

BENZOFULVENE SYNTHESIS AND EMISSION  
BASED SPECTROSCOPY

by

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A THESIS

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## **An Abstract of the Thesis of**

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Title: Benzofulvene Synthesis and Emission Based Spectroscopy

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Primary Thesis Advisor

Benzofulvenes and their derivatives have implications as synthetic precursors, molecular materials, and in medicinal applications. The interesting conjugation-based properties of benzofulvenes raises the possibility of color tunability and other optical properties. Our work focuses on the synthesis of various benzofulvenes and investigations into their optical effects through absorbance and fluorescence spectroscopy. We are specifically looking to explore push/pull dynamics related to different substituents on our title compounds regarding conjugation and optical effects. This will allow us to determine the Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital (HOMO-LUMO) energy gaps that may be tunable based on which substituents are involved. Overall, our goal is to increase the reproducibility of benzofulvene synthesis, optimize yield, and manipulate the compounds with varying substituents to gain a better understanding of their optical properties and implications in applied scenarios. At this point in our research, we have gathered strong evidence supporting the tunability of our benzofulvene dimers.

## **Acknowledgements**

I would like to thank my primary thesis advisor, Dr. Adam Glass, for providing undergraduates like myself valuable research experience. Without his intrinsic enthusiasm for organic chemistry, I would have never imagined that I could undergo a project such as this one. I would also like to thank Dr. Rebecca Altman for being my Clark Honors College advisor and offering such helpful insight as to how to complete this project. I would like to thank my fellow undergraduates in this lab who supported me and helped make this thesis possible. I would also like to thank my family and friends for their support, particularly my parents who put a lot of effort into making sure I was able to pursue higher education.

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## Introduction

Fairly recently, the chemistry community has become very interested in the physical and chemical properties of pentafulvenes and benzofulvenes. These molecules have unique properties in aromaticity, fluorescence, and, potentially, electron push/pull dynamics. Aromaticity is an important organic chemistry concept because aromatic molecules are more stable, have altered bond lengths that are shorter than non-aromatic compounds, and have specific  $\pi$ -electron ring formations due to the double bonds which allow for electron delocalization that respond to external magnetic fields which causes specific values in nuclear magnetic resonance spectroscopy (NMR) [1].

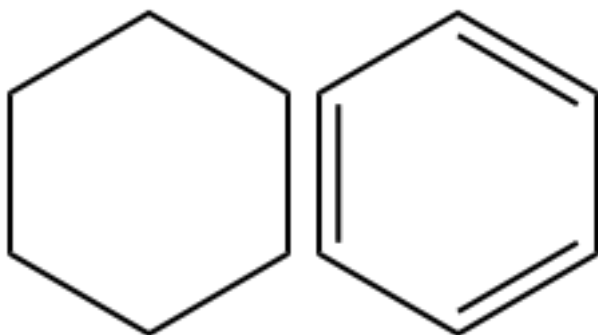


Figure 1: Non-aromatic cyclic hexane (left) versus aromatic benzene (right)

Fluorescent substances are defined as being able to absorb a photon and emit or produce a longer wavelength of light upon excitation. As far as fluorescence in benzofulvenes, aggregate induced emission (AIE) is a large topic of interest in organic chemistry research today [2]. AIE is the phenomenon of fluorescence in a solid or aggregate state but not in the solution state. The issue with organic fluorescent molecules is that they are typically inefficient for long term effects in applications such as optoelectronics. The findings from our research surrounding emission and fluorescence of benzofulvenes may be relevant towards these applications in the future. These optoelectronics are potentially good alternatives to technologies such as computer hardware for

electronic communications as there is evidence to suggest they are more cost-effective and better for long term use [2]. A related concept is OLEDs, which stands for organic light-emitting diodes, that are also a potential application of these benzofulvene dimers as they could replace LED screens and lights. AIE could potentially be the key to figuring out how to make fluorophores fluoresce longer than they typically do in their usual decay pathway. This decay is called photobleaching and it occurs when prolonged high intensity illumination causes a fluorescent molecule's structure to be altered so that it can no longer fluoresce. When specific chromophores are aggregated, their shapes and therefore  $\pi$  electron structure are manipulated in a way that makes them exhibit strong fluorescence [2].

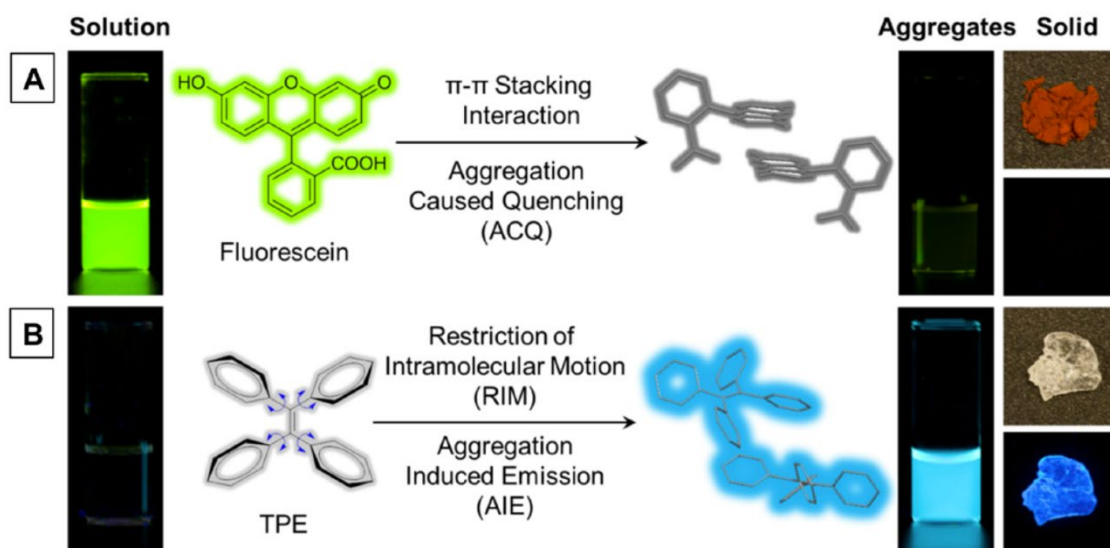


Figure 2: Model that shows conventional fluorophores (A) as emissive in solution state with fluorescence decreasing once they are in the solid or aggregate state. This is compared to a benzofulvene type structure (B) which becomes emissive once it reaches a solid or aggregate form [2].

There have been instances where using AIE ended up almost producing white light emission in diphenylbenzofulvenes (Figure 3), which are similar to the benzenofulvene dimers we have been synthesizing. It was found that these dimers have 2-4 times the white light



emission as the monomer counterparts in the aggregate forms. This is important as it allows us to understand more about why and how these molecules fluoresce. It was also determined that the diphenylbenzofulvenes produced more fluorescence in poor solvents such as water than in typically “good” solvents such as acetonitrile. Poor solvents are those in which polymer-polymer interactions between the diphenylbenzofulvenes are favored and allow a precipitate of the substance to form. Good solvents have favorable interactions where the substance is dissolved. A combination of diphenylbenzofulvenes with a methyl substitution and diphenylbenzofulvenes with two methyl substitutions in a 1:3 ratio was able to produce photoluminescence that was very similar to white light emission with a small statistical deviation [3].

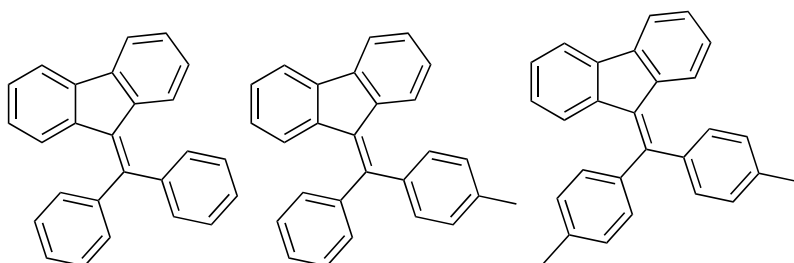


Figure 3: Diphenylbenzofulvene dimers. The center dimer has the single methyl substitution, and the right dimer has the two methyl substitutions while the dimer on the left is unsubstituted [3].

Compound	Medium	$\lambda^{abs}$ [nm]	$\lambda^{em}$ [nm]	$\Delta_{ss}$ [ $cm^{-1}$ ]	$\phi_f$
DPBF	ACN	234/258/327	420	6772	0.00004
	Agg ( $f_w=70\%$ )	237/267/313	470	10672	0.11
	Film	341	483	8622	0.044
DPBFMe	ACN	234/258/336	488	9270	0.00003
	Agg ( $f_w=80\%$ )	239/260/344	470	7793	0.0029
	Film	340	576	12051	0.0095
DPBF(Me) <sub>2</sub>	ACN	236/259/343	438	6323	0.00010
	Agg ( $f_w=95\%$ )	244/268/365	569	9823	0.018
	Film	341	582	12143	0.024

Table 1: Spectroscopic data for the diphenylbenzofulvenes [3].

This is very important to our research as we are trying to figure out the best reactants to use as well as which positions on the benzofulvenes to place substituents in order to allow them to produce the most amount of color tunability. The placement of substituents can affect electron

conjugation in ways that may or may not be optimal depending on how the fulvene reacts to either an electron donating or electron withdrawing group. Below are tables of each of the compounds our study synthesized in relation to absorbance and tunability.

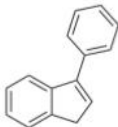
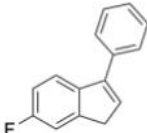
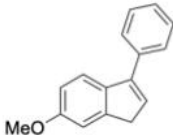
Indene <b>A</b> (Parent indene)	
Indene <b>B</b> (Fluoro-indene)	
Indene <b>C</b> (Methoxy-indene)	

Table 2: Indenes synthesized as precursors to dimers

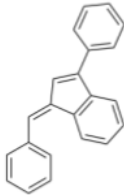
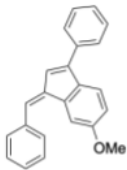
Compound <b>6</b> (Parent monomer)	
Compound <b>7</b> (Methoxy monomer)	

Table 3: Monomers synthesized that are relevant to this study

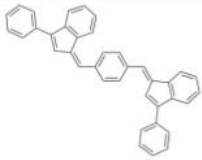
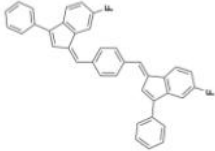
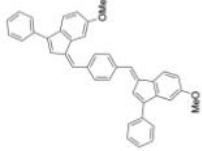
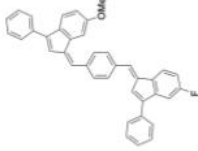
Compound <b>8</b> (Parent Dimer)	
Compound <b>10</b> (Fluoro-homodimer)	
Compound <b>11</b> (Methoxy-homodimer)	
Compound <b>12</b> (Push/pull dimer)	

Table 4: Dimers synthesized that underwent quantitative analysis

It is also important to understand the molecular tuning necessary to produce crystallization induced emission in these diphenylbenzofulvene molecules. One study compiles the results of emissions of diphenylbenzofulvene molecules in previous studies [4]. Through this analysis it is understood that a large factor in AIE dimers is the lack of twisting that is allowed to occur in the carbon-carbon double bond in the structure. Restriction of rotation about bonds is therefore a key factor in producing tunable fluorescence.

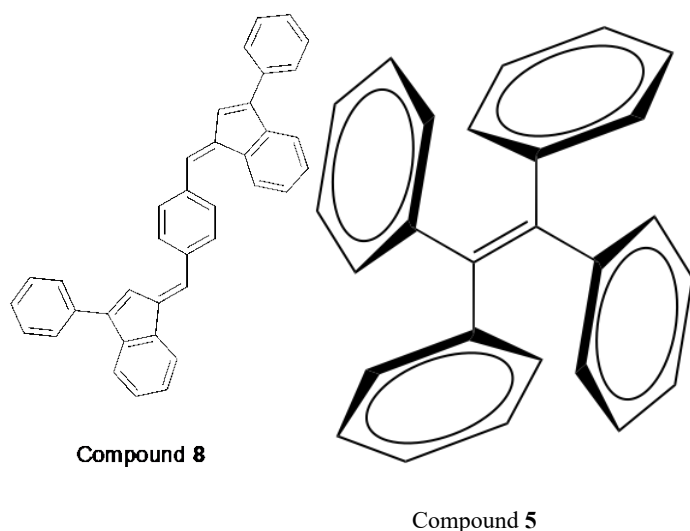


Figure 4: The *para* benzofulvene dimer (left) shown above has two single bonds on either side of the center benzene ring which allows for free rotation and prevents the dimer from being emissive. To the right is an example of an aggregate induced emission structure that allows for emission through the restriction of the intramolecular rotation due to bond conjugation with the phenyl rings.

It can be seen in Compounds **5** and **8** above that the rotation about the single bonds in a molecule prevent it from being emissive while molecules with a more rigid double-double bond are able to be tuned and fluoresce. This can be controlled by adding substituents to influence electron flow throughout the molecule, in this case, diphenylbenzofulvenes. Whether the substituents are in *ortho*, *para*, or *meta* confirmation has a large influence on whether a *trans* or *cis* dimer is produced. It was found that *para* substituted dimers produced a strong blue emission, *ortho* substituted dimers produced a moderate blue emission, and the *meta* substituted dimers produced a moderate/weak yellow-green emission. It was decided that the *para* substituted dimers underwent the least amount of structural change during excitation in the crystalline stage. This paper overall concluded that there is a linear relationship between fluorescence quantum yield and twist around the carbon-carbon double bond when it is a non-*para*-substituted dimer [4]. This is relevant to our research as we are currently producing our own *para*, *ortho*, and *meta*

substituted benzofulvenes to study the color emission they produce and ultimately to have an optimal method to be able to tune them.

The last study that addresses the background of our project outlines a lot of recent discoveries and advancements that have occurred in the research of pentafulvenes. This work reiterates and emphasizes the important properties in pentafulvenes and, consequently, benzofulvenes, and how those properties are beneficial in real world application [5]. Furthermore, this study dives into organometallic reactions with pentafulvenes which are the main types of reactions our lab is using, as well as other types of synthesis. This review is very comprehensive and provides a rich and detailed understanding that we drew a lot from when designing our experiments.

## Methods

### General Synthesis

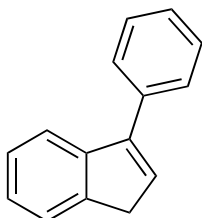
Oxygen- and moisture-sensitive manipulations (indene synthesis) were performed by using standard Schlenk line techniques using anhydrous nitrogen gas.

Reagents 2-MeTHF, DBU, THF, various benzaldehydes, and phenyl magnesium bromide were purchased from chemical manufacturers (i.e., Sigma Aldrich, TCI and Oakwood Chemical) and used without further purification.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with a Bruker 500 MHz Avance III NMR Spectrometer. All spectra were referenced to the respective solvent of  $\text{CDCl}_3$ . All dimer compounds were characterized by proton NMR in d-chloroform. All dimer compounds were analyzed through UV-Vis in chloroform and fluorimetry data was gathered using a Horiba Scientific Fluoromax-4 fluorimeter.

### Indene Synthesis

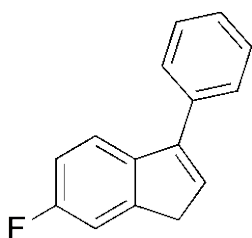
#### *Indene A*



To a round-bottom flask flushed with Schlenk line techniques, 1-indanone (1.0067 g, 7.57 mmol) was added and high-pressure vacuum was run for 5 minutes. Then, 2-MeTHF (15.5 mL) was added. The reaction was placed in an ice bath. Phenyl-

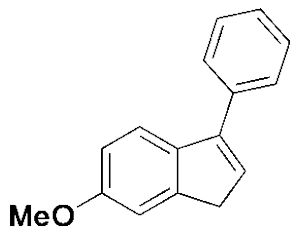
magnesium bromide (2.49 mL, 7.57 mmol) was added dropwise, and the reaction was stirred for 30 minutes. Diethyl phosphite (3.1 mL, 15.1 mmol) was added and the reaction was stirred for 24 hours. A workup was done by adding ammonium chloride (3 mL) and ethyl acetate (4 mL) to the reaction. The aqueous layer was then removed, and the organic layer was dried with anhydrous magnesium sulfide. Gravity filtration was performed and then the solvent was removed under reduced pressure.

*Indene B*



To a round-bottom flask flushed with Schlenk line techniques, 5-fluoro indanone (0.3812 g, 2.4 mmol) was added and high-pressure vacuum was run for 10 minutes. Then, 2-MeTHF (3.33 mL) was added. The reaction was placed in an ice bath. Phenylmagnesium bromide (0.934 mL, 2.6 mmol) was added dropwise, and the reaction was stirred for 30 minutes. Diethyl phosphite (0.67 mL, 4.8 mmol) was added and the reaction was stirred for 24 hours. A workup was done by adding ammonium chloride (3 mL) and ethyl acetate (4 mL) to the reaction. The aqueous layer was then removed, and the organic layer was dried with anhydrous magnesium sulfide. Gravity filtration was performed and then the solvent was removed under reduced pressure.

*Indene C*

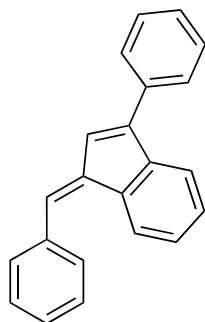


To a round-bottom flask flushed with Schlenk line techniques, 5-methoxy indanone (0.4011 g, 2.46 mmol) was added and high-pressure vacuum was run for 5 minutes. Then, 2-MeTHF (3.5 mL) was added. The reaction was placed in an ice bath. Phenylmagnesium bromide (0.87 mL, 2.46 mmol) was added dropwise, and the reaction was stirred for 30 minutes. Diethyl phosphite (0.64 mL, 4.93 mmol) was added and the reaction was stirred for 24 hours. A workup was done by adding ammonium chloride (3 mL) and ethyl acetate (4 mL) to the reaction. The aqueous layer was then removed, and the organic layer was dried with anhydrous magnesium sulfide. Gravity filtration was performed and then the solvent was removed under reduced pressure.



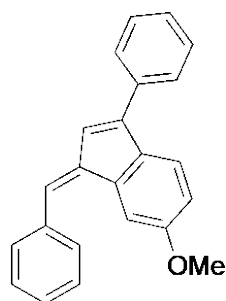
## Monomer Synthesis

### Compound 6



To a round-bottom flask, Indene **A** (0.0921 g, 0.48 mmol), 2-MeTHF (1 mL), and diazabicycloundecene (0.08 mL, 0.53 mmol) were added. The reaction was heated at 60 °C and an air condensor was added. A workup was done by adding ammonium chloride (3 mL) and ethyl acetate (4 mL) to the reaction. The aqueous layer was then removed, and the organic layer was dried with anhydrous magnesium sulfide. Gravity filtration was performed and then the solvent was removed under reduced pressure.

### Compound 7

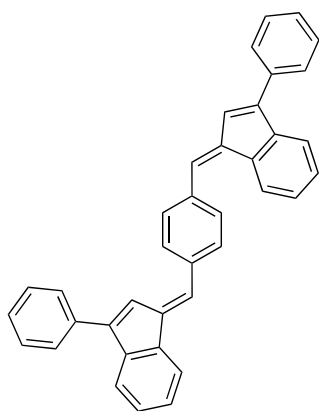


To a round-bottom flask, 5-methoxy indene (0.1658 g, 0.746 mmol), 2-MeTHF (2 mL), terephthalaldehyde (0.1517 g, 1.12 mmol), and diazabicycloundecene (0.1129 g, 0.746 mmol) were added. The reaction was heated at 60 °C and an air condensor was added. Workup was done by adding ammonium chloride (3 mL) and ethyl acetate (4 mL) to the reaction. The aqueous layer was then removed, and the organic layer was dried with anhydrous

magnesium sulfide. Gravity filtration was performed and then the solvent was removed under reduced pressure.

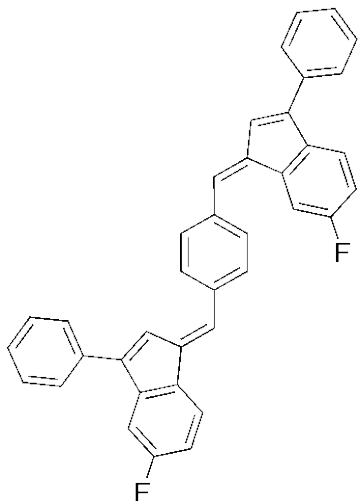
## Dimer Synthesis

### *Compound 8*



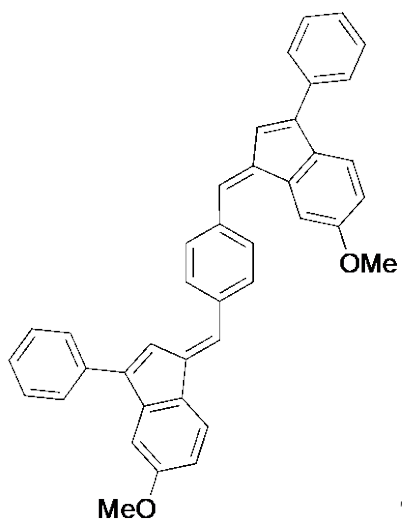
To a round-bottom flask, 3-phenyl-1H-indene (0.1994 g, 1.037 mmol), terephthalaldehyde (0.0973 g, 0.346 mmol), 2-MeTHF (4 mL), and triazabicyclodecene (0.1063 g, 0.694 mmol) were added with a stir bar and sealed. The mixture was stirred at room temperature for 15 minutes. A work-up was done with ammonium chloride (3 mL), ethyl acetate (5 mL), and magnesium sulfate. The mixture underwent gravity filtration and after performing vacuum filtration, yield was found to be 0.3580 g (0.74 mmol, 40%). Single crystal x-ray diffraction was obtained for this sample.

*Compound 10*



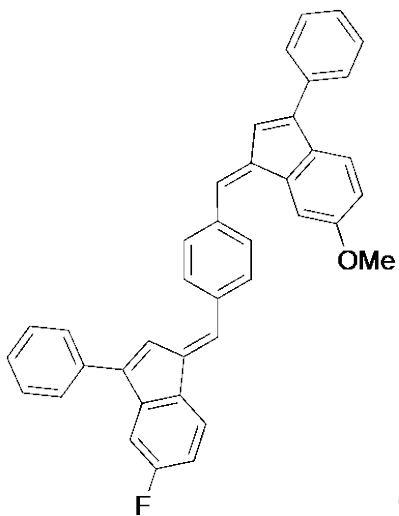
To a reaction vial, 5-fluoro indene (0.176 g, 0.8371 mmol), 2Me-THF (2 mL), terephthalaldehyde (0.0398 g, 0.279 mmol), triazabicyclodecene (0.0778 g, 0.5581 mmol) and a stir bar were added. The mixture was stirred at room temperature for 15 minutes. A workup was done with ammonium chloride (5 mL) and hexane (1 mL). The aqueous layer was then removed and the product was frit filtered, washed and transferred to a new vial with ethyl acetate. High vacuum filtration was performed for ten minutes.

*Compound 11*



To a reaction vial, 5-MeO indene (0.1444 g, 0.65 mmol), terephthaldehyde (0.0389g, 0.295 mmol), 2-MeTHF (2 mL), and triazabicyclodecene (0.0824 g, 0.65 mmol) were added and placed under high vacuum conditions for 30 minutes. A vacuum filtration was performed and the reaction was transferred to a new vial where it was washed with hexane.

*Compound 12*



To a round-bottom flask, methoxy monomer (0.0284 g, 0.0839 mmol), 5-fluoro indene (0.0194 g, 0.0839 mmol), 2-MeTHF (3 mL), triazabicyclodecene (0.019 g, 0.0839 mmol), were added and stirred for ten minutes. A column was run in dichloromethane. After high vacuum filtration, yield was found to be 0.0453 g (0.085 mmol, 25%). Single crystal x-ray diffraction was obtained for this sample.

## Results and Discussion

This research project is based around the synthesis and analysis of benzofulvene dimers. Benzofulvenes have many unique properties, particularly in optics, which is what our lab specifically aims to look at. To show that these benzofulvenes have color tunability would demonstrate many potential applications for these dimers such as in electronic devices. Our lab has previously established an optimized synthesis of the benzofulvene dimers, so our current research project is to analyze these dimers to understand the emission properties they have in solution state, crystallized state, and solid state.

We ran in-silico experiments to determine the HOMO-LUMO gap that showed, in theory, we should be able to produce color tunability with push/pull dynamics in these dimers. Push/pull dynamics refers to electron flow throughout the dimer due to substituents that are attached at either end. How electrons move through the system is determined by whether electron donating groups or electron withdrawing groups, or both, are bonded to the dimer.

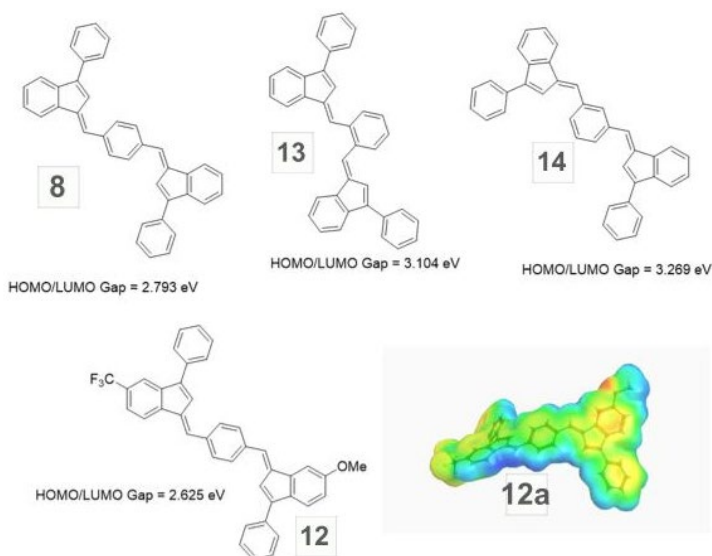


Figure 5: HOMO/LUMO gap for different types of dimers with an electron density map [6]

We see differences in HOMO/LUMO energies in dimers **8**, **13**, and **14** (Figure 5) which suggest gap tunability based on configuration. When dimers are in the para position (dimer **8**), there is a smaller HOMO/LUMO gap than the ortho (dimer **13**) and meta (dimer **14**) structures which suggest that the para dimer will have a red shift in absorbance because it requires less energy for the electron to move to the LUMO space. Gap tunability refers to how we can change the HOMO/LUMO gap values of a dimer based on what substituents we add to it. Additionally, in dimer **12**, we see that by adding push/pull substituents the HOMO/LUMO energy gap decreases further showing that this dimer is the most likely to have excited electrons with a lower energy wave. **12a** in Figure 5 illustrates an electron density map that shows how electrons will be conjugated within the push/pull mechanism. The red areas are representative of areas of high electron concentration whereas the blue areas show areas that are electron deficient. This map allows us to understand how the substituents are affecting the electron flow throughout the compound.

When synthesizing these benzofulvenes, there were a few issues we ran into with producing an adequate yield, specifically for our push/pull benzofulvene. The issues we were seeing was that by trying to add both the electron withdrawing group and the electron donating group to the dimer at the same time, we were producing two separate homodimers as well as a small percentage of the push/pull dimer. To resolve this issue, we synthesized the benzofulvene monomer with a methoxy group and then added the fluorene indene after we had a stable structure.

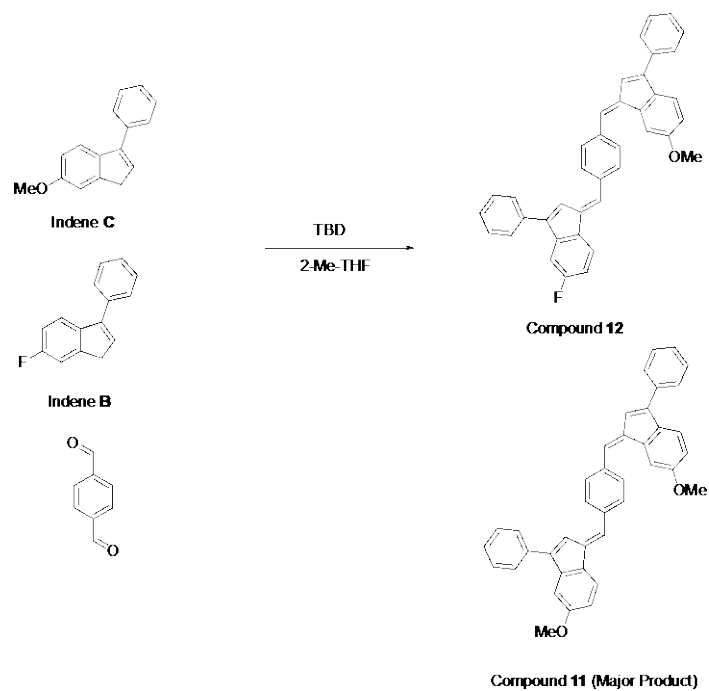


Figure 6: Proposed synthesis of how we initially approached making our push/pull benzofulvenes.

Unfortunately, we were getting many results that had two methoxy groups or two fluorine groups instead of our push-pull.

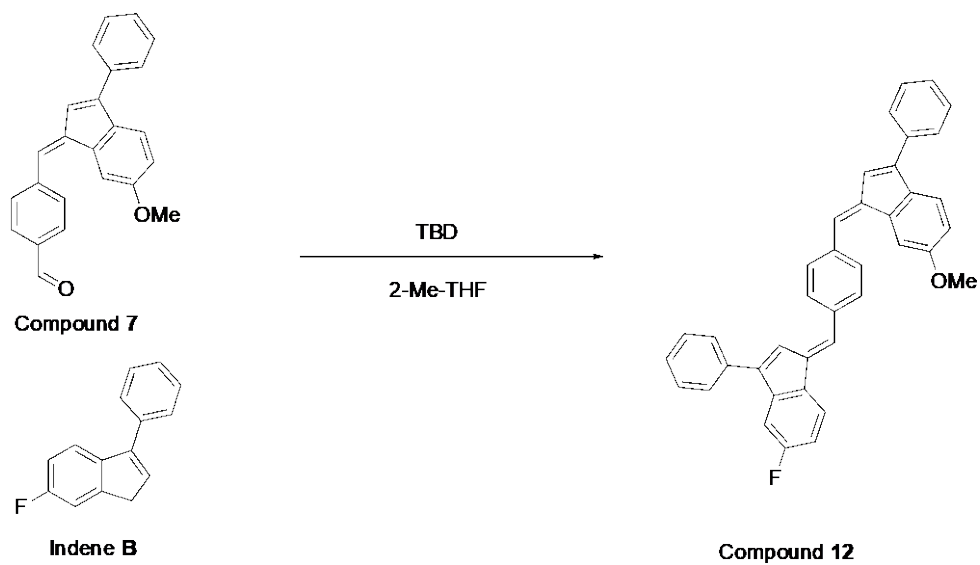




Figure 7: Our new synthesis method for creating the push/pull benzofulvene that was able to produce a much higher yield of our desired product.

To determine if we were successful in tuning our benzofulvene dimers, we analyzed them using absorbance and emission-based spectroscopy. This emission from the dimers occurs when a valence electron in a higher energy orbital relaxes to a lower energy orbital. We were able to determine the wavelength of light that is being produced from our substance with absorbance which subsequently tells us the color of light being emitted. We have been able to see light emission in the red, orange, and yellow ranges. By experimenting with our push/pull substituents we were able to confirm that the HOMO/LUMO gaps of these molecules are slightly tunable. When looking qualitatively at the fluorescence of push/pull dimer using AIE, we did see some fluorescence which is what we expected. However, fluorescence was limited due to the solution state due to the rotation of the single bonds around the central benzene ring of the dimer that are able to move freely in solution. We also looked at our parent and homodimers under UV light and they did not fluoresce whereas our push/pull dimer did fluoresce under these conditions. Therefore, it became clear that the push/pull mechanism we are examining was in fact having an effect on the fluorescent properties of the benzofulvenes.

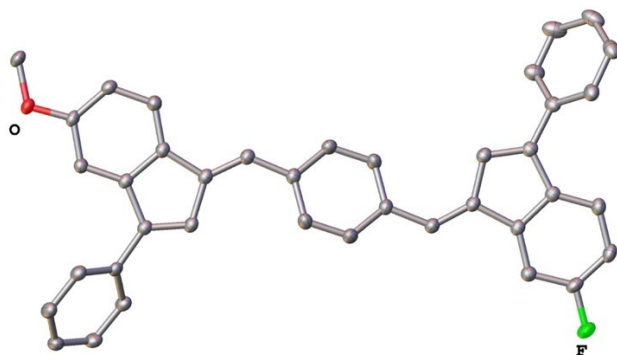


Figure 8: Ball and stick model of push/pull benzofulvene (Compound **12**) that demonstrated tunability. Qualitative data for this compound is described below



Figure 9: Optical properties of Compound **12** dissolved in different solvents.

Solvatochromism was used as a demonstration of the optical properties shown by the push/pull benzofulvene when it is dissolved in different solvents (Figure 9). The solvents from left to right are 95:5 hexane: ethyl acetate, acetone, tetrahydrofuran, ethyl acetate, dichloromethane, dimethyl sulfoxide, and dimethylformamide. From left to right these solvents range from mostly nonpolar to polar and therefore we were able to gain a better understanding of the chemical properties of our push/pull benzofulvene. We are seeing a red shift in the absorbance as the solvents become more polar which gave us valuable insight into how the solution properties affect how the dimer appears.



Figure 10: Optical properties of Compound **12** in solid state.

Solid state optics were another example we used to demonstrate fluorescence/optical properties of our push/pull benzofulvene when it is dissolved in different solvents (Figure 10). From left to right the solvents are dichloromethane, ethyl acetate, hexane, tetrahydrofuran, and acetone. Dichloromethane is the most polar solvent here followed by ethyl acetate and tetrahydrofuran and last acetone and hexane which are considered non-polar. This once again allowed us to develop a qualitative understanding of the chemical properties of our push/pull dimer. We were able to see more absorption when the push/pull dimer was in the more polar solvent even though it was in a solid state. We typically would expect a solid compound to be more fluorescent than if it was in liquid due to the restriction of bond rotation.



Figure 11: Aggregate induced emissions of Compound **12** in organic solvent (right) and inorganic solvent (left).

Aggregate induced emissions (AIE) of our push/pull benzofulvene in dimethylformamide (right) versus an aqueous solvent (left) was also used in order to demonstrate the difference in fluorescence between the solution and solid state. It can be easily seen that the benzofulvene becomes aggregated in the non-organic solvent and becomes fluorescent. The AIE works by introducing small amounts of water to the solution until you have created an aggregate which is essentially the dimer molecules coming together and forming a colloid which allows them to fluoresce with more intensity due to increased restriction of single bond rotation around the central benzene ring. Benzofulvenes are mostly nonpolar which causes them to move away from the water that is added and move towards each other. Colloids can remain dispersed across the solution evenly which is why they are valued when it comes to producing a fluorescent material.

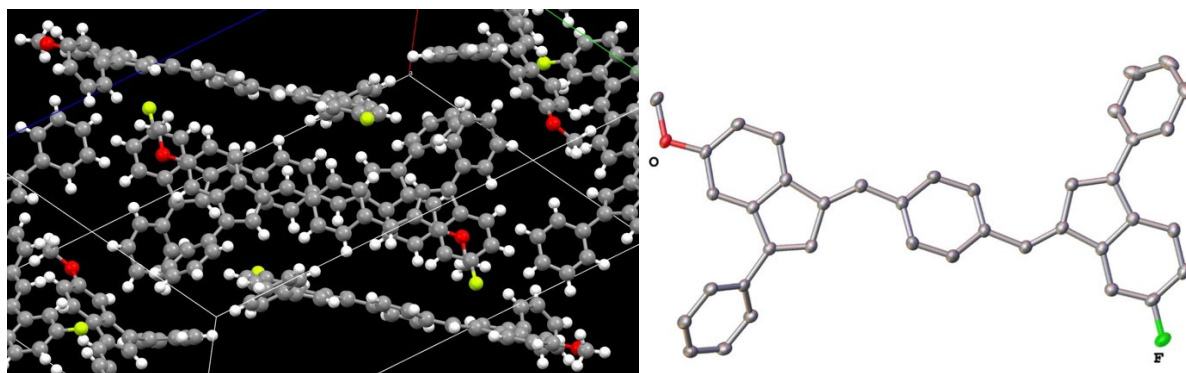


Figure 12: Crystal structures of Compound **12**.

In addition to the qualitative absorbance data we were able to gather for our push/pull benzofulvene, we were also to grow a crystal structure of the dimer which is modeled in Figure 12. The fluorescence demonstrated by our crystal structure as well as our aggregate compound seen in Figure 11 is improved due to the lack of rotation around the single bonds that are on either side of the central benzene. In solution phase, the dimer can rotate freely which decreases the amount of fluorescence it emits. When these single bonds are confined in a crystal or aggregate structure, the dimer essentially becomes locked in its 'fluorescent position'. Overall, we found through our total qualitative analysis of our push/pull dimer that color tunability is possible through manipulation of electron flow using push/pull dynamics of different substituent groups.

After seeing promising evidence for the effectiveness of Compound **12** from our qualitative data, we performed UV-Vis spectroscopy on each of our dimers.

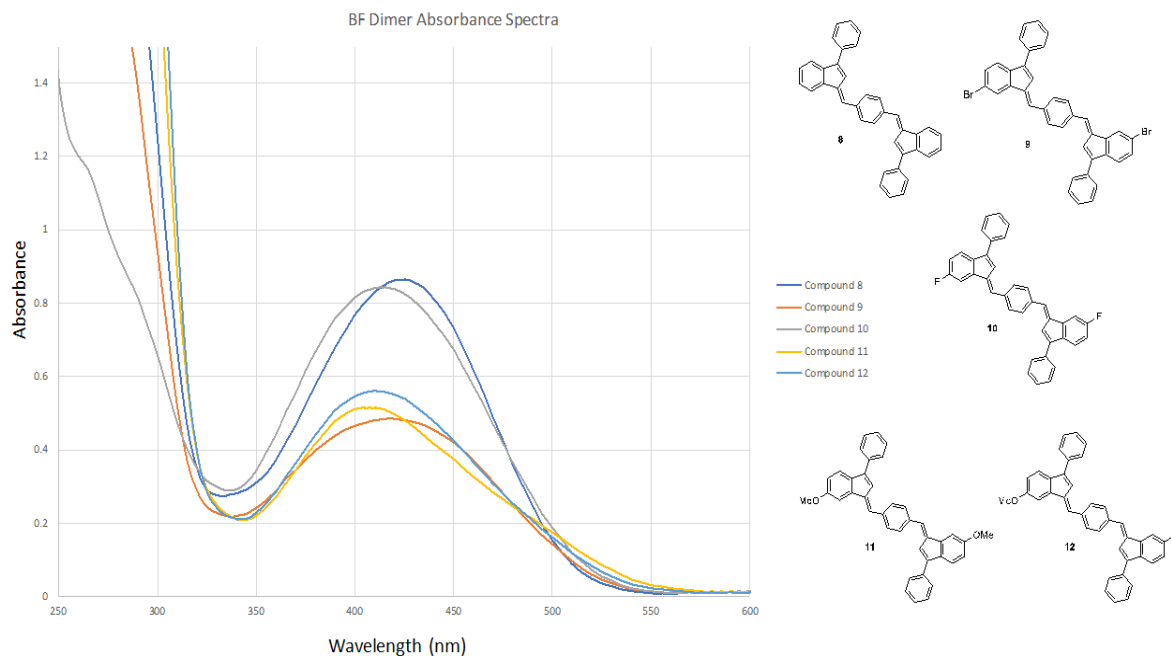


Figure 13: Absorbance spectra data for each benzofulvene dimer.

The results demonstrated in Figure 13 from our UV-Vis analysis were inconsistent with what we expected based off our computational models. Each dimer is absorbing relatively the same wavelength of light with slightly higher levels of absorbance demonstrated in the parent and fluorine homodimer. Unfortunately, we didn't observe much red shifting with our dimers which is likely due to the increased rotational ability that the dimers have as opposed to the monomers.

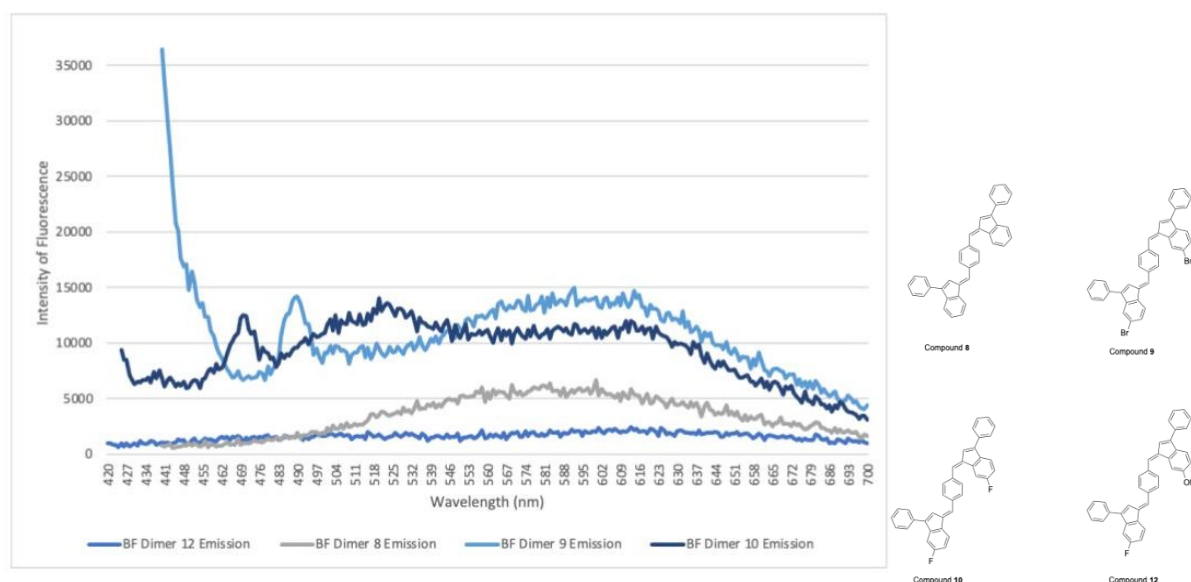


Figure 14: Benzofulvene dimer emission spectroscopy in chloroform.

After gathering absorbance data our next step was to obtain fluorimetry data for each of our dimers. We did this in chloroform because it is nonpolar, and we wanted to see how well our dimers would fluoresce in a less viscous solvent to determine if this had a major effect. It can be seen in Figure 14 that the dimers did not fluoresce very well. The most likely reason for this is because of the solvation allowing them to rotate freely around their single bonds. This rotation gives the electrons the possibility of thermal relaxation rather than fluorescence. When the dimers can do this, they don't stay in their ideal fluorescent position which may result in a

smaller quantum yield. We were unable to include Compound **11** in this graph due to its test being run at a low wavelength which resulted in an incorrect emission plot.

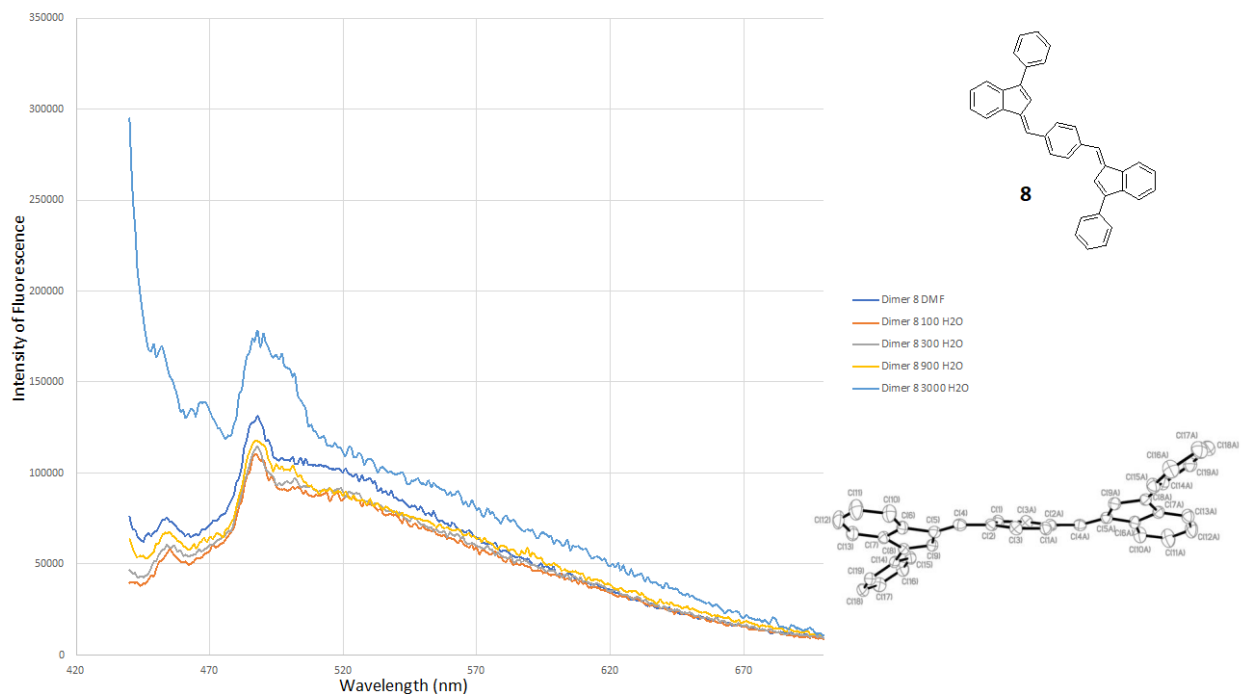


Figure 15: Aggregated induced emissions for our parent dimer in DMF.

After gathering fluorimetry and absorbance data for each of our dimers in chloroform, we wanted to observe the push/pull mechanism and the parent dimer in DMF, a more viscous and polar solvent. We expected that because DMF is more viscous the free rotation around the single bonds in the dimers would be more limited and they would be able to fluoresce more. We did see this trend and therefore wanted to proceed with gathering quantitative AIE data. As observed in Figure 15, adding increments of water initially decreased the fluorescence of our parent dimer from baseline because the aqueous properties were allowing that free rotation about the single bonds. However, once we reached a point where aggregates were forming which was about 3000 microliters of water, the fluorescence of the parent dimer skyrocketed which is consistent with our computer models and what we expected.

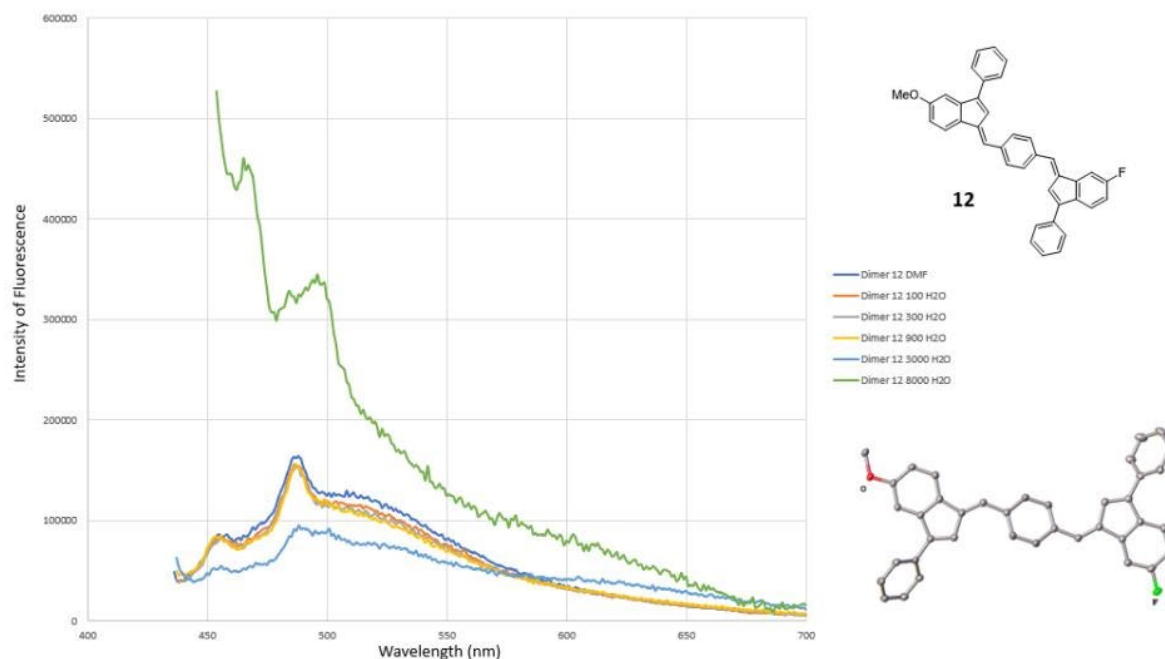


Figure 16: Aggregated induced emissions of Compound **12** dimer in DMF.

In our push/pull dimer we saw a much more intense effect when aggregating with water. The fluorescence already started out higher which we expected, and then steadily dropped off such as in the parent when we added water that made the solution less organic. However, once we reached the point where aggregates were formed, about 8000 microliters, there was a large jump in fluorescence that significantly surpassed what happened with the parent dimer. This shows that the push/pull mechanism is in fact tunable. We did require more water to reach the aggregate point than for the parent, but this makes sense considering the polarity of Compound **12** is higher. Furthermore, part of the reason we believe Compound **12** was able to fluoresce much better than the parent is due to the dihedral angle between the central benzene and the dimeric groups attached to it which we were able to measure in the crystal structure that we were able to grow for both Compounds **8** and **12** (Figure 12). In the parent benzofulvene, the dihedral angle is 26 degrees while in the push/pull the angle is only 16 degrees. This smaller angle could



be increasing the communication between these groups and allowing electrons to cross easier which contributes to higher fluorescence and quantum yield.

From our experimental data we can conclude that tunability in solution is hard to achieve for our dimers, although it has been demonstrated with our monomers. This is likely due to the increased variability in position that the dimers have because of their additional single bond that allows for rotation. This rotation makes it so that the push/pull mechanism doesn't have much of an effect on electron conjugation because communication between both sides of the dimer is hindered. However, we do see strong evidence for tunability of the dimers in the solid state as demonstrated by the AIE in Figures 15 and 16. The solid state helps to restrict the single bond rotation which allows the dimers to stay in their optimal position for communication.

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