Supporting Information

1. Syntheses of Ligands

1-(4,5-Dimethyl-oxazol-2-yl)-3,3,4,4,4-pentafluoro-but-1-en-2-ol (DMOPFB **1***)*

A 250 ml Schlenk flask was charged with 2,4,5-trimethyloxazole (1.0 ml, 9.0 mmol), pyridine (3.6 ml) and toluene (25 ml). To the resulting mixture pentafluoropropionic anhydride (5.0 ml, 25.3 mmol) was added dropwise at 0 °C. The resulting reaction mixture was stirred at room temperature for 12 h. The mixture was quenched with Na_2CO_3 (3%, 50 ml) and extracted with ethyl acetate (2 x 100 ml). After all volatiles had been removed under reduced pressure, the crude product was subjected to sublimation (45 °C, 10^{-3} mbar) giving colorless crystals in 52% yield (1.2 g, 4.7 mmol).

^{1}H-NMR (300 MHz, rt, $CDCl_3$): δ [ppm] = 11.52 (s, $\Delta_{1/2}$= 21 Hz, 1H, OH/N); 5.89 (s, 1H); 2.24 (s, 3H); 2.10 (s, 3H).

^{19}F-NMR (282 MHz, rt, $CDCl_3$): δ [ppm] = -83.4 (s, 3F); -122.8 (s, 2F).

^{13}C-NMR (75 MHz, rt, $CDCl_3$): δ [ppm] = 160.5, 157.8, 141.6, 126.1, 118.8, 111.1, 85.5, 10.0, 9.8.

CHNS (found/calculated) [%]: C (41.86/42.04); N (5.20/5.45); H (3.51/3.14).

EI-MS (20 eV, 35 °C): m/z = 257 $[M]^+$ (52%),
138 $[M-(CF_2CF_3)]$ (100%),
110 $[C_6H_7NO]^+$ (6%).

1-Ethoxy-4,4,4-trifluorobut-1-en-3-one (TFAE **7***)*

A 250 ml flask was charged with ethylvinylether (48 ml, 0.5 mol), pyridine (45 ml) and CH_2Cl_2 (150 ml). The mixture was cooled to 0 °C and trifluoroacetic anhydride (70 ml, 0.5 mol) was added dropwise at 0 °C. The resulting mixture was stirred at room temperature for 18 h. Water (500 ml) was added and the mixture was extracted with CH_2Cl_2 (2 x 100 ml). The combined organic layers were dried over Na_2SO_4. After all volatiles had been removed under reduced pressure, the crude product was subjected to distillation (27-34 °C, 10^{-3} mbar) giving the product as a yellowish liquid in 60% yield (50.5 g, 0.3 mol).

^{1}H-NMR (300 MHz, rt, $CDCl_3$): δ [ppm] = 7.82 (d, $^3J_{H,H}$ = 13 Hz, 1H), 5.78 (d, $^3J_{H,H}$ = 13 Hz, 1H), 4.03 (q, $^3J_{H,H}$ = 7 Hz, 2H), 1.30 (t, $^3J_{H,H}$ = 7 Hz, 3H).

^{19}F-NMR (282 MHz, rt, $CDCl_3$): δ [ppm] = -78.6 (s, 3F).

N,N'-Bis-(4,4,4-trifluorobut-1-en-3-on)-ethylenediamine (TFB-en **3***)*

A 100 ml flask was charged with ethylenediamine (4.5 g, 75 mmol) and CH_2Cl_2 (50 ml). To the resulting solution 1-ethoxy-4,4,4-trifluorobut-1-en-3-one (TFAE) (25 g, 150 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 2 h. The resulting precipitate was filtered off and subsequently recrystallized from CH_2Cl_2. The product was obtained as colorless crystals in 75% yield (17 g, 56.2 mmol).

^{1}H-NMR (300 MHz, rt, $CDCl_3$): δ [ppm] = 10.20 (s, 1H), 7.02 (dd, $^3J_{H,H}$ = 13 Hz, $^3J_{H,H}$ = 7 Hz, 1H), 5.42 (d, $^3J_{H,H}$ = 7 Hz, 1H), 3.55 (m, 2H).

^{19}F-NMR (282 MHz, rt, $CDCl_3$): δ [ppm] = -77.0 (s, 3F).

^{13}C-NMR (75 MHz, rt, $CDCl_3$): δ [ppm] = 179.0, 157.3, 117.0, 88.0, 50.2.

CHNS (found/calculated) [%]: C (39.94/39.48); N (9.39/9.21); H (3.62/3.31).

EI-MS (20 eV, 110 °C): m/z = 304 $[M]^+$ (56%),
235 $[M -CF_3]^+$ (6%),
165 $[M -(CF_3(CO)C_3H_3NH_2)]^+$ (100%),
151 $[M -(CF_3(CO)C_4H_4NH_2)]^+$ (96%),
113 $[CF_3CH(OH)CH_2)]^+$ (11%),
84 $[(CO)C_2H_2(NH)CH_3)]^+$ (20%).

2. Syntheses of the Uranyl Complexes

Preparation of $UO_2(DMOPFB)_2(H\text{-}DMOPFB)$ **8***:*

As already shown for $U(DMOTFP)_4$ **6**,[1] bubbling O_2 into a solution of **6** in THF and stirring a solution of **6** in THF-d_8 under air both resulted in the formation of $UO_2(DMOTFP)_2(H\text{-}DMOTFP)$. In case of U(DMOPFB) **4**, stirring **4** in water containing THF-d_8 for 5 h, during which the color changed from green to red, resulted in the formation of **8** and free ligand **1**. The compound was purified by vacuum sublimation of uncoordinated ligand (45 °C, 10^{-3} mbar) and obtained as red powder.

^{1}H-NMR (300 MHz, rt, THF-d_8): δ [ppm] = 10.25 (br s, 1H), 5.99 (br s, 2H), 5.92 (s, 1H), 2.45 (s, 12H), 2.24 (s, 3H), 2.10 (s, 3H).

Preparation of $UO_2(TFB\text{-}en)THF$ **9***:*

Stirring **5** in water containing THF-d_8 for 1 d, during which the color changed from green-brownish to bright yellow, resulted in the formation of **9** and TFB-en **3**.

^{1}H-NMR (300 MHz, rt, THF-d_8): δ [ppm] = 8.87 (2H, d, $^3J_{H,H}$ = 5 Hz), 5.75 (2H, d, $^3J_{H,H}$ = 5 Hz) and 4.43 (4H, s).

References

1 L. Appel, J. Leduc, C. L. Webster, J. W. Ziller, W. J. Evans, S. Mathur, *Angew. Chem. Int. Ed.*, 2015, **54**, 2209.