ON BENZOFULVENE MONOMERS: AN EXPLORATION OF NOVEL LEWIS ACID INDICATORS WITH TUNABLE FLUORESCENCE

by

MADELEINE KLEIN

A THESIS

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Approved: *Adam Glass, PhD*
Primary Thesis Advisor

This thesis focuses on benzofulvenes, a class of aromatic molecules with unique physical and chemical properties that have gained considerable interest over the past decade. The core research questions addressed include the optimization of benzofulvene synthesis, modulation of their optical properties via bond rotation and push-pull dynamics, and their potential application as Lewis Acid titration indicators.

The literature review highlights key aspects of aromaticity, fluorescence, and benzofulvenes. The methodology section details the experimental procedures, starting from the synthesis of benzofulvene monomers from indanone precursors, followed by purification and conversion processes. Analytical techniques such as thin-layer chromatography (TLC) and nuclear magnetic resonance (NMR) are employed to evaluate the purity and yield of the synthesized compounds. It then details an experiment that demonstrates that benzofulvenes can be used as Lewis Acid titration indicators.

In essence, this research encompasses a multifaceted exploration of molecular behavior, offering insights into the fine-tuning of emission properties, alongside an understanding of the core characteristics of pentafulvenes and their practical applicability. This approach

encompasses both practical experimentation and analytical techniques, ensuring the precision and reliability in our endeavor to understand and fine-tune fluorescent benzofulvene synthesis. This research provides evidence that benzofulvenes can be used as Lewis Acid indicators in practice, not just theory. It is a contribution to the broader field of organic chemistry, paving the way for further exploration of benzofulvene usage.

Acknowledgement

I dedicate this thesis to the professor, the myth, the local legend: Dr. Adam Glass, without whom, I might never have been introduced to the study of fluorescing molecules. Being in your lab has immensely strengthened my competency in research, collaboration, and resiliency. It also gave me some redemption for nearly flunking my first term of chemistry in college. I want to thank my awesome parents for supporting my dream of pursuing healthcare over the family meat company, as well as providing me with the most delicious farm-fresh eggs to fuel my brain during this trying season of life. I simply could not have asked for a better mom and dad. I want to thank my baby sister, Clarissa, for always answering the phone and simply being the most wonderful person I know, inside and out. You are the love of my life. Lastly, I want to thank my esteemed colleagues: Grace, Anessa, and Seth, who were a constant source of support and encouragement during the many months we worked together in the Glass Lab, both as experimental collaborators and friends. I love you all, fellas!

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Chapter 1: Background

I.I Conjugation

One of the most important concepts related to this thesis is conjugation. A conjugated system is one where double bonds are linked together by single bonds so that they alternate. When this happens, the π orbitals of the atoms arrange themselves in space so that they overlap, forming π bonds.

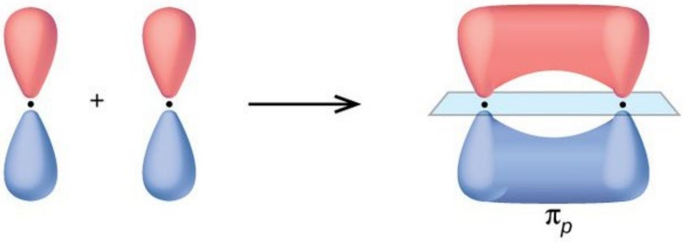

Figure 1. When molecules are conjugated and planar, the π orbitals of nearby atoms will overlap to form π bonds (π_P).

This molecular arrangement is planar and allows electrons to delocalize throughout the conjugated system, resulting in enhanced stability. Extensive conjugated systems often absorb light in the visible region. Lycopene, for example, is a pigment found abundantly in tomatoes and other red fruits with an extensive arrangement of alternating single and double bonds forming a conjugated system. This planar structure allows for the delocalization of electrons throughout the molecule, leading to enhanced stability. As a result of this extensive conjugation, lycopene efficiently absorbs light in the visible region, particularly in the blue and green wavelengths, while reflecting red wavelengths. This absorption and reflection pattern gives tomatoes their characteristic red hue.

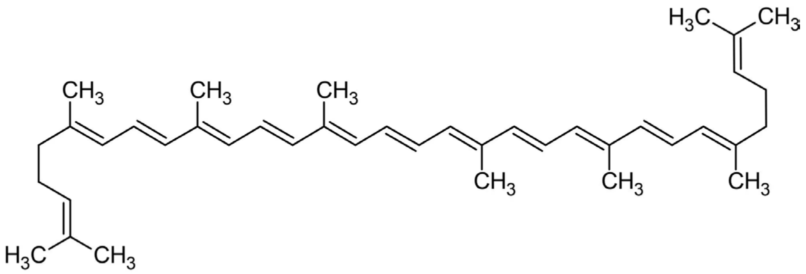

Figure 2. Lycopene is the extensive conjugated molecule that gives tomatoes red pigmentation.

I.II Aromaticity

Over the past decade, there has been a growing fascination with pentafulvenes, driven by their intriguing physical and chemical attributes. These molecules exhibit remarkable characteristics related to aromaticity, fluorescence, and electron push-pull dynamics such as tunable color in the visible region (yellow-red), enhanced stability, and altered molecular characteristics due to interaction with different solvents.

Aromatic molecules such as pentafulvenes and benzofulvenes display enhanced stability, shorter bond lengths compared to their non-aromatic counterparts, and distinct π-electron ring formations owing to the presence of double bonds. This structure permits electron delocalization, making these molecules responsive to external magnetic fields and resulting in specific nuclear magnetic resonance spectroscopy (NMR) values. (Krygowski 2001). Moreover, pentafulvenes are often referred to as "aromatic chameleons" due to their unique ability to exhibit aromaticity under certain conditions while behaving as non-aromatic compounds under others. This duality stems from their electron-rich, conjugated systems, which can adapt their electronic structure based on environmental factors such as solvent polarity. (Haberland, 2018) It adds a degree of uniqueness to the benzofulvene structures.

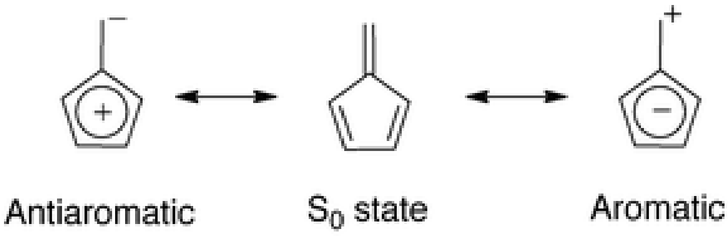

Figure. 3 Pentafulvene, an isomer of benzene with an exocyclic double bond, can transition between antiaromatic (unstable) and aromatic states (stable).

There are three qualifications that a molecule must meet to be considered aromatic. First, they must by cyclic. Second, they must have conjugation (alternating single and double bonds) throughout the entire system so their electrons can delocalize. Third, they must have 4n+2 π electrons (Hückel's rule; n is a non-negative number), which predicts a planar ring formation.

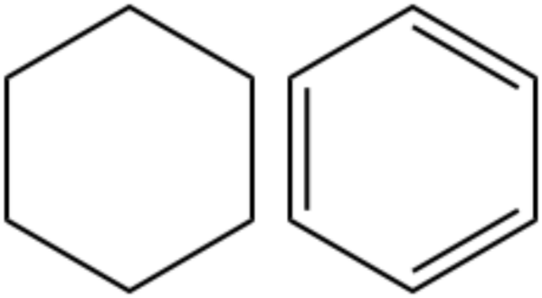

Figure 4. Non-aromatic cyclic hexane (left) versus aromatic benzene (right)

I.III HOMO-LUMO Gap

The color emitted by a fluorophore depends on the HOMO-LUMO gap. (Bredas, 2014) HOMO, meaning "Highest Occupied Molecular Orbital", is the highest energy level that contains electrons. LUMO, meaning "Lowest Unoccupied Molecular Orbital," is the lowest energy level that is empty and can accept electrons. Orbital systems contain distinct energy levels that retain electrons at varying amounts of energy. The "Gap" is the difference in energy between the HOMO and LUMO. It is crucial in determining the electronic and optical properties of a molecule, including the color/wavelength of the emitted photon. Molecules with brighter colors tend to have a small gap and are more likely to absorb visible light. As the conjugated system becomes more extended, there also tends to be stronger absorption, which can be detected using UV-Vis Spectroscopy. The specific color emitted from a molecule depends on the exact energy of the emitted photon. By tuning the HOMO-LUMO Gap, chemists can design molecules that absorb specific wavelengths of light, tuning the perceived color.

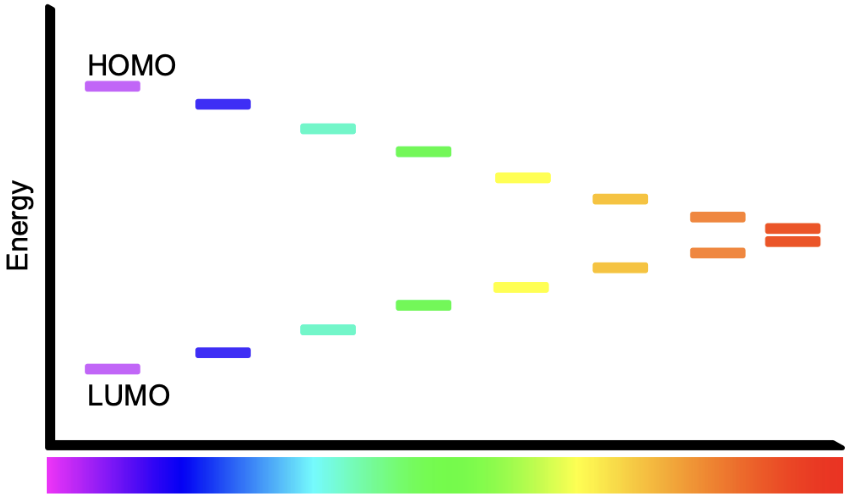

Figure 5. HOMO-LUMO Gap Visualized. A larger gap means the energy of the emitted photon is higher, which corresponds to shorter wavelengths, which are towards the blue/violet end of the visible spectrum. A smaller HOMO-LUMO gap results in lower energy photons, which have longer wavelengths so they are towards the red/orange end of the visible spectrum.

I.IV Fluorophores

Fluorescing molecules, also known as fluorophores, come in the form of synthetic polymers, proteins, and in the case of our research, small organic molecules. When the photon of a specific wavelength comes into contact with an electron, it is "excited" out of its ground state, where an electron jumps from its highest occupied molecular orbital to the lowest unoccupied molecular orbital. After which, a photon is emitted in what is known as fluorescent light, or photoluminescence is ultimately what causes the electron to return to its ground state. (Lleres, 2007)

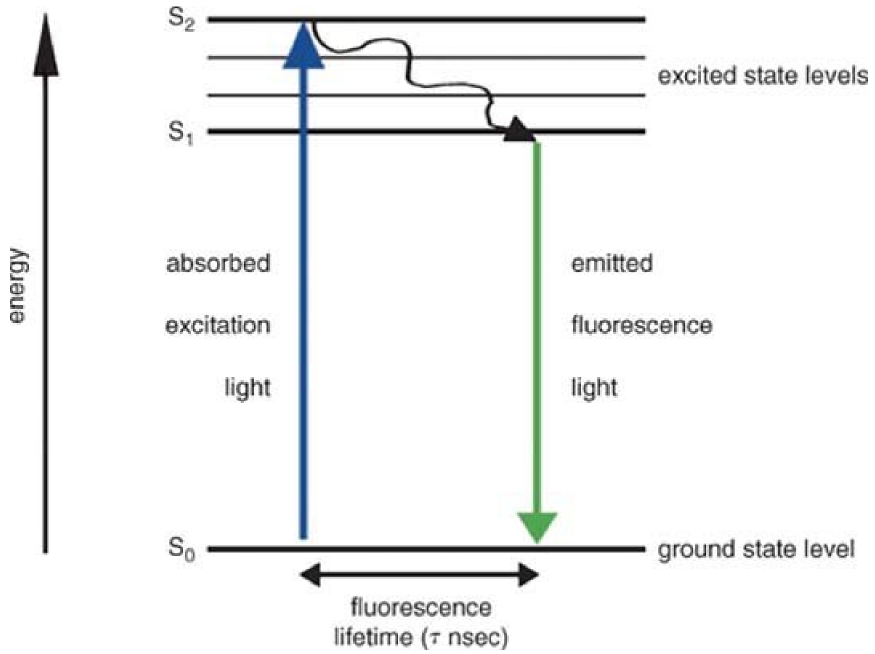

Figure 6. Fluorescence fundamentals (Lleres, 2007)

I.V Benzovulvnes as Fluorophores

Benzofulvenes have many attributes that make for a promising fluorophore. They are a class of polycyclic aromatic hydrocarbons that demonstrate significant potential as fluorophores due to their unique structural and electronic properties. The extended π-conjugated system in benzofulvenes allows for effective delocalization of π-electrons across the molecule, reducing the energy gap between the ground and excited states. This means it requires less energy to excite an electron into the LUMO to release a photon- we can ultimately tune this gap so that the photon released is at a wavelength visible to the human eye. Larger conjugation tends to red-shift emission for this reason.

This is largely intertwined with another critical factor contributing to their fluorescence properties: their potential to exhibit push-pull dynamics. A single molecule can have both electron-donating (push) groups and electron-withdrawing (pull) groups. This interaction significantly affects the electronic distribution, leading to a strong dipole moment in the excited state. This often results in enhanced fluorescence and a red shift in emission, making benzofulvenes tunable fluorophores. (Zhu, 2016) "Tunability" referring to our ability to adapt the substituents and therefore alter the optical properties. The fluorescent properties of a benzofulvene with a para-substituted dimethyl-amino group can be "turned off" if protonated by an acid, and subsequently "turned on" again if deprotonated during a titration simply by disrupting the conjugation network.

There are a few other qualities of benzofulvenes that make them interesting beyond what is researched for this thesis. The rigidity of their structure that arises from extensive π conjugation minimizes non-radiative decay pathways. (Wang, 2017) Additionally, benzofulvenes often exhibit solvatochromism due to their push-pull nature, with their emission wavelength shifting in response to polarity of solvents.

This makes them appealing as a molecule that could potentially be used in photovoltaic technology, as their fluorescent properties may have a longer shelf life and can quickly shift between different wavelengths in the visible region.

Chapter 2: Titration Experiment

II.I Lewis Acid Titration

In spectrophotometric titrations, the disappearance of the wavelength absorbed most strongly (λ_{max}) serves as a crucial indicator of the titration's progress and endpoint. This principle hinges on the fact that there are different specific absorbance characteristics of different species involved in reactions. (Scott, 2013)

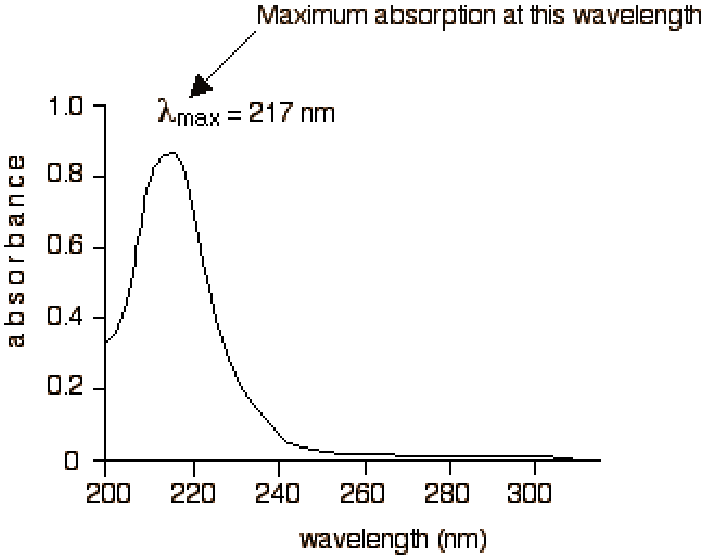

Figure 7. Idealized absorption spectrum for benzene. The strongest absorption wavelength (λ_{max}) is at 217 (the ultraviolet region). Disruption of a conjugated system can result in the disappearance of the λ_{max}.

During a titration, the colorimetric indicator (substance being titrated) undergoes a transformation, resulting in a change in absorbance at this characteristic wavelength. For instance, in complexometric titrations involving metal ions and complexing agents, the metal-indicator complex exhibits a distinct absorbance peak and an associated color. As the titrant is introduced, it reacts with the metal ions, displacing the indicator and causing both the absorbance at the λ_{max} and the color to decrease or disappear entirely. (Guo, 2004) Similarly, in acid-base titrations utilizing pH indicators, the color change associated with the pH shift corresponds to a change in absorbance. Monitoring the absorbance at the λ_{max} throughout the titration allows for the generation of a titration curve, where a sudden change in absorbance and the disappearance of color indicates the titration's endpoint. This methodology provides a quantitative and reliable means of determining the endpoint, essential for accurate and precise titrations. Thus, the disappearance or significant reduction of the longest absorption wavelength signal, along with the associated color change, is a definitive marker of the titration's effectiveness and completion.

II.II Benzofulves as Novel Lewis Acid Indicators

Benzofulvene compounds could serve as novel titrating agents due to their unique optical properties and chemical reactivity. Benzofulvenes, are characterized by their exhibition of strong absorbance in the visible region. This makes them highly suitable for spectrophotometric analysis. Their distinct absorption peaks at specific wavelengths provide a clear and measurable signal that can be monitored during a titration. (Glass, 2018) Additionally, benzofulvenes can be designed to undergo specific reactions with target analytes, leading to significant changes in their absorbance properties. It’s hypothesized that this reactivity can be harnessed to create a sensitive and selective titration indicator. The structural flexibility of benzofulvenes allows for the customization and fine-tuning of their reactivity within the visible spectrum and ideally a predictable reaction with acids and bases. The integration of benzofulvene-based compounds into titrimetric analysis could revolutionize the field by providing efficient and precise analytical tools. This thesis offers an elementary exploration of their potential as novel Lewis Acid indicators that can hopefully pave the way for future research.

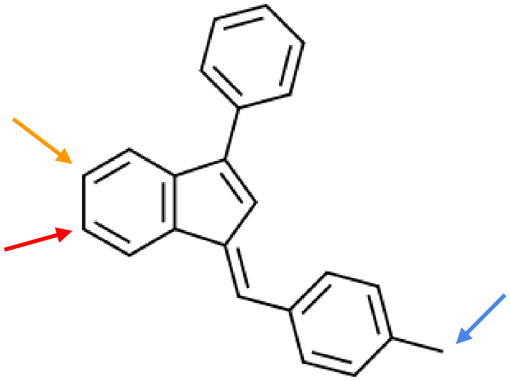

Figure 8. Basic benzofulvene with arrows marking the typical sites of customization.

Chapter 3: Materials and Methods

III.I Overview

The synthesis of benzofulvenes is largely based on schematics optimized in previous research (Glass, 2018). The synthetic route begins with a commercially available indanone, which is converted to indene via simple carbonyl coupling with 2-MeTHF, Grignard reagent (PhMgBr), and a diethyl phosphite elimination to produce an indene intermediate. For the purpose of this thesis, a 1-indanone (“parent”) and a 5-fluoro-1-indanone were ultimately utilized and compared. A DBU-mediated reaction is then used to attach 4-(Dimethylamino)benzaldehyde in good yield, ultimately producing both a “parent” benzofulvene and push-pull 5-fluorobenzofulvene. The objective of this procedure is to determine these derivatives can be used as tunable titration indicators by evaluating their UV-Vis strongest absorption wavelength changes during titration with acid.

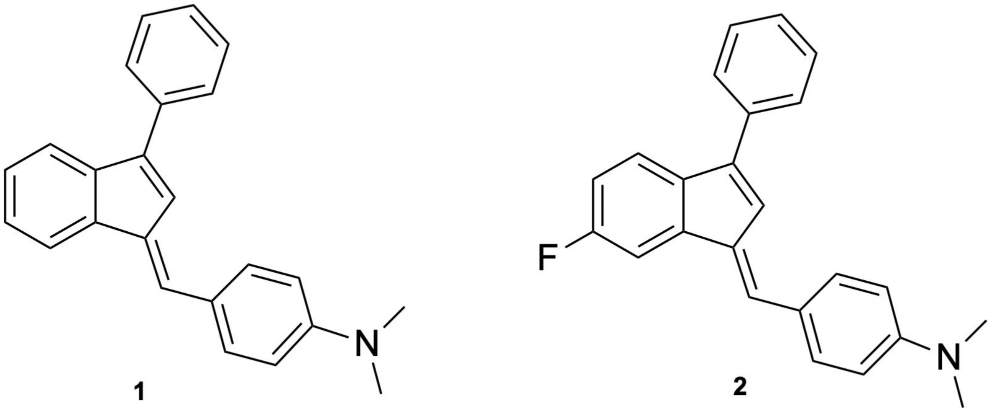

Figure 9. Parent benzofulvene (1) & 5-fluorobenzofulvene (2)

III.II Characterization

To assess our experimental results, we employ two fundamental analytical techniques. The first of these is thin-layer chromatography (TLC), a preliminary step following our experiments. It serves as a practical tool for the separation of the various components within our product (visible "streaks" on the gel plate), enabling us to gauge its purity with relative expediency (Hao 2015). While TLC doesn't provide a precise identification of the individual molecules within our product, it serves as a cost-effective and time-efficient method for assessing purity. In general, we are aware of which streaks most likely represent which compounds when observed under slow-wave blue light and can roughly assess whether our desired product turned up on a TLC plate. In cases where our TLC results indicate the presence of excess side-products or not enough desired product, we embark on a further purification process before advancing to the subsequent analytical stage – NMR (Nuclear Magnetic Resonance) analysis.

NMR analysis plays a critical role in furnishing a highly specific insight into the impurities present within our sample. It achieves this through the visualization of proton levels that correspond to specific molecules. The magic of NMR lies in its ability to exploit the magnetic properties of atomic nuclei, which are sensitive to the distinct electronic arrangements and sharing of electrons that characterize different chemical bonds (Reusch 2013). Molecules within different functional groups possess unique "spin states" which can be observed relative to one another on an NMR spectra. These nuanced variations and the spikes revealed by magnetic resonance can facilitate a better identification of impurities.

UV-Vis spectroscopy is a technique used to measure the absorbance of ultraviolet (UV) and visible (Vis) light by a sample. (Percampus, 2013) It operates on the principle that molecules absorb light at specific wavelengths, causing electronic transitions between molecular energy levels. The absorbance spectrum produced from this measurement provides insights into the molecular structure and concentration of the sample. In a UV-Vis spectrophotometer, a beam of light is passed through the sample, and the intensity of the light is measured before and after it traverses the sample. In titration experiments, UV-Vis spectroscopy is particularly useful for monitoring changes in the absorbance of a solution as a titrant is added. This method is advantageous when the analyte or the reaction product absorbs light within the UV-Vis range. The application involves several steps. Changes in the absorbance spectrum are monitored as the titrant is added, with particular attention to shifts in the absorbance maxima or changes in the intensity of absorbance peaks. These changes reflect alterations in the electronic environment of the analyte due to protonation or deprotonation.

III.III Reaction Procedures: Benzofulvene Synthesis

Part 1: Indanone → Indene Synthesis

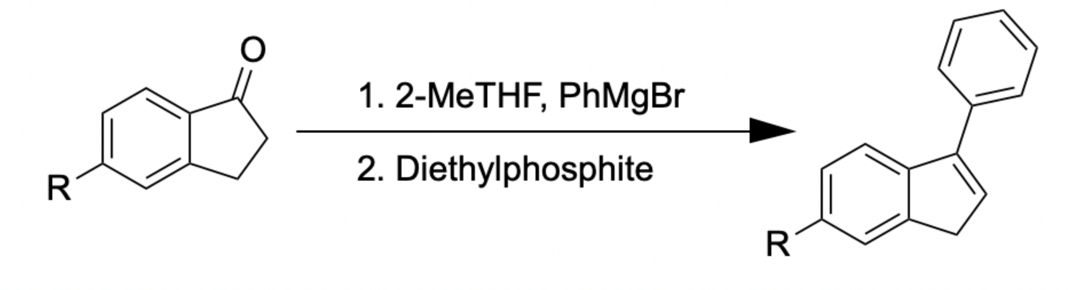

Figure 10. Indene synthesis

A standard, relatively quick, and accessible lab procedure is utilized to synthesize benzofulvenes (Glass, 2018), starting with a variation of a commercially available precursor indanone. To make the parent indene, we start with 500 mg of 1-indanone. To make the 5-fluoro-1-indene, we start with 500 mg of 5-fluoro-1-indanone. Molecular equivalents of 1 indanone: 1 PhMgBr: 2 Diethylphosphite are utilized for both (optimized in previous syntheses). An oven-dried 25 mL flask with a stir bar is capped and put under a high vacuum system by flushing it with nitrogen 3 times for 10 minutes. This ensures that there is no interaction between the system we create (our reactants) and the surrounding air- a critical step in the synthesis process. Once the flask is prepped, we add indanone to the flask and use the high vacuum system again for 10 minutes. Once the vacuuming process is complete, 2-MeTHF (3 M) is added to the flask and stirred until everything is dissolved. Phenylmagnesium bromide is added dropwise at 0 °C, and the reaction is allowed to stir for 30 minutes. Lastly, we add diethyl phosphite dropwise to the flask and allow it to stir overnight.

Part 2: Indene Purification

We begin by taking a TLC of our sample to ensure indene was produced. The TLC is performed in a 90:10 hexane: ethyl acetate solution. We quench the sample with ~ 5 mL of saturated ammonium chloride and water. Next, about 5 mL of ethyl acetate is added to make the sample more hydrophobic. After stirring, we remove the aqueous layer (which separates to the bottom of the flask). Magnesium sulfide is then added to the sample to dry out the mixture even further and remove the inorganic layer. Once the mixture appears to be dried out, it’s gravity filtered into a separate round bottom flask (RBF) and everything is rinsed with ethyl acetate to ensure all of our product is transferred into the new RBF. The solvent is removed under reduced pressure. A gravity column is run and flushed with ethyl acetate. We then take the 90:10 hexane-ethyl acetate and pack the column. We dry load our indene sample and push it through the column with more 90:10 hexane ethyl acetate and collect it in 10-15 test tubes. Then we run a second TLC with a drop from every other tube we collected to analyze further. After analyzing the TLC and determining which tubes contain the highest purity indene from our sample, those tubes are collected and transferred together into a new RBF and the solvent is removed. The indene sample is put under high-vac overnight. NMR analysis in deuterated chloroform was performed to confirm sample purity.

Part 3: Indene → Benzofulvene

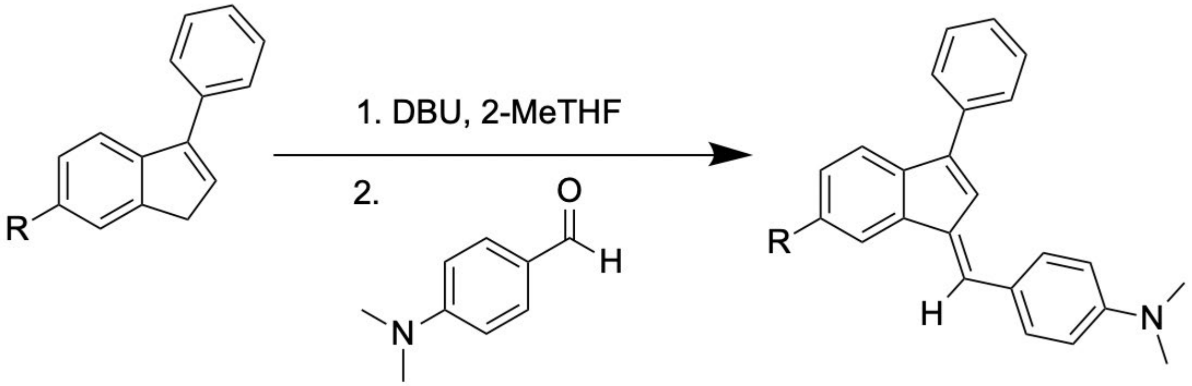

Figure 11. Benzofulvene synthesis

In the last step towards creating the benzofulvene monomers, we collect the weight of the indene samples. Each sample is transferred to a tared RBF with a minimal amount of ethyl acetate, put under the high vacuum for a few minutes, and then weighed. This amount is used to calculate how much of each reactant was needed using molar equivalents of 1 indene: 1.1 DBU: 1.1 4-dimethylaminebenzaldehyde. The reactants are all added to the flask. Our reaction is moved to a heating mantle at 60 ℃ and stirred for ten minutes, then the solvent is removed. We then run a gravity column with the same solvent and dry loading techniques as mentioned in the indene synthesis. Once again, approximately 10-15 tubes were used to collect our sample and then we ran a TLC of every other tube to determine which ones contained the highest yield of sample. These test tubes are combined into a new RBF and solvent is removed under reduced pressure. Then we load it into the high-vac overnight.

III.IV Reaction Procedures: Lewis Acid Indicator

Figure 12. Electron diagram for NMe_2, the basic electron donating group on the end of both benzofulvenes that offers a lone pair of electrons that react with acid. This sidechain amine extends the conjugation box and its protonation results in the disappearance of the strongest absorption wavelength.

To conduct this experiment, stock solutions of benzofulvene and 5-fluorobenzofulvene are prepared by dissolving a calculated amount of each compound in 95% ethanol to achieve approximately 0.0156 mM concentrations. The initial UV-Vis absorbance spectra of the benzofulvene stock solutions are measured from 200 nm to 800 nm using a quartz cuvette and the absorbance maxima is captured. 3 drops of 10% HCl were added to both solutions to protonate amine. The λ_{max} is captured using UV-Vis spectroscopy. This process is repeated with 6, 9, and 12 drops of HCl.

Under airfree conditions, we use THF as the solvent and create stock solutions of ~9 x 10^{-3} mM for the parent and 5-fluorobenzofulvene. 30 µL of BF_3 is added between each UV-Vis recording, and spectroscopy is recorded in an airfree cuvette (BF_3 is highly reactive with water in the air). For data analysis, the UV-Vis absorbance spectra of the benzofulvene and 5-fluorobenzofulvene solutions before and after titration are compared by combining the UV-Vis data onto one graph through Excel. Any shifts in absorbance maxima, up and down or left and right, are observed.. This is done to determine if either compound exhibits a clear and distinct change in the UV-Vis spectrum that might suggest a benzofulvene can be used as an indicator, specifically one that can be tuned to absorb different wavelengths of light.

III.V Experimental Results

During the titration with 10% HCl, the longest absorption wavelength disappeared as expected around 425 nm (**Figure 8**). This confirmed that the benzofulvene was titratable as expected. In the air free BF_3 titration with both the parent benzofulvene (**Figure 9**) and the 5-fluorobenzofulvene (**Figure 10**) the longest absorption wavelength also disappears around 425 nm, indicating a significant change in the electronic structure of the molecule, likely due to protonation of the acid. This interaction modifies the conjugation/ electronic distribution within the benzofulvene, resulting in the loss of the specific absorption band. Furthermore, a visible color change from yellow to transparent occurs, marking a discernible endpoint of the chemical reaction. This demonstrates that benzofulvenes are effective indicators for titrations involving HCl (Brønsted-Lowry acid) and BF_3 (Lewis acid).

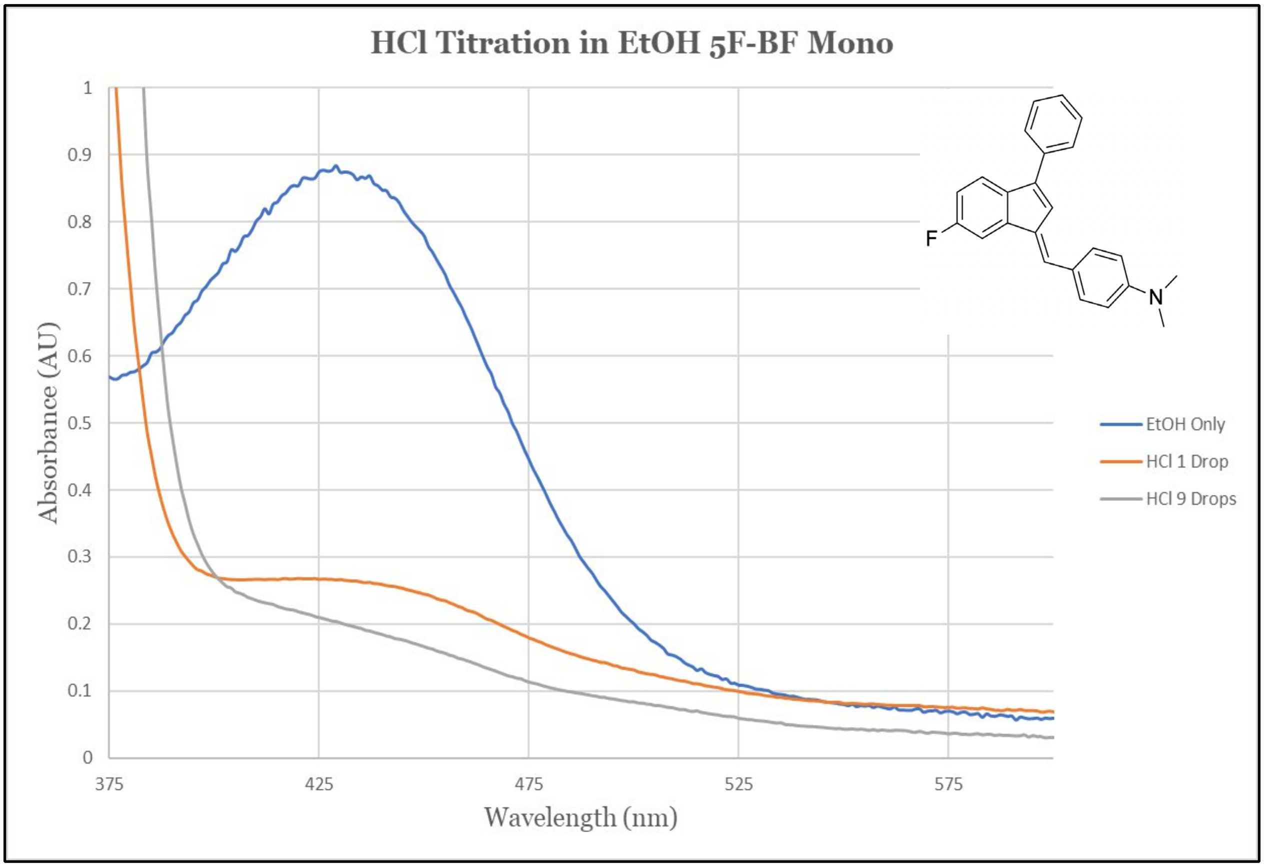

Figure 13. HCl titration of 5-fluoro-1-benzofulvene in EtOH. The maximum absorbance peak (~ 430nm) diminishes with subsequent additions of HCl.

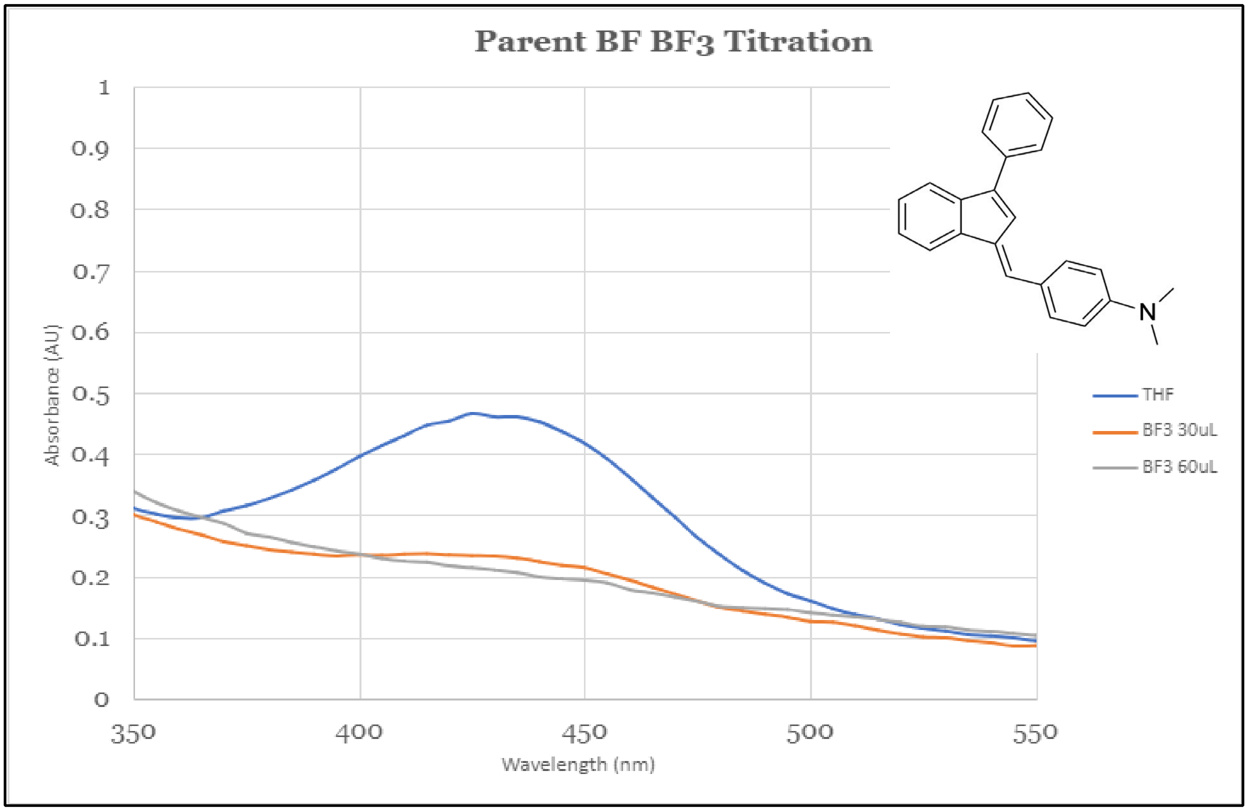

Figure 14. BF_3 Titration of the parent benzofulvene in THF. The maximum absorbance peak (~ 430 nm) diminishes with subsequent additions of BF_3.

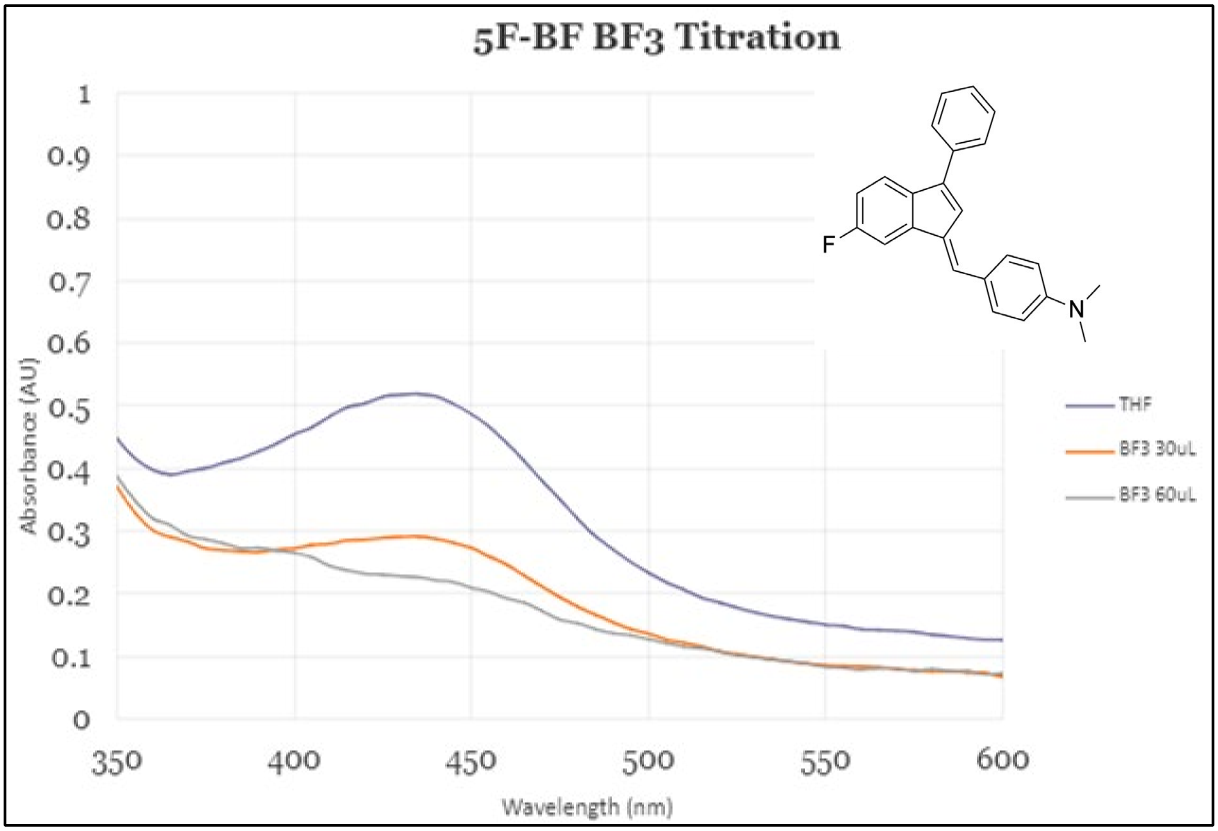

Figure 15. BF_3 Titration of the 5-Fluoro-1-benzofulvene in THF. The maximum absorbance peak (~ 430 nm) diminishes with subsequent additions of BF_3.

II.VI Discussion

The study's findings suggest that benzofulvenes can be used as novel Lewis acid titration indicators, which is special due to the high reactivity of complexes such as BF_3-THF. The push-pull dynamic, involving electron-donating and electron-withdrawing groups, amplifies the response to acid interactions, making the color change and absorption shift more pronounced. This distinctive feature underscores their potential as novel indicators in Lewis acid titrations, providing clear, reliable endpoints essential for accurate titration results.

III.VII Future Directions

This experiment could be replicated with a focus on quantifying the results to establish more precise and reliable data. Detailed quantitative studies would involve measuring the exact changes in absorbance with high-precision instruments, correlating these changes with specific pH values, and establishing clear absorbance-pH profiles for benzofulvene and its derivatives. This could lead to the development of new, efficient pH indicators or fluorescent probes with enhanced sensitivity and selectivity. Moreover, the inherent stability and fluorescence properties of benzofulvenes suggest potential applications in biological imaging and environmental sensing, where durable and reliable fluorescent markers are crucial. Further research could also explore the synthesis of new benzofulvene derivatives with tailored properties for specific applications, expanding the utility of these compounds in advanced scientific and industrial fields.

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