# Immobilization of a hexaphyrin(1.0.1.0.0.0) derivative onto a tentagel-amino resin and its use in uranyl cation detection

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**Electronic Supplementary Information** 

#### **Synthesis**

*General Procedures:* All chemicals were purchased from Aldrich or Fischer Chemical and used as received unless otherwise indicated. Polystyrene-poly(ethylene glycol) graft copolymer microspheres were purchased from Novabiochem. Starting pyrrole **S1** was provided as a gift from Phamacyclics, Inc. Dichloromethane was freshly distilled from calcium hydride, tetrahydrofuran was dried by passage through two columns of alumina (except when used as a solvent for the hydrogenation of **S6**) and *n*pentane was stirred over concentrated  $H_2SO_4$  for more than 24 h, neutralized with  $K_2CO_3$ , and distilled from CaH<sub>2</sub>. Cyclohexane was purchased from Fisher Scientific and used as received. All deuterated NMR solvents were purchased from Cambridge Isotope Labs and used as received.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury 400 MHz spectrometer or on a Varian Inova 500 MHz instrument. UV-visible spectra were recorded on a Beckman DU-640 or a Carey 5000 spectrophotometer. High-resolution mass spectra were obtained at the University of Texas at Austin, Department of Chemistry and Biochemistry, Mass Spectrometry Facility.



**S2:** Lead tetraacetate (26.4 g, 0.06 mol) was added at room temperature to a stirred solution of benzyl 3,5-dimethyl-4-(2-methoxycarbonylethyl)pyrrole-2-carboxylate 1 (18.9 g, 0.06 mol) in acetic acid (250 mL). The solution was stirred overnight at room temperature. Lead dioxide (90%, 15.9 g, 0.066 mol) was added to the solution and the mixture was heated at 80°C with stirring for 3 hours. The reaction mixture was allowed to cool to room temperature and filtered through Celite. The filtrate was poured into distilled H<sub>2</sub>O (400 mL) and extracted with ether (2 x 200 mL). The organic layer was washed with saturated NaHCO<sub>3</sub> several times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and dried in vacuo. Recrystallization from ether/hexanes (1:1) gave product **S2** (15.5 g, 78.6%). δ<sub>H</sub>(400 MHz, CDCl<sub>3</sub>) 2.28 (3 H, s, C(5)CH<sub>3</sub>), 2.54(2 H t, *J* = 7.5, CH<sub>2</sub>CH<sub>2</sub>), 3.03 (2 H, t, *J* = 7.5, CH<sub>2</sub>CH<sub>2</sub>), 3.62 (3 H, s, COOCH<sub>3</sub>), 5.31 (2 H, s, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 7.3-7.4 (5 H, m, C<sub>6</sub>H<sub>5</sub>), 9.48 (1 H, br s, NH), 9.78 (1 H, s, CHO) ; δ<sub>C</sub>(75 MHz, CDCl<sub>3</sub>) 9.76, 18.69, 34.85, 51.64, 66.59, 124.13, 126.91, 128.40, 128.56, 130.06, 131.89, 135.33, 160.57, 172.59, 179.69. CI-HRMS calc'd for C<sub>18</sub>H<sub>20</sub>N<sub>1</sub>O<sub>5</sub> : 330.1341, found: 330.1344.

S3: KMnO<sub>4</sub> (11.5 g, 0.072 mol) was dissolved in a mixture of  $H_2O$  (200 mL) and acetone (150 mL) and then was added dropwise to the solution of S2 (12.0 g, 0.036 mol) in acetone (25 0mL) for 45 minutes at room temperature. 12 hours later, more  $KMnO_4$ (3g) was added as a solid to the reaction mixture and the resulting solution was stirred for a further 4 hours. Acetone was removed from the mixture under reduced pressure. dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (250 mL), H<sub>2</sub>O (150 mL) and sodium metabisulfite (15 g, 0.079 mol) were added subsequently and the resulting mixture was stirred vigorously. Then, concentrated HCl was added dropwise, until the solution became a cloudy yellow. The solution was separated and the aqueous layer was extracted with DCM (2 x 200 mL). The combined organic layer was washed with H<sub>2</sub>O (2 x 200 mL) and brine (200 mL). After drying over sodium sulfate, the solvent was removed in vacuo. Addition of ether to the oil acted to precipitate S3 as a white solid, which was then isolated by filtration (8.35 g, 66.4%).  $\delta_{H}(400 \text{ MHz}, \text{CDCl}_{3})$  2.29 (3 H, s, C(5)CH<sub>3</sub>), 2.54 (2 H, t, J = 7.8 Hz,  $CH_2CH_2$ ), 3.05 (2 H, t, J = 7.8 Hz,  $CH_2CH_2$ ), 3.65 (3 H, s,  $COOCH_3$ ), 5.32 (2 H, s, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 7.3-7.4 (5 H, m, C<sub>6</sub>H<sub>5</sub>), 9.55 (1 H, s, NH); δ<sub>C</sub>(75 MHz, CDCl<sub>3</sub>) 9.99, 19.97, 34.37, 51.64, 66.57, 120.80, 122.65, 127.39, 128.36, 128.44, 128.65, 131.43, 135.51,

160.58, 165.29, 173.50); CI-HRMS calc'd for  $[C_{18}H_{19}N_1O_6 + H]^+$ : 346.129063, found: 346.127845.

S4: Pyrrole S3 (6.86g, 19.89 mmol) was suspended in methanol (50 mL) and an aqueous solution of saturated NaHCO<sub>3</sub> (50 mL) was added into a 500 mL three-neck RBF. The suspension was heated to 80°C. I<sub>2</sub> (5.0 5g, 19.89 mmol) and KI (9.91 g, 59.7 mmol) were dissolved in 150 mL hot water and added dropwise to the suspension. The resulting mixture was stirred at the same temperature for a further 30 minutes then cooled in an ice bath for 1 hour. The resulting white solid was filtered and washed with hot water. The solids were then dissolved in DCM (100 mL) and washed with an aqueous 3% thiosulfate solution. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and solidified with hexanes. The product, S4, was produced as a white solid (7.09g, 84%).  $\delta_{\rm H}$ (400 MHz, CDCl<sub>3</sub>) 2.31 (3 H, s, C(5)CH<sub>3</sub>), 2.42 (2 H, t, J= 8.0 Hz, CH<sub>2</sub>CH<sub>2</sub>), 2.69 (2 H, t, J = 8.0 Hz, CH<sub>2</sub>CH<sub>2</sub>), 3.66 (3 H, s, COOCH<sub>3</sub>), 5.29 (2 H, s, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 7.3-7.4 (5 H, m, C<sub>6</sub>H<sub>5</sub>), 9.04 (1 H, s, NH);  $\delta_{\rm C}$ (75 MHz, CDCl<sub>3</sub>) 10.86, 22.03, 34.28, 51.68, 65.99, 73.39, 123.64, 127.17, 128.24, 128.27, 128.59, 128.63, 136.00, 160.21, 173.50; CI-HRMS calc'd for C<sub>17</sub>H<sub>18</sub>N<sub>1</sub>O<sub>4</sub>I: 427.020860, found: 427.027024.

**S5**: Iodo-pyrrole **S4** (8.6 g, 20 mmol) was dissolved in 75 mL of DCM and then di-*tert*-butyldicarbonate (5.45 g, 25 mmol), dissolved in 45 mL of DCM, and 4dimethylaminopyridine (0.08, 0.4 mmol) were added immediately. The resulting mixture was stirred overnight at room temperature. The reaction mixture was subjected to flash chromatography over silica gel using DCM as the eluent until all of the product had been removed as judged by TLC. Evaporation of the solvent led to the desired product, **S5**, as a yellow oil (10.5 g, 99%).  $\delta_{H}(400 \text{ MHz}, \text{CDCl}_3)$  1.54 (9 H, s,  $C(CH_3)_3$ ), 2.15 (3 H, s,  $CH_3$ ), 2.52 (2 H, t, J = 7.8Hz,  $CH_2CH_2$ ), 2.99(2 H, t, J = 7.8Hz,  $CH_2CH_2$ ), 3.64 (3 H, s,  $COOCH_3$ ), 5.32(2 H, s,  $CH_2C_6H_5$ ), 7.3-7.4 (5 H, m,  $C_6H_5$ );  $\delta_C(100 \text{ MHz}, \text{CDCl}_3)$  10.988, 22.498, 27.409, 33.634, 51.613, 66.361, 85.829, 125.331, 128.141, 128.432, 129.119, 129.913, 135.672, 148.901, 160.051, 172.806; CI-HRMS m/z: calc'd for  $C_{23}H_{28}N_1O_7$ : 430.186578, found: 430.186849.

**S6**: The BOC-proteced iodo-pyrrole **S5** (12.3 g, 23.3 mmol) was dissolved in 150 mL of toluene and copper powder (12 g, 189 mmol) was added. The mixture was stirred at 120°C under Ar for 40 hours. After cooling to room temperature, the solution was

filtered through celite and washed with DCM and an ethyl acetate: hexanes (1:1/ v/v) mixture. The solvent was evaporated and the resulting black oil was heated to 180°C under high vacuum. After 1 hour, the residual oil was dissolved in hot ethanol and crystallized. The solid was collected and washed with cold ethanol. It was then redissolved in DCM and 'flashed' through a silica plug. The solution was collected and dried *in vacuo* to give **S6** as a grey solid (6.22 g, 88.9%).  $\delta_{H}(400 \text{ MHz}, \text{CDCl}_3)$  2.27(6 H, s, C(5)CH<sub>3</sub>), 2.52 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>), 2.99 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>), 3.46 (6 H, s, COOCH<sub>3</sub>), 5.24 (4 H, s, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 7.2-7.4 (10 H, m, C<sub>6</sub>H<sub>5</sub>), 11.31 (2 H, s, NH).  $\delta_{C}(75 \text{ MHz}, \text{CDCl}_3)$  10.99, 19.25, 32.91, 51.92, 65.40, 119.07, 120.49, 125.40, 127.33, 127.79, 127.90, 128.28, 136.51, 161.27, 175.02; CI-HRMS m/z: calc'd for C<sub>34</sub>H<sub>37</sub>N<sub>2</sub>O<sub>8</sub> 601.2551, found 601.2544.

**S7**: Bipyrrole **S6** (1.8 g, 3 mmol) was dissolved in THF (120 mL). In a separate flask, 10% Pd/C (0.3 g) and triethylamine (0.1 mL) were equilibrated in THF (30 mL) for 5 minutes. The bipyrrole was slowly added to this suspension. After an exchange between hydrogen and vacuum (3x), the mixture was stirred under a hydrogen atmosphere for 4 hours. The reaction mixture was filtered through celite and washed with THF (50 mL) and DCM (50 mL). The filtrate was concentrated and hexanes (50 mL) were added. The product, **S7**, was obtained as a white solid (1.26 g, quantitative). Found: C, 56.72; H, 5.88; N, 6.49; calc'd for  $C_{20}H_{25}N_2O_8$ : C, 57.14; H, 5.75; N, 6.66;  $\delta_{\rm H}$  (400 MHz, DMSO-d<sub>6</sub>) 2.22 (6 H, s, C(5)CH<sub>3</sub>), 2.29 (4 H, t, J = 8.0Hz, CH<sub>2</sub>CH<sub>2</sub>), 2.57(4 H, t, J = 8.0Hz, CH<sub>2</sub>CH<sub>2</sub>), 3.50(6 H, s, COOCH<sub>3</sub>), 11.25 (2 H, s, COOH), 12.12 (2 H, s, NH).  $\delta_{\rm C}$  (75 MHz, DMSO-d<sub>6</sub>)10.42, 19.56, 33.77, 51.23, 119.27, 122.09, 124.39, 125.09, 162.38, 172.96; CI-HRMS m/z: calc'd for  $C_{20}H_{25}N_2O_8$  421.161091, found 421.161709.

**S8**: The bis-carboxylic acid bipyrrole **S7** (0.42 g, 1 mmol) was placed in a RBF and evacuated for 30 minutes prior to an argon purge. It was then cooled to 0°C and freshly degassed TFA (10 mL) was added dropwise. The resulting green solution was stirred for 20 min. at 0°C under argon and covered from light. The solution was diluted with DCM (100 mL). It was transferred to a seperatory funnel and washed with saturated NaHCO<sub>3</sub> (3 x 100 mL) and brine (1 x 100 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and dried *in vacuo*. The product, **S8**, was obtained as a green liquid (0.30 g, 90%).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 2.08 (6 H, s, C(5)CH<sub>3</sub>), 2.68 (4 H, t, J = 6.7 Hz, CH<sub>2</sub>CH<sub>2</sub>), 2.80 (4 H,

t, J = 6.7 Hz, CH<sub>2</sub>CH<sub>2</sub>), 3.61(6 H, s, COOCH<sub>3</sub>), 6.56 (2 H, d, J = 1.4 Hz, C(5)-*H*), 9.91 (2 H, br s, N*H*);  $\delta_{\rm C}$ (75 MHz, CDCl<sub>3</sub>) 10.88, 19.87, 33.72, 51.80, 115.30, 116.47, 118.01, 122.72, 175.0; CI-HRMS m/z calc'd for C<sub>18</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>: 333.181433, found: 333.181501.

**Diformyl bipyrrole 3**: 2.14 mL POCl<sub>3</sub> was added dropwise to 3mL DMF at 0°C under argon. The mixture was then stirred at room temperature for 10 minutes and then cooled back down to 0° C. A solution of **S8** (0.3811 g, 1.15 mmol) in a minimal amount of DMF (~2mL) was then slowly added over the course of 10 minutes while protected from light. Once the addition was complete, the reaction mixture was warmed to room temperature and stirred for 2 hours still protected from light. After this delay, 100 equivalents of NaCO<sub>3</sub> (12.19 g) and 1 mL of MeOH were slowly added to the mixture. It was stirred for an additional hour. An excess of water was then added to the solution, turning the green solution to yellow. The mixture was stirred for an additional 3 hours before filtering off the solution and washing the solid with an excess of water to give **3** (0.1459 g 32.7 %).  $\delta_{H}(400 \text{ MHz}, \text{CDCl}_3)$  2.370 (6 H, s, C(5)CH<sub>3</sub>), 2.821-2.799 (8 H, m, CH<sub>2</sub>CH<sub>2</sub>), 3.696 (6 H, s, COOCH<sub>3</sub>), 9.714 (2 H, s, CHO), 11.650 (2 H, s, NH).  $\delta_{C}(100 \text{ MHz}, \text{CDCl}_3)$  9.300, 19.030, 29.624, 32.832, 52.331, 121.504, 128.141, 130.013, 175.281; HRMS (CI+) m/e calc'd. for [C<sub>20</sub>H<sub>25</sub>N<sub>2</sub>O<sub>6</sub> + H]<sup>+</sup>: 389.171262, found: 389.172425.

**Hexapyrrin 5:** 0.159 g (0.41 mmol) of diformyl bipyrrole **3** was dissolved in approximately 700 mL of methanol and heated to 60 °C. Once the solid was completely dissolved, 0.195 g (0.90 mmol, 2.2 equiv.) of methyl ethyl bipyrrole was added in two aliquots. In the first aliquot, 0.8 equivalents, 0.07 g was added to the solution followed by 4 drops conc. HCl. The solution was stirred for 5 minutes and only then was the remaining bipyrrole added (~ 0.125 g). The solution was stirred for approximately 20 hrs at 60°C. At that time, the methanol was removed *in vacuo* and the purple-red solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>: hexanes to give a 0.199 g of a brick-red solid (57.5% yield). UV-visible: UV-vis:  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 525 ( $\epsilon$  /dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup> 98000), 752 (25000), 434 (22000);  $\delta_{\rm H}$ (400 MHz, CDCl<sub>3</sub>) 1.096 (6 H, t, J = 7.6 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.272 (6 H, t, J = 7.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.200 (6 H, s, C(5)CH<sub>3</sub>), 2.216, (6 H, s, C(5)CH<sub>3</sub>), 2.399-2.370 (10 H, m, 10H, C(5)CH<sub>3</sub> and CH<sub>2</sub>CH<sub>3</sub>), 2.546 (2 H, t, J = 8.2 Hz, CH<sub>2</sub>CH<sub>2</sub>), 2.764 (2 H, q, J = 8 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.991 (2 H, t, J = 8Hz, CH<sub>2</sub>CH<sub>2</sub>), 3.589 (6 H, s, COOCH<sub>3</sub>), 6.318 (2 H, s,

C(5)-*H*), 7.097 (2 H, s, *meso*-CH), 11.625 (4 H, s, N*H*), 12.527 (2 H, s, N*H*);  $\delta_{C}$ (75 MHz, CDCl<sub>3</sub>) 10.945, 12.406, 13.005, 14.252, 15.794, 18.942, 18.952, 21.253, 34.167, 51.987, 115.207, 120.076, 124.325, 125.256, 126.021, 127.045, 129.161, 129.477, 131.731, 135.264, 136.895, 150.785, 151.230, 173.506; HRMS (ESI+) m/e calc'd for C<sub>48</sub>H<sub>61</sub>N<sub>6</sub>O<sub>4</sub> (M<sup>+</sup>): 785.47566, found: 785.47488.

**Di-methyl ester hexaphyrin(1.0.1.0.0.0), 6**: Hexapyrrin **5** (0.183 g, 0.22 mmol) was dissolved in 20 mL CH<sub>2</sub>Cl<sub>2</sub>. 10 mL of 0.5 M FeCl<sub>3</sub> in 2 M HCl was added and the biphasic mixture was stirred for 4 hours or until judged complete by TLC (silica gel plates; 8% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub>, eluent). The layers were then separated and the organic layer was washed several times with water (3 x 100 mL) and 1 M HCl (2 x 100 mL) before being dried over sodium sulfate and dried in vacuo. The resulting solid was purified by column chromatography over silica gel column using 2-5% CH<sub>3</sub>OH / CH<sub>2</sub>Cl<sub>2</sub> as the eluent, with the first red fraction (major product) being collected. The fraction was concentrated in vacuo and washed with 1 M HCl, dried over Na<sub>2</sub>SO<sub>4</sub> and again dried in *vacuo*. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub> layered with hexanes afforded green crystals with a metallic luster (0.0734 g, 40% yield). Crystals suitable for X-ray diffraction analysis were grown from the slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> / cyclohexane mixture. UV-vis:  $\lambda_{max}$  $(CH_2Cl_2)/nm 378 (\epsilon/dm^3 mol^{-1} cm^{-1} 24 600), 494 (81 100), 596 (32 500); \delta_H(400 MHz,$  $CDCl_3$ ) 0.497 (6 H, t, J = 7.4 Hz,  $CH_2CH_3$ ), 0.622 (6 H, t, J = 7.4 Hz,  $CH_2CH_3$ ), 0.900 (6 H, s, C(5)CH<sub>3</sub>), 1.039 (6 H, s, C(5)CH<sub>3</sub>), 1.125 (6 H, s, C(5)CH<sub>3</sub>), 1.410-1.342 (8 H, m, CH<sub>2</sub>CH<sub>3</sub>), 1.484 (4 H, t, J = 8 Hz, CH<sub>2</sub>CH<sub>2</sub>), 2.281 (4 H, t, J = 8Hz, CH<sub>2</sub>CH<sub>2</sub>), 3.582 (2 H, s, meso-CH), 3.919 (6 H, s, COOCH<sub>3</sub>), 22.689 (2 H, s, NH), 23.088 (2 H, s, NH), 23.340 (2 H, s, NH); δ<sub>C</sub>(75MHz, CDCl<sub>3</sub>) 9.284, 9.543, 10.664, 12.999, 13.881, 16.358, 16.941, 19.280, 33.024, 52.102, 118.750, 123.849, 126.075, 131.608, 131.826, 132.271, 132.660, 135.003, 137.589, 138.079, 141.560, 151.649, 157.760, 173.010; HRMS (ESI<sup>+</sup>) m/e calc'd. for C<sub>48</sub>H<sub>59</sub>N<sub>6</sub>O<sub>4</sub> (M<sup>+</sup>): 783.456, found: 783.45923.

**Diacid isoamethyrin 7:** Isoamethyin diester **6** (0.1221 g, 0.143 mmol) was placed in a 2-neck round bottom flask under argon. A solution of 5.5 mL TFA from a freshly opened container and 5.5 mL concentrated HCl were added to the flask and the reaction was stirred for 24 hours. At that time, ~150 mL H<sub>2</sub>O was added and the product was extracted from  $CH_2Cl_2$ . The organic layers were combined washed with 1 M HCl and dried over Na<sub>2</sub>SO<sub>4</sub>. The solid was then purified by column chromatography over silica gel using 10% CH<sub>3</sub>OH / CH<sub>2</sub>Cl<sub>2</sub> as the eluent, until the majority of impurities were removed. 0.1% TFA was then added to the eluting solution and the orange-red band was collected to give **6** (0.1181 g, 85 % yield). UV-vis:  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 377 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 18 500), 497 (57 000), 599 (22 500);  $\delta_{H}$ (400 MHz, CDCl<sub>3</sub>) 0.496 (6 H, t, J = 7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.647 (6 H, t, J = 7.6 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.948 (6 H, s, C(5)CH<sub>3</sub>), 1.055 (6 H, s, C(5)CH<sub>3</sub>), 1.216 (6 H, s, C(5)CH<sub>3</sub>), 1.406 (8 H, br-m, CH<sub>2</sub>CH<sub>3</sub>), 1.601 (4 H, br-m, CH<sub>2</sub>CH<sub>2</sub>), 2.376 (4 H, br-t, CH<sub>2</sub>COOH), 3.712 (2 H, s, *meso*-CH), 22.207 (2 H, s, NH), 22.620 (2 H, s, NH), 22.891 (2 H, s, NH); Isoamethyrin 7 had a low solubility and / or stability in all common NMR solvents and a proper Carbon NMR could not be obtained. HRMS (ESI+): m/e calc'd. for C<sub>46</sub>H<sub>35</sub>N<sub>6</sub>O<sub>4</sub> (M<sup>+</sup>): 755.4289, found: 755.42793.

**Uranyl-isoamethyrin 8:** First, the 'free base' form of **6** was obtained by dissolving the solid in CH<sub>2</sub>Cl<sub>2</sub> and washing with a 10% NaOH solution and then drying over molecular sieves (4 Å). This 'free base' (0.012 g, 0.147 mmol ) was then dissolved in a 50:50 v/v mixture of CH<sub>2</sub>Cl<sub>2</sub>: CH<sub>3</sub>OH. Uranyl acetate (0.0082 g, 0.193 mmol, 1.2 equiv) dissolved in CH<sub>3</sub>OH was added and the solution was allowed to stir overnight. After this delay, the solvent was removed in vacuo and the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub>. The product was purified by column chromatography over neutral alumina (50-200 µm) using a 2:3 v/v mixture of ethyl acetate: hexanes as the eluent. The first red band was isolated and the solvent was removed in vacuo. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes to give 8 (0.0037 g, 25%) as metallic green crystals. Crystals suitable for X-ray diffraction analysis were grown from the slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> / CH<sub>3</sub>OH mixture. UV-vis: λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>)/nm 531 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 98 000), 839 (24 000), 793 (17 000); δ<sub>H</sub>(500 MHz, CDCl<sub>3</sub>) 1.823-1.912 (6 H, m, CH<sub>2</sub>CH<sub>3</sub>), 2.805 (4 H, t, J = 8.33 Hz, CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub>), 3.373 (12 H, s, C(5)CH<sub>3</sub>), 3.581 (6 H, s, C(5)CH<sub>3</sub>), 3.662 (6 H, s, COOCH<sub>3</sub>), 4.043 (4 H, q, J = 7.40 Hz, CH<sub>2</sub>CH<sub>3</sub>), 4.082 (4 H, q, J = 7.38, CH<sub>2</sub>CH<sub>3</sub>), 4.329 (4 H, t, CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub>), 9.926 (2 H, s, meso-H). δ<sub>C</sub>(125 MHz, CDCl<sub>3</sub>) 12.29, 15.88, 16.52, 17.12, 17.992, 20.05, 21.30, 24.09, 35.99, 51.49, 107.61, 134.86, 136.63, 138.30, 144.25, 145.34, 145.58, 147.27, 147.95, 148.63, 149.39, 151.27, 151.52. HRMS (ESI+) m/e calc'd. for  $C_{48}H_{55}N_6O_6U$  (M<sup>+</sup>): 1049.4691, found: 1049.4683.

*Bead immobilization*: The polysyrene beads were 'activated' by shaking them in a solution containing DMF and 10 equivalents N,N-diisopropyl amine (DIPA). After 30 min, the solution was removed and the beads were washed with DMF. The beads were then re-suspended in a solution containing DMF, 4 equiv. of DIPA, 1.9 equiv PyBOP (benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate) and  $1/10^{\text{th}}$ ,  $1/15^{\text{th}}$ ,  $1/20^{\text{th}}$  and  $1/25^{\text{th}}$  molar equivalents of 7. The suspension was shaken until the DMF solution had lost its pigmentation (~6 hours). The beads were then washed repeatedly with 1M HCl (aq) and 1M NaOH (aq) to remove the PyBOP and DMF.

Individual beads were placed on a silicon wafer and then fitted into an encapsulated flow cell. Both the wafer and flow cell were designed and have been described in detail by Goodey *et al.*<sup>1</sup> The flow cell was then placed on the stage of an Olymupus SZX12 stereomicroscope with bottom light illumination. Images of the array were obtained using an Optronics DEI-750 3-chip charge-coupled device (CCD) and an Integral Technology Flashbus capture card. Once images of the beads were captured, numerical data representing the red, green and blue (RGB) intensities could be analyzed. The 'effective absorbance', A, was determined for individual red, green, and blue channels using the equation  $A_{red}$ = -log(R/R<sub>blank</sub>) where R is the measured absorbance in the red channel and R<sub>blank</sub> is the measured absorbance in the red channel for a blank bead. Similar calculations may be made for the green and blue channels using the equations  $A_{green}$ = -log(G/G<sub>blank</sub>) and  $A_{blue}$ = -log(B/B<sub>blank</sub>)

#### **Additional Figures:**



Fig. S1. Top and side views of H<sub>2</sub>6·2Cl<sup>-</sup> showing a partial atom labelling scheme (50% probability ellipsoids). All hydrogen atoms, a molecule of cyclohexane and the alkyl substituents in the side view have been removed for clarity. Hydrogen bond distances (N-H...Cl) range from 3.573(3) to 3.225(4) Å. C<sub>48</sub>H<sub>61</sub>C<sub>12</sub>N<sub>6</sub>O<sub>4.50</sub>, M = 864.93, Orthorhombic, a = 25.8233(3) Å, b =10.4391(10) Å, c = 33.9936(16) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 90^{\circ}$ ,  $\gamma = 90^{\circ}$ , U = 9163.7(10) Å<sup>3</sup>, T = 153(2) K, space group Pbca, Z = 8,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $\mu = 0.193$  mm<sup>-1</sup>, crystal size 0.40 x 0.07 x 0.04 mm, 8068 reflections collected, 8068 unique ( $R_{int} = 0.0779$ ). The final  $wR(F_2)$  was 0.1512 (all data). CCDC 661301.



Figure S2: UV-visible spectrum of the *bis*-Cl salts of 1 (green line) and 6 (blue line) in  $CH_2Cl_2$ .



Figure S3: UV-visible spectrum of 2 (red line) and 8 (pink line) in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S4:** Calculated color changes observed in the red, green and blue channels with 5.0% immobilized isoamethyrin (white column) and after exposure to uranyl acetate (0.0024 M in MeOH for 9 days) (grey column).<sup>16</sup> Values were calculated from an average of three to five beads; the error bars indicate the standard deviation in the measurements.



**Figure S5:** Color change observed on an isoamethyrin-immobilized bead upon exposure to a solution of 0.024 M uranyl acetate in methanol for 9 days. a) blank bead; b) bead containing 6.4% amine coverage with isoamethyrin c) bead containing 8.4% amine coverage with isoamethyrin; d) color change of (b) upon exposure to uranyl acetate; e) color change of (c) upon exposure to uranyl acetate.

### **X-ray Experimental**

6  $[(C_{48}H_{60}N_6O_4)^{2+} \cdot 2Cl^{1-} \cdot \frac{1}{2}H_2O]$ : Crystals grew as black lathes by slow evaporation of a solution of 6 in  $CH_2Cl_2$ / cyclohexane. The data crystal was a long lathe that had approximate dimensions; 0.40 x 0.07 x 0.04 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKa radiation ( $\lambda = 0.71073$ Å). A total of 524 frames of data were collected using  $\omega$ -scans with a scan range of 0.8° and a counting time of 141 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.<sup>2</sup> The structure was solved by direct methods using SIR97<sup>3</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-97.<sup>4</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.044*P)^2]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$ refined to 0.151, with R(F) equal to 0.0779 and a goodness of fit,  $S_{1} = 1.09$ . Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>5</sup> The data were corrected for secondary extinction effects. The correction takes the form:  $F_{corr} =$  $kF_c/[1 + (7.5(13)x10^{-7})*F_c^2 \lambda^3/(sin2\theta)]^{0.25}$  where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>6</sup> All figures were generated using SHELXTL/PC.7

8 [5(C<sub>48</sub>H<sub>54</sub>N<sub>6</sub>O<sub>4</sub>)UO<sub>2</sub> · C<sub>6</sub>H<sub>14</sub>]: Crystals grew as black laths by slow evaporation from a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH mixture. The data crystal was cut from a larger crystal and had approximate dimensions; 0.27 x 0.06 x 0.04 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK $\alpha$  radiation ( $\lambda$  =

0.71073Å). A total of 675 frames of data were collected using  $\omega$ -scans with a scan range of 0.5° and a counting time of 140 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.<sup>2</sup> The structure was solved by direct methods using SIR97<sup>3</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-97.<sup>4</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The methyl ester moieties had very large atomic displacement parameters that made refinement difficult. A static disorder model was attempted for the most severely affected groups without success. It appeared that the disorder was dynamic in nature. The ester moieties were refined with their geometries restrained to be equivalent. The displacement parameters of all atoms except U were refined anisotropically with restraints to keep them approximately isotropic. The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.02*P)^2]$  and P = $(|F_0|^2 + 2|F_c|^2)/3$ . R<sub>w</sub>(F<sup>2</sup>) refined to 0.167, with R(F) equal to 0.100 and a goodness of fit, S, = 1.33. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>5</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>6</sup> All figures were generated using SHELXTL/PC.<sup>7</sup>

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- 4) G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures,* 1994 University of Gottingen, Germany.
- 5)  $\begin{aligned} R_{W}(F^{2}) &= \{ \Sigma w (|F_{0}|^{2} |F_{c}|^{2})^{2} / \Sigma w (|F_{0}|)^{4} \}^{1/2} \text{ where } w \text{ is the weight given} \\ \text{ each reflection.} \\ R(F) &= \Sigma (|F_{0}| |F_{c}|) / \Sigma |F_{0}| \} \text{ for reflections with } F_{0} > 4(\sigma(F_{0})). \\ S &= [\Sigma w (|F_{0}|^{2} |F_{c}|^{2})^{2} / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of refined parameters.} \end{aligned}$
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  4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
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Figure S6: View of the macrocycle in 6 showing the atom labelling scheme. Displacement ellipsoids are scaled to the 50% probability level. Most hydrogen atoms have been removed for clarity. Dashed lines are indicative of H-bonding interactions.

Empirical formula	C48 H61 Cl2 N6 O4.50	
Formula weight	864.93	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 25.8233(3) Å	α= 90°.
	b = 10.4391(10) Å	β= 90°.
	c = 33.9936(16) Å	$\gamma = 90^{\circ}$ .
Volume	9163.7(10) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.254 Mg/m <sup>3</sup>	
Absorption coefficient	0.193 mm <sup>-1</sup>	
F(000)	3688	
Crystal size	0.40 x 0.07 x 0.04 mm	
Theta range for data collection	2.40 to 25.00°.	
Index ranges	0<=h<=30, 0<=k<=12, -40<=l<=0	
Reflections collected	8068	
Completeness to theta = $25.00^{\circ}$	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8068 / 0 / 563	
Goodness-of-fit on F <sup>2</sup>	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0779, wR2 = 0.1187	
R indices (all data)	R1 = 0.2221, wR2 = 0.1512	
Extinction coefficient	$7.5(13) \times 10^{-7}$	
Largest diff. peak and hole 0.414 and -0.405 e.Å <sup>-3</sup>		

## Table S1: Crystal data and structure refinement for 6.



**Figure S7:** View of the macrocycle 1 in **8** showing the atom labelling scheme. Displacement ellipsoids are scaled to the 30% probability level. The hydrogen atoms have been removed for clarity.



Figure S8: View of the macrocycle 2 in 8 showing the atom labelling scheme. Displacement ellipsoids are scaled to the 30% probability level. The hydrogen atoms have been removed for clarity.



**Figure S9:** View of the macrocycle 3 in **8** showing the atom labelling scheme. Displacement ellipsoids are scaled to the 30% probability level. The hydrogen atoms have been removed for clarity. The complex lies around a crystallographic two-fold rotation axis along <sup>1</sup>/<sub>2</sub>, y, <sup>1</sup>/<sub>4</sub>. The UO<sub>2</sub> ion lies on the two-fold. Atoms with labels appended by a ' are related by 1-x, y, <sup>1</sup>/<sub>2</sub>-z.

Empirical formula	C123 H142 N15 O15 U2.50	
Formula weight	2665.59	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Р	
Unit cell dimensions	a = 40.592(2)  Å	α= 90°.
	b = 16.1043(6) Å	$\beta = 94.662(2)^{\circ}.$
	c = 17.9271(6)  Å	$\gamma = 90^{\circ}$ .
Volume	11680.3(8) Å <sup>3</sup>	
Ζ	4	
Density (calculated)	1.516 Mg/m <sup>3</sup>	
Absorption coefficient	3.528 mm <sup>-1</sup>	
F(000)	5340	
Crystal size	0.27 x 0.06 x 0.04 mm	
Theta range for data collection	2.92 to 23.75°.	
Index ranges	-43<=h<=45, -18<=k<=16, -20<=l<=19	
Reflections collected	41835	
Independent reflections	17429 [R(int) = $0.1480$ ]	
Completeness to theta = $23.75^{\circ}$	97.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.872 and 0.450	
Refinement method	Full-matrix-block least-squares on F <sup>2</sup>	
Data / restraints / parameters	17429 / 968 / 1401	
Goodness-of-fit on F <sup>2</sup>	1.427	
Final R indices [I>2sigma(I)]	R1 = 0.1001, $wR2 = 0.1416$	
R indices (all data)	R1 = 0.2303, wR2 = 0.1669	
Largest diff. peak and hole 1.683 and -2.841 e.Å $^{-3}$		

## Table S2. Crystal data and structure refinement for 8.