



Electrochemistry, Electrogenerated Chemiluminescence, and Electropolymerization of Oligothieryl-BODIPY Derivatives



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ABSTRACT

We report the electrochemistry, electrogenerated chemiluminescence, and electropolymerization of a series of oligothieryl boron dipyrromethene (BODIPY) compounds in acetonitrile (MeCN) solution. For each compound, **1-5**, the first oxidation wave was attributed to the first one electron (1e) oxidation of the BODIPY core. For **1**, the second oxidation wave at $E_p = 0.8$ V vs. the ferrocene/ferrocenium couple ($\text{Cp}_2\text{Fc}^{0/+}$), attributed to the oxidation of the first thieryl substituent, is irreversible. In the case of **2-5**, the oxidation of the first thiophene is reversible, suggesting stability of the radical dication. In each case of **1-5**, the first BODIPY reduction peak was irreversible due to the instability of the radical anion, which is due to the lack of complete substitution in the β' and *meso* positions on the indacene periphery. ECL was detected for each compound; however, only **1** displayed enough light capable of generating an ECL spectrum ($\lambda_{\text{ECL}} = 674.5$ nm) with the aid of a co-reactant, tripropylamine (TPrA). This wavelength is bathochromically shifted compared to the fluorescence spectrum of the compound ($\lambda_{\text{FL}} = 654$ nm). Compounds **1** and **2** showed evidence of electropolymerization. Each of these polymers, when deposited on a glassy carbon electrode and put into a fresh solution of MeCN and supporting electrolyte, showed peak currents increasing linearly with scan rate, which is indicative of an adsorption process on the electrode surface. Further, the electropolymerization product of **1** showed stable ECL in MeCN and produced a similar spectrum as observed with the free molecules. The polymer also produced ECL in water, which quickly decayed to zero due to the aqueous environment.

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1. Introduction

Organic π conjugated fluorophores, in particular borondipyrromethene (BODIPY) dyes, have attracted considerable attention due to their easy synthesis, low cost, compatibility with electron acceptors, and tunable intrinsic properties (electronic, optical, and conductivity) offered by the structural design. [1,2] One of the most attractive ways to tune the optical properties is to extend the conjugation length by aryl, ethynylphenyl, styryl or polymethine substitutions, [3–10] aromatic ring fusion, [11–13] introduction of a nitrogen atom in the *meso* position (aza-BODIPY), [14–16] and combinations thereof. [17–19]

The substitution of heteroaromatic residues, especially in the 3,5 positions, endow BODIPY's significant red shifted spectral transitions. [20,21] We have previously demonstrated that 3,5-dithienyl BODIPYs [22–24] exhibit comparable red shifted emission with respect to the 3,5-diphenyl analogue. [23,24] There are even

fewer examples of oligothiophenes attached to BODIPY derivatives, [25–29] some being those with oligothiophenes attached in the *meso* position to give donor/acceptor materials. We recently reported the grafting of short conjugated oligothiophene chains to the 3,5 positions of BODIPY derivatives. [30,31]

Many recent applications include biological labeling, [32–34] artificial light harvesters, [35] mechanical rotors, [36] lasing, [37–39] fluorescent switches, chemosensors, molecular photonic wires, electron-transfer reagents, [40] dye sensitized solar cells, [41,42] bulk heterojunctions, [43] electroluminescence, [44] and electrogenerated chemiluminescence. [45] The incorporation of BODIPY dyes into conjugated polymers would offer unique perspectives from the viewpoint of molecular electronics and photovoltaic applications. BODIPY polymers and copolymers have been prepared and characterized, and appeared to be highly fluorescent and exhibit supramolecular self assembled structures. [46,47] Tunable polymeric BODIPY dyes were used as electron donors in bulk heterojunction solar cells, [48–50] or for cancer cell imaging. [51] Finally, electropolymerisation of BODIPY dyes bearing electroactive peripheral side groups have recently been studied with the aim

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to produce low band gap polymers [52], ambipolar behavior [53], conductive properties [54], and electrochromic materials. [55,56]

We herein describe the electrochemistry, electrogenerated chemiluminescence, and electropolymerization of five oligothieryl BODIPY derivatives. We also introduce a new polymer that can be used in nonaqueous electrogenerated chemiluminescence studies.

2. Experimental Section:

2.1 Materials: All solvents and electrolytes were reagent grade and used as purchased. The samples **1-5** were prepared, purified, and characterized as previously described. [30] Anhydrous acetonitrile (MeCN, 99.8%) and anhydrous benzene (Bz, 99.9%) were purchased from Fisher and transferred directly into an oxygen free glovebox (MBraun, Stratham, NH) without further purification. A platinum L type electrode, which is an electrode fabricated in an L shape such that the electrode surface directly faces the opening of the spectrometer or photomultiplier tube, was employed for ECL experiments and polished with a 0.5–1 μm alumina (Buehler, Ltd, Lake Bluff, IL) slurry. All potentials are referenced against ferrocene unless otherwise noted. The salt $[\text{NBu}_4][\text{PF}_6]$ (>99%) was purchased from Sigma Aldrich. Tri-*n*-propylamine (98%) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Before each electrochemical experiment, all samples were prepared under inert atmospheric conditions in a glove box.

2.2 Electrochemistry: Electrochemical measurements were carried out using a three electrode system. A glassy carbon ($A=0.07\text{ cm}^2$) or platinum ($A=0.07\text{ cm}^2$) disk electrode was used as the working electrode. A platinum wire and a silver wire were used for the auxiliary and quasi-reference electrodes, respectively. Reagent grade ferrocene was used as an internal standard. All glassware was washed first overnight in a 1:3 solution of nitric acid to hydrochloric acid and then placed in the oven for at least 24 hours after extensive rinsing with acetone and water. Platinum electrodes were washed in a 1:1 solution of sulfuric acid and hydrogen peroxide and placed in the oven for at least 24 hours before the experiment. For the experiment, electrodes and glassware were purged for at least one hour under vacuum in the antechamber, transferred into an inert glovebox, where each solution was prepared. Cells for electrogenerated chemiluminescence were also prepared and capped in the glovebox and taken out for

spectra to be taken. Cyclic voltammetry, square wave voltammetry, and chronoamperometry were measured with a CH Instruments (Austin, TX) model 660D electrochemical workstation. The parameters for square wave voltammetry are as follows: The increase was 1 millivolt, with 25 mV amplitude and 20 Hz frequencies. Quiet time for each experimental run was 5 seconds for the 3 mm glassy carbon electrode.

2.3 Electrogenerated Chemiluminescence: The spectra for ECL were generated by the reaction of the redox species with a coreactant (tri-*n*-propylamine). 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 750 V to the PMT. The signal from the PMT to the potentiostat was transferred using a multimeter (Keithley, Solon, OH).

3. Results and Discussion

3.1. Electrochemistry of **1-5**

The oxidation of **1-5**, shown in Chart 1, demonstrates a reversible peak at *ca.* 0.4V vs. the ferrocene/ferrocenium couple ($\text{Cp}_2\text{Fe}^{0/+}$). Fig. 1 shows a usual cyclic voltammogram (CV) of **1**. Voltammograms of the other compounds can be found in the supporting information. The first oxidation wave is attributed to the one electron oxidation of ferrocene to ferrocenium, which has been added to the solution of **1**. The irreversible reduction peak corresponds to the reduction of the BODIPY core. The reduction peak is irreversible because of the lack of substitution about the periphery of the indacene core, particularly in the meso and β' positions. The reversible oxidation of BODIPY at about 1V (second peak in CV) indicates stability of the radical cation, which also indicates the feasibility of obtaining electrogenerated chemiluminescence (ECL) with these fluorophores by using a coreactant.

In CV, we observed a third oxidation wave, which is attributed to the oxidation of thiophene (See Supporting Information for more details). This oxidation causes electropolymerization (*vide infra*).

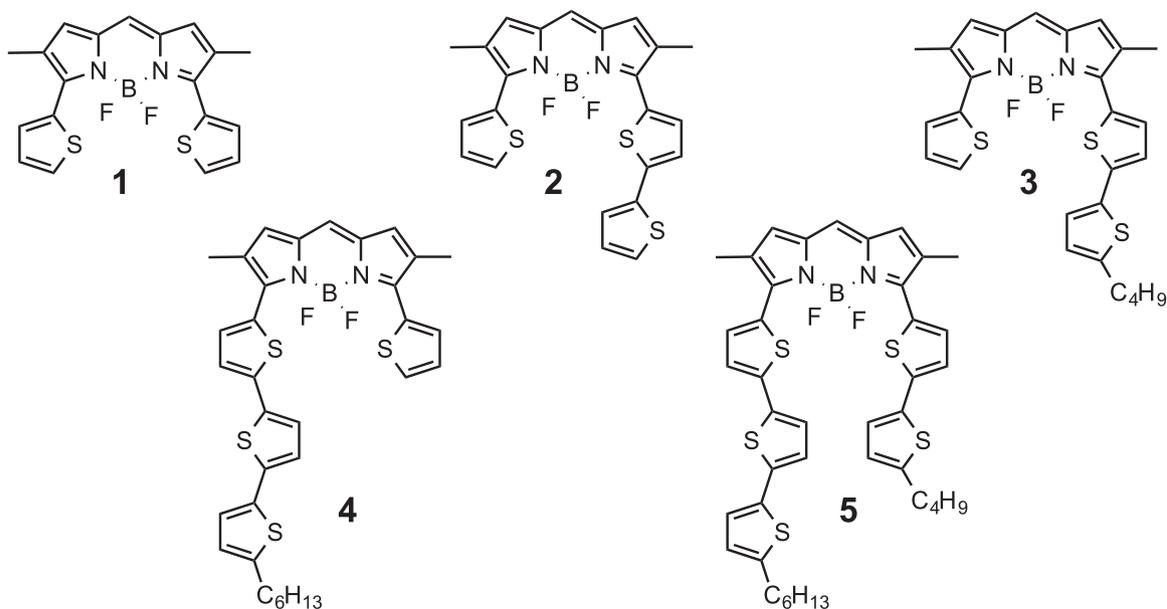


Chart 1.

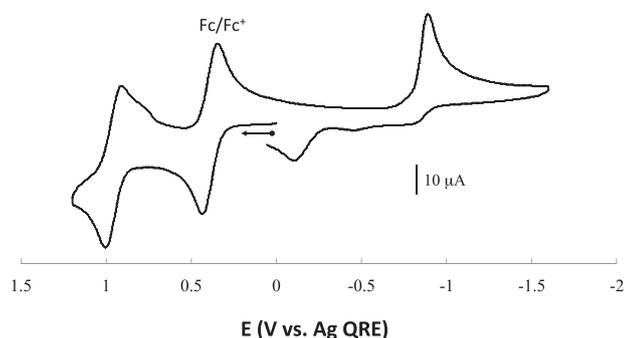


Fig. 1. A general cyclic voltammogram of 0.5 mM **1**. The first reversible oxidation wave is ferrocene (Fc). The scan rate was 100 mV/s on a 3 mm glassy carbon electrode.

Further oxidation at more positive potentials in MeCN gives further waves in the case of **3–5**. These waves can be seen in figures given in the supporting information, and no polymer peak was observed for **3–5**.

Table 1 gives experimental information for each compound. All compounds were referenced against ferrocene. The diffusion coefficient of each compound was calculated using the Randles-Sevcik relationship. For the square wave voltammetry (SWV) analysis, the full width at half max (FWHM) can give information on the number of electrons transferred. Because ferrocene is a well-known one-electron transfer reaction, the FWHM for ferrocene is equated to a one-electron transfer. Using these values, we can compare the FWHM for ferrocene to that of BODIPY oxidation and reduction and the thiophene oxidation. From this analysis, unsurprisingly, all oxidation and reduction reactions occurred through a one-electron transfer.

An analysis of the diffusion coefficients of each compound, **1–5**, evidenced diffusion coefficients decreasing upon addition of thiophene. It is interesting to plot the diffusion coefficient as a function of the number of thiophenes and use the relationship to derive the diffusion coefficient for a BODIPY molecule without thiophenes and compare to literature values. **Fig. 2** shows a plot of diffusion coefficient versus the number of thiophenes. The diffusion coefficient decreases linearly upon addition of each thiophene. Because compounds **4** and **5** are similar and differ by a hexyl substituent, the average value was taken for the plot. Extrapolating to 0 gives a diffusion coefficient of $2\text{E}-6\text{ cm}^2\text{s}^{-1}$, which agrees well with previously reported work for unsubstituted BODIPY species in various non-aqueous media. [57]

3.2. Electrogenated Chemiluminescence

Red and near IR emitters are of interest in both fluorescence and ECL. Only **1** gave adequate ECL to collect a spectrum. **Fig. 3A**

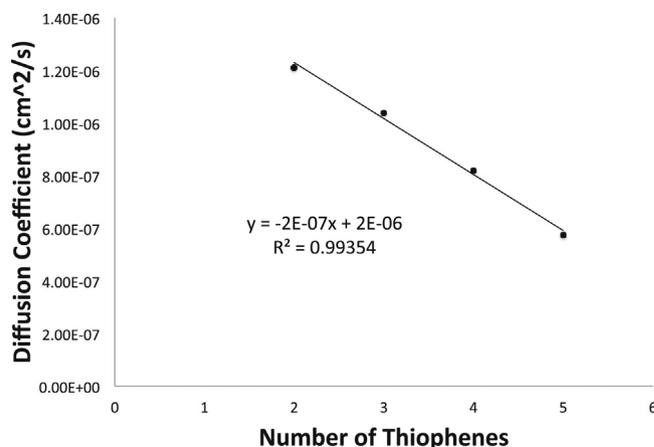


Fig. 2. Diffusion coefficient versus number of thiophenes for **1–5**.

shows the ECL generated during a cyclic voltammogram of **1** and 25 mM TPrA, and **Scheme 1** gives two possible ECL mechanisms by which light is generated. The red trace is the ECL generated during the sweep in arbitrary units. **Fig. 3B** shows ECL transients of the same system by pulsing the electrode from 0 to 0.9 V. In chronoamperometry, the peak heights were consistently high for the initial pulse, but the decay over time is likely due to trace oxygen or water in the MeCN system.

Because of the intense ECL that was generated for **1**, an ECL spectrum was collected and compared to the emission spectrum. **Fig. 4** shows an overlay of the fluorescence spectrum ($\lambda_{\text{exc}} = 450\text{ nm}$) and the ECL spectrum, which was generated using the pulsing technique. The spectra, in general, agree well with other BODIPY molecules. The ECL spectrum of BODIPY is bathochromically shifted, which is likely because the oxidation product of this reaction polymerizes on the electrode surface, as discussed below. Another reason for this shift could be due to inner filter effects between measurements on different instruments.

3.3. Electropolymerization

1 and **2** showed electropolymerization activity, i.e. polymer formation was observed on a 3 mm glassy carbon working electrode in CV. Attempts were made at using a platinum electrode to form the polymer, but the polymer disappeared after deposition, likely due to the hydrophilicity of the platinum surface. The forward scan that contained only the BODIPY oxidation/reduction showed no polymer growth in CV. Only until the first thiophene was oxidized did we observe a reduction peak for the polymer, which indicates that polymerization is occurring through the thiophene rings. For **1**, the polymer reduction was seen at 0.19 V and for **2**, the polymer was

Table 1
Electrochemical data from each compound.

Compound:	1	2	3	4	5
Diffusion Coefficient (cm^2/s)	1.2E-05	1.0E-05	9.0E-06	8.2E-06	5.7E-06
Ferrocene FWHM	0.108	0.106	0.108	0.111	-
BODIPY Oxidation $E_{1/2}$ (V)	0.565	0.488	0.452	0.425	-
BODIPY Ox $E_{1/2}$ from SWV (V)	0.564	0.486	0.451	0.423	0.351
BODIPY Oxidation FWHM (V)	0.108	0.107	0.101	0.110	-
BODIPY Oxidation ΔE_p (V)	0.093	0.084	0.072	0.074	-
2 nd BODIPY Ox from SWV (V)	1.74	1.69	1.73	1.56	-
BODIPY Reduction E_{pc} (V)	-1.23	-1.23	-1.26	-1.27	-
BODIPY Reduction FWHM (V)	0.097	0.10	0.097	0.094	-
1st Thiophene $E_{1/2}$ from SWV (V)	1.03	0.829	0.735	0.576	0.530
First Thiophene $E_{1/2}$ (V)	1.03	0.825	0.717	0.579	-
First Thiophene FWHM (V)	-	0.103	0.100	0.112	-

*All voltammetric data referenced versus ferrocene/ferrocenium couple.

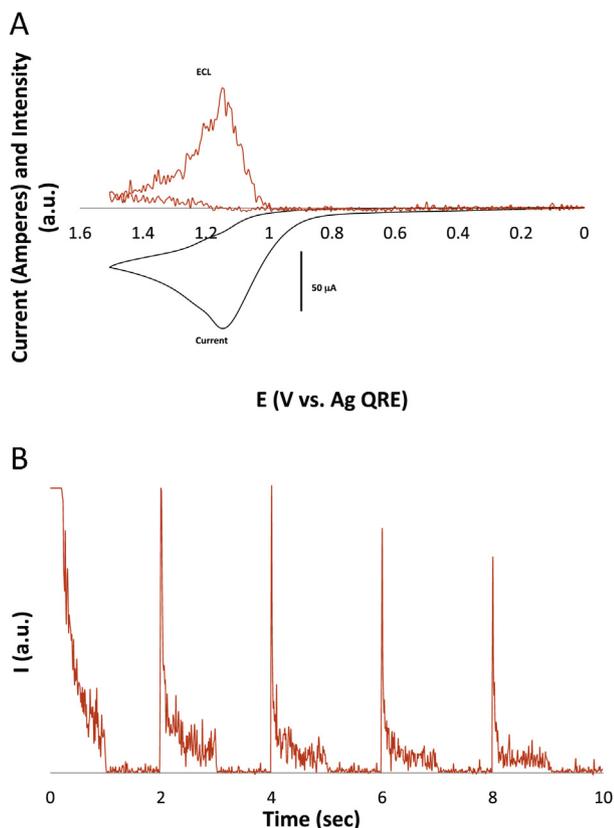
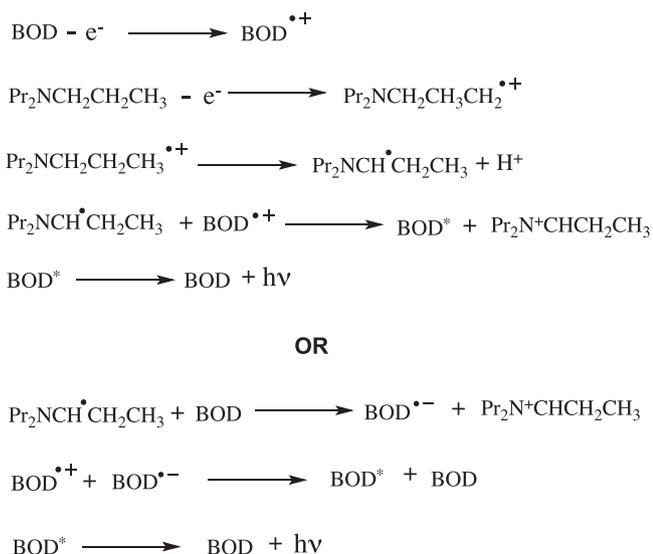


Fig. 3. A.) CV of **1** in the presence of 25 mM TPrA (black trace) and ECL generated during CV (red trace). B.) ECL transients taken while pulsing the current between 0 and 0.9 V. Experiments were performed on a 2.5 mm platinum electrode.

reduced at 0.13 V. In order to confirm polymerization, we used CV to observe the polymer growth by scanning multiple times (see supporting information as an example) on a glassy carbon working electrode. After these multiple scans, the electrode was taken out of the solution, washed with water, and put into a fresh MeCN solution containing only electrolyte, and CVs displayed a surface process (Fig. 5A). As expected [58], the current varies linearly with the scan rate (Fig. 5B), which implies a surface process is present, i.e., the polymer is adsorbed onto the surface of the electrode.



Scheme 1. Pathways to generating ECL using BODIPY as the ECL luminophore.

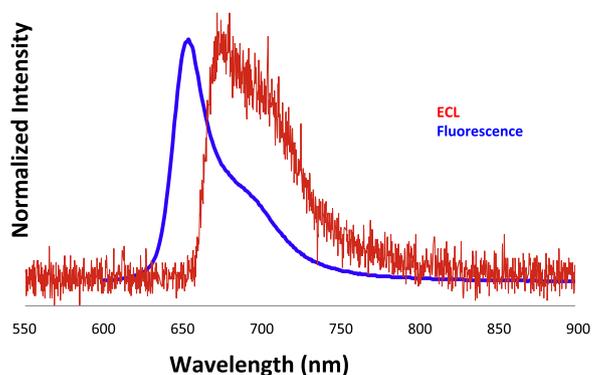


Fig. 4. Overlay of the fluorescence and ECL spectra for **1**. The excitation wavelength was 450 nm for fluorescence, and ECL was generated using the coreactant TPrA by pulsing between 0V and 0.9V on a 2.5 mm platinum electrode.

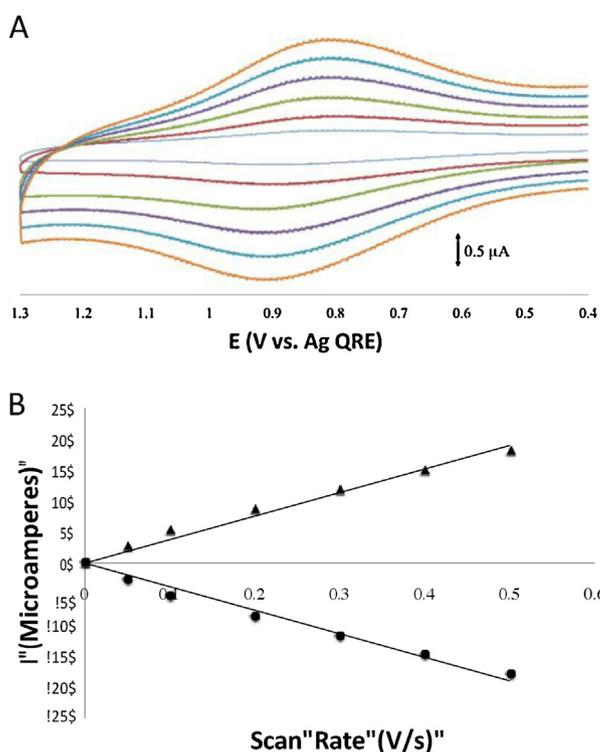


Fig. 5. A.) CVs at multiple scan rates for the polymer in a fresh solution of MeCN on a 3 mm GC working electrode. B.) Current versus scan rate dependence for anodic and cathodic processes.

ECL of the adsorbed species was collected in acetonitrile and water. Fig. 6 shows ECL CV traces in MeCN (A) and water (B) as well as ECL transients in MeCN (C) and water (D). Adequate light was generated in a fresh solution of MeCN (Fig. 6A), and the ECL transients, which decayed very little over the experimental time, indicate a stable ECL generating species (Fig. 6C). In an attempt to study the polymer's ECL in water, we probed the ECL in an aqueous solution buffered in phosphate buffer saline. The polymer showed an initial spike of ECL and rapidly died, as evidenced in the ECL spike in CV (Fig. 6B) and in the ECL transients (Fig. 6D). Unsurprisingly, the lack of ECL in an aqueous system is due to the instability of the radical species, which is reactive toward water.

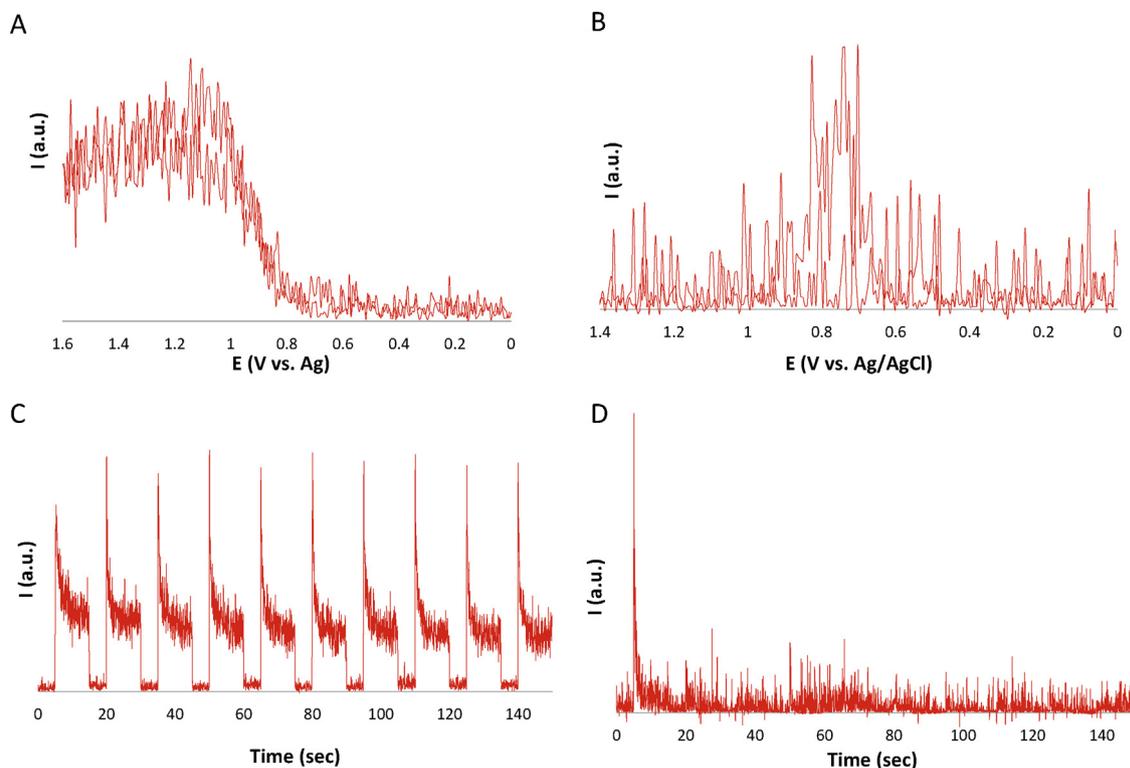


Fig. 6. A.) ECL generated for polymerized species of **1** taken on the glassy carbon electrode at 200 mV s^{-1} in the presence of 25 mM TPrA in acetonitrile. B.) ECL generated for the polymer in water and 40 mM phosphate buffer. C.) ECL transients of the polymer of **1** in acetonitrile. D.) ECL transient by using the pulse technique in aqueous solution in the presence of 5 mM TPrA.

4. Conclusion

In this report, we have studied 5 potentially useful BODIPY derivatives and have reported their electrochemical and ECL properties. For the purposes of ECL, however, only **1** displayed adequate light to attain a spectrum, which was bathochromically shifted from the emission spectrum due to electropolymerization. Further, both **1** and **2** electropolymerized to form a polymer on an inert, hydrophobic glassy carbon electrode. This was confirmed by observing that a plot of scan rate versus the current peak height was linear. This finding adds to the small list of polymers formed by BODIPY derivatives and is the first of such BODIPY polymers that polymerize through thiophene substituents. The reported molecules have the potential to be used in different non-aqueous and aqueous ECL systems and for electrochemical collision research [59,60], as do the polymers formed from these molecules.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2015.07.112>

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