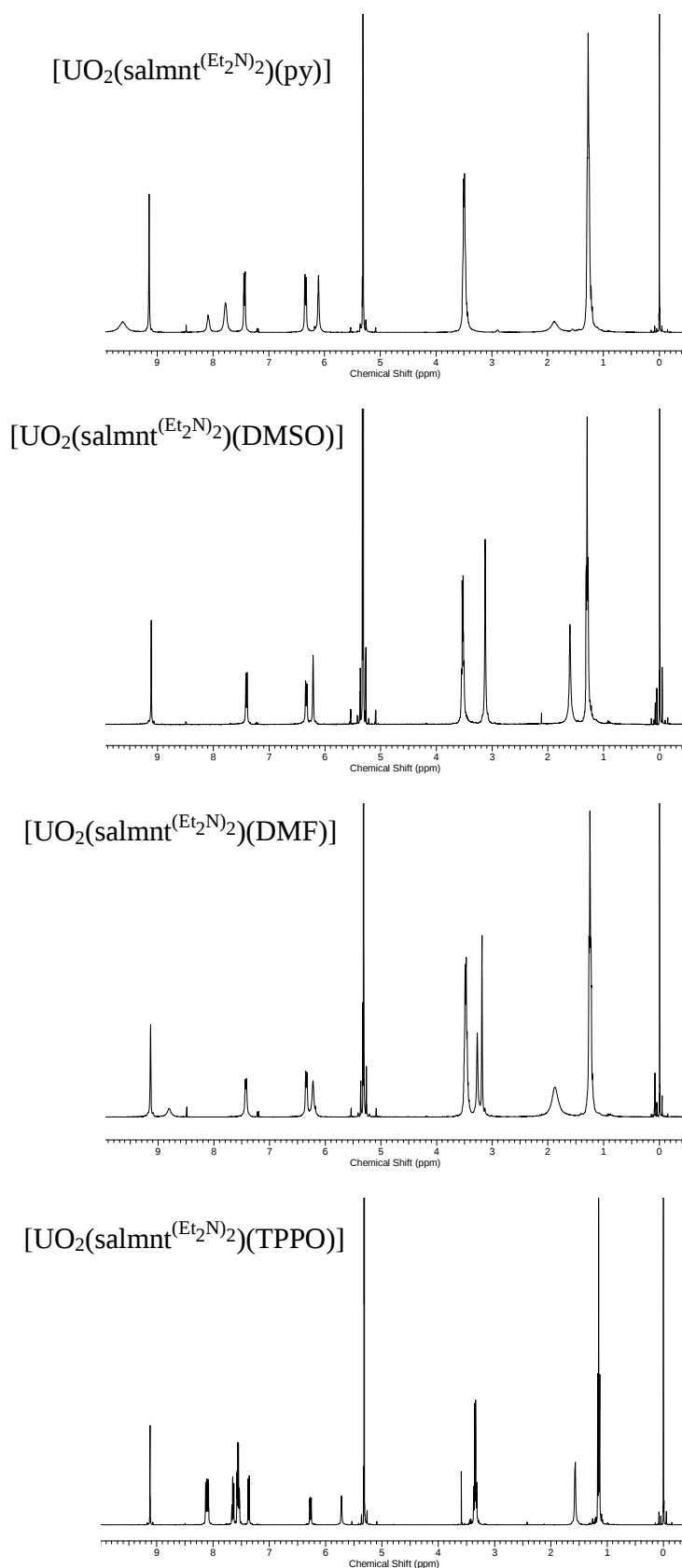
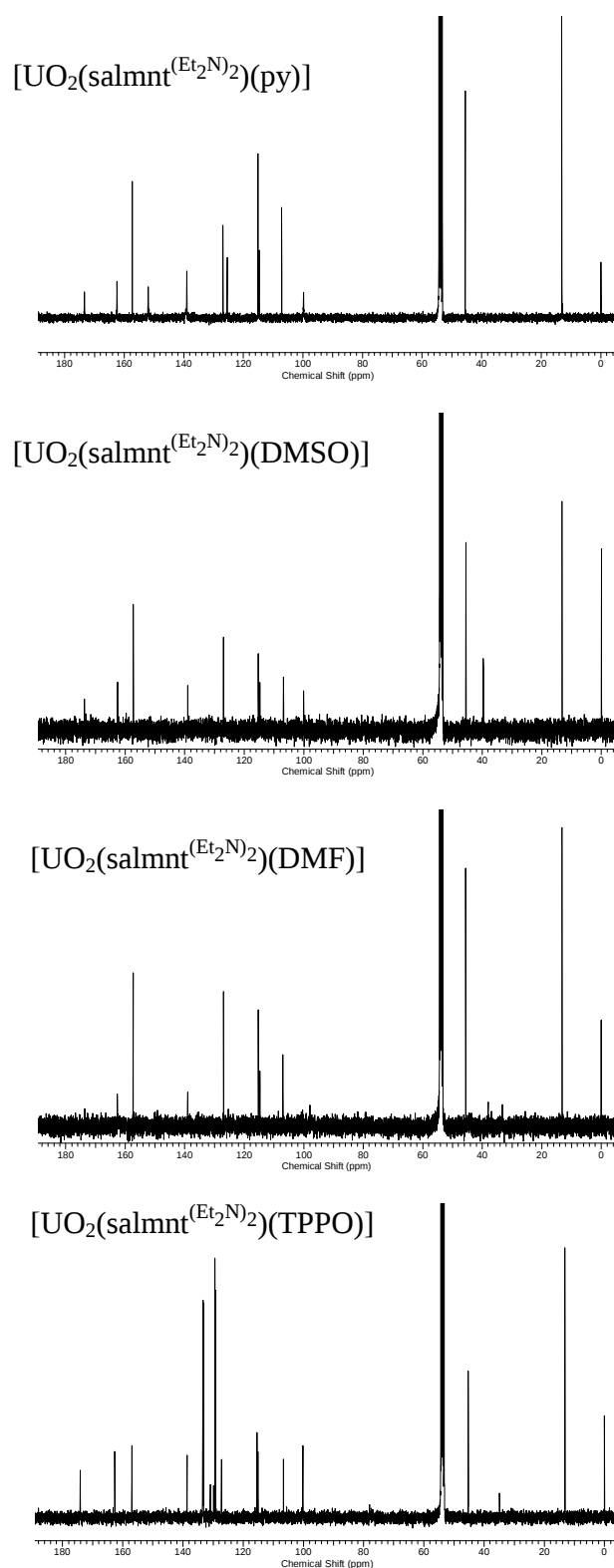


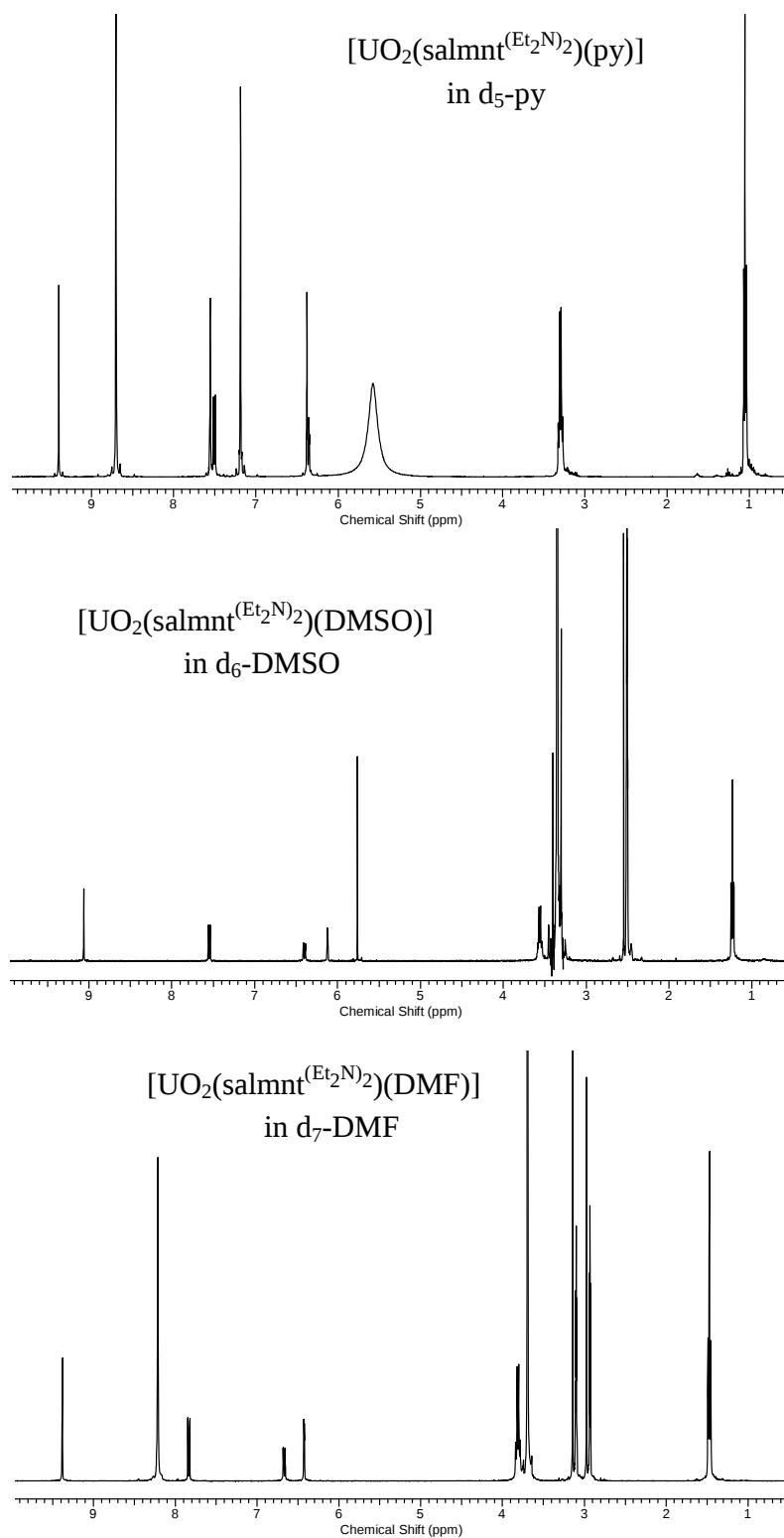
## NMR Spectra



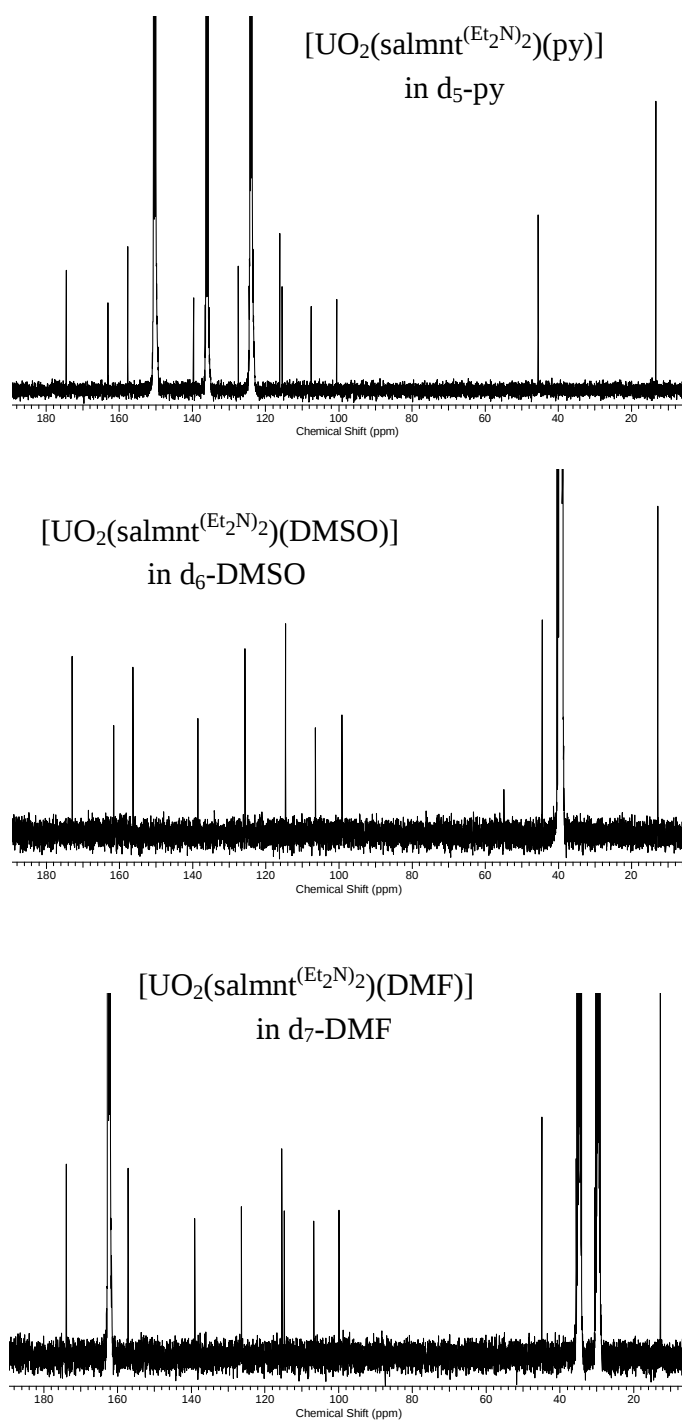
**Figure S1.**  $^1\text{H}$  NMR spectra of  $[\text{UO}_2(\text{salmnt}(\text{Et}_2\text{N})_2)(\text{L})]$  in  $\text{d}_2\text{-DCM}$  ( $\text{L} = \text{py}, \text{DMSO}, \text{DMF}, \text{TPPO}$ )



**Figure S2.**  $^{13}\text{C}$  NMR spectra of  $[\text{UO}_2(\text{salmnt}(\text{Et}_2\text{N})_2)(\text{L})]$  in  $\text{d}_2\text{-DCM}$  (L = py, DMSO, DMF, TPPO)



**Figure S3.**  $^1\text{H}$  NMR spectra of  $[\text{UO}_2(\text{salmnt}^{(\text{Et}_2\text{N})_2}(\text{L}))]$  in deuterated L (L = py, DMSO, DMF)



**Figure S4.**  $^{13}\text{C}$  NMR spectra of  $[\text{UO}_2(\text{salmnt}^{(\text{Et}_2\text{N})_2}(\text{L}))]$  in deuterated L (L = py, DMSO, DMF)

## Solution NMR and vibrational spectroscopic data

[UO<sub>2</sub>(salen)(py)]. <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N): δ<sub>H</sub> 4.44 (s, 4H, -CH<sub>2</sub>-N), 6.81, (ddd, J<sup>1</sup> = 8.0 Hz, J<sup>2</sup> = 7.2 Hz, J<sup>3</sup> = 1.2 Hz, 2H, Ph-H); 7.30 (d, J = 8.0 Hz, 2H, Ph-H); 7.63 – 7.68 (m, 4H, Ph-H); 9.35 (s, 2H, HC=N) ppm. <sup>13</sup>C NMR (C<sub>5</sub>D<sub>5</sub>N): δ<sub>C</sub> 64.8 (CH<sub>2</sub>); 117.8, 121.5, 135.7, 136.3 (Ph-H); 125.1 (Ph) 124.3, 136.2 (Ph<sub>(py)</sub>-H); 150.7 (Ph<sub>(py)</sub>-N); 169.9 (CH=N); 170.8 (Ph-O) ppm. IR spectrum (solid): 1622 (s, C=N); 1594 (s, C=N); 1545 (s, C=C); 888 (s, U=O<sub>asym</sub>) cm<sup>-1</sup>. Raman spectrum (solid): 1630 (s, C=N); 1597 (m, C=N); 1549 (s, C=C); 817 (m, U=O<sub>sym</sub>) cm<sup>-1</sup>.

[UO<sub>2</sub>(salophen)(py)]. <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N): δ<sub>H</sub> 6.75 (ddd, J<sup>1</sup> = 7.6 Hz, J<sup>2</sup> = 7.4 Hz, J<sup>3</sup> = 1.0 Hz, 2H, Ph-H), 7.25 (d, J = 8.4 Hz, 2H, Ph-H); 7.36 (dd, J = 5.8 Hz, J = 3.4 Hz, 2H, Ph-H); 7.59 (ddd, J = 7.2 Hz, 7.2 Hz, J = 1.8 Hz, 2H, Ph-H); 7.83 (dd, J = 7.6 Hz, J = 1.6 Hz, 2H, Ph-H); 9.59 (s, 2H, HC=N) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>C</sub> 120.0, 122.4, 123.3, 131.2, 138.4, 138.9 (Ph-H); 127.0, 149.4 (Ph); 125.8, 137.8 (Ph<sub>(py)</sub>-H); 152.3 (Ph<sub>(py)</sub>-N); 168.8 (CH=N); 173.0 (Ph-O) ppm. IR spectrum (solid): 1600 (s, C=N); 1573 (m, C=C); 1536 (s, C=C); 891 (s, U=O<sub>asym</sub>) cm<sup>-1</sup>. Raman spectrum (solid): 1605 (m, C=N); 1578 (s, C=C); 1539 (s, C=C); 811 (m, U=O<sub>sym</sub>) cm<sup>-1</sup>.

[UO<sub>2</sub>(salen)(DMSO)]. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO): δ<sub>H</sub> 2.60 (s, 6H, -CH<sub>3</sub>(DMSO)); 4.54 (s, 4H, -CH<sub>2</sub>-N); 6.75 (ddd, J<sup>1</sup> = 7.0 Hz, J<sup>2</sup> = 7.2 Hz, J<sup>3</sup> = 1.0 Hz, 2H, Ph-H); 7.01 (d, J = 8.0 Hz, 2H, Ph-H); 7.6 – 7.7 (m, 4H, Ph-H); 9.52 (s, 2H, HC=N) ppm. <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO): δ<sub>C</sub> 63.7 (-CH<sub>2</sub>-N); 116.1, 120.4, 134.4, 134.8 (Ph-H); 123.7 (Ph); 168.7 (CH=N); 169.0 (Ph-O) ppm. IR spectrum (solid): 1619 (s, C=N); 1593 (m, C=C); 1544 (m, C=C); 881 (s, U=O<sub>asym</sub>) cm<sup>-1</sup>. Raman spectrum (solid): 1628 (s, C=N); 1595 (m, C=C); 1547 (s, C=C); 811 (m, U=O<sub>sym</sub>) cm<sup>-1</sup>.

[UO<sub>2</sub>(salophen)(DMSO)]. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO): δ<sub>H</sub> 2.55 (s, 6H, -CH<sub>3</sub>(DMSO)); 6.72 (ddd, J<sup>1</sup> = 7.4 Hz, J<sup>2</sup> = 7.4 Hz, J<sup>3</sup> = 1.2 Hz, 2H, Ph-H); 7.00 (d, J = 8.4 Hz, 2H, Ph-H); 7.54 – 7.57 (m, 2H, Ph-H); 7.62 (ddd, J<sup>1</sup> = 7.0 Hz, J<sup>2</sup> = 6.8 Hz, J<sup>3</sup> = 1.6 Hz, 2H, Ph-H); 7.78 – 7.82 (m, 4H, Ph-H); 9.63 (s, 2H, HC=N) ppm. <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO): δ<sub>C</sub> 40.4 (-CH<sub>3</sub>(DMSO)); 116.7, 120.3, 120.6, 128.7, 135.9, 136.0 (Ph-H); 124.2 146.7 (Ph); 166.7 (CH=N); 169.8 (Ph-O) ppm. IR spectrum (solid): 1576 (m, C=C); 1531 (s, C=C) cm<sup>-1</sup>. Raman spectrum (solid): 1610 (s, C=N); 1581 (s, C=C); 1536 (s, C=C); 814 (m, U=O<sub>sym</sub>) cm<sup>-1</sup>.

[UO<sub>2</sub>(salen)(DMF)]. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>NCDO): δ<sub>H</sub> 2.60, 2.77 (p, J = 2.0 Hz 3H, -CH<sub>3</sub>(DMF)); 4.45 (s, 4H, -CH<sub>2</sub>-N); 6.57 (ddd, J<sup>1</sup> = 7.6 Hz, J<sup>2</sup> = 7.2 Hz, J<sup>3</sup> = 0.8 Hz, 2H, Ph-H); 6.86 (d, J = 8.4 Hz, 2H, Ph-H); 7.44 (ddd, J<sup>1</sup> = 8.4 Hz, J<sup>2</sup> = 8.4 Hz, J<sup>3</sup> = 1.6 Hz, 2H, Ph-H); 7.51 (dd, J<sup>1</sup> = 7.6 Hz, J<sup>2</sup> = 2.0 Hz 7.4 Hz, 2H, Ph-H); 7.88 (s, 1H, HCO(DMF)); 9.39 (s, 2H, HC=N) ppm. <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>NCDO): δ<sub>C</sub> 34.8 (-CH<sub>3</sub>(DMF)); 64.2 (-CH<sub>2</sub>-N); 116.1, 120.9, 134.6, 134.9 (Ph-H); 124.2 (Ph); 161.5 (-CHO(DMF)); 169.1 (CH=N); 169.9 (Ph-O) ppm. IR spectrum (solid): 1620 (s, C=N); 1594 (s, C=C); 1547 (m, C=C); 883 (s, U=O<sub>asym</sub>) cm<sup>-1</sup>. Raman spectrum (solid): 1626 (s, C=N); 1595 (m, C=C); 1547 (s, C=C); 814 (m, U=O<sub>sym</sub>) cm<sup>-1</sup>.

[UO<sub>2</sub>(salophen)(DMF)]. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>NCDO): δ<sub>H</sub> 2.93, 3.10 (p, J = 2.0 Hz, 3H, -CH<sub>3</sub>(DMF)); 6.93 (ddd, J<sup>1</sup> = 7.4 Hz, J<sup>2</sup> = 7.4 Hz, J<sup>3</sup> = 1.2 Hz, 2H, Ph-H); 7.00 (d, J = 8.0 Hz, 2H, Ph-H); 7.76 – 7.84, 8.04 – 8.10 (m, 4H, Ph-H); 8.21 (s, 1H, HCO(DMF)); 9.91 (s, 2H, HC=N) ppm. <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>NCDO): δ<sub>C</sub> 35.6, 40.7 (-CH<sub>3</sub>(DMF)); 117.0, 120.5, 121.3, 129.1, 136.2, 136.3 (Ph-H); 124.8 147.5 (Ph); 162.5 (-CHO(DMF)); 167.0 (CH=N); 170.8 (Ph-O) ppm. IR spectrum (solid): 1577 (m, C=C); 1531 (s, C=C) cm<sup>-1</sup>. Raman spectrum (solid): 1610 (s, C=N); 1582 (s, C=C); 1536 (s, C=C); 817 (w, U=O<sub>sym</sub>) cm<sup>-1</sup>.

[UO<sub>2</sub>(salen)(TPPO)].TPPO. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>H</sub> 4.54 (s, 4H, -CH<sub>2</sub>-N); 6.46 (d, J = 8.4 Hz, 2H, Ph-H); 6.66 (ddd, J<sup>1</sup> = 7.6 Hz, J<sup>2</sup> = 7.2 Hz, J<sup>3</sup> = 1.0 Hz, 2H, Ph-H); 7.42 (ddd, J<sup>1</sup> = 7.2 Hz, J<sup>2</sup> = 7.2 Hz, J<sup>3</sup> = 1.8 Hz, 2H, Ph-H); 7.48 (dd, J = 7.6 Hz, J = 1.6 Hz, 2H, Ph-H) 7.52, 7.61, 8.11 (s br, 30H, Ph<sub>(TPPO)</sub>-H); 9.25 (s, 2H, CH=N) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>C</sub> 65.2 (CH<sub>2</sub>); 116.6, 121.2, 134.4, 135.2 (Ph-H); 124.0, (Ph); 129.1, 132.5, 133.2 (Ph<sub>(TPPO)</sub>-H); 168.8 (CH=N); 170.4 (Ph-O) ppm. <sup>31</sup>P NMR<sub>S5</sub> (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>P</sub> 43.2 ppm. IR spectrum (solid): 1628 (s, C=N); 1592 (m, C=C); 1546 (m, C=C); 1120

(s, P=O); 889 (s, U=O<sub>asym</sub>) cm<sup>-1</sup>. Raman spectrum (solid): 1639 (m, C=N); 1592 (m, C=C); 1548 (m, C=C); 816 (w, U=O<sub>sym</sub>) cm<sup>-1</sup>.

[UO<sub>2</sub>(salophen)(TPPO)].xTPPO. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>H</sub> 6.45 (d, J = 8.4 Hz, 2H, Ph-H); 6.58 (t, J = 7.4 Hz, 2H, Ph-H); 7.34 – 7.51 (m br, Ph-H and Ph-H<sub>(TPPO)</sub>); 8.03 (s br, Ph-H<sub>(TPPO)</sub>); 9.25 (s, 2H, CH=N) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>C</sub> 115.9, 119.0, 120.5, 127.9, 134.5, 135.1 (Ph-H); 123.5, 146.8 (Ph); 131 – 133 (Ph<sub>(TPPO)</sub>); 164.9 (CH=N); 170.1 (Ph-O) ppm. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>P</sub> 43.7 ppm. IR spectrum (solid): 1602 (s, C=N); 1575 (m, C=C); 1535 (s, C=C); 1118 (s, P=O); 893 (s, U=O<sub>asym</sub>) cm<sup>-1</sup>. Raman spectrum (solid): 1608 (m, C=N); 1579 (s, C=C); 1538 (s, C=C); 812 (m, U=O<sub>sym</sub>) cm<sup>-1</sup>.

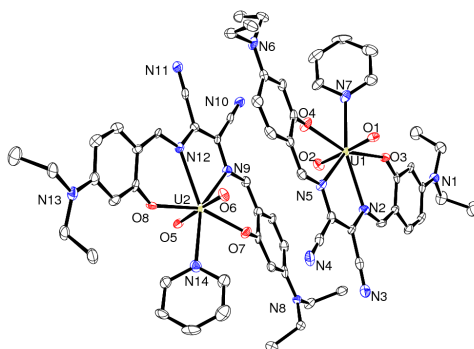
[Zn(salmnt<sup>(Et<sub>2</sub>N)</sup>)<sub>2</sub>]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>H</sub> 1.19 (t, J = 6.8 Hz, 12H, -CH<sub>3</sub>); 3.36 (q, J = 6.8 Hz, 8H, -CH<sub>2</sub>-); 5.79 (s, 2H, Ph-H); 6.14, 6.91 (d, J = 8.8 Hz, 2H, Ph-H); 8.00 (s, 2H, HC=N) ppm. IR spectrum (solid): 2210 (w, C≡N); 1615 (s, C=N); 1568 (s, C=C); 1539 (w, C=C); 1513 (s, C=C) cm<sup>-1</sup>. Raman spectrum (solid): 2210 (m, C≡N); 1573 (w, C=C); 1538 (s, C=C) cm<sup>-1</sup>.

**Table S1.** Selected electronic absorption data.

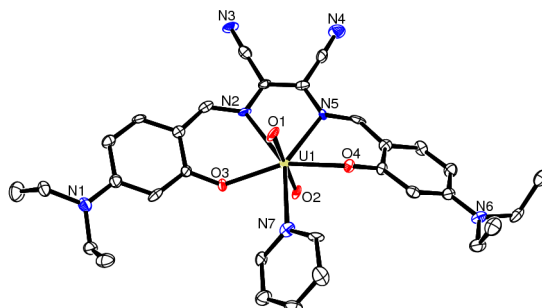
| Compound                                                              | Solvent           | λ <sub>max</sub> (nm) |     |     |
|-----------------------------------------------------------------------|-------------------|-----------------------|-----|-----|
| <b>salmnt<sup>(Et<sub>2</sub>N)</sup><sub>2</sub>H<sub>2</sub></b>    | DCM               | 568                   | 436 | 378 |
| <b>2</b>                                                              | DCM               | 579                   | 436 | 379 |
|                                                                       | py                | 595                   | 435 | 380 |
| <b>3</b>                                                              | DCM               | 583                   | 434 | 379 |
|                                                                       | DMSO              | 598                   | 435 | 381 |
| <b>4</b>                                                              | DCM               | 574                   | 436 | 380 |
|                                                                       | DMF               | 594                   | 431 | 378 |
| <b>5</b>                                                              | DCM               | 584                   | 432 | 377 |
| [Ni(salmnt <sup>(Et<sub>2</sub>N)</sup> ) <sub>2</sub> ] <sup>a</sup> | CHCl <sub>3</sub> | 584                   | -   | -   |
| [Cu(salmnt <sup>(Et<sub>2</sub>N)</sup> ) <sub>2</sub> ] <sup>a</sup> | CHCl <sub>3</sub> | 574                   | -   | -   |
| [Zn(salmnt <sup>(Et<sub>2</sub>N)</sup> ) <sub>2</sub> ] <sup>a</sup> | CHCl <sub>3</sub> | 586                   | -   | -   |

<sup>a</sup> Reference 18. No other transitions reported.

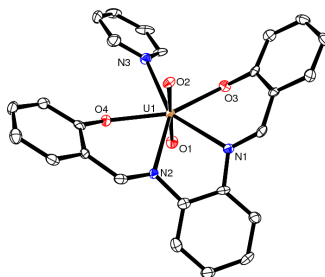
## Crystal Structures



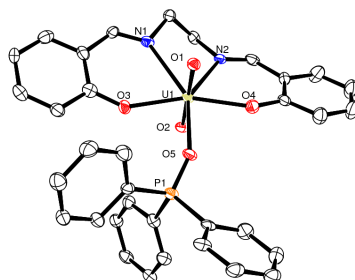
**Figure S5.** ORTEP plot of the asymmetric unit of **2a** with crystallographic numbering (hydrogens omitted)



**Figure S6.** ORTEP plot of the complex molecule of **2b** with crystallographic numbering (hydrogens omitted)

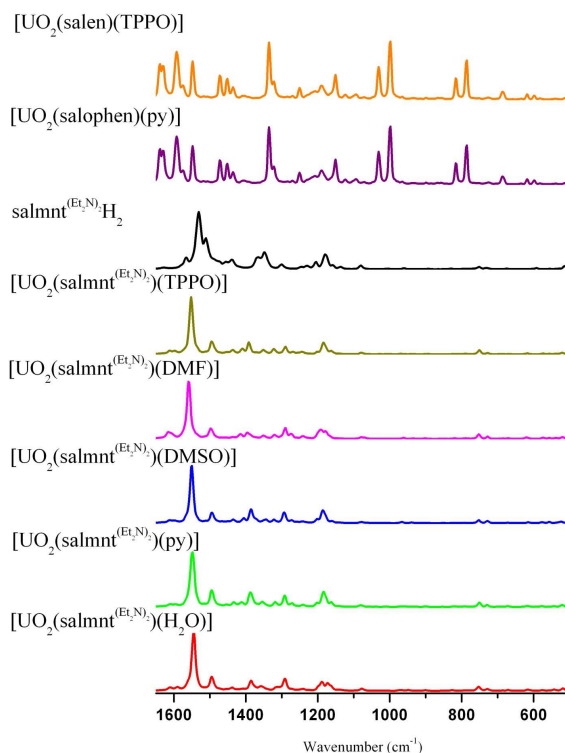


**Figure S7.** ORTEP plot of  $[\text{UO}_2(\text{salophen})(\text{py})]$  with crystallographic numbering (hydrogens omitted)

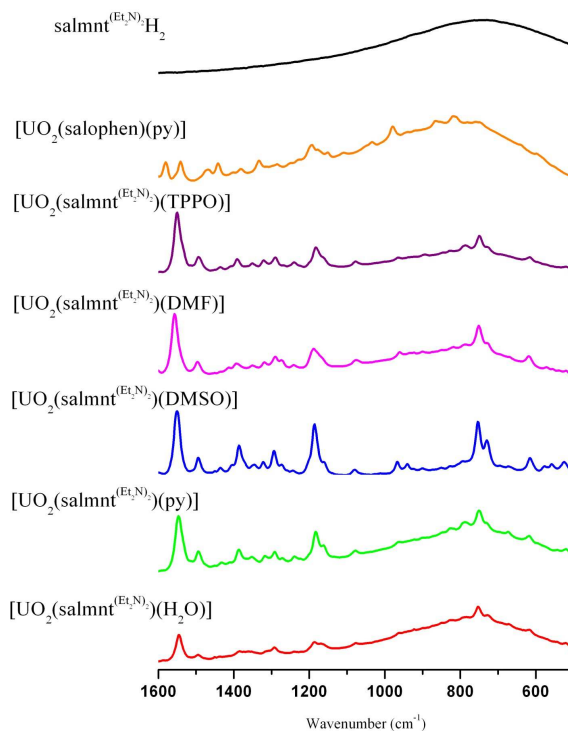


**Figure S8.** ORTEP plot of the complex molecule of  $[\text{UO}_2(\text{salen})(\text{TPPO})].\text{TPPO}$  with crystallographic numbering (hydrogens omitted)

## Raman Spectroscopy

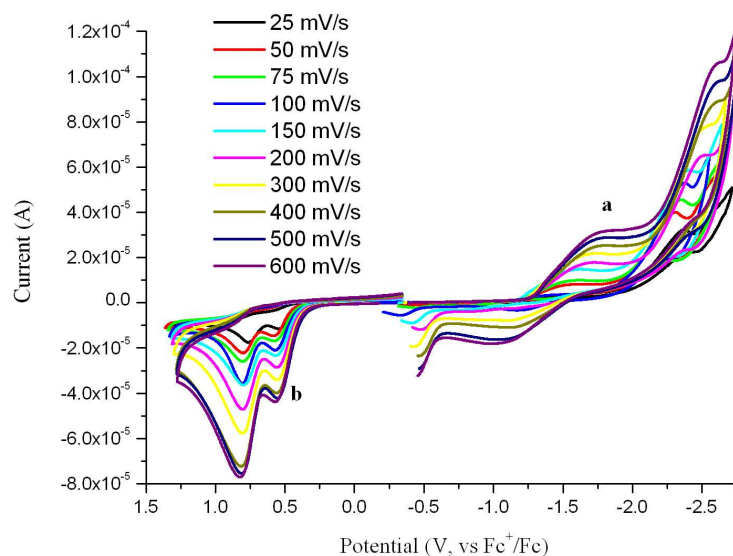


**Figure S9.** Solid state Raman spectra (laser excitation at  $\lambda = 1064$  nm)



**Figure S10.** Solid state Raman spectra (laser excitation at  $\lambda = 785$  nm)

## Cyclic Voltammetry

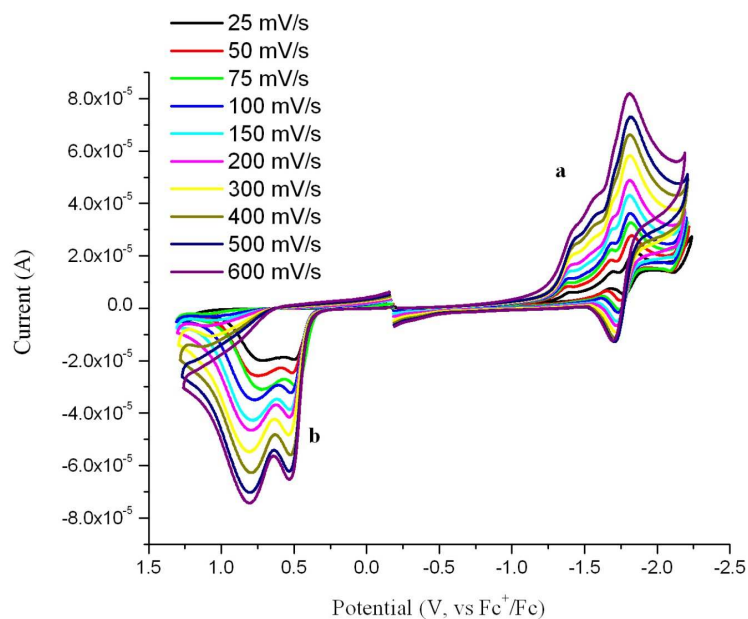


**Figure S11.** Cyclic voltammograms of salmnt<sup>(Et<sub>2</sub>N)</sup><sub>2</sub>H<sub>2</sub> (**a** - Scan range ~ -0.35 V to ~ -2.70 V, vs Fc<sup>+</sup>/Fc, Initial scan direction - cathodic; **b** - Scan range ~ -0.33 V to ~ +1.31 V, vs Fc<sup>+</sup>/Fc, Initial scan direction – anodic: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DCM).

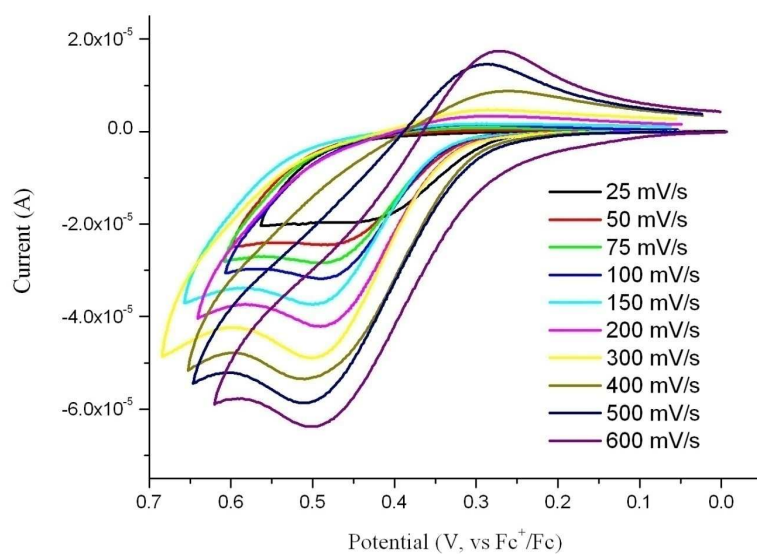
**Table S2.** Cyclic voltammetric data for salmnt<sup>(Et<sub>2</sub>N)</sup><sub>2</sub>H<sub>2</sub> in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DCM.

| Scan rate (mV/s) | E <sub>pc1</sub> (V) <sup>a</sup> | i <sub>pc1</sub> (μA) | E <sub>pc2</sub> (V) <sup>a</sup> | i <sub>pc2</sub> (μA) | E <sub>pa1</sub> (V) <sup>b</sup> | i <sub>pa1</sub> (μA) | E <sub>pa2</sub> (V) <sup>b</sup> | i <sub>pa2</sub> (μA) |
|------------------|-----------------------------------|-----------------------|-----------------------------------|-----------------------|-----------------------------------|-----------------------|-----------------------------------|-----------------------|
| 25               | -2.37                             | 6.09                  | -                                 | -                     | +0.55                             | 11.3                  | +0.76                             | 17.3                  |
| 50               | -2.31                             | 7.49                  | -1.61                             | sh                    | +0.58                             | 14.4                  | +0.80                             | 21.9                  |
| 75               | -2.35                             | 7.84                  | -1.68                             | 5.88                  | +0.58                             | 16.5                  | +0.80                             | 25.5                  |
| 100              | -2.37                             | 8.12                  | -1.66                             | sh                    | +0.57                             | 20.5                  | +0.81                             | 35.1                  |
| 150              | -2.41                             | 8.41                  | -1.70                             | 13.1                  | +0.57                             | 22.4                  | +0.80                             | 35.1                  |
| 200              | -2.47                             | 8.83                  | -1.72                             | 15.3                  | +0.56                             | 27.8                  | +0.81                             | 46.0                  |
| 300              | -2.47                             | sh                    | -1.75                             | 21.2                  | +0.56                             | 33.0                  | +0.81                             | 56.3                  |
| 400              | -                                 | -                     | -1.81                             | 24.0                  | +0.56                             | 38.4                  | +0.82                             | 70.2                  |
| 500              | -                                 | -                     | -1.83                             | 25.4                  | +0.56                             | 41.0                  | +0.81                             | 73.9                  |
| 600              | -                                 | -                     | -1.90                             | sh                    | +0.57                             | 42.0                  | +0.83                             | 74.6                  |

<sup>a</sup> Potentials internally referenced vs Fc<sup>+</sup>/Fc <sup>b</sup> Potentials externally referenced vs Fc<sup>+</sup>/Fc



**Figure S12.** Cyclic voltammograms of **2** (**a** - Scan range  $\sim -0.22$  V to  $\sim -2.40$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.22$  V to  $\sim +1.28$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic: 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM).



**Figure S13.** Cyclic voltammograms of **2** (Scan range  $\sim +0.05$  V to  $\sim +0.65$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic: 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM)

**Table S3.** Cyclic voltammetric data for **2** for scan range  $\sim -0.22$  V to  $\sim -2.4$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate (mV/s) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc}}/i_{\text{pa}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | -1.84               | 8.05                              | -1.77               | 8.76                              | 68              | -1.80         | 0.92                          |
| 50               | -1.85               | 12.0                              | -1.76               | 12.3                              | 88              | -1.80         | 0.98                          |
| 75               | -1.85               | 15.0                              | -1.76               | 15.2                              | 85              | -1.80         | 0.99                          |
| 100              | -1.84               | 16.3                              | -1.76               | 17.8                              | 84              | -1.80         | 0.92                          |
| 150              | -1.85               | 19.9                              | -1.75               | 19.7                              | 92              | -1.80         | 1.01                          |
| 200              | -1.85               | 22.9                              | -1.75               | 22.9                              | 98              | -1.80         | 1.00                          |
| 300              | -1.85               | 27.2                              | -1.75               | 26.8                              | 104             | -1.80         | 1.02                          |
| 400              | -1.86               | 30.2                              | -1.75               | 31.0                              | 107             | -1.80         | 0.97                          |
| 500              | -1.86               | 33.2                              | -1.75               | 33.7                              | 113             | -1.80         | 0.99                          |
| 600              | -1.86               | 35.2                              | -1.74               | 34.8                              | 120             | -1.80         | 1.02                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S4.** Cyclic voltammetric data for **2** for scan range  $\sim +0.05$  V to  $\sim +0.65$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

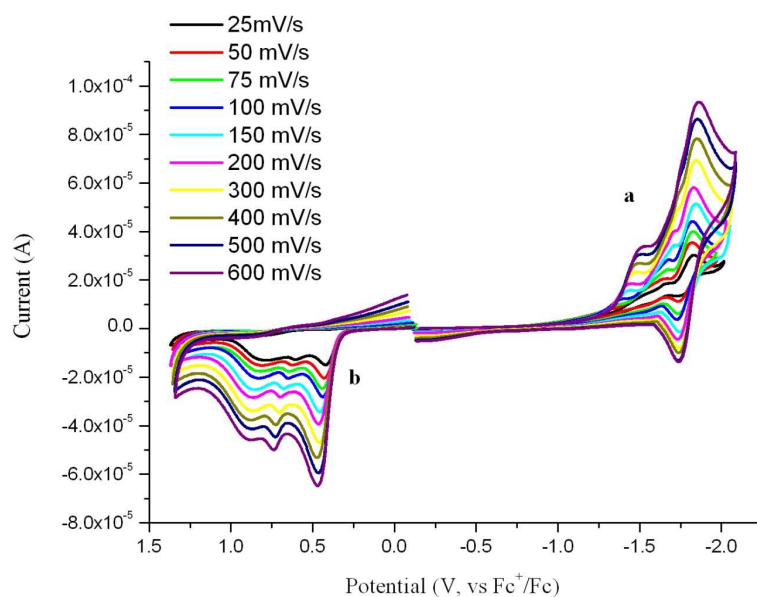
| Scan rate (mV/s) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pa}}/i_{\text{pc}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | +0.48               | 18.8                              | -                   | -                                 | -               | -             | -                             |
| 50               | +0.49               | 23.9                              | -                   | -                                 | -               | -             | -                             |
| 75               | +0.49               | 27.6                              | -                   | -                                 | -               | -             | -                             |
| 100              | +0.49               | 30.9                              | +0.41               | < 5                               | 82              | +0.45         | -                             |
| 150              | +0.50               | 36.5                              | +0.39               | < 5                               | 102             | +0.45         | -                             |
| 200              | +0.49               | 42.1                              | +0.39               | < 5                               | 104             | +0.44         | -                             |
| 300              | +0.50               | 48.9                              | +0.39               | < 5                               | 115             | +0.44         | -                             |
| 400              | +0.50               | 52.7                              | +0.38               | < 5                               | 117             | +0.44         | -                             |
| 500              | +0.51               | 57.4                              | +0.39               | 5.06                              | 121             | +0.45         | 11.3                          |
| 600              | +0.50               | 60.0                              | +0.38               | 9.60                              | 119             | +0.44         | 6.25                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

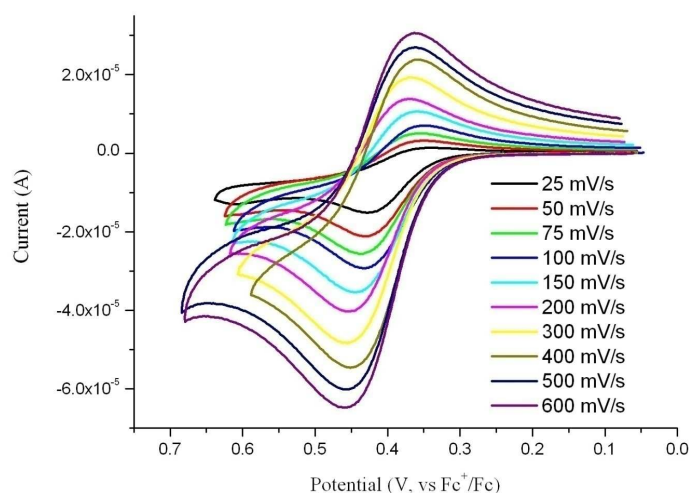
**Table S5.** Cyclic voltammetric data for **2** for scan range  $\sim -0.22$  V to  $\sim +1.28$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate (mV/s) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa2}}$ (V) | $i_{\text{pa2}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | +0.52                | 19.1                               | +0.65                | 19.4                               |
| 50               | +0.49                | 24.3                               | +0.72                | 25.4                               |
| 75               | +0.49                | 29.5                               | +0.67                | 30.8                               |
| 100              | +0.50                | 31.5                               | +0.70                | 33.9                               |
| 150              | +0.49                | 38.5                               | +0.71                | 42.4                               |
| 200              | +0.50                | 40.7                               | +0.73                | 45.4                               |
| 300              | +0.51                | 48.2                               | +0.73                | 54.7                               |
| 400              | +0.51                | 55.1                               | +0.74                | 61.6                               |
| 500              | +0.50                | 61.7                               | +0.73                | 69.7                               |
| 600              | +0.50                | 64.4                               | +0.74                | 73.0                               |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$



**Figure S14.** Cyclic voltammograms of **3** (**a** - Scan range  $\sim -0.22$  V to  $\sim -2.40$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.22$  V to  $\sim +1.28$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM).



**Figure S15.** Cyclic voltammograms of **3** (Scan range  $\sim -0.02$  V to  $\sim +0.60$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM).

**Table S6.** Cyclic voltammetric data for **3** for scan range  $\sim -0.22$  V to  $\sim -2.40$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate (mV/s) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc}}/i_{\text{pa}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | -1.83               | 8.00                              | -1.75               | 6.18                              | 77              | -1.79         | 1.29                          |
| 50               | -1.82               | 11.6                              | -1.75               | 7.86                              | 76              | -1.78         | 1.47                          |
| 75               | -1.82               | 14.1                              | -1.74               | 11.6                              | 83              | -1.78         | 1.22                          |
| 100              | -1.82               | 14.3                              | -1.74               | 13.6                              | 83              | -1.78         | 1.05                          |
| 150              | -1.84               | 19.4                              | -1.74               | 17.8                              | 108             | -1.79         | 1.09                          |
| 200              | -1.83               | 22.1                              | -1.73               | 21.2                              | 101             | -1.78         | 1.05                          |
| 300              | -1.85               | 26.4                              | -1.72               | 26.9                              | 123             | -1.78         | 0.98                          |
| 400              | -1.85               | 29.4                              | -1.71               | 28.0                              | 137             | -1.78         | 1.05                          |
| 500              | -1.85               | 32.0                              | -1.71               | 35.0                              | 141             | -1.78         | 0.91                          |
| 600              | -1.86               | 36.5                              | -1.71               | 34.8                              | 153             | -1.78         | 1.05                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S7.** Cyclic voltammetric data for **3** for scan range  $\sim -0.02$  V to  $\sim +0.60$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

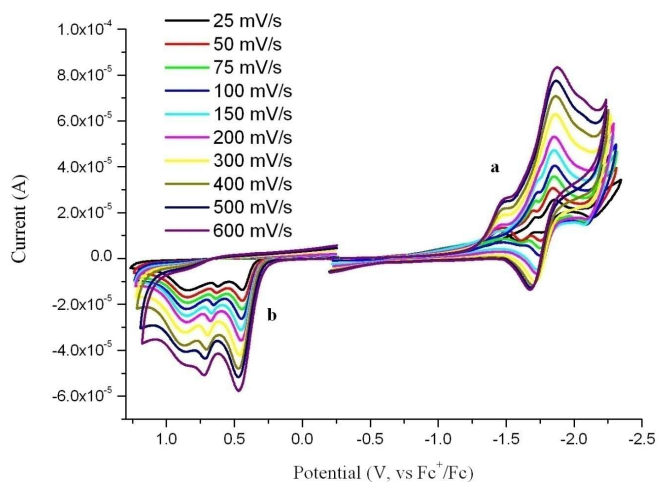
| Scan rate (mV/s) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pa}}/i_{\text{pc}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | +0.43               | 14.7                              | +0.37               | 5.56                              | 61              | +0.40         | 2.64                          |
| 50               | +0.43               | 20.6                              | +0.36               | 5.53                              | 68              | +0.40         | 3.73                          |
| 75               | +0.44               | 25.2                              | +0.37               | 7.31                              | 71              | +0.40         | 3.45                          |
| 100              | +0.43               | 28.6                              | +0.36               | 8.28                              | 72              | +0.40         | 3.45                          |
| 150              | +0.44               | 34.6                              | +0.36               | 12.9                              | 89              | +0.40         | 2.68                          |
| 200              | +0.45               | 40.3                              | +0.36               | 17.0                              | 99              | +0.40         | 2.36                          |
| 300              | +0.46               | 47.5                              | +0.35               | 22.6                              | 107             | +0.40         | 2.11                          |
| 400              | +0.45               | 52.9                              | +0.35               | 24.7                              | 101             | +0.40         | 2.14                          |
| 500              | +0.46               | 57.7                              | +0.35               | 32.1                              | 108             | +0.40         | 1.80                          |
| 600              | +0.46               | 92.9                              | +0.34               | 38.0                              | 118             | +0.40         | 1.66                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

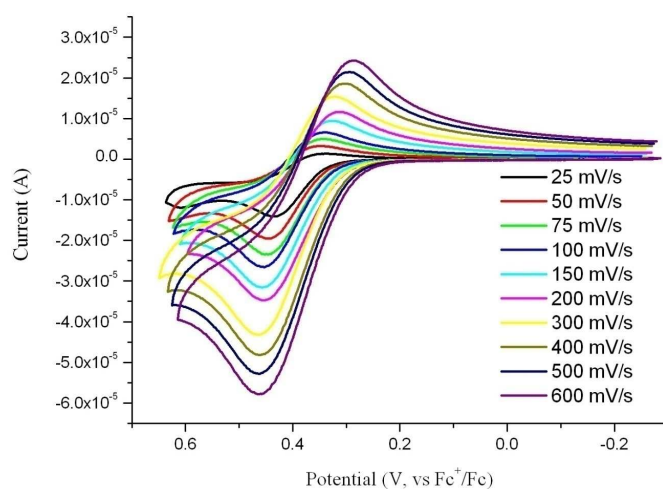
**Table S8.** Cyclic voltammetric data for **3** for scan range  $\sim -0.22$  V to  $\sim +1.28$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate (mV/s) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa2}}$ (V) | $i_{\text{pa2}}$ ( $\mu\text{A}$ ) | $E_{\text{pa3}}$ (V) | $i_{\text{pa3}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | +0.42                | 14.7                               | +0.64                | 12.4                               | +0.78                | 12.6                               |
| 50               | +0.43                | 20.0                               | +0.65                | 14.6                               | +0.81                | 14.5                               |
| 75               | +0.44                | 24.2                               | +0.66                | 17.1                               | +0.82                | 16.8                               |
| 100              | +0.44                | 27.4                               | +0.67                | 19.4                               | +0.83                | 19.0                               |
| 150              | +0.46                | 33.5                               | +0.69                | 23.7                               | +0.85                | 23.8                               |
| 200              | +0.46                | 38.6                               | +0.70                | 27.0                               | +0.86                | 26.9                               |
| 300              | +0.46                | 45.8                               | +0.71                | 32.8                               | +0.86                | 31.9                               |
| 400              | +0.47                | 51.4                               | +0.71                | 37.0                               | +0.88                | 34.6                               |
| 500              | +0.46                | 58.8                               | +0.72                | 44.8                               | +0.87                | 40.4                               |
| 600              | +0.47                | 63.6                               | +0.72                | 48.5                               | +0.87                | 44.2                               |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$



**Figure S16.** Cyclic voltammograms of **4** (**a** - Scan range  $\sim -0.22$  V to  $\sim -2.42$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.22$  V to  $\sim +1.28$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM).



**Figure S17.** Cyclic voltammograms of **4** (Scan range  $\sim -0.28$  V to  $\sim +0.60$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM).

**Table S9.** Cyclic voltammetric data for **4** for scan range  $\sim -0.22$  V to  $\sim -2.42$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate (mV/s) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc}}/i_{\text{pa}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | -1.86               | 6.28                              | -1.77               | 8.54                              | 87              | -1.82         | 0.74                          |
| 50               | -1.85               | 8.80                              | -1.77               | 9.59                              | 79              | -1.81         | 0.92                          |
| 75               | -1.85               | 14.9                              | -1.76               | 10.7                              | 89              | -1.81         | 1.40                          |
| 100              | -1.85               | 17.5                              | -1.76               | 14.3                              | 93              | -1.81         | 1.22                          |
| 150              | -1.85               | 20.5                              | -1.76               | 19.3                              | 92              | -1.81         | 1.06                          |
| 200              | -1.86               | 23.7                              | -1.75               | 21.6                              | 102             | -1.80         | 1.10                          |
| 300              | -1.86               | 27.2                              | -1.75               | 25.6                              | 111             | -1.81         | 1.06                          |
| 400              | -1.86               | 29.8                              | -1.75               | 28.1                              | 118             | -1.81         | 1.06                          |
| 500              | -1.87               | 31.8                              | -1.75               | 29.0                              | 118             | -1.81         | 1.10                          |
| 600              | -1.88               | 33.5                              | -1.74               | 30.5                              | 134             | -1.81         | 1.10                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S10.** Cyclic voltammetric data for **4** for scan range  $\sim -0.28$  V  $\rightarrow \sim +0.60$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

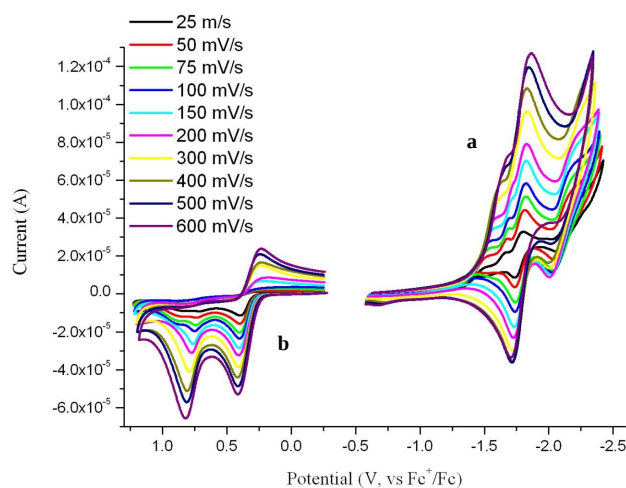
| Scan rate (mV/s) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pa}}/i_{\text{pc}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | +0.44               | 13.8                              | +0.37               | 6.96                              | 64              | +0.40         | 1.97                          |
| 50               | +0.45               | 19.1                              | +0.38               | 7.41                              | 70              | +0.41         | 2.58                          |
| 75               | +0.45               | 23.4                              | +0.38               | 8.01                              | 65              | +0.42         | 2.92                          |
| 100              | +0.45               | 26.3                              | +0.38               | 9.87                              | 72              | +0.42         | 2.67                          |
| 150              | +0.46               | 31.5                              | +0.38               | 12.3                              | 81              | +0.42         | 2.56                          |
| 200              | +0.46               | 34.3                              | +0.38               | 15.0                              | 78              | +0.42         | 2.28                          |
| 300              | +0.46               | 42.5                              | +0.37               | 20.8                              | 92              | +0.42         | 2.05                          |
| 400              | +0.46               | 47.6                              | +0.37               | 23.1                              | 95              | +0.41         | 2.06                          |
| 500              | +0.46               | 52.0                              | +0.36               | 26.5                              | 99              | +0.41         | 1.96                          |
| 600              | +0.46               | 56.9                              | +0.36               | 29.0                              | 99              | +0.41         | 1.96                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

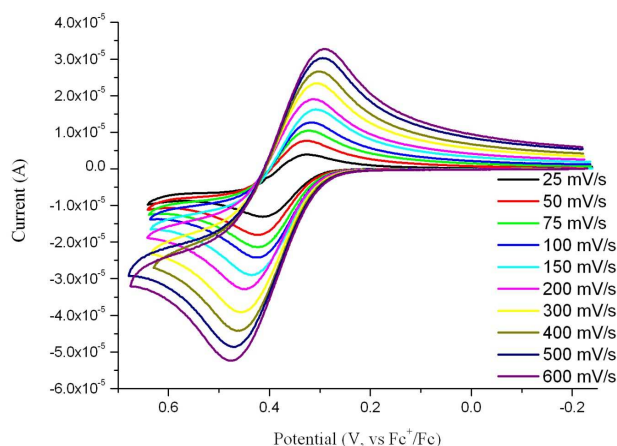
**Table S11.** Cyclic voltammetric data for **4** for scan range  $\sim -0.22$  V to  $\sim +1.28$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate (mV/s) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa2}}$ (V) | $i_{\text{pa2}}$ ( $\mu\text{A}$ ) | $E_{\text{pa3}}$ (V) | $i_{\text{pa3}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | +0.44                | 13.3                               | +0.66                | 11.7                               | +0.84                | 13.3                               |
| 50               | +0.44                | 17.9                               | +0.64                | 14.2                               | +0.84                | 16.0                               |
| 75               | +0.44                | 21.3                               | +0.65                | 16.5                               | +0.86                | 18.0                               |
| 100              | +0.45                | 25.6                               | +0.66                | 19.4                               | +0.85                | 20.9                               |
| 150              | +0.45                | 30.5                               | +0.67                | 23.0                               | +0.85                | 23.9                               |
| 200              | +0.45                | 35.5                               | +0.68                | 27.0                               | +0.86                | 27.3                               |
| 300              | +0.46                | 40.9                               | +0.70                | 31.7                               | +0.86                | 30.0                               |
| 400              | +0.47                | 47.0                               | +0.71                | 38.3                               | +0.87                | 36.3                               |
| 500              | +0.47                | 50.5                               | +0.71                | 41.9                               | +0.87                | 38.7                               |
| 600              | +0.47                | 56.4                               | +0.72                | 49.1                               | sh                   | -                                  |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$



**Figure S18.** Cyclic voltammograms of **5** (**a** - Scan range  $\sim -0.64$  V to  $\sim -2.40$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.26$  V to  $\sim +1.20$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM).



**Figure S19.** Cyclic voltammograms of **5** (Scan range  $\sim -0.22$  V to  $\sim +0.60$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic: 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM)

**Table S12.** Cyclic voltammetric data for **5** for scan range  $\sim -0.64$  V to  $\sim -2.40$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate (mV/s) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc}}/i_{\text{pa}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | -1.80               | 11.9                              | -1.74               | 9.7                               | 65              | -1.77         | 1.23                          |
| 50               | -1.81               | 18.1                              | -1.74               | 14.5                              | 78              | -1.78         | 1.25                          |
| 75               | -1.82               | 21.2                              | -1.74               | 19.9                              | 79              | -1.78         | 1.07                          |
| 100              | -1.83               | 29.7                              | -1.74               | 23.4                              | 87              | -1.78         | 1.27                          |
| 150              | -1.83               | 30.5                              | -1.73               | 29.6                              | 96              | -1.78         | 1.03                          |
| 200              | -1.83               | 33.6                              | -1.73               | 33.5                              | 100             | -1.78         | 1.00                          |
| 300              | -1.83               | 42.6                              | -1.72               | 41.1                              | 110             | -1.78         | 1.04                          |
| 400              | -1.83               | 48.9                              | -1.72               | 48.2                              | 109             | -1.77         | 1.01                          |
| 500              | -1.84               | 53.8                              | -1.71               | 53.2                              | 130             | -1.78         | 1.01                          |
| 600              | -1.87               | 58.0                              | -1.66               | 54.1                              | 211             | -1.76         | 1.07                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S13.** Cyclic voltammetric data for **5** for scan range  $\sim -0.22$  V  $\rightarrow \sim +0.60$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

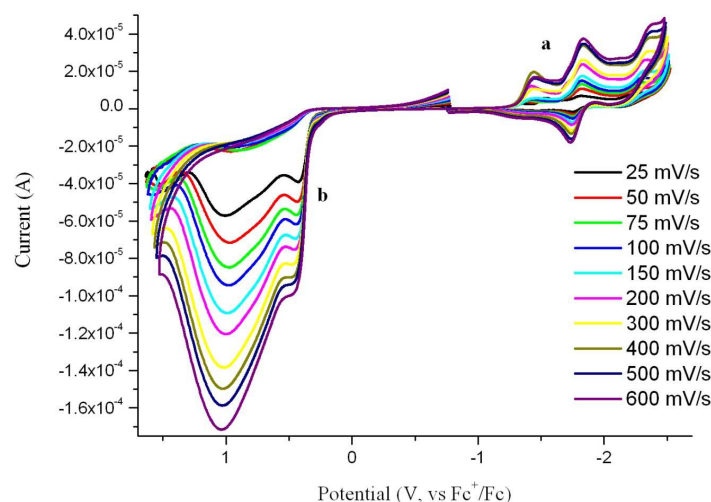
| Scan rate (mV/s) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc}}/i_{\text{pa}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | +0.33               | 12.9                              | +0.41               | 9.30                              | 75              | +0.37         | 1.38                          |
| 50               | +0.34               | 17.7                              | +0.42               | 13.1                              | 82              | +0.38         | 1.35                          |
| 75               | +0.33               | 21.4                              | +0.42               | 14.9                              | 90              | +0.38         | 1.43                          |
| 100              | +0.33               | 23.7                              | +0.42               | 17.7                              | 97              | +0.38         | 1.34                          |
| 150              | +0.33               | 28.7                              | +0.42               | 21.6                              | 107             | +0.37         | 1.33                          |
| 200              | +0.32               | 32.3                              | +0.43               | 25.9                              | 107             | +0.38         | 1.25                          |
| 300              | +0.32               | 38.5                              | +0.43               | 30.9                              | 109             | +0.38         | 1.25                          |
| 400              | +0.32               | 43.2                              | +0.43               | 32.6                              | 111             | +0.38         | 1.32                          |
| 500              | +0.32               | 48.3                              | +0.44               | 38.0                              | 117             | +0.38         | 1.27                          |
| 600              | +0.32               | 51.8                              | +0.44               | 43.6                              | 126             | +0.38         | 1.19                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S14.** Cyclic voltammetric data for **5** for scan range  $\sim -0.26$  V  $\rightarrow \sim +1.20$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate (mV/s) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa2}}$ (V) | $i_{\text{pa2}}$ ( $\mu\text{A}$ ) | $E_{\text{pa3}}$ (V) | $i_{\text{pa3}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | +0.40                | 11.3                               | +0.71                | 9.14                               | +0.87                | sh                                 |
| 50               | +0.41                | 15.3                               | +0.73                | 11.8                               | +0.88                | sh                                 |
| 75               | +0.40                | 20.1                               | +0.74                | 15.9                               | +0.88                | sh                                 |
| 100              | +0.41                | 23.2                               | +0.75                | 18.9                               | +0.88                | sh                                 |
| 150              | +0.41                | 28.1                               | +0.76                | 25.6                               | -                    | -                                  |
| 200              | +0.42                | 31.7                               | +0.77                | 29.6                               | -                    | -                                  |
| 300              | +0.41                | 38.0                               | +0.78                | 39.7                               | -                    | -                                  |
| 400              | +0.43                | 43.3                               | +0.79                | 50.0                               | -                    | -                                  |
| 500              | +0.43                | 48.3                               | +0.80                | 56.5                               | -                    | -                                  |
| 600              | +0.43                | 51.5                               | +0.80                | 63.2                               | -                    | -                                  |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$



**Figure S20.** Cyclic voltammograms of **2** (**a** - Scan range  $\sim -0.75$  V to  $\sim -2.50$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.78$  V to  $\sim +1.60$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in py).

**Table S15.** Cyclic voltammetric data for **2** for scan range  $\sim -0.75$  V  $\rightarrow$   $\sim -2.50$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in py.

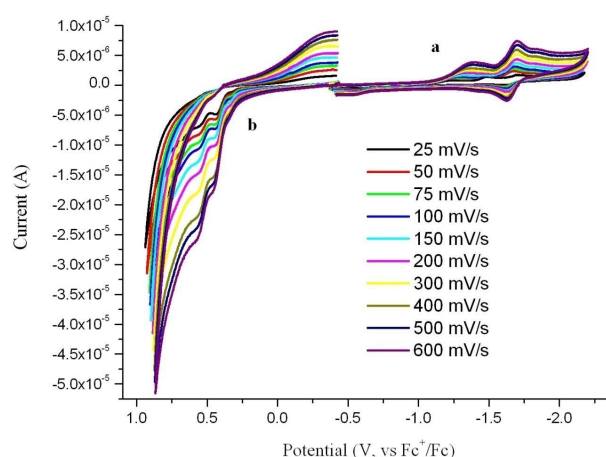
| Scan rate (mV/s) | $E_{\text{pc1}}$ (V) | $i_{\text{pc1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc1}}/i_{\text{pa1}}$ | $E_{\text{pc2}}$ (V) | $i_{\text{pc2}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|-----------------|---------------|---------------------------------|----------------------|------------------------------------|
| 25               | -1.83                | 2.31                               | -1.75                | 2.11                               | 73              | -1.79         | 1.09                            | -1.37                | 0.79                               |
| 50               | -1.83                | 5.24                               | -1.76                | 3.19                               | 70              | -1.79         | 1.64                            | -1.37                | 1.53                               |
| 75               | -1.82                | 7.46                               | -1.75                | 4.17                               | 73              | -1.79         | 1.79                            | -1.37                | 2.69                               |
| 100              | -1.82                | 8.62                               | -1.75                | 4.80                               | 71              | -1.79         | 1.80                            | -1.39                | 2.60                               |
| 150              | -1.83                | 9.85                               | -1.75                | 6.44                               | 81              | -1.79         | 1.53                            | -1.40                | 2.63                               |
| 200              | -1.83                | 12.39                              | -1.75                | 8.89                               | 83              | -1.79         | 1.39                            | -1.41                | 7.70                               |
| 300              | -1.84                | 13.48                              | -1.75                | 11.29                              | 90              | -1.79         | 1.19                            | -1.42                | 5.59                               |
| 400              | -1.83                | 16.71                              | -1.74                | 13.69                              | 88              | -1.79         | 1.22                            | -1.43                | 12.24                              |
| 500              | -1.84                | 16.89                              | -1.75                | 15.67                              | 91              | -1.79         | 1.08                            | -1.44                | 8.85                               |
| 600              | -1.84                | 17.62                              | -1.74                | 17.64                              | 95              | -1.79         | 1.00                            | -1.44                | 8.76                               |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S16.** Cyclic voltammetric data for **2** for scan range  $\sim -0.78$  V  $\rightarrow \sim +1.60$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in py.

| Scan rate (mV/s) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa2}}$ (V) | $i_{\text{pa2}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | +0.42                | 38.3                               | +0.93                | 22.8                               |
| 50               | +0.44                | 48.7                               | +0.97                | 33.3                               |
| 75               | +0.44                | 58.8                               | +0.97                | 42.1                               |
| 100              | +0.45                | 60.4                               | +0.98                | 47.4                               |
| 150              | +0.46                | 66.8                               | +0.99                | 54.9                               |
| 200              | +0.46                | 73.6                               | +1.00                | 60.6                               |
| 300              | +0.48                | 80.9                               | +1.01                | 68.8                               |
| 400              | +0.48                | sh                                 | +1.03                | 72.1                               |
| 500              | +0.48                | sh                                 | +1.03                | 75.5                               |
| 600              | +0.48                | sh                                 | +1.04                | 79.5                               |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$



**Figure S21.** Cyclic voltammograms of **3** (**a** - Scan range  $\sim -0.40$  V to  $\sim -2.20$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.43$  V to  $\sim +0.90$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DMSO).

**Table S17.** Cyclic voltammetric data for **3** for scan range  $\sim -0.40$  V to  $\sim -2.20$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DMSO.

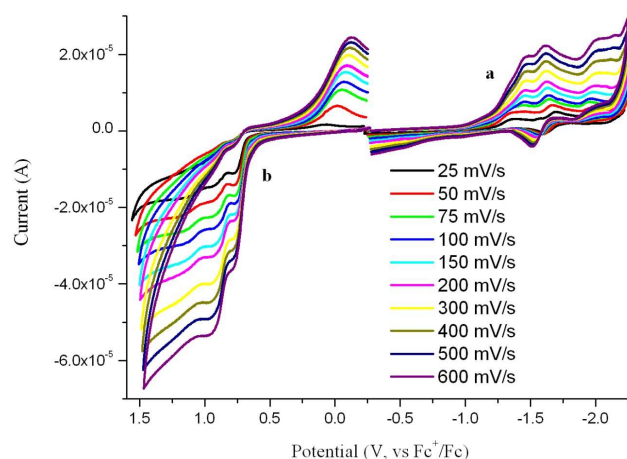
| Scan rate (mV/s) | $E_{\text{pc1}}$ (V) | $i_{\text{pc1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc1}}/i_{\text{pa1}}$ | $E_{\text{pc2}}$ (V) | $i_{\text{pc2}}$ ( $\mu\text{A}$ ) | $E_{\text{pc3}}$ (V) | $i_{\text{pc3}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|-----------------|---------------|---------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | -1.71                | 0.42                               | -1.62                | 0.45                               | 92              | -1.67         | 0.93                            | -1.30                | 0.30                               | -1.49                | 0.41                               |
| 50               | -1.68                | 0.79                               | -1.60                | 0.68                               | 79              | -1.64         | 1.16                            | -1.23                | 0.40                               | -1.46                | 0.33                               |
| 75               | -1.67                | 1.07                               | -1.61                | 0.92                               | 64              | -1.64         | 1.16                            | -1.24                | 0.46                               | -1.46                | 0.20                               |
| 100              | -1.69                | 1.38                               | -1.62                | 1.11                               | 69              | -1.65         | 1.24                            | -1.29                | 0.46                               | -1.47                | sh                                 |
| 150              | -1.70                | 1.75                               | -1.63                | 1.45                               | 64              | -1.66         | 1.21                            | -1.32                | 0.53                               | -                    | -                                  |
| 200              | -1.70                | 2.05                               | -1.63                | 1.78                               | 70              | -1.66         | 1.15                            | -1.34                | 0.89                               | -                    | -                                  |
| 300              | -1.70                | 2.49                               | -1.63                | 2.32                               | 76              | -1.66         | 1.07                            | -1.36                | 0.99                               | -                    | -                                  |
| 400              | -1.70                | 2.89                               | -1.62                | 2.82                               | 75              | -1.66         | 1.02                            | -1.38                | 1.11                               | -                    | -                                  |
| 500              | -1.70                | 3.19                               | -1.63                | 3.11                               | 75              | -1.67         | 1.03                            | -1.38                | 1.38                               | -                    | -                                  |
| 600              | -1.70                | 3.48                               | -1.63                | 3.58                               | 69              | -1.66         | 0.97                            | -1.39                | 1.54                               | -                    | -                                  |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S18.** Cyclic voltammetric data for **3** for scan range  $\sim -0.43$  V  $\rightarrow$   $\sim +0.90$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DMSO.

| Scan rate (mV/s) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa2}}$ (V) | $i_{\text{pa2}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | +0.44                | 4.55                               | +0.55                | sh                                 |
| 50               | +0.44                | 5.05                               | +0.54                | sh                                 |
| 75               | +0.44                | 5.86                               | +0.55                | sh                                 |
| 100              | +0.45                | 6.39                               | +0.55                | sh                                 |
| 150              | +0.45                | 7.69                               | +0.54                | sh                                 |
| 200              | +0.45                | 8.89                               | +0.54                | sh                                 |
| 300              | +0.45                | sh                                 | +0.54                | sh                                 |
| 400              | +0.45                | sh                                 | +0.54                | sh                                 |
| 500              | +0.45                | sh                                 | +0.54                | sh                                 |
| 600              | +0.45                | sh                                 | +0.54                | sh                                 |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$



**Figure S22.** Cyclic voltammograms of **4** (**a** - Scan range  $\sim -0.25$  V to  $\sim -2.24$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.25$  V to  $\sim +1.50$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DMF).

**Table S19.** Cyclic voltammetric data for **4** for scan range  $\sim -0.25$  V to  $\sim -2.24$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DMF.

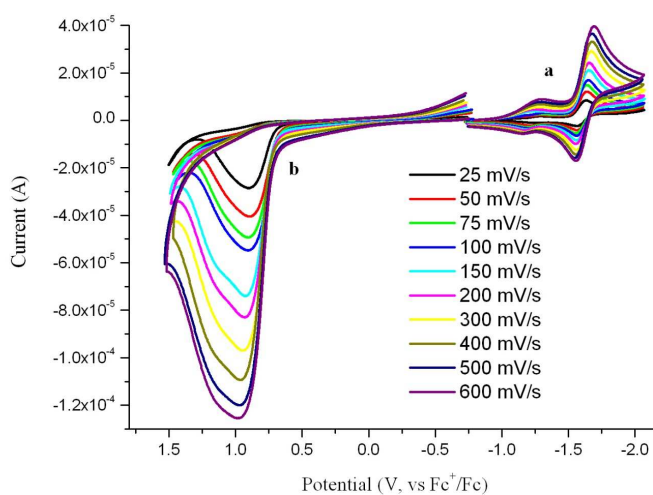
| Scan rate (mV/s) | $E_{\text{pc1}}$ (V) | $i_{\text{pc1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc1}}/i_{\text{pa1}}$ | $E_{\text{pc2}}$ (V) | $i_{\text{pc2}}$ ( $\mu\text{A}$ ) | $E_{\text{pc3}}$ (V) | $i_{\text{pc3}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|-----------------|---------------|---------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | -1.69                | 1.77                               | -1.62                | 1.86                               | 73              | -1.66         | 0.95                            | -1.38                | 2.54                               | -                    | -                                  |
| 50               | -1.68                | 1.86                               | -1.60                | 2.44                               | 79              | -1.64         | 0.76                            | -1.45                | 1.89                               | -1.96                | 0.70                               |
| 75               | -1.64                | 1.95                               | -1.58                | 2.78                               | 66              | -1.61         | 0.70                            | -1.45                | 2.15                               | -1.95                | 1.04                               |
| 100              | -1.64                | 2.13                               | -1.57                | 2.89                               | 77              | -1.60         | 0.74                            | -1.47                | 1.85                               | -1.97                | 1.08                               |
| 150              | -1.63                | 2.59                               | -1.55                | 3.37                               | 81              | -1.59         | 0.77                            | -1.46                | 1.93                               | -1.98                | 1.14                               |
| 200              | -1.63                | 2.69                               | -1.55                | 3.61                               | 79              | -1.59         | 0.75                            | -1.46                | 2.03                               | -2.01                | 1.26                               |
| 300              | -1.63                | 2.87                               | -1.53                | 4.34                               | 96              | -1.58         | 0.66                            | -1.47                | 2.27                               | -2.03                | 1.54                               |
| 400              | -1.63                | 2.98                               | -1.53                | 5.01                               | 99              | -1.58         | 0.59                            | -1.48                | 2.72                               | -2.05                | sh                                 |
| 500              | -1.62                | 3.11                               | -1.52                | 5.45                               | 101             | -1.57         | 0.57                            | -1.49                | 3.02                               | -2.05                | sh                                 |
| 600              | -1.62                | 3.11                               | -1.52                | 5.87                               | 102             | -1.57         | 0.53                            | -1.49                | sh                                 | -2.02                | sh                                 |

<sup>a</sup> All potentials externally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S20.** Cyclic voltammetric data for **4** for scan range  $\sim -0.25$  V to  $\sim +1.50$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DMF.

| Scan rate (mV/s) | $E_{\text{pa1}}$ (V) | $i_{\text{pa1}}$ ( $\mu\text{A}$ ) | $E_{\text{pa2}}$ (V) | $i_{\text{pa2}}$ ( $\mu\text{A}$ ) |
|------------------|----------------------|------------------------------------|----------------------|------------------------------------|
| 25               | +0.79                | 10.4                               | +0.96                | sh                                 |
| 50               | +0.79                | 13.3                               | +0.96                | sh                                 |
| 75               | +0.77                | 15.8                               | +0.96                | sh                                 |
| 100              | +0.77                | 18.1                               | +0.96                | sh                                 |
| 150              | +0.78                | sh                                 | +0.96                | sh                                 |
| 200              | +0.79                | sh                                 | +0.96                | sh                                 |
| 300              | +0.79                | sh                                 | +0.96                | sh                                 |
| 400              | +0.79                | sh                                 | +0.96                | sh                                 |
| 500              | +0.79                | sh                                 | +0.96                | sh                                 |
| 600              | +0.79                | sh                                 | +0.96                | sh                                 |

<sup>a</sup> All potentials externally referenced vs  $\text{Fc}^+/\text{Fc}$



**Figure S23.** Cyclic voltammograms of  $[\text{UO}_2(\text{salen})(\text{py})]$  (**a** - Scan range  $\sim -0.75$  V to  $\sim -2.10$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.75$  V to  $\sim +1.50$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - anodic: 0.1 M  $\text{Bu}_4\text{NPF}_6$  in py).

**Table S21.** Cyclic voltammetric data for [UO<sub>2</sub>(salen)(py)] for scan range ~ -0.75 V to ~ -2.10 V (vs Fc<sup>+</sup>/Fc)<sup>a</sup> in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in py.

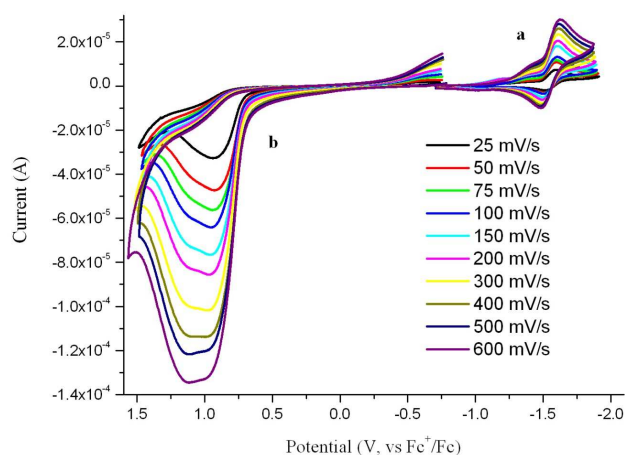
| Scan rate (mV/s) | E <sub>pc</sub> (V) | i <sub>pc</sub> (μA) | E <sub>pa</sub> (V) | i <sub>pa</sub> (μA) | ΔE (mV) | E <sub>1/2</sub> (V) | i <sub>pc</sub> /i <sub>pa</sub> |
|------------------|---------------------|----------------------|---------------------|----------------------|---------|----------------------|----------------------------------|
| 25               | -1.63               | 4.77                 | -1.57               | 4.06                 | 64      | -1.60                | 1.17                             |
| 50               | -1.64               | 7.04                 | -1.57               | 5.74                 | 72      | -1.60                | 1.23                             |
| 75               | -1.64               | 7.17                 | -1.57               | 6.35                 | 71      | -1.60                | 1.13                             |
| 100              | -1.65               | 7.56                 | -1.57               | 6.60                 | 81      | -1.61                | 1.15                             |
| 150              | -1.66               | 10.9                 | -1.56               | 8.89                 | 92      | -1.61                | 1.23                             |
| 200              | -1.66               | 12.4                 | -1.56               | 10.2                 | 96      | -1.61                | 1.22                             |
| 300              | -1.67               | 13.5                 | -1.56               | 12.3                 | 108     | -1.61                | 1.10                             |
| 400              | -1.67               | 14.5                 | -1.55               | 13.2                 | 120     | -1.61                | 1.10                             |
| 500              | -1.68               | 15.0                 | -1.56               | 13.6                 | 125     | -1.62                | 1.10                             |
| 600              | -1.69               | 15.4                 | -1.55               | 15.3                 | 144     | -1.62                | 1.01                             |

<sup>a</sup> All potentials internally referenced vs Fc<sup>+</sup>/Fc

**Table S22.** Cyclic voltammetric data for [UO<sub>2</sub>(salen)(py)] for scan range ~ -0.75 V to ~ + 1.50 V (vs Fc<sup>+</sup>/Fc)<sup>a</sup> in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in py.

| Scan rate (mV/s) | E <sub>pa1</sub> (V) | i <sub>pa1</sub> (μA) | E <sub>pa2</sub> (V) | i <sub>pa2</sub> (μA) |
|------------------|----------------------|-----------------------|----------------------|-----------------------|
| 25               | +0.90                | 30.9                  | -                    | -                     |
| 50               | +0.90                | 45.0                  | -                    | -                     |
| 75               | +0.91                | 53.4                  | -                    | -                     |
| 100              | +0.91                | 60.9                  | -                    | -                     |
| 150              | +0.93                | 72.7                  | -                    | -                     |
| 200              | +0.93                | 81.0                  | +1.14                | sh                    |
| 300              | +0.95                | 96.1                  | +1.15                | sh                    |
| 400              | +0.96                | 108                   | +1.16                | sh                    |
| 500              | +0.97                | 109                   | +1.17                | sh                    |
| 600              | +0.98                | 111                   | +1.18                | sh                    |

<sup>a</sup> All potentials internally referenced vs Fc<sup>+</sup>/Fc



**Figure S24.** Cyclic voltammograms of  $[\text{UO}_2(\text{salophen})(\text{py})]$  (**a** - Scan range  $\sim -0.70$  V to  $\sim -1.88$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction - cathodic; **b** - Scan range  $\sim -0.75$  V to  $\sim +1.50$  V, vs  $\text{Fc}^+/\text{Fc}$ , Initial scan direction – anodic: 0.1 M  $\text{Bu}_4\text{NPF}_6$  in py).

**Table S23.** Cyclic voltammetric data for  $[\text{UO}_2(\text{salophen})(\text{py})]$  for scan range  $\sim -0.70$  V to  $\sim -1.88$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in py.

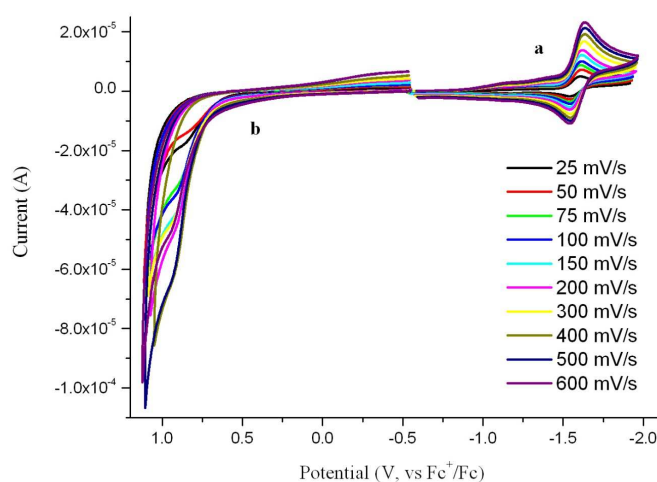
| Scan rate (mV/s) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) | $\Delta E$ (mV) | $E_{1/2}$ (V) | $i_{\text{pc}}/i_{\text{pa}}$ |
|------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|-----------------|---------------|-------------------------------|
| 25               | -1.60               | 6.57                              | -1.54               | 4.78                              | 64              | -1.57         | 1.37                          |
| 50               | -1.60               | 9.02                              | -1.54               | 6.90                              | 63              | -1.57         | 1.31                          |
| 75               | -1.60               | 11.2                              | -1.53               | 8.50                              | 67              | -1.57         | 1.31                          |
| 100              | -1.61               | 12.6                              | -1.53               | 9.94                              | 71              | -1.57         | 1.27                          |
| 150              | -1.61               | 15.8                              | -1.53               | 13.1                              | 76              | -1.57         | 1.21                          |
| 200              | -1.61               | 17.9                              | -1.53               | 14.3                              | 82              | -1.57         | 1.25                          |
| 300              | -1.61               | 20.9                              | -1.52               | 18.3                              | 89              | -1.57         | 1.14                          |
| 400              | -1.61               | 23.3                              | -1.52               | 20.6                              | 91              | -1.57         | 1.13                          |
| 500              | -1.62               | 25.1                              | -1.52               | 22.6                              | 96              | -1.57         | 1.11                          |
| 600              | -1.62               | 26.7                              | -1.52               | 24.4                              | 106             | -1.57         | 1.09                          |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$

**Table S24.** Cyclic voltammetric data for [UO<sub>2</sub>(salophen)(py)] for scan range ~ -0.75 V to ~ +1.50 V (vs Fc<sup>+</sup>/Fc)<sup>a</sup> in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in py.

| Scan rate (mV/s) | E <sub>pa1</sub> (V) | i <sub>pa1</sub> (μA) | E <sub>pa2</sub> (V) | i <sub>pa2</sub> (μA) |
|------------------|----------------------|-----------------------|----------------------|-----------------------|
| 25               | +0.94                | 27.1                  | -                    | -                     |
| 50               | +0.93                | 37.9                  | -                    | -                     |
| 75               | +0.94                | 45.7                  | -                    | -                     |
| 100              | +0.96                | 50.1                  | -                    | -                     |
| 150              | +0.96                | 68.2                  | -                    | -                     |
| 200              | +0.97                | 74.8                  | +1.15                | sh                    |
| 300              | +0.98                | 87.6                  | +1.17                | sh                    |
| 400              | +1.01                | 97.9                  | +1.19                | sh                    |
| 500              | +1.02                | sh                    | +1.20                | 105                   |
| 600              | +1.04                | sh                    | +1.21                | 109                   |

<sup>a</sup> All potentials internally referenced vs Fc<sup>+</sup>/Fc

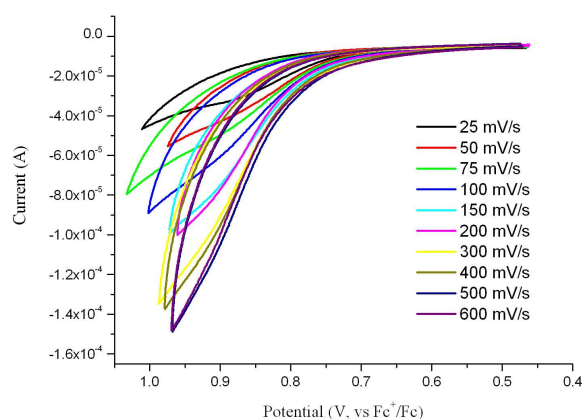


**Figure S25.** Cyclic voltammograms of [UO<sub>2</sub>(salen)(DMSO)] (**a** - Scan range ~ -0.55 V to ~ -1.95 V, vs Fc<sup>+</sup>/Fc, Initial scan direction - cathodic; **b** - Scan range ~ -0.55 V to ~ +1.10 V, vs Fc<sup>+</sup>/Fc, Initial scan direction – anodic: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DMSO).

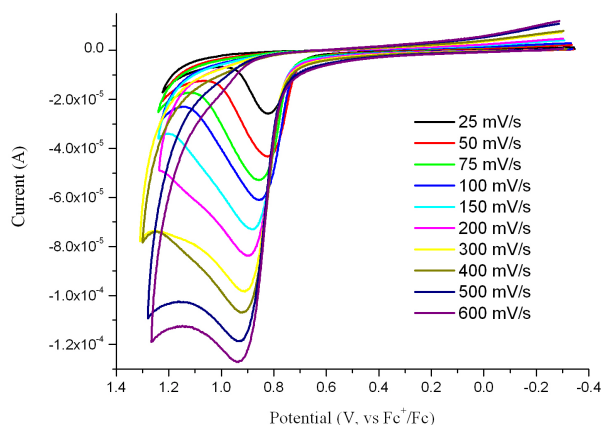
**Table S25.** Cyclic voltammetric data for [UO<sub>2</sub>(salen)(DMSO)] for scan range ~ -0.55 V to ~ -1.95 V (vs Fc<sup>+</sup>/Fc)<sup>a</sup> in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DMSO.

| Scan rate (mV/s) | E <sub>pc</sub> (V) | i <sub>pc</sub> (μA) | E <sub>pa</sub> (V) | i <sub>pa</sub> (μA) | ΔE (mV) | E <sub>1/2</sub> (V) | i <sub>pc</sub> /i <sub>pa</sub> |
|------------------|---------------------|----------------------|---------------------|----------------------|---------|----------------------|----------------------------------|
| 25               | -1.61               | 3.98                 | -1.53               | 2.72                 | 71      | -1.57                | 1.46                             |
| 50               | -1.61               | 5.68                 | -1.54               | 4.30                 | 79      | -1.57                | 1.32                             |
| 75               | -1.61               | 7.05                 | -1.53               | 5.32                 | 82      | -1.57                | 1.33                             |
| 100              | -1.62               | 7.82                 | -1.53               | 6.26                 | 91      | -1.57                | 1.25                             |
| 150              | -1.62               | 9.58                 | -1.52               | 7.69                 | 94      | -1.57                | 1.25                             |
| 200              | -1.62               | 10.2                 | -1.52               | 8.81                 | 105     | -1.57                | 1.15                             |
| 300              | -1.63               | 12.1                 | -1.52               | 10.7                 | 112     | -1.57                | 1.14                             |
| 400              | -1.63               | 14.1                 | -1.51               | 12.6                 | 125     | -1.57                | 1.12                             |
| 500              | -1.64               | 15.4                 | -1.50               | 13.1                 | 133     | -1.57                | 1.17                             |
| 600              | -1.64               | 16.2                 | -1.50               | 14.8                 | 138     | -1.57                | 1.09                             |

<sup>a</sup> All potentials internally referenced vs Fc<sup>+</sup>/Fc



**Figure S26.** Cyclic voltammograms of [UO<sub>2</sub>(salophen)(DMSO)] (Scan range ~ +0.45 V to ~ +1.00 V, vs Fc<sup>+</sup>/Fc, Initial scan direction – anodic: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DMSO).

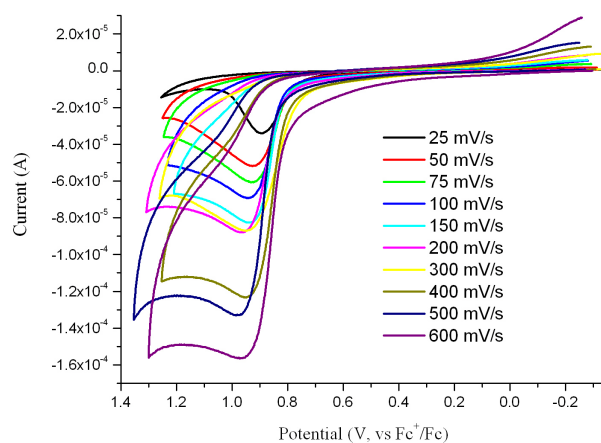


**Figure S27.** Cyclic voltammograms of [UO<sub>2</sub>(salen)(DMF)] (Scan range ~ -0.33 V to ~ +1.28 V, vs Fc<sup>+</sup>/Fc, Initial scan direction – anodic: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DMF).

**Table S26.** Cyclic voltammetric data for [UO<sub>2</sub>(salen)(DMF)] for scan range ~ -0.33 V to ~ +1.28 V (vs Fc<sup>+</sup>/Fc)<sup>a</sup> in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DMF.

| Scan rate (mV/s) | E <sub>pa1</sub> (V) | i <sub>pa1</sub> (μA) |
|------------------|----------------------|-----------------------|
| 25               | +0.82                | 24.6                  |
| 50               | +0.82                | 41.9                  |
| 75               | +0.86                | 51.2                  |
| 100              | +0.86                | 59.0                  |
| 150              | +0.88                | 70.9                  |
| 200              | +0.90                | 81.4                  |
| 300              | +0.91                | 95.7                  |
| 400              | +0.92                | 103.7                 |
| 500              | +0.93                | 113.1                 |
| 600              | +0.94                | 120.8                 |

<sup>a</sup> All potentials internally referenced vs Fc<sup>+</sup>/Fc

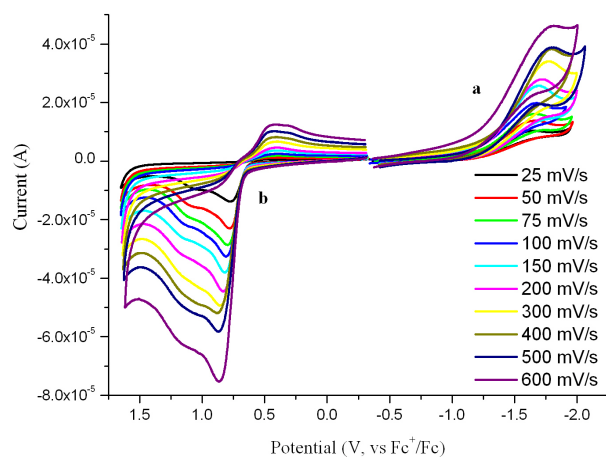


**Figure S28.** Cyclic voltammograms of [UO<sub>2</sub>(salophen)(DMF)] (Scan range ~ -0.30 V to ~ +1.25 V, vs Fc<sup>+</sup>/Fc, Initial scan direction – anodic: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DMF).

**Table S27.** Cyclic voltammetric data for [UO<sub>2</sub>(salophen)(DMF)] for scan range ~ -0.30 V to ~ + 1.25 V (vs Fc<sup>+</sup>/Fc)<sup>a</sup> in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DMF.

| Scan rate | E <sub>pa1</sub> (V) | i <sub>pa1</sub> (μA) |
|-----------|----------------------|-----------------------|
| 25        | +0.90                | 33.1                  |
| 50        | +0.93                | 50.2                  |
| 75        | +0.93                | 58.6                  |
| 100       | +0.94                | 67.7                  |
| 150       | +0.94                | 80.3                  |
| 200       | +0.97                | 85.5                  |
| 300       | +0.95                | 82.6                  |
| 400       | +0.95                | 119.3                 |
| 500       | +0.98                | 126.8                 |
| 600       | +0.97                | 144.7                 |

<sup>a</sup> All potentials internally referenced vs Fc<sup>+</sup>/Fc

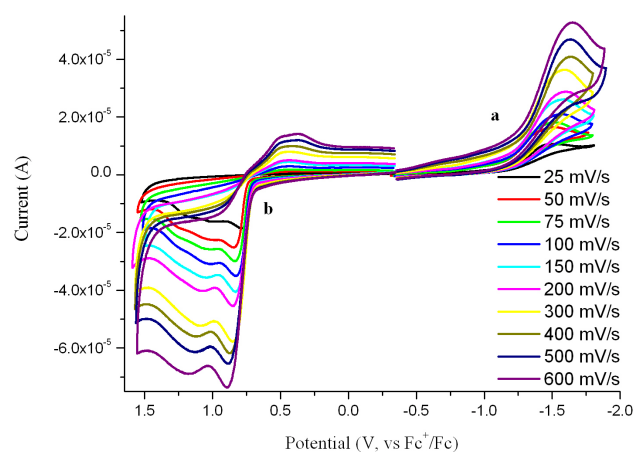


**Figure S29.** Cyclic voltammograms of [UO<sub>2</sub>(salen)(TPPO)] (**a** - Scan range ~ -0.40 V to ~ -2.00 V, vs Fc<sup>+</sup>/Fc, Initial scan direction - cathodic; **b** - Scan range ~ -0.32 V to +1.65 V, vs Fc<sup>+</sup>/Fc, Initial scan direction – anodic: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DCM).

**Table S28.** Cyclic voltammetric data for [UO<sub>2</sub>(salen)(TPPO)] (vs Fc<sup>+</sup>/Fc) in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DCM.

| Scan rate (mV/s) | E <sub>pc</sub> (V) <sup>a</sup> | i <sub>pc</sub> (μA) | E <sub>pa1</sub> (V) <sup>b</sup> | i <sub>pa1</sub> (μA) | E <sub>pa2</sub> (V) <sup>b</sup> | i <sub>pa2</sub> (μA) |
|------------------|----------------------------------|----------------------|-----------------------------------|-----------------------|-----------------------------------|-----------------------|
| 25               | -1.65                            | 8.90                 | +0.77                             | 13.3                  | +1.06                             | sh                    |
| 50               | -1.66                            | 11.2                 | +0.78                             | 22.4                  | +1.07                             | sh                    |
| 75               | -1.67                            | 14.1                 | +0.80                             | 27.7                  | +1.13                             | sh                    |
| 100              | -1.68                            | 16.2                 | +0.81                             | 31.5                  | +1.15                             | sh                    |
| 150              | -1.69                            | 20.7                 | +0.82                             | 36.5                  | +1.15                             | sh                    |
| 200              | -1.72                            | 23.1                 | +0.83                             | 42.6                  | +1.16                             | sh                    |
| 300              | -1.77                            | 27.4                 | +0.83                             | 47.3                  | +1.16                             | sh                    |
| 400              | -1.80                            | 29.9                 | +0.86                             | 49.0                  | +1.12                             | sh                    |
| 500              | -1.81                            | 34.6                 | +0.87                             | 54.4                  | +1.15                             | sh                    |
| 600              | -1.81                            | 32.8                 | +0.87                             | 72.0                  | +1.21                             | sh                    |

<sup>a</sup> Potentials internally referenced vs Fc<sup>+</sup>/Fc      <sup>b</sup> Potentials externally referenced vs Fc<sup>+</sup>/Fc

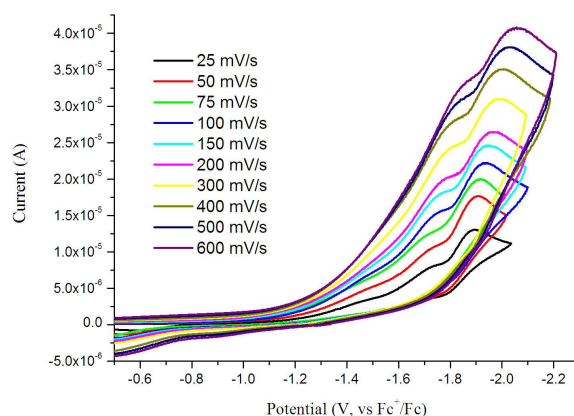


**Figure S30.** Cyclic voltammograms of [UO<sub>2</sub>(salophen)(TPPO)] (**a** - Scan range ~ -0.35 V to ~ -1.80 V, vs Fc<sup>+</sup>/Fc, Initial scan direction - cathodic; **b** - Scan range ~ -0.33 V to ~ +1.55 V, vs Fc<sup>+</sup>/Fc, Initial scan direction – anodic: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DCM).

**Table S29.** Cyclic voltammetric data for [UO<sub>2</sub>(salophen)(TPPO)] in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DCM.<sup>a</sup>

| Scan rate (mV/s) | E <sub>pc</sub> (V) | i <sub>pc</sub> (μA) | E <sub>pa1</sub> (V) | i <sub>pa1</sub> (μA) | E <sub>pa2</sub> (V) | i <sub>pa2</sub> (μA) |
|------------------|---------------------|----------------------|----------------------|-----------------------|----------------------|-----------------------|
| 25               | -1.51               | 8.88                 | +0.79                | 18.1                  | -                    | -                     |
| 50               | -1.51               | 13.2                 | +0.85                | 24.1                  | -                    | -                     |
| 75               | -1.52               | 15.0                 | +0.84                | 29.0                  | +1.02                | sh                    |
| 100              | -1.57               | 16.4                 | +0.83                | 33.1                  | +1.01                | sh                    |
| 150              | -1.58               | 20.0                 | +0.83                | 38.6                  | +1.04                | sh                    |
| 200              | -1.60               | 22.7                 | +0.85                | 43.1                  | +1.07                | 37.4                  |
| 300              | -1.59               | 27.3                 | +0.85                | 54.9                  | +1.08                | 48.9                  |
| 400              | -1.64               | 29.1                 | +0.88                | 58.6                  | +1.12                | 52.1                  |
| 500              | -1.63               | 31.4                 | +0.89                | 61.8                  | +1.13                | 57.1                  |
| 600              | -1.65               | 36.6                 | +0.89                | 68.9                  | +1.18                | 63.0                  |

<sup>a</sup> All potentials externally referenced vs Fc<sup>+</sup>/Fc



**Figure S31.** Cyclic voltammograms of [Zn(salmnt<sup>(Et<sub>2</sub>N)<sub>2</sub>)</sup>)] (Scan range -0.50 V to ~ -2.10 V, vs Fc<sup>+</sup>/Fc, Initial scan direction - cathodic: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DCM).

**Table S30.** Cyclic voltammetric data for  $[\text{Zn}(\text{salmnt}^{(\text{Et}_2\text{N})_2})]$  for scan range  $\sim -0.70$  V to  $\sim -2.50$  V (vs  $\text{Fc}^+/\text{Fc}$ )<sup>a</sup> in 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DCM.

| Scan rate<br>(mV/s) | $E_{\text{pc}}$ (V) | $i_{\text{pc}}$ ( $\mu\text{A}$ ) | $E_{\text{pa}}$ (V) | $i_{\text{pa}}$ ( $\mu\text{A}$ ) |
|---------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|
| 25                  | -1.90               | 3.87                              | -1.80               | sh                                |
| 50                  | -1.90               | 4.78                              | -                   | -                                 |
| 75                  | -1.92               | 6.54                              | -                   | -                                 |
| 100                 | -1.94               | 7.64                              | -                   | -                                 |
| 150                 | -1.95               | 7.80                              | -                   | -                                 |
| 200                 | -1.97               | 8.20                              | -                   | -                                 |
| 300                 | -1.99               | 8.88                              | -                   | -                                 |
| 400                 | -2.01               | 9.92                              | -                   | -                                 |
| 500                 | -2.03               | 12.4                              | -                   | -                                 |
| 600                 | -2.06               | 13.4                              | -                   | -                                 |

<sup>a</sup> All potentials internally referenced vs  $\text{Fc}^+/\text{Fc}$