Supplementary Information for

Easy access to stable pentavalent uranyl(V) complexes

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Experimental

The complexes described below are very sensitive to moisture and oxygen.

Syntheses and manipulations of the compounds were carried out under ultra high purity argon atmosphere with rigorous exclusion of air and water, using Shlenk-vessel and vacuum-line techniques or in a glove box.

UO₂(OTf)₂ was prepared as previously described (Ref. 4d in the communication)

Diethyl ether and tetrahydrofuran were dried over a mixture of sodium-benzophenone and pyridine or acetonitrile over KH.

KI, purchased from Aldrich or Prolabo, was crushed and dried under vacuum for 48 h at 150°C before use.

IR samples were prepared as Nujol mulls between KBr round cell windows and the spectra recorded on a Perkin-Elmer FT-IR 1725X spectrometer. The ¹H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany).

Synthesis of UO₂(py)_{2.2}I₂K (2):

Pyridine (15 mL) was condensed at -70 °C under vacuum into a 50 mL round bottom flask containing UO₂I₂(thf)₃ (250 mg, 0.33 mmol) and KC₅Me₅ (59 mg, 0.33 mmol). The orange suspension was stirred for 2 h at room temperature. After condensation of 5 mL of thf, the orange powder was filtered off. During drying under vacuum (20 h at 23 °C), the colour of the powder turned from bright orange to ochre (200 mg, 80%). Similar procedure with KC₅H₅ gave identical results; the yield of **2** was almost quantitative after precipitation by addition of diethyl ether into the pyridine suspension.

¹H NMR (200 MHz, thf- d_8 , 20 °C) : signals of free pyridine are observed. $\delta = 8.75$, 7.60, 7.21; Elemental analyses calcd. for C₁₁H₁₁I₂KN_{2.2}O₂U (736.96) : C 17.93, H 1.50; N 4.34; I 34.44; found C 18.03, H 1.48; N 4.24; I 34.66.

An NMR tube was charged with $UO_2I_2(thf)_3$ (10 mg, 0.013 mmol) and 1 eq. of 2% K(Hg) (27 mg, 0.013 mmol of K) and 0.5 mL of pyridine. The tube was then immersed in an ultrasound bath for 30 mn, and a bright orange suspension was obtained.

Thin orange needles of $\{[UO_2(py)_5][KI_2(py)_2]\}_{\infty}$ (1) suitable for X-ray diffraction analysis were deposited in a few hours when the 1/1 mixture of $UO_2I_2(thf)_3$ and KC_5Me_5 was heated at 100 °C in pyridine and then cooled down to room temperature. Slow diffusion of diethyl ether into a pyridine solution of **2** also gave crystals of **1**.



IR spectrum of UO₂(py)_{2.2}I₂K:



IR Reference (KBr + Nujol):

Synthesis of UO₂I(thf)_{2.75} (3)

Tetrahydrofuran (15 mL) was condensed at -70° C under vacuum into a 50 mL round bottom flask containing UO₂I₂(thf)₃ (298 mg, 0.40 mmol) and 1 eq. of yellow needles of the freshly sublimed TlC₅H₅ (111 mg, 0.41 mmol). The suspension was then stirred at room temperature for 6 h, affording a brown solution with a yellow precipitate of TlI. After decantation and slow filtration of the solution which was repeated three times, the solution was concentrated to 5 mL and a brown powder precipitated upon addition of pentane (15 mL). (175 mg, 73%) Elemental analyses calcd. for C₁₁H₂₂IO_{4.75}U (595.22) : C 22.20, H 3.72, I 21.32; found C 21.91, H 3.46, I 20.95

IR spectrum of UO₂I(thf)_{2.75}:



Synthesis of $UO_2(OTf)(thf)_n$ (n = 1.5, 2) (4)

Synthesis of UO₂(OTf)(thf)_{1.5}: A flask was charged UO₂(OTf)₂ (300 mg, 0.53 mmol) and KC₅Me₅ (92 mg, 0.53 mmol) and thf (20 mL) was condensed in it. The suspension was stirred at 20 °C for 15 h, affording a brown solution with a white precipitate. Two extractions from the salts with a mixture of toluene-thf (15mL-10mL) and evaporation of the solvents afforded a brown powder which was recrystallized in thf-pentane (5mL-20mL). The beige powder was then dried under vacuum for 15 h at room temperature. (233 mg, 84%).

Elemental analyses calcd. for $C_7H_{12}F_3O_{6.5}SU$ (527.26) : C 15.95, H 2.29, F 10.81; found C 16.32, H 2.14, F 10.44.



IR spectrum of UO₂(OTf)(thf)_{1.5}

Synthesis of UO₂(Otf)(thf)₂: Following similar procedure from UO₂(Otf)₂ (306 mg, 0.54 mmol) and KC₅H₅ (58 mg, 0.55 mmol), the resulting beige powder was dried for 10 h at 20 °C (220 mg, 72%).

Elemental analyses calcd. for $C_9H_{16}F_3O_7SU$ (563.31): C 19.19, H 2.86, F 10.12; found C 19.03, H 2.43, F 9.88.

IR spectrum of UO₂(OTf)(thf)₂



An NMR tube was charged with $UO_2(OTf)(thf)_2$ (10 mg, 0.017 mmol) and 1 eq. of KC₅Me₅ (3.1 mg, 0.017 mmol) and 0.5 mL of pyridine. Addition of excess KI led to a brown-red solution. The tube was immersed for 5 h in an ultrasound bath and then heated for 48 h at 100 °C. Small orange needles of **1** were deposited after some days at room temperature.