Provisional chapter

Redox Chemistry of BODIPY Dyes

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Additional information is available at the end of the chapter

Abstract

The implementation of BODIPY dyes in electron transfer reactions is an exciting new frontier that expands the toolbox of the dye molecule that has primarily been implemented in biological and chemical sensing applications. BODIPY dyes are capable of reversible reductions at the average reduction potential of −1.53 V vs. ferrocene/ferrocenium, varying about 700 mV from this average value depending on the substitution of the BODIPY core. BODIPY dyes are also capable of reversible oxidations, exhibiting an average oxidation potential of 610 mV with the ability to manipulate the oxidation potential up to 600 mV from the average potential. The respective azaBODIPY dyes are on average about 600 mV easier to reduce (more positive potentials) and are oxidized at almost identical oxidation potentials to the respective BODIPY dyes. The oxidation and reduction potentials of BODIPY dyes are heavily dependent on substitution of the BODIPY core, which allows for a high degree of tunability in the redox potentials. This characteristic makes BODIPY dye molecules good candidates for use as photoredox catalysts, redox flow batteries, redox-active ligands, light harvesting antenna, and many other applications in materials science, biology, and chemical synthesis.

Keywords: BODIPY, redox, oxidation, reduction, chemiluminescence, photoredox, electron transfer, electrochemistry

1. Introduction

Electron transfer reactions, oxidations (removal of an electron) and reductions (addition of an electron), are involved in energy conversion processes, analytical methods, synthetic procedures, and even data processing systems. With the advent of new energy sources, the search for new chemical redox reagents is at the forefront of energy research. With many chemical

redox reagents consisting of metallocene or quinone fragments, the search for new redox platforms exhibiting unique redox characteristics and are amenable to tunable redox potentials is at the cutting edge of electron transfer research.

Fluorescent dyes have been widely utilized as chemical sensors, laser dyes, and in therapeutic applications, but exploitation of their redox-active nature in chemical and electron transfer reactions has remained mostly unexplored. Fluorescent dyes are attractive substrates for introducing redox capabilities, as their fluorescent nature demonstrates their capability of redox behavior [1]. Two dye molecules that have been of recent interest due to their electrochemical behavior is 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) and the related 4,4-difluoro-4-bora-3a,4a,8-triaza-s-indacene (azaBODIPY) (**Figure 1**) [2]. BODIPY and azaBODIPY molecules are attractive as redox fragments for the incorporation into molecular scaffolds, as the BODIPY and azaBODIPY cores can be readily synthesized and incorporated into molecular frameworks [3]. For example, diamines have been employed in many biological and catalytic applications, but the incorporation of additional functionality (e.g. redox behavior) into the diamine scaffold could open up additional chemical reactivity not previously accessible. One and two BODIPY fragments have been incorporated into a diamine scaffold, resulting in a complex that exhibits one and two redox events, respectively [4].

One of the appealing characteristics of BODIPY compounds is their tunable electrochemical properties. Substitution at different positions effects the electronic environment surrounding the BODIPY core (**Figure 1**), causing characteristic changes to the oxidation and reduction potentials [2]. Upon examination of the BODIPY and azaBODIPY scaffolds, a conjugated system is observed, suggesting some degree of aromatic character. Using a NICS(0) calculation to investigate the degree of aromaticity of the BODIPY and azaBODIPY core, the parent-BODIPY dye is seen to exhibit greater aromatic character than the parent-azaBODIPY dye. Given the aromatic nature of a BODIPY molecule, the BODIPY core can act as an electron-withdrawing substituent. Appending an amino group to the 8-position of the BODIPY core has been shown to result in an amine that is more electron deficient than if appended to a pentafluorophenyl or a tosyl group [4]. The electron deficient nature of BODIPY dyes suggest that the BODIPY core could be susceptible to the addition of electrons. In addition to BODIPY dyes being susceptible to reductions, BODIPY dyes are also capable of undergoing oxidation reactions. This chapter will discuss the recent advances of BODIPY dyes as chemical redox agents in reductions, oxidations, and photopromoted reactions. The ability to manipulate BODIPY dyes to tune the redox potential of these dye molecules will also be discussed. To simplify comparisons

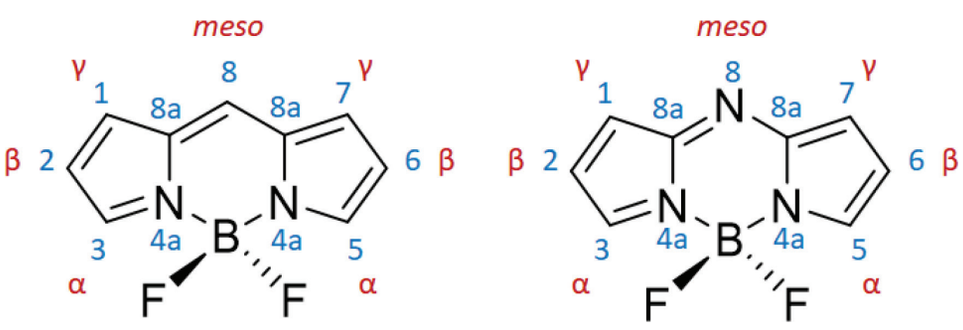

Figure 1. Numbering system for describing the substitution of (left) BODIPY and (right) azaBODIPY cores.

between BODIPY molecules, all redox potentials described within are referenced to the ferrocene/ferrocenium couple (Cp_2Fe/Cp_2Fe^+, where Cp = η^5-cyclopentadienyl). To convert a redox potential described vs. Cp_2Fe/Cp_2Fe^+ to NHE (normal hydrogen electrode), SCE (saturated calomel electrode), Ag/Ag^+, or Pt/Pt^+ reference electrodes, +0.270 V, +0.424 V, +0.469 V, or + 1.069 V, respectively, can be added to the redox potential described vs. Cp_2Fe/Cp_2Fe^+.

2. Reduction of BODIPY and azaBODIPY dyes

The electron deficient nature of the BODIPY core makes the dye molecule an attractive electron acceptor in electron transfer reactions. The reduction potential of a BODIPY core can be manipulated by almost 1.40 V, ranging from a potential as reducing as −2.40 V to a potential as moderate as −0.35 V vs. Cp_2Fe/Cp_2Fe^+. Although the reduction potentials can span a large range, depending on the substitution of the BODIPY core, the average reduction potential of a BODIPY core resides at −1.53 V vs. Cp_2Fe/Cp_2Fe^+, with about 2/3 of the reported BODIPY molecules exhibiting a reduction potential within 460 mV of the average value.

Using unpaired spin density plots of the reduced parent-BODIPY and reduced parent-azaBODIPY molecules, the likely location of the added electron can be determined (**Figure 2**). Using the M06-2X/6-31G(d,p) level of theory, an unpaired spin density plot of a reduced parent-BODIPY molecule revealed 32% of the electron density resided in the 8-position, about 24% of the electron density resided in the 1,7-positions (12% each), and about 16% of the electron density resided in the 3,5-positions (8% each). Only about 2% of the unpaired spin density resided in each of the 2,6-positions of the BODIPY dye. About 3% of the unpaired spin density resided in each of the nitrogen centers, and about 7% resided in each of the carbon atoms in the 8a-position (between the 1,7-positions and the 8-position). Surprisingly, the most electronegative atoms, boron and fluorine, contained negligible spin density.

Although the 8-position of the reduced parent-azaBODIPY contained the largest unpaired spin density (**Figure 2**), the 8-position of the reduced azaBODIPY contained about 6% less unpaired spin density than the reduced parent-BODIPY molecule. Where there was a reduction in the spin density in the 8-position of the reduced parent-azaBODIPY molecule, when

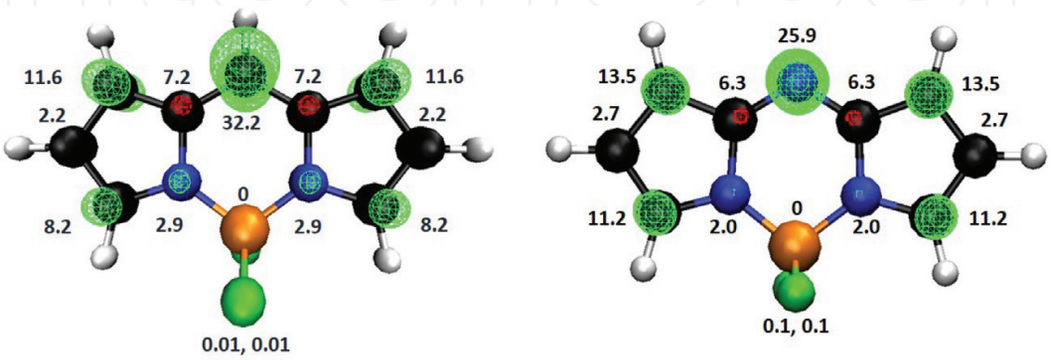

Figure 2. Unpaired spin density plots of the reduced (left) parent-BODIPY and (right) parent-azaBODIPY molecules. Isovalue = 0.01 e^-/a.u. The numbers indicate the percent of unpaired spin density present on each atom.

compared to the reduced parent-BODIPY dye, there was an increase of about 2 and 3% in the unpaired spin density at the 1,7- and 3,5-positions, respectively. As with the reduced parent-BODIPY dye, a negligible unpaired spin density resided on the boron and fluorine atoms.

Analysis of bond lengths and bond orders upon reduction of a BODIPY and azaBODIPY core revealed an increase in aromaticity of the BODIPY and azaBODIPY core (**Figure 3**). The increase in aromaticity was further verified by Wiberg bond index analysis, where bond orders of the BODIPY core become more alike in the reduced BODIPY and azaBODIPY dyes than in the parent compounds. Upon reduction, lengthening of the bonds between the 1,7- and 2,6-positions and the 3,5- and 4a-positions occurred. A contraction of the bonds between the 1,7- and 8a-positions and the 2,6 and 3,5-positions also resulted from the reduction of the parent-BODIPY dye. The greatest changes in bond distance occurred between the 8- and 8a-positions (+0.03 Å) and between the 2,6- and 3,5-postions (−0.03 Å). Analysis of the Mulliken charges of the reduced BODIPY core revealed that the carbon center residing in the 8-position contained most of the anionic charge. In contrast to the reduced BODIPY dye, the reduced azaBODIPY dye contained most of the negative charge on the carbon centers residing in the 8a positions (between the 1,7 and 8-position of the azaBODIPY core). The nitrogen atom in the 8-position of the reduced azaBODIPY actually exhibited less of a negative charge than the other two nitrogen atoms.

To analyze the influence of substitution on the unpaired spin density of a reduced BODIPY or azaBODIPY dye, the presence of methyl, phenyl, or chloride substituents on the reduction potential and unpaired spin density was investigated. Incorporation of a phenyl substituent in the 1- or 2-position of a BODIPY or azaBODIPY core resulted in a 2% lower spin density in the 5-position than in the 3-position. A phenyl substituent in the 1-position also resulted in a 3% decrease in spin density in the 8-position. Phenyl substitution in the 8-position of a BODIPY dye resulted in a 6% decrease in unpaired spin density in the 8-position. Methyl and chloride substitution had a minimal effect on the unpaired spin density of the BODIPY and azaBODIPY core, where no changes beyond a 1% difference occurred. The presence of a methyl substituent generated a BODIPY dye that was about 100–150 mV more difficult to reduce (more negative

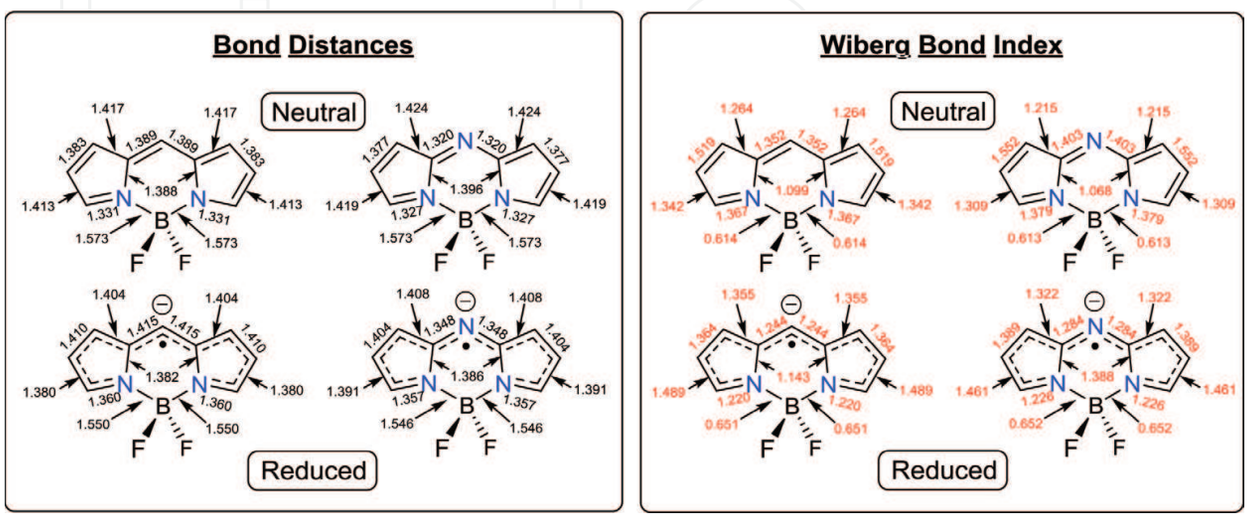

Figure 3. Lists of computed bond distances (black, Å) and Wiberg bond indices (red) for the (top) parent-BODIPY and parent-azaBODIPY cores and the (bottom) reduced parent-BODIPY and parent-azaBODIPYcore.

potentials). Investigation of the influence of substitution on the reduction potential of a BODIPY dye, revealed that substitution in the 3-postion resulted in the most negative reduction potential, followed by the 8-position, 1-position, and the 2-position. Similar results were obtained for the reduction of a substituted azaBODIPY dye. The reverse trend is observed for the stabilization of the LUMO (easiest to reduce), where substitution in the 2-position resulted in the lowest energy LUMO, demonstrating a correlation between the LUMO energy and reduction potential. Substituents consisting of electron-withdrawing groups lower the LUMO energy of the BODIPY and azaBODIPY core, resulting in dye molecules that are reduced at milder (more positive) potentials. The opposite trend occurs for substitution of a BODIPY and azaBODIPY core with electron-donating groups.

Analysis of the reduction potentials of substituted azaBODIPY and BODIPY dyes revealed the reduction potential of azaBODIPY dyes were on average about 600 mV easier to reduce (more positive potentials) than the respective BODIPY dyes. The increased ability to reduce an azaBODIPY dye when compared to the respective BODIPY dye is attributed to the reduced azaBODIPY dye gaining a greater degree of aromaticity than a BODIPY dye upon reduction. Connecting the reduction potentials to the molecular orbitals of the parent BODIPY and azaBODIPY dyes revealed a linear correlation between the LUMO energy and the reduction potential. The milder reduction potentials for azaBODIPY dyes is also attributed to the energy of the LUMO which is about 12 kcal lower (easier to oxidize) in energy than the respective BODIPY dye.

From the computational analysis of the unpaired spin density plots, substitution at the 8-position would suggest the greatest influence in the reduction potential and stabilization of the reduced BODIPY dye. Electrochemical analysis of substitution of the parent-BODIPY dye with a phenyl, chloride, methanesulfide, amide, and diethylamide substituent in the 8-position resulted in an ability to shift the reduction potential by 600 mV (**Figure 4**). Substituted electron acceptors in the 8-position resulted in the greatest stabilization of the radical anion

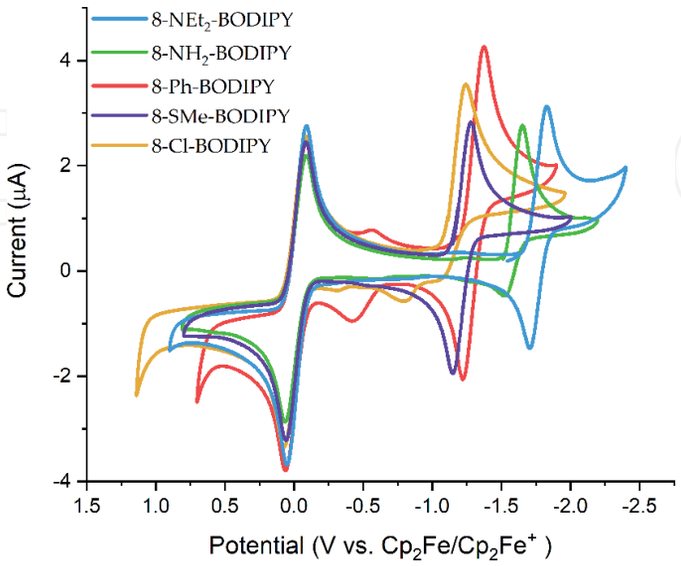

Figure 4. Stacked cyclic voltammograms of 8-SMe-BODIPY, 8-Cl-BODIPY, 8-Ph-BODIPY, 8-NH_2-BODIPY, and 8-NEt_2-BODIPY in dichloromethane. Scan rate = 100 mV/s and electrolyte = Bu_4NPF_6. The wave at 0 V is attributed to the ferrocene internal standard.

from the reduction of a BODIPY or azaBODIPY core (more reversible reduction waves) [5]. Bard and coworkers have shown that the inductive electron-withdrawing effect of a cyanide substituent in the 8-position results in an easier reduction by about 300 mV, when compared to a methylated-BODIPY. However, introduction of a more electron-donating group, such as diethylamine, results in the opposite effect [6]. Lack of the substitution in the 8-position causes for a reduced BODIPY core to be a more reactive/less stable radical anion [5]. Substitution at the 8-position of a BODIPY core can stabilize a radical anion, but substituents bearing an acidic proton residing near the 8-position, such as carboxylic acids, can result in electrophilic attack on the radical center by the acidic proton upon reduction [5].

Although no unpaired spin density resides on the boron or fluorine atoms in the reduced BODIPY or azaBODIPY dyes, substitution at the boron center also influences the reduction potential of a BODIPY core. Substituting one or both fluorine atoms with fused benzene rings, catecholate groups, or alkynyl moieties does not affect the stability of the radical anion or cation [5]. However, substitution at the boron center introduces more electron density into the system as the electron-withdrawing fluorine's are removed, disfavoring reduction of the BODIPY core. Substitution on the boron center increases the energy of both the HOMO and the LUMO, with a larger change occurring for the LUMO, resulting in a larger separation between reduction and oxidation waves when compared to the respective BF_2-containing BODIPY dyes.

Heiden and coworkers have recently described the redox properties of diamines containing one and two BODIPY molecules [4]. The redox-active behavior of the BODIPY fluorophores is showcased with the presence of quasi-reversible and irreversible redox events, in relation to the free diamines. All of the BODIPY-containing diamines exhibit either quasi-reversible or irreversible reductions between the range of −0.82 V to −1.95 V (**Table 1**). The incorporation of two BODIPY fragments into the diamine scaffold resulted in two separate reduction events, with a separation of about 100 mV. BODIPY-appended diamines derived from electron deficient diamines (e.g. ortho-phenylenediamine) resulted in milder reduction potentials than more electron rich diamines (e.g. trans-1,2-diaminocyclohexane or ethylenediamine).

Diamine	E° potential (V)
One BODIPY	
Ethylenediamine	−1.89
Phenylenediamine	−1.70
Diaminocyclohexane	−1.86
Diphenylethylenediamine	−1.80
Two BODIPYs	
Ethylenediamine	−1.85, −1.95
Phenylenediamine	0.82, −1.26, −1.35
Diaminocyclohexane	−1.74, −1.89
Diphenylethylenediamine	−1.67, −1.80

Table 1. Redox potentials for BODIPY-appended diamines.

Although there are several examples of reductions of BODIPY molecules, the reductions are often undertaken *in situ*, without isolation of the reduction product. A reduced BODIPY molecule with an appended 1,1,3,3-tetramethylguanidine fragment (BoTMG) has been recently reported by Heiden and coworkers [7]. Electrochemical analysis of acetonitrile solutions of BoTMG revealed a reversible reduction at −1.86 V vs. Cp_2Fe/Cp_2Fe^+. The reduced BoTMG was isolated by reducing BoTMG with 1.5 equivalents KC_8 in the presence of one equivalent 18-crown-6. 18-crown-6 was employed to coordinate the potassium cation to aid in solubility of the reduced BoTMG. Although the resulting red solution/solid exhibited a 15 nm hypsochromic shift when compared with the absorbance spectrum of BoTMG, the solution did not fluoresce under UV light. The presence of an unpaired electron was verified by EPR spectroscopy (g value = 2.00289; **Figure 5**). Crystallographic analysis of the reduction of BoTMG revealed the presence of an anionic BoTMG molecule with the fluorine atoms of the BODIPY residing 2.627(1) and 3.181(1) Å away from the potassium ion (**Figure 5**). The potassium ion resided within the 18-crown-6 and also exhibited a coordinated THF molecule 2.816(1) Å away (**Figure 5**), yielding an overall formula of [K(18-crown-6)(THF)][BoTMG]. The $[BoTMG]^-$ fragment showed a lengthening of the C(2)—C(3) and the C(7)—C(8) bonds by about 0.03 Å, suggesting a greater degree of single-bond character, when compared to the neutral BoTMG. The N(3)—C(5) bond length increased by about 0.09 Å and the N(3)—C(10) shortened by about 0.06 Å upon reduction of BoTMG. From the bond distances and the unpaired spin density plot of $[BoTMG]^-$ (**Figure 5**), the free electron resides primarily on C(5). The reduced BoTMG was reported to be stable in acetonitrile, THF, benzene, and fluorobenzene, reacting with halogenated and protic solvents.

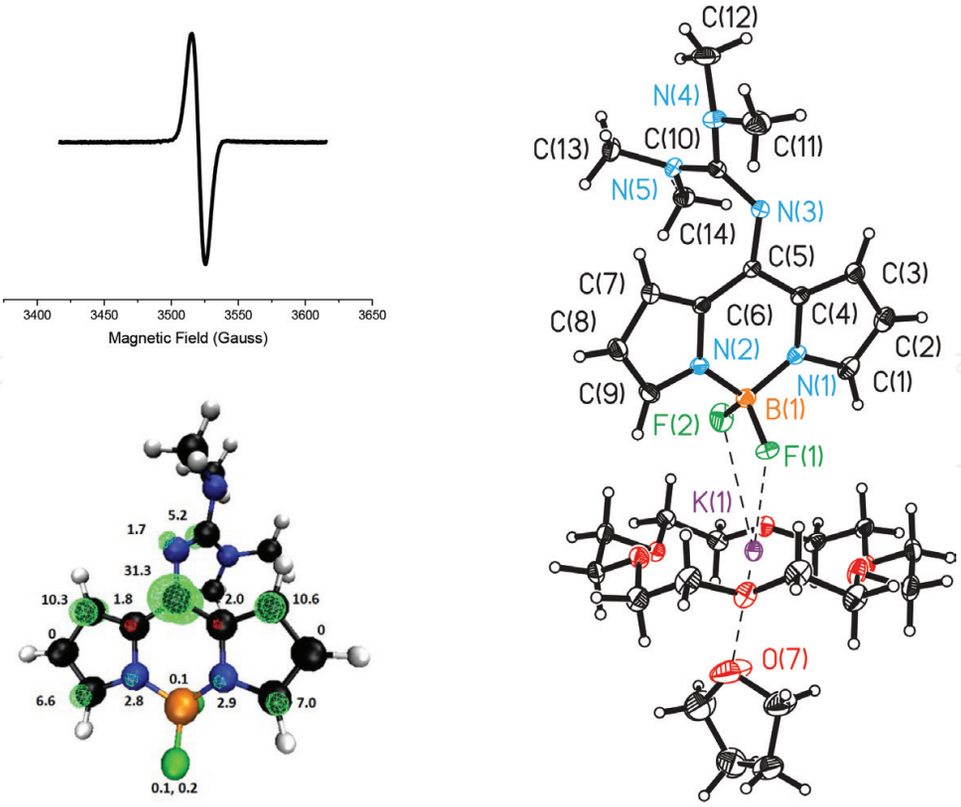

Figure 5. (top left) EPR spectrum of [K(THF)(18-crown-6)][BoTMG], (bottom left) unpaired spin density plot (isovalue = 0.01 e^-/a.u.) for $[BoTMG]^-$, and (right) molecular structure of [K(THF)(18-crown-6)][BoTMG]. Thermal ellipsoids are drawn at 50% probability.

Other redox agents have been appended to BODIPY cores. Cosa and coworkers have incorporated an ubiquinone fragment into a BODIPY core at the 3-position, resulting in +50 and +430 mV shifts in the reduction potential of the ubiquinone fragment, respectively [8]. The more positive shift of the second reduction is proposed to be stabilized via resonance through the BODIPY core. In a related study, Misra and coworkers have described the influence of appending a BODIPY core to each of the nitrogen centers of phenylenediamine and to each of the oxygen centers of phenylenediols [9]. Appending two BODIPYs to para-phenylenediol resulted in a slightly more favorable reduction than the meta- or ortho-substituted phenylenediol, respectively. In the case of two BODIPY cores appended to a phenylenediamine, the meta-substituted complex exhibited the mildest reduction potentials, followed by the para- and ortho-substituted phenylenediamine, respectively.

3. Oxidation of BODIPY and azaBODIPY dyes

Although BODIPY dyes are prone to reductions, many also are capable of undergoing oxidations. The oxidation potential of a BODIPY core can be manipulated by about 1.3 V, ranging from a potential as high as 1.55 V to a potential as low as 0.18 V vs. Cp_2Fe/Cp_2Fe^+. Although the oxidation potentials can vary a large potential range, depending on the substitution of the BODIPY core, the average reduction potential of a BODIPY core resides at 610 mV vs. Cp_2Fe/Cp_2Fe^+, with about 2/3 of the reported BODIPY molecules exhibiting a reduction potential about 330 mV from the average value.

An unpaired spin density plot of an oxidized parent-BODIPY molecule (**Figure 6**) revealed 18% of the electron density resided on the 8a-positions. About 13% of the electron density resided in each of the 3,5-positions, and about 12% of the electron density resided in the 8-position. Only about 6% of the unpaired spin density resided in each of the 2,6-positions of the BODIPY dye. About 4% of the unpaired spin density resided in each of the nitrogen centers (4a-position). As seen with the unpaired spin density plots for the reduced parent-BODIPY dye, the most electronegative atoms, boron and fluorine, contained negligible spin density in the oxidized

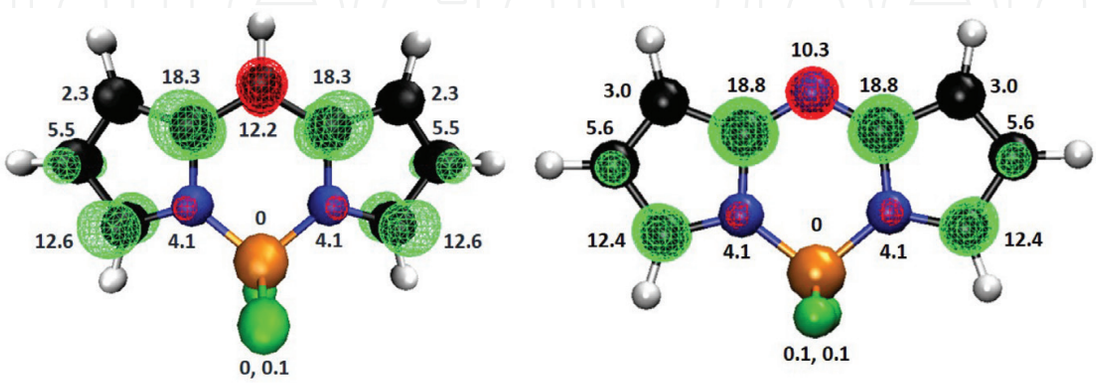

Figure 6. Unpaired spin density plots of the oxidized (left) parent-BODIPY and (right) parent-azaBODIPY dyes. Isovalue = 0.01 e^-/a.u. The numbers indicate the percent of unpaired spin density present on each atom.

parent-BODIPY dye. Whereas there were measureable differences between the unpaired spin densities for the reduced parent-BODIPY dye and the reduced parent-azaBODIPY, the unpaired spin densities observed for the oxidized parent-azaBODIPY dye were almost identical to the unpaired spin densities for the oxidized parent-BODIPY dye (**Figure 6**).

Analysis of the bond distance and bond order changes of a BODIPY and an azaBODIPY core revealed a decrease in aromaticity upon oxidation (**Figure 7**). Upon oxidation, contractions of the bonds between the 1,7- and 2,6-positions and the 3,5- and 4a-positions resulted. Lengthening of the bonds between the 1,7 and 8a-positions and the 2,6 and 3,5-positions also occurred upon oxidation. Using Mulliken charge analysis, the location of the greatest positive charge of the oxidized parent-BODIPY and parent-azaBODIPY dyes resided on the carbon atoms in the 1,7-positions.

Analysis of the oxidation potentials of substituted azaBODIPY and BODIPY dyes revealed that the oxidation potential of azaBODIPY dyes were on average about 20 mV easier to oxidize (more negative potentials) than the respective BODIPY dyes [10]. The small difference in oxidation potentials between azaBODIPY and BODIPY dyes is attributed to the similarity in changes in aromaticity upon oxidation. A NICS(0) calculation of the parent-azaBODIPY and BODIPY dyes showed almost an identical change in aromaticity upon oxidation, with the azaBODIPY dye exhibiting a slightly smaller change in aromaticity upon oxidation. The slightly reduced change in aromaticity of the azaBODIPY dye is attributed to its ability to be oxidized slightly more readily than the parent-BODIPY dye. Molecular orbital analysis also revealed a linear correlation between the HOMO energy and the oxidation potential of the BODIPY and azaBODIPY dye. The slightly more favorable oxidation of an azaBODIPY is also attributed to the HOMO energy of the azaBODIPY dye being on average 2.8 kcal lower (more easily oxidized) than the respective BODIPY dye.

Substitution of the BODIPY or azaBODIPY core can also influence the oxidation potential. Substitution in the 2-position of a BODIPY and azaBODIPY dye resulted in a large difference in unpaired spin density for the oxidized BODIPY. In the case of phenyl substitution in the

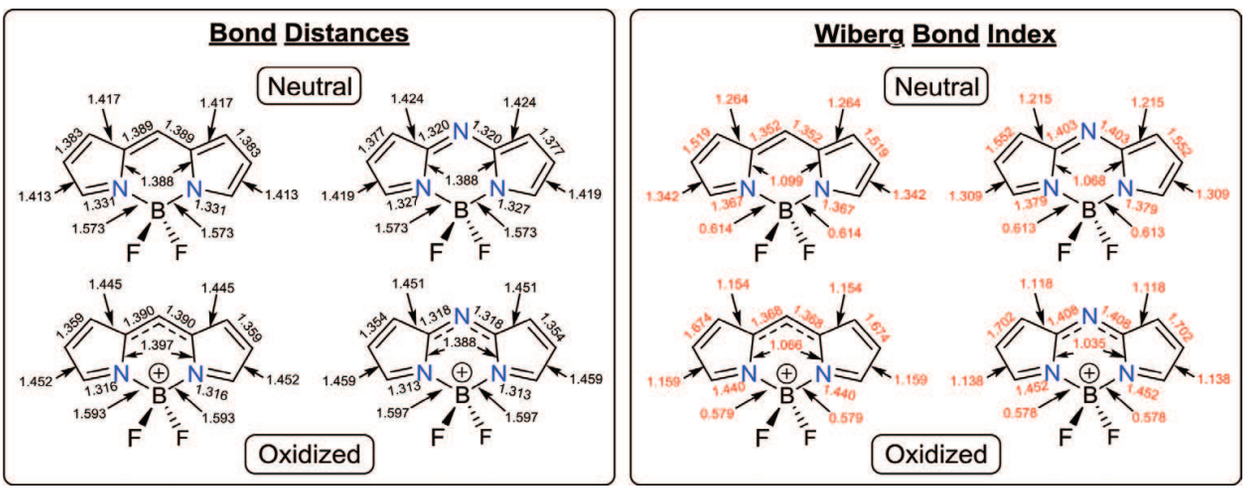

Figure 7. Lists of computed bond distances (black, Å) and Wiberg bond indices (red) for the (top) parent-BODIPY and parent-azaBODIPY cores and the (bottom) oxidized parent-BODIPY and parent-azaBODIPY core.

2-position or 3-position, a 10% difference in unpaired spin density was observed between the 2- and 6-positions and the 3- and 5-positions of the oxidized BODIPY core. A similar result was observed for methyl and chloride substitution at the 2- or 3-positions, but to a lesser extent (3–4% instead of 10%). Substitution at the 3-position resulted in the least positive oxidation potential, followed by the 2-, 1-, and 8-positions. Similar results were obtained for the oxidation of a substituted azaBODIPY dye. Where substitution in the 3-postion resulted in the most positive oxidation potential, the highest energy HOMO was also observed. A direct correlation between the energy of the HOMO and oxidation potential resulted. Substituents consisting of electron-withdrawing groups resulted in lower energy HOMO energies and higher (more positive) oxidation potentials. The opposite trend is observed for substitution of a BODIPY and azaBODIPY core with electron-donating groups.

Further verifying the computational results, Cosa and coworkers have shown that the introduction of a cyanide group in the 2-position of a BODIPY dye results in a more difficult oxidation by 400 mV, with no influence on the reversibility of the reduction. The addition of a second cyanide, in the 6-position, shifts the oxidation potential to a more positive value by an additional +200 mV (more difficult to oxidize), but the reduction of the BODIPY dye is no longer reversible [11]. Whereas the incorporation of a cyanide in the 2,6-positions of the BODIPY core can shift the oxidation potential by +400 and +200 mV, the incorporation of a chloride in the 2,6-positions increases the oxidation potential by +200 mV (more difficult to oxidize) with each substitution.

An additional method to generate a BODIPY dye capable of undergoing an oxidation is to incorporate a ferrocene fragment. Li and coworkers have incorporated two ferrocenyl fragments in the 3,5-positions through a vinyl linker [12]. The resulting ferrocenyl BODIPY complex exhibits a reversible reduction at −1.49 V and a reversible oxidation at 0.51 V that are BODIPY-based. The ferrocene-based oxidations occur at −0.01 V, where a single two electron oxidation is observed for scan rates greater than 50 mV/s. Bulk electrolysis at 0.21 V resulted in a color change from blue to purple. The color change is attributed to the oxidation of both of the ferrocenyl fragments, as evidenced by the adsorption band of the BODIPY core remaining unchanged and the loss of the adsorption at 700 nm and growth of the adsorption at 600 nm. Ravikanth and coworkers have examined the influence of placing a ferrocene and an ethynyl-ferrocene fragment in different locations on a BODIPY-core [13]. Introduction of a ferrocenyl fragment generated reversible ferrocene-based oxidations 230–360 mV more positive than free ferrocene, irreversible BODIPY-based oxidations 990–1190 mV more positive than free ferrocene, and reversible BODIPY-based reductions 1010–1110 mV more negative than free ferrocene. Similar results have been observed by several other groups that have incorporated ferrocene fragments into BODIPY cores [14–18]. Although incorporation of a ferrocenyl fragment into a BODIPY dye can introduce an additional oxidation wave, the reduction of the BODIPY dye is nearly unaffected by the presence of ferrocene moieties, which is primarily due to the added electron residing on the BODIPY core [19]. The separation of the oxidation potentials of multiple ferrocene-appended BODIPY dyes largely depends on the interactions between the two ferrocene moieties. Non-interacting redox centers normally display a difference of 35 mV between their redox potentials [20]. If a small splitting is observed between the two oxidation waves associated with the ferrocene oxidations, then the difference in oxidation potentials is attributed to electrostatic effects [18]. Although small separations between the ferrocene oxidations are

often observed, Kovtun and coworkers have shown that the implementation of a non-coordinating electrolyte did not change the reversibility of redox processes, but increased the separation between the first and second ferrocene oxidation waves from 250 mV ($[Bu_4N][ClO_4]$) to 340 mV($[Bu_4N][B(C_6F_5)_4]$) [21]. Examination of the influence of peripheral electron-donating or electron-withdrawing groups on a BODIPY core on the oxidation potential of an appended ferrocene fragment is quite small, often only shifting the potential by 30–60 mV. Although substitution of the BODIPY core weakly influences the oxidation potential of an appended ferrocene moiety, exposure to Lewis acidic cations can have a greater effect. Kaur and coworkers have shown that a +130 mV shift in the oxidation of the appended ferrocene and +80 mV shift in the BODIPY reduction results when a ferrocenyl-appended BODIPY is exposed to Hg^{2+} ions [22].

Plenio and coworkers have incorporated the BODIPY core into N-heterocyclic carbene scaffolds coordinated to iridium and rhodium centers for use in carbon monoxide detection. Plenio and coworkers have incorporated two different BODIPY cores into a N-heterocyclic carbene scaffold, where each of the BODIPY cores are connected to the carbene through a five carbon linker [23]. With the free BODIPY dyes having oxidation potentials of 0.90 and 1.01 V, coordination to an IrCl(COD) fragment, where COD = cis-cyclooctadiene, shifts the oxidation potentials to 0.92 and 1.02 V, respectively. Whereas coordination to an iridium center resulted in slightly more difficult oxidations of the BODIPY dyes, coordination to a RhCl(COD) fragment resulted in BODIPY dyes that were slightly easier to oxidize (0.89 and 1.00 V). As expected, the large distance between the appended-BODIPY dyes and metal centers results in very little influence of the metal center on the electrochemistry of the BODIPY dye.

4. Manipulating the redox chemistry of BODIPY dyes

The redox chemistry of a BODIPY and azaBODIPY core can be influenced through substitution of the BODIPY core. Computational analysis of the influence of substitution on the redox potential of the BODIPY fragment revealed that substitution in the 3,5-positions resulted in the highest energy HOMO and LUMO, but the smallest HOMO-LUMO gap. Substitution in the 3,5-positions of a BODIPY core resulted in the most negative reduction potentials. Complete alkylation of a BODIPY core exhibits one reversible one-electron oxidation and one reversible one-electron reduction, indicating the generation of stable radical ions. In aprotic solvents, radical stability correlates with electrochemical reversibility [2]. Absence of substitution in the 2-, 3-, 5-, or 6-positions destabilizes the radical cation produced upon oxidation. A similar destabilization is observed in the absence of substitution in the 1-, 3-, 5-, 7-, or 8-positions upon generation of a radical anion from a reduction.

Lack of substitution in the 3,5-positions of a BODIPY core results in a radical cation that is vulnerable to nucleophilic attack and is capable of dimerization. The rapid dimerization of radical BODIPY cations lacking substitution in 3,5-positions result in irreversible anodic waves in the cyclic voltammogram [5]. The presence of sterically bulky substituents at the 3,5-positions protect the radical cation from nucleophilic attack by a neutral BODIPY dye, leading to dimerization, or attack by surrounding solvent molecules, such as acetonitrile. Electron withdrawing substituents in the 3,5-positions may also induce a partial positive charge on the 2,6-positions, increasing the susceptibility for dimerization

at the 2,6-positions. When BODIPY cores lacking substitution in the 2,6-positions dimerize, the dimerized BODIPY dyes are often easier to oxidize than the original BODIPY dye. The increased ability to oxidize the BODIPY dimer over the original BODIPY dye can lead to the generation of oligomers of the BODIPY dye. Although dimerization of BODIPY dyes often occurs at BODIPY dyes lacking substitution, Heiland and coworkers have shown that 2,6-substituted BODIPY dyes are still prone to dimerization upon oxidation through the loss of a substituent [5]. The possibility of dimerization of a BODIPY dye can be investigated through the analysis of the reversibility of the oxidation wave as a function of scan rate. At faster scan rates, the oxidation processes exhibit increased reversibility due to the suppression of rate of dimer formation. Functionalization at the 1-, 7-, or 8-positions of a BODIPY dye do not influence the stability of the radical cation.

5. Use of redox to manipulate basicity of appended bases

The fact that BODIPY molecules are susceptible to reductions suggests that the BODIPY fragment can act as an electron-withdrawing group. Heiden and coworkers have found that the addition of an amine center to the BODIPY molecule in the 8-position does not result in Lewis acid-base adduct formation with strong Lewis acids (e.g. $B(C_6F_5)_3$). Further verifying this result, Akkaya and coworkers were able to show that a 1,7-bis(2-pyridyl)-2,5-diphenyl-azaBODIPY can be used as a near-IR sensor for Hg^{2+} ions [24]. Although this azaBODIPY can be utilized as a chemical sensor, 20 equivalents of the heavy metal is needed to see a response. Similar results have been observed by other research groups, where excess heavy metal ions are needed to show a fluorescent response [25–29]. The requirement of large amounts of Lewis acid to see a fluorescent response, suggests that azaBODIPY- and BODIPY-derived sensors act as a poor ligands for coordination to metal ions.

To counteract the strong electron-withdrawing nature of the BODIPY dye, Heiden and coworkers have shown that appending a 1,1,3,3-tetramethylguanidine fragment to a BODIPY molecule in the 8-position (BoTMG) results in a decrease of the basicity of the tetramethyl-guanidine fragment by 15 pK_a units. Protonation of the guanidinylated BODIPY, generating $[BoTMGH]^+$, resulted in a bathochromic shift by about 100 nm (45 nm in the emission) and a slight decrease in the quantum yield, from 0.17 to 0.13. In addition to influencing the photophysical properties, a shift of 870 mV to a more positive value was observed in the reduction peak upon protonation of the guanidine fragment. Further analysis of the electrochemical reactions, revealed the presence of an irreversible reduction peak at −0.99 V and a quasireversible reduction at −1.86 V. These results were attributed to the reduction of $[BoTMGH]^+$ at −0.99 V, which undergoes an electrochemical, followed by a chemical reaction leading to the unstable complex ([BoTMGH]), which decays into BoTMG through the transfer of H-atoms (H•). Although H_2 generation from the coupling of two H• was exergonic by 19.3 kcal/mol, no H_2 was observed experimentally. The absence of H_2 was further verified by electrochemical experiments, where the addition of 1, 2, 5, 10, and 20 equivalents of trifluoroacetic acid resulted in an increase in current at a potential of −1.19 V, but no current increase was observed after 20 equivalents of acid (**Figure 8**). To further investigate the influence of an added electron

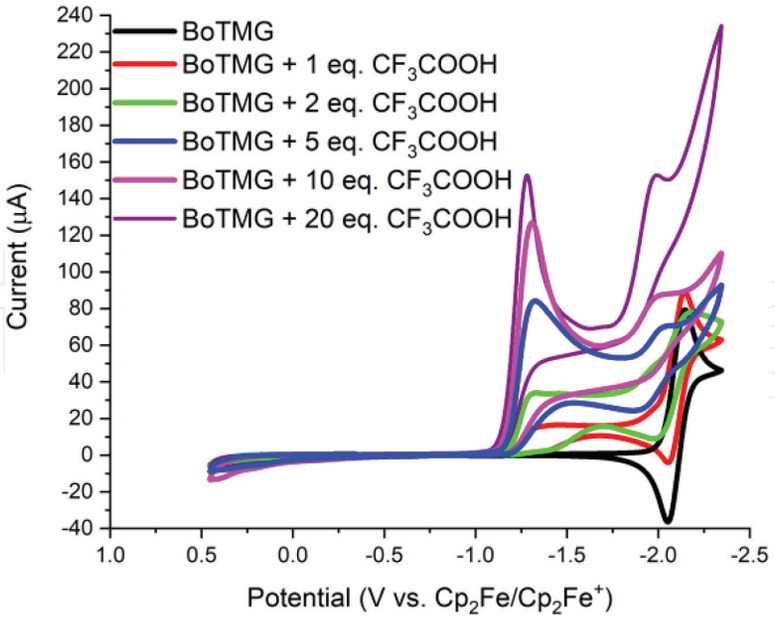

Figure 8. Cyclic voltammogram of an acetonitrile solution of BoTMG in the presence of 0–20 equivalents of trifluoroacetic acid (CF_3COOH). Electrolyte = Bu_4NPF_6 and scan rate = 50 mV/s.

to a BODIPY core on the basicity of the appended guanidine, the acidity of [BoTMGH] was measured experimentally to be 23.4 in MeCN. This result shows that by reducing the BODIPY core, the basicity of an appended amine can be increased by about 14 pK_a units.

6. Electrochemical chemiluminescence of BODIPY dyes

Recent investigations into the electrochemistry of BODIPY dyes has shown that many BODIPY dyes exhibit electrogenerated chemiluminescence (ECL). ECL occurs when radical anions and cations generated in an electrochemical experiment combine to generate an excited state, which emits light upon relaxation to the ground state (Eqs. (1)–(4)) [2]. ECL is a function of radical stability, where stable and long-lived singlet or triplet radicals, with high photoluminescent quantum yields, tend to produce bright ECL. BODIPY singlet lifetimes are in the nanosecond range, while triplet lifetimes are in the microsecond range. BODIPY cores lacking substitution in the 2,6-positions result in unstable radical cations, leading to low annihilation intensity upon reduction. Long wavelength ECL, above 700 nm, can be generated by the formation and annihilation of dimerized BODIPY cores [2, 30].

$$\text{BODIPY} + e^- \rightarrow \text{BODIPY}^{\bullet -} \quad (1)$$

$$\text{BODIPY} - e^- \rightarrow \text{BODIPY}^{\bullet +} \quad (2)$$

$$\text{BODIPY}^{\bullet -} + \text{BODIPY}^{\bullet +} \rightarrow 2\,\text{BODIPY}^* \quad (3)$$

$$\text{BODIPY}^* \rightarrow \text{BODIPY} + h\nu \quad (4)$$

ECL can be enhanced through the substitution of the BODIPY core. For example, Hesari and coworkers have successfully enhanced ECL in a BODIPY dye by appending an electron donating biphenyl carboxylic acid in the 8-position, and two styryl groups containing long alkyl chains in the 3,5-positions of the BODIPY core [31]. The biphenyl and styryl substituents increased intermolecular π-interactions, providing a feasible route for energy transfer. The 1,7-positions were substituted with methyl groups, to increase the stability of the electro-generated radicals, and discourage dimerization. An ECL efficiency as high as 100% relative to $[Ru(bpy)_3]^{2+}$, where bpy = bipyridine, was observed [31]. In addition to a single BODIPY dye exhibiting ECL, bipyridine and thiolate-separated BODIPY dimers can produce ECL signals corresponding to the simultaneous transfer of two electrons to non-interacting BODIPY groups. The bipyridine and thiolate-separated BODIPY dimers exhibit substitution in the 2-, 3-, 5-, and 6-positions to increase radical stability [2]. BODIPY dyes lacking substitution in critical locations are vulnerable to dimerization, leading to multiple ECL signals. As reported by Bard and coworkers, upon comparison of two poly(ethylene glycol)-substituted BODIPY dyes, the BODIPY that did not exhibit enough steric bulk in the 3,5-positions resulted in two ECL signals while the other BODIPY resulted in only one ECL signal [6].

7. Photoredox chemistry with BODIPY dyes

The implementation of light to promote the conversion of difficult organic transformations has received increased interest from the organic community. The illumination of organic reactions utilizing a photoredox catalyst, a light-sensitive compound that mediates the transfer of electrons (via single-electron transfer events) between chemical compounds when illuminated, can promote reactions that progress slowly or not at all. Dye molecules are attractive photoredox catalyst motifs due to their strong light absorbing capabilities [32–35].

Photocatalysis often involves the excitation of a photocatalyst from a singlet ground state to a singlet excited state upon illumination. The higher energy excited state results in a catalyst molecule that acts as a stronger reductant due to the presence of an electron in a high-energy state. Similarly, the photoexcited catalyst molecule also acts as a stronger oxidant than the ground state molecule due to the presence of a low energy singly occupied orbital which is capable of accepting an electron. Functionalized BODIPY dyes can act as good photocatalyst candidates as they can have long lived triplet excited states, in the microsecond range, as well as tunable redox potentials. To achieve long-lived triplet states, the incorporation of heavy atoms (e.g. iodide) into the BODIPY core can promote intersystem crossing from a singlet excited state to a triplet excited state. BODIPY dyes capable of intersystem crossing events exhibit triplet excited state lifetimes (μs) about 1000 times longer than a singlet excited state (ns) [36].

BODIPY photocatalysts have recently been used to oxidize 1,4-dihydropyridines [37]. A key characteristic of the BODIPY photocatalysts is the presence of methyl groups in the 1,7-positions of the BODIPY core to prevent rotation of the phenyl group in the 8-position, which reduces non-radiative decay of the excited state. The presence of iodide in the 2,6-positions increases the likelihood of intersystem crossing through the heavy atom effect, which increases the lifetime of the excited state. The incorporation of a single styryl phenyl group with a para-alkylamine in the 3,5-positions lengthens the conjugated π-system, providing

enough electron donation from the dimethylamine fragment to stabilize the radical anion without hindering catalytic reactivity. A BODIPY photocatalyst, **Figure 9**, generated 98% of the pyridine product in 28 min. Without the presence of a styryl amino substituent in the 3,5-positions on the BODIPY core, the reaction conversion slightly decreased by 3%. The yield decreased an additional 1% with the addition of an electron-withdrawing cyanide group into the styryl substituent at the 3,5 positions. The oxidation reaction was more drastically effected by the addition of an electron-withdrawing nitro group onto the para-position of the phenyl group located at the 8-position of the BODIPY photocatalyst, resulting in a 30% reduction in product conversion. The decrease in catalytic activity is attributed to the increased stabilization of the radical anion, which reduces the reactivity of the radical anion, preventing the loss of H^+ (**Figure 9**). When a styryl group with a para-alkylamine is added to the 3,5-position on the nitro-containing BODIPY, the reaction yield decreased further, to 11.9%, as both of the substitutions stabilize BODIPY radical anions.

BODIPY cores containing iodide substituents have also been utilized in aerobic oxidation reactions through the photocatalytic generation of singlet oxygen ($^1O_2$). For example, Zhao and coworkers have described the aerobic oxidative coupling of amines and the photooxidation of dihydroxylnaphthalenes, via C—H functionalization of 1,4-naphthoquinone, to produce *N*-aryl-2-amino-1,4-naphthoquinones. All of the iodide-containing BODIPY dyes tested outperformed the traditional [Ir(2-phenylpyridine)(bpy)]$^+$ (37% conversion) and [Ru(bpy)$_3$]$^{2+}$ (58% conversion) photocatalysts with 100% conversion in 1 h. Rose Bengal, another traditional photocatalyst, exhibited only an 81% conversion in 1 h [38]. Cozzi and coworkers have showed iodide-containing BODIPY dyes are able to photocatalytically promote the Atom-Transfer Radical Addition (ATRA) reaction between brominated alkanes and alkenes using sodium ascorbate as a sacrificial reductant. The proposed reaction mechanism utilizes a BODIPY-based long-lived triplet excited state to generate an organic radical from the brominated alkane. The photocatalytic reaction generated yields greater than 50% for all 20 substrates described, utilizing only 1 mol% of the BODIPY dye [39].

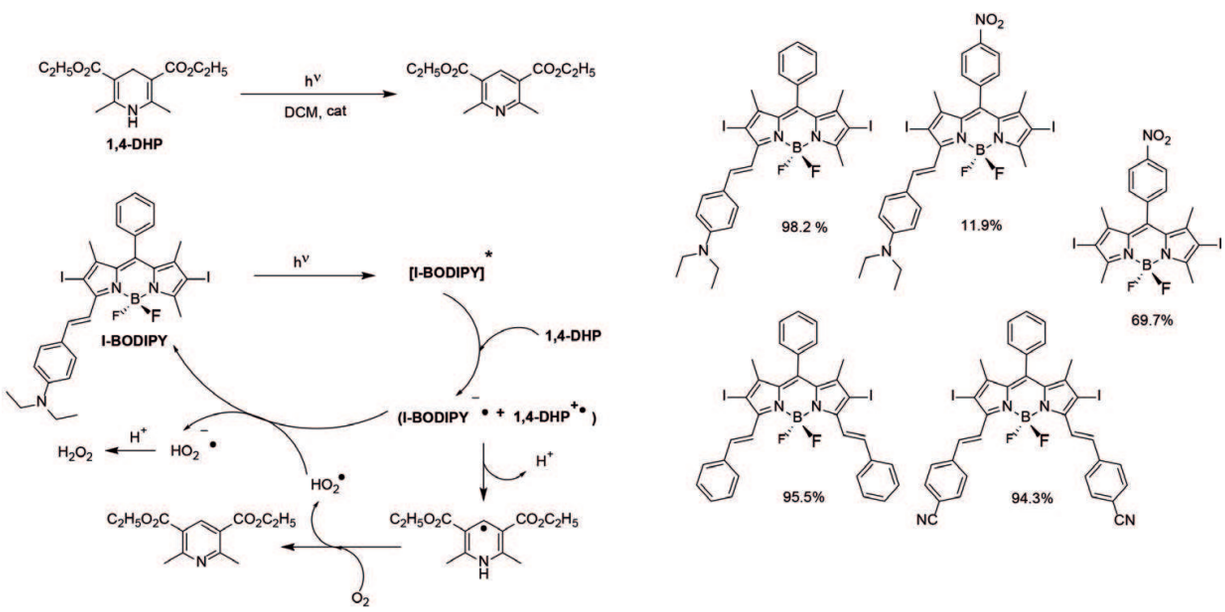

Figure 9. Reaction scheme (top left) and mechanism (bottom left) of the catalytic oxidation of 1,4-dihydropyridines with various BODIPY photocatalysts (right). The numbers shown below the BODIPY photocatalysts indicate product yields after 60 min.

BODIPY dyes have also been utilized as heterogeneous photoredox catalysts. Zhao and coworkers have affixed a BODIPY dye containing iodide substituents in the 2,6-positions to porous silica. The heterogeneous photocatalyst was employed in tandem oxidation and [3 + 2]-cycloaddition reactions of tetrahydroisoquinoline with *N*-phenylmaleimides to generate pyrrolo[2,1-a] isoquinoline in 82% isolated yield after 1 h [40]. BODIPY cores affixed via aza-linkers to fullerene molecules have also shown some catalytic ability, specifically for the tandem oxidation/[3 + 2] cycloaddition of tetrahydroisoquinoline with *N*-phenylmaleimide to produce pyrrolo[2,1-a]isoquinolines [41]. A C_{60}-appended BODIPY dye has been shown to perform oxidative [3 + 2] cyclizations on varying phenylmaleimides, generating product yields greater than 80% in an hour, which was twice as much product as $Ru(bpy)_3Cl_2$ promoted over 4 h [41].

8. Conclusions

BODIPY and azaBODIPY dyes are capable redox reagents, which can act as electron reservoirs in electron transfer reactions. The reduction potential of a BODIPY core can be manipulated by almost 1.4 V, ranging from a potential as reducing as −2.4 V to a potential as moderate as −0.35 V vs. Cp_2Fe/Cp_2Fe^+. The respective azaBODIPY dyes are on average about 600 mV easier to reduce (more positive potentials) than the respective BODIPY dyes. In addition to reductions, the oxidation potential of a BODIPY core can be manipulated by about 1.3 V, ranging from a potential as high as 1.55 V to a potential as low as 0.18 V vs. the Cp_2Fe/Cp_2Fe^+ couple. Although a large shift between the reduction potentials of a BODIPY and azaBODIPY-core result, the difference in oxidation potentials is less profound (about 20 mV). Reduction at a BODIPY or azaBODIPY core results in an increase of aromaticity of the BODIPY or azaBODIPY core. The opposite trend occurs upon oxidation of a BODIPY or azaBODIPY core. The redox nature of a BODIPY core can be utilized to modulate the basicity of an appended amine center by 14 pK_a units, exhibit electrochemically generated chemiluminescence, and promote photoredox reactions. The redox behavior of the BODIPY and azaBODIPY cores opens up the possibility of implementing these dye molecules in many exciting future electron transfer applications, such as redox flow batteries [5] and switchable catalysis [42].

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