

Controlled and sequential single-electron reduction of the uranyl dication

Tom J. N. Obey, Gary S. Nichol, Jason B. Love*

EaStCHEM School of Chemistry, Joseph Black Building, University of Edinburgh, Edinburgh EH9 3FJ, UK

Contents

General Details.....	2
Abbreviations.....	3
Synthesis	3
H ₃ L	3
[UO ₂ (HL)] ₂ , 1.....	5
UO ₂ (LiL)(py) ₃ , 3.....	7
U ^{VI} O ₂ (KNaL)(N(SiMe ₃) ₂), 4-Na/K.....	10
[U ^V O ₂ (K ₂ L)(py) ₄] ₂ , 5-K.....	13
[U ^V O ₂ Zn(L)(py) ₂] ₂ , 6-Zn.....	14
[U ^V O ₂ Y(Cl)(L)(py) ₂] ₂ , 6-Y.....	15
[U ^V O ₂ Dy(Cl)(L)(py) ₂] ₂ , 6-Dy.....	16
[U ^V O ₂ Sm(Cl)(L)(py) ₂] ₂ , 6-Sm.....	16
[U ^V O ₂ Y(Cl)(LiCl) ₂ (L)(py) ₆], 6-Y'.....	17
[U ^V O ₂ Dy(Cl)(LiCl) ₂ (L)(py) ₆], 6-Dy'.....	18
[U ^{IV} O ₂ Y(L)] ₂ (THF) ₂ , 7-THF.....	18
Infrared Spectroscopy.....	20
Electrochemistry.....	22
Crystallographic details.....	25
References	39

General Details

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. All manipulations and reactions were carried out in monitored fumehoods or a glovebox with an inert atmosphere of dry dinitrogen in a lab equipped with α - and β -counting equipment.

The synthesis of all air- and moisture-sensitive compounds was done either on a Schlenk line using standard Schlenk technique under an atmosphere of dry argon or in MBraun gloveboxes under an atmosphere of dry dinitrogen. Vacuum atmospheres and MBraun gloveboxes were used to store and handle the air- and moisture-sensitive compounds. Solvents pyridine- d_5 and benzene- d_6 were refluxed over potassium metal overnight, freeze-pump-thaw degassed three times and distilled under reduced pressure prior to use. All glassware and cannulae were stored in a 160°C oven overnight before use. Dry solvents were collected from a solvent purification system (Innovation Technologies) and stored in Teflon-tapped ampules over pre-dried 4 \AA molecular sieves. Tetrabutylammonium hexafluorophosphate, $[\text{nBu}_4\text{N}][\text{PF}_6]$, was recrystallised twice from ethanol and dried under reduced pressure before use. All other chemicals were used as received without further purification unless specified. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR were recorded on a Bruker AVA400 spectrometer at 399.90 MHz, Bruker AVA500 spectrometer at 500.12 MHz or Bruker AVA600 spectrometer at 599.81 MHz. $^{29}\text{Si}\{^1\text{H}\}$ NMR was recorded on a Bruker PRO500 spectrometer at 470.59 MHz. All chemical shifts are reported in parts per million (ppm). ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR were referenced to residual solvent signals, calibrated against SiMe_4 ($\delta = 0$ ppm). Spectra were recorded at 298 K. Data was processed using MestReNova 14.0.0. Single-crystal X-ray diffraction data were collected on an Oxford Diffraction Excalibur diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation equipped with an Eos charge-coupled device detector ($\lambda = 0.71073 \text{ \AA}$) at 120 K, or on a Supernova, Dual, Cu at zero Atlas diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 120 K. All structures were solved using ShelXT direct methods and refined using a full-matrix least-squares refinement on $|F|^2$ using ShelXL.^{1, 2} All programs were used within the Olex2 suite.³ Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were constrained to parent atoms and refined using a riding model. Structures were analysed and illustrated in Mercury 4.3.1.⁴ The x-ray crystal structures of 2-THF, 2-py, 4-Na and 7-py were solved as two-component twins. Mass spectrometry was recorded using a 12T Bruker Solarix with APPI source with a portable glovebox flushed with argon surrounding the injection port. All FT-IR spectra were recorded using a Shimadzu IRSpirit Fourier Transform Infrared Spectrophotometer (serial no. A224157). Relevant peaks are reported in cm^{-1} . Cyclic voltammetry measurements were made using an Autolab 302 potentiostat and data processed in NOVA 2.1.5. All experiments were carried out at room temperature in a glovebox under a dinitrogen atmosphere. A

glassy-carbon working electrode, platinum counter electrode and silver wire pseudo-reference electrode were used with a 0.1 M solution of either $[\text{nBu}_4\text{N}][\text{BPh}_4]$, $[\text{nBu}_4\text{N}][\text{BAR}^{\text{F}}]$ or $[\text{nBu}_4\text{N}][\text{PF}_6]$ in THF. All experiments were referenced against $[\text{FeCp}_2]^{+/\text{0}}$ ($E_{1/2}$, $[\text{FeCp}_2]^{+/\text{0}} = 0.0\text{V}$). Elemental analysis was carried out by the London Metropolitan University and measured in duplicate.

Abbreviations

THF = tetrahydrofuran

Py = pyridine

S = solvent

HMDS = hexamethyldisilazane

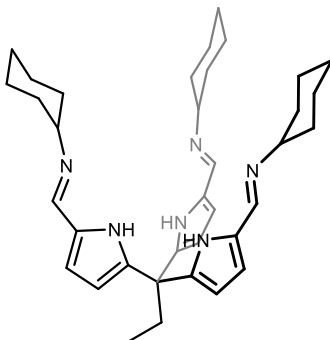
$\text{C}_6\text{D}_6 = d_6\text{-benzene}$

Cy-CH = cyclohexyl-CH

Im-CH = imino-CH

Py-CH = pyrrol-CH

Synthesis



H₃L: $\text{H}_3\text{L}(\text{H}_2\text{O})_x$ was synthesised following literature procedures.⁵ This was dried by dissolving 9.57 g, (0.017 mol, assuming $x = 1$) in dry toluene under an argon atmosphere and trimethylsilyl chloride (7 mL, 0.055 mol) was added. A pale brown precipitate formed immediately. This solid was washed with dry toluene (3 x 30 mL) and suspended in toluene. A solution of 1,4-Diazabicyclo[2.2.2]octane (DABCO) (1.89 g, 0.017 mol) in dry toluene was added to the suspension and the mixture stirred for 16 hours. The mixture was filtered under argon and the solvent removed from the filtrate under reduced pressure to afford a pale brown solid. This solid was washed with acetonitrile to give the pure product as a colourless solid (4.78 g, 8.43 mmol, 50 %). ^1H NMR (500 MHz, pyridine- d_5): δ_{H} 10.59 (br. s, 3H, NH), 8.05 (s, 3H, CH imine), 6.52 (d, $J = 3.6$ Hz, 3H, CH pyrrole), 6.26 (d, $J = 3.6$ Hz, 3H, CH pyrrole), 2.99 (m, 3H, cy), 2.69 (q, $J = 7.4, 6.9$ Hz, 2H, CH_2 ethyl) 1.68 – 1.62 (m, 12H, cy), 1.55 – 1.49 (m, 3H, cy), 1.42

(m, 6H, cy), 1.29 – 1.18 (m, 6H, cy), 1.09 (m, 3H, cy), 0.99 – 0.91 (t, 3H, CH₃ ethyl). ¹³C{¹H} NMR (126 MHz, Pyr): δ_c 149.74 (imine CH), 140.04 (pyrrole C), 131.80 (pyrrole C), 114.09 (pyrrole CH), 109.65 (pyrrole CH), 69.69 (cy CH), 48.30 (cy CH₂), 47.23 (Et C), 35.37 (cy CH₂), 33.14 (Et CH₂), 26.35 (cy CH₂), 25.35 (cy CH₂), 10.55 (Et CH₃). APPI-MS: [H₃L](H⁺) 567.41764 m/z.

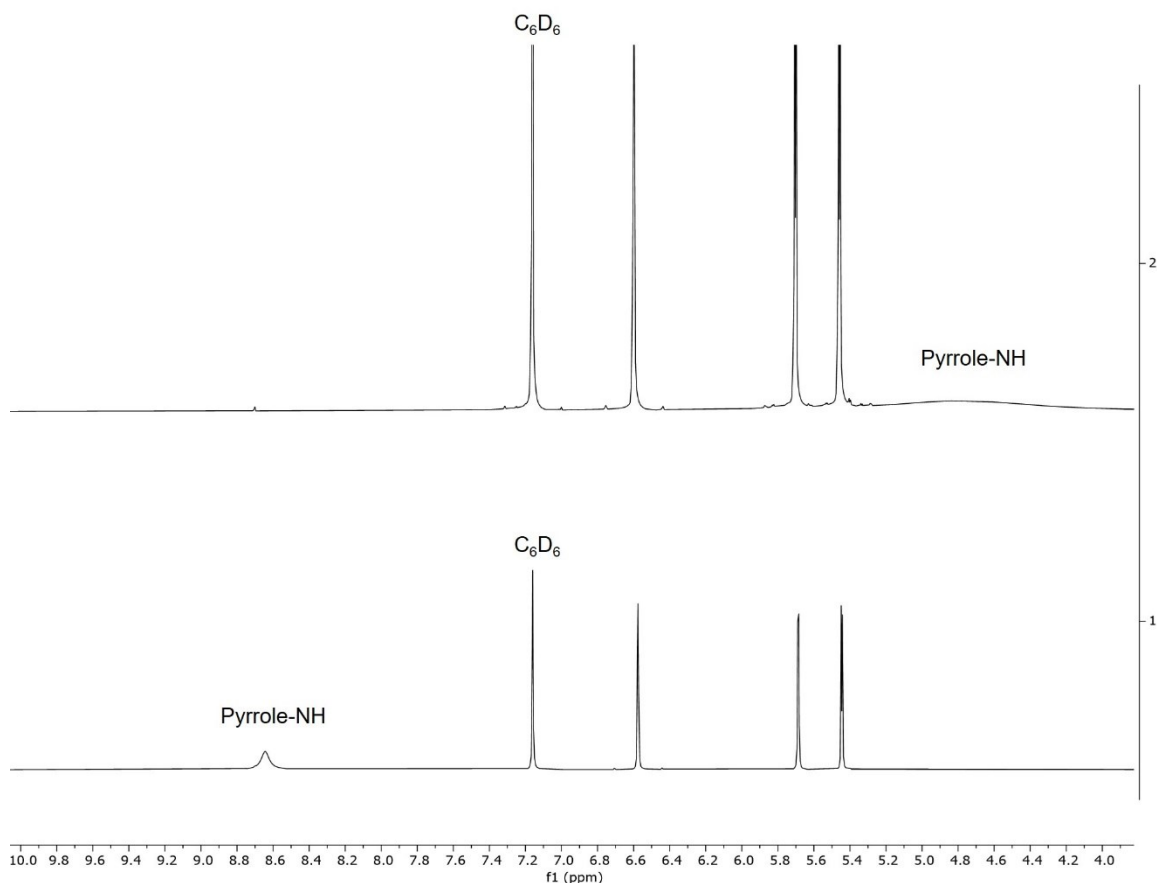
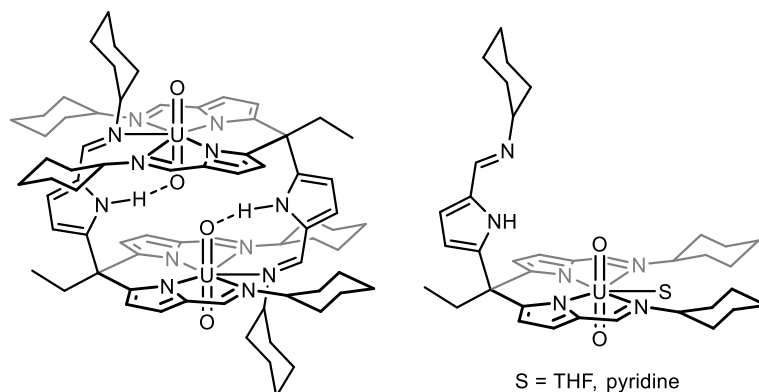


Figure SI 1. ¹H NMR spectra of **H₃L·H₂O** (TOP) and “dry” **H₃L** (BOTTOM) in *d*₆-benzene (7.16 ppm) in the range 10.0 – 4.0 ppm in *d*₆-benzene. The NH peak in **H₃L·H₂O** (4.79 ppm) is much broader and shifted upfield compared to the NH peak in **H₃L** (8.64 ppm). There is no shifting in the imine-CH (6.58 ppm) or pyrrole-CH (5.69 ppm, 5.45 ppm).



[UO₂(HL)]₂, 1: A solution of UO₂(N(SiMe₃)₂)₂(THF)₂ (1.50 g, 2.04 mmol) in dry toluene (20 mL) was added to a stirred solution of H₃L (1.15 g, 2.03 mmol) in dry toluene (50 mL). The mixture immediately became dark brown and was stirred for 6 hours, after which a dark brown precipitate forms. The mixture was filtered and the precipitate isolated and washed with cold toluene and hexane to afford **1** as a brown solid (1.16 g, 0.695 mmol, 68%). X-ray quality crystals of **1** were obtained by precipitation from toluene at -20°C over several weeks. When dissolved in pyridine or THF, **1** is converted to the monomer [UO₂(HL)(py)] (**2-py**) or [UO₂(HL)(THF)] (**2-THF**) respectively, of which X-ray quality crystals were isolated by vapour diffusion of hexane into either a pyridine or THF solution. ¹H NMR (500 MHz, pyridine-*d*₅): δ_H 11.23 (s, 1H, py NH), 9.46 (s, 2H, CH imine), 8.21 (s, 1H, CH imine), 7.16 (d, *J* = 3.5 Hz, 2H, CH pyrrole), 6.83 (d, *J* = 3.5 Hz, 1H, CH pyrrole), 6.70 (d, *J* = 3.5 Hz, 1H, CH pyrrole), 6.56 (d, *J* = 3.5 Hz, 2H, CH pyrrole), 3.27 (m, 2H, cy), 3.02 (q, *J* = 7.3 Hz, 2H, et), 2.06 (d, *J* = 12.6 Hz, 2H, cy), 1.95 (d, *J* = 12.5 Hz, 2H, cy), 1.70 – 1.59 (m, 13H, cy), 1.52 – 1.38 (m, 13H, cy), 1.12 (t, *J* = 7.5 Hz, 3H, cy). ¹³C{¹H} NMR (126 MHz, pyridine-*d*₅): δ_C 160.07 (imine CH), 159.20 (pyrrole C), 150.69 (pyrrole C), 144.03 (pyrrole C), 138.59 (pyrrole C), 131.41 (pyrrole C), 121.58 (pyrrole CH), 113.83 (pyrrole CH), 113.08 (pyrrole CH), 108.80 (pyrrole CH), 70.06 (cy CH), 64.50 (cy CH), 52.30 (Et C), 38.82 (Et CH₂), 35.54 (cy CH₂), 35.40 (cy CH₂), 34.54 (cy CH₂), 27.04 (cy CH₂), 26.96 (cy CH₂), 26.48 (cy CH₂), 26.26 (cy CH₂), 25.44 (cy CH₂), 11.34 (Et CH₃). APPI-MS: [UO₂(HL)](H⁺) 835.44532 m/z. IR: **1**; pyrrole N-H 3283.59 cm⁻¹, imine C=N 1604.01 cm⁻¹, pyrrole C-N 1047.96 cm⁻¹, asymmetric O-U-O stretch 909.65 cm⁻¹. EA: **2-THF**; Expected: C, 52.97; H, 6.22; N, 9.27; %. Found: C, 52.88; H, 6.26; N, 9.25; %.

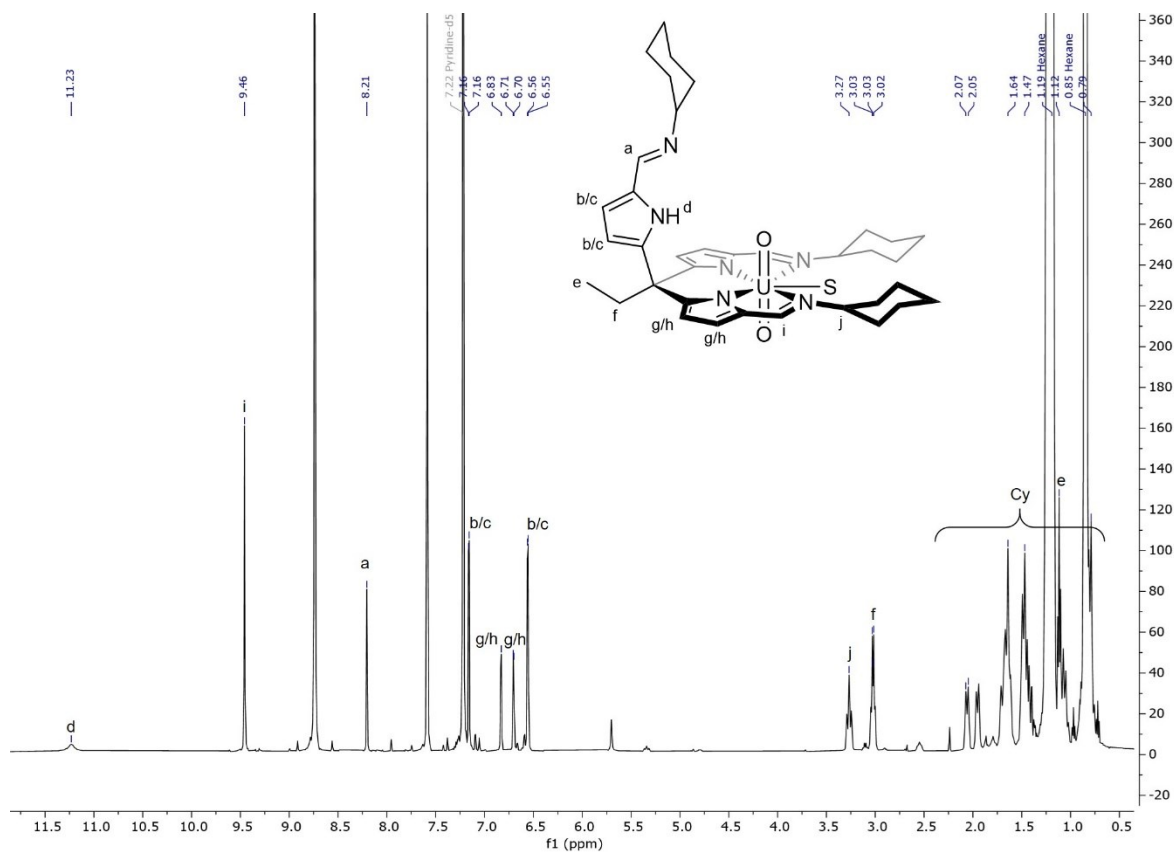


Figure SI 2. ^1H NMR spectrum of **2-py** in d_5 -pyridine.

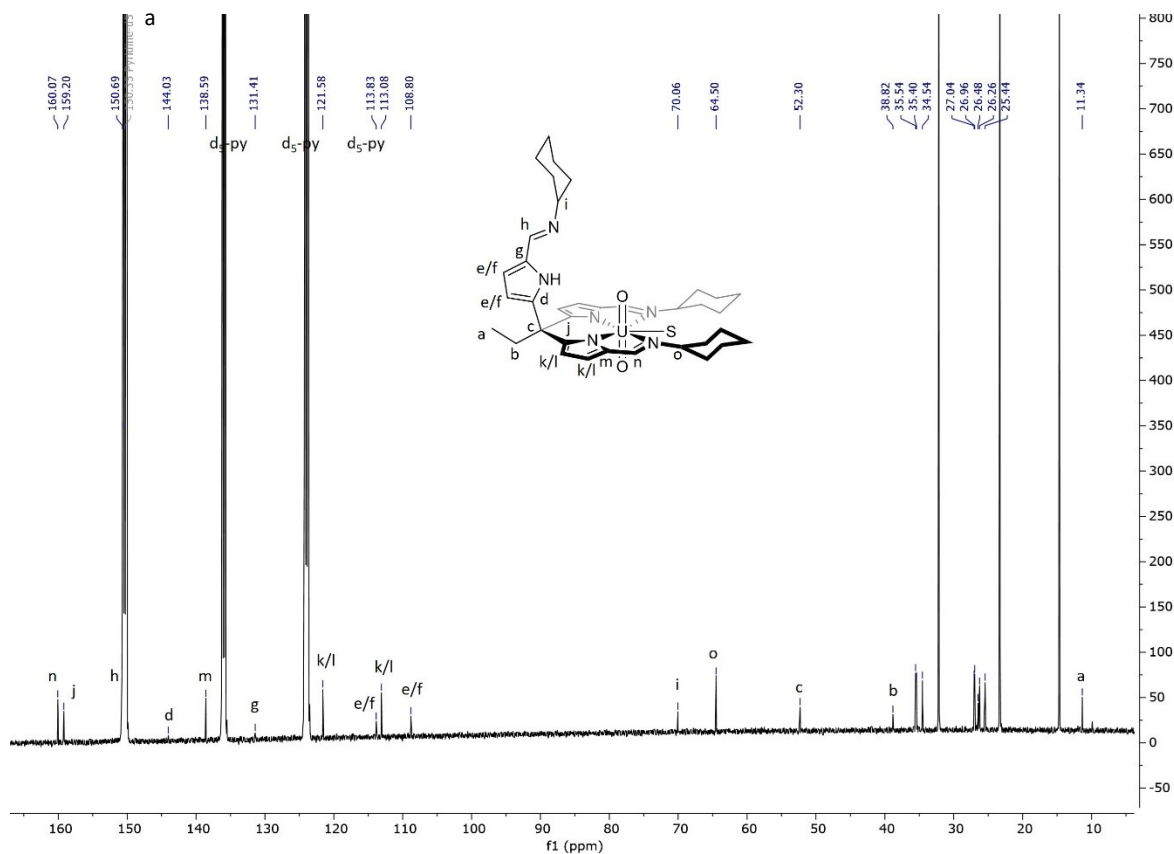
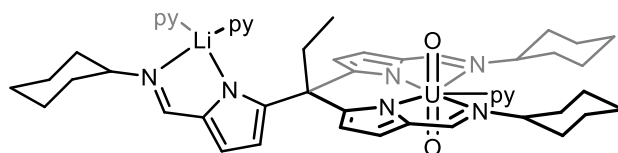


Figure SI 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-py** in d_5 -pyridine.



$UO_2(LiL)(py)_3$, 3: A solution of $LiN(SiMe_3)_2$ (0.09 g, 0.54 mmol, 2 eq.) in dry pyridine (5 mL) was added to a solution of **1** (0.45 g, 0.27 mmol) in pyridine (20 mL) under a nitrogen atmosphere. The resulting dark brown solution was stirred at room temperature for 30 minutes. The solution was concentrated under vacuum and layered with hexane to obtain the product as dark brown, X-ray quality crystals of **3** (0.32 g, 0.30 mmol, 56 %) after several days. 1H NMR (500 MHz, pyridine- d_5): δ_H 9.37 (s, 2H, imine CH), 8.29 (s, 1H, imine CH), 7.05 (d, $J = 3.1$ Hz, 1H, pyrrole CH), 6.95 (d, $J = 3.1$ Hz, 1H, pyrrole CH), 6.87 (d, $J = 3.4$ Hz, 2H, pyrrole CH), 6.66 (d, $J = 3.4$ Hz, 2H, pyrrole CH), 5.43 – 5.32 (m, 2H, cy), 3.71 – 3.63 (m, 1H, cy), 3.21 (q, $J = 7.1$ Hz, 2H, ethyl CH_3), 2.62 – 2.51 (m, 4H, cy), 1.90 – 1.85 (m, 3H, cy), 1.81 – 1.75 (m, 3H, cy), 1.72 – 1.64 (m, 4H, cy), 1.59 – 1.42 (m, 4H, cy), 1.44 (s, 1H, cy), 1.27 – 1.15 (m, 8H, cy), 1.22 – 1.18 (m, 3H, cy), 1.08 (t, $J = 14.5$ Hz, 3H, ethyl CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, pyridine- d_5): δ_C 163.10 (pyrrole C), 158.17 (imine CH), 158.12 (imine CH), 157.34 (pyrrole C), 139.06 (pyrrole C), 138.08 (pyrrole C), 129.86, 129.12, 119.26 (pyrrole CH), 116.59 (pyrrole CH), 113.40 (pyrrole CH), 109.97 (pyrrole CH), 68.33 (cyclohexane CH), 62.18 (cyclohexane CH), 54.25 (ethyl C), 38.77 (ethyl CH_2), 36.64, 36.41, 34.89, 27.08, 26.86, 26.75, 26.55, 26.27, 26.09, 19.92, 12.23 (ethyl CH_3). $^7Li\{^1H\}$ NMR (194 MHz, pyridine- d_5): δ_{Li} 3.55. APPI-MS: $[UO_2LiL](H^+)$ 841.45693 m/z. IR: Asymmetric O-U-O stretch 911.08 cm^{-1} . Expected: C, 56.82; H, 5.80; N, 11.69; %. Found: C, 56.96; H, 5.82; N, 11.51; %.

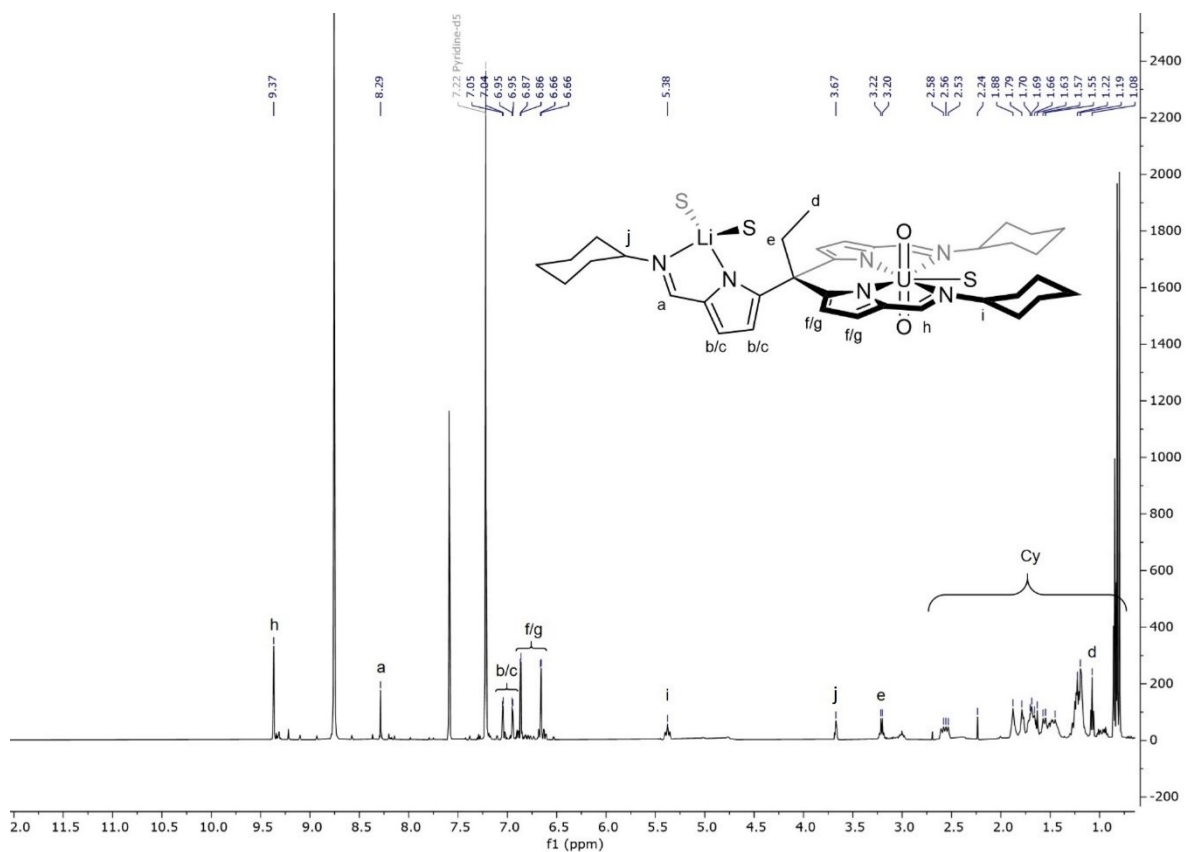


Figure SI 4. ^1H NMR spectrum of **3** in d_5 -pyridine.

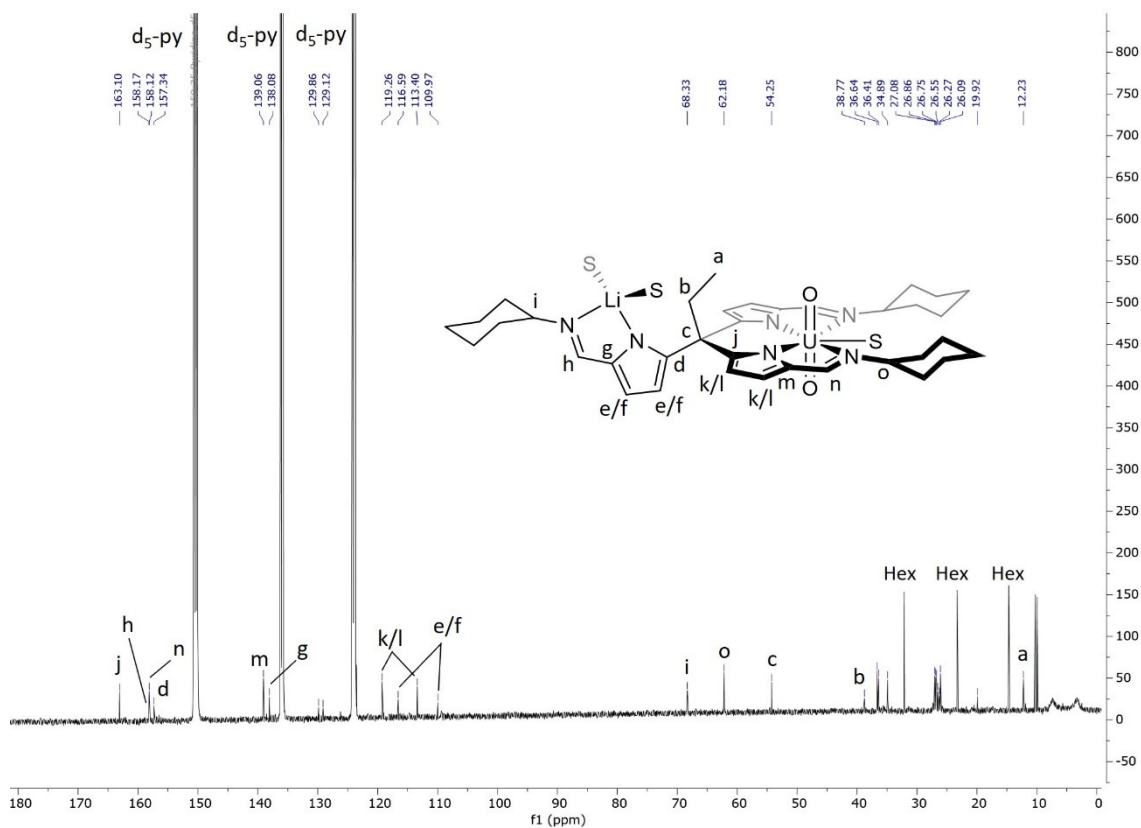


Figure SI 5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in d_5 -pyridine.

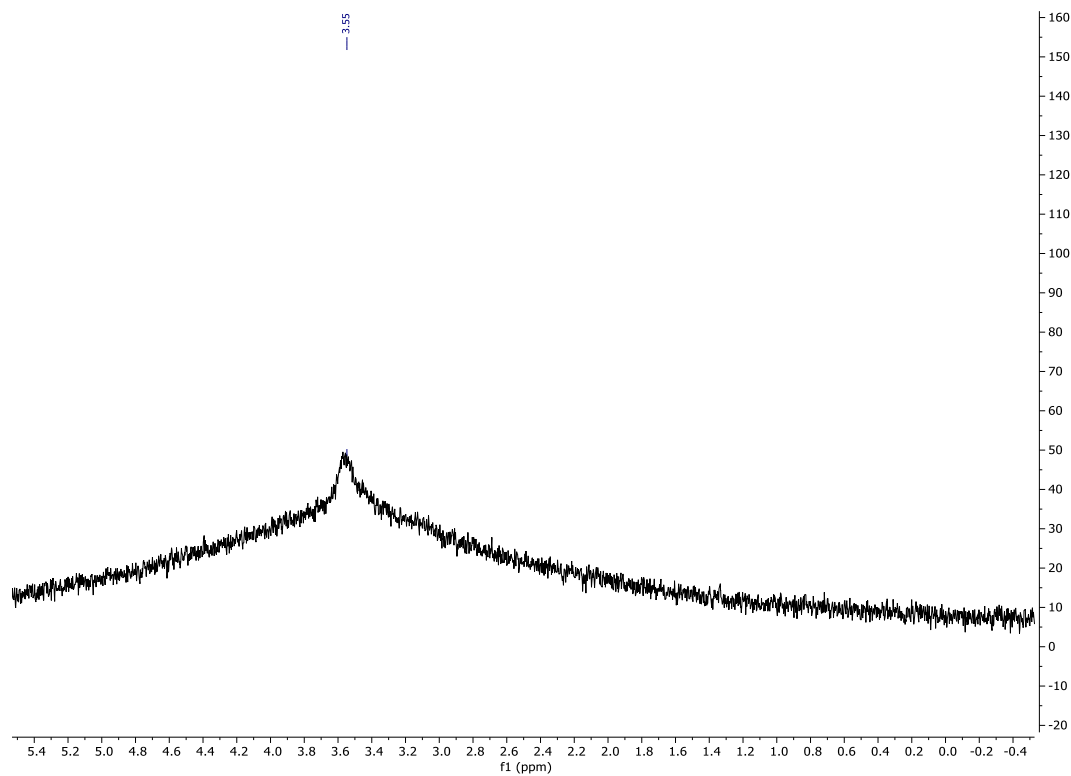


Figure SI 6. ${}^7\text{Li}\{{}^1\text{H}\}$ NMR spectrum of **2-py** in d_5 -pyridine.

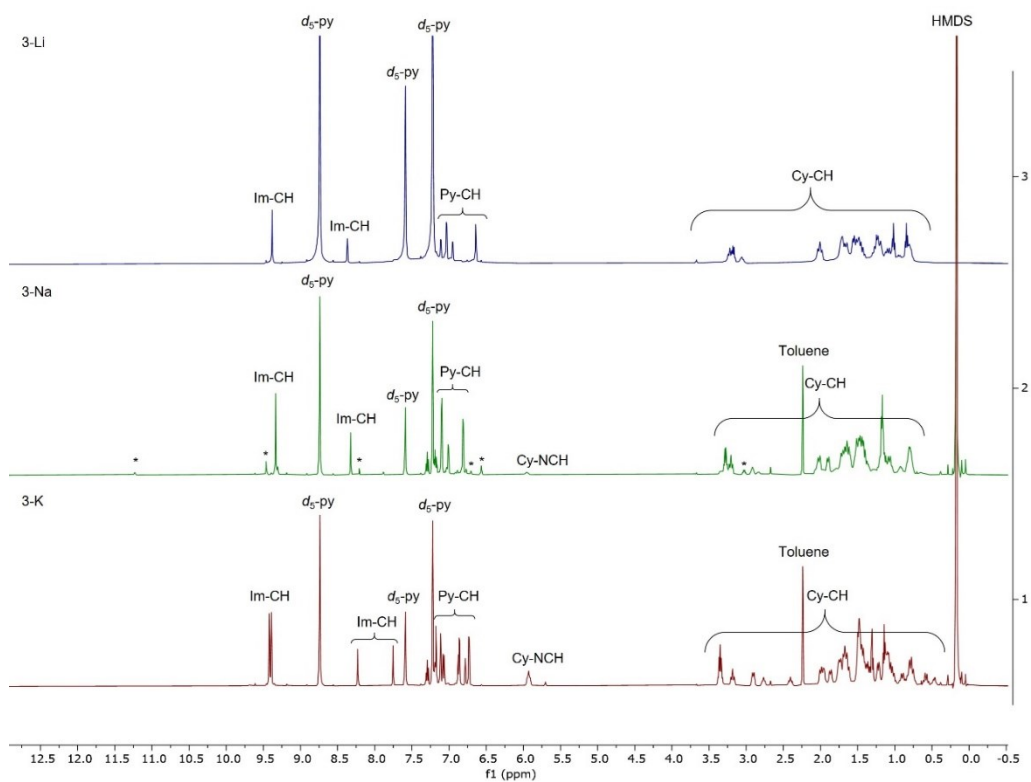
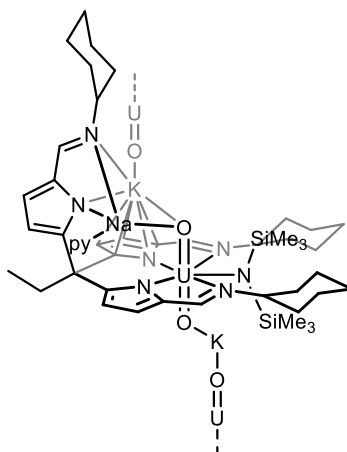


Figure SI 7. Stacked ${}^1\text{H}$ NMR spectra of **3-Li** (TOP), **3-Na** (MIDDLE) and **3-K** (BOTTOM) in d_5 -pyridine. * = **2**.



$U^{VI}O_2(KNaL)(N(SiMe_3)_2)$, 4-Na/K: A solution of $NaN(SiMe_3)_2$ (0.021 g, 0.115 mmol, 3.8 eq.) in dry pyridine (5 mL) was added to a solution of **1** (0.050 g, 0.030 mmol) in pyridine (15 mL) under a nitrogen atmosphere and stirred for 16 hours at room temperature. The solvent and $HN(SiMe_3)_2$ was removed under vacuum and the brown solid mixture of **4-Na/K** and the presumed **5-Na** were re-dissolved in pyridine. X-ray quality crystals of **4-Na/K** were obtained by vapour diffusion of hexane into the pyridine solution. No yield of pure **4-Na/K** was obtained. X-ray quality crystals were grown by slow diffusion of dry hexane layered on a saturated pyridine solution of **4-Na/K** and **5-Na**. The origin of the potassium in the structure is unknown, but likely due to contamination of the $NaN(SiMe_3)_2$. 1H NMR (500 MHz, pyridine- d_5): δ_H 9.36 (s, 2H, imine CH), 7.67 (s, 1H, imine CH), 7.12 (d, $J = 3.4$ Hz, 2H, pyrrole CH), 6.82 (d, $J = 3.4$ Hz, 2H, pyrrole CH), 6.64 (d, $J = 3.1$ Hz, 1H, pyrrole CH), 6.60 (d, $J = 3.2$ Hz, 1H, pyrrole CH), 5.17 – 5.05 (m, 2H, cy NCH), 3.23 (q, $J = 7.3$ Hz, 2H, ethyl CH_2), 2.53 – 2.44 (m, 1H, cy NCH), 2.36 (dd, $J = 26.5, 12.3$ Hz, 4H, cy), 1.82 – 1.77 (m, 8H, cy), 1.71 – 1.67 (m, 5H, cy), 1.49 – 1.40 (m, 2H, cy), 1.35 (t, 3H, ethyl CH_3), 1.26 (dd, $J = 12.4, 3.7$ Hz, 4H, cy), 1.08 – 0.99 (m, 2H, cy), 0.94 – 0.86 (m, 2H, cy), 0.82 (d, $J = 6.3$ Hz, 2H, cy), 0.72 (s, 9H, $SiMe_3$), 0.68 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, pyridine- d_5): δ_C 161.80 (pyrrole C), 160.05 (pyrrole C), 158.18, 157.18, 137.75 (pyrrole C), 136.57 (pyrrole C), 121.33 (pyrrole CH), 117.06 (pyrrole CH), 111.67 (pyrrole CH), 105.40 (pyrrole CH), 67.83 (cy CH), 62.50 (cy CH), 53.57 (Et C), 36.01, 35.28, 34.96, 33.98 (Et CH_2), 26.69, 26.44, 26.36, 26.34, 26.19, 25.44, 11.92 (Et CH_3), 9.69 ($SiMe_3$), 9.27 ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (99 MHz, pyridine- d_5): δ_{Si} -6.34, -7.14. APPI-MS: $[UO_2(KNaL)(N(SiMe_3)_2)](H^+)$ 1056.50492 m/z.

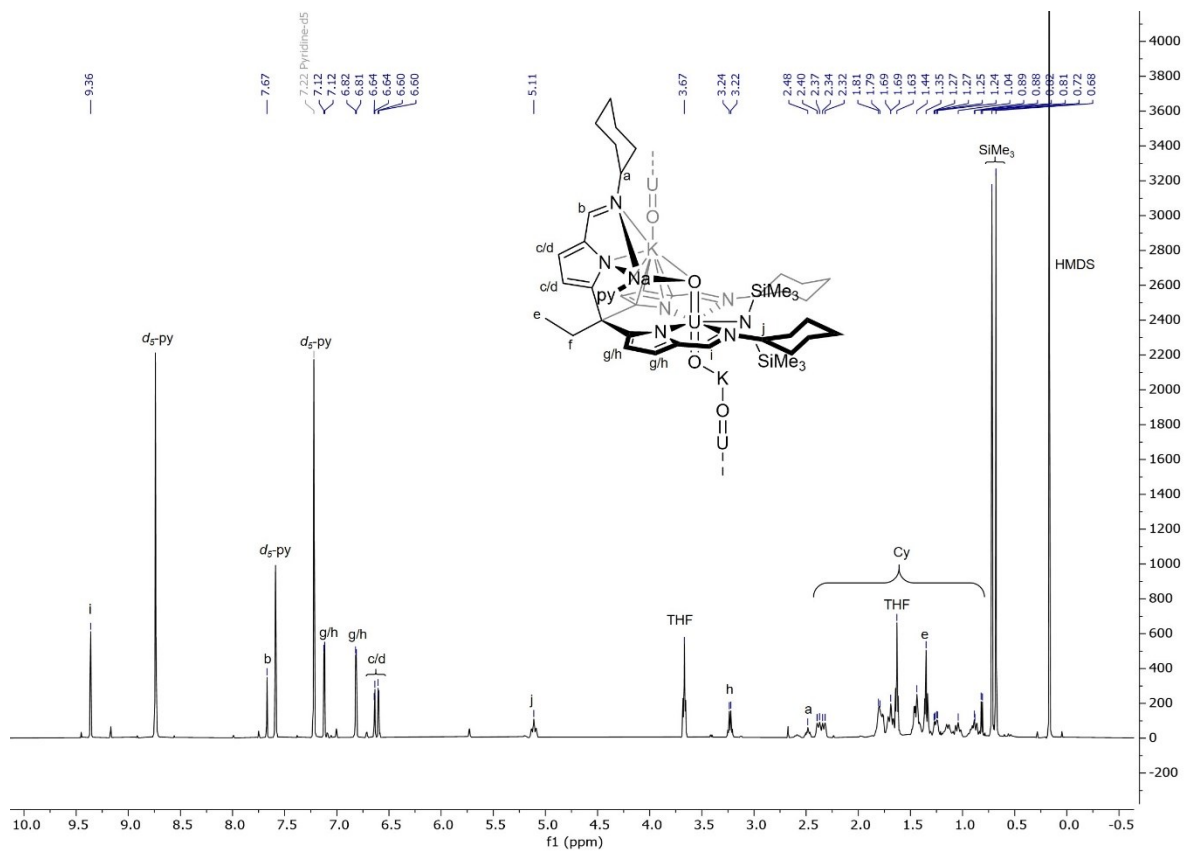


Figure SI 8. ^1H NMR spectrum of **4-Na/K** in d_5 -pyridine.

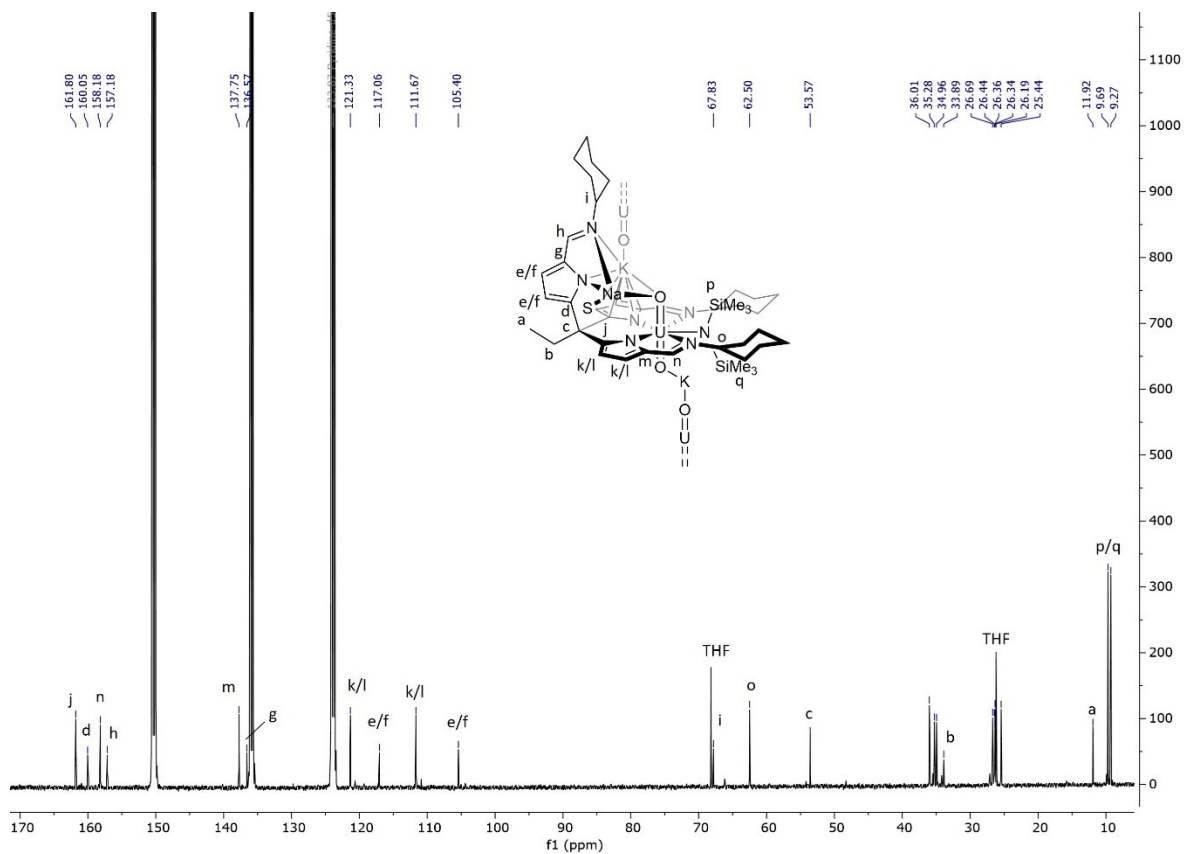


Figure SI 9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4-Na/K** in d_5 -pyridine.

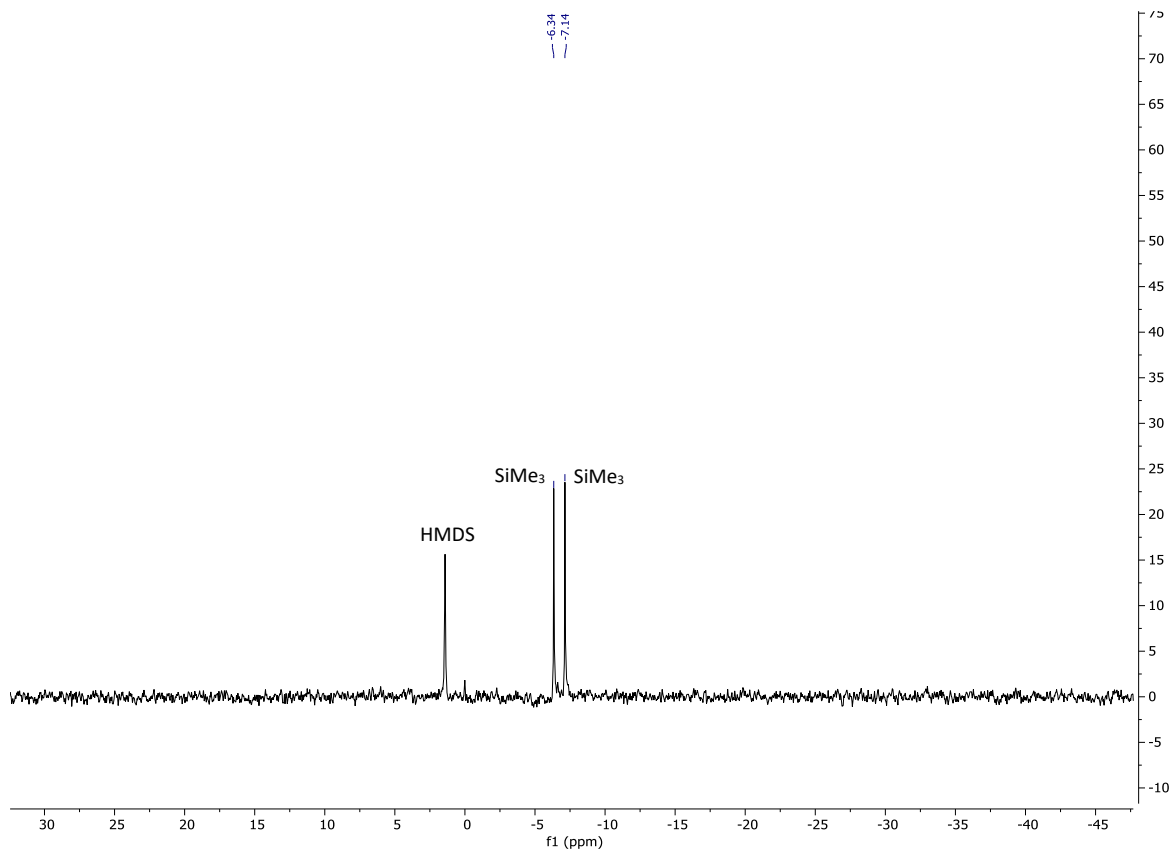


Figure SI 10. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **4-Na** in d_5 -pyridine.

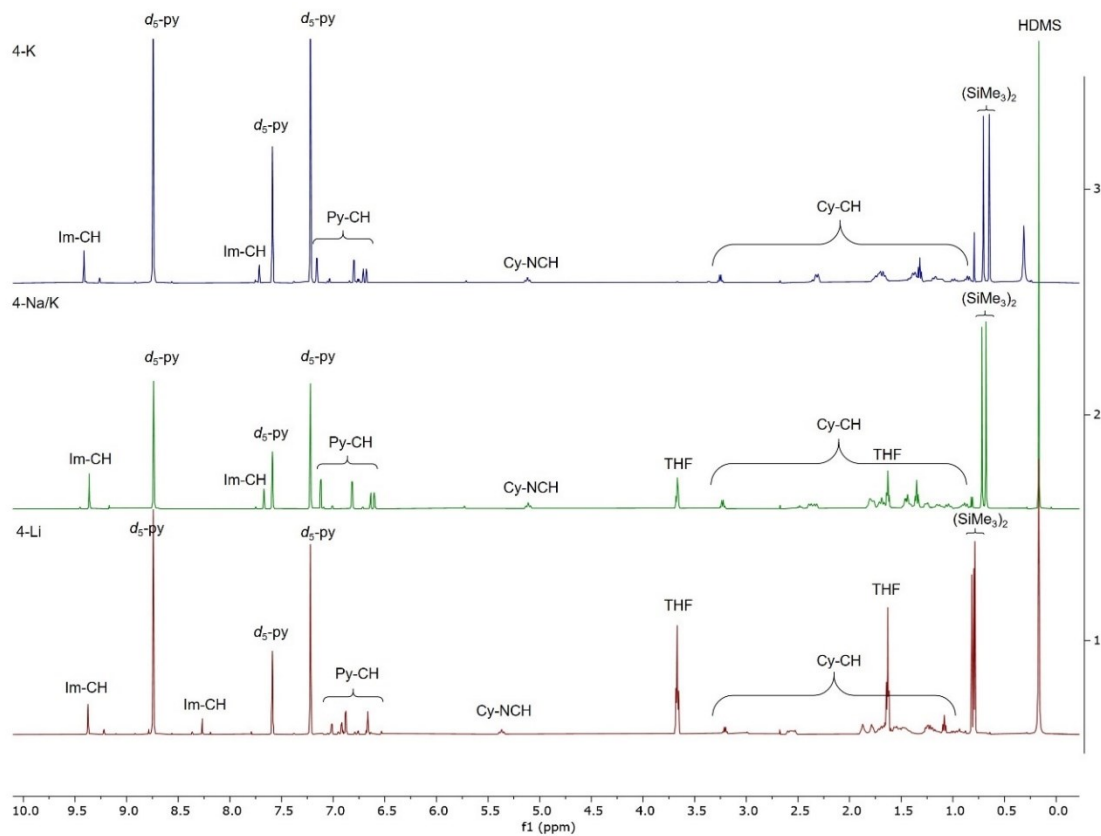
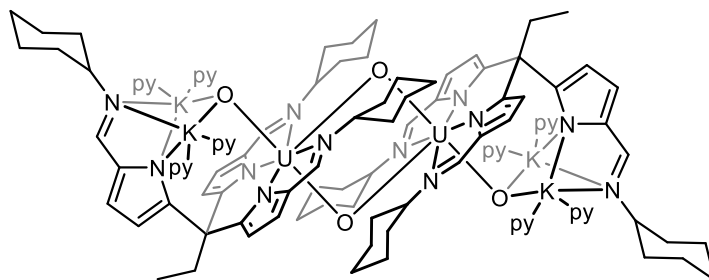


Figure SI 11. Stacked ^1H NMR spectra of **4-K** (TOP), **4-Na** (MIDDLE) and **4-Li** (BOTTOM) in d_5 -pyridine.



[U^VO₂(K₂L)(py)₄]₂, 5-K: A solution of KN(SiMe₃)₂ (0.184 g, 0.922 mmol, 4 eq.) in dry pyridine (10 mL) was added to a solution of **1** (0.389 g, 0.233 mmol, 1 eq.) and DHA (0.084 g, 0.466 mmol, 2 eq.) in pyridine (20 mL) under an argon atmosphere. The dark purple/brown solution was stirred at room temperature for 2 hours before the solvent was removed under reduced pressure. The resulting pale brown solid was washed with dry hexane to afford the product (0.270 g, 0.110 mmol, 47 %). X-ray quality crystals of **5-K** were obtained by vapour diffusion of hexane into a pyridine solution. ¹H NMR (500 MHz, pyridine): δ_H 14.72, 14.15, 10.54, 10.39, 7.90, 6.22, 5.63, 5.59, 3.01, -1.00, -1.02, -2.71, -3.00, -3.02, -4.23, -4.25, -4.47, -4.49, -5.23, -6.15, -6.77, -7.85, -8.07, -8.90, -11.35, -12.01, -13.54, -36.89. APPI-MS: [U^VO₂(K₂L)](H⁺) 912.36153 m/z, [U^VO₂(K₂L)]₂(H⁺) 1823.72833 m/z. IR: Imine C=N 1601.16 cm⁻¹, pyrrole C-N 1045.10 cm⁻¹, U-O 665.84 cm⁻¹.

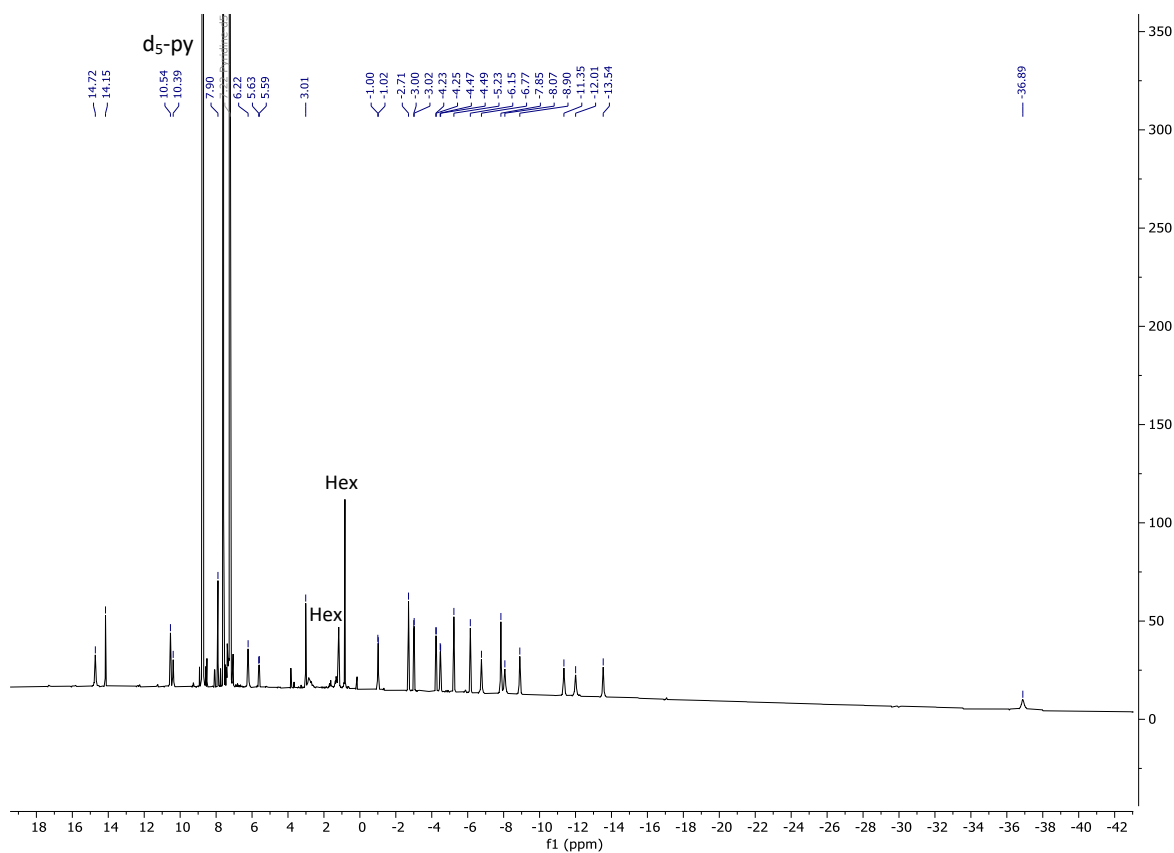
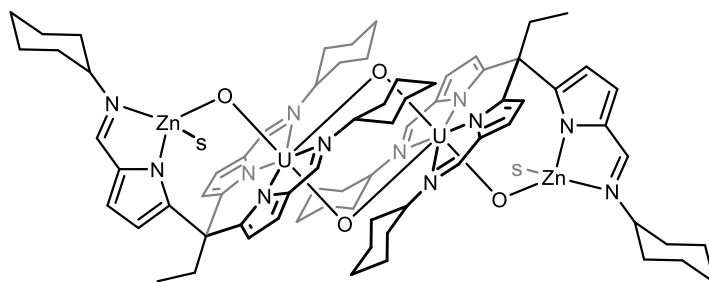


Figure SI 12. ¹H NMR spectrum of **5-K** in *d*₅-pyridine.



[U^VO₂Zn(L)(py)₂]₂, 6-Zn: A solution of ZnCl₂ (13 mg, 0.093 mmol, 2 eq.) in dry THF (5 mL) was added to a solution of **5-K** (100 mg, 0.048 mmol) in (5 mL) and the mixture was stirred at room temperature for 16 hours, after which a colourless precipitate formed. The mixture was filtered and the solvent removed from the pale orange/brown filtrate under reduced pressure. The brown solid was washed with dry hexane to obtain the product (30 mg, 0.015 mmol, 37 %). X-ray quality crystals were grown by vapour diffusion of hexane into a solution of **6-Zn** in pyridine. ¹H NMR (500 MHz, pyridine-*d*₅): δ_H 18.78 (s, 4H), 17.23 (s, 2H), 14.38 (s, 2H), 13.84 (s, 4H), 9.82 (d, *J* = 2.0 Hz, 2H), 6.97 (s, 4H), 5.83 (s, 4H), 5.37 (s, 2H), 5.14 (s, 2H), 3.66 (s, 4H), 1.66 – 1.59 (m, 4H), 0.28 – 0.21 (m, 4H), -1.10 (d, *J* = 3.6 Hz, 4H), -2.10 (d, *J* = 11.1 Hz, 4H), -3.47 (q, *J* = 12.4 Hz, 4H), -3.66 – -3.70 (m, 8H), -3.92 (s, 4H), -4.22 (s, 4H), -6.20 (s, 4H), -7.94 (s, 4H), -8.17 (d, *J* = 12.9 Hz, 4H), -9.92 (s, 4H), -10.35 (s, 4H), -12.60 (d, *J* = 11.0 Hz, 4H), -29.39 (s, 4H). IR: Imine C=N 1588.33 cm⁻¹, pyrrole C-N 1043.68 cm⁻¹, U-O 660.14 cm⁻¹. APPI-MS: [UO₂ZnL]⁺ 897.36390 m/z.

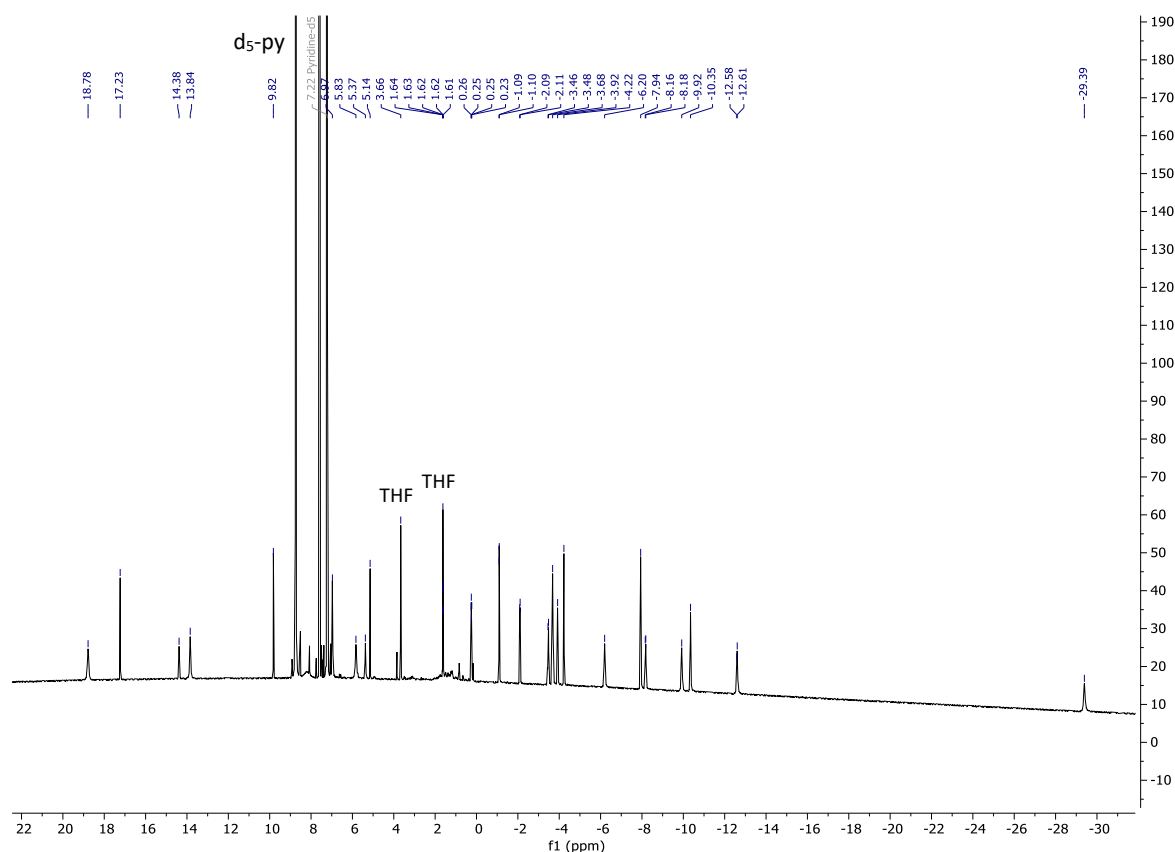
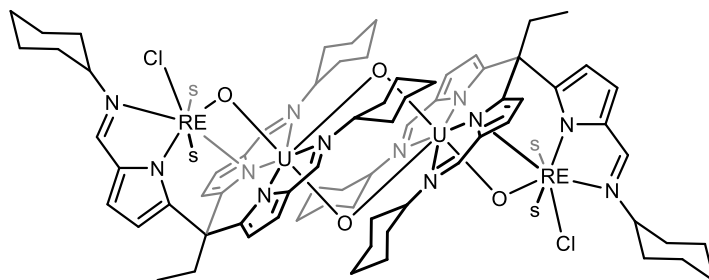


Figure SI 13. ¹H NMR spectrum of **6-Zn** in *d*₅-pyridine.



[U^{VO₂Y(Cl)(L)(py)₂]₂, 6-Y:} A solution of **5-K** (60 mg, 0.048 mmol) in dry THF (5 mL) was added to a suspension of YCl₃ (11 mg, 0.096 mmol, 2 eq.) in THF (5 mL) and the mixture was stirred at room temperature for 16 hours, after which a the solution became paler and a colourless precipitate formed. The mixture was filtered and the solvent removed from the pale brown filtrate under vacuum. After washing with hexane the product was obtained as a pale yellow solid (55 mg, 0.025 mmol, 89 %). X-ray quality crystals were grown by vapour diffusion of hexane into a solution of **6-Y** in pyridine. ¹H NMR (601 MHz, pyridine-*d*₅): δ_H 17.38, 17.16, 13.79, 13.72, 11.69, 11.49, 10.48, 9.45, 8.59, 8.51, 8.42, 7.70, 7.22, 6.59, 6.06, 5.60, 5.49, 5.03, 4.79, 4.51, 4.33, 4.27, 3.66, 3.65, 3.64, 3.09, 1.62, 1.16, 0.61, 0.14, -0.36, -1.55, -2.23, -2.38, -2.39, -3.71, -3.87, -4.41, -4.62, -4.81, -5.16, -5.45, -5.78, -5.99, -7.77, -8.03, -9.51, -10.17, -10.30, -11.45, -11.95, -12.35, -13.08, -16.08, -17.72, -30.80. IR: Imine C=N 1595.46 cm⁻¹, pyrrole C-N 1046.53 cm⁻¹, U-O 671.55 cm⁻¹. APPI-MS: [UO₂Y(Cl)(L)]⁺ 957.31107 m/z.

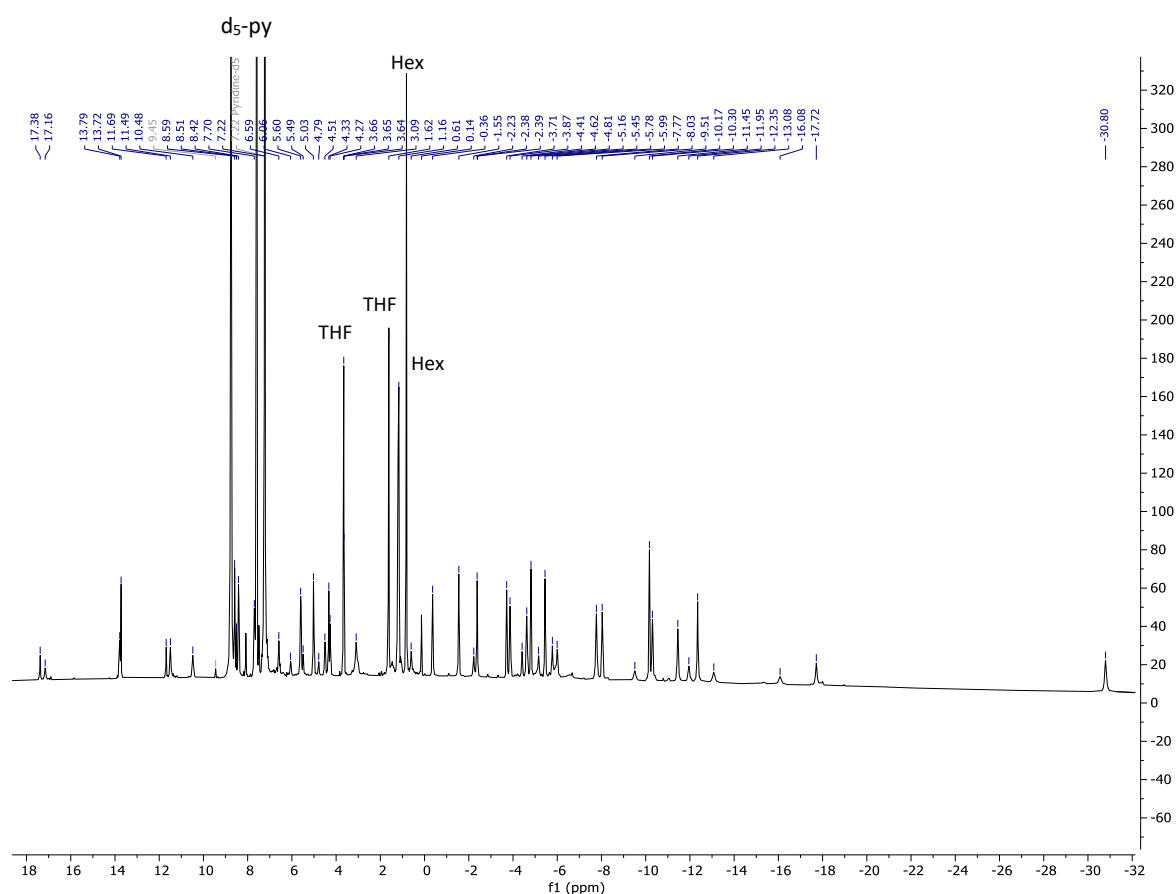


Figure SI 14. ¹H NMR spectrum of **6-Y** in *d*₅-pyridine.

[U^vO₂Dy(Cl)(L)(py)₂]₂, 6-Dy: A solution of DyCl₃(THF)₂ (47 mg, 0.114 mmol, 2 eq.) in THF (5 mL) was added to a solution of **5-K** (140 mg, 0.057 mmol) in dry THF (5 mL) and the solution was stirred at room temperature for 16 hours, after which a colourless precipitate formed. The mixture was filtered and the solvent removed from the brown filtrate under vacuum. After washing with hexane the product was obtained as a pale yellow-brown solid (64 mg, 0.027 mmol, 48 %). X-ray quality crystals were grown by vapour diffusion of hexane into a solution of **6-Dy** in pyridine. ¹H NMR (500 MHz, pyridine-*d*₅): δ_H 96.77, 85.91, 80.48, 63.09, 57.10, 44.06, 22.39, 21.95, 19.66, 18.15, 15.67, 12.90, 7.22, 3.05, -1.43, -2.93, -4.03, -4.49, -5.19, -5.62, -6.97, -7.60, -8.68, -9.44, -10.93, -12.25, -12.47, -18.93, -20.46, -26.48, -28.53, -33.63, -38.56, -41.26, -68.29. IR: Imine C=N 1598.31 cm⁻¹, pyrrole C-N 1047.96 cm⁻¹, U-O 670.12 cm⁻¹. APPI-MS: [UO₂DyCl]⁺ 1032.33980 m/z.

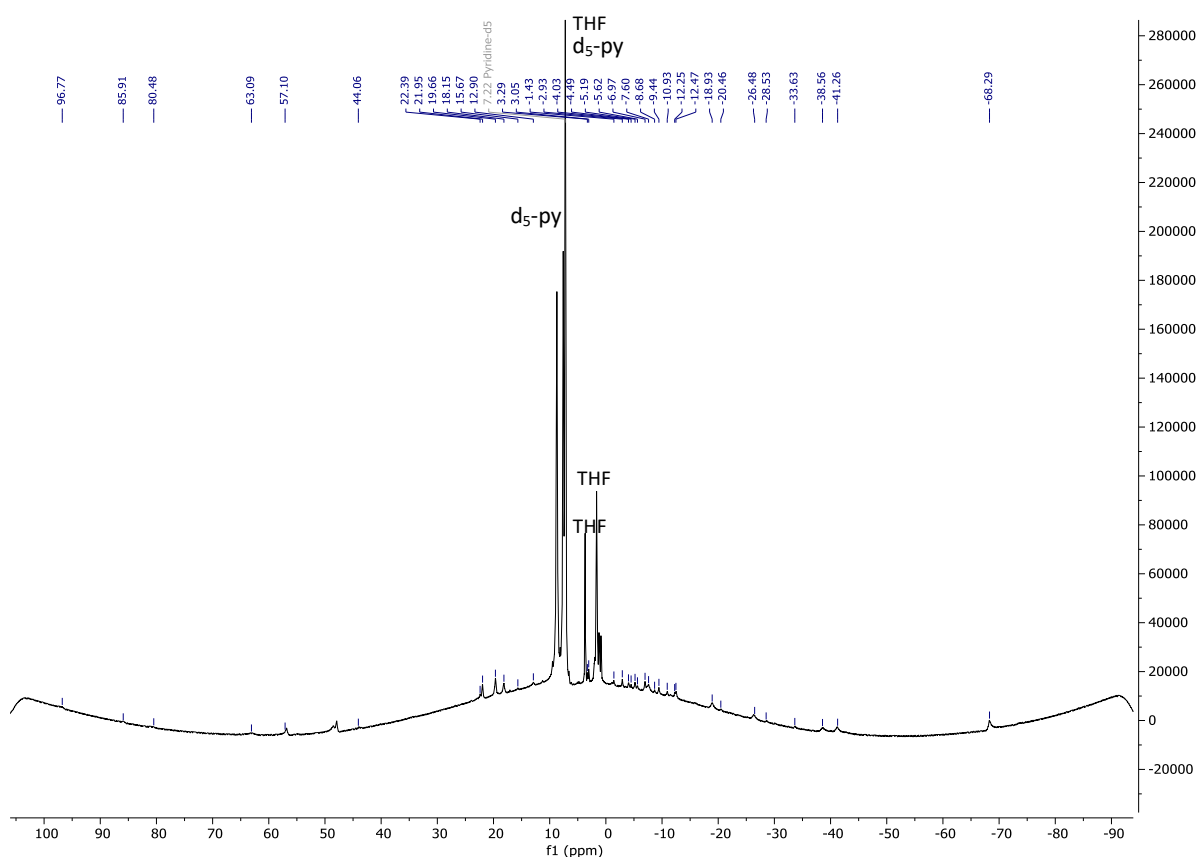
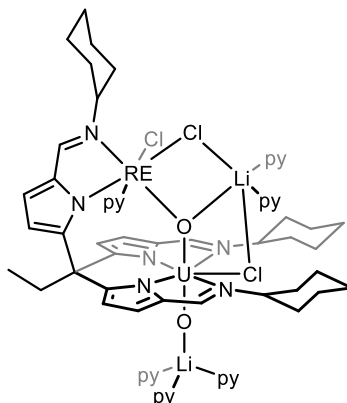


Figure SI 15. ¹H NMR spectrum of **6-Dy** in *d*₅-pyridine.

[U^vO₂Sm(Cl)(L)(py)₂]₂, 6-Sm: A solution of SmCl₃(THF)₂ (2 eq., 28 mg, 0.070 mmol) in dry THF (5 mL) was added to a stirred solution of **5-K** (85 mg, 0.035 mmol) in THF under a nitrogen atmosphere. The mixture was stirred at room temperature for 16 hours, after which a colourless precipitate formed. The mixture was filtered and the solvent removed from the brown filtrate under vacuum. After washing the resulting brown solid with hexane the product was obtained as a pale yellow solid (72 mg, 0.031 mmol, 86 %). X-ray quality crystals were grown by vapour diffusion of hexane into a solution

of **6-Sm** in pyridine. No NMR data could be obtained. IR: Imine C=N 1601.16 cm^{-1} , pyrrole C-N 1046.53 cm^{-1} , U-O 668.70 cm^{-1} . APPI-MS: $[\text{UO}_2\text{SmCl}]^+$ 1022.33421 m/z .



$[\text{U}^{\text{V}}\text{O}_2\text{Y}(\text{Cl})(\text{LiCl})_2(\text{L})(\text{py})_6]$, 6-Y': A solution of LiCl (3 mg, 0.071 mmol) in dry pyridine (2 mL) was added to a solution of **6-Y** (40 mg, 0.019 mmol) in dry pyridine (5 mL) under a nitrogen atmosphere. The mixture was stirred for 16 hours before the solvent was removed under reduced pressure. The resulting solid was washed with hexane to give the product as a pale yellow solid (34 mg, 0.022 mmol, 58%). X-ray quality crystals were grown by vapour diffusion of hexane into a pyridine solution of **6-Y'** in pyridine. ^1H NMR (601 MHz, pyridine- d_5): δ_{H} 13.44, 12.81, 5.37, 4.70, 4.69, 4.07, 4.04, 2.09 (br), -0.47, -1.24, -1.94, -2.84, -3.34, -3.99, -4.38, -4.92, -6.54 (br), -7.32, -8.59 (br). IR: Imine C=N 1596.88 cm^{-1} , pyrrole C-N 1047.96 cm^{-1} , U-O 668.70 cm^{-1} .

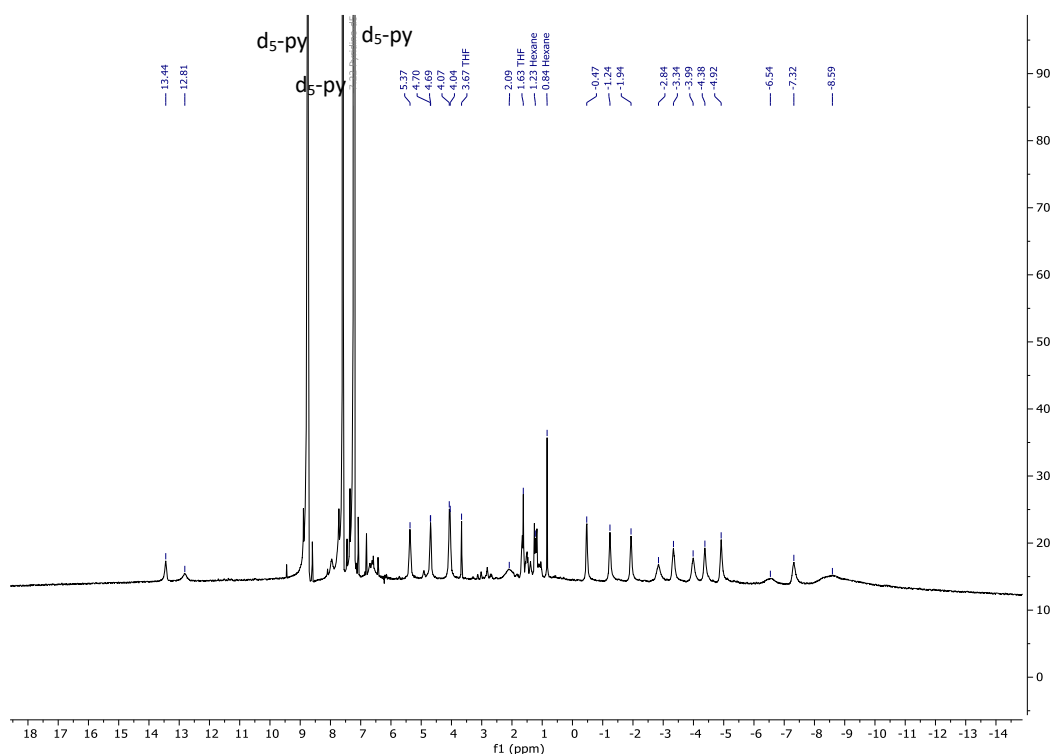


Figure SI 16. ^1H NMR spectrum of **6-Y'** in d_5 -pyridine.

$[U^{IV}O_2Dy(Cl)(LiCl)_2(L)(py)_6]$, 6-Dy': A solution of LiCl (3 mg, 0.071 mmol, 4 eq) in dry pyridine (2 mL) was added to a solution of **6-Dy** (37 mg, 0.016 mmol) in dry pyridine (5 mL) under a nitrogen atmosphere. The mixture was stirred for 16 hours before the solvent was removed from the resulting brown solution under reduced pressure. The resulting solid was washed with hexane to give the product as a pale yellow solid (29 mg, 0.018 mmol, 56%). X-ray quality crystals were grown by vapour diffusion of hexane into a pyridine solution of **6-Dy'** in pyridine. IR: Imine C=N 1598.31 cm^{-1} , pyrrole C-N 1047.96 cm^{-1} , U-O 670.12 cm^{-1} .

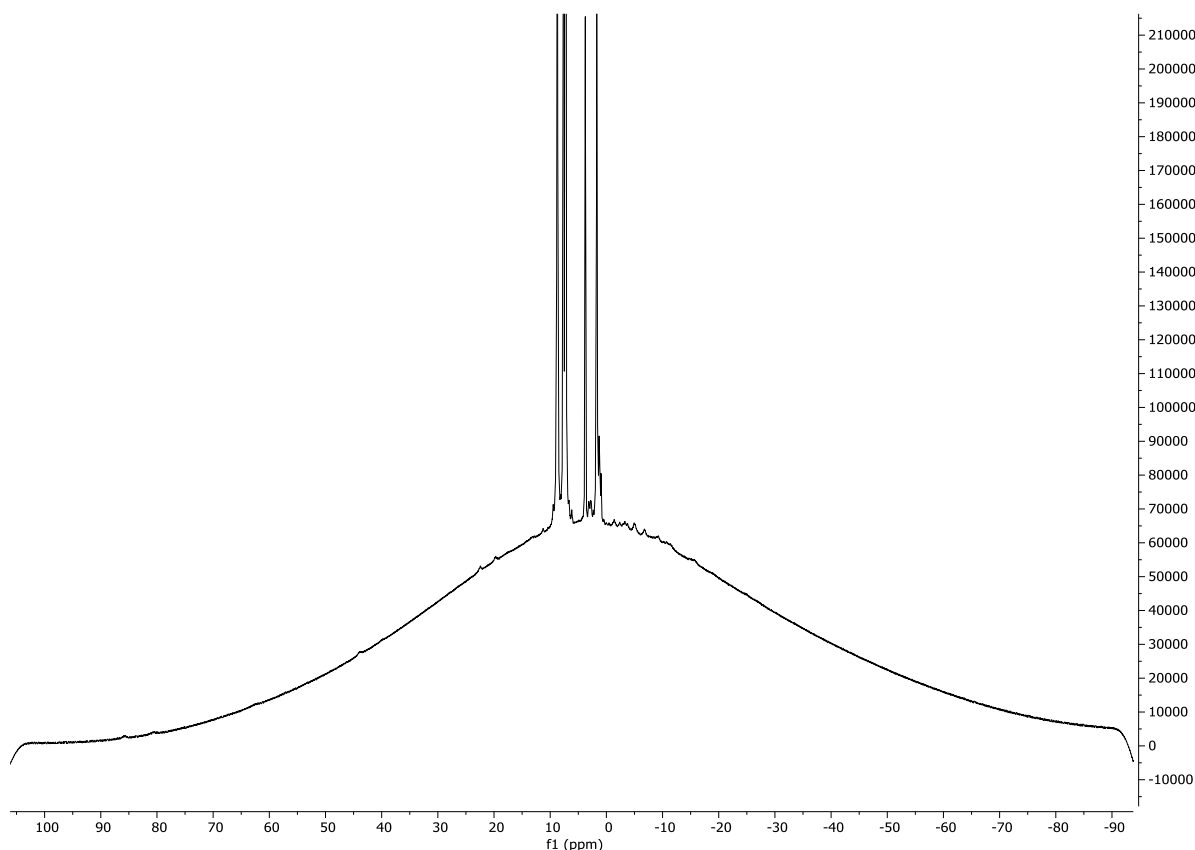
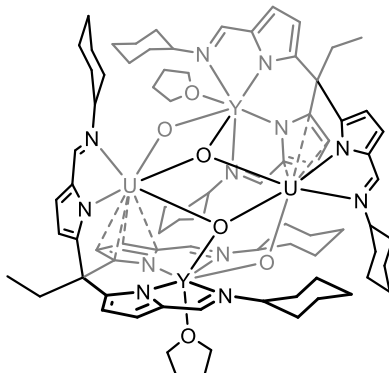


Figure SI 17. 1H NMR spectrum of **6-Dy'** in d_5 -pyridine.



$[U^{IV}O_2Y(L)]_2(THF)_2$, 7-THF: KC_8 (12 mg, 0.089 mmol) was added to a solution of **6-Y** (90 mg, 0.041 mmol) in dry THF (5 mL) and stirred for 1 hour at room temperature, after which the brown solution darkened

and a black precipitate formed (graphite and KCl mixture). The solid graphite and KCl were removed by filtration and the solvent removed under vacuum to give the product as a brown solid after washing with hexane (68 mg, 0.034 mmol, 84%). X-ray quality crystals were grown by slow evaporation of a THF solution of **7-THF** (or by vapour diffusion of hexane into a pyridine solution to give $[(U^{IV}O_2Y(L))_2\{py\}_3]$, **7-py**). 1H NMR (500 MHz, pyridine- d_5): δ_H 79.29, 66.04, 57.96, 56.34, 40.58, 40.41, 31.34, 31.24, 28.91, 24.83, 23.84, 23.25, 23.16, 23.12, 22.62, 21.93, 21.90, 18.30, 17.78, 16.48, 16.43, 15.27, 14.69, 14.12, 10.53, 10.37, 9.90, 8.09, 7.86, 7.00, 6.76, 6.22, 5.85, 3.85, 2.97, 2.52, 0.60, 0.38, 0.17, -1.07, -1.39, -1.79, -2.70, -3.00, -3.02, -3.19, -3.23, -3.41, -3.45, -4.19, -4.47, -4.61, -5.16, -6.11, -6.82, -7.70, -8.11, -8.82, -9.07, -11.53, -11.85, -13.44, -16.66, -16.71, -17.41, -18.95, -25.90, -26.42, -26.47, -35.81, -62.06, -77.65. IR: Imine C=N 1586.90 cm^{-1} , pyrrole C-N 1046.53 cm^{-1} , U-O 537.52 cm^{-1} .

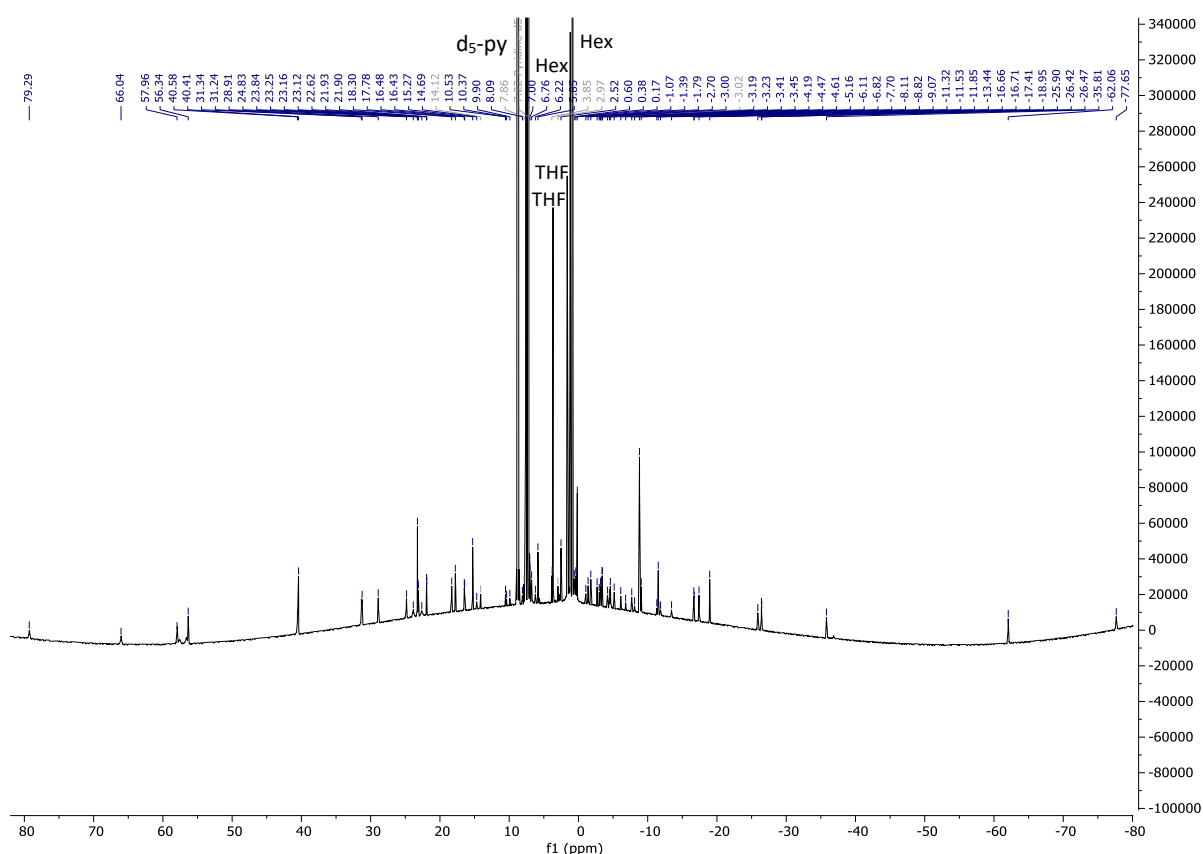


Figure SI 18. 1H NMR spectrum of **7-py** in d_5 -pyridine.

Infrared Spectroscopy

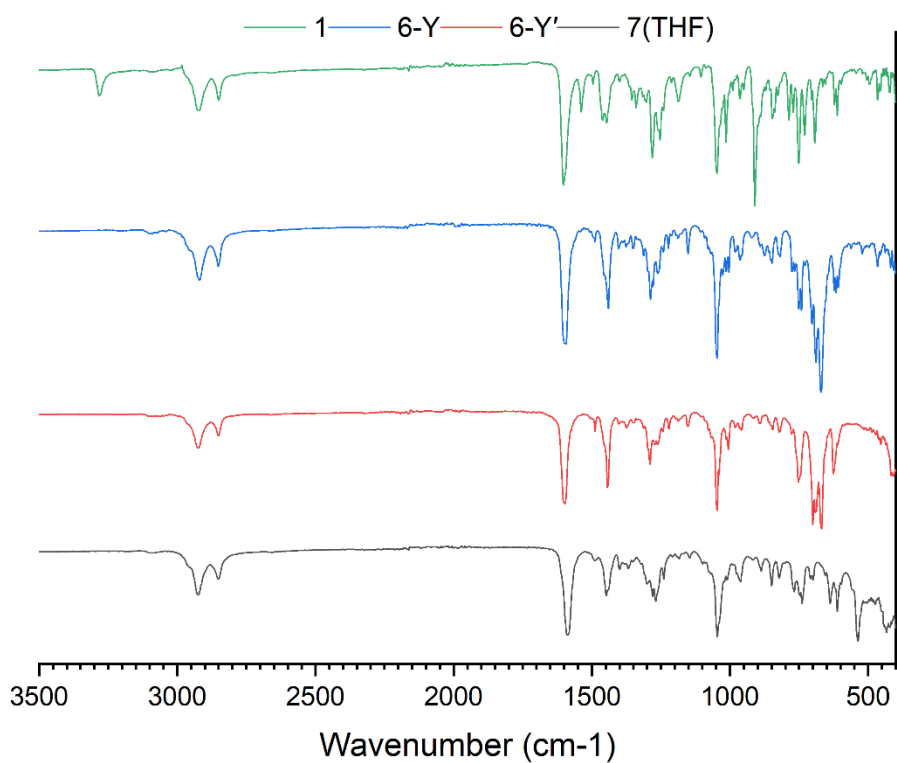
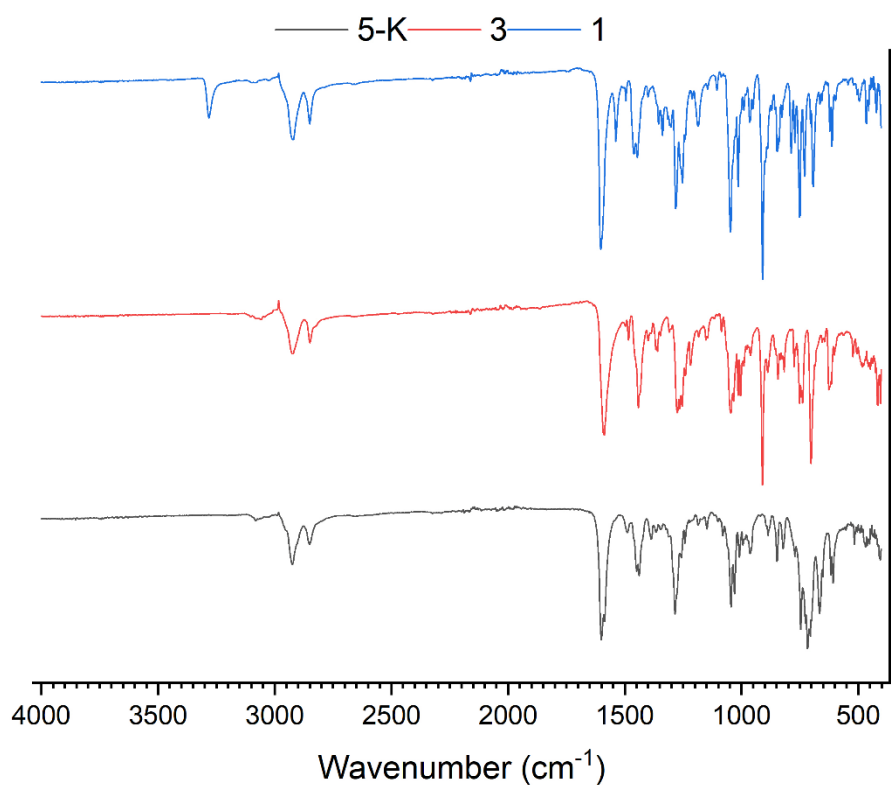
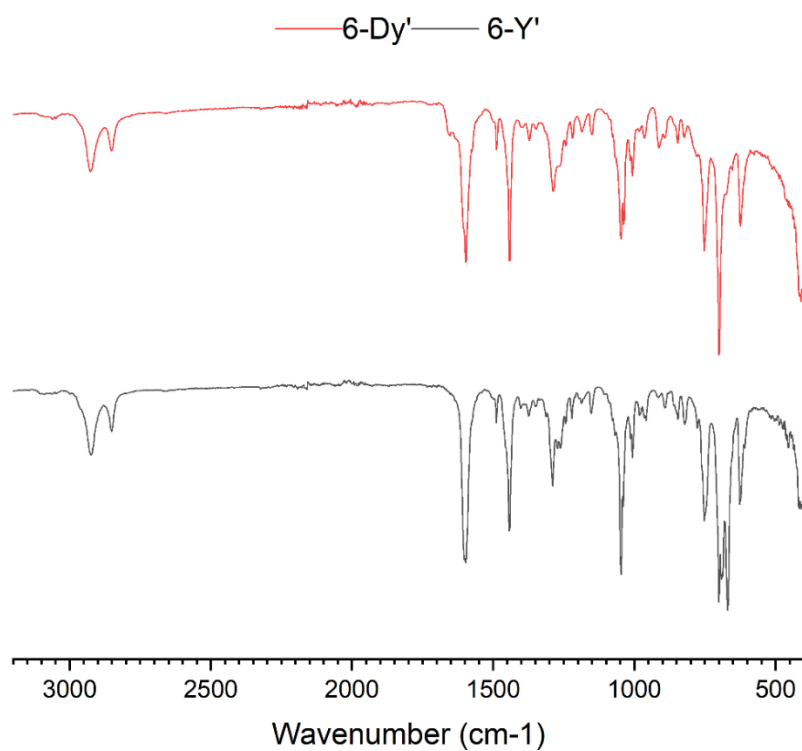


Figure SI 19. Stacked IR spectra of complexes 1, 3 and 5-K.

Figure SI 20. Stacked IR spectra of complexes **1**, **6-Y**, **6-Y'** and **7(THF)**.



Figure

SI 21. Stacked IR spectra of complexes **5-K**, **6-Zn**, **6-Y**, **6-Sm** and **6-Dy**.

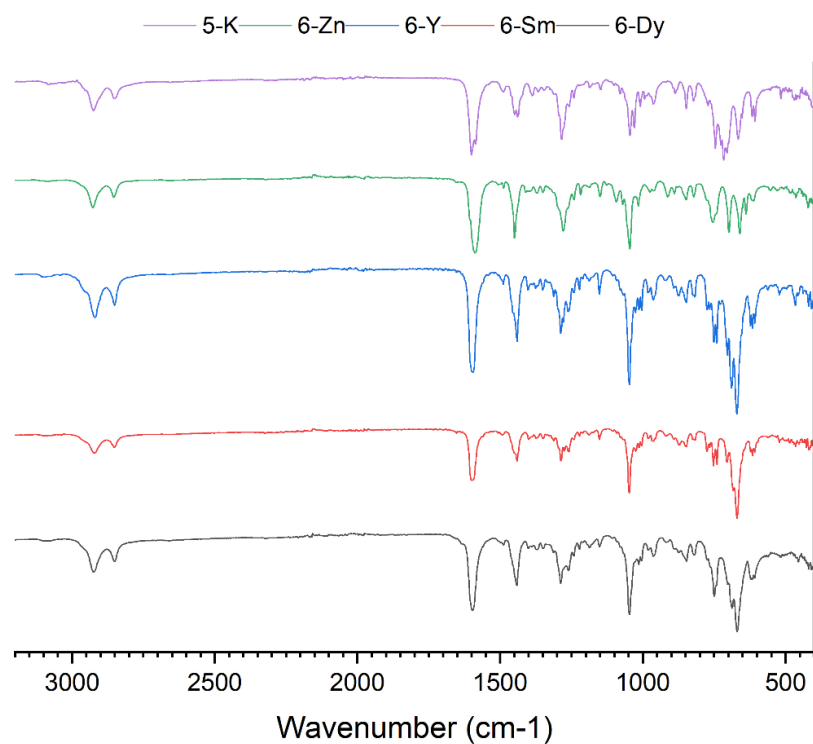


Figure SI 22. Stacked IR spectra of complexes **6-Y'** and **6-Dy'**.

Electrochemistry

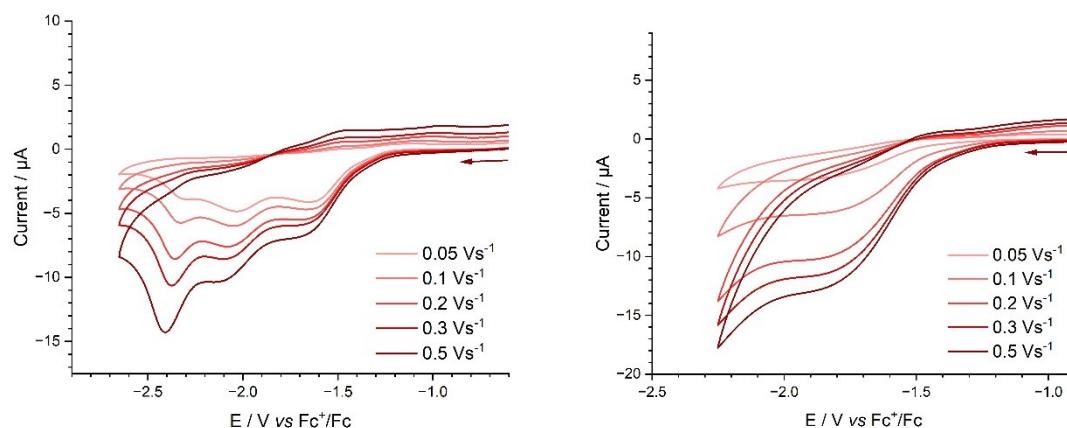


Figure SI 23. Cyclic voltammetry of a 2 mM solution of **2-THF** in 0.1 M [ⁿBu₄N][PF₆] electrolyte using a glassy-carbon working electrode, platinum gauze counter electrode and a silver wire pseudo-reference electrode. The spectra were referenced to ferrocene (Fc⁺/Fc) and run at scan-rates 0.05, 0.1, 0.2, 0.3 and 0.5 V s⁻¹.

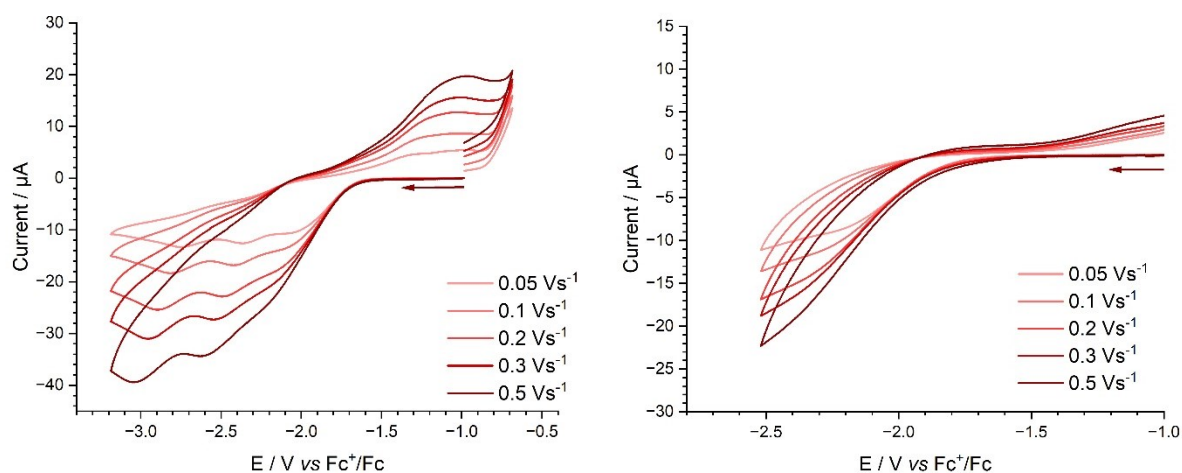


Figure SI 24. Cyclic voltammetry of a 10 mM solution of **3** in 0.1 M [ⁿBu₄N][PF₆] electrolyte using a glassy-carbon working electrode, platinum gauze counter electrode and a silver wire pseudo-reference electrode. The spectra were referenced to ferrocene (Fc⁺/Fc) and run at scan-rates 0.05, 0.1, 0.2, 0.3 and 0.5 V s⁻¹.

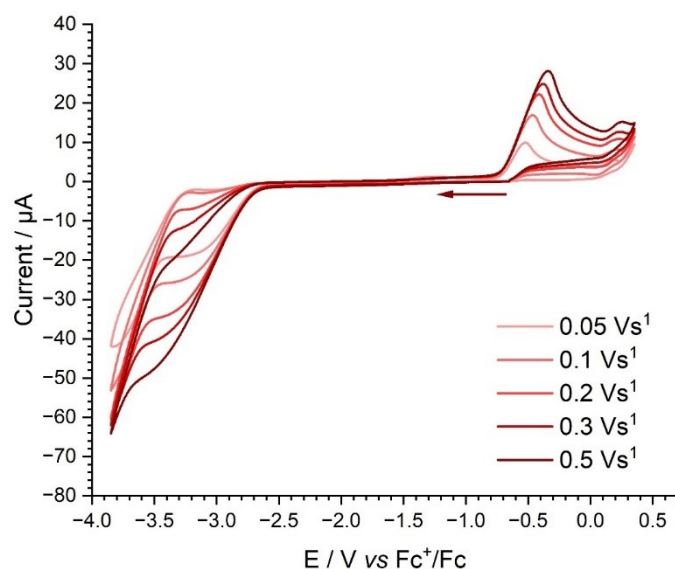


Figure SI 25. Cyclic voltammetry of a 10 mM solution of **H₃L** in 0.1 M [ⁿBu₄N][PF₆] electrolyte using a glassy-carbon working electrode, platinum gauze counter electrode and a silver wire pseudo-reference electrode. The spectra were referenced to ferrocene (Fc⁺/Fc) and run at scan-rates 0.05, 0.1, 0.2, 0.3 and 0.5 V s⁻¹. The irreversible oxidation at E_{p_a} = -0.52 V vs Fc⁺/Fc is only present when scanning to the potential of the irreversible reduction at E_{p_c} = -3.25 V vs Fc⁺/Fc.

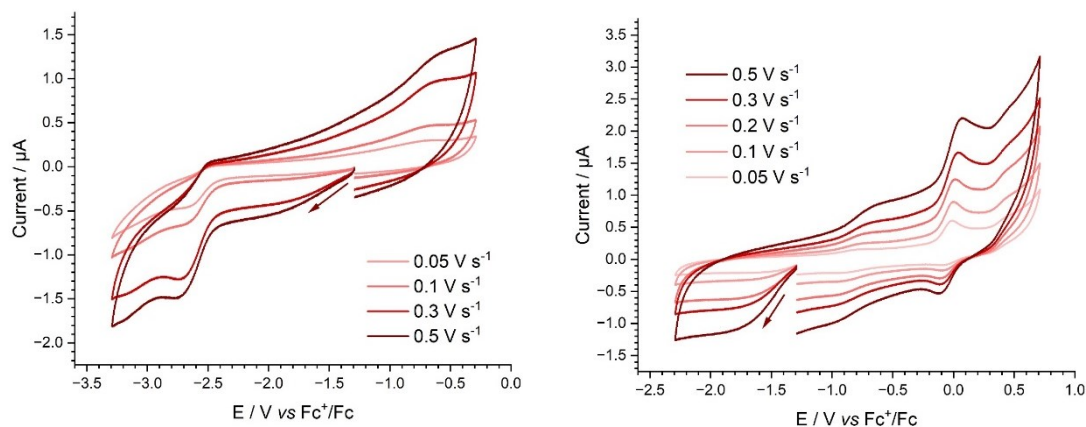


Figure SI 26. Cyclic voltammetry of a 1 mM solution of **6-Zn** in 0.1 M [ⁿBu₄N][PF₆] electrolyte using a glassy-carbon working electrode, platinum gauze counter electrode and a silver wire pseudo-reference electrode. The spectra were referenced to ferrocene (Fc⁺/Fc = 0 V) and run at scan-rates 0.05, 0.1, 0.2, 0.3 and 0.5 V s⁻¹. The reversible reduction at 0 V is the Fc⁺/Fc redox couple.

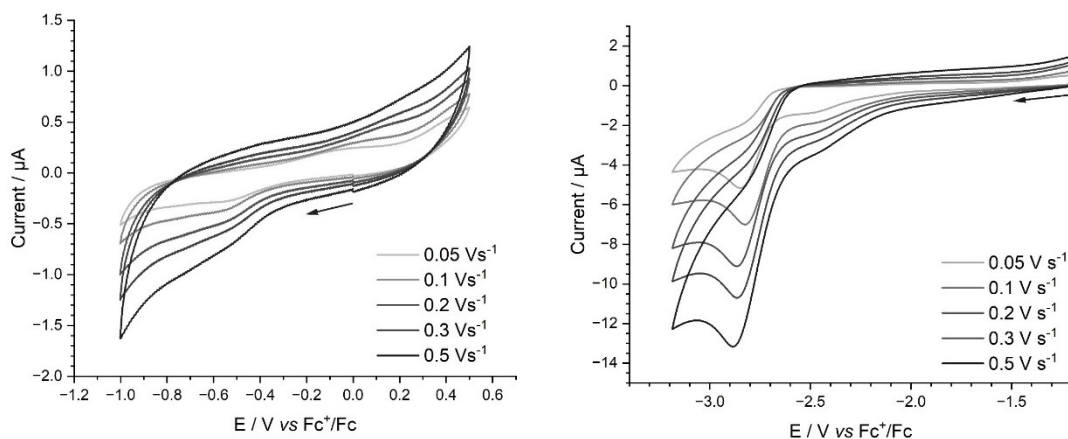


Figure SI 27. Cyclic voltammetry of a 1 mM solution of **6-Y** in 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ electrolyte using a glassy-carbon working electrode, platinum gauze counter electrode and a silver wire pseudo-reference electrode. The spectra were referenced to ferrocene ($\text{Fc}^+/\text{Fc} = 0 \text{ V}$) and run at scan-rates 0.05, 0.1, 0.2, 0.3 and 0.5 V s^{-1} .

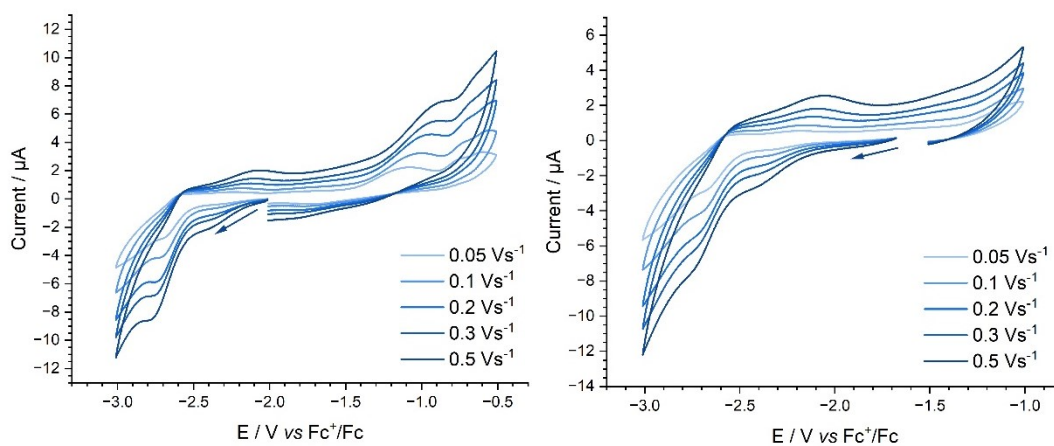


Figure SI 28. Cyclic voltammetry of a 1 mM solution of **5-K** in 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ electrolyte using a glassy-carbon working electrode, platinum gauze counter electrode and a silver wire pseudo-reference electrode. The spectra were referenced to ferrocene ($\text{Fc}^+/\text{Fc} = 0 \text{ V}$) and run at scan-rates between 0.05 and 0.5 V s^{-1} .

Crystallographic details

	[UO ₂ (HL)] ₂ , 1
CCDC Number	2313497
Crystal data	
Chemical formula	C ₃₆ H ₄₈ N ₆ O ₂ U·C ₇ H ₈
<i>M</i> _r	926.96
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.6782 (2), 16.9971 (2), 18.3318 (2)
β (°)	91.987 (1)
<i>V</i> (Å ³)	4570.79 (10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.59
Crystal size (mm)	0.31 × 0.26 × 0.12
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst. A</i> 51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T</i> _{min} , <i>T</i> _{max}	0.805, 0.915
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	51279, 11102, 9250
<i>R</i> _{int}	0.032
(sin θ/λ) _{max} (Å ⁻¹)	0.690
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.054, 1.02
No. of reflections	11102
No. of parameters	470
H-atom treatment	H-atom parameters constrained
Δ _{max} , Δ _{min} (e Å ⁻³)	0.98, -0.68

	[UO ₂ (HL)(THF)], 2-THF
CCDC Number	2313498
Crystal data	
Chemical formula	C ₄₀ H ₅₆ N ₆ O ₃ U
<i>M</i> _r	906.93
Crystal system, space group	Triclinic, <i>P</i> ⁻ 1
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.5408 (7), 11.7266 (6), 15.0732 (7)
α, β, γ (°)	81.684 (4), 84.377 (4), 75.615 (5)
<i>V</i> (Å ³)	1951.09 (19)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.20
Crystal size (mm)	0.22 × 0.14 × 0.06
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Multi-scan <i>CrysAlis PRO</i> 1.171.42.81a (Rigaku Oxford Diffraction, 2023) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T</i> _{min} , <i>T</i> _{max}	0.596, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	15591, 15591, 12658
<i>R</i> _{int}	?
(sin θ/λ) _{max} (Å ⁻¹)	0.612
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.100, 0.99
No. of reflections	15591
No. of parameters	453
No. of restraints	460
H-atom treatment	H-atom parameters constrained
Δ _{max} , Δ _{min} (e Å ⁻³)	2.24, -1.21

	[UO ₂ (HL)(py)], 2-py
CCDC Number	2313499
Crystal data	
Chemical formula	C ₄₁ H ₅₃ N ₇ O ₂ U
<i>M</i> _r	913.93
Crystal system, space group	Triclinic, <i>P</i> ⁻ 1
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.3701 (3), 11.9785 (5), 14.9463 (4)
α, β, γ (°)	83.518 (3), 85.015 (2), 75.569 (3)
<i>V</i> (Å ³)	1955.15 (11)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.20
Crystal size (mm)	0.31 × 0.09 × 0.07
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst.</i> A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T</i> _{min} , <i>T</i> _{max}	0.631, 0.892
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	36204, 7952, 6812
<i>R</i> _{int}	0.055
(sin θ/λ) _{max} (Å ⁻¹)	0.625
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.038, 0.090, 1.07
No. of reflections	7952
No. of parameters	507
No. of restraints	516
H-atom treatment	H-atom parameters constrained
Δ _{max} , Δ _{min} (e Å ⁻³)	2.97, -1.42

	[UO ₂ (LiL)(py) ₃], 3
CCDC Number	2313500
Crystal data	
Chemical formula	C ₅₁ H ₆₂ LiN ₉ O ₂ U
<i>M_r</i>	1078.06
Crystal system, space group	Monoclinic, <i>P2₁/c</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	18.3220 (7), 13.2763 (4), 20.5072 (9)
β (°)	108.143 (4)
<i>V</i> (Å ³)	4740.3 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.47
Crystal size (mm)	0.14 × 0.1 × 0.03
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst.</i> A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T_{min}</i> , <i>T_{max}</i>	0.593, 0.839
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	50829, 10030, 7881
<i>R_{int}</i>	0.077
(sin θ/λ) _{max} (Å ⁻¹)	0.633
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.040, 0.064, 1.03
No. of reflections	10030
No. of parameters	582
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δ _{max} , Δ _{min} (e Å ⁻³)	1.20, -0.77

	[UO ₂ (NaL)K(N(SiMe ₃) ₂)(py)], 4-Na/K
CCDC Number	2313501
Crystal data	
Chemical formula	C ₄₇ H ₇₀ KN ₈ NaO ₂ Si ₂ U·1.5(C ₆ H ₁₄)
<i>M</i> _r	1264.66
Crystal system, space group	Monoclinic, <i>I</i> 2/ <i>a</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	26.8382 (18), 15.5671 (10), 28.998 (3)
β (°)	92.423 (2)
<i>V</i> (Å ³)	12104.4 (17)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.84
Crystal size (mm)	0.36 × 0.05 × 0.04
Data collection	
Diffractometer	Bruker <i>APEX</i> -II CCD
Absorption correction	Empirical (using intensity measurements) TWINABS-2012/1 (Bruker,2012) was used for absorption correction. Final HKLF 4 output contains 595361 reflections, <i>R</i> _{int} = 0.0925 (208722 with <i>I</i> > 3σ(<i>I</i>), <i>R</i> _{int} = 0.0572)

No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	21269, 21269, 16103
<i>R</i> _{int}	?
(sin θ/λ) _{max} (Å ⁻¹)	0.676
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.052, 0.106, 1.10
No. of reflections	21269
No. of parameters	741
No. of restraints	246
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + 129.8202P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	1.23, -1.24

	[UO ₂ (K ₂ L)(py) ₄] ₂ , 5-K
CCDC Number	2313502
Crystal data	
Chemical formula	C _{112.003} H _{136.003} K ₄ N _{20.001} O ₄ U ₂
M_r	2458.86
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	120
a, b, c (Å)	12.5339 (3), 12.5763 (2), 19.5151 (5)
α, β, γ (°)	76.777 (2), 79.539 (2), 68.993 (2)
V (Å ³)	2778.75 (12)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	3.12
Crystal size (mm)	0.62 × 0.47 × 0.24
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst.</i> A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{\min}, T_{\max}	0.069, 0.274
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	51201, 13766, 12167
R_{int}	0.051
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.698
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.074, 1.05
No. of reflections	13766
No. of parameters	752
No. of restraints	301
H-atom treatment	H-atom parameters constrained
$\Delta_{\text{max}}, \Delta_{\text{min}}$ (e Å ⁻³)	2.42, -1.12

	[UO ₂ (ZnL)(py) _{1.5}] ₂ , 6-Zn
CCDC Number	2313503
Crystal data	
Chemical formula	C ₈₇ H ₁₀₉ N ₁₅ O ₄ U ₂ Zn ₂
<i>M_r</i>	2035.69
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.3634 (6), 18.9972 (7), 15.4266 (6)
β (°)	100.975 (2)
<i>V</i> (Å ³)	4132.4 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.54
Crystal size (mm)	0.23 × 0.21 × 0.05
Data collection	
Diffractometer	Bruker <i>APEX</i> -II CCD
Absorption correction	Multi-scan <i>SADABS</i> 2016/2 (Bruker,2016/2) was used for absorption correction. <i>wR</i> 2(int) was 0.0886 before and 0.0493 after correction. The Ratio of minimum to maximum transmission is 0.7390. The λ/2 correction factor is Not present.
<i>T_{min}</i> , <i>T_{max}</i>	0.552, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	196713, 15026, 12811
<i>R</i> _{int}	0.044
(sin θ/λ) _{max} (Å ⁻¹)	0.758
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.023, 0.051, 1.03
No. of reflections	15026
No. of parameters	611
H-atom treatment	H-atom parameters constrained
Δ _{max} , Δ _{min} (e Å ⁻³)	1.93, -2.16

	[UO ₂ (YL)(Cl)(py) ₂] ₂ , 6-Y
CCDC Number	2313504
Crystal data	
Chemical formula	C ₉₂ H ₁₁₄ Cl ₂ N ₁₆ O ₄ U ₂ Y ₂
<i>M</i> _r	2232.77
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.5026 (9), 17.0392 (9), 17.5819 (9)
β (°)	104.439 (2)
<i>V</i> (Å ³)	5077.8 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.42
Crystal size (mm)	0.06 × 0.05 × 0.02
Data collection	
Diffractometer	Bruker <i>APEX</i> -II CCD
Absorption correction	Empirical (using intensity measurements) <i>SADABS</i> 2016/2 (Bruker,2016/2) was used for absorption correction. <i>wR</i> 2(int) was 0.0803 before and 0.0702 after correction. The Ratio of minimum to maximum transmission is 0.9251. The λ/2 correction factor is Not present.
<i>T</i> _{min} , <i>T</i> _{max}	0.690, 0.745
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	176971, 10409, 8731
<i>R</i> _{int}	0.089
(sin θ/λ) _{max} (Å ⁻¹)	0.626
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.067, 1.07
No. of reflections	10409
No. of parameters	533
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 17.603P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	1.06, -0.96

	[UO ₂ (SmL)(Cl)(py) ₂] ₂ , 6-Sm
CCDC Number	2313505
Crystal data	
Chemical formula	C ₉₂ H ₁₁₄ Cl ₂ N ₁₆ O ₄ Sm ₂ U ₂
M_r	2355.65
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
a, b, c (Å)	17.5417 (2), 17.1342 (2), 17.6710 (2)
β (°)	104.591 (1)
V (Å ³)	5139.95 (10)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	4.37
Crystal size (mm)	0.26 × 0.13 × 0.04
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst.</i> A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{\min}, T_{\max}	0.363, 0.756
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	133748, 13125, 11074
R_{int}	0.053
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.692
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.056, 1.03
No. of reflections	13125
No. of parameters	533
H-atom treatment	H-atom parameters constrained
$\Delta_{\text{max}}, \Delta_{\text{min}}$ (e Å ⁻³)	2.04, -0.73

	[UO ₂ (DyL)(Cl)(py) ₂] ₂ , 6-Dy
CCDC Number	2313506
Crystal data	
Chemical formula	C ₉₂ H ₁₁₄ Cl ₂ Dy ₂ N ₁₆ O ₄ U ₂ ·3(C ₅ H ₅ N)
<i>M</i> _r	2617.24
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.5882 (7), 17.0832 (4), 17.6031 (5)
β (°)	104.739 (4)
<i>V</i> (Å ³)	5115.0 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.71
Crystal size (mm)	0.46 × 0.26 × 0.24
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Multi-scan <i>CrysAlis PRO</i> 1.171.42.81a (Rigaku Oxford Diffraction, 2023) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T</i> _{min} , <i>T</i> _{max}	0.755, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	28997, 9868, 7702
<i>R</i> _{int}	0.046
(sin θ/λ) _{max} (Å ⁻¹)	0.625
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.051, 0.136, 1.13
No. of reflections	9868
No. of parameters	641
No. of restraints	200
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 66.7969P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	3.02, -2.34

	[UO ₂ (YL)(Cl)(LiCl) ₂], 6-Y'
CCDC Number	2313507
Crystal data	
Chemical formula	C ₆₆ H ₇₇ Cl ₃ Li ₂ N ₁₂ O ₂ UY·C ₅ H ₅ N
<i>M</i> _r	1596.66
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.0604 (3), 17.0605 (2), 24.4496 (4)
β (°)	106.506 (2)
<i>V</i> (Å ³)	7622.9 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.03
Crystal size (mm)	0.39 × 0.38 × 0.09
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst.</i> A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T</i> _{min} , <i>T</i> _{max}	0.203, 0.653
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	153359, 18097, 13924
<i>R</i> _{int}	0.071
(sin θ/λ) _{max} (Å ⁻¹)	0.679
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.072, 1.02
No. of reflections	18097
No. of parameters	839
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 10.9349P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	1.19, -1.18

	[UO ₂ (DyL)(Cl)(LiCl) ₂], 6-Dy'
CCDC Number	2313508
Crystal data	
Chemical formula	C ₆₆ H ₇₇ Cl ₃ DyLi ₂ N ₁₂ O ₂ U·2(C ₃ H ₅ N)
<i>M_r</i>	1749.35
Crystal system, space group	Monoclinic, <i>P2₁/n</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.0653 (4), 17.0891 (3), 24.4481 (5)
β (°)	106.566 (2)
<i>V</i> (Å ³)	7634.8 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.25
Crystal size (mm)	0.46 × 0.24 × 0.06
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst.</i> A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T_{min}</i> , <i>T_{max}</i>	0.224, 0.752
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	79648, 17518, 13292
<i>R_{int}</i>	0.067
(sin θ/λ) _{max} (Å ⁻¹)	0.680
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.042, 0.079, 1.04
No. of reflections	17518
No. of parameters	893
No. of restraints	100
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 10.4983P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	1.36, -1.26

	[UO ₂ (YL)(THF) ₂] ₂ , 7-THF
CCDC Number	2313509
Crystal data	
Chemical formula	C ₈₀ H ₁₁₀ N ₁₂ O ₆ U ₂ Y ₂
<i>M</i> _r	1989.67
Crystal system, space group	Triclinic, <i>P</i> ⁻ 1
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.3299 (4), 16.2642 (4), 21.1749 (4)
α, β, γ (°)	74.514 (2), 87.911 (2), 82.799 (2)
<i>V</i> (Å ³)	5047.7 (2)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	10.77
Crystal size (mm)	0.36 × 0.09 × 0.06
Data collection	
Diffractometer	SuperNova, Dual, Cu at home/near, Atlas
Absorption correction	Empirical (using intensity measurements) <i>SADABS2016/2</i> (Bruker,2016/2) was used for absorption correction. <i>wR2(int)</i> was 0.1210 before and 0.0749 after correction. The Ratio of minimum to maximum transmission is 0.1867. The λ/2 correction factor is Not present.
<i>T</i> _{min} , <i>T</i> _{max}	0.110, 0.588
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	107929, 20831, 16990
<i>R</i> _{int}	0.074
(sin θ/λ) _{max} (Å ⁻¹)	0.629
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.058, 0.146, 1.07
No. of reflections	20831
No. of parameters	949
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 69.4686P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	4.56, -5.13

	[UO ₂ (YL)(py) ₂] ₂ (py), 7-Py
CCDC Number	2313510
Crystal data	
Chemical formula	C ₈₇ H ₁₀₉ N ₁₅ O ₄ U ₂ Y ₂ ·C ₆ H ₁₄ ·[+solvents]
<i>M</i> _r	2168.94
Crystal system, space group	Triclinic, <i>P</i> ⁻ 1
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.1503 (3), 16.1749 (4), 24.3853 (7)
α, β, γ (°)	79.382 (2), 82.241 (2), 85.201 (2)
<i>V</i> (Å ³)	4658.7 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.76
Crystal size (mm)	0.50 × 0.14 × 0.12
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst.</i> A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T</i> _{min} , <i>T</i> _{max}	0.311, 0.650
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	93776, 19017, 15700
<i>R</i> _{int}	0.070
(sin θ/λ) _{max} (Å ⁻¹)	0.625
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.063, 0.146, 1.11
No. of reflections	19017
No. of parameters	1049
No. of restraints	1233
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 76.4691P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	4.14, -2.02

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