Appendix A

METHODOLOGY AND INSTRUMENTATION

Materials: Solvents, including dichloromethane, acetonitrile, acetone, methanol, ethyl acetate, tetrahydrofuran, benzene, and toluene were purchased from the Caltech VWR stockroom, generally through EMD Chemicals, and were used without further purification in most cases. Solvents used for air- and moisture-sensitive reactions were degassed with argon and dried on columns of activated alumina in a glove box. Solvents for air-sensitive photophysical measurements were subjected to three freeze-pump-thaw cycles after being purged with dry nitrogen gas. Deuterated NMR solvents were purchased from the Caltech chemistry stockroom through Cambridge Isotope Laboratories (or occasionally Sigma-Aldrich) and were used as received. Reagents were purchased from Sigma-Aldrich, and largely used as received. $[Ir(cod)Cl]_2$ was occasionally purchased from Alfa Aesar instead. Crystallization of the discussed complexes was achieved by slow evaporation of concentrated methylene chloride solutions with small amounts of methanol and/or hexanes added.

Nuclear Magnetic Resonance Spectroscopy: One-dimensional proton NMR experiments were performed on two different Varian Mercury 300 MHz NMR spectrometers and one Varian Mercury 600 MHz NMR spectrometers. All ^{19}F 1D NMR experiments were performed on one of the 300 MHz spectrometers because of the lack of an appropriate probe on the 600 MHz instrument. Two-dimensional experiments, including ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{13}C H2BC, ^{1}H-^{15}N HSQC, and ^{1}H-^{15}N HMBC, were performed exclusively on the 600 MHz instrument. COSY refers to COrrelation SpectroscopY and detects interactions between two vicinal nuclei of identical type. HSQC stands for Heteronuclear Single Quantum Correlation, and detects one-bond interactions between two different types of nuclei. HMBC is an acronym for Heteronuclear Multiple Bond Correlation, and detects two- and three-bond couplings between two different types of nuclei. Finally, H2BC, which stands for Heteronuclear Two Bond Correlation, acts as a variant of HMBC wherein the three-bond interactions are attenuated dramatically and the signal corresponds primarily to two-bond coupling.

Mass spectrometry: MS was performed by electrospray ionization into a Thermofinnigan LCQ ion trap mass spectrometer. Solutions of 1–10 μM analyte concentration were prepared in CH_3OH for injection when possible; in the case of material less soluble in methanol, a mix of 7:3 $CH_3OH/CHCl_3$ was employed instead. Ions were examined primarily in positive mode.

UV-visible spectroscopy: For the work presented in Chapters 1 and 2, UV-vis spectra were obtained on a Hewlett-Packard 8452A Diode Array Photospectrometer. Titrations of corrole compounds by oxidants were performed by adding small amounts of stock oxidant solution to corrole solutions in CH_2Cl_2. For the rest of the work presented here, UV-vis spectra were obtained on a Varian Cary 50 Scanning Photospectrometer. In all cases, the error in reported wavelength values is at most ± 0.5 nm. Extinction coefficients were measured for gravimetrically prepared solutions, and should be accurate to ± 10%.

Cyclic voltammetry: The data presented in Chapter 2 were collected on a WaveNow USB Potentiostat/Galvanostat (Pine Research Instrumentation) using Pine AfterMath Data Organizer software. All other CV experiments were performed using a BAS100B/W Electrochemical Analyzer. For the experiments presented in Chapter 1, tetraethylammonium hexafluorophosphate (0.3 M) was employed as the electrolyte; for all other experiments tetrabutylammonium hexafluorophosphate (0.1–0.5 M) was used instead. All electrochemical experiments involving the corroles were performed in CH_2Cl_2 to avoid the ligand substitution problems that occasionally appeared when CH_3CN (a more traditional electrochemistry solvent with a larger non-redox-active window) was used instead. All CV measurements were referenced to the ferrocenium/ferrocene (Fc^+/Fc^0) reduction potential and then back-converted to potentials vs. the standard saturated calomel electrode (SCE) by addition of 0.465 V to the values vs. Fc^+/Fc^0. A three-electrode setup was employed for CV measurements, with a glassy carbon disc working electrode, a platinum wire counter electrode, and a Ag/AgCl quasi-reference electrode prepared by dipping a silver wire into HCl for four hours and then inserting it into a tube filled with electrolyte solution (separated from the bulk CV solution by a Vykor frit).

Spectroelectrochemistry: Spectroelectrochemical measurements were performed, using a Varian Cary 50 Scanning Photospectrometer (with attached software scanning kinetics package), in a homemade cuvet with a one mm path length at the beam and a one cm well at the top. Optically transparent platinum mesh was employed as the working electrode and a platinum wire was used as the auxiliary electrode. A silver wire, coated in AgCl by a four-hour stay in a concentrated HCl bath and then immersed in electrolyte solution, was separated by a Vykor frit from the bulk solution and allowed to act as a quasi-reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M in CH_2Cl_2) was employed as the electrolyte.

Electron Paramagnetic Resonance: EPR measurements were performed using a Bruker EMX Biospin instrument, with a Gunn diode microwave source. Most EPR was performed in CH_2Cl_2, which does not generally glass as well as toluene but which gave us better results in general and which can dissolve both of the oxidants we employed in experiments (iodine and (tris)-4-bromophenylaminium hexachloroantimonate). Solutions were pre-cooled by rapid freezing in liquid nitrogen; spectra of samples at 20 K, where signal was found to be optimal for these systems, were obtained using liquid helium as a coolant. The SPINCOUNT package by Michael Hendrich was used to simulate EPR parameters.

Quantum Yield, Lifetime, and Emission Measurements: Steady-state and time-resolved emission measurements were conducted at the Beckman Institute Laser Resource Center. Emission spectra were recorded on samples dissolved in solution (room temperature) or frozen glass (77 K). Samples were degassed by three freeze-pump-thaw cycles. For steady-state emission spectra, the 496.5 nm line of an argon ion laser (Coherent Inova 70) was used to excite samples. Right angle emission was collected *via* a Melles Griot Fiber Optic Spectrometer (MGSPEC-2048-SPU). Quantum yields were obtained by comparing signal intensity (corrected through use of a pre-made software file) to a tetraphenylporphyrin standard. Absorption values for the samples at 496.5 nm were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. For time-resolved measurements, samples were excited at 440 nm. Pulses of 8 ns duration from the third harmonic of a Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series) operating at 10 Hz were used to pump an optical parametric oscillator (OPO, Spectra-Physics Quanta-Ray MOPO-700) to provide laser pulses at 440 nm. Emitted light was detected with a photomultiplier tube (PMT, Hamamatsu R928). PMT current was amplified and recorded using a transient digitizer (Tektronix DSA 602).

Computational Methods: The calculations presented in Chapter 4 were performed using Jaguar 7.0 (Schrödinger, L.L.C.), employing the hybrid functional B3LYP (Becke 3 Parameter, Lee, Yang, and Parr). The pseudopotentials of Hay and Wadt were used to model core electrons, which were not treated explicitly due to the computational costs involved. Geometries were computed with 2-ζ valence functions on the metal and 6-31G** for all other atoms. Meanwhile, single point energies were computed with 3-ζ valence functions on the metal and 6-31G**$^{++}$ for all other atoms. Solvation energies were obtained using the Poisson-Boltzmann continuum solvation model, with a dielectric constant of $\varepsilon = 8.93$ and probe radius of 2.33 Å to represent dichloromethane. The work described in the Epilogue employed the ORCA program, developed by Frank Neese at the University of Bonn in Germany.