Supplementary Information:

Uranium complexes supported by an aryloxide—functionalised triazacyclononane macrocycle: Synthesis and characterisation of a six-coordinate U(III) species and insights into its reactivity

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Experimental Section

General Procedures:

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glove box. Solvents were purified using a two-column solid-state purification system (Glasscontour System, Irvine, CA) and transferred to the glove box without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed and stored over activated molecular sieves prior to use.

Starting materials:

$[(THF)_4UI_3]$ and $[U(N(SiMe_3)_2)_3]$ were prepared as described by Clark et al.[1-3] Uranium turnings were purchased from Alfa Aesar and activated according to literature proceedings.

Complex Synthesis:

$[((ArO)_3tacn)U]$(**1**): A solution of $[U(N(SiMe_3)_2)_3]$ (1.5 g, 2.09 mmol) in hexane (17 mL) was added to a solution of 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane ($(ArO)_3tacn$) (1.55 g, 1.98 mmol) in hexane (20 mL) and stirred for 12 h at room temperature. The resulting red-brown solution was filtered and stored at –40 °C. Within 12 h, a red-brown microcrystalline precipitate formed, filtered, washed with cold hexane, and dried in vacuum (yield: 1.39 g, 1.36 mmol, 69 %).
Yield: ~70%, based on $[U(N(Si(CH_3)_3)_2)_3]$. ^1H NMR (400 MHz, benzene-d_6, 20 °C): δ = 12.19 (s, 1H, $\Delta\nu_{1/2}$ = 15.7 Hz), 9.05 (s, 1H, $\Delta\nu_{1/2}$ = 12.7), 4.15 (s, 9H, $\Delta\nu_{1/2}$ = 15.6 Hz), 2.63 (s, 9H, $\Delta\nu_{1/2}$ = 7.08 Hz), −1.53 (s, 1H, $\Delta\nu_{1/2}$ = 41.4 Hz), –4.01 (s, 1H, $\Delta\nu_{1/2}$ = 20.8 Hz), −7.43 (s, 1H, $\Delta\nu_{1/2}$ = 23.7 Hz), −12.41 (s, 1H, $\Delta\nu_{1/2}$ = 44.1 Hz), −18.98 (s, 1H, $\Delta\nu_{1/2}$ = 32.9 Hz), –21.84 (s, 1H, $\Delta\nu_{1/2}$ = 45.1 Hz); elemental analysis (%) calcd for **1**: C 60.10, H 7.71, N 4.12; found: C 60.02, H 7.84, N 4.18.

$[((ArO)_3tacn)U(OAr)]$(**2**): A solution of 2,4-di-*tert*-butylphenol (101 mg, 0.490 mmol) in hexane (3 mL) was added to a solution of **1** (250 mg, 0.245 mmol) in hexane (7 mL) and stirred at room temperature for 1 h. The resulting white precipitate of **2** was filtered, washed with hexane, and dried in vacuum. Room temperature recrystallization of the

crude product from a saturated solution of hexane yielded rectangular crystals of **2** • C_5H_{12} suitable for X-ray diffraction analysis.
^1H NMR (400 MHz, benzene-d_6, 20 °C): $\delta = 42.99$ (s, H, $\Delta v_{1/2} = 12.8$ Hz), 37.29 (s, 3H, $\Delta v_{1/2} = 21.2$), 16.88 (s, H, $\Delta v_{1/2} = 9.0$ Hz), 16.33 (s, H, $\Delta v_{1/2} = 18.1$ Hz), 8.88 (s, 3H, $\Delta v_{1/2} = 4.4$ Hz), -3.55 (s, 9H, $\Delta v_{1/2} = 4.8$ Hz), -4.59 (s, H, $\Delta v_{1/2} = 10.9$ Hz), -8.72 (s, H, $\Delta v_{1/2} = 12.8$ Hz), -12.58 (s, 9H, $\Delta v_{1/2} = 61.0$ Hz), -21.84; elemental analysis (%) calcd for **2**: C 63.75, H 8.15, N 3.43; found: C 63.79, H 8.22, N 3.33.

[{((ArO)$_3$tacn)U}$_2$(μ-O)](**3**): A solution of **1** (100 mg, 0.10 mmol) in THF (15 mL) was stirred at room temperature for 1 h. After two weeks pale aquamarine blue hexagonal microcystals precipitated. The crystals were filtered, washed with THF, and dried in vacuum (yield: 100 mg, 0.05 mmol, >95 %). Recrystallization of the crude product from a dilute solution of Et_2O/pentane at room temperature yielded rectangular crystals of **3** • Et_2O suitable for X-ray diffraction analysis.
Elemental analysis (%) calcd for **3:** C 59.63, H 7.65, N 4.09; found: C 59.55, H 7.58, N 4.13.

Crystallographic details:

Crystallographic details for **2**: Colorless rectangular crystals grown from a solution of di-ethylether/pentane at room temperature were coated with Paratone N oil on a microscope slide. A crystal of approximate dimensions 0.25 x 0.25 x 0.10 mm^3 was selected and mounted on a glass fiber. A total of 58665 reflections ($-46 \leq h \leq 46$, $-19 \leq k \leq 19$, $-33 \leq l \leq 32$) were collected at $T = 228(2)$ K in the θ range of 1.14 to 27.57° of which 15962 were unique ($R_{\text{int}} = 0.0730$); $\text{Mo}_{K\alpha}$ radiation ($\lambda = 71073$Å). The structure was solved by Direct Methods (Shelxtl Version 6.10, Bruker AXS, Inc., **2000**). With the exception of hydrogen atoms, all atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions. The residual peak and hole electron density was 1.918 and -0.748 eA^{-3}. The absorption coefficient was 2.340 mm^{-1}. The least square refinement converged normally with residuals of $R_1 = 0.0672$ (all data), $wR_2 = 0.1380$ and GOF = 1.017 ($I > 2\sigma(I)$). $C_{65}H_{99}N_3O_4U$, space group $C2/c$, monoclinic $a = 35.737(3)$, $b = 15.0416(12)$, $c = 26.266(2)$ Å, $\beta = 90.188(2)°$, $V = 14119(2)$ A^3, $Z = 8$, $\rho_{\text{calcd}} = 1.152$ mg/m^3, $F(000) = 5072$, $R(F) = 0.0422$, $wR(F^2) = 0.1334$.

Crystallographic details for **3**: Pale aquamarine blue rectangular crystals grown from a solution of pentane at room temperature were coated with Paratone N oil on a microscope slide. A crystal of approximate dimensions 0.20 x 0.20 x 0.13 mm^3 was selected and mounted on a glass fiber. A total of 22661 reflections ($-19 \leq h \leq 19$, $-19 \leq k \leq 19$, $-19 \leq l \leq 19$) were collected at $T = 296(2)$ K in the θ range of 1.50 to 27.55° of which 11787 were unique ($R_{\text{int}} = 0.0489$); $\text{Mo}_{K\alpha}$ radiation (λ=71073Å). The structure was solved by Direct Methods (Shelxtl Version 6.10, Bruker AXS, Inc., **2000**). The symmetry transformation used to generate equivalent atoms was: -x+1,-y+1,-z+1. With the exception of hydrogen atoms, all atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions. The residual peak and hole electron density was 5.185 and -3.406 eA^{-3}. The absorption coefficient was 3.032 mm^{-1}. The least square refinement converged normally with residuals of $R_1 = 0.0938$ (all data), $wR_2 = 0.1674$ and GOF = 1.033 ($I>2\sigma(I)$). $C_{55}H_{88}N_3O_{4.5}U$, space group $P1$, triclinic $a = 14.8550(17)$, $b = 15.0174(17)$, $c = 15.2609(17)$ Å, $\alpha = 60.832(2)$, $\beta = 74.682(2)$, $\gamma = 66.580(2)°$, $V = 2717.3(5)$ A^3, $Z = 2$, $\rho_{\text{calcd}} = 1.346$ mg/m^3, $F(000) = 1134$, $R(F) = 0.0646$, $wR(F^2) = 0.1525$.

Methods:

Magnetization of crystalline powdered samples was recorded with a SQUID magnetometer (Quantum Design) at 10 kOe between 5—300 K for samples **1**, **2**, and **3**, respectively. Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment ($\chi_{\text{dia}} = -782 \cdot 10^{-6}$ cm^{3}mol^{-1} (**1**), $-929 \cdot 10^{-6}$ cm^{3}mol^{-1} (**2**), $-1654 \cdot 10^{-6}$ cm^{3}mol^{-1} (**3**)) by using tabulated Pascal constants and the effect of the blank sample holders (gelatine capsule/straw). Samples used for magnetization measurement were recrystallized multiple times and checked for chemical composition and purity by elemental analysis (C, H, and N) and ^{1}H NMR spectroscopy. Data reproducibility was also carefully checked.

The ADF2000.01 program suite was utilized for geometry optimization of the core structure. The Vosko, Wilk, and Nusair (VWN) local density approximation was used. Becke's (1988) exchange correlation and Perdew (1986) correlation for the gradient correction were also applied. The spin-unrestricted option was utilized together with ZORA relativistic formalism. No symmetry was specified in the calculation of the $[((ArO)_3tacn)U]$ species, starting from the X-ray refined geometry of the crystallographically characterised seven-coordinate $[((ArO)_3tacn)U(NCCH_3)]$. The latter is reported elsewhere (CCDC reference number: 192194). U: triple-ζ basis set with polarization and frozen core 6p. N: triple-ζ basis set with polarization. O: triple-ζ basis set with polarization. C: triple ζ-basis set with polarization. H: triple-ζ basis set with polarization including H-polarization.

^{1}H NMR spectra (300 or 400 MHz) were recorded at probe temperature of 20°C on Varian (Mercury 300/400) in C_6D_6. Chemical shifts were referenced to *protio* solvent impurities (δ 7.15 (C_6D_6)) and are reported in ppm.

Infrared spectra (400—4000 cm^{-1}) of solid samples were obtained on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer as KBr pellets.

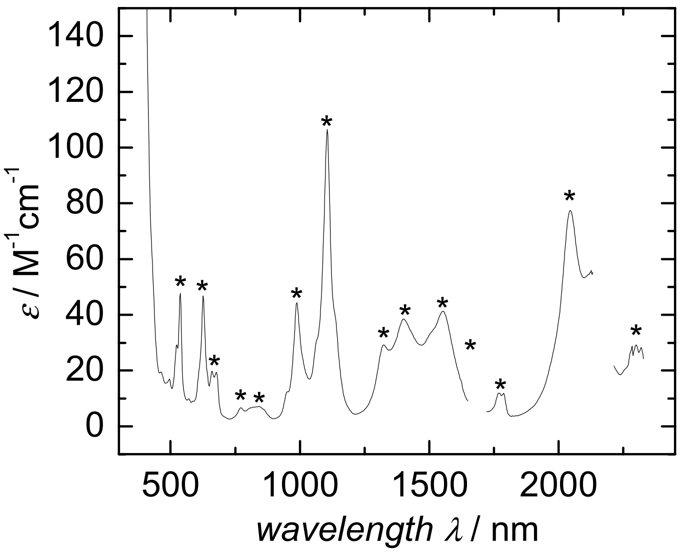
Electronic absorption spectra were recorded from 200 nm to 2500 nm (Shimadzu (UV-3101PC)) or from 190 to 820 (HP 8452A Diode Array) UV/vis/NIR spectrophotometer.

Results from elemental analysis were obtained from Kolbe Microanalytical Laboratory (Muelheim/Ruhr, Germany).

References:

1 D. L. Clark, A. P. Sattelberger, R. A. Andersen, *Inorg. Synth.*, 1997, **31**, 307-315.
2 L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin, B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 2248-2256.
3 D. L. Clark, A. P. Sattelberger, S. G. Bott, R. N. Vrtis, *Inorg. Chem.*, 1989, **28**, 1771-1773.

Fig. S1: Electronic absorption spectra of **2**, recorded in benzene solution.



wavelength λ_{max} / nm	Extinction Coefficient ε_{max} / M^{-1}cm^{-1}
538	48
626	47
660/678	20/19.5
774	6.6
830	7
990	44
1106	107
1324	30
1402	38.5
1554	41
1768/1790	12/11
2044	77.5
2304	28

Fig. S2: Temperature dependence of the effective magnetic moment μ_{eff} of solid samples of **1**, **2**, and **3**.

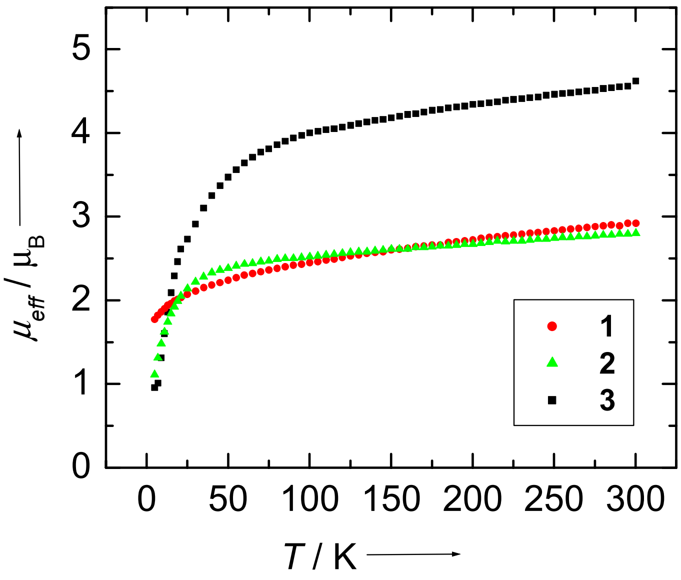


Table S1: Mulliken populations for [((ArO)$_3$tacn)U]. For electronically equivalent atoms, mean values are given.

Atom	Charge	Spin-density	Spin	S	P	D	F
U	1.5740	3.1118	α	1.1948	2.9828	0.6376	2.9537
			β	1.0433	2.9324	0.4337	0.2478
Oav	-0.6931	-0.0425	α	1.9099	2.3924	0.0247	0.0000
			β	1.9141	2.4037	0.0339	0.0000
Nav	-0.5876	-0.0139	α	1.7863	1.9591	0.0414	0.0000
			β	1.7897	1.9710	0.0401	0.0000