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

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ABSTRACT

We report the electrochemistry, electrogenerated chemiluminescence, and electropolymerization of a series of oligothienyl 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 ($Cp_2Fc^{0/+}$), attributed to the oxidation of the first thienyl 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 (λ_{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 (λ_{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.

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 oligothienyl 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 $[NBu_4][PF_6]$ (>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 ($A=0.07\,cm^2$) or platinum ($A = 0.07\,cm^2$) 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.* 0.4 V vs. the ferrocene/ferrocenium couple ($Cp_2Fe^{0/+}$). 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 1 V (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*).
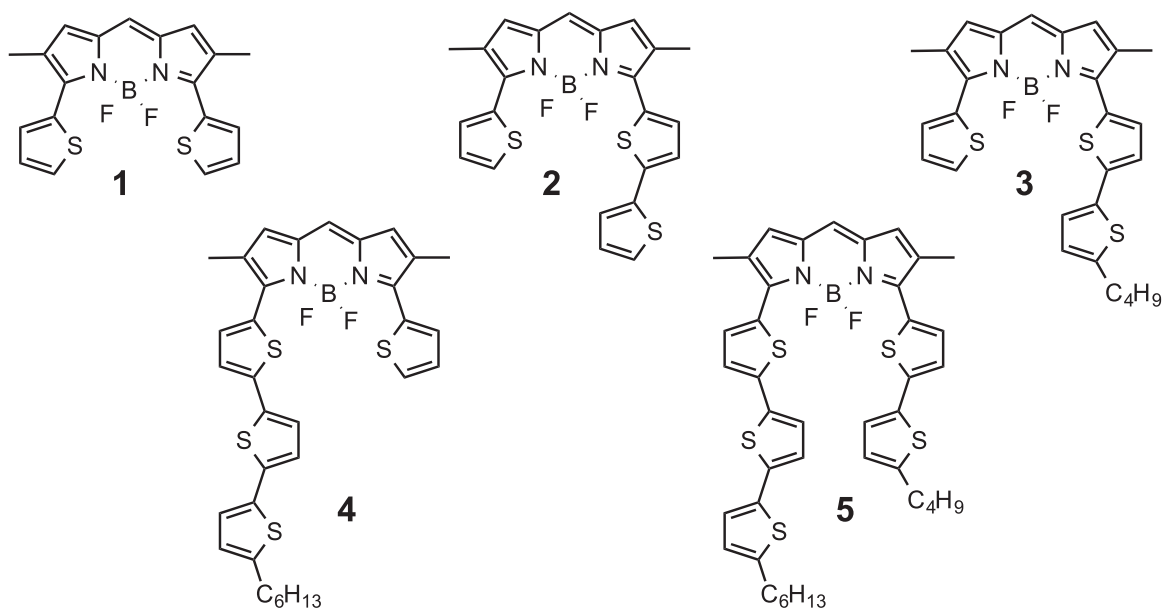

Chart 1.