

# Electrogenerated Chemiluminescence 71. Photophysical, Electrochemical, and Electrogenerated Chemiluminescent Properties of Selected Dipyrromethene–BF<sub>2</sub> Dyes

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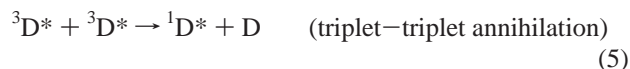
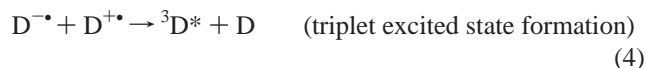
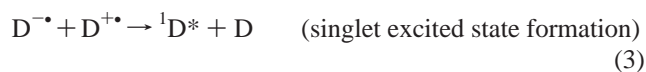
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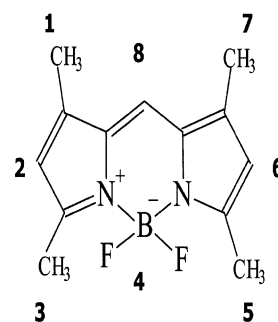
The photochemistry, electrochemistry, and electrogenerated chemiluminescence (ECL) of five boron-based laser dyes (BODIPY, PM 546, PM 567, PM 580, PM 597) have been investigated. These show high fluorescence quantum yields ( $\Phi > 0.85$ ) for all dyes except PM 597 ( $\Phi \approx 0.41$ ), because of the high degree of substitution and inductive effects of the substituents. Moderately intense ECL was observed from the three dyes, exhibiting reversible electrochemical oxidation and reduction with ECL efficiencies of  $\sim 0.009$  for PM 567,  $\sim 0.007$  for PM 580, and  $\sim 0.003$  for PM 597. The parent fluorophore, BODIPY, displayed both irreversible oxidation and reduction, because of the lack of substituents at positions 2, 6, and 8, and, hence, higher reactivity of the electrogenerated radical ions. Substituting a methyl group at position 8 stabilized the radical anion, causing a reversible reduction, as shown in PM 546. However, for both BODIPY and PM 546, irreversible chemical side reactions, such as oxidative polymerization, were responsible for the lack of ECL or low ECL efficiency.

## Introduction

Over the past decades, a wide variety of compounds have been employed in electrogenerated chemiluminescence (ECL) experiments, but few studies have involved highly fluorescent laser dyes.<sup>1</sup> We show, in this paper, photophysical and electrochemical characterization of several commercially available boron-containing dipyrromethene–BF<sub>2</sub> (PM–BF<sub>2</sub>) dyes (Figure 1), as well as the ECL that results from radical ion annihilation. Classical ECL occurs when the electron transfer between electrochemically generated species, often radical ions, results in an excited species that emits light. The simplest ECL process is the radical ion annihilation reaction, which can be represented as



where D, for example, is a polycyclic aromatic hydrocarbon (PAH), such as rubrene.<sup>2</sup> In some situations, however, the radical cation or anion cannot be generated prior to the background oxidation or reduction of the solvent/supporting electrolyte used for electrochemistry. In this case, a second compound must be



Dye	2	6	8
BODIPY	H	H	H
PM 546	H	H	CH <sub>3</sub>
PM 567	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>
PM 580	n-C <sub>4</sub> H <sub>9</sub>	n-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>
PM 597	t-C <sub>4</sub> H <sub>9</sub>	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>

Figure 1. Molecular structures of PM–BF<sub>2</sub> complexes.

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added to generate a stable radical counterion (a second reductant or oxidant to react with the radical cation or anion), which is required for annihilation.<sup>2</sup> In recent years, an important advance in ECL was the discovery of reaction schemes for generating ECL via the use of coreactants or other electrogenerated species capable of reacting with either the anion or cation alone to produce the desired excited state. These reactions could be observed on the basis of their ability to generate energetic precursors at less-extreme potentials upon bond cleavage of a coreactant such as  $C_2O_4^{2-}$  and  $S_2O_8^{2-}$ . Currently, the most widely used ECL coreactants are aliphatic amines such as tri-*n*-propylamine, because they appear to be the most efficient, in regard to generating light.

The search for new, highly efficient, and stable organic and inorganic ECL emitters has been a continuous theme in ECL (for example, as emitting labels in analytical applications). Successful ECL emitters must be capable of generating radical cations and anions that are stable even after prolonged electrochemical cycling and ECL production.<sup>3,4</sup> Among the most efficient ECL emitters are PAHs such as rubrene and 9,10-diphenylanthracene (DPA), which are compounds that fulfill the stability criterion, in addition to possessing fluorescence quantum yields close to unity.<sup>2</sup> Although a high fluorescence quantum yield is key to generating efficient and strong ECL, there have been only a few attempts to produce ECL from commercially available fluorescence dyes with high fluorescence efficiencies. Generally, these attempts have not been very successful, with only weak ECL emission observed, because of the instability in the radical ions and formation of byproducts incapable of ECL.<sup>1</sup>

In the late 1980s and early 1990s, PM-BF<sub>2</sub>, which is a new class of laser dyes with higher lasing efficiencies, were synthesized.<sup>5,6</sup> These PM-BF<sub>2</sub> complexes show fluorescence efficiencies and lasing wavelengths similar to those of the well-known rhodamine dyes and do not form aggregates, even at relatively high concentration. With these advantages over traditional fluorescence dyes, PM-BF<sub>2</sub> complexes have been utilized in almost every area where fluorescence dyes are used, especially in tagging proteins and DNA in biochemical research.<sup>7,8</sup> In recent years, derivatives capable of analytical applications, such as proton or anion recognition, have also been synthesized.<sup>9–11</sup> Most studies, however, have focused on their photophysical properties, with only a few recent studies investigating the electrochemical properties of these compounds.<sup>9,12–14</sup> To our knowledge, only one brief study reported ECL from a PM-BF<sub>2</sub> compound. This species was similar to PM 567, with the only structural difference being the replacement of a phenyl group at position 8 of the dye.<sup>11</sup> The possibility of ECL of other dyes from this group has not been investigated, although their high fluorescence efficiencies make them interesting candidates for ECL sensors and display devices.

We report here a new class of fluorescence dyes that are capable of ECL. Five compounds were chosen; all are commercially available PM-BF<sub>2</sub> dyes. The selection was made based on the chemical structure of the dyes as shown in Figure 1. The selected dyes were BODIPY, PM 546 (8-Me), PM 567 (2,6-Et), PM 580 (2,6-<sup>*n*</sup>Bu), and PM 597 (2,6-<sup>*i*</sup>Bu). The fluorescence and electrochemical properties of these compounds were investigated to locate energies and evaluate their potential for ECL. The high degree of substitution on three of these compounds would be expected to block possible decomposition pathways of the radical ions and, thus, lead to stable ECL. The results of ECL studies of these three dyes are compared with two dyes with fewer substituents in an attempt to understand

the influence of electron-donating substitutions at positions 2, 6, and 8 of the parent fluorophore. These results provide further insight into future development of similar compounds for ECL, using variations of the core PM-BF<sub>2</sub> structure.

## Experimental Section

Laser-grade PM-BF<sub>2</sub> dyes were obtained from Exciton, Inc. (St. Louis, MO) or Molecular Probes (Eugene, OR) and used without further purification. The structural names of these dyes are given in the Supporting Information. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>), was recrystallized twice and dried in a vacuum oven at 100 °C prior to transferring it directly into an inert atmosphere drybox (Vacuum Atmospheres Corp., Hawthorne, CA). 10-methylphenothiazine (10-MP, Aldrich) and anhydrous acetonitrile (ACS spectrophotometric grade, Aldrich) were used as received. All solutions were prepared in the drybox with fresh anhydrous solvents and sealed in airtight vessels for measurements completed outside the drybox.

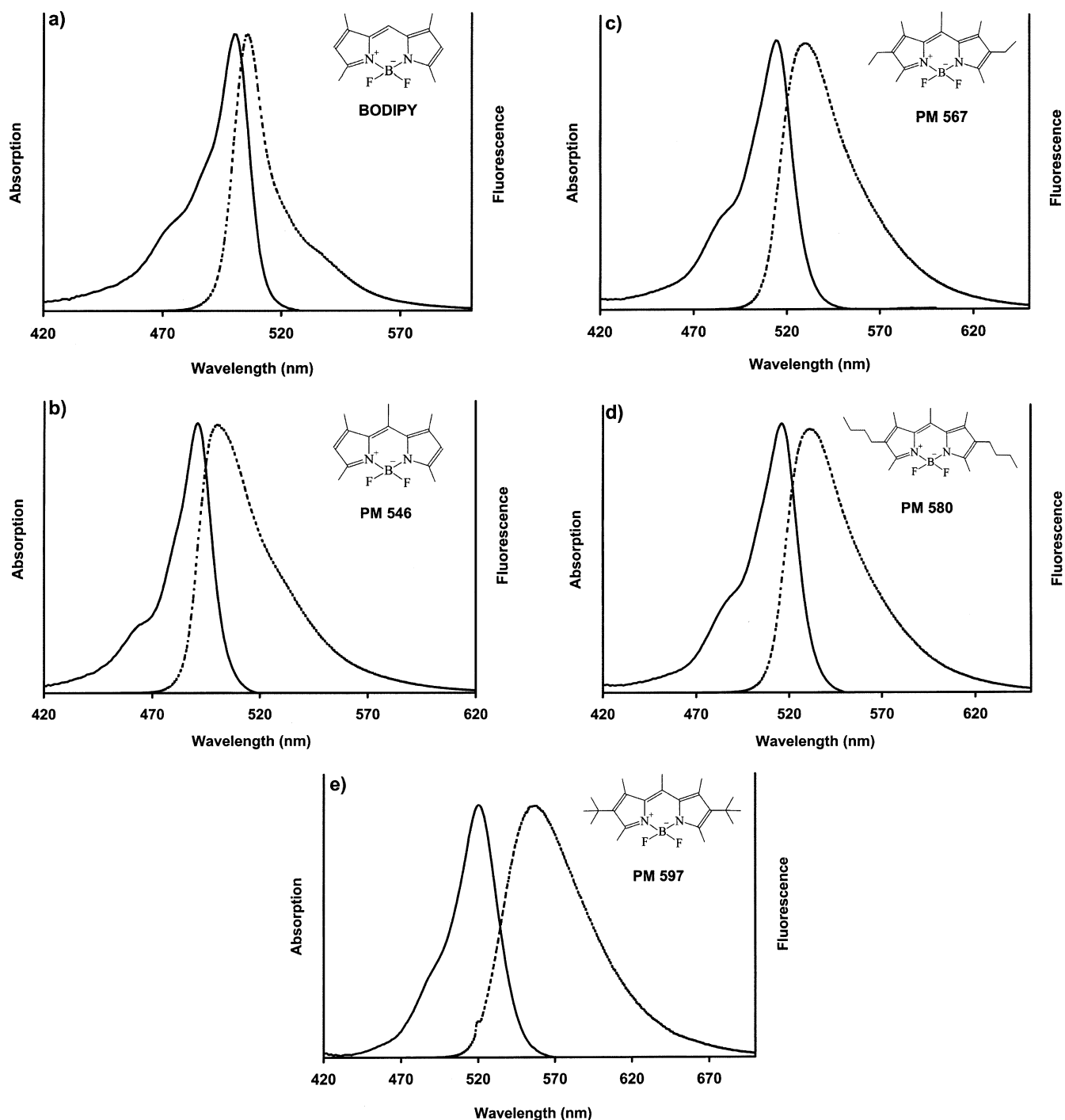
All fluorescence spectra were recorded on a Fluorolog-3 spectrofluorimeter (ISA-Jobin Yvon Hariba, Edison, NJ), using a slit width of 1 nm and a resolution of 1.5 nm. All UV-visible spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer. The absorbance and fluorescence spectra of the PM-BF<sub>2</sub> dyes were obtained with 2 μM solutions in MeCN. The relative fluorescence efficiency was measured using a 2 μM solution in MeCN with PM 567 as a standard ( $\lambda_{exc} = 514$  nm;  $\Phi_{PM567(2,6-Et)} = 0.87$  in MeCN).<sup>15</sup>

Cyclic voltammograms were recorded on a CH Instruments electrochemical work station (Austin, TX). The working electrode, in most cases, consisted of an inlaid platinum disk (1.5–2.0 mm in diameter) that was polished on a felt pad with 0.05 μm alumina (Buehler, Ltd., Lake Bluff, IL), sonicated in water and absolute ethanol for 3 min, and then dried in an oven at 100 °C before being transferred into the inert atmosphere drybox. A platinum ultramicroelectrode (25 μm) was also utilized as the working electrode to obtain steady-state cyclic voltammograms for compounds that show irreversible electrochemistry. A platinum wire served as a counter electrode, and a silver wire was utilized as a quasi-reference electrode. The concentrations used to obtain each voltammogram are given in the corresponding figure captions. All potentials were calibrated versus an aqueous SCE by the addition of ferrocene (Fc) as an internal standard, taking  $E^\circ(Fc/Fc^+) = 0.424$  V, vs SCE.<sup>16</sup>

All ECL measurements were performed as previously reported.<sup>17</sup> Measurements were obtained with solution concentrations of 1 mM in 0.1 M TBAPF<sub>6</sub> in MeCN. To generate the annihilation reaction, the working electrode was pulsed between the first oxidation and reduction peak potentials of the compound with a pulse width of 0.1 s. The resulting emission spectra were obtained with a charged-coupled device (CCD) camera (model CH260, Photometrics—Roper Scientific, Tucson, AZ) that was cooled to -100 °C. Integration times were 2 min. The CCD camera and grating system were calibrated with a mercury lamp before each measurement.

## Results and Discussion

**Absorption and Emission Spectroscopy.** The absorption and emission spectra for the five PM-BF<sub>2</sub> dyes are shown in Figure 2. As shown, the absorption and fluorescence maxima are affected by the substituents in positions 2 and 6 of the fluorophore, leading to a shift to lower energies when compared to the less-substituted compounds, BODIPY and PM 546 (8-Me). Ethyl groups (PM 567 versus PM 546) cause spectral shifts



**Figure 2.** Optical absorption and fluorescence spectra of  $2 \mu\text{M}$  (a) BODIPY, (b) PM 546 (8-Me), (c) PM 567 (2,6-Et), (d) PM 580 (2,6- $n\text{Bu}$ ), and (e) PM 597 (2,6- $t\text{Bu}$ ) in MeCN. (Excitation wavelengths were as follows: 500 nm, BODIPY; 491 nm, PM 546 (8-Me); 514 nm, PM 567 (2,6-Et); 515 nm, PM 580 (2,6- $n\text{Bu}$ ); and 521 nm, PM 597 (2,6- $t\text{Bu}$ ).)

in MeCN of 23 and 30 nm in the absorption and fluorescence bands, respectively. Similarly, *n*-butyl ( $n\text{Bu}$ ) groups (PM 580 versus PM 546) cause a red shift of 24 nm in the absorption band and  $\sim 31$  nm in the fluorescence band, whereas *tert*-butyl ( $t\text{Bu}$ ) groups (PM 597 versus PM 546) give rise to larger shifts (30 and 56 nm in the absorption and emission bands, respectively). These bathochromic shifts are due to inductive effects of the substituents at positions 2 and 6, causing those positions of the molecules to undergo a decrease in electron density in their excited state, with respect to the ground state.<sup>15</sup> Thus, a gradual decrease in absorption energy is observed with substituents with increasing electron-donating properties.

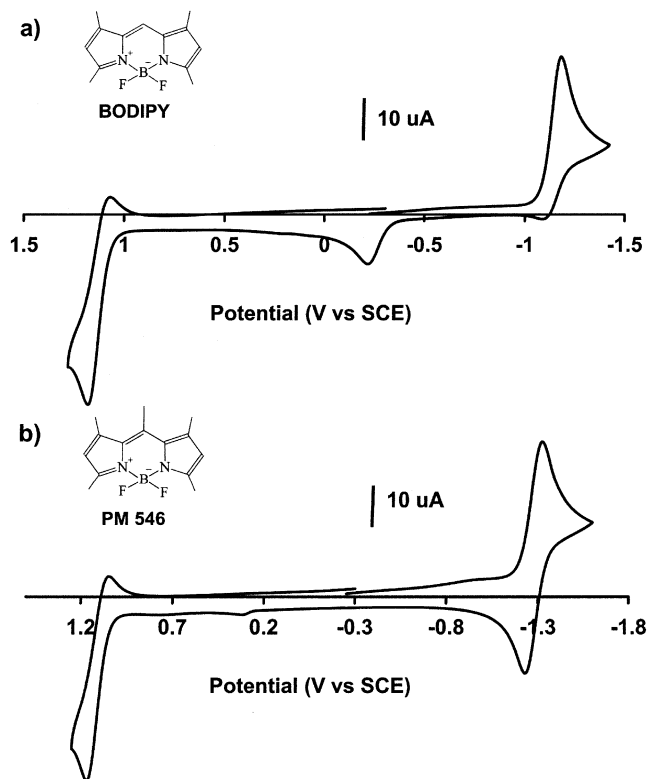
As shown in Table 1, a relatively large Stokes shift of 30 nm was observed between the absorption and emission maxima of PM 597 (2,6- $t\text{Bu}$ ), whereas a smaller Stokes shift, 6 nm, was observed in BODIPY, which is the only one of the dyes studied without substituents in positions 2, 6, and 8. A gradual increase in the Stokes shift is observed with increasing degree of substitution, because of changes in the molecular structure of the compound upon excitation. In particular, the difference in energy between the geometrically relaxed ground state and the nonrelaxed excited singlet state is larger than the energy difference between the geometrically relaxed excited state and the nonrelaxed ground state.<sup>18</sup> In addition, an increase in the

**TABLE 1: Electrochemical, Photophysical, and ECL Data for the Various PM–BF<sub>2</sub> Dyes**

compound	V, vs SCE		$\lambda_{\max(\text{ab})}$ (nm)	$\epsilon_{\max}$ (10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{\max(\text{fl})}$ (nm)	$\Phi_{\text{fl}}$	$E_s(\text{eV})$	$\lambda_{\max(\text{ECL})}$ (nm)	$\Phi_{\text{ECL}}$
	$E_{1/2(\text{R/R}^+)}$	$E_{1/2(\text{R/R}^-)}$							
BODIPY	1.17	-1.15	500	8.0	506	0.92	2.47		
PM 546	1.22	-1.18	491	8.1	501	0.95	2.50	530	
PM 567	1.02	-1.29	514	7.9	531	0.87	2.37	550	~0.009
PM 580	0.95	-1.36	515	7.7	532	0.85	2.37	555	~0.007
PM 597	1.01	-1.24	521	6.8	557	0.41	2.32	585	~0.003

Stokes shift in dyes with larger and more-flexible substituents could be due to different rearrangement of the solvent molecules in the transient ground state and singlet-excited state. As observed, both PM 567 (2,6-Et) and PM 580 (2,6-<sup>n</sup>Bu) showed a shift of 17 nm, suggesting similarities in the inductive effects and degree of flexibility caused by the ethyl and <sup>n</sup>Bu groups at those positions. When compared to the four PM–BF<sub>2</sub> dyes, BODIPY displayed a slightly different photophysical behavior. Although it is the least substituted among the dyes in this study, the absorption and fluorescence bands of BODIPY are slightly lower in energy than those in PM 546 (8-Me). The fluorescence spectrum obtained in the same solvent was narrower and had more-defined vibrational structures than other highly substituted PM–BF<sub>2</sub> dyes, because of the lack of solvation broadening effects. The small Stokes shift (6 nm) also indicates rigidity and the lack of steric hindrance in the dye, when compared to other dyes in this study.

The fluorescence efficiencies of BODIPY, PM 546 (8-Me), PM 567 (2,6-Et), PM 580 (2,6-<sup>n</sup>Bu), and PM 597 (2,6-<sup>n</sup>Bu) measured in MeCN are 0.95, 0.96, 0.87, 0.85, and 0.41, respectively, which are in good agreement with similar values in a recent study on these dyes in MeCN.<sup>15</sup> Slightly different values were obtained in another study where the solvent and dye concentrations used were different.<sup>6</sup> Overall, the observed fluorescence efficiencies appear to decrease as the substitution increases, in agreement with recent studies with similar dyes. The differences in fluorescence efficiency among the dyes are mainly due to differences in the rate of nonradiative deactivation, such as internal conversion. Nonradiative deactivation is controlled by the flexibility of the molecule; therefore, molecules such as PM 597 (2,6-<sup>n</sup>Bu) with large <sup>n</sup>Bu groups are less efficient than small and rigid molecules, such as PM 546 (8-Me). The nonradiative rate constants were shown to increase as the substitution in positions 2 and 6 increases with this type of dye in many solvents.<sup>15</sup> In addition, the internal conversion rate constant is directly related to the lack of planarity in this molecule. To determine the planarity of this molecule, seven difference resonance structures were drawn and are given in the Supporting Information. Among the seven resonance structures, only two structures showed a positively charged nitrogen atom with sp<sup>2</sup> (planar) hybridization. This suggests that the nitrogen atom is mostly in its neutral form with sp<sup>3</sup> (nonplanar) hybridization. Every resonance structure contributes to the structure of the actual molecule; therefore, this molecule probably is nonplanar.<sup>6,15</sup> Thus, the presence of electron-donating substituents in positions 2, 6, and 8 of the molecule would further stabilize the nonplanar resonance structures, leading to an increase in the degree of nonplanarity, which controls the rate of internal conversion. Moreover, steric hindrance caused by the higher degree of substitution may also contribute to the nonplanarity among dyes with larger side groups. Overall, this assumption agrees well with our observations that PM 597 (2,6-<sup>n</sup>Bu), with <sup>n</sup>Bu groups in both positions 2 and 6, displayed the lowest fluorescence efficiency among the five PM–BF<sub>2</sub> dyes.

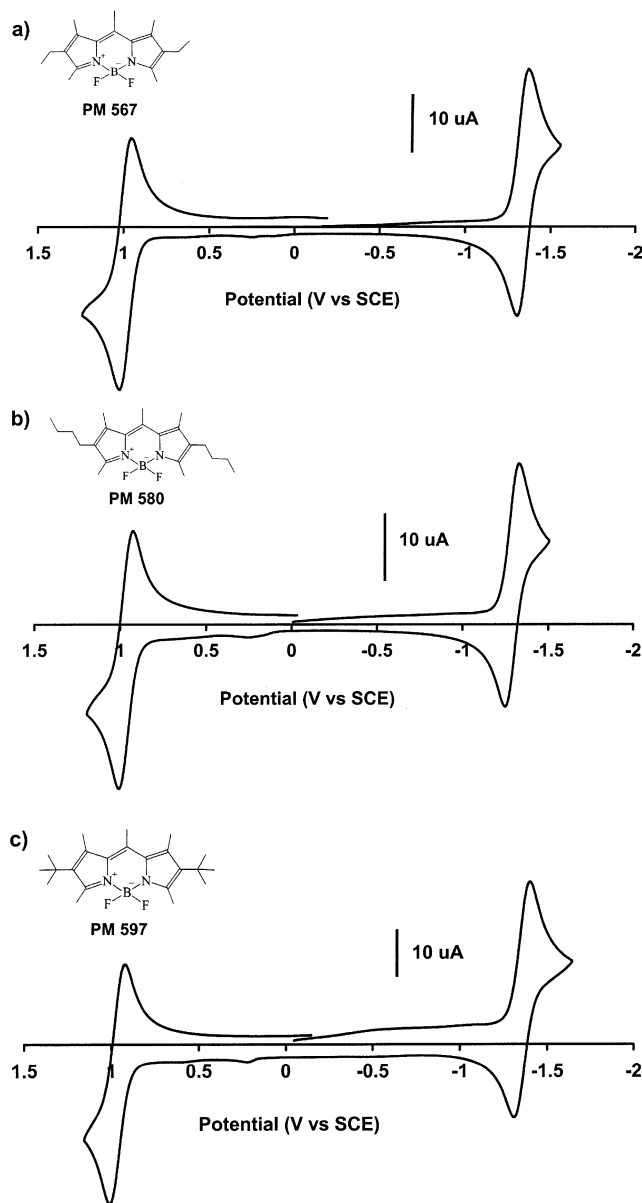


**Figure 3.** Cyclic voltammograms of (a) 1 mM BODIPY and (b) 1 mM PM 546 (8-Me) in 0.1 M TBAPF<sub>6</sub> in MeCN at a platinum electrode. (Scan rate was 200 mV/s.)

In summary, on the basis of the emission wavelengths in the fluorescence spectra (Figure 2), the energy needed to generate the first singlet-excited state of each of these dyes is in the range of 2.32–2.50 eV. This energy must be generated in the electrochemical annihilation reaction of the radical ions to generate directly the singlet-excited state and ECL emission.

**Electrochemical Properties of PM–BF<sub>2</sub> Dyes.** Cyclic voltammetry was used to investigate the electronic effects of the aliphatic substituents at positions 2, 6, and 8 on the core fluorophore. Cyclic voltammograms of the five PM–BF<sub>2</sub> dyes in 0.1 M TBAPF<sub>6</sub> in MeCN obtained at a platinum electrode are shown in Figures 3 and 4. As observed, all five dyes displayed a one-electron oxidation and reduction in MeCN. No second oxidation or reduction was observed in this group of dyes prior to the oxidation or reduction of the background. However, aromatic substitutions onto certain positions of the parent fluorophore are known to lead to second redox steps.<sup>9,13</sup>

In MeCN, BODIPY, which is the compound without substituents in positions 2, 6, and 8, showed irreversible cyclic voltammetric (CV) oxidation and reduction at half-wave potentials of +1.17 and -1.15 V at a scan rate,  $\nu$ , of 200 mV/s, as shown in Figure 3a. These potentials were obtained from a steady-state voltammetric scan using a 25  $\mu\text{m}$  UME (voltammogram not shown). Reversibility was obtained at scan rates above 50 V/s for both oxidation and reduction. Upon bulk



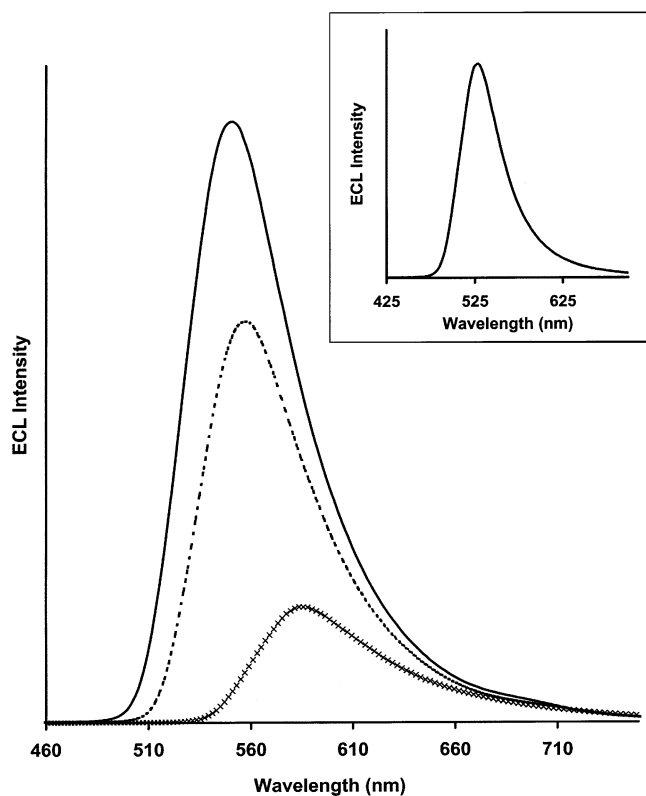
**Figure 4.** Cyclic voltammograms of (a) 1 mM PM 567, (b) 1 mM PM 580, and (c) 1 mM PM 597 in 0.1 M TBAPF<sub>6</sub> in MeCN at a platinum electrode. (Scan rate was 200 mV/s.)

electrolysis at positive potentials, a red film was formed on the surface of the electrode. In addition, prolonged electrolysis led to a visible color change in the solution, which turned bright red from its original green color. In the absence of substituents on both positions 2 and 6, the radical cations generated are unstable and react rapidly to form byproducts. Products of oxidative polymerization have not been identified, but a recent study suggested that these byproducts could be analogous to polypyrrole.<sup>12</sup> PM 546 (8-Me), a derivative of BODIPY substituted with a methyl group at position 8, showed reversible reduction and irreversible oxidation waves at 200 mV/s. As shown in Figure 3b, upon scanning in the negative direction, one reversible reduction wave with a half-wave potential of  $-1.18$  V (vs SCE) was observed, whereas upon scanning to positive potentials, an irreversible one-electron oxidation wave was observed with a half-wave potential of  $+1.22$  V (vs SCE). The observed peak separation for the reversible wave was  $\sim 60$  mV, demonstrating essentially nernstian behavior. In addition, the peak current ratio ( $i_{pa}/i_{pc}$ ) was approximately unity down to a scan rate of 50 mV/s, indicating the absence of a following

chemical reaction, suggesting that the reduction results in a stable radical anion. However, this was not observed for the oxidation which showed electrochemical reversibility only at  $v > 50$  V/s. As with BODIPY, the irreversibility in the oxidation of the molecule suggests a following chemical reaction such as polymerization. Prolonged anodic electrolysis also led to film formation in addition to a visible color change in the solution, as observed with BODIPY.

PM 567 (2,6-Et), with a higher degree of substitution, displayed somewhat different electrochemical behavior. As shown in Figure 4a, PM 567 (2,6-Et) showed reversible oxidation and reduction waves at half-wave potentials of 1.21 and  $-1.4$  V (vs SCE), respectively, in MeCN. PM 580 (2,6-<sup>n</sup>Bu) and PM 597 (2,6-<sup>t</sup>Bu) showed similar electrochemistry (Figure 4b and c), characterized by reversible oxidation and reduction. Details of their redox potentials, in addition to photophysical and ECL properties, are tabulated in Table 1. In all three compounds, the observed oxidation and reduction peak separations were  $\sim 60$  mV, demonstrating near-nernstian behavior. For PM 567 (2,6-Et), PM 580 (2,6-<sup>n</sup>Bu), and PM 597 (2,6-<sup>t</sup>Bu), the peak current ratio ( $i_{pa}/i_{pc}$  or  $i_{pc}/i_{pa}$ ) for both oxidation and reduction were approximately unity, down to a scan rate of 50 mV/s, indicating the absence of following chemical reactions and reasonable stability of the radical ions. PM 567 (2,6-Et), PM 580 (2,6-<sup>n</sup>Bu), and PM 597 (2,6-<sup>t</sup>Bu), which are the three compounds substituted with aliphatic groups at positions 2 and 6, showed less-positive potentials for oxidation than those without substituents at those positions. The inductive properties of alkyl substituents probably stabilize the cation and shift the potential for oxidation to slightly more-positive values. Similarly, with higher electron density within the molecule, the observed potentials for reduction of PM 567 (2,6-Et), PM 580 (2,6-<sup>n</sup>Bu), and PM 597 (2,6-<sup>t</sup>Bu) were slightly more negative than BODIPY and PM 546 (8-Me), where no substituents are found in either position.

As a final note, the total free energy of the annihilation reaction,  $\Delta H_{ann} = \Delta G_{ann} + T\Delta S$ , is based on the difference between the half-wave potentials of the first oxidation and first reduction wave in the cyclic voltammogram, with correction for entropy effects ( $\sim 0.1$  eV). This energy, which becomes available upon radical ion annihilation, should be greater than  $E_s$ , as determined from the fluorescence spectrum, to directly populate the singlet-excited state. As calculated from the highest energy fluorescence at  $\lambda_{max}$ , the energies available from the radical ion annihilation reaction for all the dyes in this study are less than those required for direct population of the singlet-excited states but are presumably able to produce the triplet states.<sup>19</sup> Thus, observed singlet ECL emission from these dyes would be a result of triplet-triplet annihilation (TTA), which is observed in many PAHs. Rubrene, for example, undergoes ECL via both singlet and triplet routes.<sup>20,21</sup> In addition, the annihilation energies of these compounds decrease upon increased substitution, mirroring their absorption energies. These potentials are also a measure of the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps, which should correlate with the compounds' absorption energies. Among the five compounds, PM 546 (8-Me) has the highest annihilation energy whereas PM 597 (2,6-<sup>t</sup>Bu) has the lowest annihilation energy. This correlates well with the photophysical properties of the compounds, because PM 597 (2,6-<sup>t</sup>Bu) has the smallest  $E_s$  value and PM 546 (8-Me) has the highest  $E_s$  value. PM 567 (2,6-Et) and PM 580 (2,6-<sup>n</sup>Bu) showed very similar annihilation energies, suggesting that the inductive effects of ethyl and <sup>n</sup>Bu groups do not differ



**Figure 5.** ECL spectra of 1 mM PM 567 (2,6-Et) (solid line), PM 580 (2,6-*t*-Bu) (dotted line), and PM 597 (2,6-*t*-Bu) (×) in 0.1 M TBAP in MeCN with pulsing (0.1 s) between the oxidation and reduction peak potentials of the respective dyes. Inset: ECL spectrum of 1 mM PM 546 (8-Me) and 1 mM 10-MP obtained under the same conditions.

significantly, thus no major electrochemical and photochemical differences were observed between PM 567 (2,6-Et) and PM 580 (2,6-*t*-Bu) in MeCN. The only observable difference is their solubility in MeCN, where PM 567 (2,6-Et) is soluble up to 5 mM, versus 1 mM for PM 580 (2,6-*t*-Bu).

**Electrogenerated Chemiluminescence.** To generate ECL, the platinum working electrode was pulsed between peak potentials where oxidized and reduced forms were alternately produced. Among the five compounds, moderately strong ECL was observed from only three compounds—PM 567 (2,6-Et), PM 580 (2,6-*t*-Bu), and PM 597 (2,6-*t*-Bu)—upon radical ion annihilation. Under the same conditions, very weak emission was observed from PM 546 (8-Me) and none was observed from BODIPY, probably because of the instability of the cations and anions in solution. However, upon the addition of 10-MP, which is a compound that is capable of generating stable cations at potentials less positive than the oxidation potential of PM 546 (8-Me), relatively intense green emission was observed. This again indicates that the energy required to populate the singlet-excited state of PM 546 (8-Me) (2.50 eV) is much higher than the total free energy of the annihilation reaction between 10-MP and PM 546 (8-Me) (~1.87 V). The ECL of 10-MP was not observed here, because its singlet energy (~2.76 eV) is higher than that of PM 546 (8-Me). The triplet energy of PM 567 (2,6-Et) was recently shown to be ~1.63 eV, and, because of the similarities between PM 546 (8-Me) and PM 657, the free energy of annihilation obtained here should be sufficient to generate the triplet state of PM 546 (8-Me).<sup>19</sup>

Figure 5 shows the ECL spectra of 1 mM solutions of PM 567 (2,6-Et), PM 580 (2,6-*t*-Bu), and PM 597 (2,6-*t*-Bu) in MeCN containing 0.1 M TBAPF<sub>6</sub> as the supporting electrolyte during

repeated pulsing (pulse width of 0.1 s) between their oxidation and reduction peak potentials. The inset of Figure 5 shows the ECL spectrum of PM 546 (8-Me) obtained from repeated pulsing between its reduction peak potential and the oxidation peak potential of 10-MP. For these ECL experiments, solutions similar to those used for the electrochemistry experiments were utilized.

The ECL efficiency of PM 567 (2,6-Et), PM 580 (2,6-*t*-Bu), and PM 597 (2,6-*t*-Bu) was determined by comparing the number of photons emitted per electron or annihilation event, by comparison to a standard system with known ECL efficiency, Ru(bpy)<sub>3</sub><sup>2+</sup> (where bpy represents 2,2'-bipyridine).<sup>22</sup> This yielded efficiencies of  $\Phi_{\text{ECL}} = 0.009$  for PM 567 (2,6-Et), 0.007 for PM 580 (2,6-*t*-Bu), and 0.003 for PM 597 (2,6-*t*-Bu). The efficiency of PM 567 (2,6-Et) is about one-fifth that of Ru(bpy)<sub>3</sub><sup>2+</sup> ( $\Phi_{\text{ECL}} = 0.05$ ).<sup>22</sup> The ECL efficiency of PM 546 (8-Me) in the presence of 10-MP was not determined, but the light obtained was comparable in intensity to that of PM 597 (2,6-*t*-Bu). The light produced from a 1 mM solution of these four compounds was easily visible in a darkened room and appeared green for PM 546 (8-Me), yellow for both PM 567 (2,6-Et) and PM 580 (2,6-*t*-Bu), and orange for PM 597 (2,6-*t*-Bu). However, the ECL intensity depended on the condition of the electrode surface, and more-intense ECL was observed on a freshly polished electrode that had not been exposed to the dye solution for a long period of time before the ECL experiment. As shown in Figure 5, the ECL emission of PM 546 (8-Me), PM 567 (2,6-Et), PM 580 (2,6-*t*-Bu), and PM 597 (2,6-*t*-Bu) centered around 530, 550, 555, and 585 nm, respectively. When compared to the fluorescence spectra, the ECL spectra appear slightly broader in shape and slightly shifted to lower energy. This is probably due to an inner filter effect as a result of the high concentrations of the compound needed to obtain measurable ECL, as well as the difference in resolution between the two instruments where the spectra were collected. The observed ECL intensity of PM 597 (2,6-*t*-Bu) was lower than PM 567 (2,6-Et) and PM 580 (2,6-*t*-Bu), because of its lower fluorescence efficiency. The fluorescence efficiency of these dyes was previously shown to decrease with increasing size or electron-donating ability of the side groups.<sup>15</sup> PM 546 (8-Me) possesses the highest fluorescence efficiency among the dyes in this study; however, because of the instability of its radical cations, very weak ECL was observed upon radical ion annihilation. In the presence of 10-MP, the ECL of PM 546 (8-Me) was more intense than, but not comparable to, that of PM 567 (2,6-Et), which is the most efficient ECL emitting compound in this study. BODIPY, another highly fluorescent dye, showed no ECL, because of the instability of both the radical cation and anion. Even at higher pulse rates, where the contributions of the follow-up chemical reactions were smaller, no ECL was observed.

## Conclusion

The electrochemical, photochemical, and electrogenerated chemiluminescence (ECL) properties of five boron-containing dipyrromethene-BF<sub>2</sub> (PM-BF<sub>2</sub>) dyes were investigated. Dyes with a lower degree of substitution showed higher fluorescence efficiencies, as exemplified by BODIPY and PM 546 (8-Me); however, the lack of electron-donating substituents in positions 2, 6, and 8 caused a decrease in the stability of the cation and anion radicals, leading to irreversible electrochemical oxidation and reduction. This instability gave rise to a lack of ECL or a low ECL efficiency, in addition to film formation on the electrode upon radical ion annihilation. For PM 546 (8-Me),

more-intense ECL was observed only upon the addition of 10-methylphenothiazine (10-MP) as a source of stable cations. Highly substituted dyes such as PM 567 (2,6-Et), PM 580 (2,6-<sup>n</sup>Bu), and PM 597 (2,6-<sup>t</sup>Bu) demonstrated reversible electrochemical behavior, and moderately intense ECL was observed from these three dyes. Overall, the calculated ECL efficiencies for PM 567 ( $\Phi_{\text{ECL}} = 0.009$ ), PM 580 ( $\Phi_{\text{ECL}} = 0.007$ ), and PM 597 ( $\Phi_{\text{ECL}} = 0.003$ ) correlated well with their respective fluorescence efficiencies in the same solvent.

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**Supporting Information Available:** Figures showing the seven resonance structures of PM-BF<sub>2</sub> and structural names of the five dyes used in this study (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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