

Supplementary Information

Synthesis and Characterization of an Amethyrin-Uranyl Complex Displaying Aromatic Character

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Materials & General Methods

All reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. Tetrahydrofuran (THF), anhydrous, >99.9%, inhibitor-free was purchased from Sigma Aldrich and stored over molecular sieves (3.0 Å) for 48 hours prior to use. Analytical thin-layer chromatography (TLC) was performed using commercial precoated silica gel plates containing a fluorescent indicator. Column chromatography was carried out using basic alumina (aluminum oxide, basic, Brockmann 1, 50-200 µm, 60 Å; Acros Organics). High-resolution mass spectrometric (HRMS) measurements were made using an Ion Spec Fourier Transform mass spectrometer (9.4 T). Proton and carbon NMR spectra were recorded using a Varian 400 spectrometer at room temperature. Chemical shifts are reported in ppm using TMS or solvent residual signals as the internal reference standards. All NMR spectroscopic solvents were purchased from Cambridge Isotope Laboratories. UV-Vis spectra were recorded from 250 to 800 nm using a Varian Cary 5000 spectrophotometer at room temperature. Unless otherwise indicated, a cell length of 10 mm was used for all UV-Vis spectral studies. Electrochemical experiments were carried out under nitrogen in a glove box using the GPES software from Eco Chemie B. V. and an Autolab Potentiostat (PGSTAT30). The electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate [(n-Bu)₄N][PF₆] in dry dichloromethane (CH₂Cl₂). The electrolyte was purified through three recrystallizations from hot ethanol before drying under vacuum for three days at 100 °C. Electrochemical experiments were carried out in a 20 mL electrochemical vial using a Pt button working electrode (1.6 mm diameter), a Ag/AgNO₃ (silver wire in a 0.01 M AgNO₃ and 0.1 M TBAPF₆ in a dry acetonitrile solution), a nonaqueous reference electrode, and a Pt wire coil counter electrode. Cyclic voltammetry was done by cycling within the range of -1.9 V to 1.8 V (vs. Ag/Ag⁺) for three scans at a scan rate of 100 mV s⁻¹. All potentials are reported relative to the ferrocene/ferrocenium couple (Fc/Fc⁺), which was used as an external standard to calibrate the reference electrode. Ferrocene was purified by sublimation at 95 °C. Metalation studies were carried out under inert glove box conditions.

Synthesis and Characterization Data

Amethyrin-uranyl complex (**5**)

In an inert atmosphere glove box, $\text{UO}_2[\text{N}(\text{SiMe}_3)_2]_2 \cdot 2\text{THF}$ (32 mg, 0.044 mmol) was added to a stirred solution of amethyrin **4** [1] (25 mg, 0.043 mmol) in 5 mL of dry THF. The mixture was heated to reflux for 14 h, at which time the solution was observed to turn a dark red. The reaction mixture was removed from the inert atmosphere glove box and concentrated *in vacuo*. The residue was purified by basic alumina (Al_2O_3) chromatography (eluent: 2% acetone: CH_2Cl_2) on the bench top to yield **5** as a dark red solid with green metallic luster. Yield: 83% (30 mg).

^1H NMR (400 MHz, CDCl_3) δ 9.90 (s, 2H), 3.85 (s, 12H), 3.61 (s, 12H), 3.42 (s, 12H). ^{13}C NMR (101 MHz, δ -value in CDCl_3) δ 152.6, 147.3, 147.0, 146.5, 136.5, 135.5, 77.2, 29.7, 16.1, 15.4, 12.2, 1.0. UV-Vis (λ_{max} (nm) in CH_2Cl_2 ; (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)) 520 (89,200), 826 (29,400). HRMS (ESI $^+$) calcd. for $\text{C}_{38}\text{H}_{38}\text{N}_6\text{O}_2\text{U}$ ($\text{M}+\text{H}^+$) 849.3564, found 849.3633.

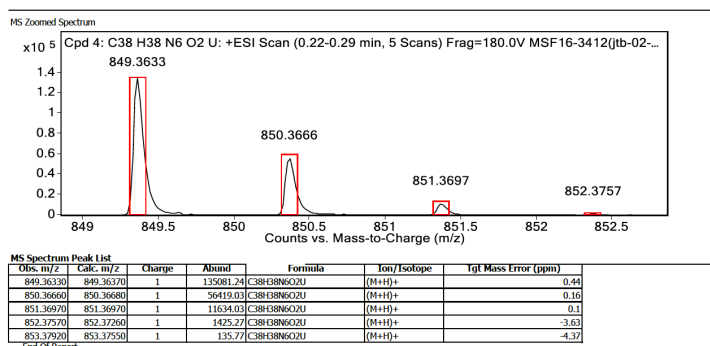


Figure S1. High-resolution mass spectrometry data of amethyrin-uranyl complex **5**.

NMR Spectral Data

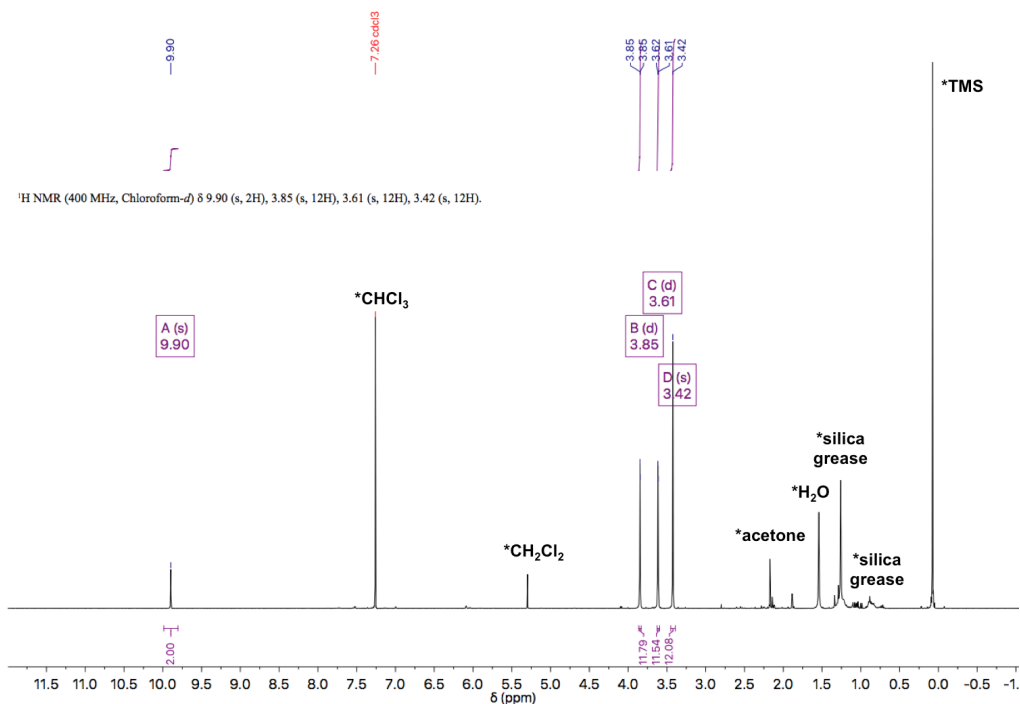


Figure S2. Proton NMR spectrum of the amethyrin-uranyl complex **5** recorded in CDCl_3 .

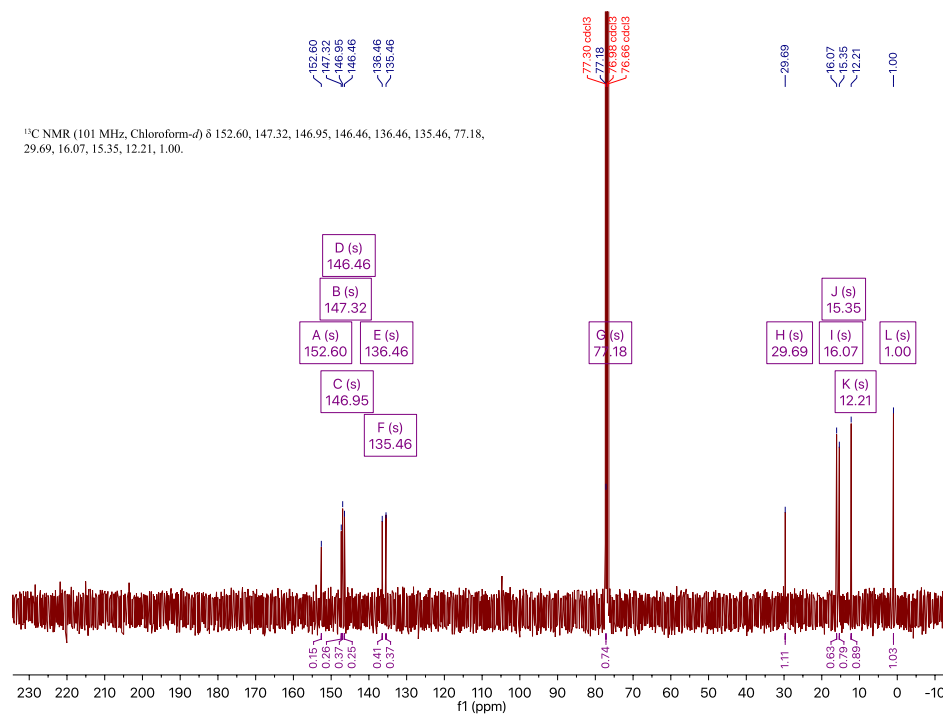


Figure S3. Carbon NMR spectra of amethyrin-uranyl complex **5** recorded in CDCl₃.

Cyclic Voltammetry

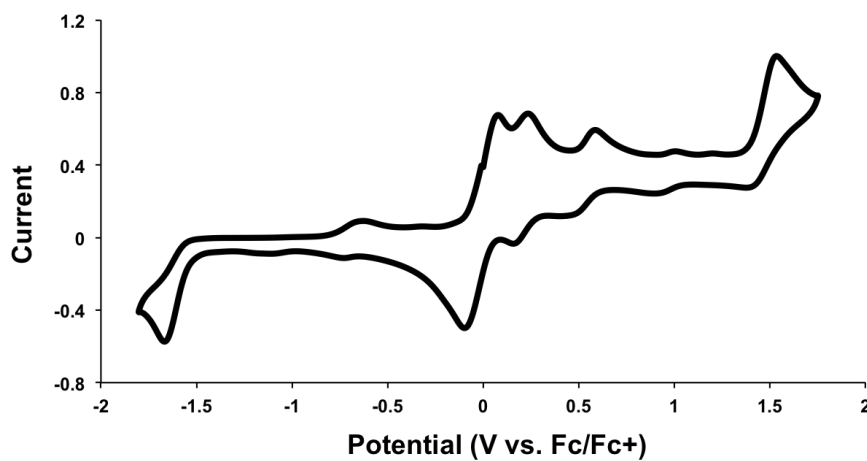


Figure S4. Cyclic voltammogram of free-base amethyrin **4** as measured in CH₂Cl₂.

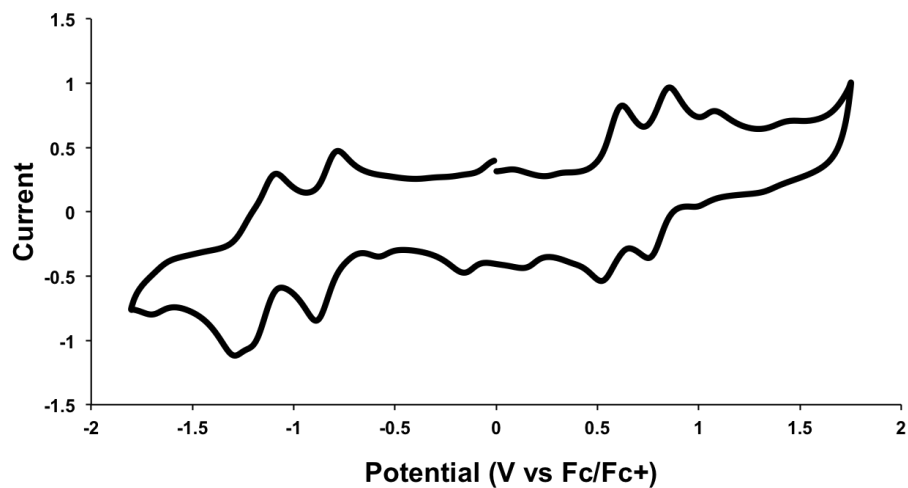


Figure S5. Cyclic voltammogram of amethyrin-uranyl complex **5** as measured in CH₂Cl₂.

References

[1] (a) Sessler, J. L.; Weghorn, S. J.; Hiseada, Y.; Lynch, V. *Chem. Eur. J.* **1**, 56 (1995). (b) Hannah, S.; Seidel, D.; Sessler, J. L.; Lynch, V. *Inorg. Chim. Acta.* **317**, 211 (2001).