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Synthesis and Characterization of Hydrazine-Appended BODIPY Dyes and the Related Aminomethyl Complexes

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Abstract

The synthesis and characterization of three new organic hydrazines containing BODIPY dyes is described. The respective aminomethyl complexes were also synthesized to aid in the assignment of the physical properties that were hydrazine-based vs. BODIPY-based. Incorporation of a BODIPY dye into an organic hydrazine introduced a reduction event (average value of -1.70 V vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$). Although two irreversible oxidation events were observed, it was unclear whether the oxidation events arose from BODIPY-based or amine/hydrazine-based oxidations. The respective BODIPY-appended hydrazine complexes exhibited excited state lifetimes on the order of 2–6 ns, suggesting the presence of a singlet excited state. The excited state lifetimes of the BODIPY-appended hydrazine complexes were about a factor of ten greater than the respective aminomethyl complexes. Computational analysis showed that by appending a BODIPY dye to a hydrazine fragment the hydrazine fragment becomes more susceptible to transfer H_2 equivalents as protons and hydrides as opposed to H-atoms, which occurs with common organic hydrazines. Computational analysis also revealed that the BODIPY-based redox events can be used to manipulate the mechanism for H_2 transfer from the BODIPY-appended hydrazine, where a BODIPY-based reduction favors H-atom transfer and a BODIPY-based oxidation favors proton transfer followed by hydride transfer.

Graphical Abstract

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Conflicts of interest

There are no conflicts to declare.

[†]Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: multinuclear NMR spectra, cyclic voltammograms, normalized UV-Vis and fluorescence spectra of all reported complexes, computed free energies for H_2 , H-atom, proton, and hydride transfer from the examined hydrazine and aminomethyl complexes, computed energy gaps between the frontier molecular orbitals of the examined hydrazines and aminomethyl complexes, gas phase energies and 3D coordinates of all computed structures. See DOI: [10.1039/c9nj02859e](https://doi.org/10.1039/c9nj02859e)

The synthesis and characterization of three new organic hydrazines containing BODIPY dyes and the respective aminomethyl complexes is described.

Introduction

Hydrazine has many applications, whether it be reductions, rearrangements, or the synthesis of heterocycles or peptides.¹ Although hydrazine has been widely employed in organic synthesis, its most important uses are as polymerization initiators, blowing agents for foamed plastics, the production of pesticides, and the generation of organic hydrazines.² About 80–90% of hydrazine production is converted into its organic derivatives.^{2–3} Although organic hydrazines are widely known, little has been studied in the ability to coordinate a redox-active fragment to a hydrazine moiety to influence the reactivity of the hydrazine center. An approach that introduces redox capabilities into organic hydrazines is by appending fluorescent dyes to the hydrazine fragment. Fluorescent dyes are attractive candidates for introducing redox capabilities, as they exhibit reversible redox chemistry.^{4–5} One dye molecule that has been utilized in reversible electrochemistry is the metal-free 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) molecule (Figure 1).⁵ The BODIPY molecule has been widely employed as a fluorescent dye,⁶ in photodynamic therapy,⁷ and as a sensor for molecules such as cyanide,^{8–9} nitric oxide,¹⁰ carbon dioxide,¹¹ and heavy metals.¹²

Several groups have shown that a hydrazine fragment can be appended to a BODIPY dye. Song and coworkers have reported the synthesis of a hydrazine group appended to a BODIPY dye in the 8-position and have implemented this hydrazine-appended dye for the detection of formaldehyde in aqueous solutions.¹³ Upon treatment of the hydrazine-appended dye (which does not emit) with formaldehyde the fluorescence of the dye molecule turns on. Bane and coworkers have synthesized hydrazine appended BODIPYs by nucleophilic substitution in the 3-position and investigated the influence of BODIPY substitution on the resulting UV-Vis and fluorescence spectra.¹⁴ Xu and coworkers have shown that a hydrazine appended BODIPY dye (3-position) can be used as a fluorescent probe for hypochlorite.¹⁵

Related to the reported hydrazine-appended BODIPY complexes, Hiroto and coworkers have synthesized a diazo-bridged BODIPY dimer by the oxidation of an amino-substituted BODIPY dye.¹⁶ Filarowski and coworkers have reported the generation of a BODIPY-Schiff dye by the Schiff base condensation of a hydrazine-appended BODIPY (in the 3-position) to an aldehyde, to examine their photophysical properties.¹⁷ Niu and coworkers have described the E-Z isomerization of a hydrazone, where they have been able to show reversible “on/off” fluorescence switching by exposure to irradiation or the addition of an acid/base.¹⁸

Although hydrazine-appended BODIPY dyes have been synthesized, the influence of the BODIPY dye on the reactivity beyond its utilization as a fluorescent probe has not been investigated. We have previously shown that by appending a 1,1,3,3-tetramethylguanidine fragment to a BODIPY dye, the basicity of the tetramethylguanidine fragment could be modulated by 14 pK_a units through a BODIPY-based redox event.¹⁹ We have also shown that by appending a BODIPY dye to a nitrogen center, the basicity of that nitrogen center is

greatly diminished.^{19–20} Based on these results, we hypothesized that by appending a BODIPY fragment to a hydrazine or organic hydrazine fragment would allow for control of the chemistry that occurred at a hydrazine center. In this manuscript we describe the synthesis and characterization of three new hydrazine-appended BODIPY dyes and the related 8-aminomethyl-BODIPY derivatives to investigate the influence of a BODIPY dye on the reactivity of an appended hydrazine fragment.

Results and Discussion

Synthesis and Characterization of New BODIPY Appended Hydrazine Complexes

The generation of hydrazine-appended BODIPY dyes can occur through the nucleophilic aromatic substitution of 8-methylthio-BODIPY (**BoSMe**) in 40–90 % yields with aryl or alkyl hydrazines. This approach has been utilized by Bañuelos and coworkers in the synthesis of blue-emitting laser dyes.^{21–28} For example, the addition of 1.2 equivalents of hydrazine monohydrate to one equivalent of **BoSMe** in acetonitrile resulted in **BoNHNH₂** in a 90 % yield. (Equation 1). Similar results were obtained by the addition of phenylhydrazine or 2-pyridylhydrazine to **BoSMe**, resulting in **BoNHNHPh** and **BoNHNHPy**, respectively (Equation 1). Song and coworkers have recently reported the synthesis of **BoNHNH₂** utilizing 8-chloro-BODIPY (**BoCl**) as a BODIPY source, but were only able to obtain a 60 % yield.¹³ The resulting BODIPY-appended hydrazines exhibited a 1:1:1:1 quartet centered around –145 ppm in the ¹⁹F NMR spectrum. A 1:1:1:1 quartet in the ¹⁹F NMR spectrum arises from the one bond coupling (~ 28 Hz) between the fluorine atoms and ¹¹B (I = 3/2), which is 80% abundant. A slight shoulder on the 1:1:1:1 quartet is attributed to coupling between the fluorine atoms and ¹⁰B (I = 3,

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(2)

20% abundant). The ^{11}B NMR spectrum for each complex exhibited a triplet, at 1.7–1.9 ppm for the aryl hydrazine complexes and at 0.58 ppm for **BoNHNH₂**. Each had $^1J_{\text{BF}} = 28$ Hz coupling constant in the ^{11}B NMR spectrum, verifying the addition of a BODIPY fragment to the hydrazine fragments.

Treatment of **BoNHNH₂** with an additional equivalent of **BoSMe** did not result in the incorporation of a second BODIPY dye onto the hydrazine fragment, even with heating. Incorporation of a second BODIPY dye was achieved by treating **BoNHNH₂** with **BoCl** in the presence of a base. We have observed a similar result in appending multiple BODIPY dyes to chiral and achiral diamines.²⁰ Treatment of the tan colored **BoNHNH₂** with one equivalent of **BoCl** in the presence of four equivalents of K_2CO_3 (Equation 2) for 24 hours resulted in an orange colored solid (**BoNHNHBo**) that weakly fluoresced blue-green in methanol. **BoNHNH₂** does not fluoresce under the same conditions. Whereas the ^1H NMR spectrum of **BoNHNH₂** revealed six evenly spaced pyrrole resonances between 6.5 and 8.0 ppm (see Supporting Information, Figure S1), the ^1H NMR spectrum of the pyrrole resonances of **BoNHNHBo** exhibited almost a ppm upfield shift from the resonances of **BoNHNH₂** (see Supporting Information, Figure S5). The incorporation of a second BODIPY dye onto a hydrazine fragment resulted in a slight downfield shift in the ^{19}F NMR spectrum (from -145 ppm to -143.65 ppm) and a two ppm downfield shift in the ^{11}B NMR spectrum. The downfield shifts observed in the NMR spectra are attributed to the deshielding effect of an additional electron deficient BODIPY dye attached to the hydrazine fragment. Samples of **BoNHNHBo** stored on the benchtop were found to slowly decompose over the course of a week. No change was observed in samples of **BoNHNH₂**, when stored under similar conditions.

To determine the influence of a BODIPY dye on a hydrazine fragment, the respective aminomethyl compounds were also generated (Figure 2). For example, the addition of two equivalents of 2-(aminomethyl)pyridine to a solution of **BoSMe** in acetonitrile produced the yellow colored (aminomethyl)pyridine-appended BODIPY, **BoNHCH₂Py**, in 73 % yield. The respective benzylamine (**BoNHCH₂Py**) was also prepared as reported by Banuelos and coworkers.²⁵

Molecular Structure Analysis of Hydrazine-Appended BODIPYs

To investigate the orientation of the hydrazine moiety in relation to the appended BODIPY dye, crystallization of the BODIPY-appended hydrazines was attempted. X-ray quality crystals of **BoNHNH₂** were grown by the diffusion of hexanes into an ethyl acetate solution. X-ray structural analysis revealed that the nitrogen proximal to the BODIPY dye exhibited a trigonal planar type geometry (Figure 3), similar to the NH_2 group in the structure of 8- NH_2 -BODIPY.²⁹ The distal nitrogen center exhibited more of a tetrahedral geometry, with the lone pair residing in the same plane as the pyrroles of the BODIPY dye. The fact that **BoNHNH₂** does not emit is intriguing, as the BODIPY dye is nearly planar (deviation from planarity is less than 8°), where dyes with deviations of greater than 15° have been shown to not emit.²⁹ Crystallization attempts of **BoNHNHPh**, **BoNHNHPy**, and **BoNHNHBo** resulted in amorphous solids, twinned crystals that were not solvable, and crystals that did not diffract, respectively. Crystals of **BoNHCH₂Py** were grown from slowly cooling a hot

(77 °C) ethyl acetate solution to –13 °C. Molecular structure analysis revealed the presence of a hydrogen bond between N(3)H and the pyridyl nitrogen (Figure 3). The co-planarity of the pyridine ring and the BODIPY dye is attributed to this hydrogen bonding interaction. Bañuelos and coworkers have shown that the phenyl group of **BoNHCH₂Ph** does not reside in the same plane as the BODIPY dye.²⁵

Photophysical Properties of Hydrazine-Appended BODIPYs

To investigate the influence of incorporating a BODIPY dye into a hydrazine fragment, the photophysical properties of the generated hydrazine and aminomethyl-appended BODIPY dyes were investigated. Whereas appending a phenyl group to the distal nitrogen of **BoNHNH₂** resulted in no effect on the absorption or emission spectra, appending a pyridyl group on the distal nitrogen of **BoNHNH₂** resulted in a 15 nm bathochromic shift in the absorption. Addition of a second BODIPY dye to the distal nitrogen of **BoNHNH₂**, generating **BoNHNHBo**, resulted in a five nm bathochromic shift in the absorption spectrum and the presence an additional emission (three as opposed to two) in the emission spectrum (see Supporting Information). The origin of the additional excited state is attributed to the presence of an additional BODIPY dye in **BoNHNHBo**. The excited state lifetimes of the BODIPY-appended hydrazines all exhibited 2–6 ns lifetimes, suggesting the presence of a singlet excited state.⁵ The respective BODIPY-appended hydrazine complexes also exhibited excited state lifetimes about a factor of ten more than the respective amino-methyl complexes. Computational analysis of the excited states using time-dependent density functional theory of the BODIPY-appended hydrazine and aminomethyl complexes revealed that the hydrazine-appended BODIPY dyes exhibited an excited state transition (HOMO-1 to LUMO) from the arene-hydrazine moiety to the BODIPY dye, generating a charge-separated state. This transition was not present in the respective aminomethyl complexes, which only exhibited excited states with BODIPY to BODIPY transitions. The presence of a charge-separated state in the hydrazine-appended BODIPY dyes, and not in the aminomethyl-appended BODIPY dyes, is proposed to be the origin of the longer excited state lifetimes of the hydrazine-appended BODIPY dyes. The quantum yields of the BODIPY-appended hydrazines were also very low, except for the two complexes (**BoNHNHPy** and **BoNHCH₂Py**) that exhibit intramolecular hydrogen bonding between the nitrogen of a pyridyl group and an amine or hydrazine proton (see below). The intramolecular hydrogen bonding of **BoNHNHPy** and **BoNHCH₂Py** contributes to the increased fluorescence quantum yields through the increased rigidity of the molecular frameworks.

Electrochemical Analysis of Hydrazine-Appended BODIPYs

The redox properties of the hydrazine-appended BODIPY dyes were investigated using cyclic voltammetry (CV), in a 0.1 M acetonitrile solution of Bu₄NPF₆, referenced to Cp₂Fe/Cp₂Fe⁺. BODIPY dyes are capable of reversible reductions at the average reduction potential of –1.53 V vs. Cp₂Fe/Cp₂Fe⁺, with the reduction potentials varying about 700 mV from this average value depending on the substitution of the BODIPY core.⁵ 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.⁵ To examine the influence of appending a BODIPY dye to hydrazine, the

electrochemistry of **BoNHNH₂** was compared to the phenyl (**PhNHNH₂**) and pyridyl (**PyNHNH₂**) hydrazines (Table 1). Whereas the cyclic voltammogram of **PhNHNH₂** revealed the presence of two irreversible oxidation events (Table 1 and Supporting Information, Figure S21), the cyclic voltammogram of **PyNHNH₂** only exhibits a single oxidation at 1.19 V. The incorporation of a pyridyl group into a hydrazine also introduced an irreversible reduction at -2.75 V (Table 1 and Supporting Information, Figure S22). The cyclic voltammogram of **BoNHNH₂** (see Supporting Information, Figure S23) exhibited an irreversible reduction about one volt more positive (easier to reduce) than **PyNHNH₂** and two irreversible oxidation waves.

To examine the influence of appending groups to the distal nitrogen atom, the electrochemistry of disubstituted hydrazines were also investigated. Adding a second phenyl group to **PhNHNH₂**, resulting in **PhNHNHPh**, yielded an additional irreversible reduction at -0.95 V and a second oxidation at 1.61 V and a slight anodic shift (harder to oxidize) of the existing oxidation events. Replacement of one of the phenyl groups of **PhNHNHPh** with a BODIPY dye introduced an irreversible reduction event and shifted most of the redox events in a cathodic direction (easier to oxidize). Replacement the phenyl group of **BoNHNHPh** with a pyridyl group resulted in an anodic shift (easier to reduce) of the reduction waves. Substitution of the phenyl group of **PhNHNHPh**, with a BODIPY dye resulted in a cathodic shift (easier to oxidize, harder to reduce) of the oxidation and reduction waves.

To help determine which of the observed redox events were BODIPY-based and which redox events were hydrazine-based, the respective amino-methyl complexes were examined. Upon comparison of the cyclic voltammogram of **BoNHNHPh** and **BoNHCH₂Ph**, the reduction events at -1.76 V and -1.77 V, respectively are BODIPY-based reductions. Although three irreversible oxidation events were observed for **BoNHNHPh** and two irreversible oxidation events were observed **BoNHCH₂Ph**, it was unclear whether the oxidation events arose from BODIPY-based or amine/hydrazine-based oxidations, preventing further assignment of the oxidation events. Similar results can be seen from the comparison of the redox chemistry of **BoNHNHPy** and **BoNHCH₂Py**.

Computational Analysis

To obtain further insight into the influence of hydrazine fragments appended to a BODIPY dye, computational analysis, using density functional theory employing the M06-2X functional,³⁰ of the hydrazine and respective amino-methyl complexes described within was undertaken. Examination of the bond distance between the nitrogen appended to a phenyl/pyridyl/BODIPY and the *ipso*-carbon of the phenyl/pyridyl/BODIPY group in **PhNHNH₂**, **PyNHNH₂**, and **BoNHNH₂** showed a 0.01 Å contraction when comparing **PyNHNH₂** to **PhNHNH₂** and a 0.08 Å contraction upon when comparing **BoNHNH₂** to **PhNHNH₂**. The contraction of the N-C bond is attributed to the increased electron withdrawing nature when going from phenyl to pyridyl to BODIPY. Comparison of the distance between the nitrogen-appended to the BODIPY dye and the *ipso*-carbon of BODIPY dye in **BoNHNHPh**, **BoNHNHPy**, **BoNHCH₂Ph**, and **BoNHCH₂Py** showed a 0.01 Å longer bond in the BODIPY-appended hydrazines than in the BODIPY-appended aminomethyl complexes. A

lengthening of the N-N bond in the BODIPY hydrazines also occurred upon moving from **BoNHNHPh** to **BoNHNHPy** to **BoNHNHBo**.

Computational analysis of **BoNHCH₂Py** revealed that the hydrogen bonding interaction between the NH and the pyridyl group resulted in a complex that was 2.9 kcal/mol more stable than if the nitrogen of the pyridyl group was pointed away from the amine center. In the case of **BoNHNHPy**, the hydrogen bonding with the proton on the nitrogen center proximal to the pyridine center was 2.2 kcal/mol more favorable than the hydrogen bonding interaction with the distal nitrogen atom (Figure 4). The observed hydrogen bonding interactions of **BoNHCH₂Py** and **BoNHNHPy** are proposed to be the origin of the increased quantum yields, when compared to the respective phenyl complexes (see above).

Examination of the frontier molecular orbitals revealed that by appending a phenyl group to hydrazine, the HOMO-LUMO gap decreased about 40 kcal, but only a seven kcal decrease in the HOMO-LUMO gap was observed by the addition of a second phenyl group (e.g. phenylhydrazine to 1,2-diphenylhydrazine). Appending a BODIPY dye, as opposed to a phenyl group to hydrazine (e.g. **BoNHNH₂**) resulted in the reduction of the HOMO-LUMO gap by 75 kcal, and a reduction of HOMO-LUMO gap by an additional eight kcal upon addition of a second BODIPY dye (e.g. **BoNHNH₂** to **BoNHNHBo**). Appending a BODIPY dye to phenylhydrazine resulting in **BoNHNHPh**, resulted in a 37 kcal reduction in the HOMO-LUMO gap, whereas appending a phenyl group to **BoNHNH₂** to generate **BoNHNHPh** resulted in only a three kcal reduction in the HOMO-LUMO gap. Appending a pyridyl group (e.g. **BoNHNHPy**) as opposed to a phenyl group (**BoNHNHPh**) resulted in almost a negligible (< 1 kcal) change to the HOMO-LUMO gap when compared to **BoNHNH₂**. The respective aminomethyl complexes (e.g. **BoNHCH₂Ph** and **BoNHCH₂Py**) exhibited a HOMO-LUMO gap about 2.5 kcal larger than the respective hydrazine complexes.

Hydrazine have been shown to act as reductants in several organic reactions.¹ To examine the ability of hydrazines and the respective aminomethyl complexes to act as a hydrogen source in reduction reactions, computational analysis of the ability of these complexes to lose H₂ was computed (Equation 3). As a benchmark, the loss of H₂ from hydrazine to generate diazene was computed to be endergonic by 20.8 kcal/mol, with the subsequent loss of H₂ to generate N₂ being exergonic by about 50 kcal/mol (Table 2). Appending one phenyl group to hydrazine increased the ability to lose H₂ by about one kcal/mol and about 11 kcal/mol upon appending two phenyl groups to hydrazine. Although appending phenyl groups to hydrazine made H₂ loss more favorable, appending BODIPY dyes to hydrazine fragments decreased the ability to lose H₂. Appending one BODIPY dye to hydrazine disfavored H₂ loss by about 18 kcal/mol when comparing H₂ loss from **BoNHNH₂** to H₂ loss from hydrazine. The addition of a second BODIPY dye had a minimal effect on the ability to lose H₂, as H₂ loss from **BoNHNHBo** was only about one kcal/mol less favorable than from **BoNHNH₂**. The addition of a phenyl or pyridyl group to **BoNHNH₂**, generated hydrazines that were about ten and six kcal/mol more favorable to lose H₂ (Table 2). Upon comparison of H₂ loss from the respective aminomethyl complexes, **BoNHCH₂Ph** and **BoNHCH₂Py** were four and eight kcal/mol, respectively, more favorable to lose H₂ than the

respective hydrazine complexes. This result is attributed to the increased stability of the imine vs. diazene complexes upon loss of H₂.

(3)

Since hydrazines have been employed in the reduction of organic substrates, the thermodynamics for the transfer of protons, H-atoms, and hydrides from the examined hydrazines was also investigated. This investigation was targeted to provide insight into the possible mechanisms for H₂ transfer from BODIPY-appended hydrazines. Given that H₂ loss from a hydrazine results in a diazene fragment, the transfer of H-atoms (Equations 4, S3, and S4), as opposed to hydrides or protons was hypothesized to be more favorable mechanism for H₂ loss and was investigated first. Computational analysis of the loss of a H-atom from hydrazine was about 14 kcal/mol less favorable than TEMPOH (G_{H•} = 66.5 kcal/mol).³¹ Appending a phenyl group to hydrazine caused the H-atom proximal to phenyl group to be about two kcal/mol more favorable for H-atom transfer than

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the distal H-atom (Figure 5). A similar result occurred for **BoNHNH₂**, but the proximal H-atom was about four kcal/mol more favorable for H-atom loss than the distal H-atom. The attachment of a BODIPY dye to a hydrazine fragment had little effect on the ability to transfer H-atoms, as the transfer of the first H-atom from **BoNHNH₂** exhibited very similar thermodynamics to H-atom loss from hydrazine. Upon loss of the first H-atom, the loss of the second H-atom resulted in a H-atom loss about 10 kcal/mol less favorable than the loss of the second H-atom from hydrazine or a phenyl appended hydrazine. The reduced ability to transfer H-atoms from **BoNHNH₂** is attributed to the electron withdrawing nature of the BODIPY dye. Upon examination of the respective aminomethyl complexes, H-atom loss from the C-H bond was found to be about 20 kcal/mol more favorable than H-atom loss from the N-H bond (Figure 5).

Instead of an initial H-atom transfer from a hydrazine fragment, a proton could be initially removed (Equation 5). Computational analysis of the pK_a of hydrazine (pK_a = 60.1 in MeCN) revealed a high basicity of hydrazine. Appending a phenyl group to hydrazine (**PhNHNH₂**) results in the nitrogen center proximal to the phenyl group to be acidified by about 15 pK_a units and the distal nitrogen center to be acidified by about six pK_a units, when

compared to hydrazine (Figure 6). Upon appending a second phenyl group, the nitrogen center is acidified by an additional eight pK_a units, when compared to **PhNHNH₂**. As seen with appending BODIPY dyes to amine centers,²⁰ the hydrazine fragment of **BoNHNH₂** is acidified by 40 pK_a units at the proximal nitrogen and 16 pK_a units at the distal nitrogen center, when compared to hydrazine (Figure 6). Appending a second BODIPY dye to **BoNHNH₂** further acidifies the nitrogen centers, exhibiting pK_a 's almost 50 pK_a units more acidic than hydrazine. As expected, appending a pyridyl or a

(5)

phenyl group to **BoNHNH₂** resulted in an increase in the acidification of the proximal nitrogen center by one and two pK_a units, respectively. When compared to the respective aminomethyl complexes, the hydrazine complexes were about eight pK_a units more acidic than the respective aminomethyl complexes. These results suggest that the incorporation of an electron deficient BODIPY dye into a hydrazine fragment results in a hydrazine fragment that favors proton transfer.

In addition to the ability of proton and H-atom transfer from a hydrazine fragment, hydrazine fragments also present the possibility to transfer hydrides. Computational analysis of the hydride donor ability of hydrazine (Equation 6) showed that hydride transfer from hydrazine is as favorable as PhSiH_3 ($G_{\text{H}^-} = 96.3$ kcal/mol).³² Appending a phenyl group to hydrazine (**PhNHNH₂**) increased the ability to transfer a hydride from the proximal nitrogen by seven kcal/mol and the distal nitrogen by three kcal/mol (Figure 7). Addition of a second phenyl group (**PhNHNHPh**) generated a hydride donor that was 17 kcal/mol favorable than hydrazine and ten kcal/mol more favorable than phenylhydrazine (Figure 7). As expected, appending a highly electron withdrawing BODIPY dye to hydrazine results in a hydrazine that is about 22 kcal/mol less favorable to transfer a hydride than hydrazine. Appending a second BODIPY dye (**BoNHNHBo**) further disfavored hydride transfer by an additional 14 kcal/mol. Appending a phenyl or pyridyl group to **BoNHNH₂** resulted in complexes that were nine and four kcal/mol more favourable, respectively, for hydride transfer than **BoNHNH₂**. Comparison of hydride transfer from **BoNHNHPh** and **BoNHNHPy** to the respective aminomethyl complexes revealed that the aminomethyl complexes were about 15 kcal/mol more likely to transfer a hydride, with the hydride coming from the CH_2 fragment as opposed to the N-H bond, which was about 50–70 kcal/mol less favorable for hydride transfer. These results suggest that the incorporation of an electron deficient BODIPY dye into a hydrazine fragment results in a hydrazine fragment that disfavors hydride transfer.

From the analysis of proton, hydride, and H-atom loss from hydrazine and the investigated organic hydrazines, when not considering kinetic barriers, H-atom transfer appeared to be the most favorable method for H₂ transfer from hydrazine, **PhNHNH₂**, **PyNHNH₂**, and **PhNHNHPh**. In the case of the BODIPY-appended hydrazines, proton transfer followed by hydride transfer appears to be a more favorable pathway for H₂ transfer than H-atom transfer. The ability of BODIPY dyes to undergo redox reactions also allows for the ability to influence the mechanism of H₂ transfer. Oxidation of the BODIPY-appended hydrazines disfavored H-atom and hydride loss and favored proton loss, followed by hydride loss. Reduction of the BODIPY-appended hydrazines disfavored proton loss and favored H-atom and hydride followed by proton loss, with the loss of H-atoms being more favorable than an initial hydride loss followed by proton loss. These results suggest that the redox chemistry of a BODIPY-appended hydrazine can be utilized to control the reduction mechanism of substrate molecule employing a BODIPY-appended hydrazine as a H₂ source.

Conclusions

The synthesis of three new BODIPY-appended hydrazines and one new BODIPY-appended aminomethyl complex was reported. The incorporation of one or two BODIPY dyes within the hydrazine scaffold resulted in organic hydrazines that weakly fluoresced. The BODIPY-appended hydrazine and aminomethyl complex that exhibited the greatest fluorescence contained intramolecular hydrogen bonding between a pyridyl group and an amine/hydrazine center. Cyclic voltammetry experiments showcased the redox-nature of the BODIPY core, exhibiting a BODIPY-based reduction event at about -1.70 V vs. Cp₂Fe/Cp₂Fe⁺. In addition to the BODIPY-based reduction, each BODIPY-appended hydrazine and aminomethyl complex exhibited two irreversible oxidations, but it was unclear whether the oxidation events were BODIPY-based or amine/hydrazine-based. Computational analysis revealed that H-atom transfer is more likely to occur from organic hydrazines in reduction reactions and proton followed by hydride transfer is most likely to occur from BODIPY-appended hydrazines. Computational analysis also revealed that the redox nature of a BODIPY dye can be utilized to alter the mechanism of H₂ transfer from BODIPY-appended hydrazines. For example, the reduction of BODIPY-appended hydrazines disfavors proton followed by hydride loss and favors the loss of two H-atoms in reduction reactions. The exploitation of BODIPY fluorophores beyond the fields of biochemistry, medicine, and chemical sensing, will continue to remain in the foreground of synthetic chemists for the foreseeable future.

Experimental

Synthetic Techniques

All preparations and manipulations were performed on a double manifold N₂/vacuum line with Schlenk-type glassware or in a N₂-filled VAC glovebox, unless indicated otherwise. Solvents were dried using an Innovative Technologies solvent system, and degassed before use. NMR solvents were purchased from Cambridge Isotopes, and used as received. All remaining reagents were purchased from Sigma Aldrich, Acros Organics, or Alfa Aesar and were used without further purification. **BoSMe** and **BoCl** were prepared according to the

literature procedures.^{20, 33} **BoNHCH₂Ph** was prepared according to procedure published by Bañuelos.²⁵

BoNHNH₂

A 30 mL acetonitrile solution containing 312 mg (1.3 mmol) of 8-methylthio-BODIPY (**BoSMe**) was treated with 80 μ L (1.6 mmol) hydrazine monohydrate resulting in an immediate color change from red to olive green. The solution was stirred for 30 min, then the solvent was removed under reduced pressure, producing a tan solid. Yield: 282.2 mg (1.27 mmol, 96%) ¹H NMR (600 MHz, CD₃CN): δ 4.84 (br, 2H, NH-NH₂), 6.40 (m, 1H, pyrrolic proton), 6.51 (m, 1H, pyrrolic proton), 7.06 (m, 1H, pyrrolic proton), 7.37 (m, 1H, pyrrolic proton), 7.53 (m, 1H, pyrrolic proton), 8.01 (m, 1H, pyrrolic proton), 9.27 (br, 1H, NH-NH₂). ¹¹B NMR (192 MHz, CD₃CN): δ 0.58 (t, ¹J_{BF} = 28.6 Hz, 1B). ¹³C NMR (150 MHz, CD₃CN): δ 113.86, 114.63, 115.24, 122.67, 123.95, 126.81, 131.17, 134.32, 147.91. ¹⁹F NMR (564 MHz, CD₃CN): δ -145.83 (q, ¹J_{BF} = 28.6 Hz, 2F). λ_{max} (MeCN) = 390 nm. $\lambda_{\text{emission}}$ (MeCN) = 463 nm, 504 nm. ϵ = 18820 L cm⁻¹mol⁻¹.

BoNHNHBo

To a solution of **BoNHNH₂** (127.2 mg, 0.57 mmol) in 25 mL acetonitrile 129.6 mg of **BoCl** (0.57 mmol) and 333 mg anhydrous K₂CO₃ (4 eq) were added. The burnt orange solution began to darken around 30 min after the addition of base. After 24 hours, the bittersweet solution was filtered through a pad of celite, and the solvent removed under reduced pressure. The bittersweet residue was triturated in diethyl ether, and the orange solid product filtered and dried. Yield: 211 mg (0.51 mmol, 90%). ¹H NMR (600 MHz, CD₃CN): δ 6.10 (t, 2H, pyrrolic protons), 6.20 (t, 2H, pyrrolic protons), 6.78 (s, 2H, pyrrolic protons), 6.95 (s, 4H, pyrrolic protons), 7.00 (s, 2H, pyrrolic protons), ¹¹B NMR (192 MHz, CD₃CN): δ 2.28 (t, ¹J_{BF} = 31.2 Hz, 1B). ¹³C NMR (150 MHz, CD₃CN): δ 107.84, 110.72, 122.47, 124.04, 127.53, 133.47, 140.44. ¹⁹F NMR (564 MHz, CD₃CN): δ -143.65 (q, ¹J_{BF} = 31.2 Hz, 2F). λ_{max} (MeCN) = 395 nm. $\lambda_{\text{emission}}$ (MeCN) = 387 nm, 446 nm, 504 nm. ϵ = 13936 L cm⁻¹mol⁻¹.

BoNHNHPh

To a solution of **BoSMe** (204 mg, 0.68 mmol) in 25 mL of acetonitrile was added 0.2 mL of phenyl hydrazine (2 mmol). The solution was stirred for 2 hours at room temperature, after which the solvent was removed under reduced pressure. The resulting brown residue was treated with ethyl acetate and hexanes to recrystallize the product, which was collected as a yellow powder. Yield: 78 mg (0.26 mmol, 39%) ¹H NMR (600 MHz, CD₃CN): δ 6.49 (d, 2H, pyrrolic protons), 6.96 (d, 2H, phenyl protons), 6.98 (t, 1H, phenyl proton), 7.23 (s, 1H, pyrrolic proton) 7.31 (t, 2H, phenyl protons), 7.51 (s, 1H, pyrrolic proton) 7.59 (s, 1H, pyrrolic proton) 7.79 (s, 1H, pyrrolic proton) 9.38 (br, 1H, Bo-NH-NH), ¹¹B NMR (192 MHz, CD₃CN): δ 1.71 (t, ¹J_{BF} = 27.7 Hz, 1B). ¹³C NMR (150 MHz, CD₃CN): δ 114.55, 114.85, 115.80, 117.73, 122.73, 127.08, 130.53, 133.60, 136.44, 146.45, 150.34. ¹⁹F NMR (564 MHz, CD₃CN): δ -145.52 (q, ¹J_{BF} = 27.7 Hz, 2F). λ_{max} (MeCN) = 390 nm. $\lambda_{\text{emission}}$ (MeCN) = 461 nm, 503nm. ϵ = 35575 L cm⁻¹mol⁻¹.

BoNHNHPy

To a solution of BoSMe (208 mg, 0.87 mmol) in 15 mL of acetonitrile was added a solution of 2-hydrazinopyridine (117 mg, 1.07 mmol) in 15 mL of acetonitrile. The solution was stirred for 2 hours, and the product collected as an orange precipitate. Additional product can be obtained by cooling the filtrate. Yield: 108 mg (0.36 mmol, 42%) ^1H NMR (600 MHz, CD_3CN): δ 6.40 (d, 2H, pyrrolic proton), 6.94 (t, 1H, pyridinic proton), 7.08 (d, 1H, pyridinic proton), 7.21 (s, 1H, pyrrolic proton), 7.33 (s, 1H, pyrrolic proton), 7.45 (m, 2H, pyrrolic protons), 7.78 (t, 1H, pyridinic proton), 8.09 (d, 1H, pyridinic proton). ^{11}B NMR (192 MHz, CD_3CN): δ 1.90 (t, $^1J_{\text{BF}} = 28.8$ Hz, 1B). ^{13}C NMR (150 MHz, CD_3CN): δ 110.05, 112.43, 113.18, 113.72, 115.89, 121.56, 128.94, 131.64, 140.37. ^{19}F NMR (564 MHz, CD_3CN): δ -145.50 (q, $^1J_{\text{BF}} = 28.8$ Hz, 2F). λ_{max} (MeCN) = 405 nm. $\lambda_{\text{emission}}$ (MeCN) = 458 nm, 506 nm. $\epsilon = 20196 \text{ L cm}^{-1}\text{mol}^{-1}$.

BoNHCH₂Py

To a solution of BoSMe (104 mg, 0.44 mmol) in seven mL of acetonitrile was added 95 mg of 2-(aminomethyl)pyridine (0.88 mmol) in five mL of acetonitrile resulting in a color change from sunset orange to yellow after about 30 seconds, accompanied by the solution fluorescing a blue color. The solution was stirred for five minutes, after which the solvent was removed under vacuum. The product was recrystallized from ethyl acetate, producing a yellow crystalline solid. Yield: 95 mg (0.32 mmol, 73%) ^1H NMR (600 MHz, CD_3CN): δ 5.07 (s, 2H, CH_2), 6.48 (s, 1H, pyrrolic proton), 6.58 (s, 1H, pyrrolic proton), 7.30 (s, 1H, pyrrolic proton), 7.38 (t, 1H, pyridinic proton), 7.43 (s, 2H, pyrrolic protons), 7.50 (d, 1H, pyridinic proton), 7.62 (s, 1H, pyrrolic proton), 7.84 (t, 1H, pyridinic proton), 8.65 (d, 1H, pyridinic proton), 9.17 (br, 1H, NH). ^{11}B NMR (192 MHz, CD_3CN): δ 1.73 (t, $^1J_{\text{BF}} = 28.9$ Hz, 1B). ^{13}C NMR (150 MHz, CD_3CN): δ 50.57, 114.56, 115.74, 116.38, 123.01, 123.62, 124.29, 125.10, 126.32, 132.32, 135.68, 138.59, 148.99, 149.85, 154.19. ^{19}F NMR (564 MHz, CD_3CN): δ -145.37 (q, $^1J_{\text{BF}} = 28.9$ Hz, 2F). λ_{max} (MeCN) = 400 nm. $\lambda_{\text{emission}}$ (MeCN) = 450 nm. $\epsilon = 22549 \text{ L cm}^{-1}\text{mol}^{-1}$.

Spectroscopic Techniques

NMR spectra were obtained on a Varian 600 MHz spectrometer, and spectra were referenced to residual solvent (^1H , ^{13}C) or externally (^{11}B ; $\text{BF}_3\cdot\text{OEt}_2$, ^{19}F ; CCl_3F).³⁴ Chemical shifts are reported in parts per million (ppm), and the chemical shifts of multiplets (multiplicities beyond singlets) are reported in respect to the center of the multiplet. All UV-Vis spectra were obtained on a Cary 60 UV-Vis spectrometer. Cyclic voltammetry (CV) experiments were carried out at room temperature in nitrogen-purged acetonitrile solutions using a CH Instruments Model CHI600E electrochemical workstation. All CV experiments were performed using a glassy carbon working electrode (3.0 mm diameter). The electrode surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use and in between runs. The counter electrode was a carbon rod and the pseudo reference electrode was an Ag/AgCl electrode. The concentration of the sample and supporting electrolyte, tetrabutylammonium hexafluorophosphate, were 1.0 mM and 0.1 M, respectively. The supporting electrolyte was recrystallized from acetonitrile and stored in a desiccator prior to use. To employ moisture free conditions, the CV cell was dried in an oven

(140 °C for 24 hours) prior to use. Voltammograms were referenced to 1.0 mM ferrocene/ferrocenium.

Molecular Structure Refinement Information

X-ray diffraction data for **BoNHNH₂** and **BoNHCH₂Py** were collected at 100 K on a Bruker D8 Venture using MoK α -radiation ($\lambda=0.71073$ Å) using APEX3³⁵ software. The crystal selected of **BoNHNH₂** was an orange rod with dimensions of 0.18 mm x 0.18 mm x 0.02 mm. Data have been corrected for absorption using SADABS³⁶ area detector absorption correction program. The crystal selected of **BoNHCH₂Py** was a yellow prism with dimensions of 0.24 mm x 0.20 mm x 0.14 mm. Data have been corrected for absorption using SADABS³⁶ area detector absorption correction program. Crystallographic data were solved using Olex2.³⁷ A Hirshfeld Atom Refinement³⁸ of the solved X-ray structures of **BoNHNH₂** and **BoNHCH₂Py** resulted in a reduction in the R1 value for **BoNHCH₂Py** from 3.80% to 2.33 % and for **BoNHNH₂** from 3.25% to 1.94%.

Computational Methods

All structures were fully optimized without symmetry constraints using the M06–2X³⁹ functional as implemented in Gaussian 09,⁴⁰ using the 6–31G(d,p) basis set.^{41–42} The exchange-correlation functional M06–2X was chosen for the good overall performance observed in the description of main group compounds and BODIPY complexes.^{30, 32, 39, 43} In all calculations, the ultrafine integration grid was employed to ensure the stability of the optimization procedure for the molecules of interest. Each stationary point was confirmed by a frequency calculation at the same level of theory to be a real local minimum on the potential energy surface. The 6–311++G(d,p) basis set was used to compute more accurate electronic energies for the optimized geometries.^{44–45} All reported pK_a's are for acetonitrile solutions at the standard state (T = 298 K, P = 1 atm, 1 mol/L concentration of all species in acetonitrile) as modeled by a polarized continuum model.⁴⁶ An error of 1.3 pK_a units is estimated for all computed pK_a values. All G_{H●} free energy values employed TEMPOH (G_{H●} = 66.5 kcal/mol) as an anchor for the scale.³¹

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Parent BODIPY molecule, demonstrating numbering system.

Figure 2.
BODIPY and hydrazine complexes examined in this study. The new complexes are highlighted in red.

Figure 3. Molecular structures of (left) **BoNHNH₂** and (right) **BoNHCH₂Py**. Thermal ellipsoids are drawn at 50% probability.

Figure 4. Drawing of the hydrogen bond interactions between the pyridyl group of BoNHNHPy with each of the hydrazine protons. The free energy is in units of kcal/mol.

Figure 5.

List of $G_{H\bullet}(1)$ values for the aminomethyl and hydrazine complexes investigated in this study. The values listed are located near the atom where the H-atom is removed.

Figure 6.

List of computed pK_a values in MeCN for the aminomethyl and hydrazine complexes investigated in this study. The values indicated are for the pK_a value of the nearest proton.

Figure 7.

List of G_{H-} values for the loss of a hydride from the aminomethyl and hydrazine complexes investigated in this study. The values indicated are for the hydride donor ability of the nearest hydride.

Table 1.

Summary of the photophysical and redox properties of the hydrazine-appended BODIPY dyes described within. All spectra and data were collected in acetonitrile, unless noted.

Compound	λ_{max} (nm)	$\lambda_{\text{emission}}$ (nm)	τ (ns)	Φ	E° (V vs Fc/Fc ⁺)
PhNHNH ₂	-	-	-	-	0.01, 1.29
PyNHNH ₂	-	-	-	-	-2.75, 1.19
BoNHNH ₂	390	463 504	2.18 ± 0.05 5.13 ± 0.13	0.0017	-1.76, 0.92, 1.21
BoNHNHPh	390	461 503	1.98 ± 0.05 2.90 ± 0.07	0.0010	-1.76, -1.56 0.76, 1.15, 1.50
BoNHCH ₂ Ph	403 ^a	454 ^a	0.49 ^a	0.09 ^a	-1.77, 1.19, 1.64
BoNHNHPy	405	458, 506	4.06 ± 0.19 4.06 ± 0.38	0.20	-1.57, -1.21, 1.33, 1.51
BoNHCH ₂ Py	400	450	0.26 ± 0.19	1.0	-1.83, 1.09, 1.32, 1.61
PhNHNHPh	-	-	-	-	-0.95, 0.15, 1.34, 1.60
BoNHNHBo	395	387 446 504	2.89 ± 0.33 2.98 ± 0.04 5.82 ± 0.11	0.0011	-2.48, -1.85 -0.07, 1.21

^a Values are for methanol solutions and are taken from reference 25.

Table 2.

Computed free energies for H₂ loss from the hydrazines examined in this study. The values were reported at the M06–2X/6–31G(d,p)//M06–2X/6–311++G(d,p) level of theory in MeCN.

Hydrazine	G _{H2} (kcal/mol)
H ₂ N-NH ₂	20.81
HN=NH	–49.98
PhNHNH ₂	19.65
BoNHNH ₂	38.32
PhNHNHPh	9.59
BoNHNHBo	39.24
BoNHNHPh	27.62
BoNHNHPy	32.55