Supplementary Information "Co-linear, double-uranyl complexation in an expanded Schiff-base polypyrrole macrocycle"

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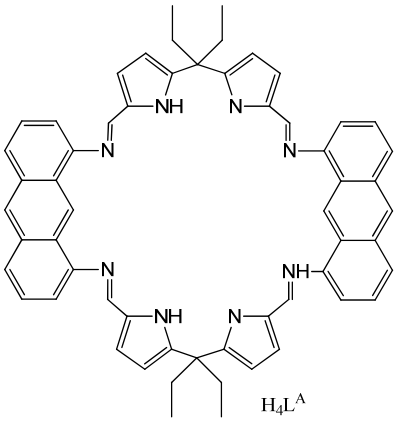
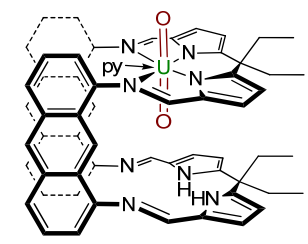
General Experimental Details

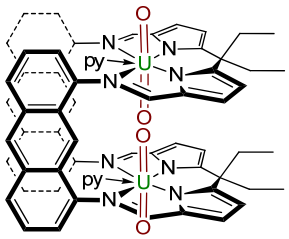
All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in an MBraun Labstar glovebox unless otherwise stated. Solvents were degassed and dried using a Vacuum Atmospheres solvent system prior to use. Deuterated solvents were boiled over potassium, vacuum transferred, and freeze-pump-thaw degassed three times prior to use. H_4L^{A} [1] and $[UO_2\{N(SiMe_3)_2\}_2(py)_2]$[2] were synthesised according to literature procedures. ^{1}H NMR spectra were recorded on a Bruker AVA 400 spectrometer operating at 399.90 MHz, ^{13}C NMR spectra where recorded on a Bruker AVA 500 operating at 125.76 MHz. All spectra were recorded at 298 K. Chemical shifts are reported in parts per million, and referenced to residual proton resonances calibrated against external TMS. All spectra were recorded at 298 K unless otherwise stated. Infrared spectra were recorded on a Jasco 410 spectrophotometer, w = weak, m = medium, s = strong intensity. Cyclic voltammetry experiments were performed using an Autolab 302 potentiostat and the data processed using GPES manager version 4.9. Experiments were performed in a glovebox using a 15 mL glass vial as the cell. The working electrode consisted of a platinum wire embedded in glass, the counter electrode a platinum wire and the reference electrode silver wire. The solution employed was 1 mmol $[\{UO_2(py)\}_2(L)]$ **2** and 0.2 M $[Bu_4N][BF_4]$ with scan rates 300-1000 mVs^{-1}. All potentials are reported versus $[Cp_2Fe]^{0/+}$.

Abbreviations and compound numbering and lettering scheme





1



2

py = 

Synthesis and Characterisation

^{1}H NMR Spectrum of H_4L^A synthesised by literature methods

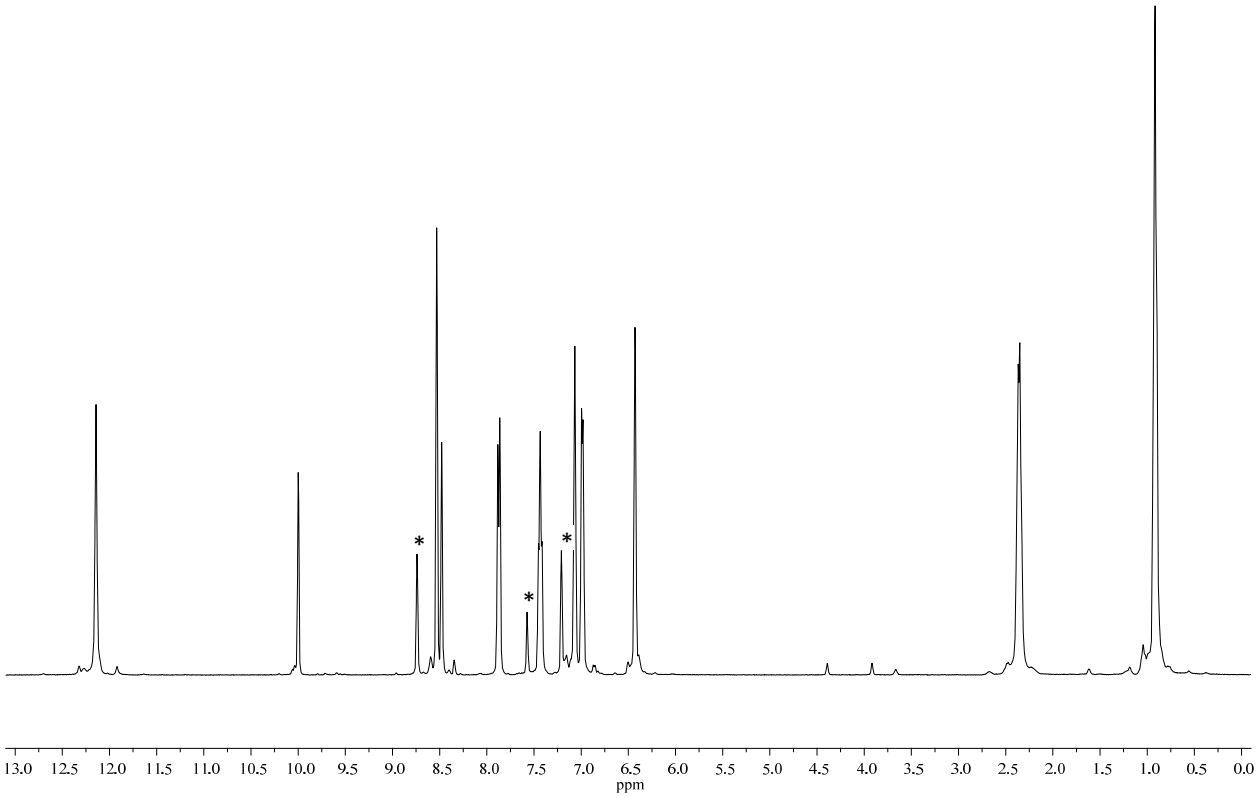


Fig. SI.1: ^{1}H NMR spectrum of H_4L^A in d_5-pyridine, * = residual C_5D_4HN

Synthesis of $[(UO_2)(py)(H_2L^A)]$ 1 and $[\{UO_2(py)\}_2(L^A)]$ 2

To a solution of H_4L^A (100 mg, 0.116 mmol) in pyridine (2 mL) was added a solution of $[UO_2\{N(SiMe_3)_2\}_2(py)_2]$ (174 mg, 0.232 mmol) in pyridine (2 mL) and the resulting brown solution stirred for four days at room temperature causing the precipitation of brown solids which were isolated by filtration and dried under vacuum for one hour at 100°C (85 mg, Batch A, see below). The volume of the filtrate was then reduced under vacuum to 0.5 mL and left to stand at room temperature for 24 h resulting in the precipitation of crystals of $[\{UO_2(py)\}_2(L^A)]$ **2**. These were isolated by filtration and dried under vacuum for one hour at 100°C. The filtrate was left to stand at room temperature for one week resulting in the precipitation of a final batch of 2 which was isolated in the same manner. $[\{UO_2(py)\}_2(L^A)]$ was collected as a brown crystalline solid which contained single crystals suitable for X-Ray diffraction.

Total yield of pure **2**: 50 mg, 0.032 mmol, 28%

Batch A contained a 70:30 mixture of **1** and **2**, equating to 0.046 mmol (40 %) and 0.019 mmol (16 %), respectively.

Characterising data for **2**: ^{1}H NMR (d_5-pyridine): δ_H 9.16 (s, 2H, aryl), 9.09 (s, 4H, imine), 8.22 (s, 2H, aryl), 7.50 (d, J = 8 Hz, 4H, aryl), 7.30 (d, J = 4 Hz, 4H, pyrrolic), 7.00 (t, J = 8 Hz, 4H, aryl), 6.86 (d, J = 8 Hz, 4H, aryl), 6.78 (d, J = 4 Hz, 4H, pyrrolic), 2.48 (m, 8H, CH_2) 1.09 (t, J = 7 Hz, 6H, CH_3), 0.90 (t, J = 7 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (d_5-pyridine): δ_C 162.2 (quarternary), 160.3 (aryl CH), 151.5 (quarternary), 137.2 (quarternary), 132.7 (quarternary), 128.1 (quarternary), 127.7 (aryl CH), 125.4 (aryl CH), 125.2 (aryl CH), 125.1 (aryl CH) 120.4 (pyrrolic CH) 112.2 (pyrrolic CH) 52.1 (meso- quaternary), 39.6 (CH_2), 38.6 (CH_2), 10.8 (CH_3), 10.5 (CH_3).

Analysis. Found: C, 53.70; H, 3.76; N, 8.78 %. $C_{68}H_{58}N_{10}O_4U_2$ requires: C, 52.51; H, 3.76; N, 9.01 %. FTIR (Nujol mull, cm-1): ν 1595 (s), 1551 (m), 1306 (m), 1281 (s), 1258 (m), 112 (w), 1092 (w), 1060 (m), 1015 (m), 924 (m), 912 (m, UO_2^{2+} asymmetric stretch), 878 (w), 860 (w), 761 (w), 747 (w), 718(w).

Solubility: partial solubility in pyridine and DMSO at room temperature, full dissolution afforded upon boiling up to 20 mg ml^{-1}. Insoluble in benzene, THF and MeCN.

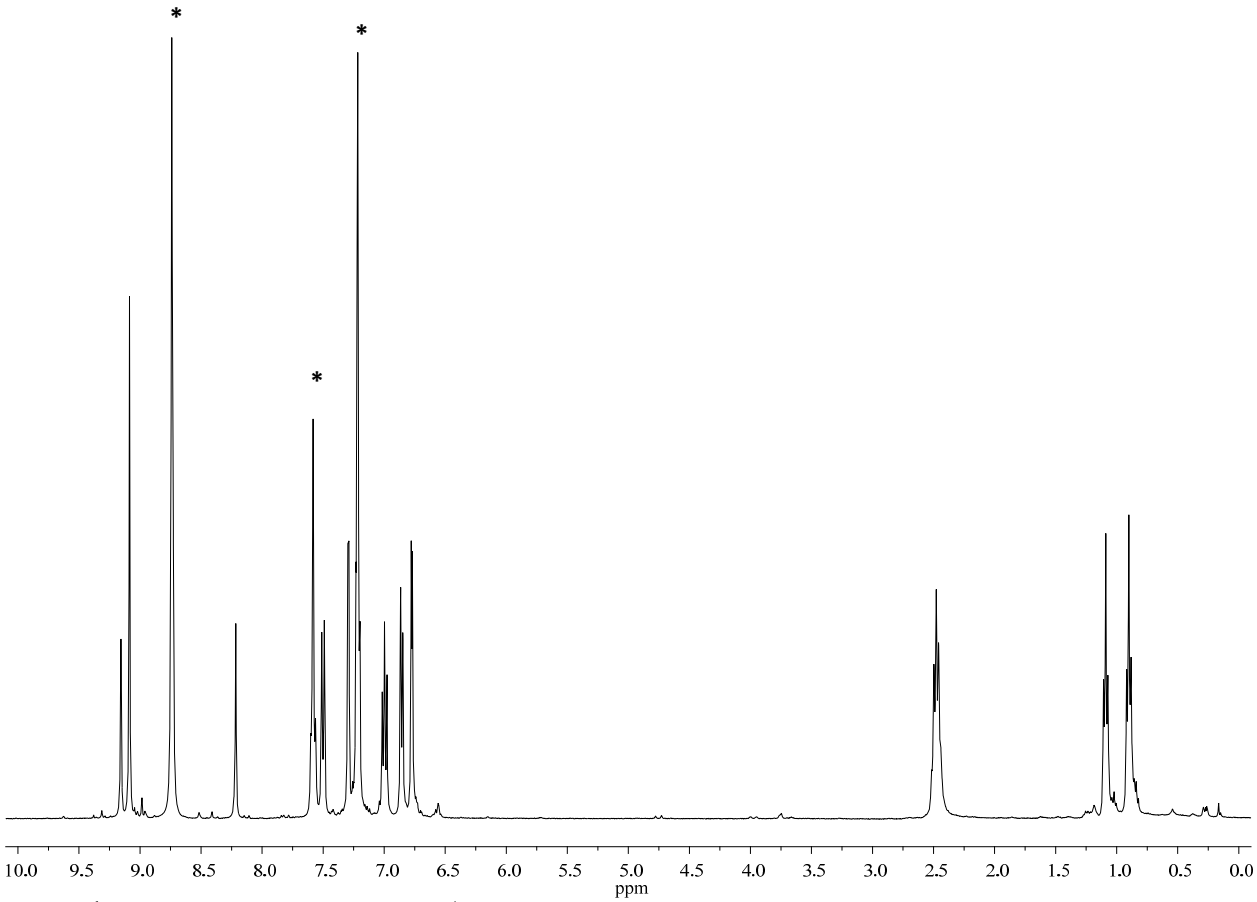


Fig. SI.2: ^{1}H NMR spectrum of [{UO_2(py)}$_2$(L^A)] **2** d_5-pyridine, * = residual C_5D_4HN

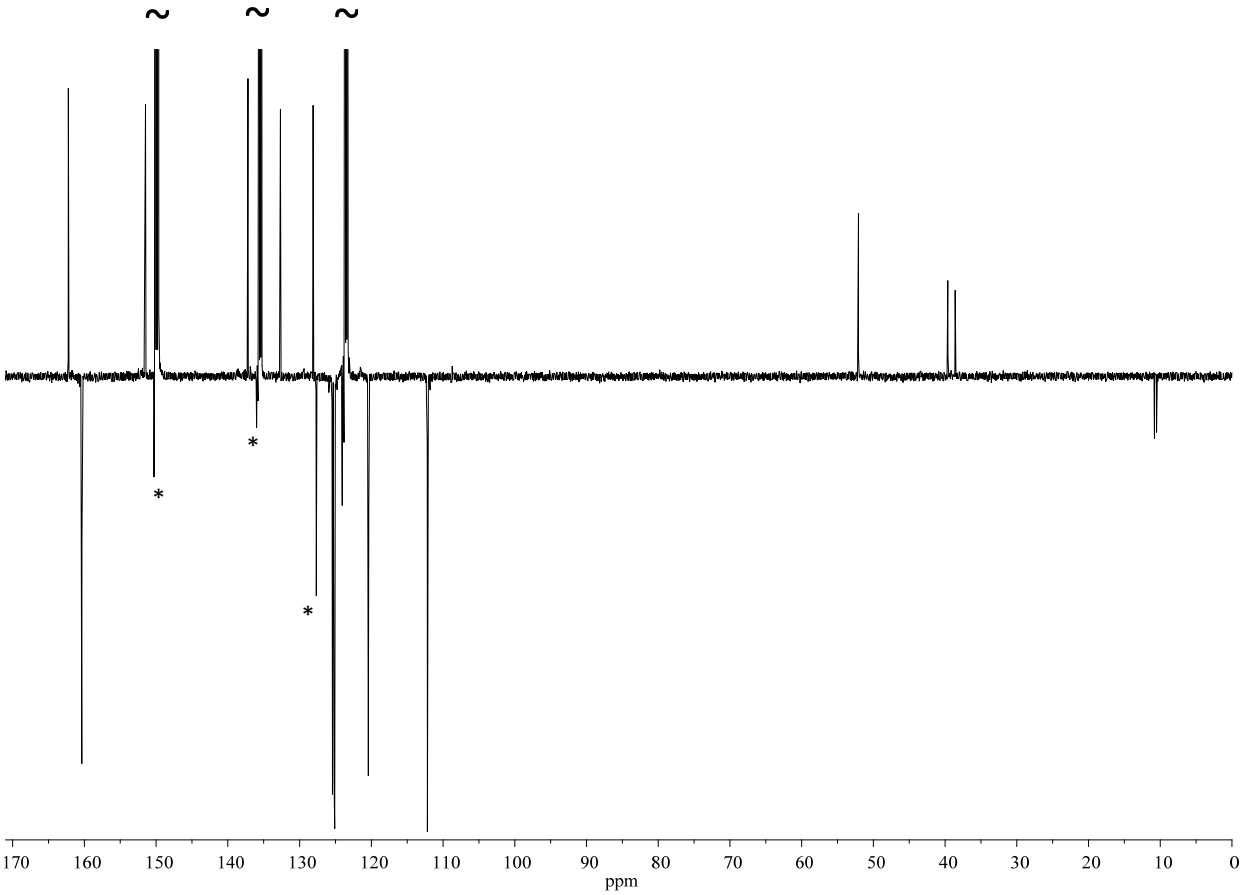


Fig. SI.3: $^{13}C\{^{1}H\}$ NMR spectrum of $[\{UO_2(py)\}_2(L^A)]$ **2** d_5-pyridine with DEPTQ135 editing. *C*D, CH_2, and quaternary carbons shown with positive phasing, *C*H and CH_3 shown with negative phasing ~ = C_5D_5N, * = residual C_5D_4HN.

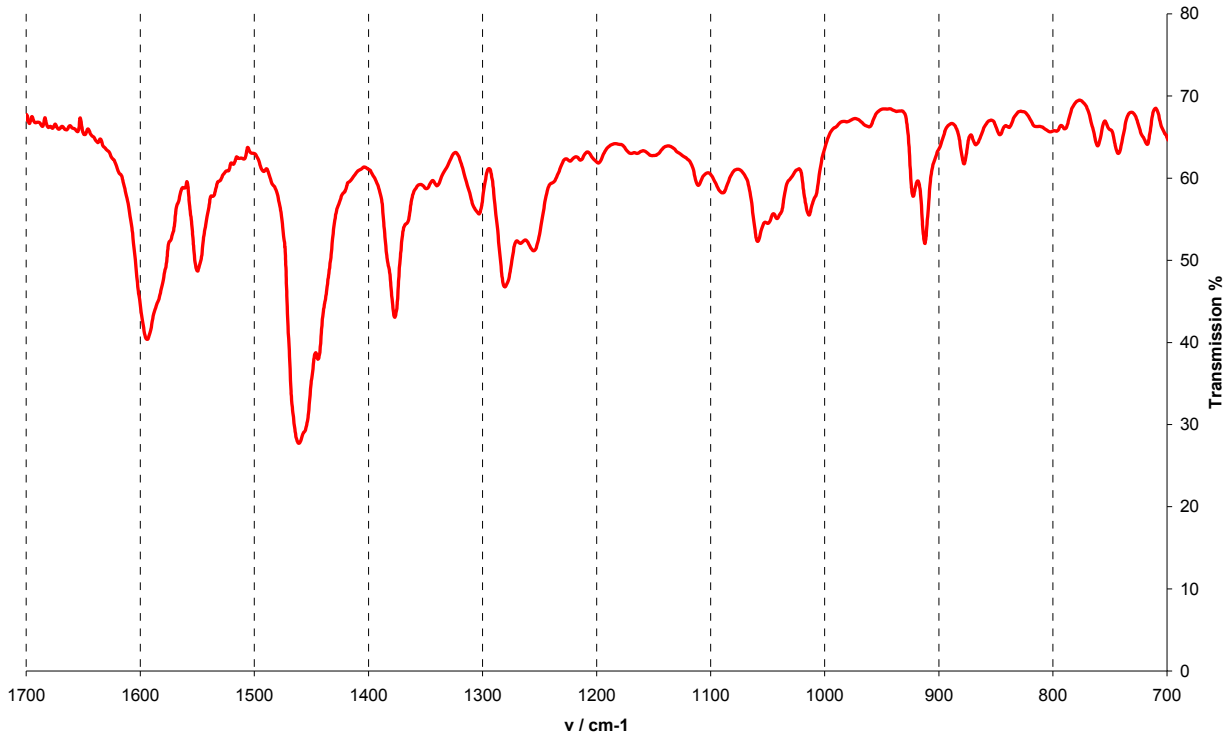


Fig. SI.4: FTIR spectrum of $[\{UO_2(py)\}_2(L^A)]$ **2** (nujol mull)

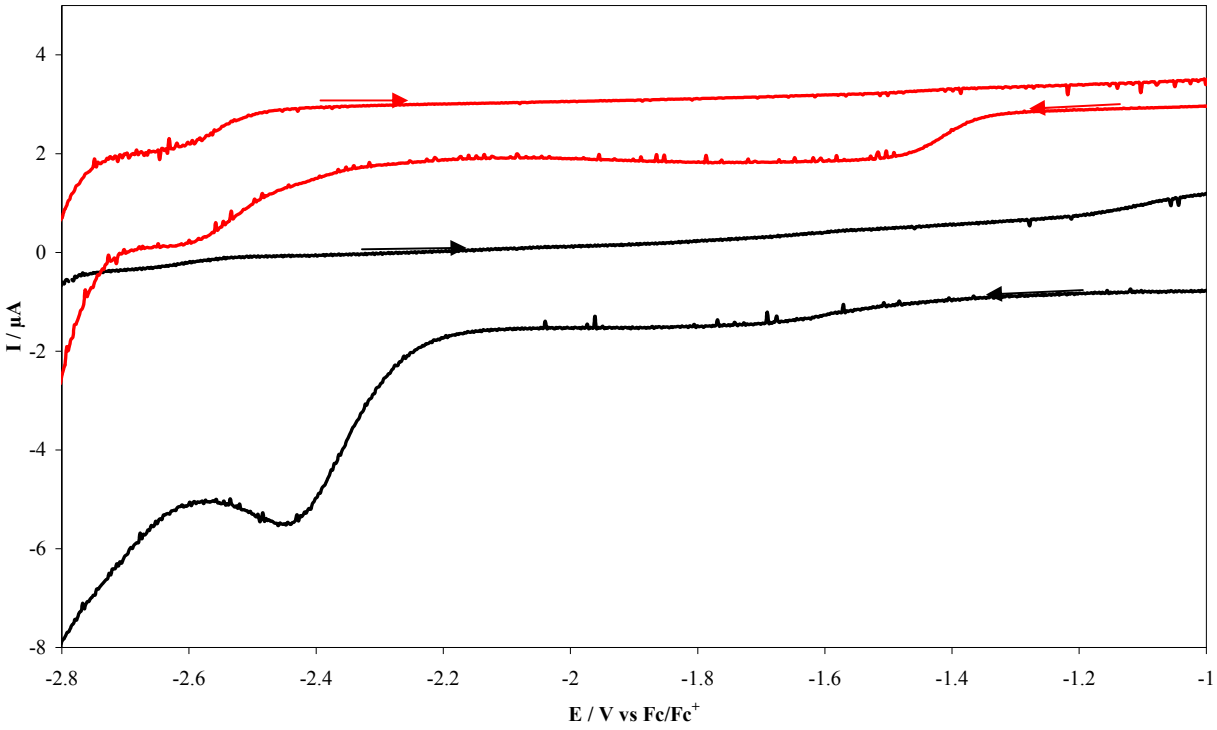


Fig. SI.5: Cyclic voltammogram of batch A (**1** + **2**, red line, current adjusted for clarity) and **2** (black line) in THF at 25 °C (Fc^+/Fc, 0.2M Bu_4NBF_4 as supporting electrolyte, 300 mV s^{-1}, Pt WE, Pt wire CE, Ag wire RE).

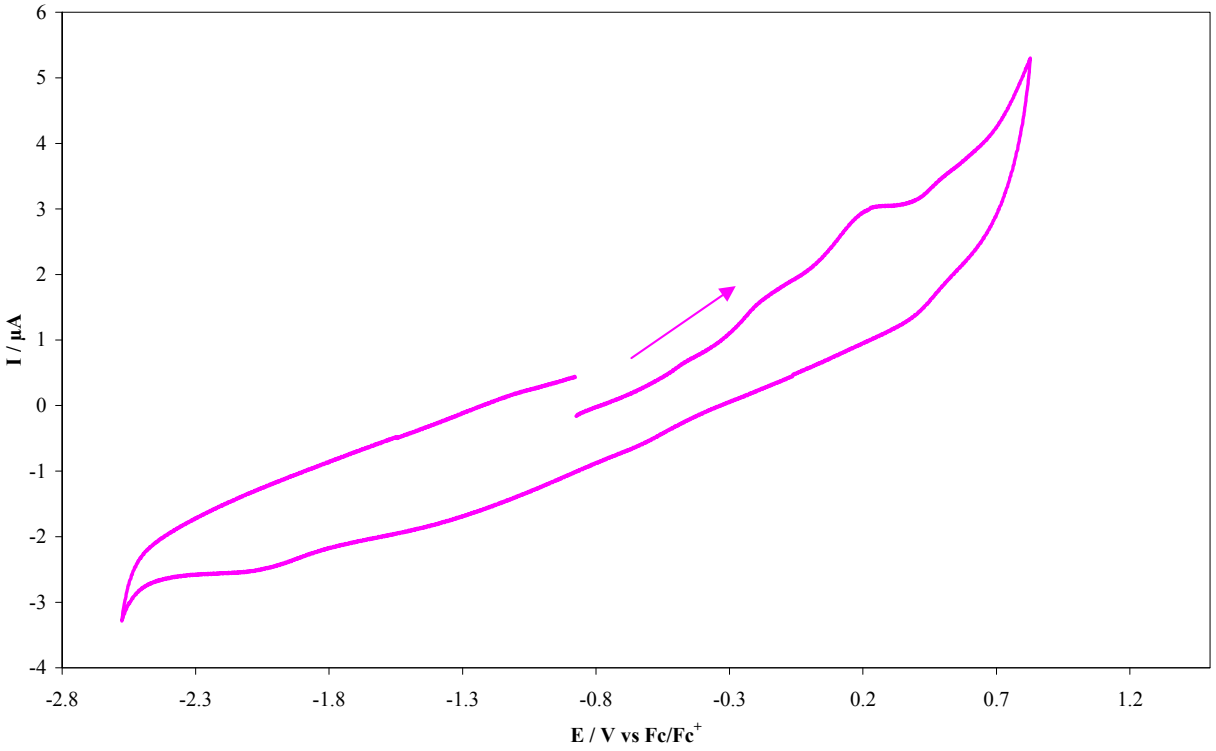


Fig. SI.6: Cyclic voltammogram of $[Zn_2(L^A)]$, which adopts a Pacman shape, for comparison. Solution in PhCN at 25 °C (Fc^+/Fc, 0.2M Bu_4NBF_4 as supporting electrolyte, 300 mV s^{-1}, Pt WE, Pt wire CE, Ag wire RE)**.**[3]

Characterisation data from Batch A: Contains 0.3 equivalents of $[\{UO_2(py)\}_2(L^A)]$ **2** (see above for resonances) and 0.7 equivalents of $[UO_2(py)(H_2L^A)]$ **1**: ^{1}H NMR (d_5-pyridine): δ_H 9.63 (s, 2H, aryl) 9.38 (s, 2H, imine), 9.01 (s, 2H, NH), 8.14 (s, 2H, aryl), 8.10 (s, 2H, imine), 7.74 (d, J = 8 Hz, 2H, aryl), 7.56 (d, J = 4 Hz, 2H, pyrrolic), 7.49 (d, J = 8 Hz, 2H, aryl), 7.32 (t, 2H, J = 8 Hz, aryl), 7.26 (t, J = 8 Hz, 2H, aryl), 7.01 (d, J = 8 Hz, 2H, aryl), 6.95 (d, J = 4 Hz, 2H, pyrrolic), 6.59 (d, J = 8 Hz, 2H, aryl), 6.55 (d, J = 4 Hz, 2H pyrrolic), 6.15 (d, J = 4 Hz, 2H pyrrolic), 2.71 (q, J = 7 Hz, 2H, CH_2), 2.54 (q, J = 7 Hz, 2H, CH_2), 2.17 (q, J = 7 Hz, 2H, CH_2), 1.60 (q, J = 7 Hz, 2H, CH_2), 1.47 (t, J = 7 Hz, 2H, CH_3), 1.05 (t, J = 7 Hz, 2H, CH_3), 0.97 (t, J = 7 Hz, 2H, CH_3), 0.54 (t, J = 7 Hz, 2H, CH_3).

MALDI (α-Cyano-4-hydroxycinnamic acid matrix):

Found **A** 1126.37 (100 %), 1127.43 (80 %), 1128.46 (100 %), 1129.51 (70 %), 1130.50 (17 %). fitted to $C_{58}H_{50}N_8O_2U$ 128.46 (100.0%), 1129.46 (63.4%), 1130.46 (21.7%), 1131.47 (4.0%), 1129.45 (3.0%).

Found **B** 1370.48 (100 %) 1371.48 (58 %) 1372.48 (6 %) 1367.54 (3 %) fitted to $C_{56}H_{46}N_8O_4U_2$: 1370.47 (100.0%), 1371.47 (61.2%), 1372.47 (20.7%), 1373.48 (3.6%), 1371.46 (3.0%), 1367.46 (1.5%), 1373.47 (1.1%).

Found: **C** 1451.53 (100 %), 1452.53180 (72 %) 1453.54224 (22 %), 1454.54682 (3 %) fitted to $C_{61}H_{53}N_9O_4U_2$ 1451.52 (100.0%), 1452.53 (66.7%), 1453.53 (22.8%), 1454.53 (5.9%), 1452.52 (3.3%), 1453.52 (2.2%), 1448.52 (1.5%).

Found: **D** 1526.55688 (100 %), 1527.554993 (100 %), 1528.55301 (35 %), 1529.55920 (3 %) fitted to $C_{66}H_{54}N_{10}O_4U_2$ 1526.53 (100.0%), 1527.54 (72.2%), 1528.54 (26.5%), 1529.54 (7.4%), 1527.53 (3.7%), 1528.53 (2.7%), 1523.53 (1.5%), 1530.55 (1.2%), 1524.53 (1.0%). $C_{54}H_{38}N_8O_4U_2$

Found 1126.36716 (100 %), 1128.41324 (100 %)

Solubility: partial solubility in boiling pyridine at low concentrations.

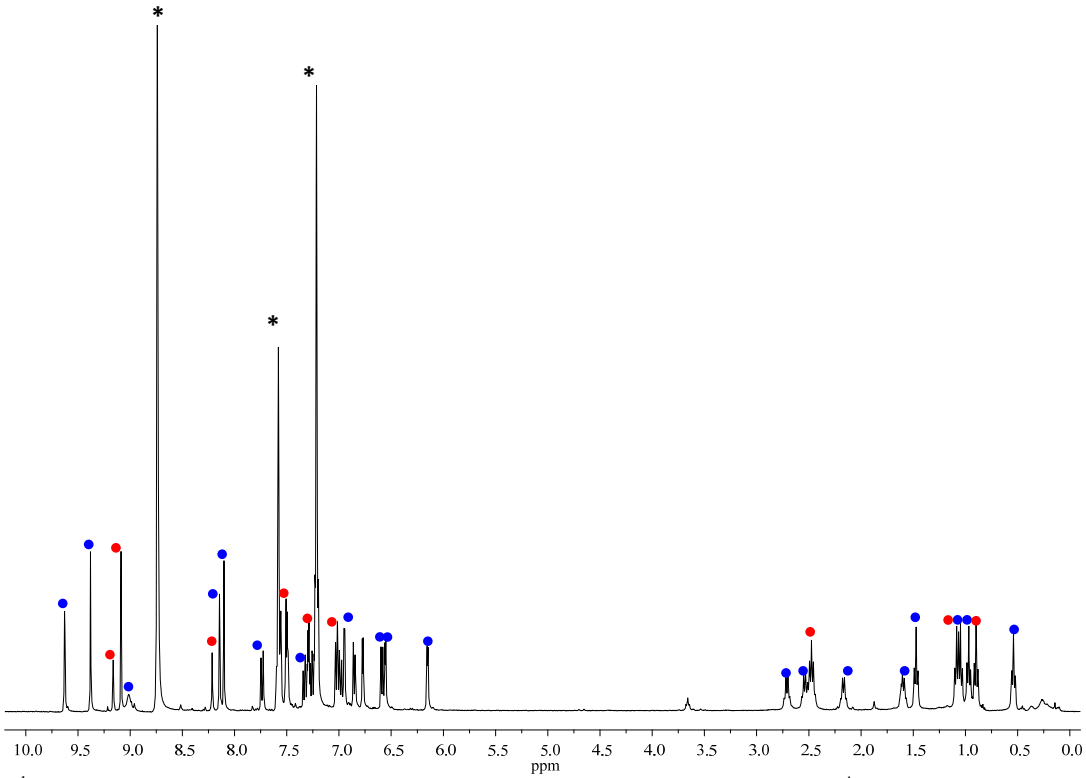


Fig. SI.7: ^{1}H NMR spectrum of Batch A in d_5-pyridine containing 30 % $[\{UO_2(py)\}_2(L^A)]$ **2** (red markers) and 70 % $[(UO_2)(py)(H_2L^A)]$ **1** (blue markers), * = residual C_5D_4HN

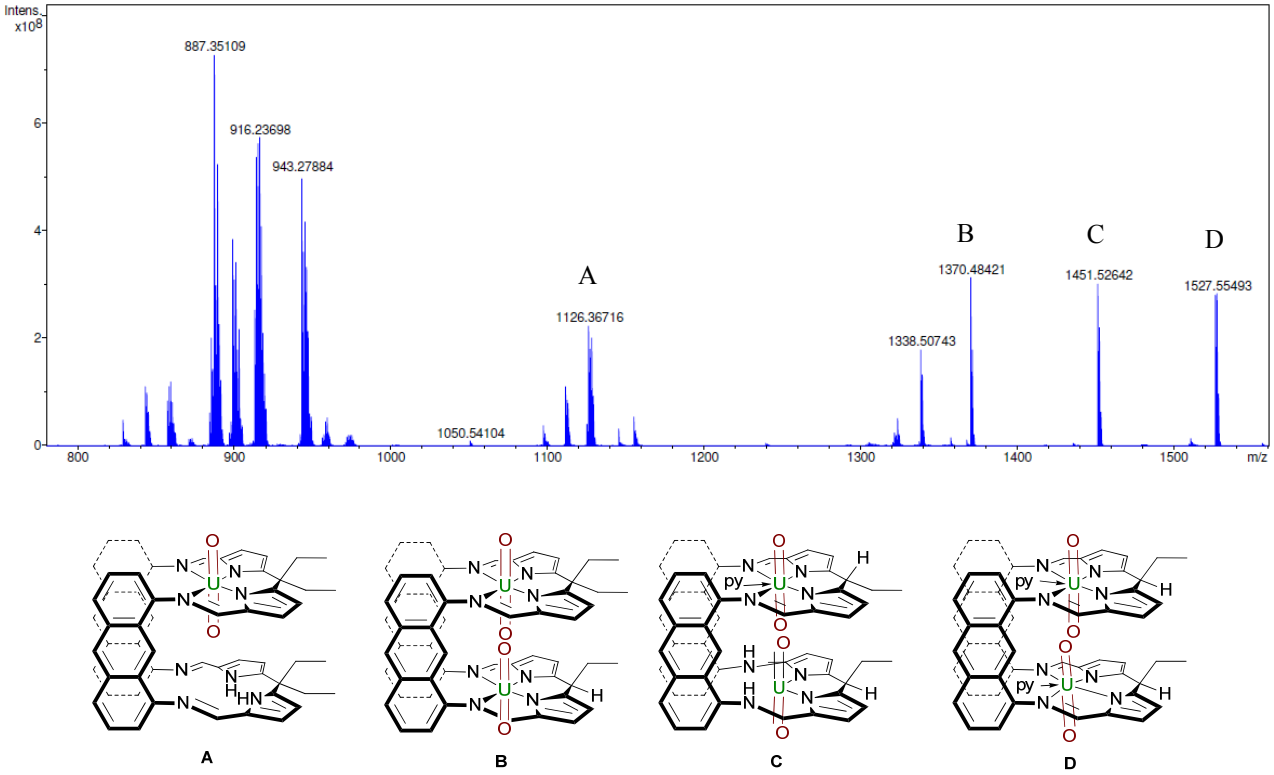


Fig. SI.8: MALDI mass spectrum of batch a and fragments fitted to **1** (A) and **2** (B, C, D)

Attempted synthesis of pure $[(UO_2)(py)(H_2L^A)]$ 1

To a solution of H_4L^A (10 mg, 0.012 mmol) in d_5-pyridine (0.3 mL) was added a solution of $[UO_2\{N(SiMe_3)_2\}_2(py)_2]$ (9 mg, 0.012 mmol) in d_5-pyridine (0.3 mL) and the resulting brown solution left for 24 h at room temperature after which $[(UO_2)(py)(H_2L^A)]$ **1**, $[(UO_2)(py)(H_2L^A)]$ **2** and H_4L^A, were present in a 71 : 14.5 : 14.5 molar ratio, in addition to two equivalents of $HN(SiMe_3)$, as observed by ^{1}H NMR spectroscopy. Heating the mixture at 120°C in an attempt to conproportionate **2** and H_4L^A caused no change in the spectrum.

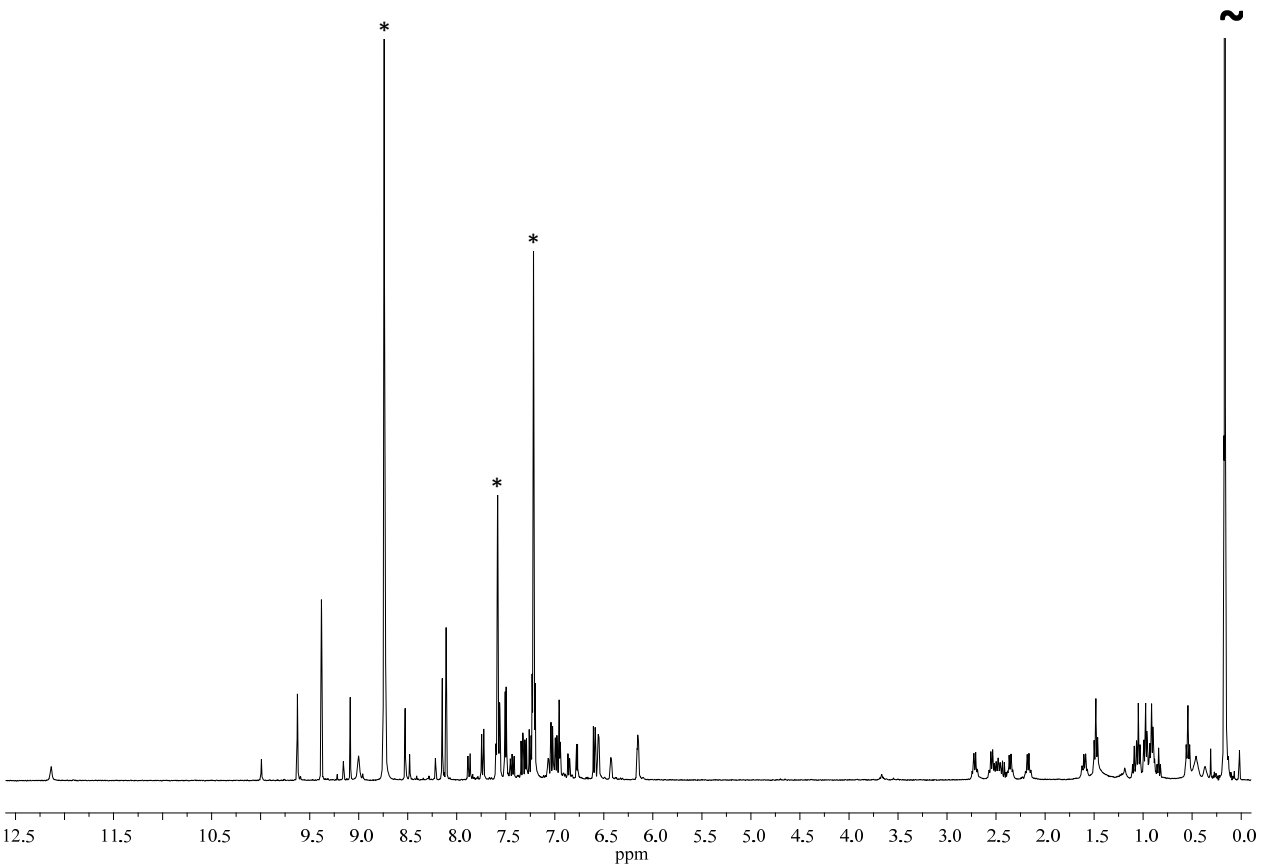


Fig. SI.9: ^{1}H NMR spectrum of the 1:1 reaction between H_4L^A and $[UO_2\{N(SiMe_3)_2\}_2(py)_2]$ in d_5-pyridine containing 71 % $[(UO_2)(py)(H_2L^A)]$ **1,** 14.5 % $[(UO_2)(py)(H_2L^A)]$ **2** and 14.5 % H_4L^A. * = residual C_5D_4HN ~ = $HN(SiMe_3)_2$.

Crystallographic details

For solid state structure of **2** absorption was corrected for by multi-scan methods, empirical absorption correction used special harmonics and was implemented in SCALE3 ABSPACK scaling algorithm. H-parameters were constrained to parent atoms and refined using a riding model. X-ray crystallographic coordinates have been deposited at the Cambridge Crystallographic Database, number 867432

Crystal Data	
Chemical formula	$C_{68}H_{58}N_{10}O_4U_2$
M_r	1555.3
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	13.5141 (2), 17.9909 (4), 23.4778 (5)
β (°)	92.443 (3)
V (Å^3)	5702.99 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.73
Crystal size (mm)	0.04 × 0.02 × 0.01
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
T_{min}, T_{max}	0.976, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34847, 12703, 9061
R_{int}	0.074
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.089, 1.03
No. of reflections	12703
No. of parameters	761
No. of restraints	18
H-atom treatment	Riding
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.62, −2.01

Table SI:1 Experimental details of crystal data collection for **2**

References

1. E. Askarizadeh, A. M. J. Devoille, D. M. Boghaei, A. M. Z. Slawin and J. B. Love, *Inorg. Chem.*, 2009, **48**, 7491-7500.
2. P. L. Arnold, G. M. Jones, S. O. Odoh, G. Schreckenbach, N. Magnani and J. B. Love, *Nat. Chem.*, 2012, **4**, 221-227.
3. A. M. J. Devoille, PhD Thesis 'New cofacial binuclear complexes for the oxygen reduction reaction and selective anion binding' University of Edinburgh, 2011.