

Supporting Information for Iridium Corroles Communication

Notes on Instrumentation: All nuclear magnetic resonance spectroscopy was performed on a Varian Mercury 300 MHz NMR spectrometer; mass spectrometry was performed by electrospray ionization into a Thermofinnigan LCQ ion trap mass spectrometer; UV-visible spectroscopy was performed on a Hewlett-Packard 8452A Diode Array Photospectrometer; and cyclic voltammetry was performed with a BAS100B/W Electrochemical Analyzer.

Notes on Solvents and Crystallization Techniques: All solvents were purchased from Sigma-Aldrich. Solvents used for air- or moisture-sensitive reactions were degassed with argon and dried on columns of activated alumina. Otherwise, all solvents were used as received. Crystallization of the discussed complexes was achieved by slow evaporation of concentrated methylene chloride solutions. Methylene chloride was also used as the solvent for all UV-visible spectroscopy.

Notes on Bromination and Trimethylamine Oxide: Bromination of metallocorroles proceeds easily in a number of cases upon allowing a methanolic solution of the corrole and many equivalents of bromine to stir overnight at room temperature.¹ Bromination of free-base corroles can also be achieved, but this procedure suffers from lower chemical yields and produces a non-aromatic tetrapyrrolic macrocycle that becomes aromatic again only after metallation.² Trimethylamine-oxide was chosen as an oxidant in the iridium corrole synthesis because it can act as both a terminal oxidant and a ligand for the complex. We have also been able to perform a similar reaction using pyridine as the ligand and atmospheric dioxygen as the terminal oxidant, but the trimethylamine-substituted corrole is easier to purify and manipulate.

Notes on Cyclic Voltammetry: CV was performed using an internal ferrocene (Fc) standard, with the Fc/Fc⁺ couple being set to 0 V. Values were converted to V vs. SCE (by adding 0.465 V) in order to facilitate comparisons with literature values for similar complexes. The original CV values are $E_{1/2} = +0.19$ and $+0.82$ V vs. Fc/Fc⁺ for **1** and $E_{1/2} = +0.72$ and -1.7 V vs. Fc/Fc⁺ for **2**.

¹ Mahammed, A.; Gray, H.B.; Meier-Callahan, A.E.; Gross, Z. *J. Am. Chem. Soc.* **2003**, *125*, 1162-1163. Golubkov, G.; Bendix, J.; Gray, H.B.; Mahammed, A.; Goldberg, I.; DiBilio, A.J.; Gross, Z. *Angew. Chem. Int. Ed. Eng.* **2001**, *40*, 2132-2134.

² Paolesse, R.; Nardis, S.; Sagone, F.; Khoury, R.G. *J. Org. Chem.* **2001**, *66*, 550-556.