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Boron Dipyrromethenes: Synthesis and Computational Analysis

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Abstract

Recently, there has been a growing interest in the boron dipyrromethene (BODIPY, 4,4′-difluoro-4-bora-3a,4a-diaza-*s*-indacene) compounds. BODIPY compounds have fascinating properties that allow for the absorption and emission of light in the near infrared region of the electromagnetic spectrum. These molecules are highly modifiable making them ideal chemicals for the use of photoelectric energy conversion such as for commercial use in dye sensitized solar cells (DSSCs). It has been previously shown that different meso compounds have only a slight effect on the absorptive capabilities of these BODIPY compounds. We believe that the BODIPY compounds' lack of planarity is one of the major obstacles in more efficient absorption in the NIR and IR regions. Because of this, we focused on modifying recently synthesized BODIPY compounds in an attempt to align their meso group with the rest of the compound's framework. Synthesis of various BODIPY compounds was attempted in order to perform the ring fusion reaction between the meso group and the body of the compound. Computational analysis on several BODIPY compounds was performed with several setups and the results were compared to x-ray crystallography from the literature.

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Introduction

Boron dipyrromethene (BODIPY, 4,4′-difluoro-4-bora-3a,4a-diaza-s-indacene) compounds are an exciting class of fluorescent molecules[1–16]. In 1968, Treibs and Kreuzer synthesized the first boron-dipyrromethene (BODIPY, Figure 2) compound using 2,4-dimethylpyrrole[17]. However, it was not until the late 1980's that it's importance began to be realized[6]. Recently, there has been a growing interest in the boron dipyrromethene compounds due to their fascinating properties such as thermal and photochemical stability, sharp fluorescence peaks, accessible and flexible synthetic routes towards functionalization, high molar absorption coefficients, and large quantum yields, making them ideal chemicals for a variety of applications including use as a fluorescent molecule in dye sensitized solar cells (DSSCs)[18,19]. Since their discovery, interest in these molecules has steadily climbed as evidenced by their publication rates and citations per year. For example, in 1997 there were not 50 published papers published with the phrase "BODIPY" but that number now reaches close to 600 per year.

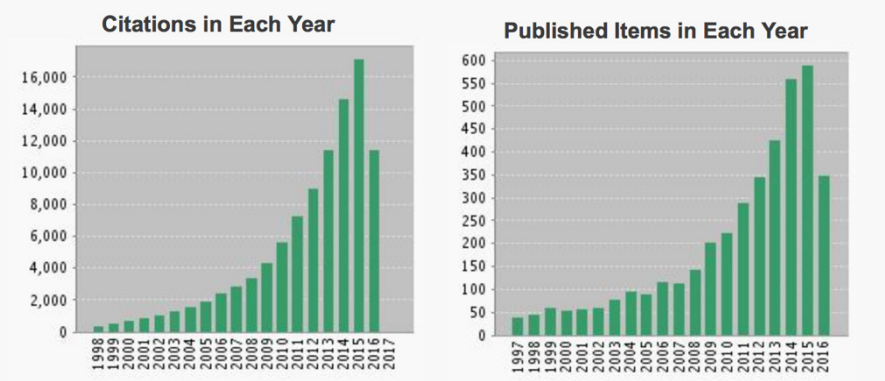

Figure 1 Web of Science search with keyword "BODIPY"

Solar cell technology is a rapidly growing field promising to provide a renewable green electricity source worldwide to meet the demands of a growing worldwide population that uses increasingly large amounts of energy[20,21,22]. Dye-sensitized solar cells

(DSSC) are appealing because they can be less expensive to manufacture than other types of solar cells and can be easily modified[12–16]. The list of possible dyes for inclusion in a solar device is extensive, but the most desirable characteristic for a dye includes absorbance in the near-IR region. Currently, silicon based solar cells dominate the market because DSSCs have a smaller wavelength window of sunlight that is possible to collect: silicon devices can collect wavelengths up to 1100 nm while DSSCs have difficulty surpassing 800 nm for light collection[23]. In order to increase efficiency of solar cells, one possibility is to find new dyes that can collect light in as large of a region as their counterparts.

The standard BODIPY structure is a fairly rigid planar structure where two pyrene rings are held in a coplanar geometry by the boron atom. It is because of this geometry that the p system of the aromatic rings become conjugated and linked, leading to absorbances starting from ~450 nm and extending all the way to the near-IR (800 nm) for some derivatives, depending upon the exact structure. Typical BODIPY molecules based on the structure below have absorbances in the visible spectral region caused by a π to π^* transition upon excitation. Understandably, removal of the boron entity causes loss of many of the interesting properties of these molecules, but replacement with other atom types seems to be permissible[24]. Other analogs have also been reported in the literature, including aza-BODIPY, PODIPY, and various fluoroborate derivatives similar to the BODIPY core. Figure 2 shows the basic BODIPY structure.

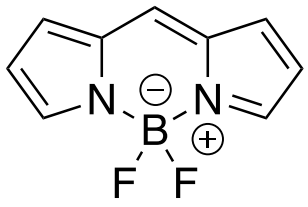

Figure 2 4,4'-difluoro-4-bora-3a,4a-diaza-s-indacene

Some of the desired properties of these molecules can be imparted by installation of simple functional groups to the core (like installing a halogen in place of a hydrogen), extending the π system with linkers, or by modifying the core itself. One of the drawbacks of the BODIPY compounds is their lack of absorbance in the near-infrared (NIR) and infrared (IR) region (700-1000 nm), and so we decided to investigate a new method to modify the BODIPY core in order to extend the absorbance wavelength into the near-IR region. Of the various methods, the extension strategy using linkers can be problematic if the geometry does not favor full conjugation with the BODIPY core, thereby mitigating any benefit that results from a larger π system. Additionally, the linker strategy can often lead to the advancement of one property (absorbance wavelength) at the cost of others (ease of synthesis)[4]. Replacement of hydrogen with functional groups has imparted small changes in the structure's behavior with other BODIPYs[25], but often much larger alterations are needed to achieve a desired photochemical property. An alternative that has been more difficult to achieve synthetically extends the π network through a fused ring system. We began studying a modified BODIPY core after the Swavey laboratory discovered a facile synthetic method for its construction. These BODIPY compounds contain more fused ring conjugation than many other examples in the literature.[1] Other modifications have been reported in the aryl-meso position. For example, substitution of a standard BODIPY core at the 3 and 5 positions with electron donating *p*-MeOPh rings accompanied by a *p*-iodo group on the aryl-meso ring induces a red shift in the absorbance maximum wavelength by roughly 80 nm as well as increasing the quantum yield by almost 10-fold while maintaining a high extinction coefficient [19]. Even though the comparisons are not perfect since they are made for molecules in different solvents (toluene and

chloroform), it demonstrates potential for modification in order to increase absorption capabilities.

Synthesis of these BODIPY compounds requires a multistep process, shown in figure 3, with the opportunity to vary certain parts of the process. This process follows the steps laid out by Lash et al. and Swavey et al[26–29]. This process yields an expanded aromatic arrangement and is easily synthesized in two steps, under mild conditions, and solvent free environment [28]. 1-nitronaphthalene can be allowed to react with *tert*-Butylimino-tri(pyrrolidino)phosphorene (BTPP) and ethyl isocyanoacetate to yield a naphtha[1,2-c]pyrrole ester. This compound can be treated with potassium hydroxide and hydrazine in ethylene glycol and heat to sever the ester unit, leaving just the naphtha[1,2-c]pyrrole. Reaction with an aldehyde and heat, followed by addition of boron trifluoride etherate and base (triethyl amine, TEA) in dichloromethane (DCM) generates the final planar BODIPY structure. Varying the pyrrole reagents yields a BODIPY core that varies in size while varying the aromatic aldehyde provides different meso position compounds. Several BODIPY compounds were created by Dr. Swavey in order to test their variability in absorption and emission of light.

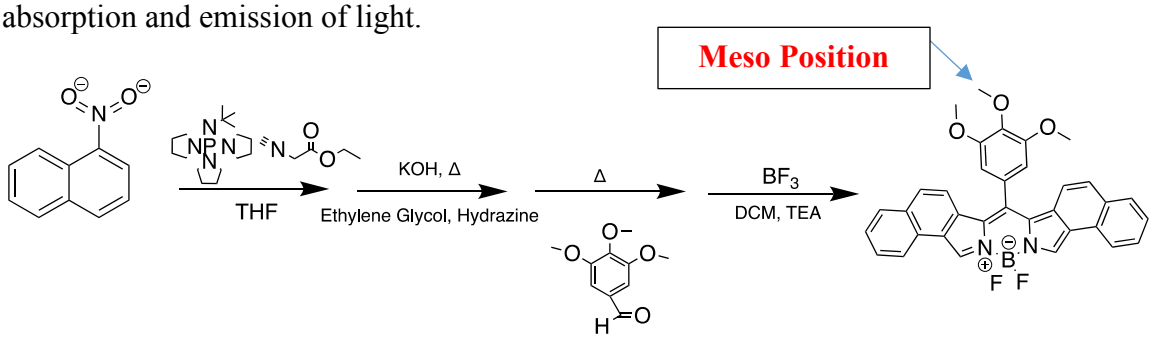

Figure 3 Overview of synthesis pathway for a BODIPY compound

Varying the meso group showed minimal differences with the absorption and emission of the compound. We decided to use this initial library of BODIPY compounds synthesized here at UD as a platform to explore the ring-fusion strategy. Iron trichloride

was used to attempt ring-fusion by forming single bonds between the meso group and the core of the BODIPY, as was reported in the literature[18]. These changes would, theoretically, allow for extended movement of the electrons through the coordinated pi system of the BODIPY due to the forced geometrical changes caused by planarization of the molecule. Since the literature contains only a few examples of this reaction, we were interested in examining the effect of different BODIPY structures on the effectiveness of this ring fusion reaction. For simplicity, we decided to explore variation of groups at the *meso* position with the BODIPY cores that we knew were possible to synthesize. Essentially, the *meso* groups can be categorized into two groups: electron withdrawing and electron donating groups. Since the mechanism for how the ring fusion reaction works is not known, we desired to test both cases. The synthesis process is time consuming and the nature of multi-step synthesis means that, even with fairly successful and high yielding reactions, the final products will be difficult to obtain in large enough quantities to study.

Along with the synthesis aspect, computational analysis of several BODIPY compounds was initiated through the Ohio Supercomputer and the PQS cluster system in the Chemistry Department computer lab. The program Gaussian/Gauss View allows for us to draw molecules in three-dimensional space. Once this is done, the program is capable of running several different calculations that will each provide different information. For this project, we used geometry optimizations, frequency calculations, and time dependent density functional theory calculations (TD-DFT). Geometry optimizations lets us visualize what the computer assumes to be an approximation to natural geometry based on how the molecule is drawn. It is essentially the program's way of "cleaning up" a "messy" structure before any other tests are performed. Frequency calculations help determine the vibrational

frequencies within the drawn chemical. These values allow for us to determine if the structure the optimization is produced is even possible by ensuring all vibrational frequencies are positive or real. If there are any negative frequencies, this means that it is an imaginary frequency and therefore, not possible. These two processes should be paired together under the same calculation method because otherwise it will produce meaningless results. Once the geometry optimization and frequency calculations are performed, we do a TD-DFT calculation which provides information regarding the photophysics of the compound such as wavelength absorbance and excited states[30,31].

Making BODIPY compounds is a difficult, expensive, and time-consuming process. We therefore want to make sure we are utilizing our resources appropriately. Computational analysis is an excellent tool that allows for us to screen potential compounds before we attempt at synthesis. It is a faster tool that can be left by itself once a calculation has started and is relatively easy to learn how to use it. If the calculations show promising results, the compound is then considered a candidate for synthesis.

Experimental Methods

This project was separated into two parts: synthesis and computational analysis. The synthesis of the BODIPY compounds requires multi-step organic synthesis with the purpose to join to pyrrolic groups with an aromatic aldehyde in the meso position. This process may yield both symmetrical and asymmetrical BODIPY compounds[28]. Computational analysis was performed on the BODIPY compounds synthesized in lab as well as other compounds considered for future synthesis.

Synthesis of BODIPY compounds

The materials used for the synthesis pathway were purified following techniques appropriate for each compound. Solvents were obtained from a five-column solvent purification system. Other important tools used throughout the process included a rotary evaporator with a pump for reduced atmospheric pressure, sand baths of varying sizes for high temperature reflux, and a *Combiflash®* that permitted quick and easy column chromatography. The product was confirmed at each step using nuclear magnetic resonance imaging.

The synthesis for BODIPY precursors was necessary due to an unavailability of these reagents as commercial products. This synthesis follows a general multi-step procedure that can be easily modified to create an incredible variety of BODIPY compounds of different sizes and group composition[32]. The following outline demonstrates the procedure used to create the BODIPY compounds.

A naphthalene of choice can be used to start the reaction. A different naphthalene will yield different core sizes for the end BODIPY product. Here, 2-nitronaphthalene is combined with ethyl isocyanoacetate and phosphazene base (added dropwise) in a stirred solution of tetrahydrofuran. This solution is then refluxed overnight. The resulting mixture was diluted with chloroform and washed with water. The product was later obtained by evaporating the solvent under reduced pressure[27].

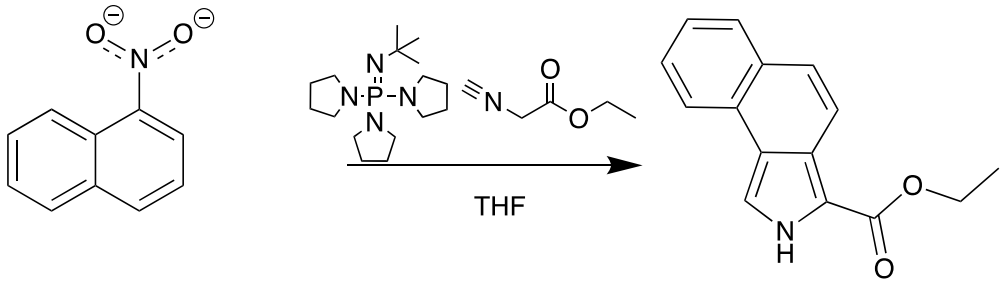

Figure 4 Step 1: reflux of a naphthalene compound

The resulting pyrrole was dissolved in ethylene glycol with potassium hydroxide. An atmosphere devoid of oxygen is required. To achieve this, nitrogen gas was bubbled through the mixture for fifteen minutes. Once this was complete, a low amount of hydrazine was added. The mixture was stirred under reflux at 190°C for thirty minutes under a nitrogen atmosphere. After reflux, the mixture is poured into ice water and the precipitate is collected under suction filtration[26].

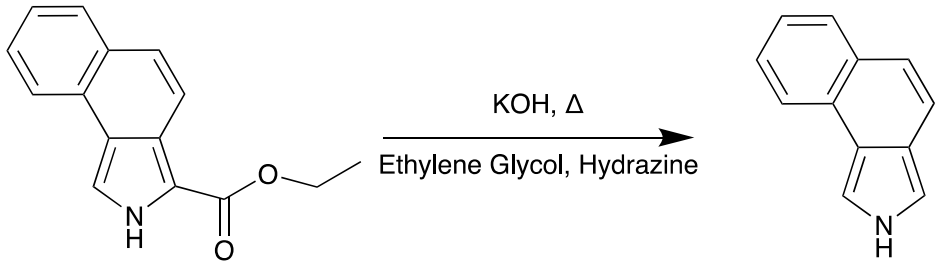

Figure 5 Step 2: decarboxylation of pyrrole through reflux

Once the pyrrole is decarboxylated, the BODIPY core can begin to form. Any aromatic aldehyde can be used for this step. For illustration purposes, 3,4,5-trimethoxybenzaldehyde was used. The pyrrole and benzaldehyde are mixed in minimal dichloromethane. Once thoroughly mixed, the dichloromethane is evaporated, and the remained solids are heated until a color change is observed. The temperature required varies per BODIPY compound, but is usually from 70-90°C. It is important to note that

some aromatic aldehydes may form an asymmetrical compound by creating an arm group[28].

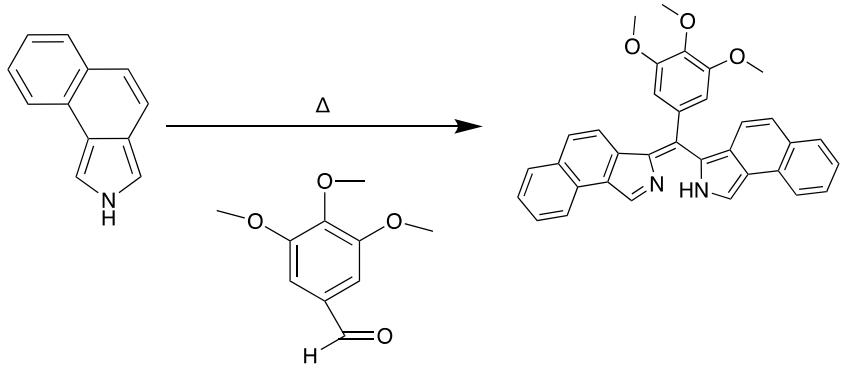

Figure 6 Step 3: Pre-BODIPY core formation using a benzaldehyde

The final step for the BODIPY compound uses boron trifluoride – diethyl ether. A flask is degassed, and dichloromethane is added along with the pre-BODIPY product from step 3. Trimethyl amine and boron trifluoride is added to the solution. This is left to stir overnight at room temperature under nitrogen. The resulting product was collected by washing with water and chromatographed using hexanes/ethyl acetate[28].

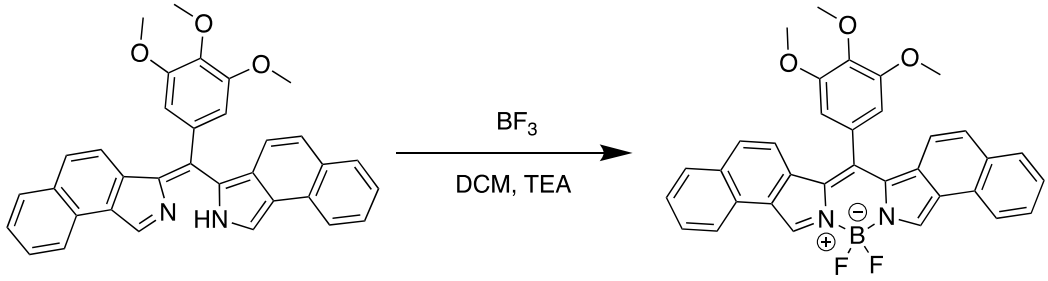

Figure 7 Step 4: Formation of BODIPY

Ring fusion is then performed by mixing the BODIPY product with iron trichloride in methylene chloride and nitromethane. This solution is left to stir overnight at room temperature and under nitrogen. The resulting solution is washed with water and chromatographed using toluene[18].

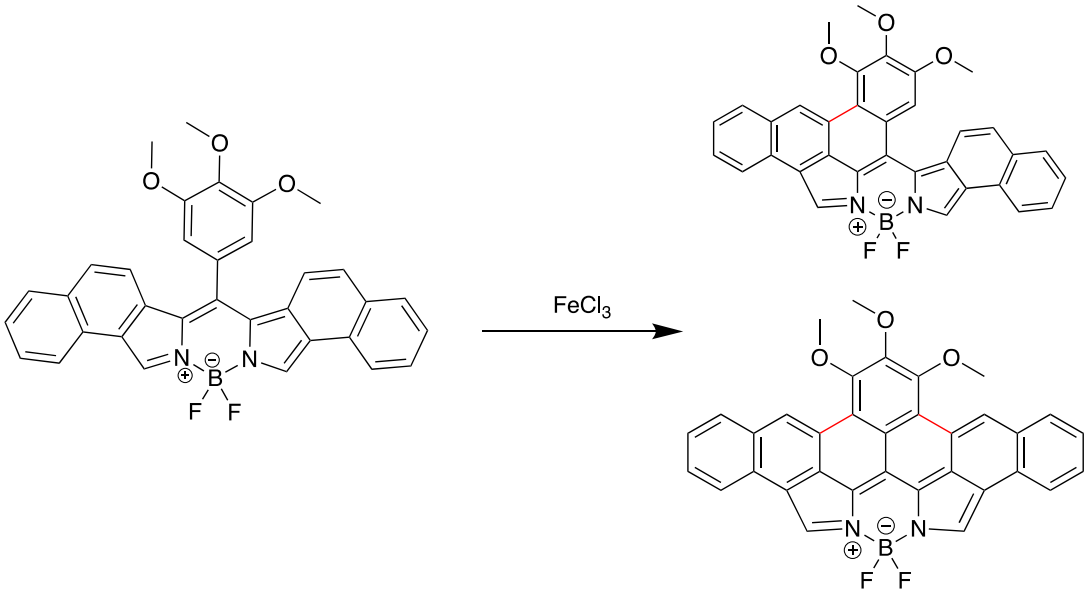

Figure 8 Ring-fusion of BODIPY compound

Computational analysis of BODIPY compounds

Computational analysis was performed by accessing the Ohio Supercomputer and by using a PQS cluster system. As previously mentioned, the compound in question was drawn on Gaussian/Gauss view. In order to ensure proper geometry, a geometry optimization and frequency calculation was performed for each compound. These calculations were performed using DFT with a basis set of 6-311+G in a methylene chloride solvent. This is followed by a TD-DFT calculation using CAM-B3LYP/cc-pVTZ as a basis set. This process was performed three times per compound: unfused, single ring-fused, and double ring-fused.

The information obtained from TD-DFT calculations regarding absorption wavelengths has been shown to not reflect the behavior of compounds in nature. In order to have a better understanding of such information, a linear correction calculation was performed, yielding a better estimate of absorption values in nature[19].

Results and Discussion

Synthesis

Overall, the multi-step synthesis pathway is successful and adaptable to various reagent changes. However, there are two major drawbacks to this procedure that could be fixed over time. The first problem is that this process is low-yield from step 1. Since the BODIPY itself is not commercially available, building a substantial amount in order to perform large scale reactions is very difficult and time consuming. This solution, however, may impact the process's low-cost. The second problem is that there seems to be no way to control for single or double ring-fusion. This process has not been frequently attempted with BODIPY compounds and further experimentation may be required to fully understand its process.

We discovered that ethyl acetate was a poor choice in solvent. Using ethyl acetate as a solvent for the dipyrromethene synthesis reaction caused fizzling to occur in solution. When this occurred, no product was obtained from column chromatography. We believe that the ester carbonyl was reacting instead of the aldehyde.

A previously unpublished BODIPY compound was discovered when synthesizing using 3,4,5-trimethoxybenzaldehyde. The literature only shows a symmetrical BODIPY synthesized when using this benzaldehyde. However, an asymmetrical BODIPY was also obtained when chromatographing the resulting products of step four. This BODIPY can be seen in figure 9.

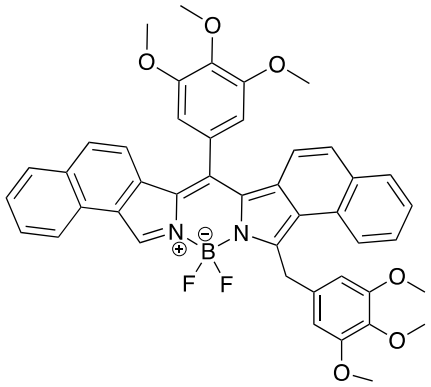

Figure 9 Asymmetrical 3,4,5-trimethoxy BODIPY

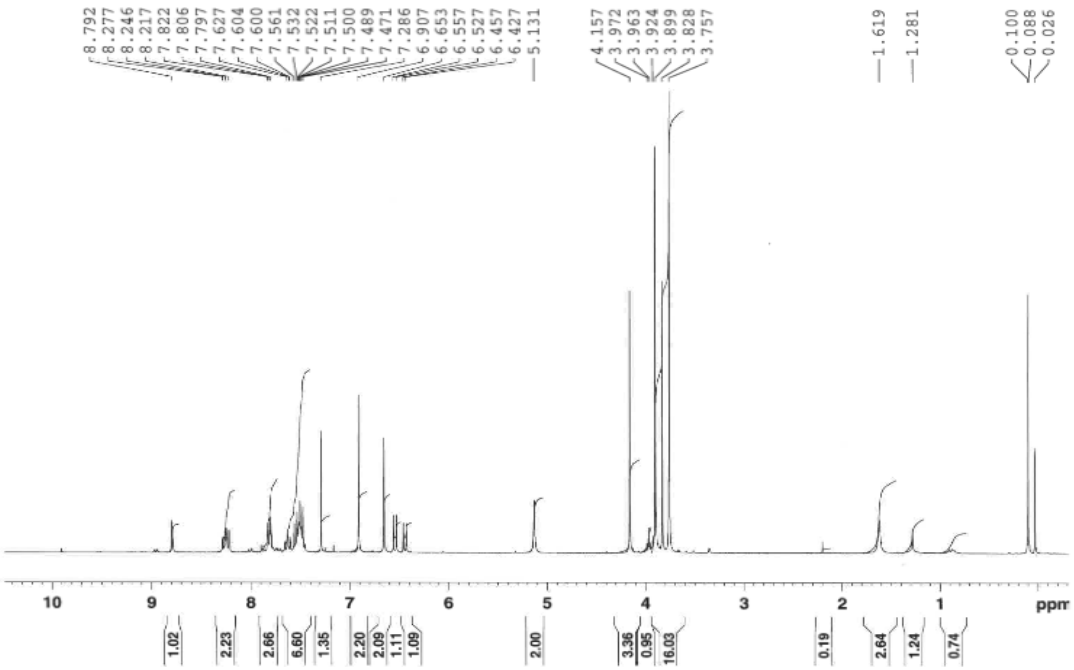

Figure 10 H NMR for asymmetrical 3,4,5-trimethoxy BODIPY

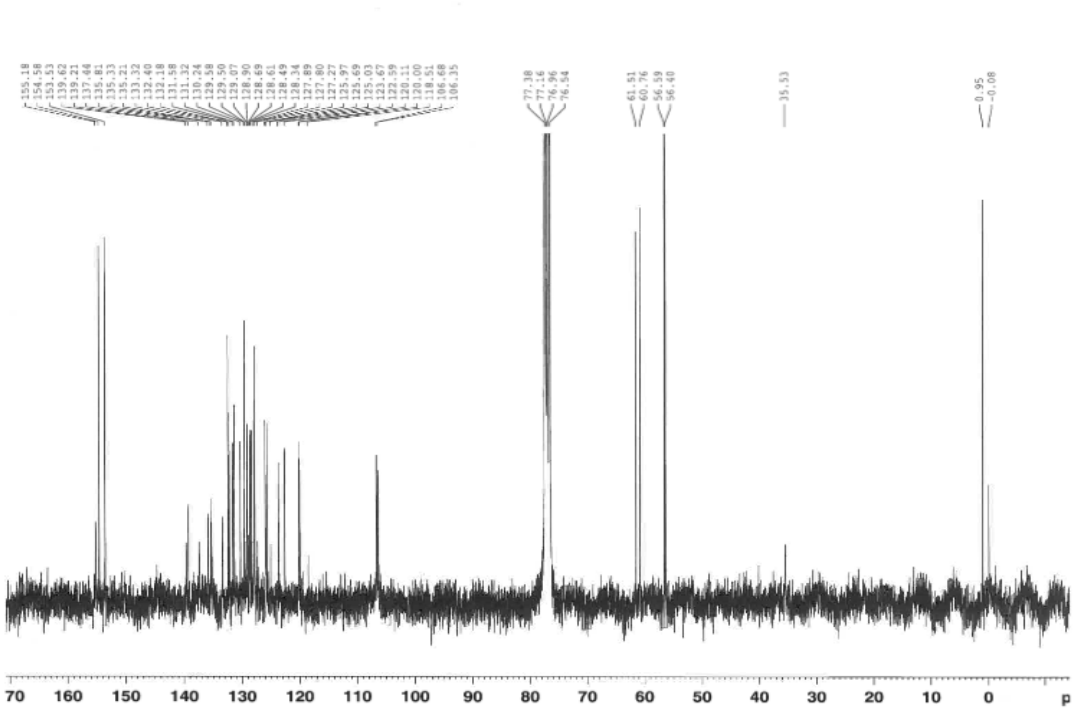

Figure 11 Carbon NMR for asymmetrical 3,4,5-trimethoxy BODIPY

The NMR spectra shown above is for the newly synthesized asymmetrical 3,4,5-trimethody BODIPY compound. A proton NMR and carbon NMR were obtained. UV-VIS spectroscopy showed a λ_{max} of 596 nm, further proving the presence of a previously unreported BODIPY. The observed yield for 3,4,5-trimethoxy BODIPY was 25.8%.

Attempts at ring fusion with the asymmetrical 3,4,5-trimethoxy BODIPY yielded a product with a λ_{max} of 613 nm in its crude state. An attempt at purification by washing with toluene yielded two compounds. They appear to be BODIPY compounds as they glow red when dissolved. However, analysis using mass spectroscopy showed that these compounds did not have the expected mass. We suspect the two compounds are a single ring-fused and double ring-fused BODIPY in which some part of the chemical also got oxidized, adding extra mass. The yield was very low. We suspect that the purification step was not entirely successful and a portion of the product was left in the column.

Computational Analysis

The process has yielded important information thus far despite the requirement that these calculations can take days or more to complete on both the cluster and the supercomputer. For example, analysis showed minimal increase (~20nm) in absorption for a single ring-fusion attempt, far less than the desired target of 150-200 nm. The ring fusion will probably have to be done in tandem with a second ring fusion or installation of different groups on the molecule in order to achieve the desired gain in absorbance.

Overall, computational analysis was used to estimate the values of maximum absorbance wavelength based on the structure. The TD-DFT calculation estimates the energy it takes to move one electron from the ground state to the excited state using the ground state geometry. This calculation is not perfect since it is an approximation (the calculation assumes that the excited state geometry of the compound is the same as the geometry of the ground state) but is known to be a good compromise between accuracy and speed. A linear correction calculation was used to adjust these computational values of λ_{max} in order to better reflect the actual values in solution[19].

Upon observation of the geometry optimization of the BODIPY compounds, it was observed that the compounds are not entirely flat. Further analysis into a double ring-fused BODIPY has shown it to planarize the molecule yet the calculated change in the absorption spectra has not changed significantly and varies per compound. Current experimentation has been performed on molecules containing electron donating groups and it was hypothesized that a greater change in shift will be achieved if the compound contains electron withdrawing groups. For this reason, computational analysis was performed on BODIPY compounds in which the meso group constitutes of a 3,4,5-trimethoxy

benzaldehyde, p-nitro benzaldehyde, and a simple benzaldehyde for comparison. Figures 12-14 shows some pictures of geometry optimization and the predicted molecular orbitals for these compounds.

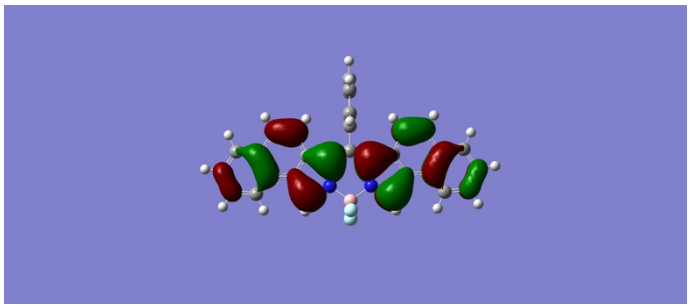

Figure 12 Front view of the highest occupied molecular orbitals for a Benzene BODIPY

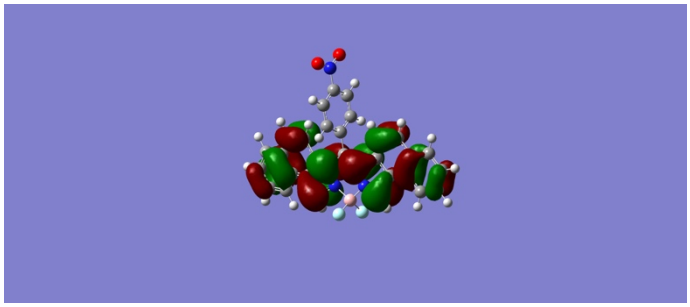

Figure 13 Front view of the highest occupied molecular orbitals for a p-Nitro BODIPY

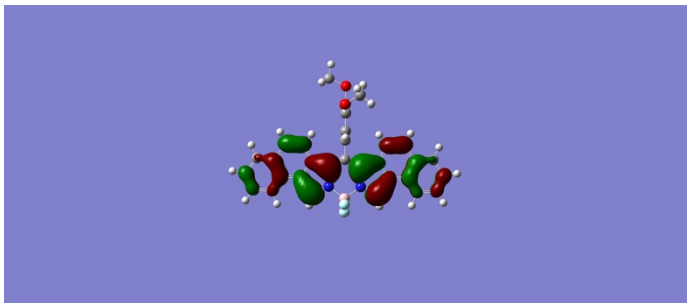

Figure 14 Front view of the highest occupied molecular orbitals for a 3,4,5 - trimethoxy BODIPY

Use of computers to predict the properties of these molecules is an incredibly useful supporting method since these molecules often take extended periods of time to synthesize. Many more computations are scheduled to run as current others finish. Computational analysis into these theoretical compounds will be able to provide additional insight into the possible effects of the ring fusion.

The results were as expected. Ring-fusion allowed for an increase in the absorption wavelength. Electron withdrawing groups also showed larger increases in the absorption wavelength when placed on a BODIPY compared to electron donating groups, especially when double ring-fused. A comparison between an electron donating group and an electron withdrawing group can be seen in figures 15 and 16.

The effects of ring-fusion vary by compound. The 3,4,5-trimethoxy BODIPY has an unfused λ_{max} of 596 nm. The single ring-fused has a λ_{max} of 614 nm. The double ring-fused has a λ_{max} of 623 nm. Each ring-fusion adds approximately 20 nm to the max absorbance. This data is the corrected λ_{max} after linear correction using y=x*0.9397+104.63 where y is the corrected value and x is the raw computed value[19]. A 3,4,5-trimethoxy BODIPY was synthesized and after a single attempt at ring-fusion showed a λ_{max} of 613 nm. We believe that this increase in absorbance is, in part, due to the compound progressively becoming more planar as ring-fusion is performed as seen on figures 15-16.

The ring-fusion also causes a shift in the electron density. A single ring-fused BODIPY has high electron density on the side of ring-fusion and the meso group is largely uninvolved. However, a double ring-fused BODIPY has an evenly distributed electron density throughout a now planar structure and the meso group becomes more involved (Figures 15-16).

This method of obtaining information via computational analysis is extremely helpful. Even though calculations may take several hours to days, it can save time in the laboratory by providing some insight into what compounds might yield promising results. The setup is relatively easy, as long as proper protocols are used to obtain the desired

information. These calculations can be left to run on their own while synthetic work in the laboratory can be completed.

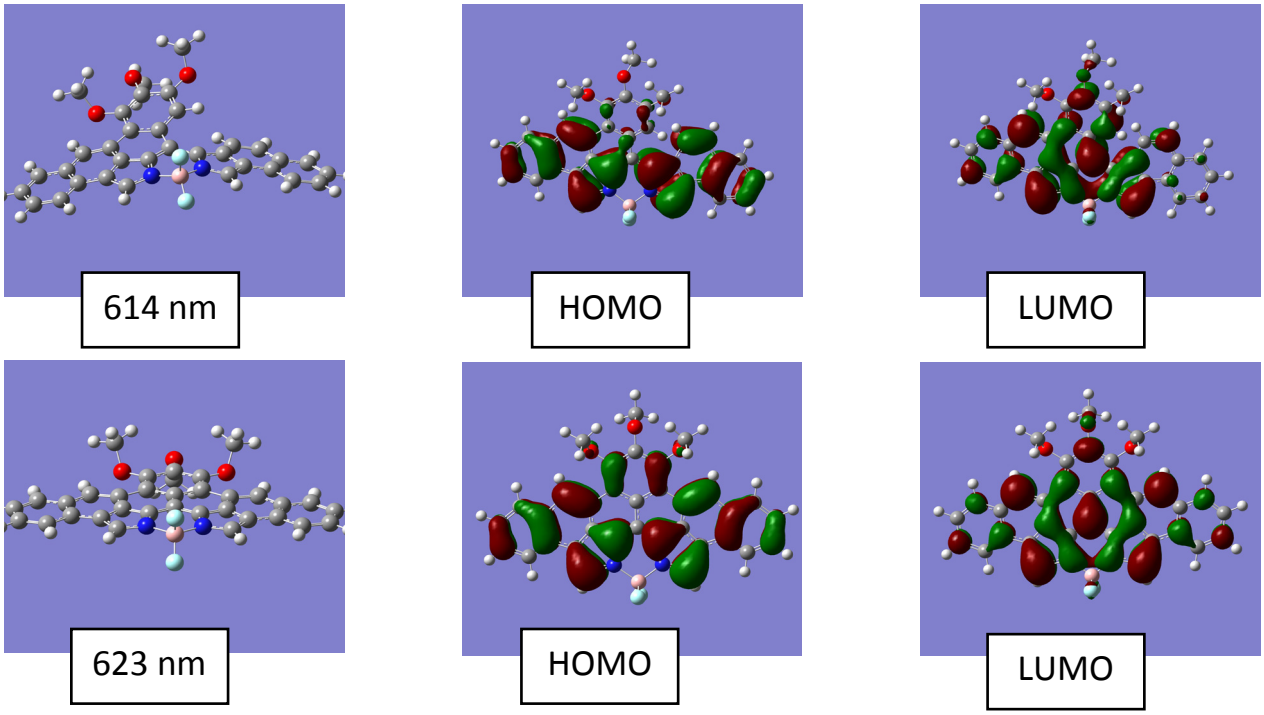

Figure 15 Single and double ring-fused 3,4,5-trimethoxy BODIPY

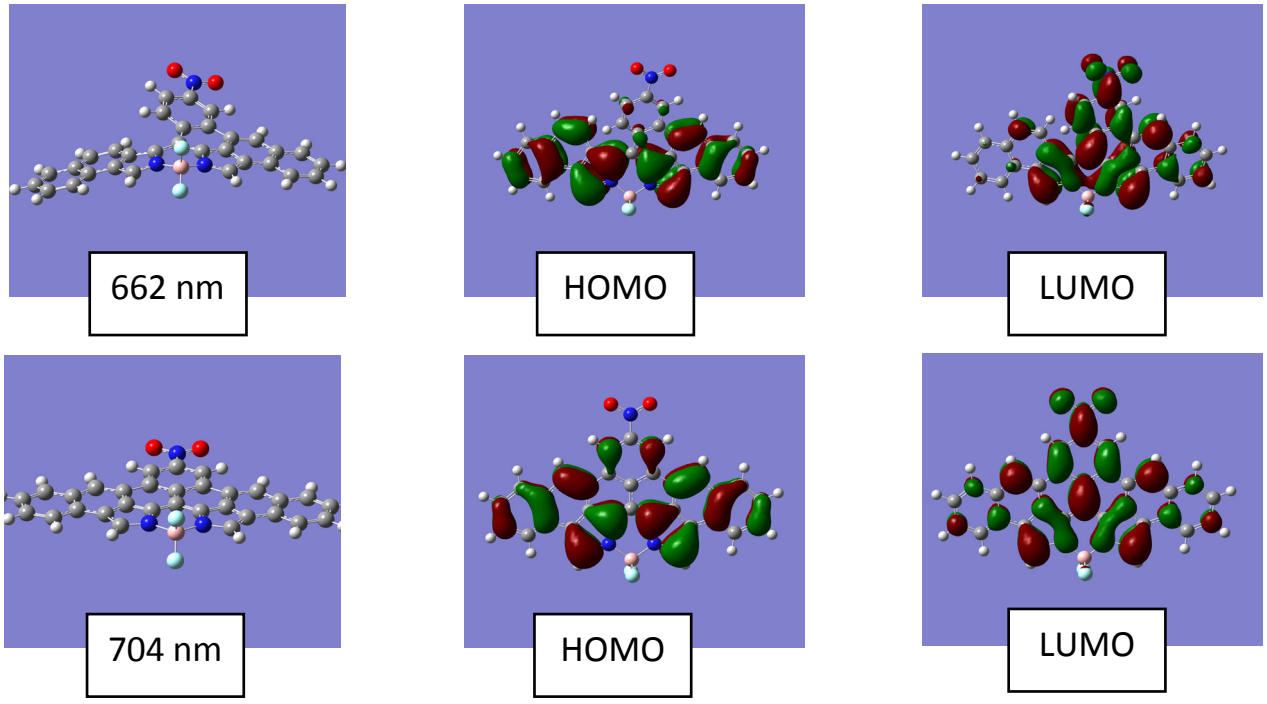

Figure 16 Single and Double ring-fused p-nitro BODIPY

Conclusion and Future Directions

The synthesis, modification, and computational analysis of BODIPY compounds yielded important information regarding its absorbance capabilities. Modification of these compounds via meso group modification and addition of functional groups showed slight increases in their absorbance capabilities. Computational analysis also showed how these compounds interact and behave when undergone ring-fusion. The NIR region of the electromagnetic spectrum was just reached by the *p*-nitro BODIPY through double ring-fusion computational analysis.

This project would benefit greatly by expanding on the work already accomplished, particularly by beginning synthesis of compounds that showed great promise through computational analysis. More work needs to be done on the ring-fusion synthesis technique in order to better understand its process and find measures to control the reaction. Expanding the BODIPY library, both synthetically and computationally, should yield more information regarding which compounds are able to achieve the desired increase in absorbance to the NIR and IR regions of the electromagnetic spectrum.

Recently, work at the University of Dayton has included a series of publications detailing the steps in synthesizing unique BODIPY compounds as well as their computational analysis through a collaborative effort between Dr. Swavey and Dr. Erb. Efforts have also expanded upon the origin idea to include the synthesis of BODIPY compounds in which the chemicals are able to coordinate with metal ions like ruthenium and lanthanides[33]. Although there is not a great deal of information regarding their photochemical capabilities, this relatively unexplored area could prove to impart unique

characteristics on BODIPY molecules. Including this aspect in the future of the project may also lead to the desired results.

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