

Electrochemistry and Electrogenenerated Chemiluminescence of BODIPY Dyes

ALEXANDER B. NEPOMNYASHCHII AND ALLEN J. BARD*

*Center for Electrochemistry, Chemistry and Biochemistry Department,
The University of Texas at Austin, Austin, Texas, 78712*

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CONSPECTUS

BODIPY (boron dipyrromethene) dyes are unique materials with spectroscopic and electrochemical properties comparable to those of aromatic hydrocarbons. Electrochemical studies are useful in understanding the redox properties of these materials and finding structure–stability relations for the radical ions; along with spectroscopy, these studies help researchers design novel compounds with desired properties.



This Account represents our attempt at a full description of the electrochemical and electrogenerated chemiluminescence (ECL) properties of the BODIPY dyes. When the dyes are completely substituted with alkyl or other groups, the radical ions of BODIPY dyes are highly stable. But if they include unsubstituted positions, the radical ions can undergo dimerization or other reactions. BODIPY dyes also show unusually large separations, ~ 1.0 V, between the first and second cyclic voltammetric (CV) waves for both oxidation and reduction half-reactions. Alkyl-substituted BODIPY dyes show good photoluminescence (PL) quantum efficiencies, and radical ion electron transfer annihilation in these molecules produces electrogenerated chemiluminescence (ECL), the intensity of which depends on the structure of the dye. The large separation between waves and the presence of strong ECL signals are both important in the design of stable ECL-based materials. The ECL spectra provide a fast method of monitoring the electrochemical formation of dimers and aggregates from the monomers. BODIPY dyes are particularly good systems for studying stepwise electron transfer in their chemically synthesized oligomers and polymers because of the small separation between the first oxidation and first reduction waves, generally about 2.0–2.4 V, and their relative ease of reduction compared with many other aromatic compounds. The larger separation between consecutive waves for oxidation compared with reduction is noticeable for all BODIPY dimers and trimers. We also observe a more difficult addition or extraction of a third electron compared with the second for the trimers, signaling the importance of electrostatic interactions. In general, BODIPY dyes combine interesting electrochemical and spectroscopic properties that suggest useful analytical applications.

Introduction

This Account is an attempt to describe comprehensively the electrochemical and electrogenerated chemiluminescence (ECL) properties of the BODIPY dyes. BODIPY dyes or boron pyrromethene or bora-indacene dyes are useful materials that have been proposed for applications in biological sensing, energy light harvesting, catalysis, optical devices, and laser materials.^{1–12}

Although the first BODIPY compounds were synthesized in 1968,¹³ the current interest began mostly in the 1990s from the work of Boyer and co-workers who applied these dyes as laser materials.¹⁴ Currently BODIPY dyes are commercially available, for example, for application as laser dyes and for biological labeling experiments of DNA, proteins, and lipids,¹⁵ from companies like Exciton, Inc., and

Invitrogen, Inc.^{15,16} Most of the research of these compounds has been concerned with their properties, with fewer publications on their electrochemical and ECL properties.^{17–31} This Account will mostly deal with the results recently obtained by our group,^{22–27} although studies of the electrochemical properties of the BODIPY dyes is an area of current interest, among other groups.^{28–34}

Electrochemical Properties of the BODIPY Dyes

Electrochemical properties of the representative BODIPY compounds are summarized in Table 1. The electrochemical properties of BODIPY dyes strongly depend on the nature of the substitution in the meso, α , and β positions (Scheme 1, Figure 1).

TABLE 1. Photophysical and Electrochemical Properties of Selected BODIPY Compounds

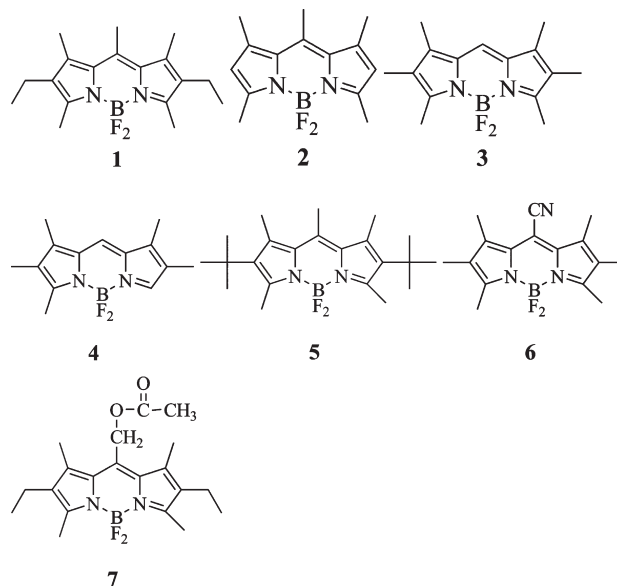
dye	$\lambda_{\max}(\text{abs})$	$\lambda_{\max}(\text{fl})$	Φ_{fluor}^b	$E_{1/2}^a(\text{SCE})$		$\lambda_{\max}(\text{ECL})$	Φ_{ECL}^c
				A/A ⁻	A/A ⁺		
1	371, 521	538	0.99	-1.37	0.95	551	0.21
2	360, 496	512	0.99	-1.22	1.12	540	0.006
3	380, 529	541	1.00	-1.30	1.11	560	0.008
4	383, 524	537	1.0	-1.32	1.12, 1.57	656	0.005
5	379, 527	566	0.75	-1.34	0.98	572	0.15
6	432, 596	623	0.50	-0.82	1.14	630	0.01
7	385, 549	572	0.92	-1.2 (E_{pc1}), -1.42 (E_{pc2})	0.98	614	0.002
8	641	655	0.28	-1.05	0.72	674	0.06
9	468, 647	682	0.30	-0.44	1.14	695	<0.001
10	389, 486, 556	643	0.7	-1.15, -1.40	0.95, 1.45	666	0.1
11	368, 526	563	0.66	-1.17, -1.29	1.09, 1.31	587	0.008
12	370, 550	587	0.60	-1.15, -1.24, -1.43	1.04, 1.17, 1.42	607	0.011
13	378, 590	614	0.35	many	many	620	<0.001
14	488, 696	720	<0.01	-0.37, -0.5	1.10, 1.24		
15	387, 489, 562	650	0.7	-1.20, -1.57	0.97, 1.47	679	0.004
16	368, 520	532	0.99	-1.33	1.02	566, 706	0.19
17	360, 526	537	0.84	-1.40	0.96	551, 741	0.006
18	497	506	0.64	-1.29	1.05	516, 581, 663, 752	0.003
19	504	528	0.39	-1.15, -1.22	1.11, 1.15	554	0.001
20	524	537	0.5	-1.5	0.9	560	<0.01

^a $E_{1/2}$ is shown for all compounds except **7**, where E_p values are used. ^bRelative to fluorescein. ^cRelative to Ru(bpy)₃²⁺ under similar conditions. The fluorescence efficiencies are normalized with respect to fluorescein (absolute fluorescence efficiency 0.81),³⁵ and ECL efficiencies are normalized with respect to Ru(bpy)₃²⁺ (absolute ECL efficiency 0.05).³⁶

SCHEME 1. Structure of the BODIPY Core

The completely substituted dye **1** shows reversible Nernstian one-electron oxidation and reduction with formation of stable radical ions (Figure 1a). Absence of substitution in positions 2, 3, 5, or 6 causes instability of the radical cation produced on oxidation, for example, **2** and **4**, and lack of the substitution in position 8 causes the radical anion produced on reduction to be more reactive, for example, **3** and **4** (Figure 1b–d). This finding corresponds to the distribution of the electron density in the BODIPY core.²³ Instability on oxidation is similar to the behavior seen for pyrroles and thiophenes, but greater steric protection prevents the fast dimerization and polymerization, which is a feature of these compounds.^{37,38} Dye **5** with *t*-butyl groups in positions 2 and 6 shows a smaller separation, about 0.1 V, between the first oxidation and reduction waves as compared with **1** (Figure 1e). The inductive electron-withdrawing effect of a cyano group in position 8, as in **6**, makes the reduction easier by about 0.3 V compared with **1** (Figure 1f). Dye **7** with an acetoxymethyl group in position 8 shows a more closely spaced second reduction wave compared with other BODIPY compounds (Figure 1g).^{23,32} Dyes like **8**, called by Ziessel et al. E-BODIPY dyes, are formed through introduction of

ethynyl or ethynylaryl groups instead of fluorine atoms on the boron.³⁹ The electrochemical reversibility was largely unaffected by the presence of the bulky groups and showed Nernstian reductions but some instability on oxidation due to absence of the substitution in positions 2 and 6 (Table 1). The radical cation stability is slightly higher compared with the weakly blocked dye **2**. Dyes **6**, **8**, and **9** show a separation of about 1.6 to 2.0 V between the first oxidation and reduction waves (Table 1)⁴⁰ and small Stokes shifts.^{20–24} Aza-BODIPY dye **9**, with an acceptor nitrogen atom in position 8, shows a shift of the potential for reduction of around 1.0 V, while the oxidation potential is the same as for



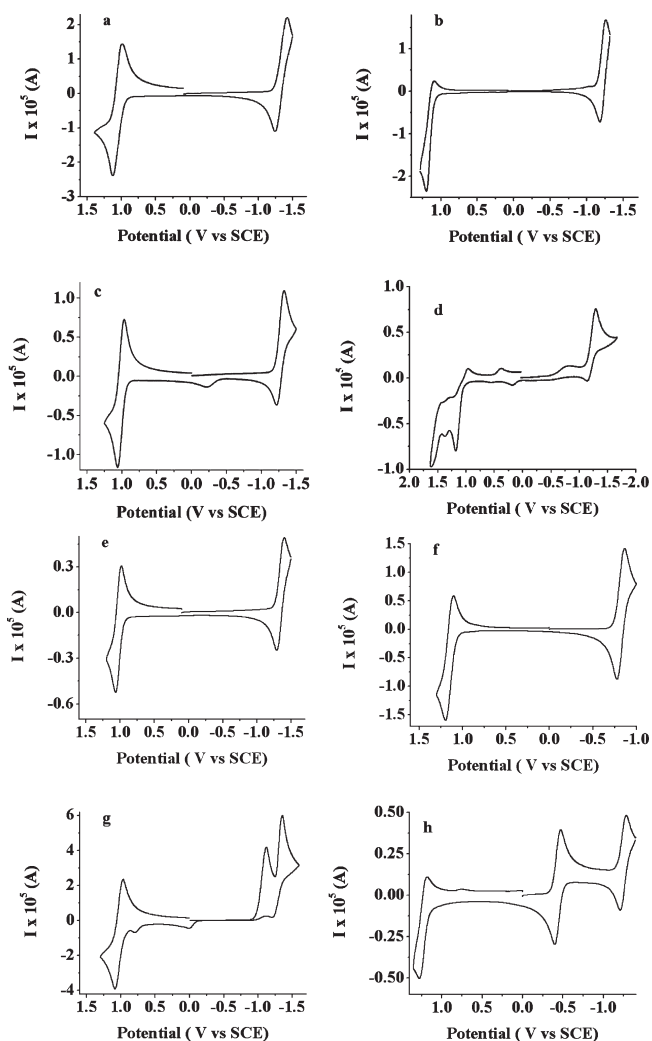


FIGURE 1. Cyclic voltammogram of dyes: (a) 3.0 mM **1**; (b) 2.2 mM **2**; (c) 1.5 mM **3**; (d) 1.5 mM **4**; (e) 0.6 mM **5**; (f) 0.6 mM **6**; (g) 7 mM **7**; (h) 0.6 mM **9**. Scan rate = 0.1 V/s; solvent = DCM. Electrode area = 0.0314 cm²; supporting electrolyte = 0.1 M TBAPF₆. Reprinted and adapted with permission from refs 23–25. Copyright 2010–2011 American Chemical Society.

the BODIPY dyes with a carbon in position 8 (represented as C⁸-BODIPY). (Figure 1h).²⁴ A second reversible wave with a separation of ~0.8 V from the first corresponds to the

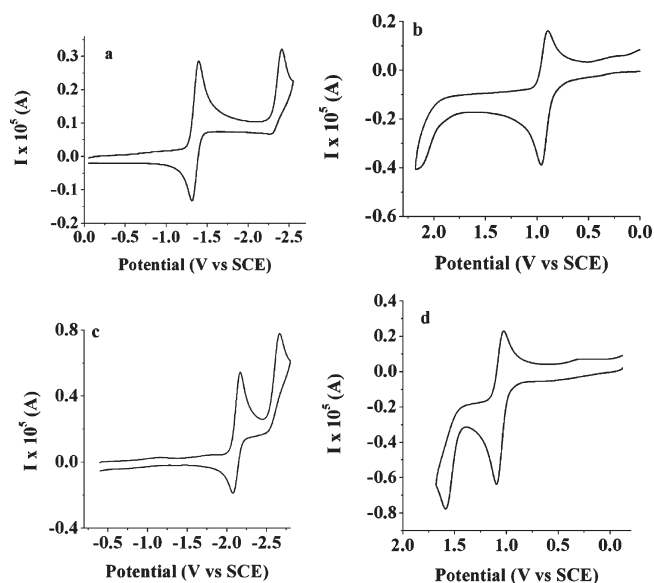
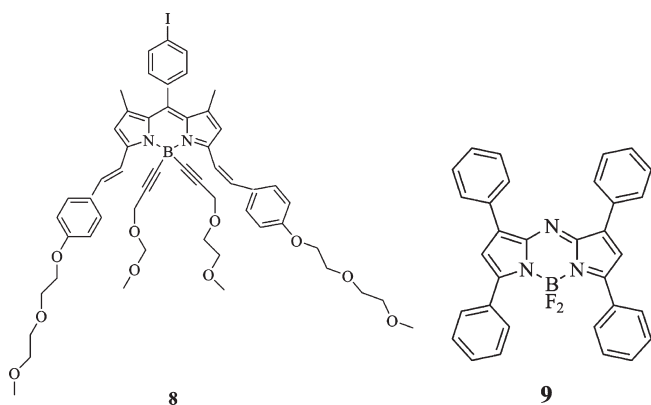
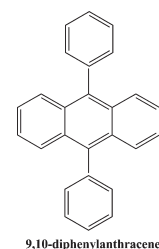


FIGURE 2. Cyclic voltammograms of (a, b) 0.5 and 0.6 mM **1** and (c, d) 1.0 mM 9,10-diphenylanthracene. Scan rate = 0.1 V/s; solvent = (a, c) THF or (b, d) acetonitrile. Electrode area = 0.0314 cm²; supporting electrolyte = 0.1 M TBAPF₆. Reprinted and adapted with permission from ref 23. Copyright 2010 American Chemical Society.

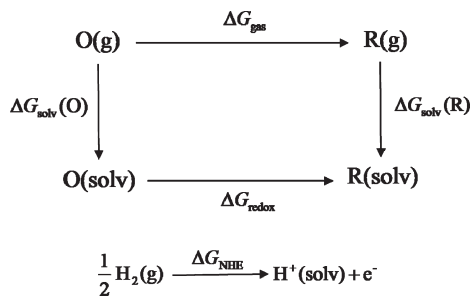
addition of a second electron; better reversibility can be achieved in methylene chloride at room temperature and in ultrahigh purity solvents like SO₂ at low temperature.^{24,41–43} Reversibility on oxidation requires substituents in positions 2 and 6, just as with C⁸-BODIPY.

As with C⁸-BODIPY, aza-BODIPY dyes show a large separation between the first and second oxidation and reduction waves, ~0.8–1.0 V, which is substantially larger than that of polycyclic aromatic compounds, ~0.5 V (Figure 2).²³

Theoretical calculations using DFT (the AM1 method) for a completely substituted dye, like **1**, show that electronic factors rather than solvation are largely responsible for this large separation (Scheme 2, Table 2).^{23,44} Similar calculations carried out for 9,10-diphenylanthracene (DPA) demonstrate the validity of these calculations and predict a separation of ~0.5 V between waves for consecutive electron transfers for DPA.



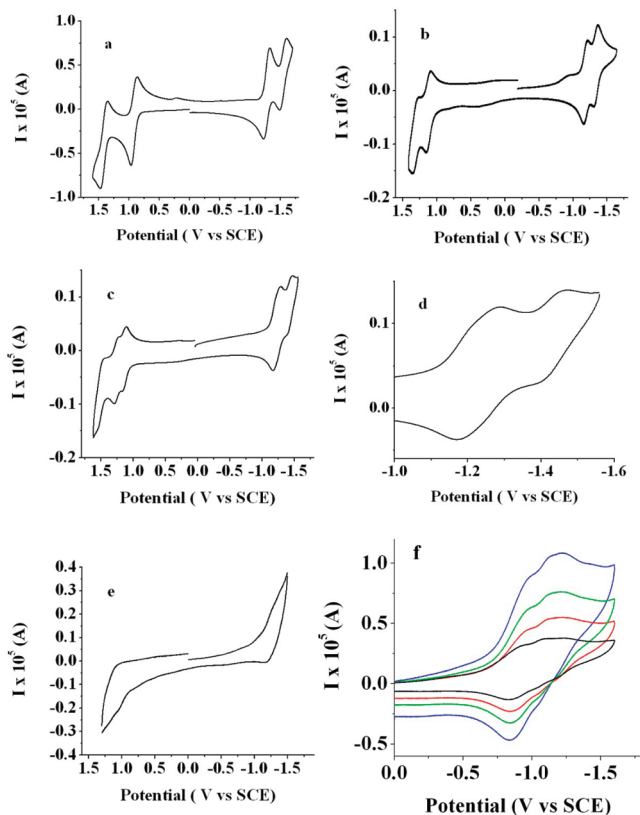
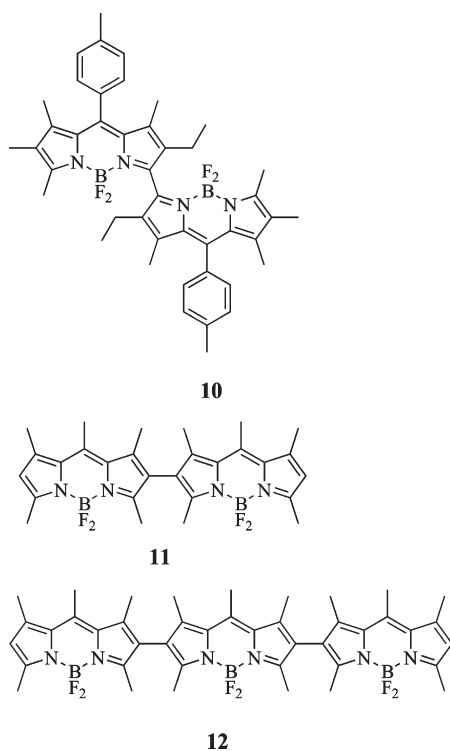
The properties of the monomers can be compared with larger units from dimer to longer oligomers. Dimers of the BODIPY dyes show interesting behavior where the

SCHEME 2. Thermodynamic Cycle Connecting the Oxidized (O) and the Reduced State (R) in a Solvent**TABLE 2.** Experimental and Calculated Reduction and Oxidation Potentials of Dye **1** and 9,10-Diphenylanthracene (DPA)

chemicals	reductions	reduction potentials, V		calculated energy, eV	
		exptl E^{a}	calcd E^{b}	$\Delta E_{\text{elec}}^{\text{c}}$	$\Delta \Delta G_{\text{solv}}^{\text{d}}$
1	ox2 \rightarrow ox1	~ 2.3	2.31	-11.08	4.59
	ox1 \rightarrow neu	~ 0.94	0.89	-6.52	1.44
	neu \rightarrow re1	approx -1.37	-1.67	-0.83	-1.70
	re1 \rightarrow re2	approx -2.46	-3.04	-3.68	-4.83
DPA	ox2 \rightarrow ox1	~ 1.7	1.71	-10.17	4.27
	ox1 \rightarrow neu	~ 1.2	0.89	-6.38	1.30
	neu \rightarrow re1	approx -2.1	-2.10	-0.34	-1.75
	re1 \rightarrow re2	approx -2.6	-2.87	-3.26	-4.58

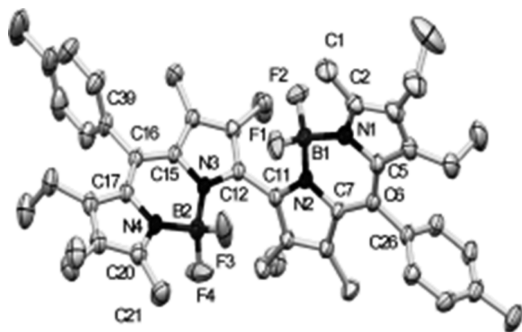
^aV vs SCE obtained based on 0.342 V vs SCE for ferrocene couple. ^bV vs SCE obtained based on SCE at 0.241 V vs NHE assuming aqueous system. ^cDifference in electronic energies in eV of reduced and oxidized species from DFT. ^dDifference in ΔG_{solv} of reduced and oxidized species in eV.

magnitude of separation between successive waves depends on the position of coupling of the monomer units (Figure 3a,b).

**FIGURE 3.** Cyclic voltammograms of BODIPY dyes: (a) 1.4 mM **10**; (b) 0.14 mM **11**; (c, d) 0.1 mM **12**; (e, f) 0.15 mM **13**. Scan rates for panels a–e = 0.1 V/s; (f) scan rate = 0.1 V/s (black line), 0.25 V/s (red line); 0.5 V/s (green line), and 1 V/s (blue line); solvent = DCM except for panel f, where THF was used. Electrode area = 0.0314 cm²; supporting electrolyte = 0.1 M TBAPF₆. Reprinted and adapted with permission from refs 22 and 24. Copyright 2010–2011 American Chemical Society.

The chemically synthesized angular dimer **10** formed through positions 3 or 5 shows the presence of two waves corresponding to the addition of one electron to each center of the molecule (Figure 3a).^{22,24}

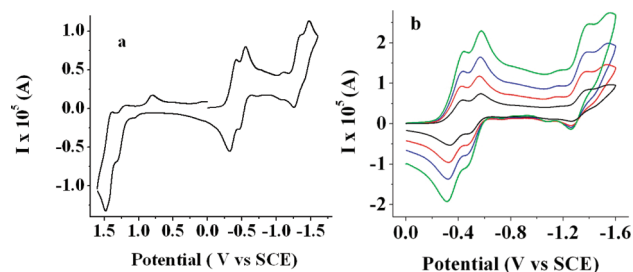
The separation of ~ 0.5 V on oxidation and 0.3 V on reduction demonstrates a substantial interaction between the two BODIPY units, which also corresponds fairly well with the exciton splitting present in the absorption spectra.^{33,45,46} This interaction exists even with a large dihedral angle of 96.52° between the C₉BN₂ planes (Scheme 3).^{45,47} Dimer **11** formed through positions 2 and 6 shows a much smaller separation of ~ 0.12 V on reduction and 0.22 V on oxidation; the absorbance and fluorescence spectra show one peak at a wavelength of 563 nm that is blue-shifted compared with the angular dimer **10**, which is at 623 nm (Figure 3b).^{25,48} There are also no exciton splitting features seen for the dimer **11**. A proposed dihedral angle of 61° between the two BODIPY units leads to the presence of the interactions and steric strain but to a smaller extent than

SCHEME 3. Molecular Structure of Dimer **10** except with Ethyl Groups Instead of the Methyl in Positions 1 and 2 for Both Rings (Molecule B; Ellipsoids Set at the 50% Probability Level)^{45a}

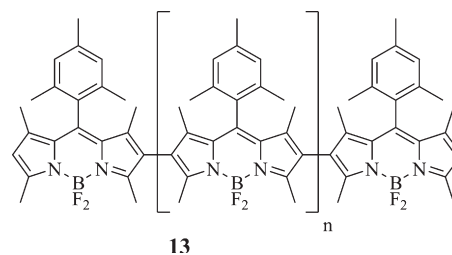
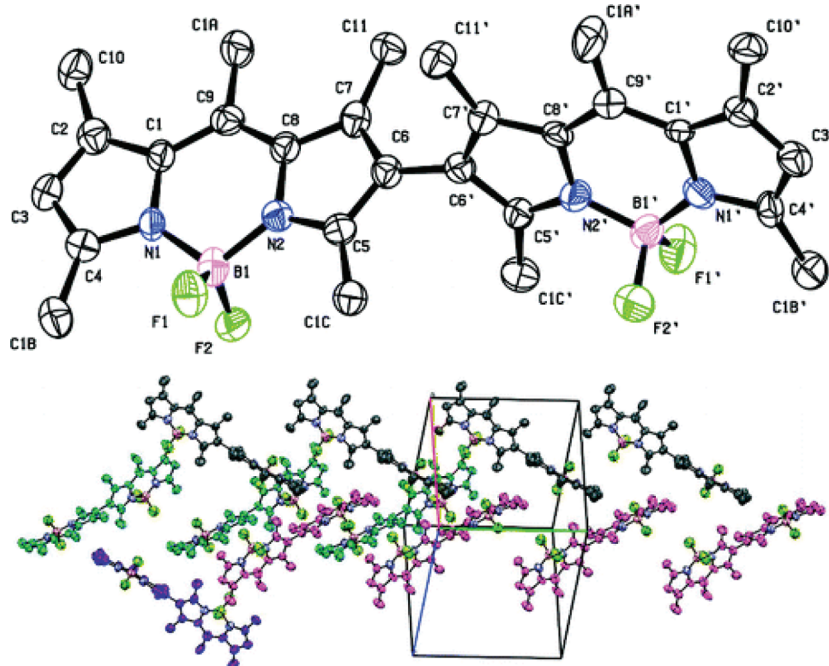
^aReprinted and adapted with permission from ref 45. Copyright 2008 Wiley-WCH.

with the angular dimer **10** (Scheme 4).⁴⁸ This is an important factor for the magnitude of potential separations of waves for angular dimer units as compared with linear ones and the role of the electrostatic interactions compared with conjugation. The larger interwave separation for oxidation compared with reduction is still under investigation.^{22–24}

The alkyl-substituted trimer **12** shows three waves with a separation of 0.09 V between the first and second waves and 0.19 V between the second and third waves on reduction and separations of 0.13 and 0.25 V on oxidation (Figure 3c,d).^{24,48} The presence of multiple electrochemical

**FIGURE 4.** Cyclic voltammogram of 0.9 mM BODIPY dye **14**. Scan rate of (a) 0.9 V/s and (b) 0.1 V/s (black line), 0.25 V/s (red line), 0.5 V/s (blue line), and 1 V/s (green line); solvent = DCM. Electrode area = 0.0314 cm²; supporting electrolyte = 0.1 M TBAPF₆. Reprinted and adapted with permission from ref 24. Copyright 2011 American Chemical Society.

waves is also seen with BODIPY polymer (Figure 3e,f). These factors correspond to multiple successive electron transfers in BODIPY polymers and might be relevant in the general area of conjugated polymer electrochemistry.^{49,50}

**SCHEME 4.** ORTEP (Oak Ridge Thermal Ellipsoid Plot Program) View for Dimer **11** with Thermal Ellipsoids Plotted at the 30% Level and Molecular Packing along the *b* Axis^{48a}

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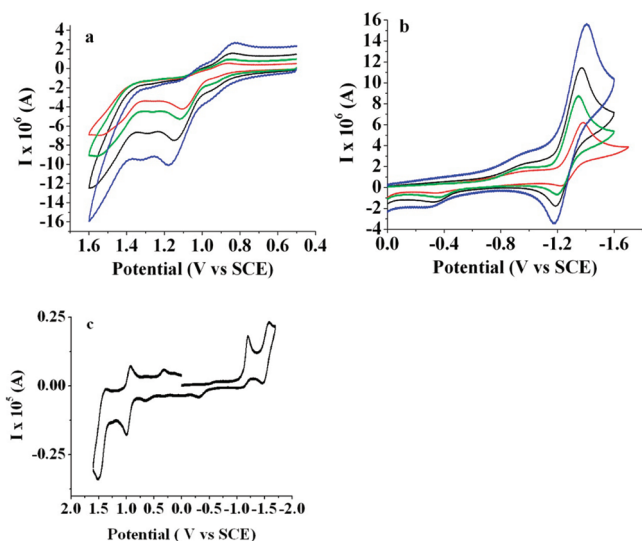
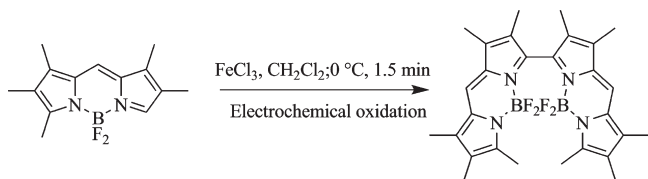
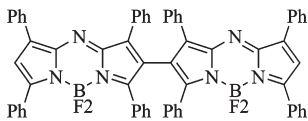


FIGURE 5. Scan rate dependence (a, b) and cyclic voltammogram (c) for 0.7 mM dye **15**; solvent = DCM. Electrode area = 0.0314 cm²; supporting electrolyte = 0.1 M TBAPF₆. Reprinted and adapted with permission from ref 25. Copyright 2011 American Chemical Society.

SCHEME 5. Chemical and Electrochemical Dimerization of Dye **4**



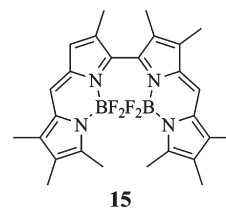
The aza-BODIPY dimer **14** shows four reduction waves that correspond to the addition of two electrons to each unit followed by an additional two electrons in second waves in the very slightly interacting groups compared with interactions in the dimer formed through positions 3 and 5 (Figure 4).



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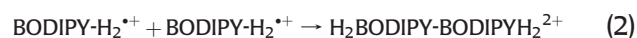
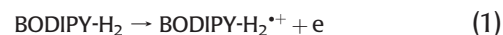
Coupling of BODIPY units to form dimers can be also monitored electrochemically through formation of a second wave on oxidation (Scheme 5, Figure 5). This coupling mechanism was fit to voltammograms obtained by digital simulations, which showed a monomer concentration dependence expected for an electrochemical dimerization. The second-order rate constant for dimerization was $4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ when the process goes through positions 3 or 5 for dye **4** as compared with dye **1** with unsubstituted 2 and 6 positions, where it is 400–2000 $\text{M}^{-1} \text{ s}^{-1}$.^{24,25} This also

corresponds to the chemical oxidative dimerization, where it occurs through positions 2 and 6 at room temperature using FeCl₃ as the oxidant, while dimerization through positions 3 and 5 takes place at 0 °C.²⁵



15

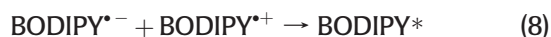
The proposed mechanism of the dimerization based on the simulation of CV scans is



Electrogenerated Chemiluminescence of BODIPY Dyes

Electrogenerated chemiluminescence (ECL) is a technique by which light is generated electrochemically.^{51–57} In addition to the scientific aspects of ECL, it has been applied as a sensitive and selective analytical technique that is used commercially in clinical analysis.⁵⁸ ECL is also very useful for characterization of organic and inorganic systems and detecting the formation of excimers, exciplexes, aggregates, and dimers.^{59–62}

Completely substituted BODIPY dyes produce stable, fairly intense ECL signals by radical ion electron transfer (annihilation) (Figure 6a):



The absence of substitution in positions 2 and 6 causes instability of the radical cations and oxidation and low annihilation intensity on the cathodic steps (Figure 6b). Addition of the reductive coreactant benzoyl peroxide (BPO) produces a higher intensity of ECL and avoids formation of the byproducts on oxidation (Figure 6c):

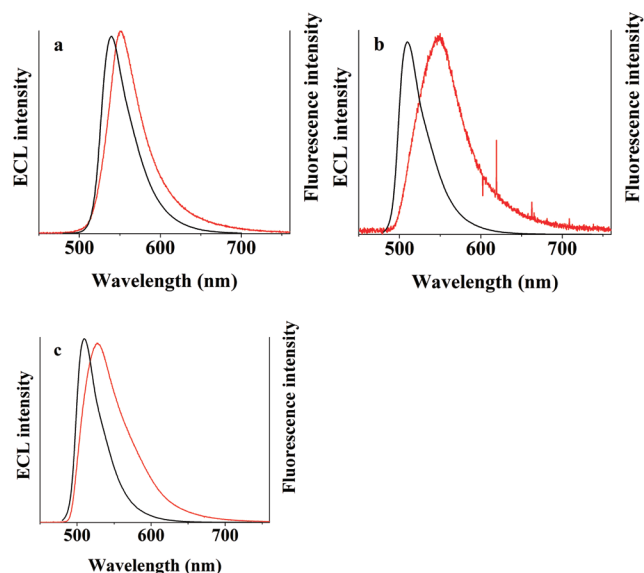


FIGURE 6. Fluorescence (black line) and electrogenerated chemiluminescence (red line) spectra for BODIPY dyes: (a) 2.2 mM **1**; (b, c) 1.0 mM **3**. Platinum electrode area = 0.0314 cm²; supporting electrolyte = 0.1 M TBAPF₆; ECL spectrum for panel b was generated in the presence of the benzoyl peroxide and for all other cases by annihilation. Reprinted and adapted with permission from refs 23 and 24. Copyright 2010–2011 American Chemical Society.

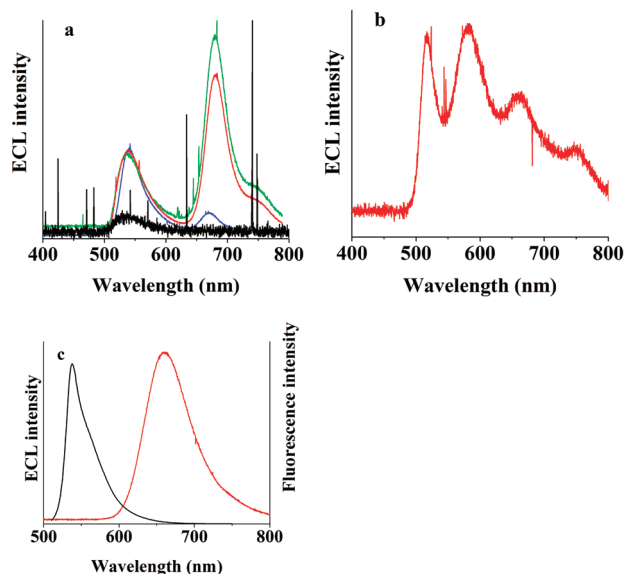
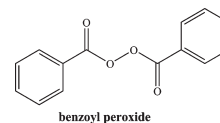
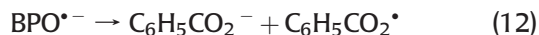
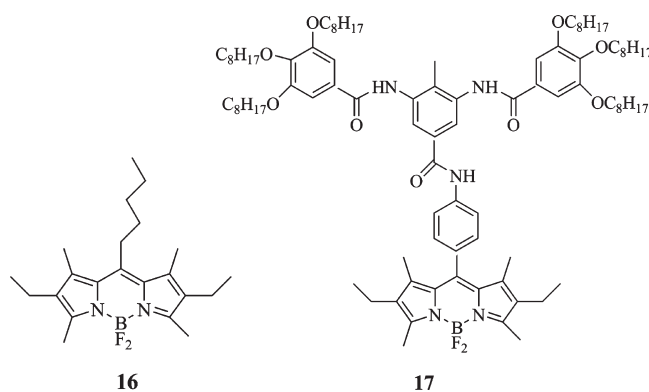
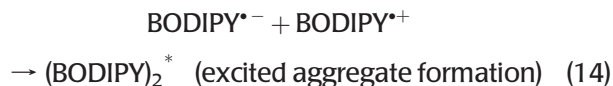


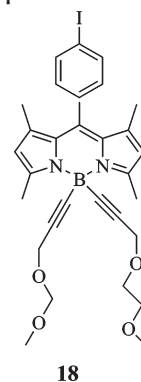
FIGURE 7. (a) ECL spectra for different concentrations of **16**: 0.01 mM (black line); 0.2 mM (blue line); 1 mM (red line); 5 mM (green line). (b) ECL spectrum of 0.2 mM **18**. (c) Fluorescence and electrogenerated spectra of 1.5 mM of **4**. Platinum electrode area = 0.0314 cm²; supporting electrolyte = 0.1 M TBAPF₆; ECL spectra were generated by annihilation. Reprinted and adapted with permission from refs 22, 25, and 27. Copyright 2010–2011 American Chemical Society.



Formation of aggregates was seen by annihilation for species with a long chain in position 8 (**16**) (Figure 7a):

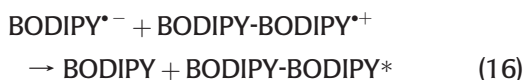


This phenomenon of formation of long wavelength ECL signal by annihilation of dye **16** with the *n*-pentyl chain is also seen with **17** with B⁸-amide chain. The concentration dependence and increase of aggregate emission with concentration is evidence for noncovalent bonding responsible for the long wavelength ECL. Addition of the reductive coreactant BPO or the oxidative coreactant tri-*n*-propylamine decreases formation of aggregates from the radical ion annihilation step. Annihilation ECL for dye **18** with a short poly(ethylene glycol) (PEG) chain shows the presence of multiple ECL emission peaks at different wavelengths, which

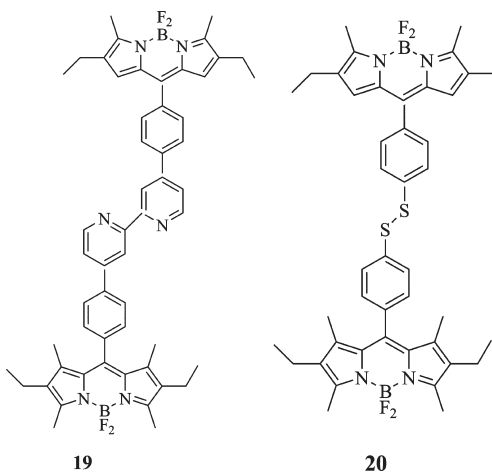


can be taken as evidence for the occurrence of chemical coupling reactions (Figure 7b).²⁷ Dye **8** from the same family but with a longer and more highly blocked BODIPY core shows just one ECL peak with a wavelength close to the fluorescence wavelength (Table 1).²⁷

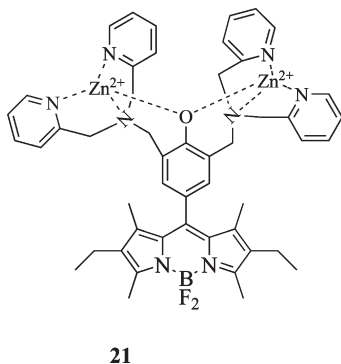
Formation of the dimer discussed above is also seen in ECL in the absence of substitution in positions 3 and 5 for dye **4** (Figure 7c), which agrees with the electrochemical results via the proposed mechanism, eqs 1–4 and 6, followed by



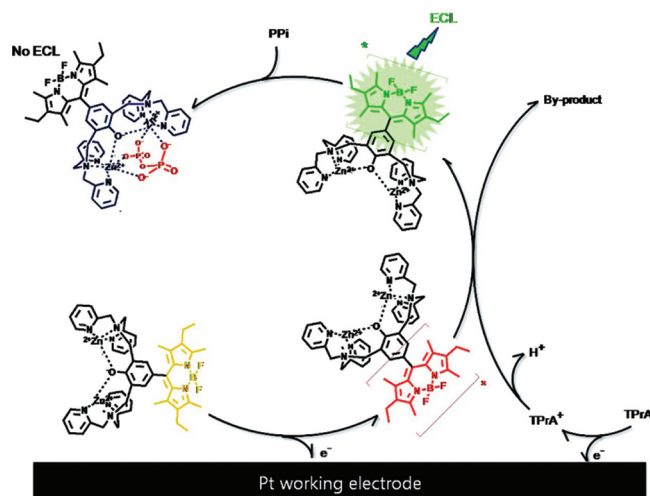
The wavelength for ECL emission of the monomeric species and of the dimer are very different, and this allows one to clearly see dimer product formation. ECL was also recorded for the bipyridine- and thiolate-separated dimers (**19** and **20**) at a wavelength close to that of the fluorescence. The behavior corresponds to simultaneous two-electron transfer to noninteracting BODIPY units:



ECL studies for recognition of pyrophosphate ion using a BODIPY dye with a phenoxo-bridged bis(Zn^{2+} -dipicolylamine) complex (**21**) demonstrate the possibility of using BODIPY



SCHEME 6. Mechanism of the ECL-Based Pyrophosphate (PPI) Sensing^{64a}



^aReprinted and adapted from ref 64. Copyright 2010 American Chemical Society.

species for ion sensing, although the reported effect relies on quenching (Scheme 6) of luminescence and a mechanism based on ECL enhancement would be preferable.⁶⁴

Summary and Future Prospects

Electrochemistry of BODIPY dyes can provide important information about properties of the compounds and also of oligomers of different sizes and polymers. Compared with aromatic hydrocarbons, they are relatively easy to reduce. As illustrated, these studies also can give unique information about the interaction between different units in oligomers and polymers and how the stepwise electron transfers correlate with conjugation and electrostatic interactions among the units. BODIPY dyes show interesting photophysics, for example, the presence of exciton splitting. The electrochemical behavior can be useful in explaining qualitatively and quantitatively phenomena like quenching of fluorescence by photo-induced electron transfer (PET), aggregation induced emission (AIE), and metal ion sensing using attached ligands, for example, crown ethers. Finding BODIPY compounds that show good electrochemistry and ECL in water could lead to analytical applications. In future studies, materials that show good photo properties might be of interest for photovoltaic applications, as are the electrochemical and luminescence properties of nanoparticles of BODIPY compounds.

BIOGRAPHICAL INFORMATION

Alexander Borisovich Nepomnyashchii was born in Saint Petersburg (Leningrad) in 1979. He obtained his specialist degree

in Chemistry and English in 2001 from the Herzen State Pedagogical University of Russia (Saint Petersburg, Russia). He started his graduate program there in 2001 under the guidance of Dr. Vyacheslav Nikolaevich Pak and obtained his Candidate of Science degree in physical chemistry in 2005. During this time, he also spent two years in the University of Northern Iowa (UNI) where he obtained his M.S. degree in chemistry working under the direction of Shoshanna R. Coon. He started his doctoral program in 2005 at the University of Texas at Austin (UT Austin) under guidance of Dr. Allen J. Bard and graduated in summer 2011 with his Ph.D. in analytical chemistry. He is currently a postdoctoral fellow in Dr. Bruce A. Parkinson's laboratory at the University of Wyoming (UW).

Allen J. Bard was born in New York City on December 18, 1933. He attended The City College of the College of New York (B.S., 1955) and Harvard University (M.A., 1956; Ph.D., 1958). Dr. Bard joined the faculty at The University of Texas at Austin in 1958. He has been the Hackerman-Welch Regents Chair in Chemistry at UT since 1985.

FOOTNOTES

The authors declare no competing financial interest.

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