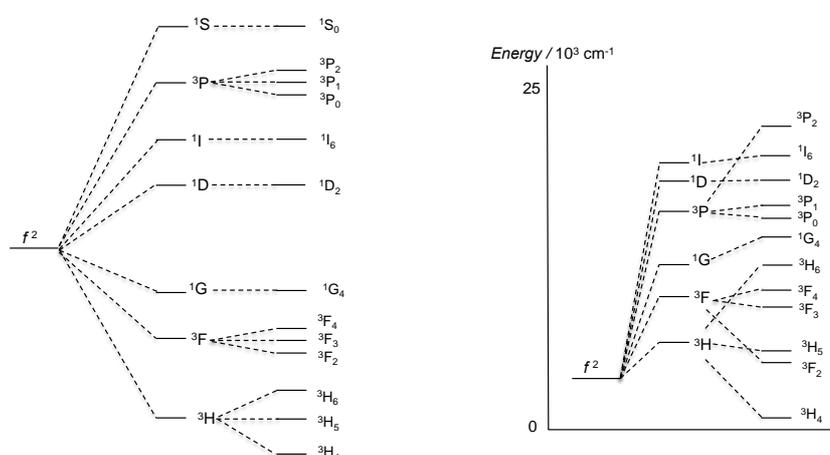
**Figure S5.** Excitation spectrum of [U(DO3A)]Br in MeOH monitoring the 415 nm emission band



**Figure S6.** Excitation spectrum of [U(DO3A)]Br in MeOH monitoring the 350 nm emission band



**Figure S7.** Excitation spectrum of [U(DO3A)]Br in MeOH monitoring the 300 nm emission band



**Figure S8.** Left; energy level diagram for the  $U^{4+}$  (and  $Pr^{3+}$ ) ion, showing the successive effects of electrostatic repulsion and spin orbit coupling; crystal field splitting of the terms not shown. Right; energy level diagram for the  $U^{4+}$  ion in an octahedral crystal field

## References

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