

Supporting Information

Electrogenerated Chemiluminescence of Common Organic Luminophores in Water Using an Emulsion System

Jeffrey E. Dick, Christophe Renault, Byung-Kwon Kim, and Allen J. Bard*

Center for Electrochemistry, Department of Chemistry, The University of Texas at Austin, Austin, TX 78712

Chemicals:

Deionized water and 5 mM phosphate buffer was used as the continuous phase. Toluene was HPLC grade (Sigma Aldrich, >99.9%). TPrA was purchased from Tokyo Chemical Industry (>98%, Tokyo, Japan). Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide (>95%) was purchased from Sigma Aldrich. Rubrene (99.99% Trace Metal Basis) was purchased from Sigma Aldrich. 9,10-Diphenylanthracene (99%) was purchased from Alfa Aesar. Pyrene (99%) was purchased from Sigma Aldrich. Perylene (>99.5%) was purchased from Sigma Aldrich. Difluoro{3-ethyl-5-[1-4-ethyl-3,5-dimethyl-2H-pyrrolo-*N*]}boron (98% HPLC grade), BODIPY, was purchased from Aldrich.

Emulsion Preparation:

The emulsions were prepared by dissolving 15-20 mM of the polycyclic aromatic hydrocarbon (PAH) in 0.1 mL of toluene. This solution was then added to 5 mL Millipore water. We dissolved 400 mM ionic liquid, trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide, as the supporting electrolyte and emulsifier. Finally, 50 μ L of tri-*n*-propylamine (TPrA) were added to the mixture. The solution was sonicated by a Q500 ultrasonic processor (Qsonica, Newtown, CT) with a microtip probe with three periods of seven second pulses (500 watts, amplitude 40%) and one period of a two second pulse at the end. This ultrasonication was performed twice before experimentation. The emulsion was vortexed or vigorously shaken periodically over the following ten minutes to ensure homogeneity.

Instrumentation:

ECL Spectra were recorded with a Princeton Instruments Spec 10 CCD camera (Trenton, NJ), equipped with an Acton SpectPro-150 monochromator cooled with liquid nitrogen to -100 °C. Simultaneous measurements of CV and ECL were taken by a multichannel Eco Chemie Autolab PGSTAT100 (Utrecht, The Netherlands). A photomultiplier tube (PMT, Hamamatsu R4220, Tokyo, Japan) was used as a photon detector. A Kepco power supply (New York, NY) was used to provide 700V to the PMT. The signal from the PMT to the potentiostat was transferred using a multimeter (Keithley, Solon, OH). Fluorescence spectra were taken on a Fluorolog-3 fluorometer (Model FL3-11) by Jobin Yvon-

Spex (Edison, NJ). The wavelength of excitation was $\lambda_{\text{ex}} = 400$ nm using a helium lamp. Light was collected through a monochromator in a PMT (Hamamatsu R4220, Tokyo, Japan). Dynamic Light Scattering data was obtained using a Zetasizer Nano ZS (Malvern, Westborough, MA). The 3 mm glassy carbon working electrode was purchased at BASi (West Lafayette, IN).

ESI-MS Analysis:

In order to gain perspective on the distribution of TPrA in the toluene and water phases, 50 microliters of TPrA were added to a tube containing 5 mL deionized water and 0.1 mL toluene. This solution was then ultrasonicated. Electrospray ionization - Mass Spectrometry analysis was completed on the two layers. One microliter of each solution was dilute 1000 x's in methanol. The area under the curve for the toluene solution was 26392828697, and the area under the curve for the water solution was 3303413769. This means that 90% of the TPrA is in the toluene phase. By calculating the concentration of TPrA in the water phase, we get about 5.5 mM. Values between 5 mM and 6 mM have been reported for TPrA as the maximum solubility in water, which agrees well with our ESI - MS results, leaving about 1.8 M of TPrA in the toluene phase.

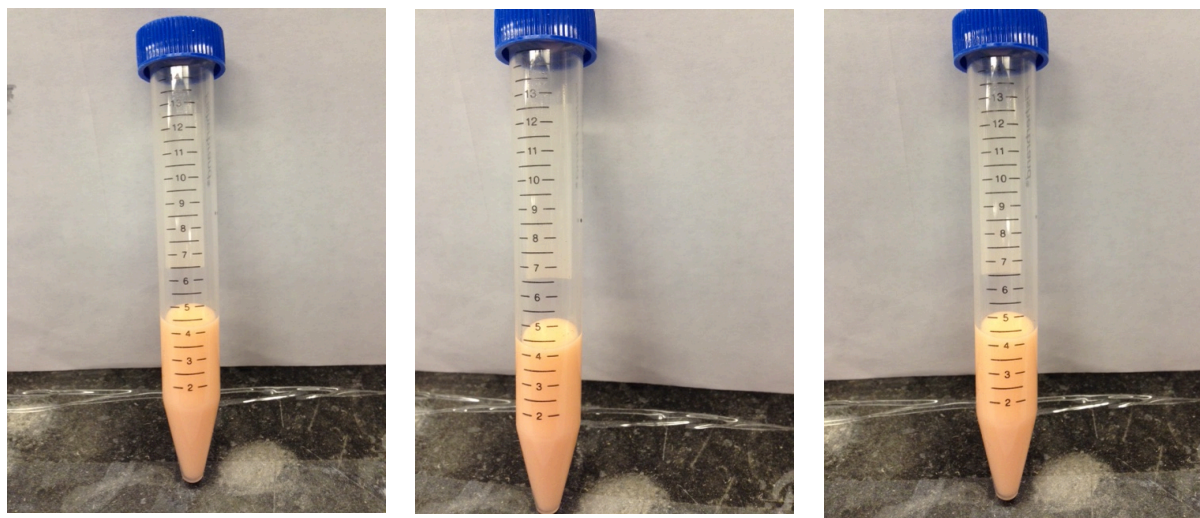


Figure S1. Pictures of the Rubrene emulsion system at 2 hours (far left), 6 hours (middle), and 10 hours (far right).

Electrochemistry:

Figure S2 shows control experiments to explain two peaks seen in oxidation. There are two peaks that are due to TPrA oxidation, which correspond well with the two peaks observed in the PAH experiments. This control experiment confirms that both peaks come from the TPrA in the aqueous phase and the emulsion. The oxidation peak at 0.95 V vs. Ag/AgCl is likely due to protonated TPrA, and the peak at 0.64 V vs. Ag/AgCl is due to deprotonated TPrA.

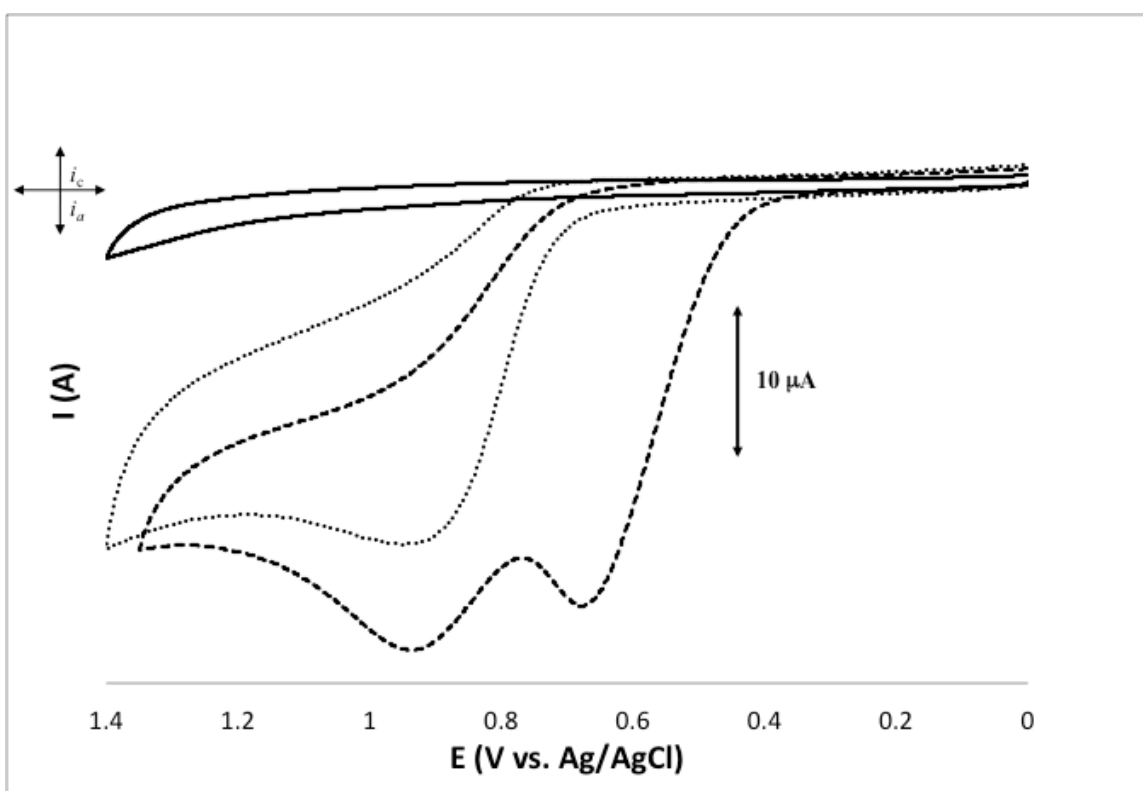


Figure S2. Cyclic voltammograms (CVs) of emulsion systems. The solid line represents the toluene/IL-PA/Ru emulsion in 5 mM PB. The dotted line represents 5 mM TPrA in 15 mM PB. The dashed trace represents 53 mM TPrA ultrasonicated in water and added to the 5 mM PB. The scan rate was 50 mV s^{-1} on a 3 mm GC working electrode for each CV.

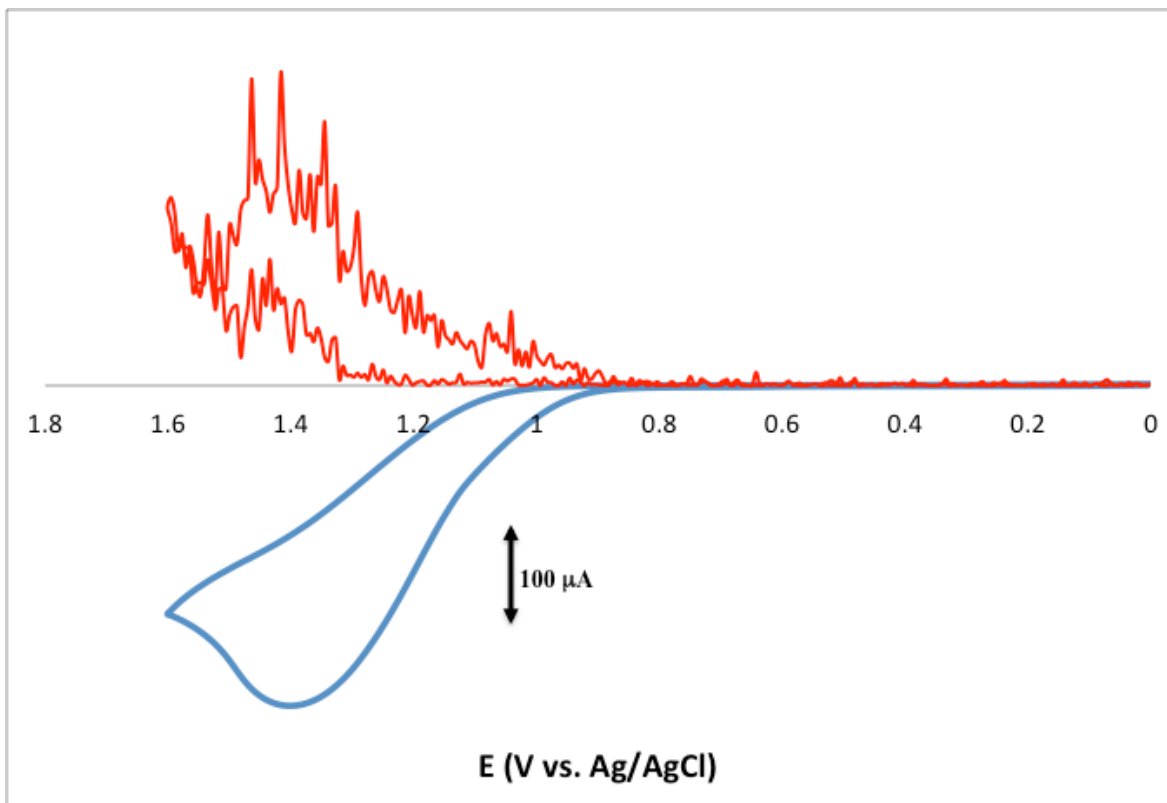


Figure S3. Cyclic Voltammograms (blue traces) and ECL (red traces) of Rubrene in 10 mM aqueous sodium oxalate solution. CV was taken at 50 mVs^{-1} on a 3 mm glassy carbon working electrode. The photomultiplier tube gain was set at 700 V, and the multimeter sensitivity was set to 200 nA. An autolab potentiostat was used to take the simultaneous current and ECL measurements. ECL intensities are normalized to the maximum current.

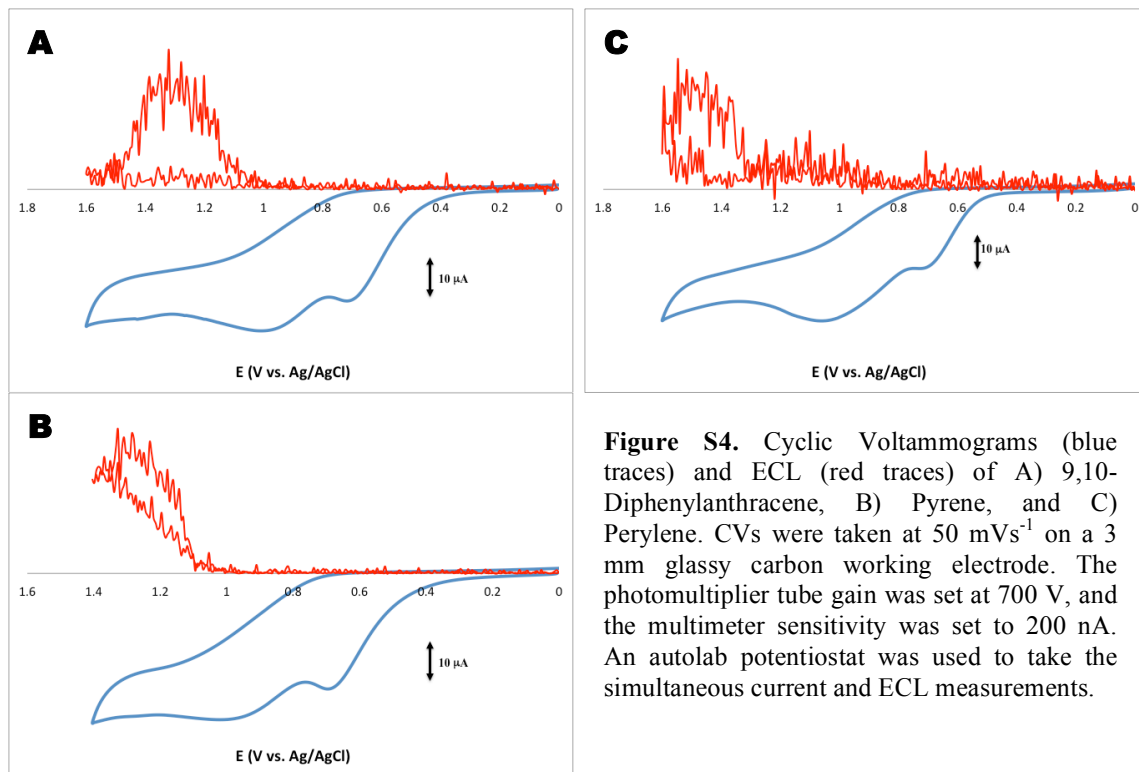


Figure S4. Cyclic Voltammograms (blue traces) and ECL (red traces) of A) 9,10-Diphenylanthracene, B) Pyrene, and C) Perylene. CVs were taken at 50 mVs^{-1} on a 3 mm glassy carbon working electrode. The photomultiplier tube gain was set at 700 V, and the multimeter sensitivity was set to 200 nA. An autolab potentiostat was used to take the simultaneous current and ECL measurements.

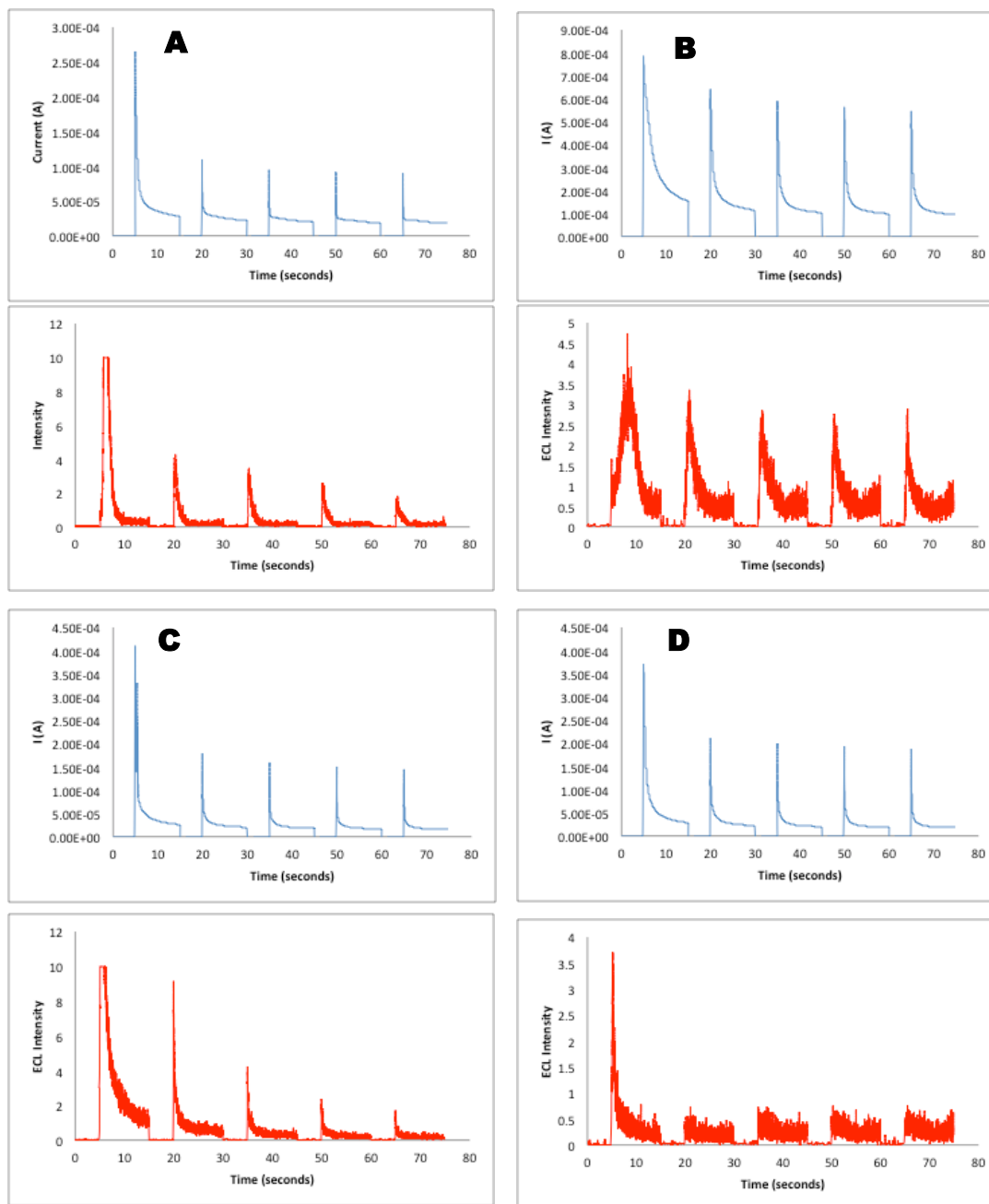
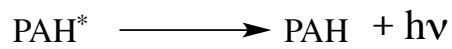
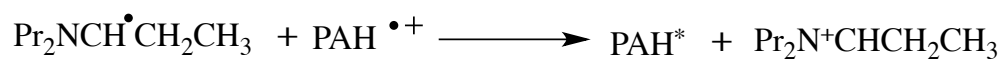
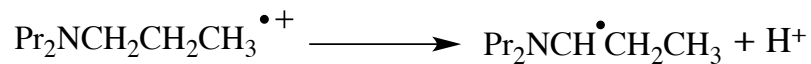
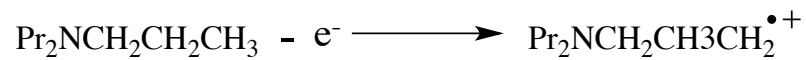
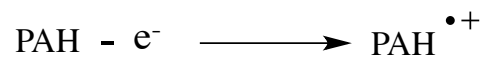


Figure S5. Current (blue trace) and ECL (red trace) transients for A) Rubrene, stepped from 0.0 V to 1.0 V, B) 9,10-Diphenylanthracene, stepped from 0.0 V to 1.35 V C) Pyrene, stepped from 0.0 V to 1.3 V and D) Perylene, stepped from 0.0 V to 1.5 V. Current transients were measured using an autolab potentiostat, which simultaneously measured the ECL transients from a photomultiplier tube (gain 700V) and multimeter (sensitivity was 200 nA).

Proposed ECL Mechanism for PAH or BODIPY:



OR

