Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information for the manuscript

The Effect of Iron Binding on Pentavalent Uranyl(V) Stability.

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1. General considerations.

All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen level were always kept at less than 1 ppm. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (diisopropylether, hexane, pyridine, toluene, benzene and THF) or freeze-degassed and stored over activated 3 Å molecular sieves (pyridine-d_5). Depleted uranium was purchased from IBILABS, USA.

$[(UO_2Py_5)(KI_2Py_2)]_n$ and UI_4 were synthesized as previously described.[1,2] $UO_2(NO_3)_2(H_2O)_6$ was purchased from Sigma-Aldrich : Fluka. $UO_2(NO_3)_2$ was obtained by high vacuum drying of $UO_2(NO_3)_2(H_2O)_6$ for 5 days at 120°C. Anhydrous FeI_2, $FeCl_3$ and PyHCl were purchased from Aldrich and were used without further purification. The H_3trensal[3] and H_3tdmba[4] ligands were prepared according to the published procedure.

Elemental analyses were performed under argon with a Thermo Scientific Flash 2000 Organic Elemental Analyzer by the EPFL elemental analyses service. ^1H NMR experiments were carried out using NMR tubes adapted with J. Young valves. ^1H NMR spectra were recorded on Bruker 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference. EPR spectra were recorded with a Bruker Elexsys E500 spectrometer working at 9.4 GHz frequency with an oxford ESR900 cryostat for 4-300 K operation. Simulation was performed with the Easyspin 5.1.3 program.

Caution: *Depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47×10^9 years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with α- and β-counting equipment.*

2. Synthetic procedures.

Synthesis of K_3trensal.

Potassium hydride (50.8 mg, 1.267 mmol, 2.9 eq.) was added slowly to a stirred solution of H_3trensal (200.0 mg, 0.436 mmol, 1 eq.) in THF (5 mL) and stirred overnight. After 12 hours of stirring, the resulting white solid was filtered off, washed with THF and dried under vacuum to give K_3trensal.$(THF)_{0.5}$ (244.3 mg, 0.379 mmol, 87 % yield). The residual amount of THF present in the solid was determined at each preparation by quantitative titration using naphthalene as standard. ^{1}H NMR (400 MHz, C_5D_5N, 298 K): δ = 8.18 (s, 3H), 7.27 (d, 3H), 7.04 (t, 3H), 6.61 (d, 3H), 6.44 (t, 3H), 3.42 (s, 6H), 2.42 (s, 6H).

Synthesis of [UO_2(trensal)K], 1.

A yellow solution of $UO_2(NO_3)_2$ (30.8 mg, 0.078 mmol, 1 eq.) in pyridine (1mL) was slowly added to a stirred suspension of K_3trensal$(THF)_{0.5}$ (50.3 mg, 0.078 mmol, 1 eq.) in pyridine (1 mL) and the mixture was stirred for 60 minutes, resulting in an orange solution. Then KNO_3 was removed by centrifugation and the resulting solution was layered with *n*.hexane (2 mL). Slow diffusion of hexane yielded [UO_2(Ktrensal)].Py as orange solid (39.0 mg, 0.046 mmol, 59%) Anal. Calcd. for [UO_2(trensal)K].Py ($C_{32}H_{32}N_5O_5KU$, MW=843.66) C 45.56, H 3.82 and N 8.30; found C 45.47, H 3.64 and N 8.15.

Synthesis of [UO_2(Htrensal)], 2.

A yellow solution of $UO_2(NO_3)_2$ (20.0 mg, 0.051 mmol, 1 eq) in pyridine (1mL) was slowly added to a stirred suspension of K_3trensal$(THF)_{0.5}$ (32.9 mg, 0.051 mmol, 1 eq.) in pyridine (1mL) and was stirred for 60 minutes, resulting in an orange solution. Then, a solution of PyHCl (5.9 mg, 0.051 mmol, 1 eq.) in pyridine (0.5 mL) was added to the reaction mixture. The reaction mixture was stirred overnight, then KNO_3 was removed by centrifugation and the resulting solution was layered with *n*.hexane (2 mL). Slow diffusion of hexane yielded [UO_2(Htrensal)].$Py_{0.5}$ as an orange microcrystalline solid (23.0 mg, 0.031 mmol, 60%) Anal. Calcd. for [UO_2(Htrensal)].$Py_{0.5}$ ($C_{29.5}H_{30.5}N_{4.5}O_5U$, MW=766.07) C 46.25, H 4.01 and N 8.23; found C 46.58, H 3.80 and N 8.07. ^{1}H NMR (400 MHz, C_5D_5N, 298 K) δ = 11.94 (s, 1H), 6.26 (m, 3H), 6.16 (dd, 2H), 6.05 (m, 4H), 5.86 (m, 2H), 5.61 (t, 1H), 5.38 (t, 2H), 3.74 (t, 2H), 3.08 (dd, 2H), 2.93 (t, 2H), 2.74 (m, 5H), 2.57 (td, 2H). Orange single crystals of **2.py** suitable for X-ray diffraction were obtained by slow diffusion (one week) of hexane into pyridine solution of **2**.

Synthesis of [UO_2(trensal)K]K, 3.

An orange solution of $[(UO_2Py_5)(KI_2Py_2)]_n$ (20.0 mg, 0.018 mmol, 1 eq.) in pyridine (2mL) was slowly added to a stirred suspension of K_3trensal$(THF)_{0.5}$ (11.6 mg, 0.018 mmol, 1 eq.) in pyridine (2 mL). The reaction mixture was stirred for 2 hours, resulting in a bright blue solution and a white precipitate. The white precipitate was centrifuged out. Upon slow diffusion of n.hexane into the resulting solution, a blue solid was obtained (13.0 mg, 0.014 mmol, 70%). Anal. Calcd for [UO_2(trensal)K]K.$KI_{0.6}$ ($C_{27}H_{27}N_4O_5I_{0.6}K_{2.6}U$, MW=903.363) C 35.9, H 3.01 and N 6.20; found C 36.13, H 2.63 and N 6.43.

Synthesis of [UO_2(trensal)(K(2.2.2crypt)] [K(2.2.2crypt)], 4.

An orange solution of $[(UO_2Py_5)(KI_2Py_2)]_n$ (47.6 mg, 0.040 mmol, 1 eq.) in pyridine (1.5 mL) was slowly added to a stirred suspension of K_3trensal$(THF)_{0.5}$ (25.8 mg, 0.040 mmol, 1 eq.) in pyridine (0.5 mL) resulting in a dark blue solution. The solution was stirred for 30 minutes and then a solution of 2.2.2.cryptand (60.2 mg, 0.016 mmol, 4 eq.) in pyridine (0.5 mL) was added resulting in a colour change to bright green. The resulting solution was stirred for 30 minutes, the solvent was evaporated and the residue was dissolved in THF (2 mL). The resulting green solution was filtered to remove K(2.2.2cryptand)I and the filtrate was layered with DIPE (2 mL). Upon slow diffusion of DIPE, complex

4.THF was obtained as green crystals (40.0 mg, 0.025 mmol, 62%). Anal. Calcd. for [UO$_2$(trensal)(K(2.2.2crypt)][K(2.2.2crypt)].THF ($C_{67}H_{107}N_8O_{18}K_2U_1$, MW=1628.859) C 49.40, H 6.62 and N 6.88; found C 49.43, H 6.69 and N 7.03. ^{1}H NMR (400 MHz, C_5D_5N, 298 K) δ = 6.94 (m, 3H), 5.99 (s, 1H), 5.24 (s, 3H), 4.47 (s, 4H), 4.26 (s, 4H), 3.84 (s, 24H), 3.78 (s, 24H), 2.73 (s, 24H), -2.16 (s, 2H), -3.32 (s, 2H), -4.63 (s, 2H), -7.71 (s, 2H), -9.49 (s, 2H), -10.04 (s, 2H). Bright green single crystals of **4** suitable for X-ray diffraction were obtained after slow diffusion (4 weeks) of DIPE (1 mL) into a THF (1 mL) solution of **4**.

Synthesis of [(UO$_2$(trensal))$_2$Fe(py)$_2$], 5.

A yellow solution of UO$_2$(NO$_3$)$_2$ (20 mg, 0.05 mmol, 2 eq.) in pyridine (0.5 mL) was slowly added to a stirred suspension of K$_3$trensal(THF)$_{0.5}$ (32.2 mg, 0.05 mmol, 2 eq.) in pyridine (1 mL) and was stirred for 1 hour. A suspension of FeI$_2$ (7.9 mg, 0.025 mmol, 1 eq) in pyridine (0.5 mL) was added to the resulting orange solution and the reaction mixture was stirred overnight, yielding a deep purple solution. KI was removed by centrifugation and the solution was layered with hexane (1 mL). [(UO$_2$(trensal))$_2$Fe(py)$_2$].py$_2$ was obtained as a dark brown solid after 6 days (43 mg, 0.024 mmol, 93%). ^{1}H NMR (400 MHz, C_5D_5N, 298 K): δ = 51.62 (s, 2H), 36.64 (s, 1H) 6.77-0.51 (br, 49H), -14.85 (s, 2H). Elemental analysis calcd (%) for [(UO$_2$(trensal))$_2$Fe(py)$_2$].py$_2$ ($C_{74}H_{74}N_{12}O_{10}FeU_2$, MW=1823.2) C 48.75, H 4.09 and N 9.22; found C 48.36, H 3.71 and N 9.30. Dark purple single crystals of **5** suitable for X-ray diffraction were obtained by slow diffusion (two weeks) of hexane (1 mL) into a pyridine (2 mL) solution of **5.**

Synthesis of [UO$_2$(trensal)Fe(py)$_3$], 6.

An orange solution of [(UO$_2$Py$_5$)(KI$_2$Py$_2$)]$_n$ (75.4 mg, 0.068 mmol, 1 eq.) in pyridine (3 mL) was slowly added to a stirred suspension of K$_3$trensal(THF)$_{0.5}$ (43.6 mg, 0.068 mmol, 1 eq.) in pyridine (2 mL) and was stirred for 1 hour. A suspension of FeI$_2$ (21.1 mg, 0.068 mmol, 1 eq.) in pyridine (1 mL) was added to the resulting blue solution, yielding a deep purple solution. The reaction mixture was stirred overnight, KI was removed by filtration. The resulting solution was layered with hexane (3 mL) to afford, after two weeks, a dark purple microcrystalline solid that was dried under vacuum (65.0 mg, 0.055 mmol, 81%). Electrospray ionization mass spectrometry (ESI-MS): *m/z = 859.89 {UO$_2$(trensal)Fe(Py)$^+$}*. Elemental analysis calcd (%) for [UO$_2$(trensal)Fe(py)$_3$]KI$_{0.8}$ ($C_{42}H_{42}N_7O_5I_{0.8}K_{0.8}FeU$, MW=1151.5) C 43.81, H 3.68 and N 8.51; found C 43.76, H 3.53 and N 8.60. ^{1}H NMR (400 MHz, C_5D_5N, 298 K): δ = 51.48 (s, 3H), 38.28 (s, 3H), 2.67 (s, 3H), -2.72 (s, 2H), - 4.50 (s, 2H), -5.46 (s, 2H), -7.93 (s, 2H), -10.92 (s, 2H), -12.21 (s, 3H), -14.56 (s, 2H), -27.65 (s, 1H), 31.06 (s, 1H). Dark purple single crystals of **6**.py.0.5hex suitable for X-ray diffraction were obtained by slow diffusion (two weeks) of hexane (1 mL) into a pyridine (1 mL) solution of **6**.

Synthesis of [UO$_2$(trensal)Fe(py)$_3$U(trensal)]I, 7.

A pyridine (1 mL) solution of [U(trensal)(py)]I (16.3 mg 0.020 mmol, 1 eq) prepared *in situ* (KI formed was removed by filtration) was added to a deep purple pyridine (1 mL) solution of [UO$_2$(trensal)Fe(py)$_3$] (20.2 mg, 0.020 mmol, 1 eq), prepared *in situ (*KI formed was removed by filtration*)*. The reaction mixture was stirred overnight. A white precipitate (KI formed) was removed by filtration. The resulting solution layered with hexane (2 mL). After a week [UO$_2$(trensal)Fe(py)$_3$U(trensal)]I.KI (32 mg, 0.016 mmol, 80%) was obtained as a purple crystalline powder. Electrospray ionization mass spectrometry (ESI-MS): *{UO$_2$(trensal)Fe*$_3$U(trensal)$^+$*} m/z = 1474.42;* Elemental analysis calcd (%) for [UO$_2$(trensal)Fe(py)$_3$U(trensal)]I.KI ($C_{69}H_{69}N_{11}O_8I_2KFeU_2$, MW=2005.2) C 41.33, H 3.47 and N 7.68; found C 41.36, H 3.38 and N 7.57. ^{1}H NMR (400 MHz, C_5D_5N, 298 K): δ = 53.66 (s, 1H), 49.65 (s, 1H), 41.17 (s, 1H), 35.97 (s, 1H), 27.52 (s, 1H), 23.54 (s, 1H), 21.81 (s, 1H), 17.32 (s, 1H), 16.35 (s, 1H), 15.60

(s, 1H), 13.58 (s, 1H), 12.82 (s, 1H), 11.96 (s, 1H), 11.24 (s, 1H), 10.81 (s, 1H), 9.22 (s, 1H), 8.01 (s, 1H), 4.89 (s, 1H), 4.43 (s, 1H), 4.19 (s, 1H), 3.92 (s, 1H), 3.57 (s, 2H), 3.28 (s, 1H), 2.69 (s, 1H), 2.21 (s, 1H), 1.01 (s, 2H), -1.46 (s, 2H), -4.71 (s, 1H), -5.56 (s, 1H), -8.98 (s, 1H), -9.47 (s, 1H), -9.94 (s, 1H), -11.44 (s, 1H), -11.82 (s, 1H), -12.28 (s, 1H), -13.32 (d, 2H), -14.62 (s, 1H), -17.90 (s, 1H), 18.00 (s, 1H), -18.90 (s, 1H), -20.29 (s, 1H), -21.16 (d, 3H), -29.45 (s, 1H), -31.97 (s, 1H), -35.64 (s, 1H). Dark purple single crystals of **7** suitable for X-ray diffraction were obtained by slow diffusion (two weeks) of hexane (1 mL) into a pyridine (0.5 mL) solution of **7**.

Synthesis of [(UO$_2$(trensal)Fe(py)$_3$)$_2$Fe(py)$_3$]I$_2$, 8.

An orange solution of [(UO$_2$Py$_5$)(KI$_2$Py$_2$)]$_n$ (50 mg, 0.035 mmol, 1 eq) in pyridine (0.5 mL) was slowly added to a stirred suspension of K$_3$trensal (THF)$_{0.5}$ (22.6 mg, 0.035 mmol, 1 eq) in pyridine (1 mL) and was stirred for 1 hour. A suspension of FeI$_2$ (16.3 mg, 0.053 mmol, 1.5 eq) in pyridine (1 mL) was added to the resulting blue solution, yielding a deep purple solution. The reaction mixture was left stirring overnight, KI was removed by centrifugation and filtration and the resulting solution was layered with hexane (2.5 mL). After a week [(UO$_2$(trensal)Fe(py)$_3$)$_2$Fe(py)$_3$]I$_2$].KI (63 mg, 0.023 mmol, 65%) was obtained as a purple crystalline powder. Dark purple X-ray quality crystals of **8** were obtained by slow diffusion (one week) of hexane (1 mL) into a pyridine (0.5 mL) solution **8**. Electrospray ionization mass spectrometry (ESI-MS): m/z = *859.83 {UO$_2$(trensal)Fe(Py)$^+$}*. Elemental analysis calcd (%) for [(UO$_2$(trensal)Fe(py)$_3$)$_2$Fe(py)$_3$]I$_2$].KI ($C_{99}H_{99}N_{17}O_{10}I_3K_1Fe_3U_2$, MW=2750.4) Calculated C 43.23, H 3.63 and N 8.66; found C 42.93, H 4.02 and N 8.46. ^{1}H NMR (400 MHz, Pyridine, 298 K): δ = 53.62 (s, 3H), 40.36 (s, 3H), 5.53-0.63 (m, 29H), -3.50 (s, 2H), 13.46 (s, 3H), -17.16 (s, 2H), -20.47 (s, 2H).

Synthesis of [U(trensal)(py)]I, 9.

A bright orange solution of [UI$_4$(dioxane)$_{1.8}$] (30.0 mg, 0.033 mmol, 1 eq) in pyridine (1 mL) was added to a suspension of K$_3$trensal (THF)$_{0.5}$ (21.3 mg, 0.033 mmol, 1 eq) in pyridine (0.5 mL) and was stirred for 2 hours. Residual solid (KI) was removed by centrifugation and resulting orange solution was layered with hexane (2 mL). Slow diffusion of hexane yielded [U(trensal)(py)]I.KI$_{0.1}$ as orange solid (0.02 mmol, 72%) Elemental analysis calcd (%) for [U(trensal)(py)]I.KI$_{0.1}$ ($C_{32}H_{32}N_5O_3I_{1.1}K_{0.1}U$, MW=916.17) Calculated C 41.95, H 3.52 and N 7.64; found C 41.85, H 3.31 and N 7.26. ^{1}H NMR (400 MHz, C_5D_5N, 298 K): δ = 41.26 (s, 3H), 16.30 (s, 3H), 12.39 (s, 3H), 10.64 (s, 3H), 10.35 (s, 3H), -6.83 (s, 6H), -18.82 (s, 6H). Orange single crystals of **9.**0.5py suitable for X-ray diffraction were obtained after two weeks by slow diffusion of hexane into pyridine solution of **9**.

Reaction of 2 with Cp$^*_2$Co.

A bright orange solution of [UO$_2$(trensal)K] (10.0 mg, 0.01 mmol, 1 eq) in pyridine (1 mL) was added to a pyridine solution (0.5 mL) of Cp$^*_2$Co (4.5 mg, 0.01 mmol, 1 eq) and stirred for 30 minutes. The ^{1}H NMR spectrum of the reaction mixture indicated partial disproportionation (Fig. S4).

Reaction of 3 with PyHCl.

A pyridine (0.3 mL) solution of PyHCl (3.0 mg, 0.026 mmol, 1 eq.) was slowly added to a blue pyridine solution (1.5 mL) of **3** (21.3 mg, 0.026 mmol, 1 eq.) prepared *in situ* resulting in a khaki solution. The proton ^{1}H NMR spectrum of the solution indicated partial disproportionation (Fig. S7, middle). The resulting solution was stirred for 8 hours and a second equivalent of PyHCl in pyridine solution (0.3 mL) was added to the reaction mixture. The ^{1}H NMR spectrum of the resulting orange solution indicated full disproportionation (Fig. S7, top).

Reaction of 4 with PyHCl.

A pyridine (0.3 mL) solution of PyHCl (3.0 mg, 0.026 mmol, 1 eq.) was slowly added to a green pyridine solution (1.5 mL) of **4** (40.8 mg, 0.026 mmol, 1 eq.) prepared *in situ* resulting in a khaki solution. The ^{1}H NMR spectrum of the solution indicated the presence of ^{1}H NMR silent species (Fig. S9 middle). The solution was stirred for 8 hours and a second equivalent of PyHCl in pyridine solution (0.3 mL) was added to the reaction mixture. The ^{1}H NMR spectrum of the resulting orange solution indicated full disproportionation after 3 days (Fig. S9 top).

Reaction of 6 with PyHCl.

A colourless pyridine (0.3 mL) solution of PyHCl (1.6 mg, 0.014 mmol, 1 eq.) was slowly added to a purple pyridine solution (1.5 mL) of **6** (14.3 mg, 0.014 mmol, 1 eq.) prepared *in situ*. The ^{1}H NMR of the resulting solution indicated partial disproportionation (Fig. S14 (b)). The resulting solution was stirred for 2 hours and 4 additional equivalents of PyHCl in pyridine solution (0.3 mL) were added stepwise to the reaction mixture resulting. The ^{1}H NMR spectrum of the resulting orange solution indicated full disproportionation (Fig. S14 (d)).

Reaction of 7 with PyHCl.

A colourless pyridine (0.3 mL) solution of PyHCl (1.0 mg, 0.0082 mmol, 1 eq.) was slowly added to a purple pyridine solution (1.5 mL) of **7** (16.5 mg, 0.0082 mmol, 1 eq.) prepared *in situ*. The ^{1}H NMR of the resulting solution indicated partial disproportionation (Fig. S17). The resulting solution was stirred for 2 hours and 3 additional equivalents of PyHCl in pyridine solution (0.3 mL) were added stepwise to the reaction mixture. The ^{1}H NMR spectrum of the resulting orange solution indicated full disproportionation.

Reaction of 8 with PyHCl.

A colourless pyridine (0.3 mL) solution of PyHCl (0.5 mg, 0.0044 mmol, 1 eq.) was slowly added to a purple pyridine solution (1.0 mL) of **8** (12.0 mg, 0.0044 mmol, 1 eq.) prepared *in situ*. The ^{1}H NMR spectrum of this solution indicated partial disproportionation (Fig. S20). The resulting solution was stirred for 2 hours and 4 additional equivalents of PyHCl in pyridine solution (0.3 mL) were added stepwise to the reaction mixture. The ^{1}H NMR spectrum of the resulting orange solution indicated full disproportionation.

Reaction of 3 with $FeCl_3$.

An orange pyridine (0.3 mL) solution of $FeCl_3$ (1.5 mg, 0.009 mmol, 1 eq.) was slowly added to a blue pyridine solution (0.5 mL) of **3** prepared *in situ* (7.4 mg, 0.009 mmol, 1 eq.) resulting in a dark orange solution. The ^{1}H NMR spectrum of this solution showed the formation of **5** (Fig. S21). The solution was stirred for 30 minutes, filtered and layered with hexane (1 mL). A few red single crystals of **5** suitable for X-ray diffraction were obtained after three weeks.

Reaction of 6 with [Fe(tpa)Cl_3].

A purple solution of **6** (10.0 mg, 0.008 mmol, 1 eq.) in pyridine (0.5 mL) was added to an orange solution of [Fe(tpa)Cl_3] prepared *in situ* from $FeCl_3$ and tpa (3.8 mg, 0.008 mmol, 1 eq) in pyridine (0.3 mL). The reaction mixture was stirred overnight, then centrifuged to remove KCl. The ^{1}H NMR spectrum of the reaction mixture indicated that a redox reaction had occurred (Fig.S22). A few orange single crystal of

$[Fe(tpa)Cl_2]$ suitable for X-ray diffraction were obtained after two weeks by slow diffusion of hexane (1 mL) into the resulting pyridine solution confirming that the iron was reduced.

Synthesis of [Fe(tdmba)].

A pyridine (1 mL) solution of $FeCl_3$ (24.0 mg 0.146 mmol, 1 eq) was added to a stirred solution of K_3tdmba (82.0 mg, 0.146 mmol, 1 eq.) in pyridine (1 mL) and was stirred for 1 hour. The resulting suspension was evaporated, the residue was dissolved in THF, KI was removed by filtration and the solution was layered with hexane (1 mL). [Fe(tdmba)].py was obtained as a dark brown solid after 6 days (66 mg, 0.121 mmol, 83%). Elemental analysis calcd (%) for [Fe(tdmba)].py ($C_{32}H_{35}N_2O_3Fe$, MW=551.4) C 69.71, H 6.40 and N 5.08; found C 69.96, H 6.14 and N 5.25.

Reaction of 6 with [Fe(tdmba)].

A purple solution of **6** (10.0 mg, 0.008 mmol, 1 eq.) in pyridine (0.5 mL) was added to a prepared *in situ* dark orange solution of [Fe(tdmba)] (3.8 mg, 0.008 mmol, 1 eq) in pyridine (0.3 mL). The reaction mixture was left stirring overnight. The ^1H NMR spectrum of the resulting solution indicates that no reaction occurs (Fig. S23).

Reaction of 3 with [Fe(tdmba)].

A blue solution of **3** (8.0 mg, 0.010 mmol, 1 eq.) in pyridine (0.5 mL) was added to a prepared *in situ* dark orange solution of [Fe(tdmba)] (4.7 mg, 0.010 mmol, 1 eq) in pyridine (0.3 mL). The reaction mixture was left stirring overnight, then centrifuged to remove KI. The ^1H NMR spectrum of the resulting solution shows that redox reaction has occurred between uranyl(V) and the Fe(III) complexes affording uranyl(VI) and Fe(II) complexes (Fig. S24).

3. NMR spectra.

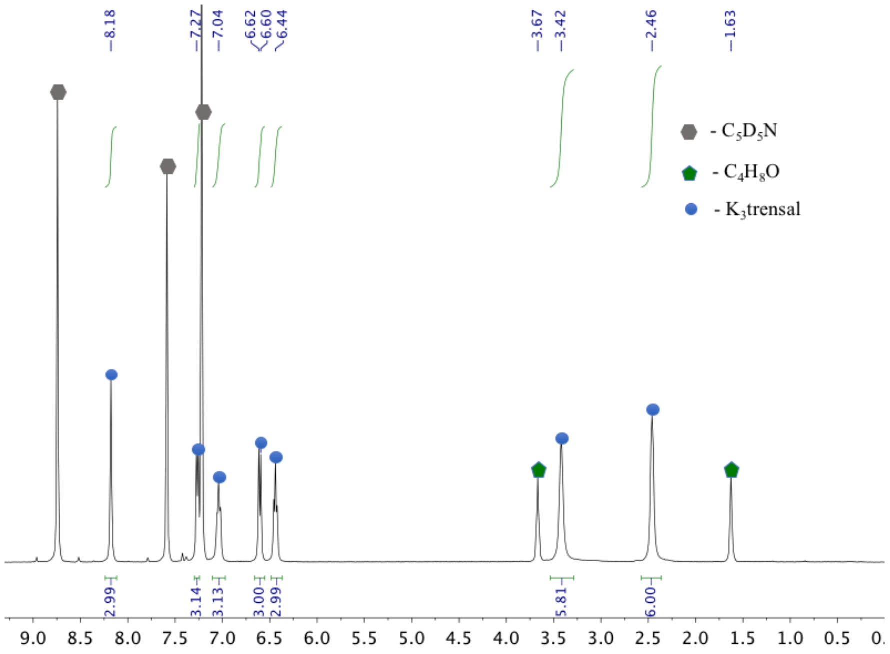

Figure S1. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the K_3trensal ligand.

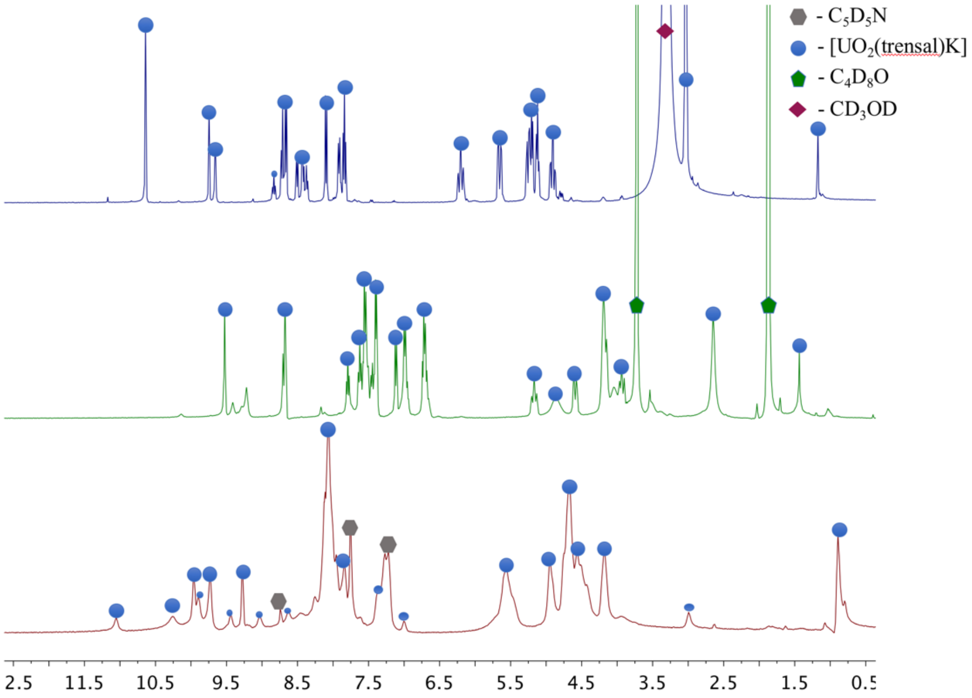

Figure S2. ^{1}H NMR spectrum (400 MHz, 298 K) of the complex $[UO_2$(trensal)K] (**1**) in C_5D_5N (bottom), **1** in C_4D_8O (middle) and **1** in CD_3OD (top).

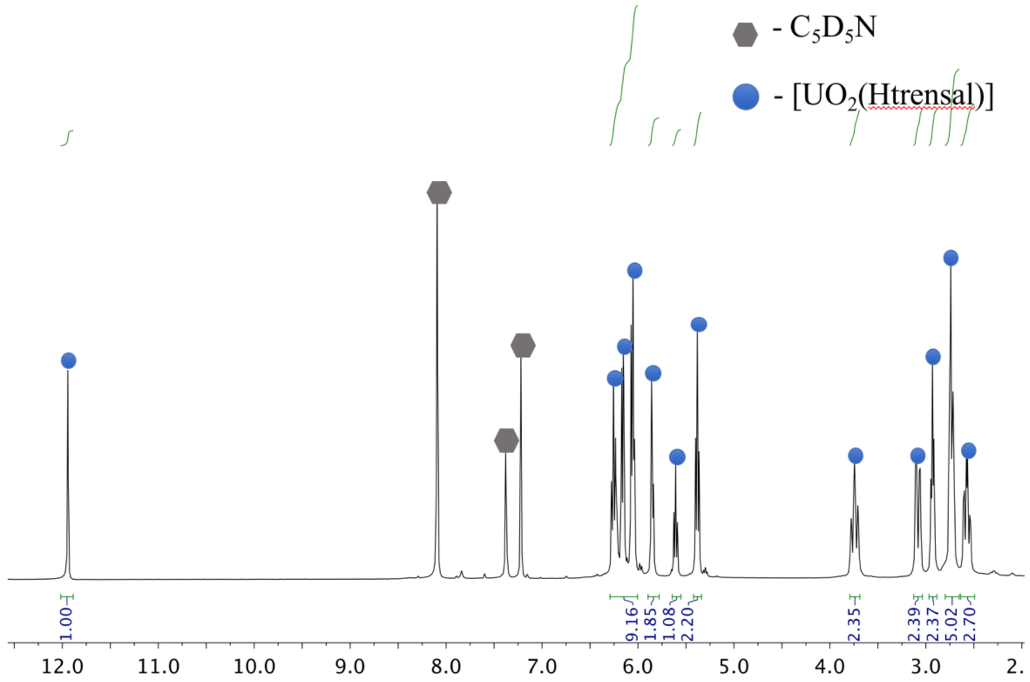

Figure S3. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the crystals of [UO_2(Htrensal)] (**2**).

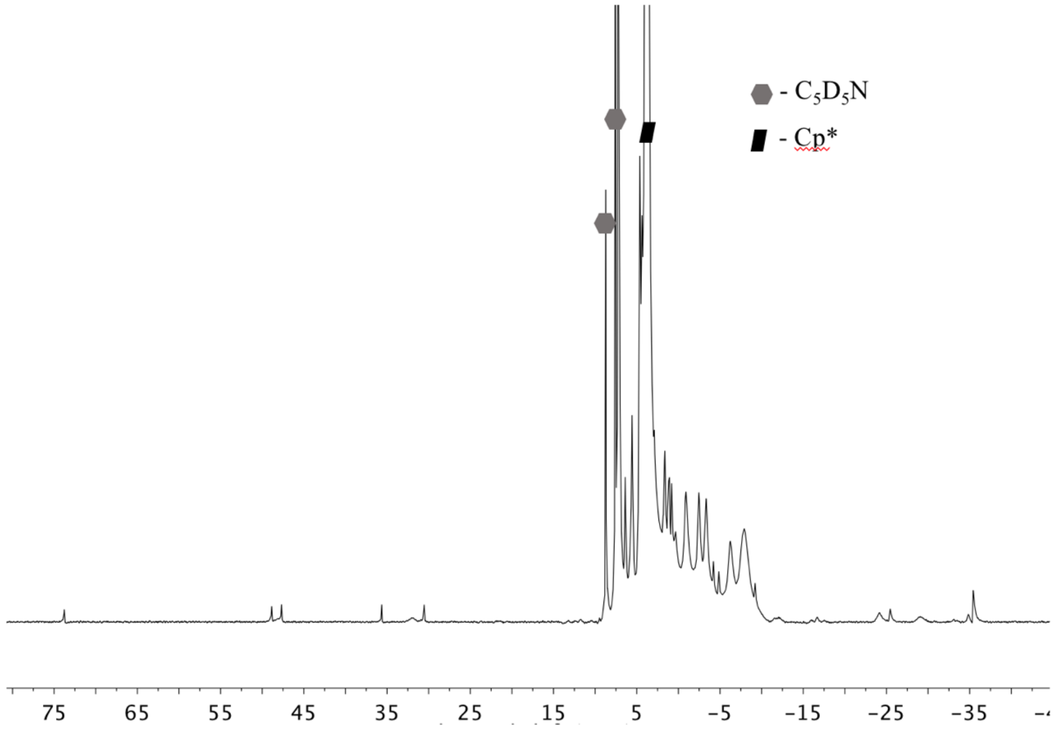

Figure S4. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the reaction mixture immediately after the addition of Cp^*_2Co to [UO_2(Htrensal)] (**2**) showing that the reduction of the protonated uranyl(VI) leads to disproportionation.

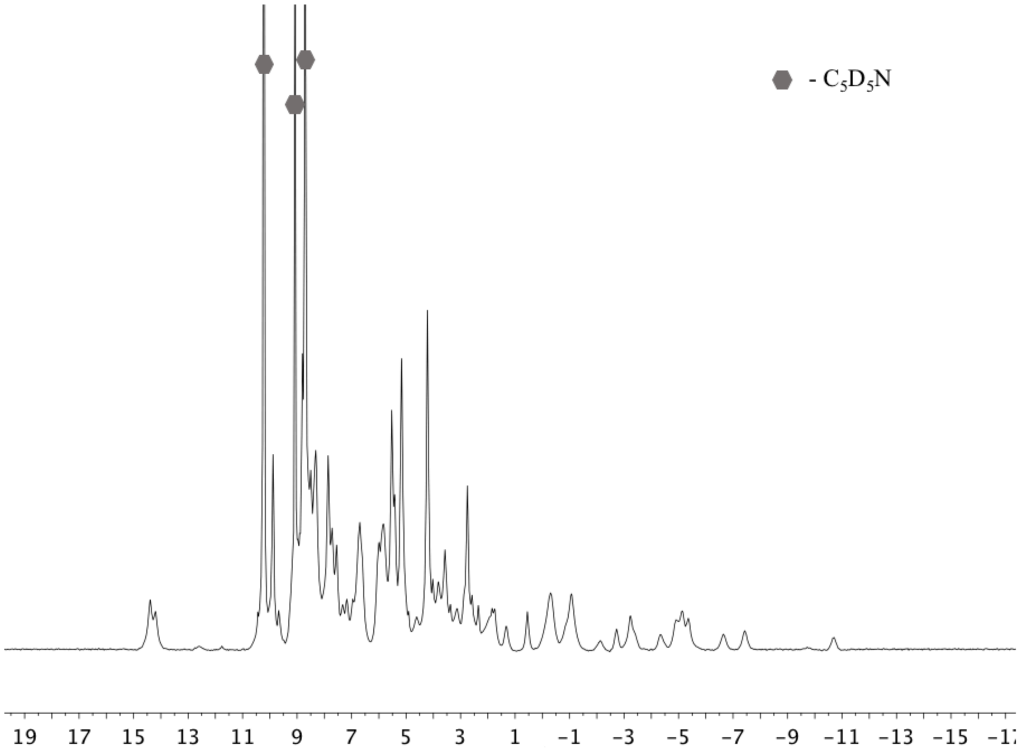

Figure S5. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of $[UO_2(trensal)K]K$ (**3**).

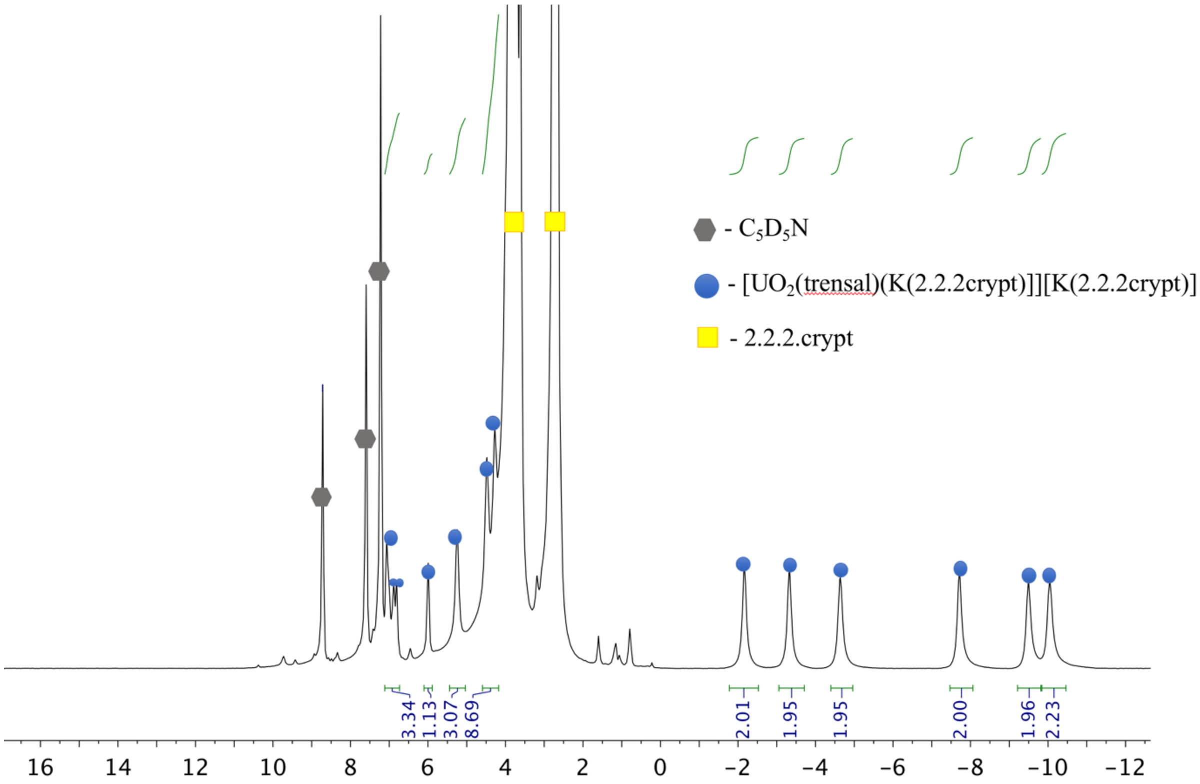

Figure S6. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of $[UO_2(trensal)(K(2.2.2crypt)]$ $[K(2.2.2crypt)]$ (**4**).

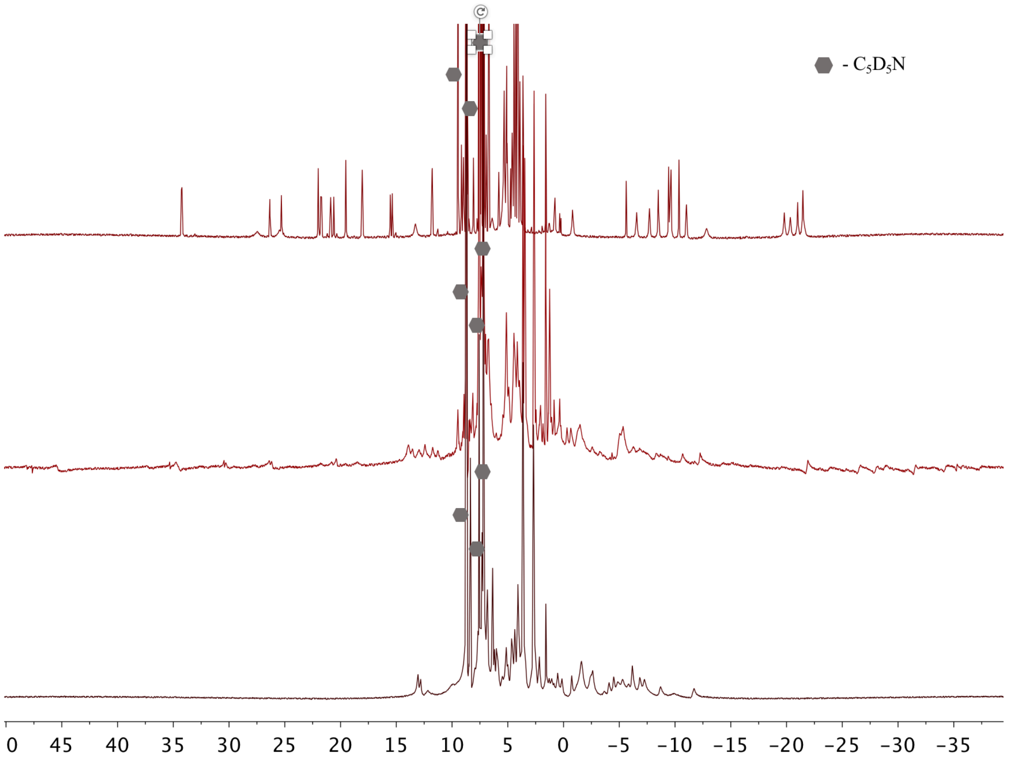

Figure S7. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of [UO_2(trensal)K]K (**3**) (bottom), of the reaction mixture of **3** + 1 eq. PyHCl (middle) and of **3** + 2 eq. PyHCl (top).

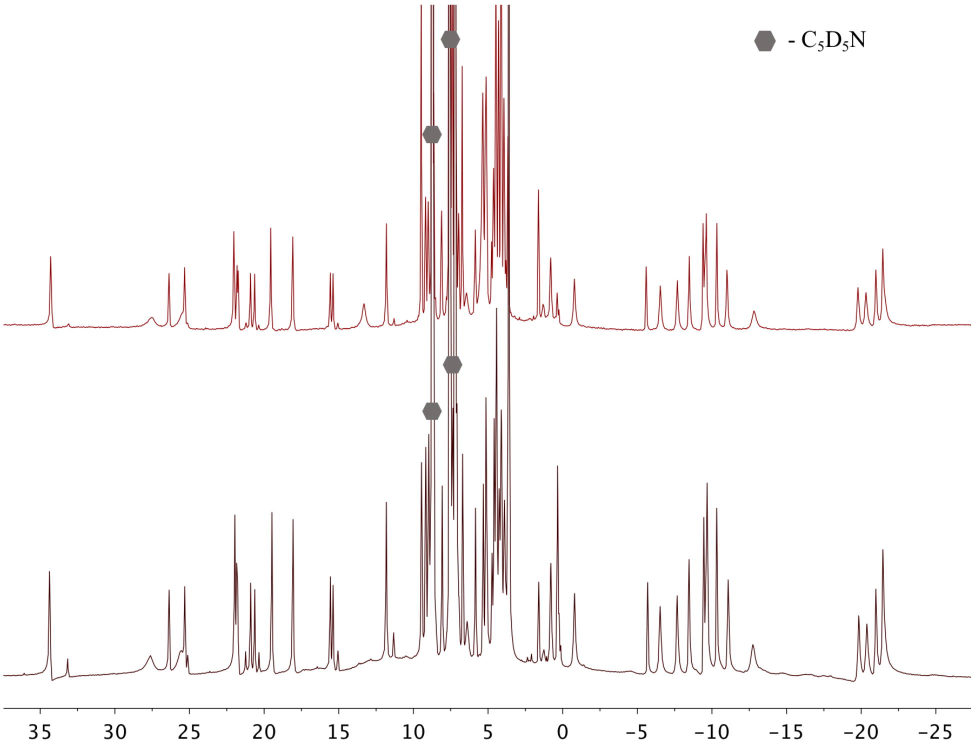

Figure S8. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the reaction mixture of [UO_2(trensal)K]K (**3**) + 2 eq. PyHCl (top) and of [UO_2(Htrensal)] **(2)** + U(trensal)I **(9)** + 2 H_2O (bottom).

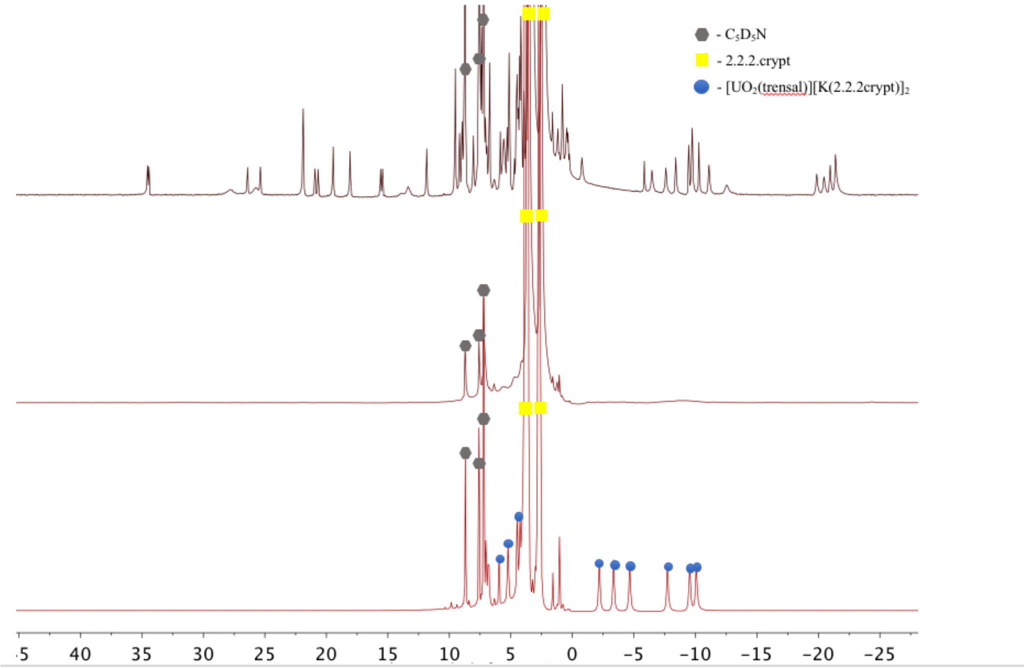

Figure S9. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of a solution of $[UO_2(trensal)(K(2.2.2crypt)][K(2.2.2crypt)]$, **4** (bottom) and immediately after the addition of 1 eq. PyHCl to **4** (middle), and 3 days after the addition of 2 eq. PyHCl to **4** (top).

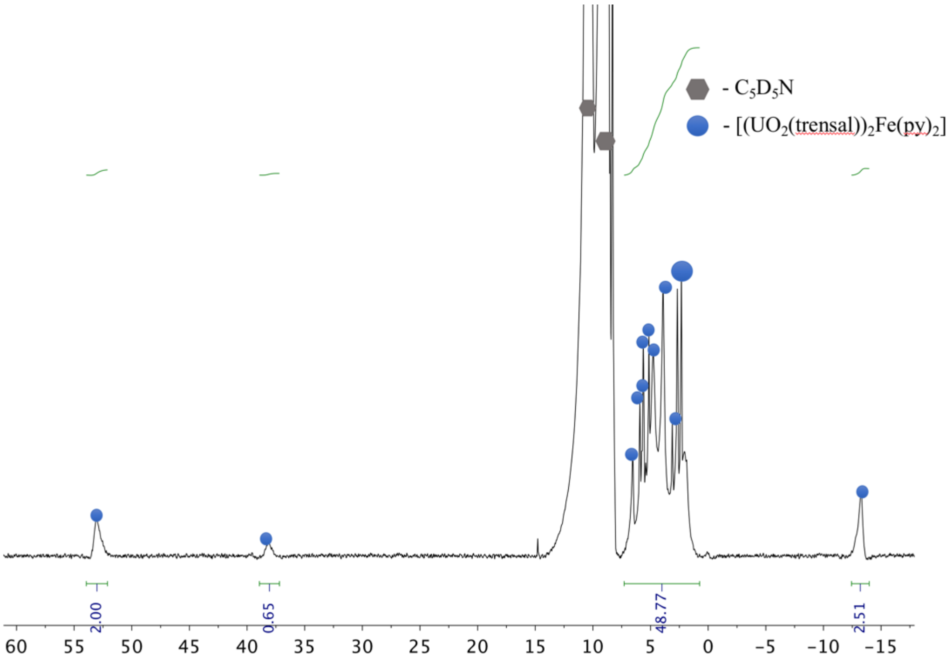

Figure S10. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of crystals of $[(UO_2(trensal))_2Fe(py)_2]$ (**5**).

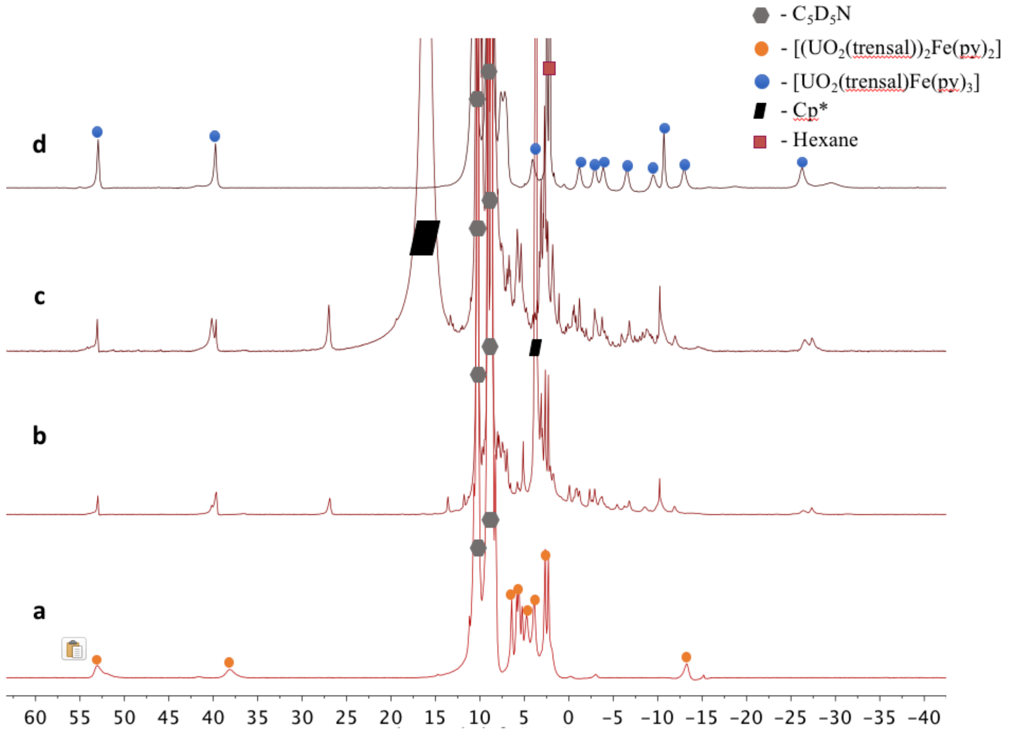

Figure S11. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of crystals of [(UO_2(trensal))$_2$Fe(py)$_2$] (**5**) (a), of the solution after addition of 1 eq. Cp_2*Co to **5** (b), addition of 2.5 eq. Cp_2*Co to **5** (c) and crystals of compound [UO_2(trensal)Fe(py)$_3$] **(6)** (d).

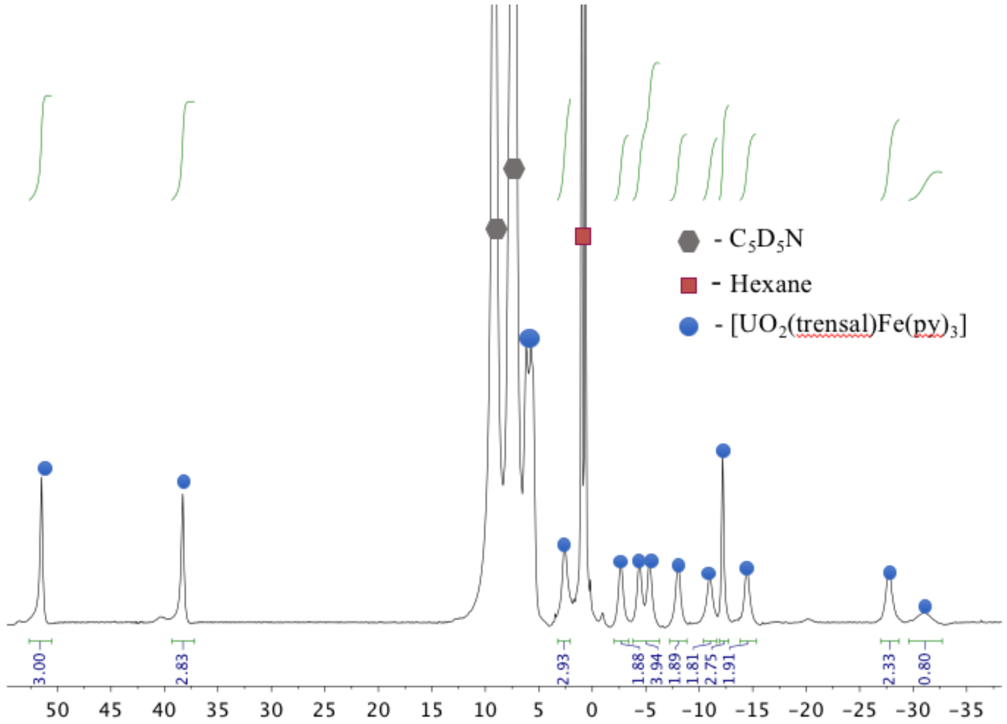

Figure S12. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of crystals of [UO_2(trensal)Fe(py)$_3$] (**6**).

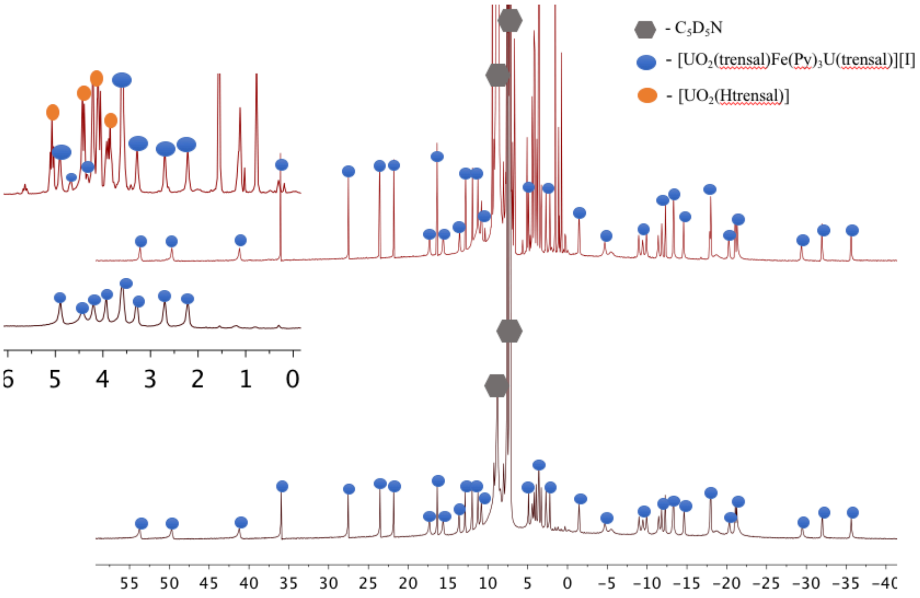

Figure S13. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of crystals of $[UO_2(trensal)Fe(py)_3U(trensal)]I$ (**7**) (bottom) and of the reaction mixture after the addition of 2 eq. of PyHCl to $[UO_2(trensal)Fe(py)_3]$ (**6**) (top)(*Inset:* Zoom of the diamagnetic region (0-6 ppm) of the spectra).

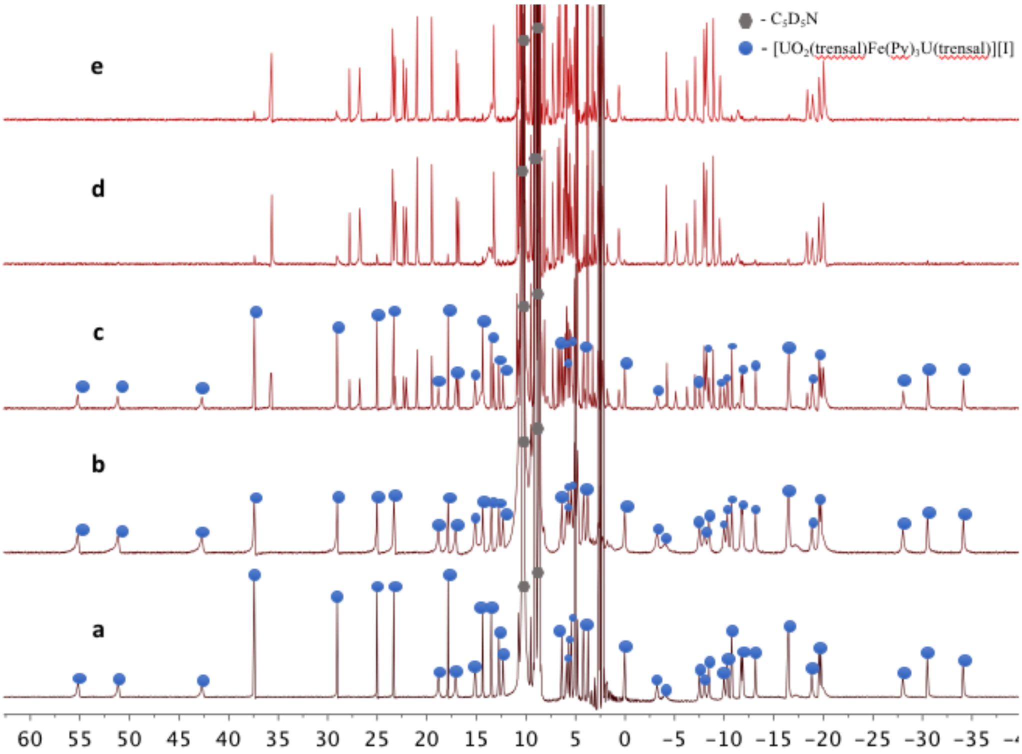

Figure S14. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the crystals of compound $[UO_2(trensal)Fe(py)_3U(trensal)]I$ (**7**) (a) and of the reaction mixtures after : addition of 1 eq. of PyHCl to $[UO_2(trensal)Fe(py)_3]$ (**6**) (b), addition of 3 eq. of PyHCl to **6** (c), addition of 5 eq. of PyHCl to **6** (d) and addition of 2 eq. of PyHCl to $[UO_2(trensal)K]K$ **(3)** (e).

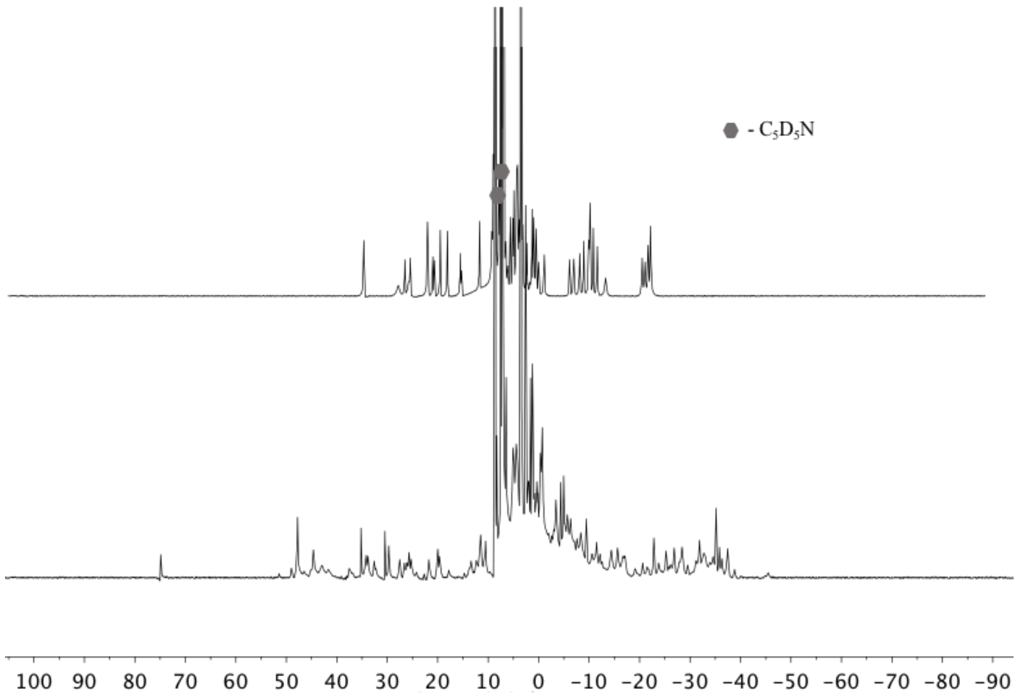

Figure S15. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the addition of [U(trensal)]I (**9**) to complex UO_2(trensal)K]K (**3**) (bottom) and addition of 2 eq. PyHCl to the 1:1 mixture of [U(trensal)]I, **9** and complex **3**.

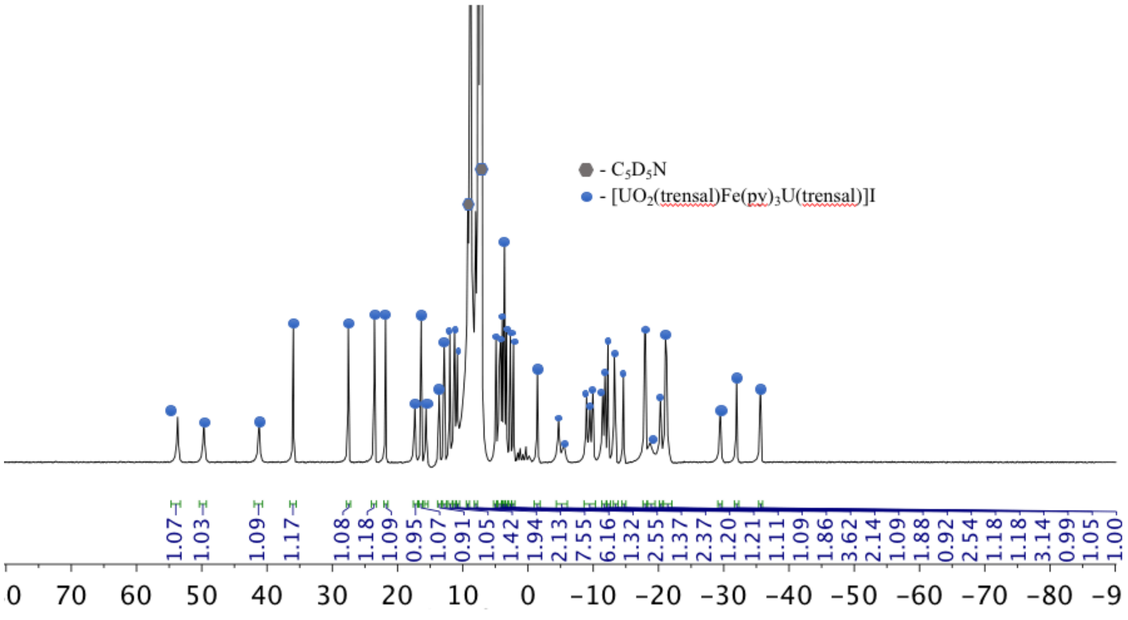

Figure S16. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of crystals of $[UO_2(trensal)Fe(py)_3U(trensal)]I$ (**7**).

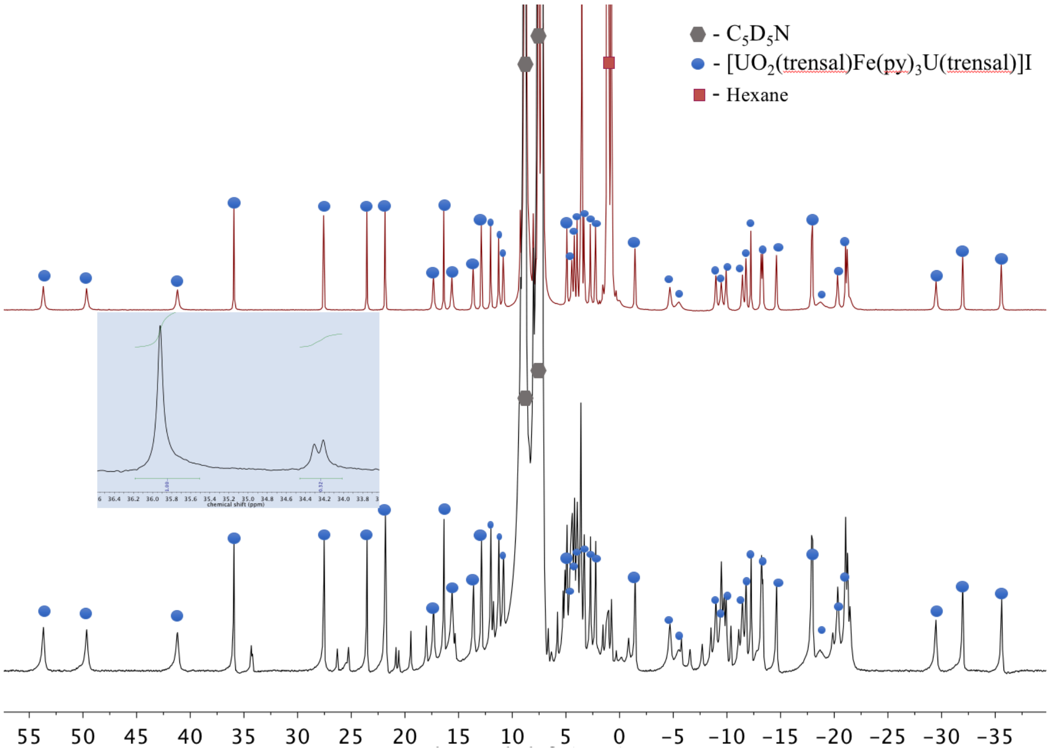

Figure S17. ^1H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the crystals of compound $[UO_2(trensal)Fe(py)_3U(trensal)]I$ (**7)** (top) and of the reaction mixture after addition of 1 eq. of PyHCl to **7** (bottom) (*Inset:* zoom in on the 33.6 – 36.6 ppm region of the bottom spectrum, showing a 3:1 ratio of **7** to decomposition products).

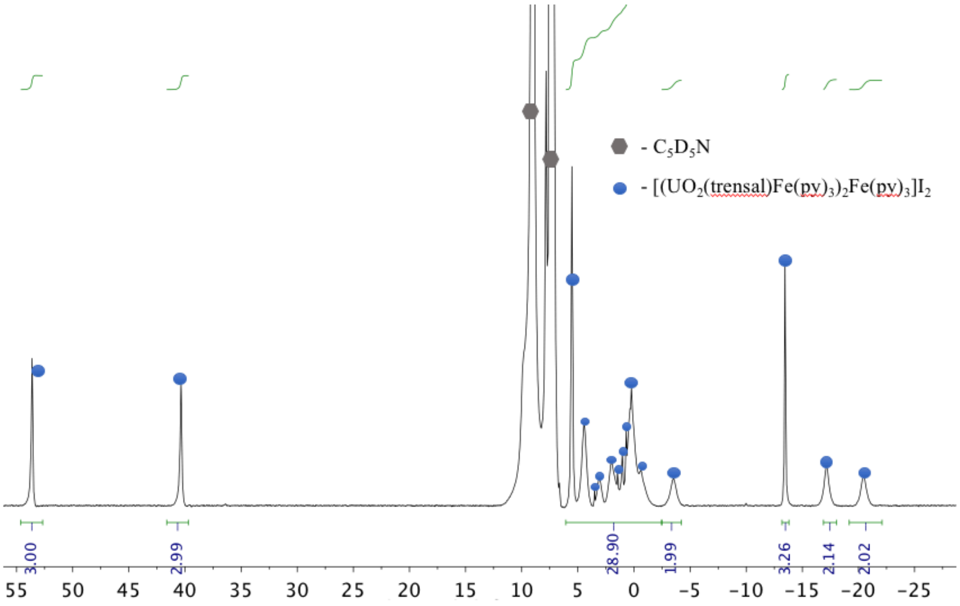

Figure S18. ^1H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the crystals of $[(UO_2(trensal)Fe(py)_3)_2Fe(py)_3]I_2$ **(8)**.

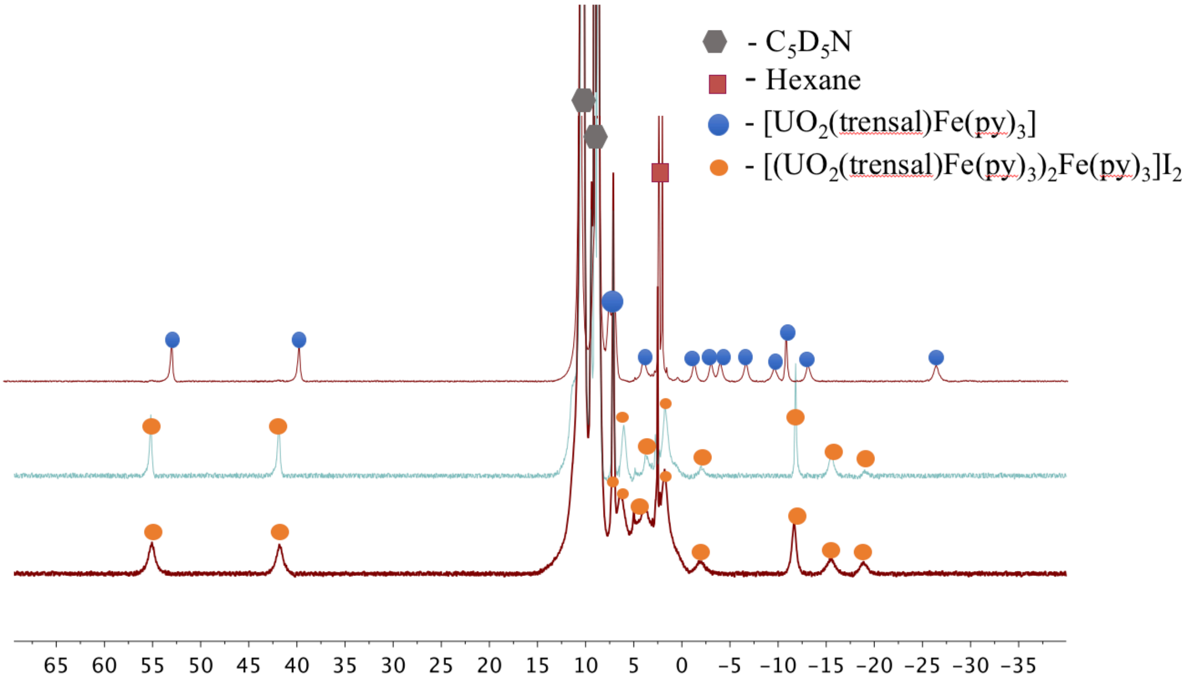

Figure S19. ^{1}H NMR spectrum (400 MHz, C$_5$D$_5$N, 298 K) of the crystals of compound [(UO$_2$(trensal)Fe(py)$_3$)$_2$Fe(py)$_3$]I$_2$ (**8**) (bottom), of crystals of [UO$_2$(trensal)Fe(py)$_3$] (**6**) (top) and of the reaction mixture after addition of 1 eq. of **6** to **8** (middle).

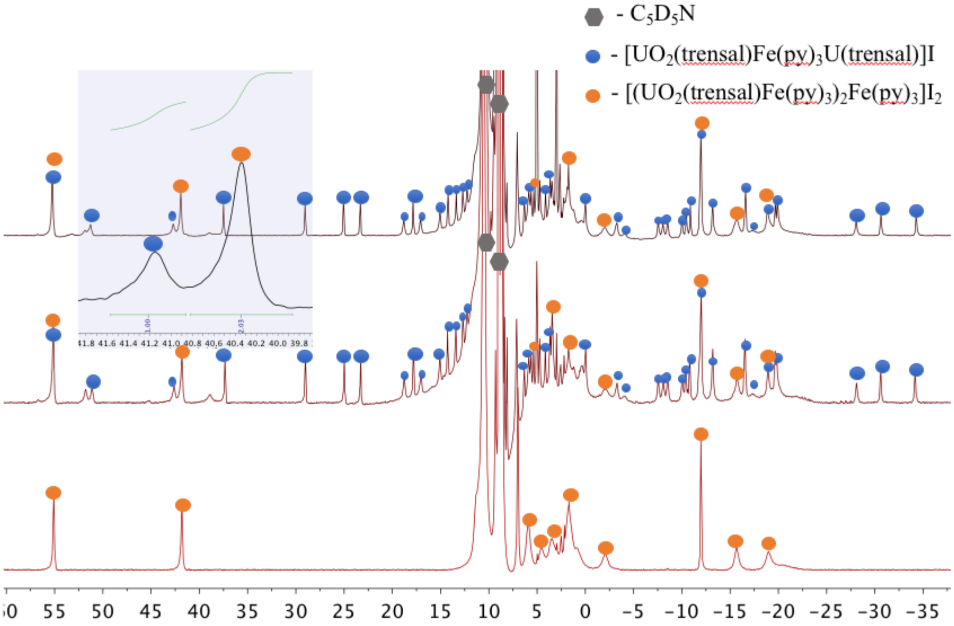

Figure S20. ^{1}H NMR spectrum (400 MHz, C$_5$D$_5$N, 298 K) of crystals of [(UO$_2$(trensal)Fe(py)$_3$)$_2$Fe(py)$_3$]I$_2$ (**8**) (bottom), of the reaction mixture after addition of 2 eq. of PyHCl to **8** (middle), of the reaction mixture after addition of 1 eq. of PyHCl to [UO$_2$(trensal)Fe(py)$_3$] (**6**) (top) *Inset:* zoom in on the 33.6 – 36.6 ppm region showing the 2:1 ratio of **8** to disproportionation product that is the same as that found for the reaction of 2 eq. of PyHCl with complex **6**.

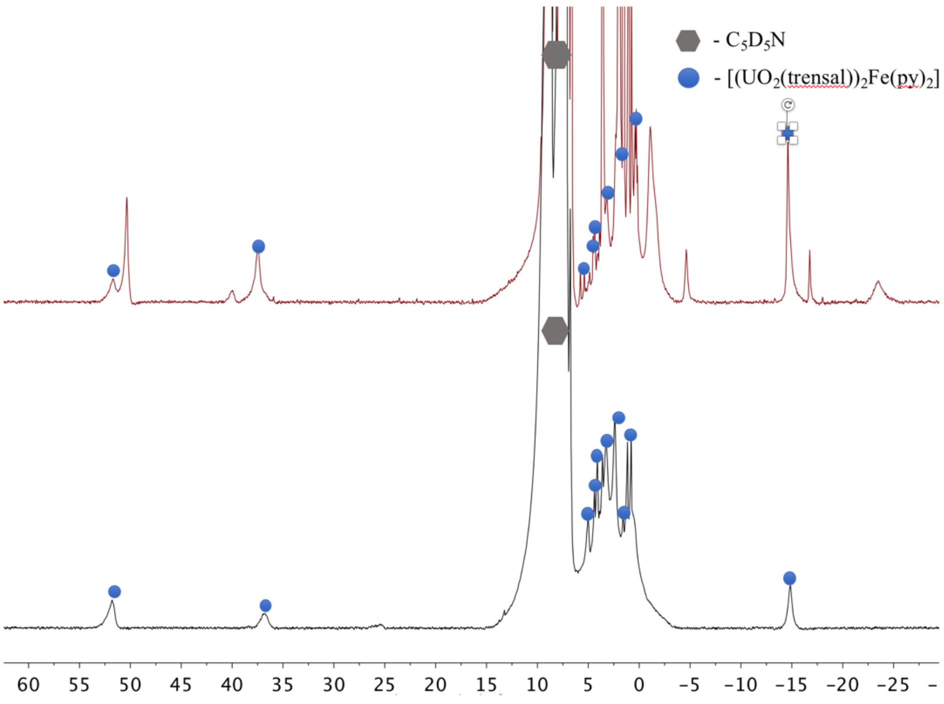

Figure S21. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the crystals of compound $[(UO_2(trensal))_2Fe(py)_2]$ **5** (bottom) and of the reaction mixture after the reaction of $[UO_2(trensal)K]K$ **(3)** with $FeCl_3$ (top).

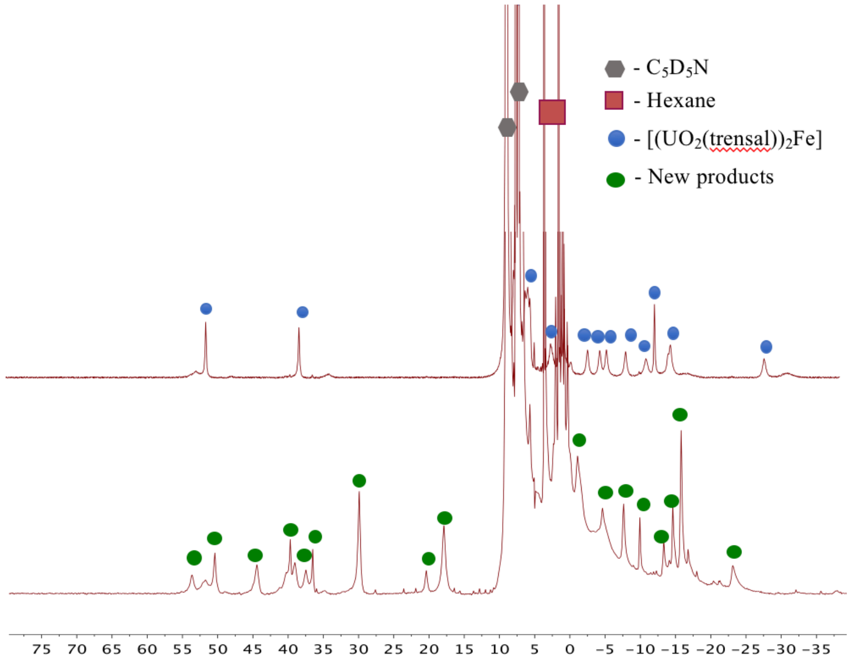

Figure S22. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the crystals of compound $[(UO_2(trensal))_2Fe(py)_2]$ **(6)** (top) and of the reaction mixture after the reaction of **6** with $[Fe(tpa)Cl_3]$ (bottom).

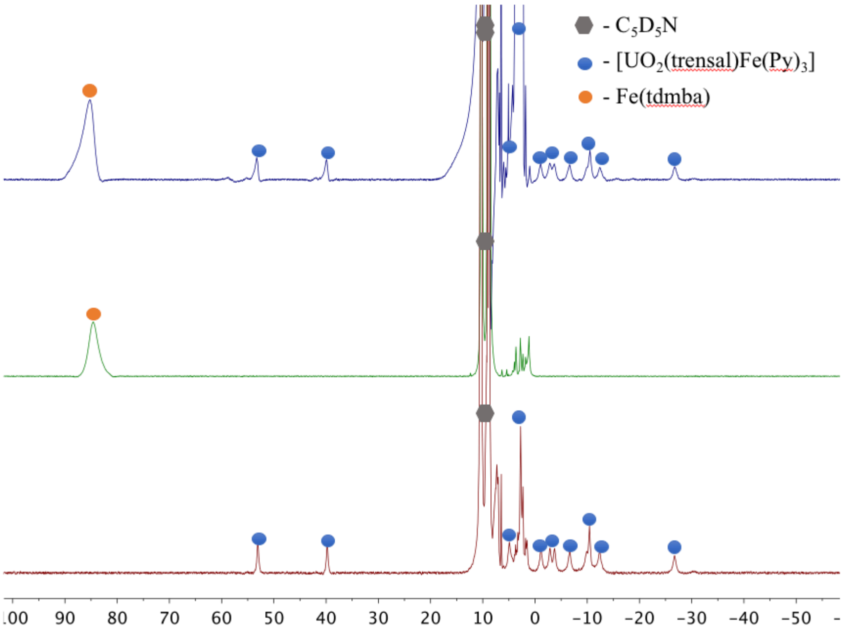

Figure S23. ^1H NMR spectrum (400 MHz, C_5D_5N, 298 K) of $[UO_2(trensal)Fe(py)_3]$ (**6**) (bottom) of [Fe(tdmba)] (middle) and after addition of [Fe(tdmba)] to **6** in pyridine (top).

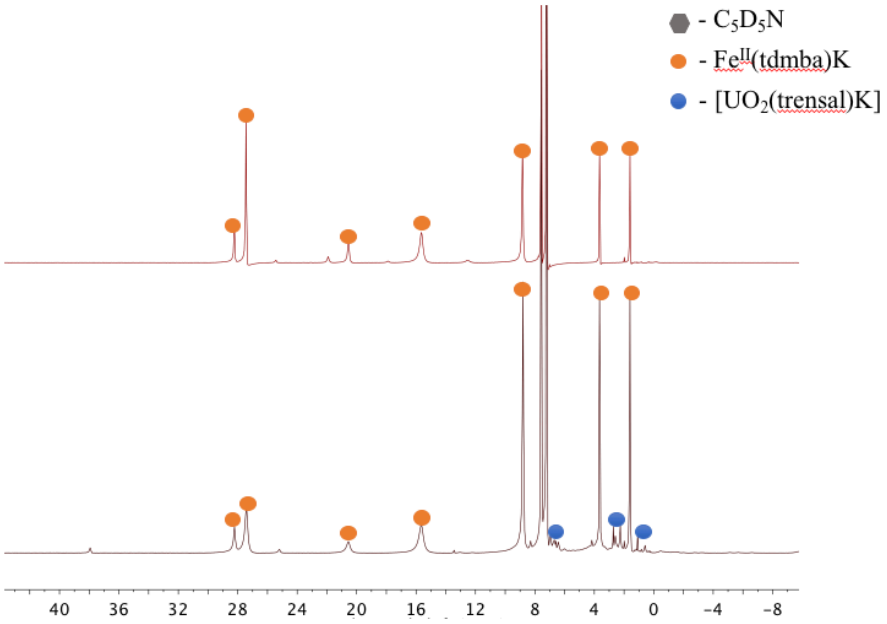

Figure S24. ^1H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the reaction mixture after addition of [Fe(tdmba)] to $[UO_2(trensal)K]K$ (**3**) in pyridine (bottom) and of the complex [Fe(tdmba)]K (top).

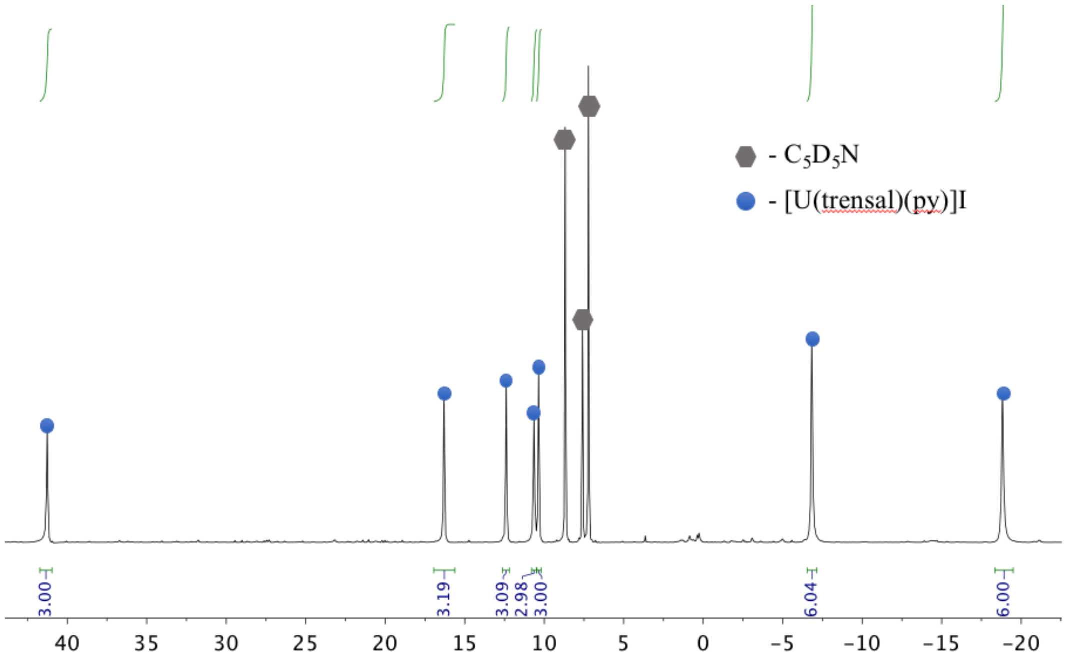

Figure S25. ^{1}H NMR spectrum (400 MHz, C_5D_5N, 298 K) of the crystals of compound [U(trensal)(py)]I (**9**).

4. Mass Spectroscopy

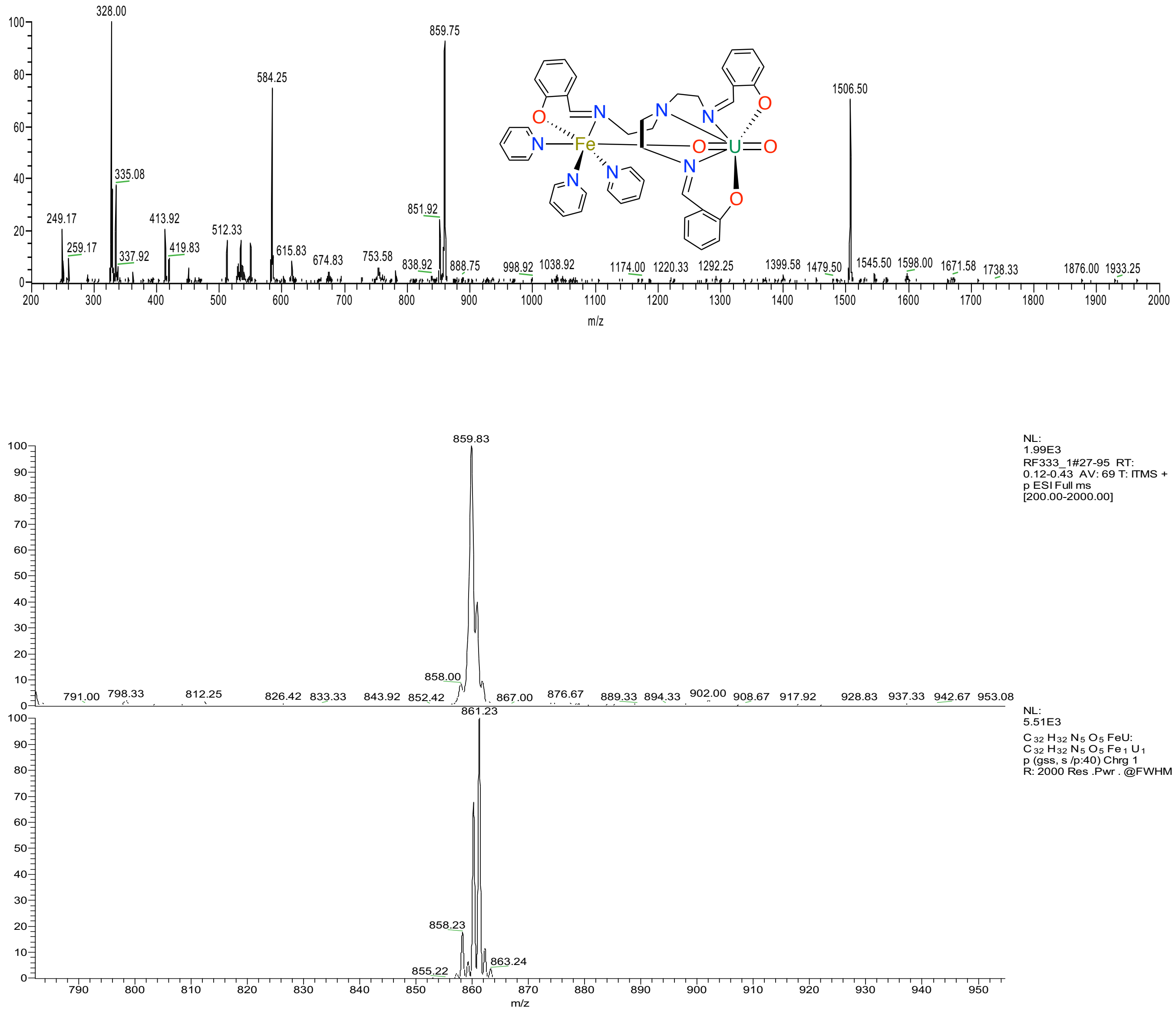

Figure S26: ESI/MS spectra of **6**-[UO$_2$(trensal)Fe(Py)$_3$], in pyridine (top) and zoom on the molecular peak (centre) compared with the theoretical isotopic (bottom) profile calculated for *{UO$_2$(trensal)Fe(Py)$^+$} m/z = 859.83.*

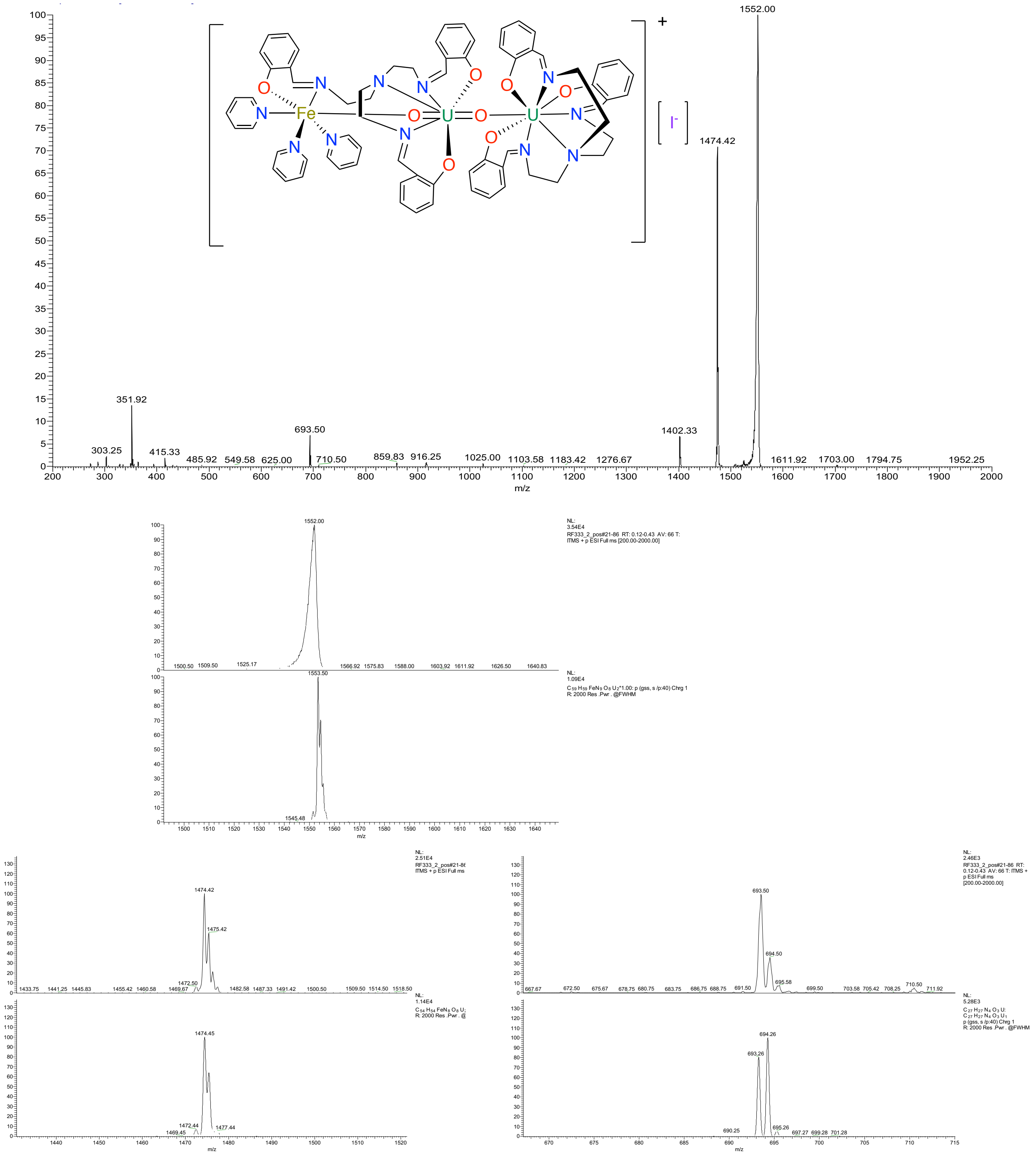

Figure S27: ESI/MS spectra of **8-**[UO$_2$(trensal)Fe(py)$_3$U(trensal)][I], in pyridine (top) and zoom on the molecular peak (centre left) compared with the theoretical isotopic profile calculated for *{UO$_2$(trensal)Fe$_3$U(trensal)(Py)$^+$} m/z = 1552.00;* zoom on the molecular peak (centre right) compared with the theoretical isotopic profile calculated for {UO$_2$(trensal)Fe$_3$U(trensal)$^+$} *m/z = 1474.42;* zoom on the molecular peak (bottom) compared with the theoretical isotopic profile calculated for {U(trensal)$^+$} *m/z = 693.50*

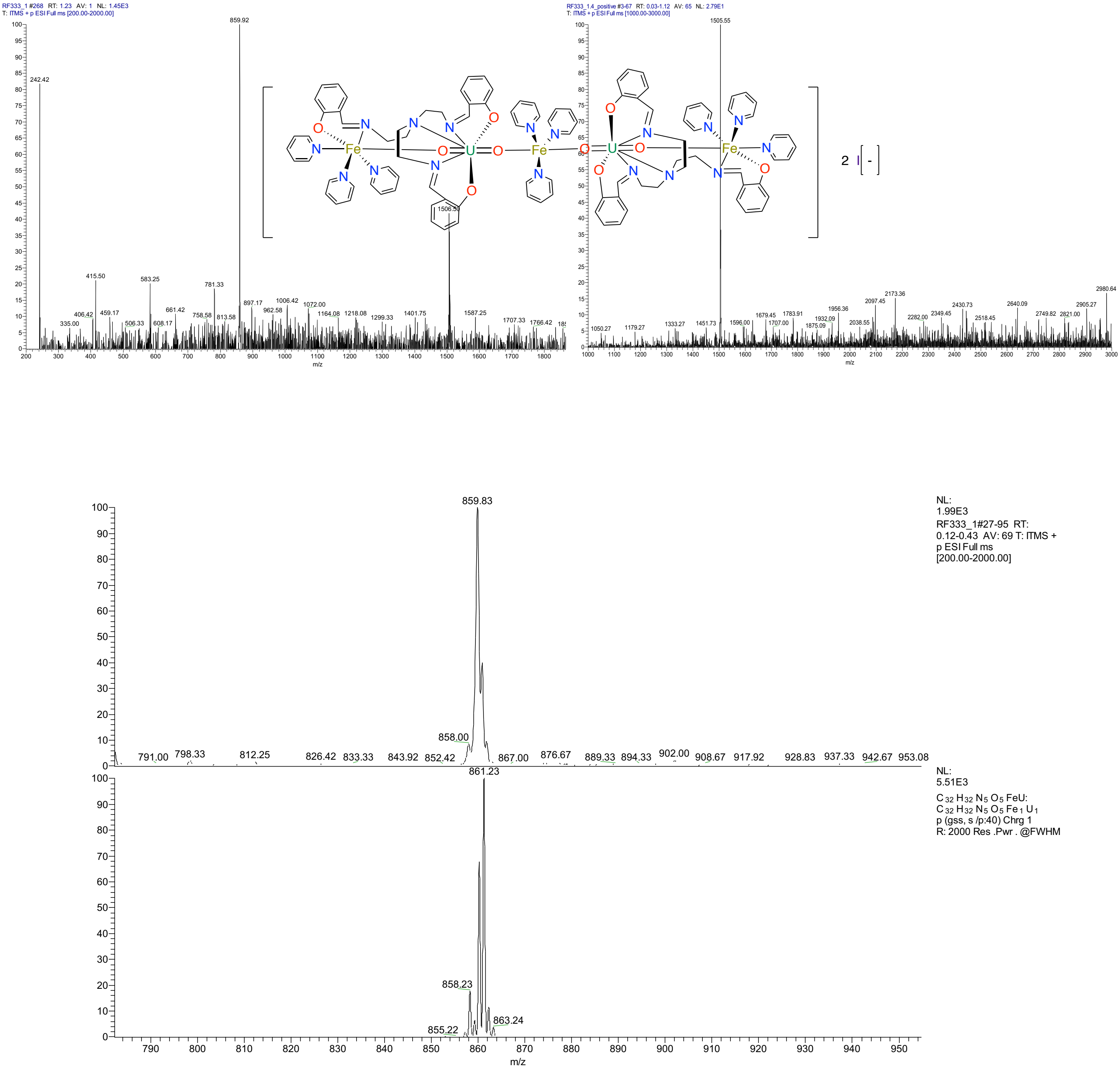

Figure S28: ESI/MS spectra of **7-**[(UO$_2$(trensal)Fe(Py)$_3$)$_2$Fe(Py)$_3$]I$_2$] in pyridine (top) and zoom on the molecular peak (bottom) compared with the theoretical isotopic profile calculated for calculated for *{UO$_2$(trensal)Fe(Py)$^+$} m/z = 859.83.*

5. EPR

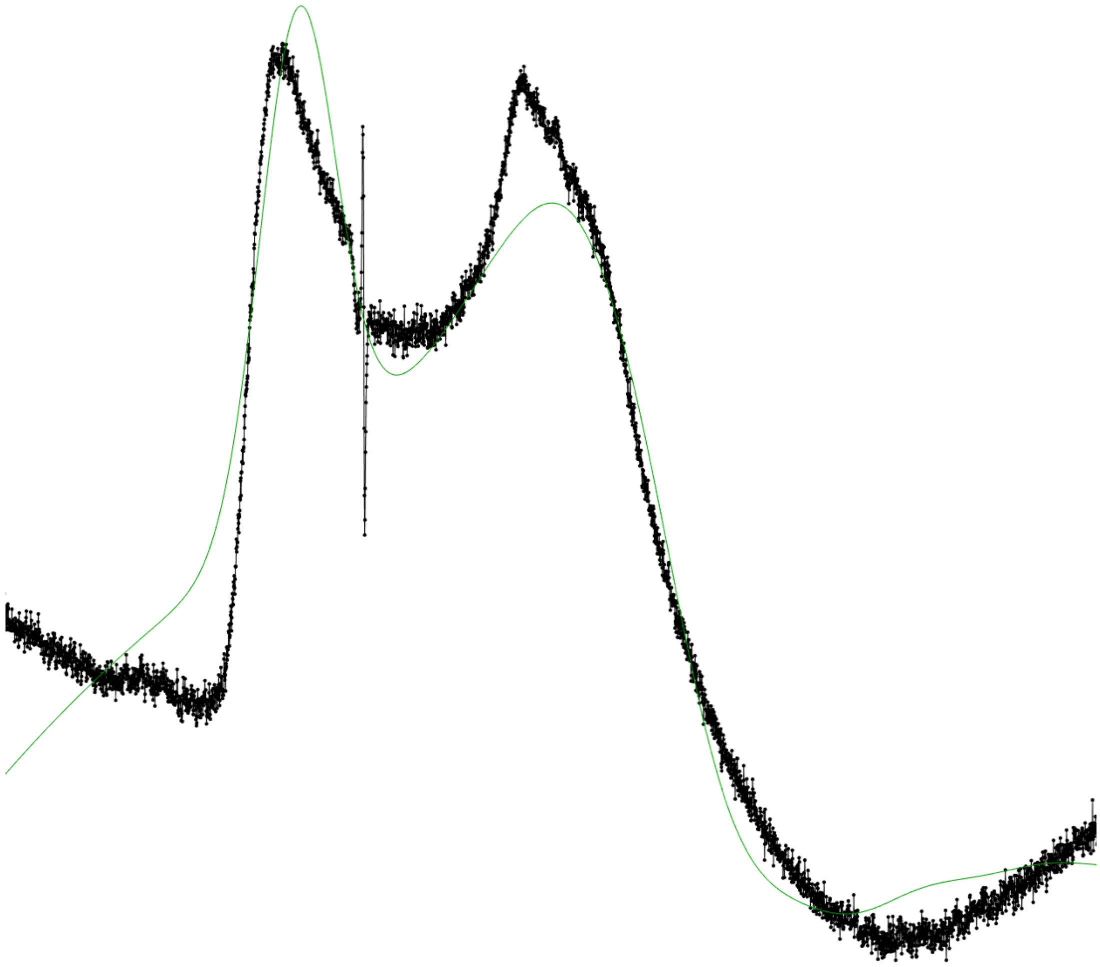

Figure S29. Band (9.40 GHz) EPR spectrum of crystals of **4** in the solid state at 10 K (black lines) and simulated EPR spectrum (green lines).

6. Electrochemistry

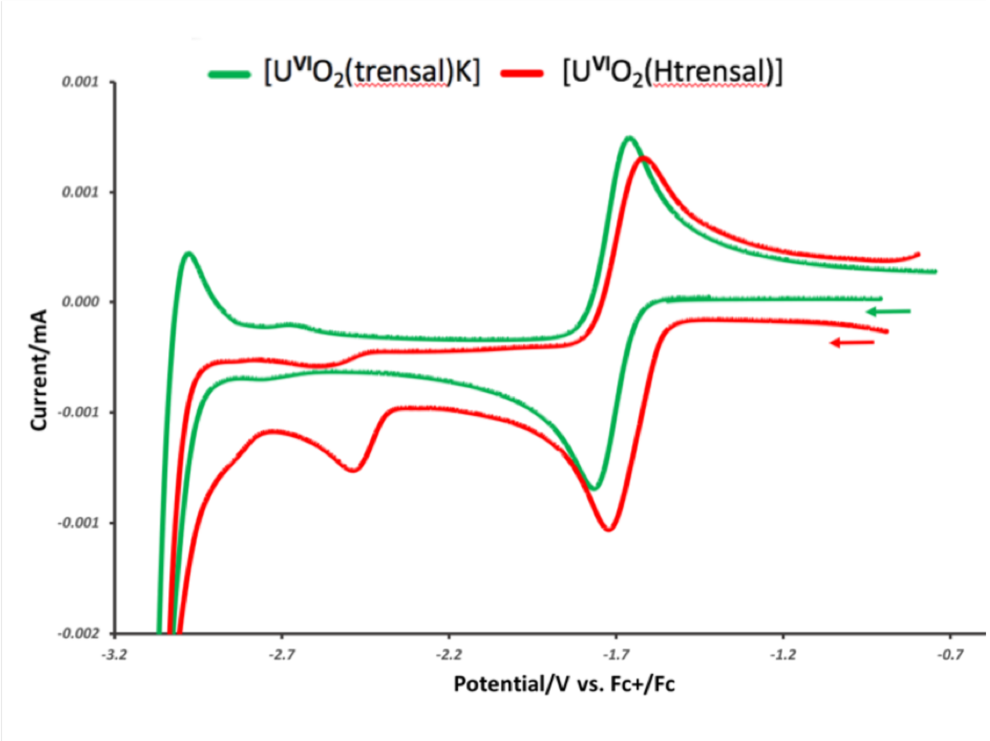

Figure SCV1. Room temperature cyclic voltammograms for [$U^{VI}O_2$(Htrensal)] **2** (red) and [$U^{VI}O_2$(trensal)K], **1** (green) recorded in 0.1 M [Bu_4N][PF_6] in 2 mM pyridine solution at 100 mV/s scan rate, Cp_2Fe/Cp_2Fe^+ corrected**.**

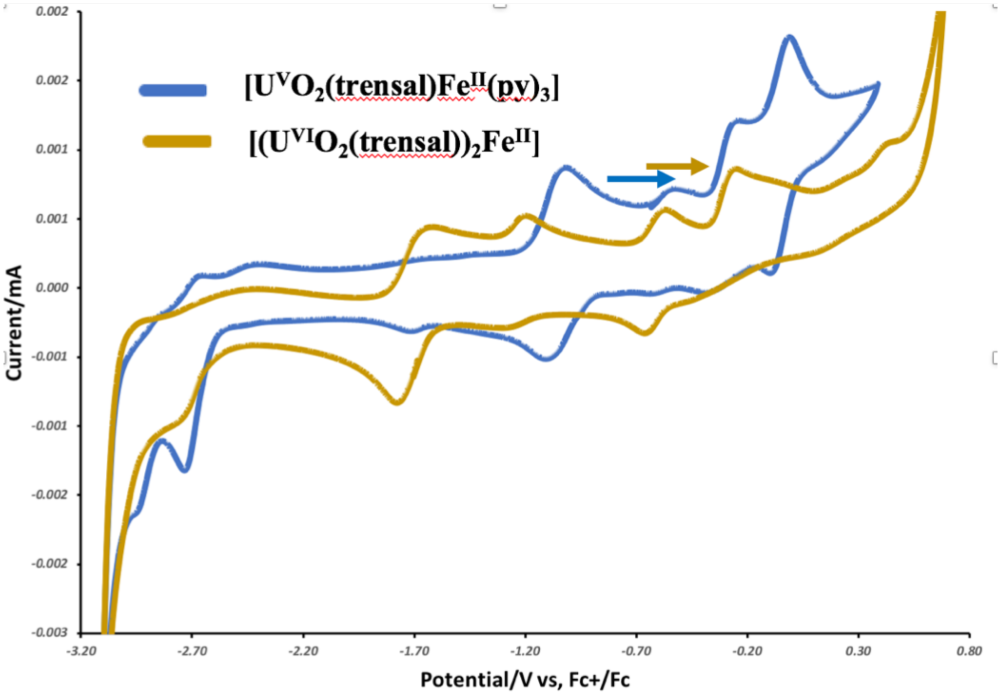

Figure SCV2. Room temperature cyclic voltammograms for and [U^VO_2(trensal)Fe^{II}(py)$_3$] **6** (blue) and [($U^{VI}O_2$(trensal))$_2Fe^{II}$] **5** (mustard) recorded in 0.1 M [Bu_4N][PF_6] in 2 mM pyridine solution at 100 mV/s scan rate, Cp_2Fe/Cp_2Fe^+ corrected.

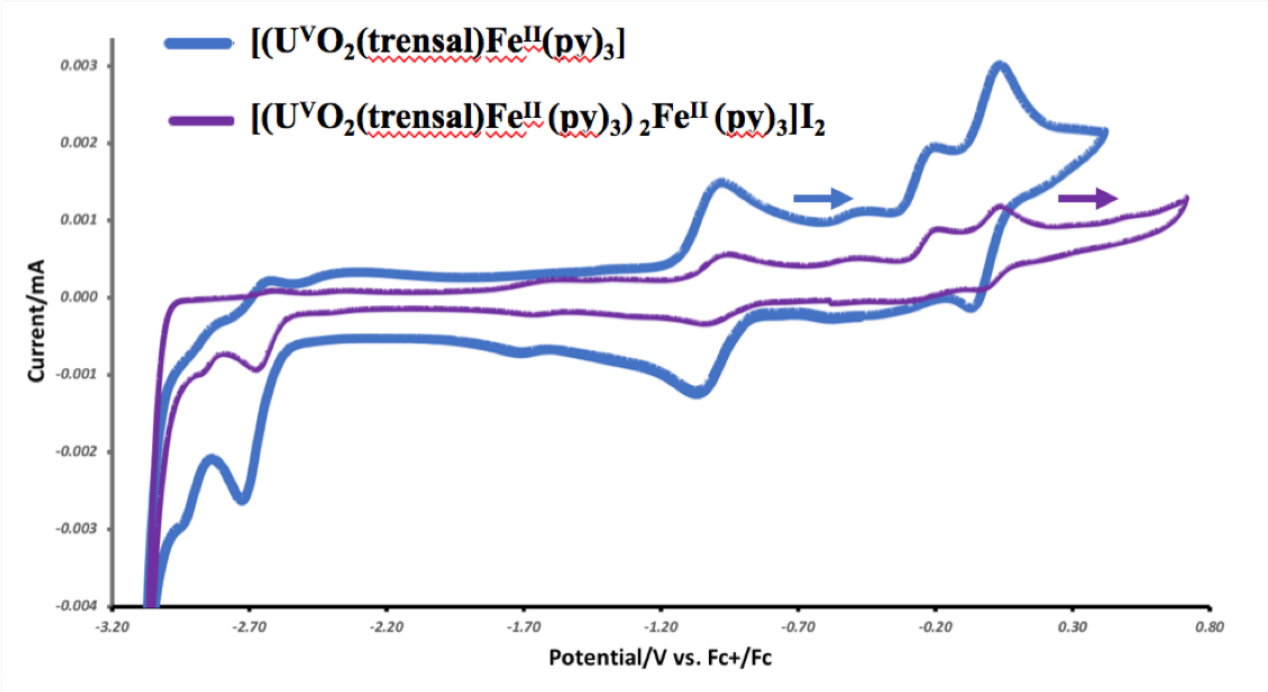

Figure SCV3. Room temperature cyclic voltammograms for $[U^VO_2(trensal)Fe^{II}(py)_3]$ **6** (blue) and $[(U^{VI}O_2(trensal)Fe^{II}(py)_3)_2Fe(py)_3]I_2$ **8** (purple) recorded in 0.1 M $[Bu_4N][PF_6]$ in 2 mM pyridine solution at 100 mV/s scan rate, Cp_2Fe/Cp_2Fe^+ corrected**.**

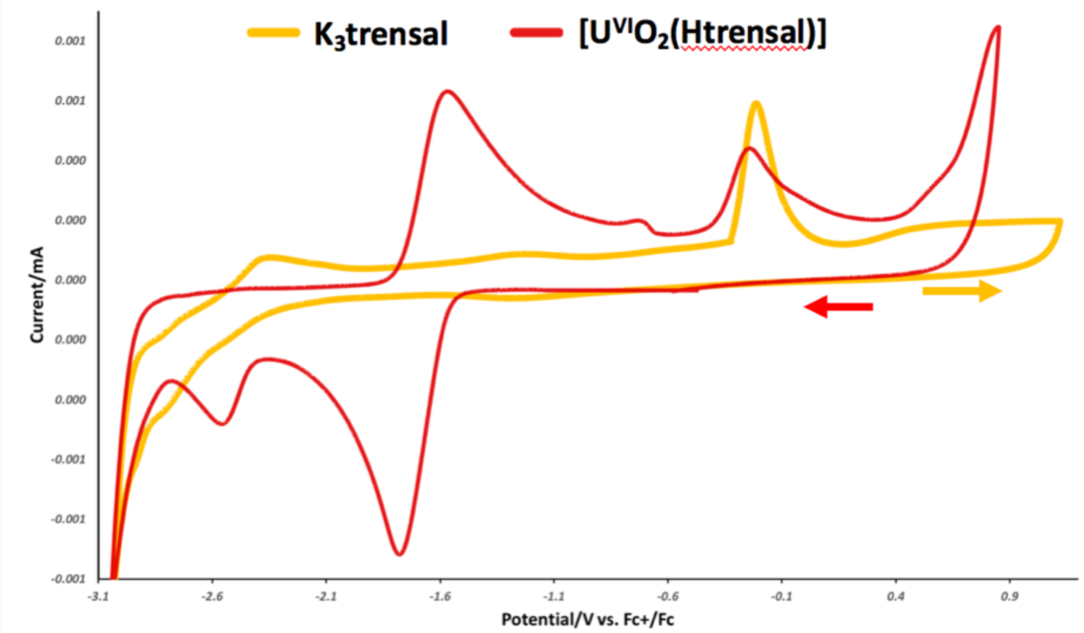

Figure SCV4. Room temperature cyclic voltammograms for $[U^{VI}O_2(Htrensal)]$ **2** (red) and $K_3trensal$ (yellow) recorded in 0.1 M $[Bu_4N][PF_6]$ in 2 mM pyridine solution at 100 mV/s scan rate, Cp_2Fe/Cp_2Fe^+ corrected**.**

Table S1. Redox potential of [UO_2(trensal)K] after addition of cryptand to increase solubility(**1**), [UO_2(trensal)H] (**2**), [(UO_2(trensal))$_2$Fe] (**5**), [UO_2(trensal)Fe(py)$_3$] (**6**) and [(UO_2(trensal)Fe(py)$_3$)$_2$Fe(py)$_3$]I_2 (**8**) complexes.

Complex	**$E_{1/2}$ U(VI)/U(V)**	**E U(V)/U(IV)**
[UO_2(trensal)K], **1**+cryptand	*-1.69 V*	-
[UO_2(trensal)H], **2**	*- 1.66 V*	*-2.47 V*
[(UO_2(trensal))$_2$Fe], **5**	*- 1.66 V*	*-2.70 V*
[UO_2(trensal)Fe(py)$_3$], **6**	*-1.03 V*	*-2.70 V*
[(UO_2(trensal)Fe(py)$_3$)$_2$Fe(py)$_3$]I_2, **8**	*-1.03 V*	*-2.70 V*

7. X-ray Crystal Structure Determination Details

The diffraction data of **4** and **7** were measured at low temperature using Mo K_α radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. Both datasets were reduced by *EvalCCD*[5] and then corrected for absorption.[6] The data collection of compounds **2**, **5**, **6** and **8** were measured at low temperature using Cu K_α radiation on an Agilent Technologies SuperNova dual system in combination with an Atlas CCD detector (type 1 or 2). The data reduction was carried out by Crysalis$^{\mathrm{Pro}}$.[7] The solutions and refinements were performed by *SHELX*.[8] The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. All hydrogen atoms (including the H forming the intramolecular bond in **2**) were placed in calculated positions by means of the "riding" model.

In the case of the crystal structure of **4**, the refinement of light atoms was difficult because crystal was very weak, being 0.953 Å the highest resolution, and rigid bond restraints (RIGU card) were used in the last stages of least-squares, in combination with *SQUEEZ*[9] to remove the electron density due to the disordered solvent. However, the connectivity is well established by the structural data. The same rigid bond restraints were employed for the crystal structure or compound **7**, whereas in the case of **8** all the pyridine solvent molecules displayed rotational disorder and were removed by the *SQUEEZE*[9] algorithm in *OLEX2*.[10]

CCDC Numbers for the crystals structures deposited at the Cambridge Crystallographic Data Center: Complex **2**: CCDC 1842376 - Complex **4**: CCDC 1842377- Complex **5**: CCDC 1842378- Complex **6**: CCDC 1842379- Complex **7**: CCDC 1842380- Complex **8**: CCDC 1842381- Complex **9**: CCDC 1842382.

Table S2. Crystallographic parameters for complexes 2, 4-9.

	2.py	**4**	**5**
Formula	$C_{32}H_{233}N_5O_5U$	$C_{63}H_{99}K_2N_8O_{17}U$	$C_{64}H_{64}FeN_{10}O_{10}U_2$
Crystal size (mm^3)	0.319 x 0.170 x 0.12	0.336 x 0.156 x 0.111	0.135 x 0.087 x 0.025
cryst syst	Triclinic	Triclinic	Monoclinic
space group	$P1$	$P1$	$C2/c$
volume (Å^3)	1500.76(7)	3997(6)	8465(4)
a (Å)	10.3182(3)	12.542(6)	46.746(5)
b (Å)	12.47104(19)	13.779(10)	13.2744(3)
c (Å)	12.8143(3)	23.86(3)	24.296(3)
α (deg)	82.2874(17)	81.55(6)	90
β (deg)	68.197(3)	78.59(5)	145.84(3)
γ (deg)	79.3609(17)	86.58(4)	90
Z	2	2	4
formula weight (g/mol)	805.66	1551.69	1665.16
density (g cm^{-3})	1.783	1.289	1.307
absorption coefficient (mm^{-1})	15.630	2.196	11.557
F(000)	784	1588	3232
temp (K)	100.01(10)	120(2)	100.01(10)
total no. reflections	10197	37059	30689
unique reflections [R(int)]	6064 [0.0183]	9507 [0.1127]	8737 [0.0238]
Final R indices [I > 2σ(I)]	$R_1 = 0.0256$, $wR_2 = 0.0673$	$R_1 = 0.1093$, $wR_2 = 0.2765$	$R_1 = 0.0182$, $wR_2 = 0.0480$
Largest diff. peak and hole (e.A^{-3})	1.890 and -2.137	2.393 and -2.380	1.461 and -0.845
GOOF	1.148	1.110	1.069

	6.py.0.5hex	**7**	**8**
Formula	$C_{50}H_{54}FeN_8O_5U$	$C_{69}H_{69}FeIN_{11}O_8U_2$	$C_{99}H_{99}Fe_3I_2N_{17}O_{10}U_2$
Crystal size (mm^3)	0.276 x 0.196 x 0.116	0.329 x 0.312 x 0.196	0.350 x 0.241 x 0.087
cryst syst	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/n$	P-1
volume (Å^3)	4717.8(3)	7359.3(14)	6888.8(2)
a (Å)	19.5691(7)	15.964(2)	13.7743(3)
b (Å)	13.9341(3)	23.884(3)	21.1783(4)
c (Å)	19.6431(6)	20.0642(9)	24.4520(5)
α (deg)	90	90	99.7615(17)
β (deg)	118.260(4)	105.849(6)	95.7326(16)
γ (deg)	90	90	98.8026(16)
Z	4	4	2
formula weight (g/mol)	1140.89	1839.16	2584.36
density (g cm^{-3})	1.606	1.660	1.246
absorption coefficient (mm^{-1})	12.500	5.062	12.901
F(000)	2272	3548	2520
temp (K)	139.99(13)	120(2)	140.00(10)
total no. reflections	34891	94039	53233
unique reflections [R(int)]	9657 [0.0454]	16710 [0.0700]	27994 [0.0443]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0326$, $wR_2 = 0.0858$	$R_1 = 0.0584$, $wR_2 = 0.1091$	$R_1 = 0.0558$, $wR_2 = 0.1438$
Largest diff. peak and hole (e.A^{-3})	2.267 and -1.771	1.896 and -3.104	5.508 and -2.564
GOOF	1.032	1.130	1.036

	9.0.5py
Formula	$C_{32}H_{32}IN_5O_3U$
Crystal size (mm^3)	0.198 x 0.140 x 0.064
cryst syst	Monoclinic
space group	$P2_1/n$
volume (Å^3)	3416.2(3)
a (Å)	14.3842(6)
b (Å)	14.1543(8)
c (Å)	16.8027(7)
α (deg)	90
β (deg)	93.045(4)
γ (deg)	90
Z	2
formula weight (g/mol)	939.11
density (g cm^{-3})	1.826
absorption coefficient (mm^{-1})	5.697
F(000)	1796
temp (K)	100.01(10)
total no. reflections	29812
unique reflections [R(int)]	8463 [0.0473]
Final R indices [I > 2σ(I)]	R_1 = 0.0447, wR_2 = 0.0900
Largest diff. peak and hole (e.A^{-3})	2.413 and -1.076
GOOF	1.079

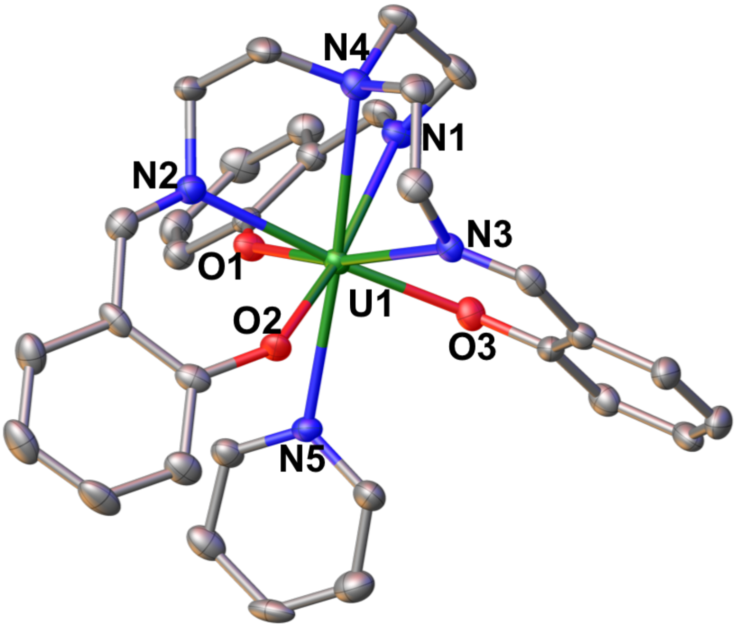

Figure S30. Ellipsoid plot at 50% probability of [U(trensal)(py)]$^+$ in complex **9** (co-crystallised pyridine molecule, I$^-$ and H were omitted for clarity, C are represented in grey, O in red, N in blue, and U in green). Selected distances (Å) U(1)–O(1) 2.193(4), U(1)–O(2) 2.199(4), U(1)–O(3) 2.185(4), U(1)–N(1) 2.546(5), U(1)–N(2) 2.523(5), U(1)–N(3) 2.548(5), U(1)-N(4) 2.855(5), U(1)-N(5) 2.655(5).

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