

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

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S Supporting Information

ABSTRACT: We describe a method to produce electrogenerated chemiluminescence (ECL) in water using a family of highly hydrophobic polycyclic aromatic hydrocarbon (PAH) luminophores and boron dipyrromethene (BODIPY). This method is based on an oil-in-water emulsion system. Various PAHs (rubrene, 9,10-diphenylanthracene, pyrene, or perylene) and BODIPY were trapped in a toluene and tri-*n*-propylamine mixed oil-in-water emulsion using an ionic liquid as the supporting electrolyte and emulsifier. ECL was observed for all the aforementioned PAHs and BODIPY, and the rubrene and BODIPY emulsion systems showed adequate light to record an ECL spectrum. ECL was also observed using oxalate as the co-reactant, which was dissolved in the aqueous continuous phase. The emulsions were stable for hours and showed a droplet size distribution that ranged from 275 to 764 nm, in accordance with dynamic light scattering data.

Electrogenerated chemiluminescence (ECL), where an emitting species is generated by an energetic electron-transfer reaction, has been demonstrated with numerous organic species, such as polycyclic aromatic hydrocarbons (PAHs), in aprotic solvents.^{1–3} However, few of these can be studied in aqueous solutions, where analytical interest is highest, because of solubility and radical ion stability problems. Currently, the aqueous luminophore of choice is the tris-(bipyridine)ruthenium(II) dication coupled with tri-*n*-propylamine (TPrA) as the co-reactant. ECL of PAHs and the boron dipyrromethene (BODIPY) dye series is well known in aprotic solvents,⁴ like acetonitrile–benzene (1:1 v/v). Aprotic systems are thoroughly dried and degassed^{5–7} to maintain stability of the radical ions, so ECL of PAHs and BODIPY in water has not been attainable because of the solubility and stability problems, as well as the small potential window of water, limiting luminophores that can be oxidized or reduced. In this work, we offer a solution to the solubility issue, expanding the library of ECL luminophores normally observed in aprotic solvents to the aqueous regime.

Previously, rubrene nanoparticles (NPs) and diphenylanthracene (DPA) nanorods (NRs) were studied for their ECL in aqueous solution using TPrA as the co-reactant.⁸ Although light was observed, this system showed very low light intensities. To increase the solubility of PAHs in water, surfactants that form micelles have been used. Haapakka et al. reported the electroluminescence (EL)⁹ at an Al electrode of

DPA in a micellar system in water (pH 7) based on Brij-35 and sodium dodecyl sulfate surfactants.¹⁰ In this experiment, high mass transfer was needed at the Al/aluminum oxide rotating disk electrode (at least 4 revolutions per second) to observe EL. Ouyang et al. reported that micelle formation in aqueous solution depressed the ECL intensity, the electrochemical response, and photoluminescence of Os(bpy)₃²⁺.¹¹

Here, we describe a solution to the solubility issue of PAHs and BODIPY in water and provide clear evidence of ECL in water. We report the ECL of these highly hydrophobic organic ECL luminophores in an aqueous system using toluene droplets suspended in the aqueous continuous phase. The small, immiscible droplets of toluene suspended in a continuous phase were stabilized by an ionic liquid (IL) acting as an emulsifier, following a recent report from our laboratory demonstrating attoliter emulsion droplet reactors of toluene in water with an IL for studying collisions on ultramicroelectrodes.¹² Drawing from this work, an emulsion system conducive to ECL was developed. To our knowledge, this is the first report of ECL of a family of PAHs and BODIPY in an emulsion system in water.

An oil-in-water emulsion was prepared by simply mixing together toluene, TPrA, the ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonamide) (IL-PA), the PAH or BODIPY, and water and sonicating with an ultrasonicator. TPrA was selected as the co-reactant because of its wide use in ECL. A detailed description of emulsion synthesis can be found in the Supporting Information. Concentrations between 15 and 20 mM of these organic ECL luminophores were dissolved in a 2:1 (v/v) toluene/TPrA solution containing 400 mM of the IL-PA as the supporting electrolyte and emulsifier, as reported previously.¹² The composition of the water phase and toluene phase as analyzed by electrospray ionization–mass spectrometry (ESI-MS, see Supporting Information) is provided in Table 1.

Table 1. Distribution of Species between Oil and Water Phases

	concentration of various species			
	TPrA	IL-PA	PAH/ BODIPY	PB
in water	<6 mM	~0 mM	~0 mM	5 mM
in the toluene droplet	~1.8 M	400 mM	15–20 mM	~0 mM

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Here, the PAH is completely dissolved in the toluene/TPrA droplet phase, and about 10% of the TPrA was dissolved in the continuous aqueous phase. The concentration of the organic ECL luminophore in the droplets, ca. 15–20 mM, corresponds to the limit of solubility in the toluene/TPrA mixture. The high solubility of TPrA in toluene allows storage of about 1.8 M TPrA per emulsion droplet. The size of the droplets was measured by dynamic light scattering (DLS), which showed a bimodal distribution of droplet sizes, with peaks at 275 and 764 nm, and a zeta potential of -14 mV. Pictures of the emulsions taken over a 10 h period show the absence of significant aggregation, indicating good stability (see Supporting Information Figure S1).

Figure 1A shows a cyclic voltammogram (CV, blue trace) and the corresponding ECL (red trace) of a ca. 40 pM of

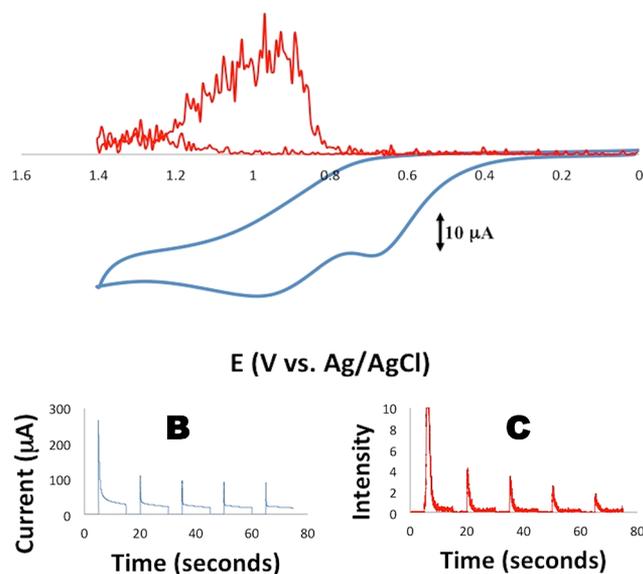


Figure 1. (A) ECL intensity (red trace) and CV (blue trace) of 40 pM emulsion with 15 mM rubrene on a 3 mm glassy carbon working electrode in 5 mM phosphate buffer (PB) at pH 7. Scan rate is 50 mV s^{-1} . (B) Current and (C) ECL transients. Electrode potential was pulsed between 0 and 1.0 V.

droplets containing rubrene. Rubrene was a good candidate for ECL in emulsions because of its high ECL efficiency and relatively low potential required to oxidize it to the radical cation.¹ In the CV, the oxidation waves are attributed largely to protonated TPrA and deprotonated TPrA in the emulsion system at $E_{pa} = 0.94$ and 0.65 V vs Ag/AgCl, respectively. The peak assignments are discussed in the Supporting Information (Figure S2). Within our studies, there were no distinctive features ascribable to the oxidation of rubrene, which is most likely because of its relatively small concentration (~ 15 mM) compared to that of TPrA (~ 1.8 M) within each droplet. As shown in Figure 1A, red trace, ECL is produced only when the potential is above 0.82 V. We assume that this potential must be positive enough to oxidize rubrene in the emulsion because light is produced. To understand the relative stability of the radical ion within the emulsions, we produced transient ECL by stepping the potential from a region where the analyte and co-reactant are not oxidized (0 V) to a potential where both are oxidized (~ 1.0 V). Figure 1B,C shows the current and ECL transients for these emulsions. After each pulse, the ECL

intensity decayed with time, which likely indicates instability of the radical cation in the emulsion system.

Figure 2 depicts the reaction between rubrene and TPrA in the droplet. It should be noted that any PAH or BODIPY could

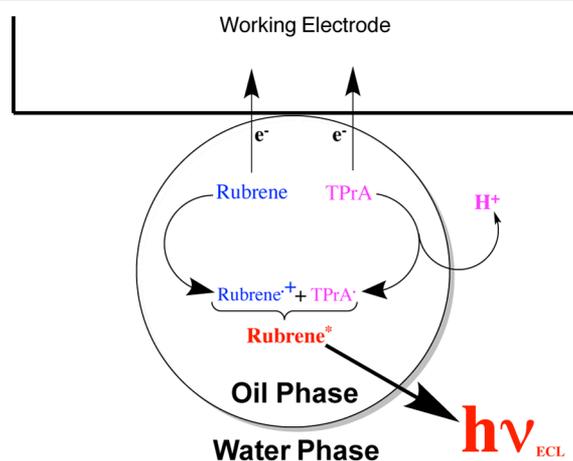


Figure 2. Proposed mechanism between rubrene and TPrA within the emulsion droplet. The figure is not drawn to scale.

be substituted for rubrene in this figure. After an electron leaves, producing rubrene $^{\bullet+}$, it is likely that a proton from the TPrA disproportionation reaction, upon oxidation of TPrA, will leave the droplet and enter the aqueous continuous phase to maintain charge neutrality. It is of interest to note that rubrene ECL can also be observed with sodium oxalate, which is only soluble in the continuous phase as the co-reactant (Figure S3). The ECL is much lower than with TPrA by over a factor of 10, which is likely due to the lower availability of co-reactant within the droplet. Observation of ECL suggests that the strong reductant $CO_2^{\bullet-}$ is made available to rubrene $^+$, despite the hydrophobicity of the toluene droplet. This observation shows that the co-reactant does not necessarily have to be inside the droplet for ECL to be observed.

In the experiments above, light intense enough to be seen with the naked eye in a dark room, is produced above 0.82 V. We assume that this light is due to the ECL mechanism of rubrene and TPrA upon TPrA and rubrene oxidation. To test our hypothesis that the observed light was from rubrene, we collected an ECL spectrum, which is shown as the red trace in Figure 3. The blue trace represents the fluorescence spectrum of rubrene for comparison. The ECL spectrum has wavelength maxima at $\lambda_{max} = 564$ and 595 nm and matches the photoemission spectrum well, as well as ECL spectra previously reported for rubrene.¹³

The emulsion method presents the flexibility of changing the luminophore to any PAH reasonably soluble in toluene. To test this, we studied DPA, perylene, and pyrene. Figure 4 depicts the relative intensities of ECL for the four different PAHs. The corresponding CV plots with ECL can be found in Figure S4, along with current and ECL transients in Figure S5. As seen in Figure 4, DPA (purple trace), pyrene (green trace), and perylene (blue trace) showed significantly lower ECL intensity than rubrene (red trace). It is of interest to note that the ECL emission decreased with increasing potential for oxidation.

The ability of TPrA to induce a PAH excited state is complicated and apparently dependent on the ECL system conditions. Previously, it was shown that TPrA was not an energetic enough co-reactant to produce ECL with DPA,

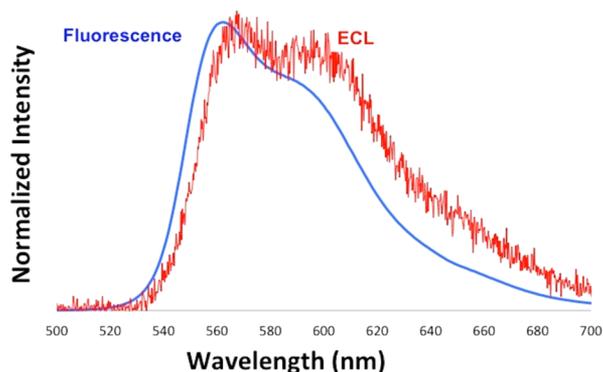


Figure 3. Fluorescence spectrum (blue trace) of 0.3 mM rubrene in toluene and ECL spectrum (red trace) of the toluene/TPrA/IL-PA/rubrene-in-water emulsion generated on a 3 mm glassy carbon working electrode.

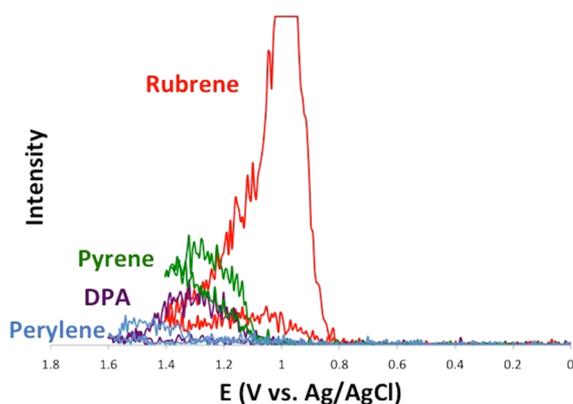


Figure 4. Relative intensities of each PAH in the toluene/TPrA/IL-PA/PAH-in-water emulsion in 5 mM PB at pH 7.

pyrene, or perylene in a dry and inert atmosphere in an acetonitrile/benzene solution as the solvent.¹⁴ However, as discussed above, rubrene NPs and DPA NRs were studied for their ECL in aqueous solution using TPrA as the co-reactant. The light intensities for these systems were low; however, light was indeed observed. Also, rubrene and DPA were shown to give ECL using TPrA as a co-reactant when immobilized onto Langmuir–Blodgett films in water at the electrode surface, giving higher intensities than the NP and NR examples.¹⁵ These examples demonstrate that the ECL mechanism via TPrA oxidation may be easier in the presence of water. As stated above, oxalate was able to produce an excited state with rubrene and DPA, which was surprising since oxalate will likely not enter the oil phase. This observation may indicate that the light generation step occurs at the droplet interface. It has been shown that the electrochemistry in electroactive oil droplets mostly occurs at the three-phase boundary between the oil droplet, the aqueous continuous phase, and the electrode surface,¹⁶ which means that some TPrA dissolved in the aqueous phase can also participate in inducing an excited state of PAH or BODIPY.

To further show the versatility of the methodology, BODIPY was tested for its ECL. This particular member of the BODIPY dye series is substituted with methyl groups around its indacene core, except for the two extreme β positions, which are substituted by ethyl groups. Light could not be observed by the naked eye in a dark room; however, sufficient light was provided to attain a spectrum. Figure 5A shows the ECL and

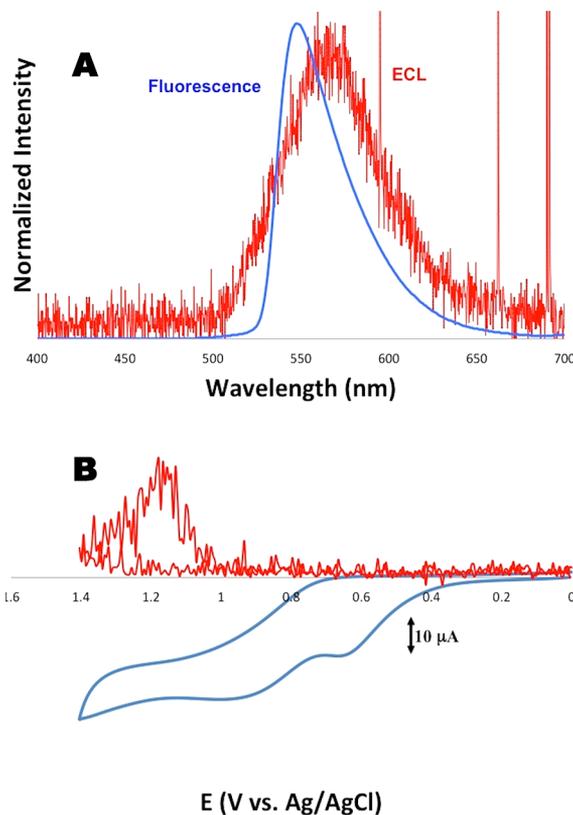


Figure 5. (A) Fluorescence spectrum (blue trace) of 0.1 mM BODIPY in toluene and ECL spectrum (red trace) of the toluene/TPrA/IL-PA/BODIPY-in-water emulsion. (B) CV and ECL trace of BODIPY emulsion system on a 3 mm glassy carbon electrode.

photoemission spectra, and Figure 5B shows the ECL intensity (red trace) and CV (blue trace) collected for the BODIPY emulsion system. The potential required to oxidize BODIPY is more positive than for rubrene, which is suggested by the onset of light around 1.05 V (as opposed to 0.82 V for rubrene). Because of the lack of light obtained for BODIPY ECL, the ECL spectrum is much less resolved than the emission spectrum. The large blips between 590 and 700 nm are cosmic ray events.

In summary, a simple emulsion system based on toluene and TPrA and emulsified by an IL has been described for the production of ECL of PAHs and BODIPY in aqueous systems. Remarkably, ECL of different PAHs and BODIPY was attained with this system in water, and spectra were taken of rubrene and BODIPY. We have shown that the library of ECL luminophores in aprotic solvents can now be extended to aqueous systems by using this simple emulsion technique. We have also shown that the technique is versatile, encompassing many ECL luminophores. One can also envisage other organic solvent emulsions (e.g., 1,2-dichloroethane), ECL luminophores, and even different co-reactants (i.e., benzoyl peroxide, persulfate) to augment to the versatility. Potentially, these droplets may be used in sensor technology or for tracking stochastic events.¹²

■ ASSOCIATED CONTENT

📄 Supporting Information

Instrumentation, chemicals used, and emulsion synthesis. Pictures of emulsions over time. CV showing control experiments for emulsion oxidation. CV and ECL traces for

DPA, pyrene, and perylene. Chronoamperometry. CV and ECL traces for rubrene and DPA in oxalate system. Proposed ECL mechanism for PAH + TPrA oxidation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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