Synthesis, Electrochemistry, and Electrogenerated Chemiluminescence of Two BODIPY-Appended Bipyridine Homologues

Honglan Qi,†,§ Justin J. Teesdale,‡ Rachel C. Pupillo,‡ Joel Rosenthal,*‡ and Allen J. Bard*†

‡ Center for Electrochemistry, Department of Chemistry and Biochemistry, The University of Texas, Austin, Texas 78712, United States
§ Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States

Supporting Information

ABSTRACT: Two new 2,2’-bipyridine (bpy) derivatives containing ancillary BODIPY chromophores attached at the 5- and 5’-positions (BB3) or 6- and 6’-positions (BB4) were prepared and characterized. In this work, the basic photophysics, electrochemistry, and electrogenerated chemiluminescence (ECL) of BB3 and BB4 are compared with those previously reported for a related bpy-BODIPY derivative (BB2) (J. Phys. Chem. C 2011, 115, 17993–18001). Cyclic voltammetry revealed that BB3 and BB4 display reversible 2e− oxidation and reduction waves, which consist of two closely spaced (50–70 mV) 1e− events. This redox behavior is consistent with the frontier molecular orbitals calculated for BB3 and BB4 and indicates that the 2,2’-bipyridine spacer of each bpy-BODIPY homologue does not facilitate efficient electronic communication between the tethered indacene units. In the presence of a coreactant such as tri-n-propylamine (TPA) or benzoyl peroxide (BPO), BB3 and BB4 exhibit strong ECL and produce spectra that are very similar to their corresponding photoluminescence profiles. The ECL signal obtained under annihilation conditions, however, is significantly different and is characterized by two distinct bands. One of these bands is centered at ~570 nm and is attributed to emission via an S- or T-route. The second band occurs at longer wavelengths and is centered around ~740 nm. The shape and concentration dependence of this long-wavelength ECL signal is not indicative of emission from an excimer or aggregate, but rather it suggests that a new emissive species is formed from the bpy-BODIPY luminophores during the annihilation process.

INTRODUCTION

Electrogenerated chemiluminescence (ECL) involves the generation of oxidized and reduced species, often radical ions, that undergo a fast electron transfer reaction to produce a species in an excited state. The various mechanisms by which ECL processes take place have been extensively discussed. A prime pathway by which ECL is achieved is radical ion annihilation. An alternative mechanism involves consumption of a coreactant, which generates a reductant upon oxidation (or oxidant upon reduction) that reacts with the emission precursor. Coreactants can often be used to help elucidate ECL reaction mechanisms by providing a contrasting pathway to that observed for annihilation ECL. ECL is often produced by direct electron transfer reactions. In the annihilation mechanism, the energy is sufficient to populate the singlet excited state. Alternatively in cases where this energy is not sufficient to populate the singlet state, ECL can be generated by triplet–triplet annihilation (T-route), which provides an alternate route to the emissive species in the singlet excited state. Another ECL mechanism involves emission from an excited state dimer such as an excimer or exciplex (E-route). Exciplex emission is often encountered for aromatic molecules, including derivatives of thianthrene, stilbene, corannulene, perylene, anthracene, and naphthalene and is characterized by broad, structureless emission bands at long wavelengths.

4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) dyes were discovered in 1968 by Treibs and Kreuzer. Based on these attractive properties, BODIPY derivatives have found utility as laser dyes, photosensitizers, fluorescent labels for in vivo imaging, and in optical devices. The electrochemical and ECL properties of BODIPY derivatives are also of note, as these compounds often display reversible redox behavior in aprotic solvents and excellent stability upon oxidation or reduction. These attractive electrochemical properties, coupled with robust and tunable photophysics,
distinguish BODIPY derivatives as excellent candidates for ECL applications.34–36

A number of electrochemical37–39 and ECL studies40–45 of BODIPY dyes have been reported. In a recent study, we described the electrochemical, photophysical, and ECL properties of a 2,2′-bipyridine-BODIPY derivative (BB2), in which the meso-position of two fully substituted BODIPY moieties were linked directly to a 2,2′-bipyridine (bpy) spacer at the 4- and 4′-positions.46 This BODIPY-appended bipyridine derivative was highly fluorescent and produced strong ECL emission in the presence of a coreactant. Given that the electronic properties of bpy derivatives are sensitive to the substitution pattern about the bpy framework, we were curious as to whether the photophysics and ECL emission might be tuned by altering the position to which the BODIPY moieties were attached. To this end, we have developed two new BODIPY-appended bipyridine derivatives, in which the BODIPY units were linked to the bpy spacer at either the 5,5′- (BB3) or 6,6′-positions (BB4). These new compounds, which are juxtaposed with our previously reported bpy-BODIPY derivative (BB2) in Chart 1, were thoroughly characterized by a combination of photophysical, electrochemical, and ECL methods. Of note is our finding that BB3 and BB4 exhibit a bifurcated ECL signal which is distinct from that simply observed by photoluminescence experiments.

### EXPERIMENTAL SECTION

#### General Materials and Methods.
Reactions were performed in oven-dried round-bottomed flasks unless otherwise noted. Reactions that required an inert atmosphere were conducted under a positive pressure of N2 using Suba-Seal rubber septa or in a nitrogen-filled glovebox (MBraun Inc., Stratham, NH) without further purging. All solvents were linked to the bpy spacer at either the 5,5′-bipyridine (bpy) spacer at the 4- and 4′-positions.46 This BODIPY-appended bipyridine derivative was highly fluorescent and produced strong ECL emission in the presence of a coreactant. Given that the electronic properties of bpy derivatives are sensitive to the substitution pattern about the bpy framework, we were curious as to whether the photophysics and ECL emission might be tuned by altering the position to which the BODIPY moieties were attached. To this end, we have developed two new BODIPY-appended bipyridine derivatives, in which the BODIPY units were linked to the bpy spacer at either the 5,5′- (BB3) or 6,6′-positions (BB4). These new compounds, which are juxtaposed with our previously reported bpy-BODIPY derivative (BB2) in Chart 1, were thoroughly characterized by a combination of photophysical, electrochemical, and ECL methods. Of note is our finding that BB3 and BB4 exhibit a bifurcated ECL signal which is distinct from that simply observed by photoluminescence experiments.

#### Compound Characterization.
1H and 13C NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Proton spectra are referenced to the residual proton resonance of the deuterated solvent (CDCl3 = 0.0 ppm), and carbon spectra are referenced to the carbon resonances of the solvent (CDCl3 = 0.0 ppm). DMSO-d6 = δ 40.45). All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. LR-GCMS data were obtained using an Agilent gas chromatograph consisting of a 6890 Series GC System equipped with a 5973 Network Mass Selective Detector. Low resolution MS data were obtained using either an LCQ Advantage from ThermoFinnigan or a Shimadzu LC/MS-2020 single quadrupole MS coupled with an HPLC system, with a dual ESI/APCI source. High-resolution mass spectrometry analyses were either performed by the Mass Spectrometry Laboratory in the Department of Chemistry and Biochemistry at the University of Delaware or at the University of Illinois at Urbana—Champaign.

#### Chart 1. Structures of BODIPY-Appended Bipyridine Derivatives

![Chart 1. Structures of BODIPY-Appended Bipyridine Derivatives](image-url)
6,6′-Bis(BODIPY)-2,2′-bipyridine (BB4). This compound was prepared according to the same method used for the preparation of 5,5′-Bis(BODIPY)-2,2′-bipyridine (BB3), using 2,2′-bipyridine-6,6′-dicarboxylic acid (2) in place of 2,2′-bipyridine-5,5′-dicarboxylic acid (1). The desired product was purified via flash column chromatography on silica using CH2Cl2 as the eluent to deliver 610 mg (36%) of the title compound as a brick red powder.1H NMR (400 MHz, CDCl3, 25 °C) δ ppm: 8.49 (d, J = 8.0 Hz, 2H), 7.92 (t, J = 7.8 Hz, 2H), 7.45 (d, J = 6.8 Hz, 2H), 2.56 (s, 12H), 2.31 (q, J = 7.5 Hz, 8H), 1.27 (s, 13H), 0.99 (t, J = 7.5 Hz, 12H). 13C NMR (101 MHz, CDCl3, 25 °C) δ 156.05, 154.67, 154.16, 138.04, 137.77, 137.26, 132.96, 130.74, 124.82, 121.43, 17.09, 14.68, 12.68, 11.49. HR-ESI-MS [M+H]+ m/z: calcd for C44H52B2F4N6, 761.4297. Found 761.4301.

Electrochemical Experiments. Electrochemistry experiments were carried out using a three-electrode setup that employed a 0.043 cm2 platinum disk working electrode (WE), a platinum counter electrode (CE), and a silver wire quasi-reference electrode (RE) calibrated using ferrocene as an internal standard (0.342 V vs SCE).48 Electrochemical Experiments were carried out in CH2Cl2 containing 0.1 M TBAPF6 as the supporting electrolyte. Cyclic voltammetry and chronoamperometry experiments were carried out with a CH Instruments (Austin, TX) model 660 electrochemical workstation. Electrochemistry experiments were carried out in CH2Cl2 containing 0.1 M TBAPF6 as the supporting electrolyte.

ECL Experiments. ECL spectra were generated by annihilation by pulsing the potential with a pulse width of 0.1 s from about 80 mV past the peak potentials, or by stepping from 0 to 80 mV from the reduction peak with a step time of 2 s using benzoyl peroxide as a coreactant or by stepping from 0 V to 80 mV from the oxidation peak with a step time of 2 s using TPA as a coreactant. ECL spectra were recorded with a Princeton Instruments Spec 10 CCD camera (Trenton, NJ) with an Acton SpectroPro-150 monochromator cooled with liquid nitrogen to ~100 °C. ECL-CV simultaneous experiments were carried out prior to spectral measurements to ensure the presence of ECL emission. In this case, a multichannel Eco Chemie Autolab PGSTAT100 (Utrecht, The Netherlands) was used to collect the signal and a photomultiplier tube (Hamamatsu R4220, Tokyo, Japan) was used as a detector. Voltage for the PMT (750 V) was provided by a Kepco power supply (New York, NY), and the signal from the PMT to the potentiostat was transferred using a multichannel Eco Chemie Autolab PGSTAT100 (Utrecht, The Netherlands).

Computed. Geometry optimizations, frequency calculations, and molecular orbital calculations were performed in Gaussian 09 using the B3LYP/6-311G(d) basis set. Only positive frequencies were found for the optimized structures. Molecular orbitals were visualized using GaussianView software. All calculations were performed in the gas phase.

RESULTS AND DISCUSSION

Synthesis. The synthetic protocols used to construct the bpy-BODIPY derivatives 5,5′-bis(BODIPY)-2,2′-bipyridine (BB3) and 6,6′-bis(BODIPY)-2,2′-bipyridine (BB4) are shown in Scheme 1. Preparation of BB3 begins with the conversion of 5,5′-dimethyl-2,2′-bipyridine to the corresponding dicarboxylic acid (1) via oxidation with K2MnO4 in water (Scheme 1a). Following purification, the dicarboxylic acid derivative was treated with excess thionyl chloride to generate the corresponding acid chloride derivative. Condensation of this intermediate with 2,4-dimethyl-3-ethylpyrrole followed by treatment with NEt3 and BF3·OEt2 afforded 5,5′-bis(BODIPY)-2,2′-bipyridine (BB3) in 44% yield. Synthesis of the homologous 6,6′-bis(BODIPY)-2,2′-bipyridine (BB4) derivative was accomplished in 36% yield from dicarboxylic acid 2 using an analogous strategy (Scheme 1b).

Electrochemistry. The basic redox properties of BB3 and BB4 were probed by cyclic voltammetry (CV). Electrochemical results obtained for both bpy-BODIPY derivatives in CH2Cl2 containing 0.1 M TBAPF6 as the supporting electrolyte are summarized in Table 1, and pertinent CVs are shown in Figure 1. As was previously observed for BB2, both BB3 and BB4 show single redox waves upon oxidation or reduction. Both these waves consist of two closely spaced one-electron (1e−) events, as confirmed by digital simulation. Overall 2e− reduction and oxidation waves were also observed for BB3 and BB4 using a platinum ultramicroelectrode (Figure S1). Fitting of the CV traces was carried out by subtraction of the background current and determining the best fit to the simulation corrected for the measured electrical double layer capacitance and the uncompensated cell resistance (Supporting Information Figures S4–S7).

Scheme 1. Synthesis of BODIPY-Appended Bipyridine Derivatives BB3 and BB4

13560 dx.doi.org/10.1021/ja406731f J. Am. Chem. Soc. 2013, 135, 13558–13566
The small separation observed for the two reductive and oxidative electron transfer events is consistent with there being negligible electronic coupling between the two BODIPY moieties via the bipy spacers of both BB3 and BB4. For two groups that are completely uncoupled, the theoretical difference between the potentials for the first and second electron transfers would be 36 mV due to entropic factors. As was the case for BB2, the weak electronic coupling between the two BODIPY groups of BB3 and BB4 is manifest in small separations in potential between the A/A+ and A+/A2+ redox processes (Table 1). If the BODIPY groups were more strongly coupled, the two oxidation and reduction waves would be more broadly separated with the A/A+ and A+/A2+ shifted toward more extreme potentials, as has been observed for BODIPY derivatives containing directly linked indacene moieties.

DFT calculations carried out for BB3 and BB4 confirm that the BODIPY moieties of both these molecules are effectively insulated from one another, as steric demands force the indacene frameworks to cant significantly with respect to the bipyridine bridges. Orthogonalization of the BODIPY moieties and bipy spacer results in the HOMO and LUMO of both BB3 and BB4 residing on the individual chromophores. These calculations provide no evidence for electronic delocalization onto the bipyridine spacer (Figure 2).

Oxidation and reduction of both BB3 and BB4 are reversible, which is consistent with the high stability of the radical cation and anion products formed at the electrode surface. This stability is a result of the BODIPY units of both bipy-BODIPY homologues being completely substituted along the indacene periphery, which prevents decomposition of the electrochemically generated radical ions. Randles–Sevcik analysis showed that the measured oxidation and reduction peaks vary linearly as a function of the square root of the scan rate (ν1/2) (Supporting Information Figures S2 and S3), indicating that these redox processes are diffusion controlled. In an effort to obtain better insight into the mechanism and kinetics of both the anodic and cathodic processes, the experimental polarization curves for BB3 and BB4 were digitally simulated (Supporting Information Figures 3 and S4–S7). Both the cathodic and anodic CVs of BB3 were characterized by two reversible 1e− transfers, with a fast heterogeneous rate constant (k° > 0.01 cm/s) for both reaction steps (Supporting Information Figures 3a, b, S4, and S5). Virtually identical parameters were also found for BB4 (Supporting Information Figures 3c, d, S6, and S7). The slight differences between simulated and experimental polarization curves may be attributed to weak adsorption of the bipy-BODIPY derivatives to the working electrode. BODIPY redox sites can often be oxidized or reduced by two electron equivalents. As such, the bipy-BODIY constructs considered here might be expected to be able to donate up to four electrons at sufficiently positive

---

**Table 1. Redox Potentials Recorded for BB2–BB4 in CH2Cl2**

<table>
<thead>
<tr>
<th></th>
<th>E1/2 (A/A+)</th>
<th>E1/2 (A+/A2+)</th>
<th>E1/2 (A/A+)</th>
<th>E1/2 (A+/A2+)</th>
<th>ΔG_{ann}</th>
<th>ΔH_{ann}</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB2</td>
<td>1.11 V</td>
<td>1.15 V</td>
<td>−1.15 V</td>
<td>−1.22 V</td>
<td>4.0 cm²/s</td>
<td>2.33 eV</td>
</tr>
<tr>
<td>BB3</td>
<td>1.14 V</td>
<td>1.19 V</td>
<td>−1.17 V</td>
<td>−1.24 V</td>
<td>4.0 cm²/s</td>
<td>2.13 eV</td>
</tr>
<tr>
<td>BB4</td>
<td>1.12 V</td>
<td>1.17 V</td>
<td>−1.18 V</td>
<td>−1.24 V</td>
<td>4.0 cm²/s</td>
<td>2.30 eV</td>
</tr>
</tbody>
</table>

*E1/2 values were obtained by fitting the experimental results to digital simulations and are reported versus SCE. Data for BB2 are reproduced from ref 46. ΔG_{ann} = E1/2(A/A+) − E1/2(A+/A2+). ΔH_{ann} = ΔG_{ann} − 0.1 eV.*

---

**Figure 1.** Cyclic voltammograms of CH2Cl2 solutions of (a) 0.59 mM BB3 and (b) 0.68 mM BB4. CVs were recorded using 0.1 M TBAPF6 as the supporting electrolyte using a platinum disk working electrode (A = 0.043 cm²) and a scan rate (ν) of 100 mV/s.

**Figure 2.** Calculated frontier molecular orbitals for BB3 and BB4 by DFT (B3LYP/6-311G(d)).
potentials. CV scans recorded for BB3 and BB4 in CH2Cl2 over the potential range of 0.1–2.4 V versus SCE revealed a second irreversible peak at ~2.05 V (Figure 4). This second oxidation wave is more positive than the first 2e\(^-\) wave by ~0.9 V, which is consistent with that observed for other BODIPY derivatives\(^2\,\,4\) and is presumed to correspond to removal of a third and fourth e\(^-\) from the bpy-BODIPY derivatives. The reductive window of CH2Cl2 precludes scanning to potentials significantly more negative than the first reduction waves; however, THF, which has a more negative working potential range, was used to study the reduction of BB3 and BB4 beyond ~1.5 V. An additional reduction wave was observed for BB4 at approximately ~2.3 V versus SCE; however, BB3 did not show a new redox wave beyond the first 2e\(^-\) reduction. This divergent behavior is likely a result of the distinct molecular topologies of the two bpy-BODIPY homologues (Chart 1).

**Photophysics.** The basic photophysical properties of BB3 and BB4 were assessed in CH2Cl2 (Figure 5) and are summarized in Table 2. Both BB3 and BB4 display optical properties analogous to those of the previously studied BB2 homologue and other related BODIPY derivatives. UV–vis absorbance and emission spectra for BB3 and BB4 are shown...
Both of these compounds display strong absorption bands in the visible region centered at approximately 528 nm ($S_0 \rightarrow S_1$ transition) and 371 nm ($S_0 \rightarrow S_2$ transition). The molar absorption coefficients of BB3 and BB4 in CH$_2$Cl$_2$ were measured to be $8.2 \times 10^4$ and $6.7 \times 10^4$ M$^{-1}$ cm$^{-1}$, respectively.

These relatively high absorptivities are consistent with there being two BODIPY chromophores appended to the bipyridine bridge for both compounds. These molar absorptivities are similar in magnitude to that determined for BB2 (Table 2).

The bipyridine spacer of BB3–BB4 causes the major absorbance band observed for each of these derivatives to undergo a hypsochromic shift of approximately 7 nm relative to the analogous BODIPY dye bearing a methyl substituent at the indacene meso-position (PM567). These hypsochromic shifts can be attributed to an inductive electron withdrawing effect of the bipyridine spacer.

Excitation of BB3 and BB4 leads to a greenish-yellow emission, centered at 545 and 543 nm, respectively (Figure 5, Table 2). The small Stokes shift observed for both bipy-BODIPY derivatives was also observed for BB2 and is typical of many BODIPY dyes. Measured quantum yields of fluorescence ($\Phi_{Fl}$) for BB3 and BB4 (0.39 and 0.47, respectively) are also similar to that determined for BB2. Notably, there was no evidence for dimerization or aggregation.

**Table 2. Photophysical and ECL Properties Recorded for BB2–BB4 in CH$_2$Cl$_2$**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{Fl}$ (nm)</th>
<th>$\Phi_{Fl}$</th>
<th>$E_{0-0}^a$ (eV)</th>
<th>$\lambda_{ECL}$ (nm)</th>
<th>$\Phi_{ECL}^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB2$^b$</td>
<td>528</td>
<td>$8.4 \times 10^4$</td>
<td>547</td>
<td>0.39</td>
<td>2.26</td>
<td>554</td>
<td>–</td>
</tr>
<tr>
<td>BB3</td>
<td>528</td>
<td>$8.2 \times 10^4$</td>
<td>545</td>
<td>0.39</td>
<td>2.27</td>
<td>570, 740</td>
<td>0.006</td>
</tr>
<tr>
<td>BB4</td>
<td>528</td>
<td>$6.7 \times 10^4$</td>
<td>543</td>
<td>0.47</td>
<td>2.28</td>
<td>571, 741</td>
<td>0.010</td>
</tr>
</tbody>
</table>

$^a$ $E_{0-0}$ approximate energy of the first singlet excited state taken as the fluorescence wavelength maximum.

$^b$ Data for BB2 are reproduced from ref 46.

$^c$ ECL efficiencies were determined using [Ru(bpy)$_3$]$^{2+}$ in MeCN as a standard, for which $\Phi_{ECL} = 0.05$.

**Figure 5.** Normalized absorbance (red) and emission (blue) spectra for (a) BB3 and (b) BB4 in CH$_2$Cl$_2$. Emission samples were excited at $\lambda_{ex} = 480$ nm.

**Figure 6.** Fluorescence (blue) and ECL (red) spectra of (a) BB3 and (b) BB4. ECL emission was generated by oscillating the potential with a pulse width of 0.1 s from ~80 mV past the first oxidation and reduction waves of each Bpy-BODIPY homologue. ECL spectra were recorded in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ with an accumulation time of 2 min.
of the bpy-BODIPY complexes in solution, as the shape and normalized intensity of the photoluminescence spectra recorded for BB3 and BB4 did not vary as a function of dye concentration.

**Electrogenerated Chemiluminescence.** Initial ECL studies for BB3 and BB4 were carried out by pulsing between the first reduction and oxidation potentials (80 mV past both the reduction and oxidation waves). ECL spectra obtained via annihilation of the ions and diions generated during these experiments are shown in Figure 6, and associated spectral data are listed in Table 2. Two ECL emission peaks are observed for both bpy-BODIPY homologues. Higher-energy ECL bands were observed at ∼570 nm, which are similar in energy to those observed in the photoluminescence spectrum. Lower-energy ECL signals were also resolved at ∼740 nm. By contrast, when the excited states of BB3 or BB4 were generated under oxidizing conditions using tripropylamine (TPA) as a coreactant, or under reducing conditions using benzoyl peroxide (BPO) as a coreactant, only the high-energy ECL peaks (λ_{ECL} ≈ 570 nm) were observed (Figure 7). These ECL emission profiles are very similar to the normal fluorescence spectra observed for BB3 and BB4 when corrected for a small difference inner filter effect (Figure 7).\textsuperscript{46} Virtually identical results were obtained previously for BB2, suggesting that all three bpy-BODIPY derivatives produce ECL via the common pathways shown in Scheme 2.\textsuperscript{46}

In order to clarify the nature of the excited state from which ECL emission is produced for BB3 and BB4, the enthalpy of annihilation (ΔH_{ann}) was assessed for both compounds. This parameter was estimated from the reversible standard potentials for the reduction and oxidation of each of the bpy-BODIPY homologues according to the expression ΔH_{ann} = ΔG_{ann} - TΔS. The free energy of annihilation (ΔG_{ann}) was calculated as the difference between E_{1/2}(A/A') and E_{1/2}(A/A^-), and TΔS was estimated to be 0.1 eV,\textsuperscript{55} leading to an estimation of ΔH_{ann} ≈ 2.20 eV. The energies of the first singlet excited state (E_0) of BB3 and BB4 were also determined based on their maximal fluorescence wavelength (λ_{Fl}) to be E_0 = 2.27 eV. The estimated values of ΔH_{ann} and E_0 for BB3 and BB4 differ by less than 0.1 eV, which suggests that the bpy-BODIPY ECL and fluorescence originate from the same excited state. Moreover, these results suggest that the ECL signal observed at ∼570 nm for BB3 and BB4 is generated through either an S- or a T-route (vide supra).

In addition to the ECL signal at ∼570 nm, long-wavelength emission at ∼740 nm was also observed under annihilation conditions. This long-wavelength signal was not observed in the photoluminescence spectra recorded for BB3 and BB4. As has been observed for previously studied BODIPY derivatives,\textsuperscript{34} long-wavelength ECL can be generated via formation of excimers; however, such signals are usually broad and structureless. That the ECL signal observed for BB3 and...
**SUMMARY**

Two new 2,2′-bipyridine derivatives containing ancillary BODIPY units at either the 5- and 5′- (BB3) or 6- and 6′-positions (BB4) were prepared, and the basic photophysics, electrochemistry, and ECL properties of these bpy-BODIPY homologues were investigated. These properties are similar to those observed for a related bpy-BODIPY derivative in which two BODIPY moieties were coupled to a 2,2′-bipyridine spacer at the 4- and 4′-positions (BB2). All three of the bpy-BODIPY constructs are strongly absorbing in the visible region and display high fluorescence quantum yields in CH2Cl2. Cyclic voltammetry showed that the new bpy-BODIPY derivatives (BB3 and BB4) also maintain redox properties that are similar to that observed for BB2. All three systems display reversible 2e− oxidation and reduction waves, which consist of two closely spaced (50–70 mV) 1e− events. These observations are consistent with the calculated frontier molecular orbitals for these compounds and indicate that the 2,2′-bipyridine spacer of each bpy-BODIPY homologue does not facilitate efficient electronic communication between the tethered indacene units, regardless of their position on the bpy bridge.

ECL experiments for BB3 and BB4 correlate with the observed electrochemistry. In the presence of a coreactant (TPA or BPO) both of these bpy-BODIPY derivatives exhibit strong ECL and produce spectra that are very similar to their corresponding fluorescence profiles. Similar results have been observed for BB2. Under annihilation conditions, however, the ECL signal obtained from BB3 and BB4 is distinct and is characterized by two major bands. One of these bands is centered at ~570 nm and is attributed to emission via an S- or a T-route. The second band occurs at longer wavelengths and is centered around ~740 nm. This long-wavelength ECL signal was not observed in the BB3 or BB4 photoluminescence spectra. The shape and concentration dependence of this long-wavelength ECL band was not indicative of luminescence from an excimer or aggregate, but rather is generated by a new species formed from the bpy-BODIPY luminophores during the annihilation process. Future work will be needed to elucidate the structure of these electrochemical products, which may be comprised of bpy-BODIPY dimers, oligomers, or more extended assemblies.

**ASSOCIATED CONTENT**

Supporting Information

Electrochemistry and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

ajbard@mail.utexas.edu; joelr@udel.edu
Acknowledgments

A.J.B. acknowledges support from the Robert A. Welch Foundation (F-0021) and the National Science Foundation (CHE-1111518). J.R. was supported through a DuPont Young Professor award. J.R. also thanks the University of Delaware and the Donors of the American Chemical Society’s Petroleum Research Fund for financial support. H.L.Q. thanks the National Science Foundation of China (Nos. 21375084, 21027007), the Natural Science Basic Research Plan in Shaanxi Province of China (No. 2013KJJX-73), and the Fundamental Research Funds for the Central Universities (No. GK261001185) for support. NMR and other data were acquired using instrumentation obtained with assistance from the NSF (CHE-0421224, CHE-0840401, CHE-1048367 and CHE-1229234).

References