Title
The Synthesis, Characterization, And Potential Applications Of Novel And Known Nitropyrenes

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THE SYNTHESIS, CHARACTERIZATION, AND POTENTIAL APPLICATIONS OF NOVEL AND KNOWN NITROPYRENES

By

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A capstone project submitted for Graduation with University Honors

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ABSTRACT

Dye sensitized solar cells (DSSC) are an emerging photovoltaic that uses organic photosensitizer dyes to produce solar energy. These cells aim to be cheaper, environmentally friendly, and eventually more efficient than conventional photovoltaics. Nitroaromatics, specifically nitropyrenes, are an attractive candidate for optimizing DSSCs. Pyrenes, which typically absorb light in the UV range, can be nitrated to bring their absorption wavelengths into the visible range, thereby increasing the efficiency of the cell. However, a challenge exists in not only preparing these nitropyrenes with linkers but also in separating the various regioisomers produced. Here we report a robust and high yield synthetic scheme for preparing three novel nitropyrenes derivatives with acetyl, propionyl, and butyrl side groups respectively. To achieve this, we introduce the use of Soxhlet extraction as a separative tool. Alternatively, we consider regioselective nitration of pyrene iimide derivatives to produce di- and tri- derivatives. Future work aims to investigate the construction of electron acceptor-donor systems for use in tandem DSSCs.

ACKNOWLEDGEMENTS

I first want to sincerely thank my faculty mentor Dr. Valentine Vullev for assisting and guiding me during this project. I also want to extend this gratitude to the graduate students in the lab for teaching me the various skills and information needed to conduct this research.

I next want to thank all my teachers and professors whose encouragement and lessons both inside and outside the classroom have helped shape me into the person I am. It’s because of them that I am able to not only conduct research but also that I am able to receive my bachelor’s degree. In a way, my degree is not just mine but also that of those who have helped and guided me.

Finally, I want to thank and honor my grandparents, Nirmala, and Gordhandas Butani for whom I owe for instilling in me the pursuit of knowledge and creativity. Their love and compassion inspire me, and I aim to carry their spirit forward through my work. Without them, I also would not be here.

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INTRODUCTION

As the world turns towards renewable technologies, the efficiency and cost of them are further scrutinized and improved characteristics are desired. During the development of photovoltaics, metal oxides, rare earth metals, and other exotic natural resources have been used as photosensitizers, doping materials, and other functional components. As the demand for higher performance photovoltaics increases, more research is being done into a certain organic chemistry's role in these new technologies. Organic photosensitizers are being researched as catalysts for fuel generation [1] and have been considered for use in photovoltaics. The posterchild for this application is dye sensitized solar cells which use a pigment or dye to absorb light and emit an electron when excited. Via charge transfer, this electron is shuttled to a conducting surface. While not currently surpassing conventional photo-voltaics, this young technology (having only been developed in the 1990's) has great potential [3]. To achieve this potential, more work must be done in developing the next generation of dyes and photo-capture systems. It is the former avenue of research that is presented in this capstone.

Pyrene is a large polyaromatic hydrocarbon e featuring many delocalized electrons and has 4 chemically active locations, these being the 1,3 6 and 8 positions. Additionally, Pyrene is photoactive, absorbing light at 336nm and emitting at 384nm (UVC). In the construction and development of organic semiconductors and tangential technologies, Pyrene has great potential and chemical diversity to match it . The goal with this molecule is to bring about the development of fully organic photosensitizers, semiconductors, and similar charge transfer based technologies. Functionalization of the active sites on Pyrene allow for the finetuning of its chemical properties such as solvent polarity sensitivity, hydrogen donation ability, and tunable fluorescence. More relevant to this work is how functionalization, in this case nitration, is able to red-shift or bathochromically shift the absorption and emission characteristics of pyrene to the visible region.

Large charge transfer systems required for applications in photovoltaics require large amounts of electrons and unique interactions between the electron-dense core and functional groups. Additionally, these molecules must be photoactive and somewhat well-studied. As such, nitropyrene is a prime candidate for such applications. Nitropyrenes are a class of polycyclic aromatic molecules that contain a nitro group. This nitro group itself is comprised of nitrogen attached to two oxygens, one double bonded to the central nitrogen. Due to the presence of these atoms, nitro groups are incredibly electron withdrawing. Nitropyrenes, along with other pyrene derivatives, are well known for their mutagenicity and biotoxicity and their chemistry is one of the most well known of the pyrene derivatives. As a result of functionalization, many nitropyrenes tend to strongly absorb wavelengths within the range of 405-410nm. Due to the pyrene core, its somewhat difficult to obtain specific regioisomers. Thus, most nitropyrene synthetic schemes begin with chemically reactive groups on the 1,3 6 and 8 positions while further techniques can make the 2 and 7 positions chemically active. Unsurprisingly, commercially synthesized sources of these molecules are expensive.

MATERIALS

Reactions

The starting reagents for the reaction were sourced through various chemical companies. 1-Aminopyrene, Acetyl Chloride, Butyryl Chloride, and Propionyl Chloride were purchased from TCI chemicals. Due to the war in The Ukraine, several compounds were unavailable from suppliers such as the dimethyl malonyl chloride and dimethyl malonyl chloride ester. To circumvent this, two halogenating agents were purchased from chem-blocs, Fluoro-activating, and Chloro-activating while the dimethyl malonic acid precursors were supplied by Acros chemicals. Dimethylformamide (DMF) was used as the reaction solvent for DBAN 1, DBAN 2 and DBAN 3. DMF is a potent amide-coupling solvent, however it is prone to forming amine and amide contaminants in the presence of water. Experience with DMF laden contaminants has had negative effects on reaction progress and yield. Thus, Lab grade DMF was distilled in-house to obtain amine and water-free DMF. To aid in the distillation process, several hygroscopic molecules were used such as sodium sulfate. Calcium Chloride and drierite were used to dry the air being vacuumed. Dichloromethane, DCM, was used as the reaction solvent for DBAN 4, DBAN 5, DBAN 6, DBAN 7, DBAN 8, DBAN 9, and DBAN 10. Radical nitration required the use of concentrated Nitric acid along with copper. To safely and efficiently produce the Dinitrogen Tetraoxide radical, copper shreds were used. Sodium bicarbonate was used to quench the production of Nitrous Oxide gas. Regarding classical nitration, the same nitric acid was used in conjunction with glacial acetic acid. Throughout the reactions, Argon and Nitrogen gas was used to purge atmospheric oxygen from the reaction mixture and to evacuate oxygen and moisture from flasks.

Purification

One of the critical tools for this project was the use of a Bucci rotovap (rotational evaporator) and its axillary systems (heat bath, chiller, vacuum). A Soxhlet apparatus attached to a condenser was used in one of the isolation attempts. This set up included a heating mantle, sand, and cold-water inlets. For the flash (column) chromatography set up, silica powder, sand and a 250mL chromatography column was used.

Characterization

In the purification steps, Ethyl Acetate and Hexanes were used with TLC plates to monitor reaction progress and detect the presence of products. To characterize the products, an Agilent Mass spectrometer was used as well as an AVANCE 600 NMR machine. Methanol and deuterated DMSO respectively were used as analytical solvents. Finally, a variety of vials were used to store, transfer, react, or act as analytical vessels throughout the experiment.

METHODS

Reaction Planning

There are several goals in designing the synthesis schemes of nitropyrene or pyrene derivatives. First, the environmental conditions should be as low demanding as possible. That is, they should produce high yields of product without the use of high pressure or temperature (as compared to the Haber process which exclusively requires the use of high pressure and temperature to create ammonia),

Prior to conducting work, the reaction mechanism and required materials had to be planned. A naming convention was used to differentiate the different reactions and are as follows: DBAN (Dev Bhatt Aidan Nguyen) 1, 2, & 3 refer to the pyrene molecules with acetyl, butyrl, and propionyl linkers (respectively). DBAN 4,5 & 6 refer to the nitrated versions of the previous molecules. DBAN 7 and 8 refer to the pyrene molecules with Amide and Iimide linkers respectively. Additionally, DBAN 9 and 10 refer to the nitrated version of these molecules.

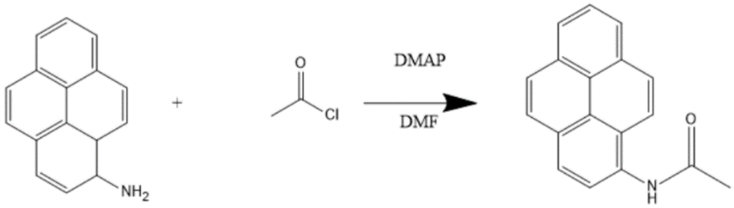
The starting material for the nitropyrenes is comprised of a pyrene core and a linker. To produce the starting material for the nitropyrenes, an amide coupling reaction connecting the pyrene core to the linker was desired. Furthermore, this reaction would need to be base-catalyzed and be done in Dimethylformamide (DMF) which is a superior amide coupling solvent. This reaction would target the amino group at the 1 position and allow for the addition of an acetyl, butyryl, or propionyl linker via a peptide bond.

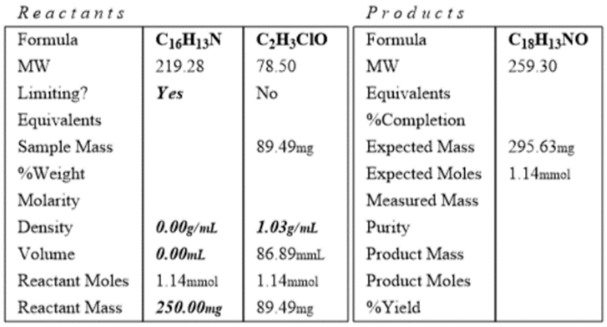
DBAN 7 and 8 differ from the previous nitropyrenes primarily due to their linker. DBAN 7's linker was a dimethyl malonyl ester, a derivative of malonic acid containing two methyl groups and an ester. DBAN 8's linker is just a derivative of malonic acid with the aforementioned methyl groups without the ester. Much like the novel nitropyrenes, the linker for these two molecules will be attached to the pyrene core via a peptide bond. However, DBAN 8's structure bonds to the nitrogen of the amino group twice, resulting in a vaguely cyclic shape. To achieve this, it was planned to use dimethyl malonyl ester chloride and dimethyl malonyl chloride however due to the war in Ukraine or other supply chain issues, this was unavailable. Thus, a workaround was created. By using the commercially available derivatives with hydroxyl (OH) groups and a halogenating agent, linkers with sufficiently reactive functional groups could be synthesized and added to the pyrene core.

Starting Material Synthesis

Novel Nitropyrenes

To produce DBAN 1, 250mg of 1-Aminopyrene, .9mL of Acetyl Chloride, and a catalytic amount of 4-Dimethylaminopyradien (DMAP) was added to approximately 30mL of DMF in a 100mL round bottom flask . DBAN 2 and 3 required 250mg of 1-Aminopyrene and DMAP as well as a slightly higher amount of butyryl and propionyl chloride (1.4 and 1.6mL respectively). Due to the exothermic nature of the reaction, an ice bath was used to cool the reaction (although depending on the number of reactants, a simple water bath could be used). The reaction was left overnight and covered in aluminum foil to prevent photodegradation of the products. Furthermore, the reaction mixture was purged with argon or nitrogen to prevent oxidation and the proliferation of byproducts. The reaction mixture for these three compounds would immediately turn from transparent to opaque and beige colored. Precipitates would also form and impede magnetic mixing, in this case 10-15mL of DMF was added. Post reaction, deionized water would be added to crash the product out of solution. Then, the contents of the flask would be initially separated via gravimetric filtration, but it was found that vacuum filtration was far more efficient. After, the filtrate would be dissolved in DCM and transferred to a separatory funnel and undergo 3 washes in lightly acidic water (to remove any DMAP), lightly basic water (to remove any contaminants as well as residual acid), and finally one wash with DI water. 25dram vial to be dried via an abderhalden apparatus to fully dry the sample overnight. From this work-up procedure, a small amount of product would be set aside to act be used in analytical measurements while the rest of the products would be used in further reactions. Figure 2 below shows the reaction mechanism and stoichiometric table for DBAN 1. DBAN 1-3 have similar mechanisms differing only in their linker reagent.





Reactants

Formula	**$C_{16}H_{13}N$**	**C_2H_3ClO**
MW	219.28	78.50
Limiting?	***Yes***	No
Equivalents		
Sample Mass		89.49mg
%Weight		
Molarity		
Density	***0.00g/mL***	***1.03g/mL***
Volume	***0.00mL***	86.89mmL
Reactant Moles	1.14mmol	1.14mmol
Reactant Mass	***250.00mg***	89.49mg

Products

Formula	**$C_{18}H_{13}NO$**
MW	259.30
Equivalents	
%Completion	
Expected Mass	295.63mg
Expected Moles	1.14mmol
Measured Mass	
Purity	
Product Mass	
Product Moles	
%Yield	

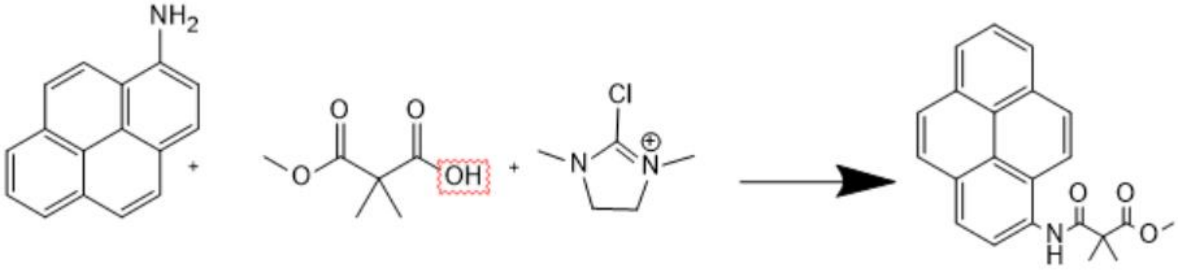
(Fig. 1. reaction mechanism and stoichiometric table for DBAN 1)

Known Nitropyrenes

DBAN 7 and 8 required the same pyrene reagent and base catalyst but with different linker reagents. 250mg of 1-Aminopyrene was added to a 100mL round bottom flask with approximately 30mL of DCM. 168.16mg of 3-methoxy-2-dimethyl-3-oxopropanoic acid was added along with 153.73g amount of the chlorinating agent, 2-Chloro-1,3 dimethylimidazolidinium hexafluorophosphate. A small amount of DMAP was added and the reaction was left overnight. For DBAN 8, 152.02mg amount of dimethyl malonic acid was added instead of the 3-methoxy-2-dimethyl-3-oxopropanoic acid along with the chlorinating agent and also left to react overnight. DBAN 7 turned into a jade-green solution with off-white precipitates. DBAN 8 turned into a reddish-brown solution with beige precipitates. Both solutions were washed via separatory funnel with 4 deionized water washes. The first wash was to remove the chlorinating agent, the second wash was with slightly acidic water to remove any residual DMAP, the third wash was with slightly basic water to remove any residual acid and charged contaminants, and the fina006C was with neutral water. After, the bottom layer was collected and rotovapped to remove the DCM. Finally, the contents were transferred to a 25-dram vial and left to fully dry in an abderhalden device. Similarly, to the previous reactions, a small amount of product was withheld to be used for analytical measurements.

Difference Between Chlorinating and Fluorinating Agents

When planning this reaction and acquiring the necessary materials, it was questioned whether a chlorinating agent would work better than a fluorinating agent. Both halogens have a similar, if not exactly the same, mechanism of action in-vitro but their reaction behavior differs. The chlorinating agent, 2-Chloro-1,3- dimethylimidazolidinium hexafluorophosphate, is shown to be more powerful at chlorinating with the downside of its products being slightly less stable. The fluorinating agent, 2-Fluoro-1,3- dimethylimidazolidinium hexafluorophosphate, produces products of higher stability but its fluorinating ability is somewhat weaker. Thus, batches of the starting material were synthesized using either the chlorinating or fluorinating agent and their yields were noted. The results of this are discussed later in the capstone. Figure 3 shows the scheme for DBAN 7. DBAN 8 differs only in the linker reagent used.



(Fig. 2. reaction mechanism for DBAN 7)

Nitration

There were two methods of nitration: Radical and Classical. To prepare the radical nitration solution, 100mL of DCM was super cooled in an acetone bath cooled by dry ice. In another large flask, a small amount of nitric acid was combined with an arbitrary amount of metallic copper and capped with a rubber stopper containing a port and tubing. The tubing was connected to a glass pipette and bubbled into the ice-cold DCM solution for several minutes. During this time, the solution would turn bright blue, signifying the formation of the Dinitrogen Tetra oxide radical. This solution was pipetted into the target molecule solution and left to react for 30 minutes at room temperature.

For classical nitration, it was found that dissolving the compound in 10mL acetic acid and around 1mL of nitric acid was enough to begin the reaction. Due to the nature of these compounds, the acetic acid would not fully dissolve them and required prior dissolution in DCM. Magnetic stir bars were added to the reaction flasks and the reactions were left to run for 2 hours.

The work-up for the radically nitrated products was simple and just required drying via rotovap. However, the work-up for the classically nitrated products was more involved. All the compounds were washed 3 times in neutral and slightly basic deionized to remove any excess acid and reactant. The DCM (organic) layer was collected and further dried via rotovap for future work. Figure 3 shows all 5 classically nitrated molecules.

(Fig. 3. Classically nitrated products in DCM (Left to Right: DBAN 1,2,3,7 & 8)

Isolation

Once all the compounds were nitrated either radically or classically, the goal then became isolating the different isomers. The first method used was flash or column chromatography which would allow for the separation of isomers using an eluent system. However, this method provided no conclusive results as the fractions collected would overlap or “bands” of a molecule would simply not move.

During a second attempt, a Soxhlet apparatus was used to selectively remove mono-nitrated products from the reaction mixture. Despite only working for isolating mono-nitrated products, this method still provided some good results.

The last isolation method involved preparative TLC. The crude nitrated mixture was spotted on a TLC plate and allowed to elute in a mixture of 50-50 hexanes: ethyl acetate or 25:75 mix. Once meaningful separation was observed, the desired spot(s) were etched out from the plate and re-dissolved in DCM. Due to the lack of special preparative plates, high yields were impossible to obtain using regular TLC plates. This process was repeated for all compounds.

Characterization

All compounds were verified via mass spectrometry and NMR was obtained for the starting materials. TLC characterization was attempted but it proved difficult due to the similarity in behavior amongst the isomers.

DISCUSSION

Reaction Yields

The reaction yields for the starting material synthesis were fairly high but do show the presence of contaminants or water. The yield for DBAN 1, DBAN 2, and DBAN 3 were 623.34mg, 651.23mg, and 545.19mg respectively. The yields for DBAN 7 and 8 were 312.11mg and 330.09mg respectively. The higher-than-expected yields may be due to impurities in the DMAP or the presence of water.

Chlorinating vs Fluorinating Agent

As previously mentioned, a key point in developing the scheme for DBAN 7 and 8 was determining which halogenating agent to use. Two batches of DBAN 7 with equal amounts of the agents were created. Their yields would be determined by post reaction and the decision would be made. Surprisingly, it was observed that there were no physical changes in the fluorinating agent reaction. Mass spectrometry data supports the position that the reaction failed while yields and physical changes were observed for the chlorinating agent. Thus, the latter was used in all future reactions.

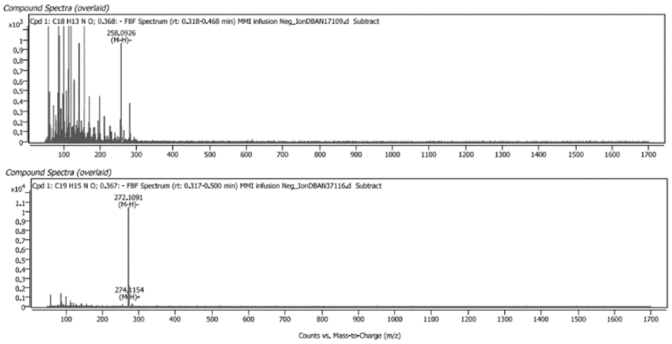
The isolation aspect of the project was arguably its most difficult. As previously mentioned, the first method used was flash (column) chromatography. This method involves the use of eluent systems to separate and move chemicals (sometimes called bands) down the length of the column to be collected. This eluent system is a mixture of ethyl acetate and hexanes in a specific, experimentally determined proportion. By tweaking this solution, certain molecules can be separated from a mix. This method was largely unsuccessful mainly because of the similarities in charge between the regioisomers. As such, many of the bands would bleed into each other and cause an overlap in the collected fractions. This method was used by Espinoza et al [2] with good results; thus, this may be a case of operator inexperience.

The Soxhlet apparatus capitalizes on selectively solubilizing certain molecules from a mixture. In this case, the goal was to selectively solubilize the mono and di nitro isomers as they had better solubility than the tri-nitro. This method worked in isolating the mono-isomers, however it failed to isolate the di-nitro isomer. In a trial with 50mg DBAN 4, 33mg of mono-nitrated products were recovered. However, more work would have to be done to find a solvent or solvent mixture that can isolate the di and possible tri nitro isomers.

The final isolation method was using a version of preparative TLC where the mixture was allowed to separate and then remove from the plate. However, this technique was conducted using regular TLC plates which significantly hindered yield and the quality of the molecule isolated. Mass spectrometry data was too muddied by the silica in the plates to be used.

Characterization

Mass spectrometry is a highly accurate and specialized analytical tool used to characterize molecules based on their mass to charge ratio. The device provided by UCR’s Analytical Chemistry Instrumentation Facility (ACIF) also allows the user to run their sample in a positive or negative infusion which can further differentiate molecules by their net charge. As such, it’s a highly specific tool for “hunting” atoms in crude product mixtures. The data obtained confirms the existence and suggests the abundance of the target compound in the sample. This latter observation also allows the chemist to see what other molecules may be present in the sample, aiding in future reaction and purification optimization. As seen in *figure 4* , the presence of the pyrenes with butyrl and propionyl linkers were very high as compared to the acetyl linker which gave a moderately sized peak. However, the acetyl linker, DBAN 1, shows the presence of many impurities.



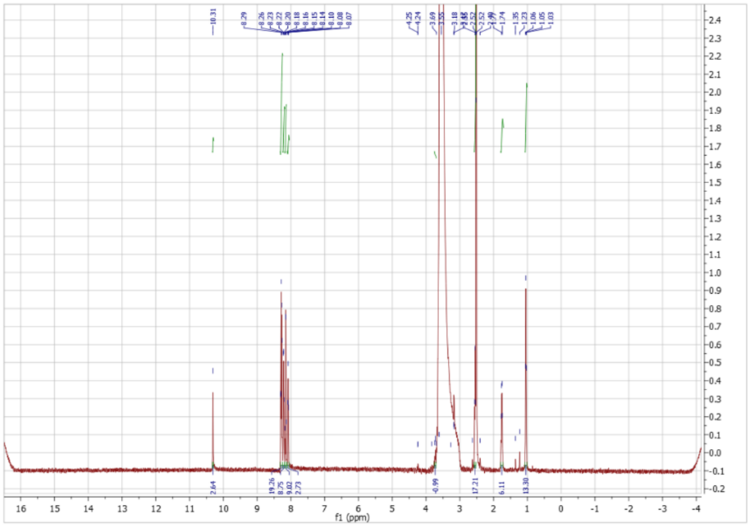
(*Fig. 4.Mass spectrometry data of DBAN1 (Top) and DBAN 3(Bottom)***)**

IMPROVEMENTS

There is quite a bit to improve within this project; the foremost area being the isolation techniques. One route of improvement would be to utilize High Pressure Liquid Chromatography (HPLC), a very powerful separation technique built for separation situations such as these. This technique is similar to column chromatography but computerized and highly precise. Alternatively, more work must be done to elucidate a proper eluent system for the Soxhlet method of separation. Its success in isolating mono-nitrated compounds suggests that the technique can be equally successful for the di-nitro and tri-nitro compounds provided a complementary solvent is used. Future solubility experiments may include a dried amount of some molecule being partially dissolved by small amounts of different solvents and measuring the amounts of di-nitro or tri-nitro compounds present in them.

The second avenue of improvement would be through reducing operator error and by placing a greater emphasis on obtaining clean and dry compounds. A key source of error is simply lack of experience with these techniques and methods. This is easily alleviated with continued work and education. Operator error should be as reduced as possible, and this can be achieved by further familiarization with good practices in synthetic and analytical chemistry.

By improving the quality of the product, higher quality and more advanced forms of characterization can be performed. For example, figure 5 shows the NMR data obtained for DBAN 3. It can be seen that the peaks are muddied and that a large contaminant peak is present at 17.21ppm



(*Fig 5. NMR graph of DBAN 3*)

Nitration Efficiency

A key improvement and potential next step are to focus on a nitration procedure. It was found that radical nitration only produced mono-nitrated molecules while classical nitration produced a variety of regioisomers. Despite this, no attempts were made to optimize this aspect of the project leaving questions and room for optimization. Future work with this aspect of the project aims to see how radical nitration can be conducted in warmed solutions to observe whether poly-nitrated products can be obtained via radical nitration at all. This may lead to an investigation in developing a robust nitration procedure which can significantly improve yields and ease isolation difficulties.

FUTURE DIRECTIONS

Reaction Optimization

One way di-nitro and tri-nitro compounds can be synthesized is by regioselective reactions which form one product in lieu of another or form one product in a higher amount than another. DBAN 7(9) and DBAN 8 (10) are good examples of this as they selectively form di-nitro and tri-nitro compounds. However, they are only able to be selective due to their linkers. Future work will investigate the possibility of selectively forming di-/tri-nitro compounds using the same linker, thereby bypassing most of the regioselective isomer separation steps.

Linker Diversity

The next step in this work is to design a system to attach these molecules to a surface. By modulating the linkers and the surface chemistry of the desired surface, the linker can be optimized specifically for that surface. Thus, it will be important to understand what different types of linkers can be added to the molecule and if these linkers hinder the charge transfer abilities of the molecule. The ideal linker would be synthetically succinct, non-problematic with regards to the electro and photochemistry of the nitropyrene and be able to adhere to a surface with relative ease. To achieve this, various nitropyrenes with unique linkers should be synthesized and have their characteristics measured.

Dye Sensitized Solar Cells

As mentioned above, Nitropyrenes can be used as organic photosensitizers for dye sensitized solar cells. The specific absorption and emission characteristics of Nitropyrenes can be harnessed in Tandem Dye sensitized solar cells. These variants allow for multiple photosensitizing dye and pigments to be used in tandem with each other in a solar cell. If the absorption wavelengths of these dyes are separate, that is they are distinct and don’t overlap significantly, broad spectrum solar cells can be obtained which improves the efficiency of these cells far beyond conventional technology.

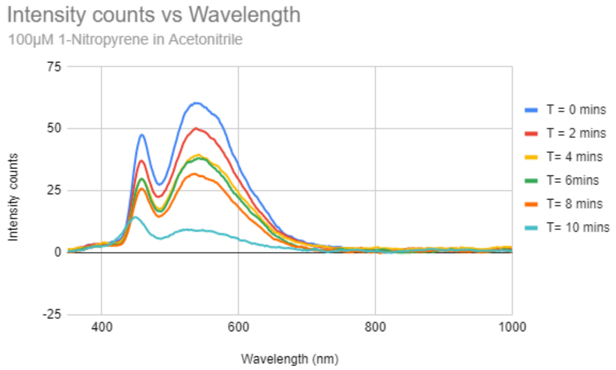
Photodegradative studies

Nitropyrene’s absorbance at in the low 400nm region (UVC) and the wealth of available research allow for it to be used as a standard for the development of photo degrative procedures. A prime example of this is the role of 1-Nitropyrene in developing the Automatic Photo-Spectral Rotational Actinometer or the APSRA. The APSRA is a device that aims to automate the process of obtaining the quantum yield of photo-degradation of a molecule. Its accomplishes this by irradiating a molecule with a 405nm laser for a set amount of time and then promptly measuring its absorbance. As time goes on, the change in absorbance can be correlated with a change in concentration which in turn can be used to obtain the number of molecules decomposed. Combined with the number of absorbed photons, the quantum yield can be obtained using the formula below.

$$\phi_D = \frac{\#molecules\ decomposed}{\#photons\ absorbed}$$

(*Fig. 6. Quantum Yield of Photodegradation formula***)**

Due to the wavelength of the laser used, 1-Nitropyrene is used to test the irradiation and absorption abilities of the device (fig 7). The Intensity counts vs Wavelength data obtained by the APSRA for 1-Nitropyrene perfectly shows that as irradiation time increases, the measured intensity drops.



(*Fig. 7. Quantum Yield of Photodegradation formula***)**

CLOSING REMARKS

This project serves as an excellent foray into pyrene chemistry and serves to outline some fundamental synthetic procedures in the development of photosynthesizers. There is of course much work to be done in establishing the synthetic procedures necessary to reliably produce these molecules.

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