The effect of electron withdrawing groups on functional conjugated systems

I. Introduction

Organic photochemistry is a broad area of study with growing applications in everything from medicine to electronics. Highly conjugated organic molecules combine the benefits of inorganic conductors with the simplicity of organic synthesis and design. Two types of organic systems are studied in this experiment with the goal of elucidating more information and further information about the applications of these molecules.

A. The photochemistry of π-conjugated organic systems:

Organic photochemistry involves absorption of photons into an organic molecule that leads to an electronically excited state. When a molecule absorbs a photon, an electron is promoted from the low energy ground state to a higher energy excited state.[1] The energy contained in the excited state electron can undergo several interactions based on the energies of the ground and excited states and their proximity to other donor or acceptor molecules.[1],[2]

The two main processes studied in this experiment are fluorescence and photolysis. Fluorescence occurs when a molecule absorbs a photon of a particular energy, promoting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), creating an electronically excited state. The energy of the excited state electron is then released as a photon as the electron falls back down to its ground state.[2] In photolysis, absorption of a photon results in the breakage of a bond in the molecule, resulting, in this case, in the photo-uncaging of protected molecules.[3]

i. Fluorescence:

Fluorescence is the radiative process where an excited singlet state molecule emits a photon and is returned to its ground singlet state. Fluorescence emission usually occurs from the lowest excited singlet state, or the excited state with the lowest vibrational energy. This is due to the instantaneous loss of vibrational energy as the molecule adjusts to form the "equilibrium" molecular formation, according to the Frank-Condon Principle.[4] This form of non-radiative decay happens quickly and it is this instantaneous loss of vibrational energy that causes the excitation energy to be higher than the emission energy.[1][5]

The singlet state of an excited state molecule exists when the promoted electron retains its molecular spin and is oriented opposite to its paired electron, which was left behind in the HOMO. The molecule is said to have overall zero spin. The triplet state occurs when the excited electron flips orientation and is thus in a parallel spin to its paired ground state electron. When the two spins are parallel, the state has an overall non-zero spin and the molecule is said to possess a different spin multiplicity.[4]

When a conjugated molecule absorbs a photon, the excited electron can either undergo a $\pi \rightarrow \pi^*$ or an $n \rightarrow \pi^*$ transition, depending on the presence and proximity of heteroatoms that contain filled nonbonding, n, orbitals. In the first type of transition ($\pi \rightarrow \pi^*$), the wave functions of the π-electrons switch from parallel to antiparallel upon the absorption of a photon.[1] The rate of intersystem crossing, or the rate of switching between the singlet and triplet states, in this type of system is very low because the energy difference between the singlet and triplet states is quite large.[2] In general, the non-bonding orbital has a higher energy than the ground state π-orbital, thus the second transition ($n \rightarrow \pi^*$) requires less energy or a lower energy photon. This also results in a higher rate of intersystem crossing because the energy difference between the singlet and triplet states is considerably lower.[6]

Quantum yield of fluorescence measures the efficiency of fluorescence and is a useful measurement in a vast number of disciplines including chemistry, physics, biology and medicine.

It is an important step in determining the photophysical behavior of the molecule in question. The quantum yield (ϕ) is defined as the ratio of number of photons emitted to the number of photons absorbed by the molecule per time unit.[7] In order to determine the absolute quantum yield, a comparison of the radiative and non-radiative rate constants must be calculated. However, a much easier method of determining the relative quantum yield will be used in this study.[7]

The purpose of this portion of the project is to determine the effect of electron withdrawing substituents on the fluorescence quantum yield of highly conjugated oligomers. A discussion of the electron withdrawing effects on fluorescence and energy transfer will be given below. We are trying to 'tune' the photophysical characteristics of highly conjugated oligomers with the potential for future application in a wide variety of disciplines.

ii. *Synthetic design of alternating PAVs and PAEs*:

Large systems of π-conjugated polymers have recently seen advancements in development that make them viable replacements for inorganic semiconductors.[8] Their ease of processability, low production cost, and optical and electronic tenability has led to their extensive study in recent years. This wide range of molecules is used in many diverse applications including laser dyes, chemical sensors, scintillators, and organic light emitting diodes, among many other applications.[9]

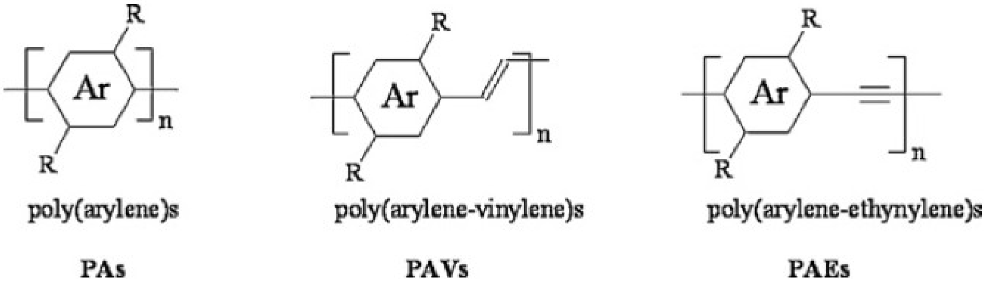

Figure 1: General model of π-conjugated systems.[9]

Three classes of π-conjugated polymers have developed in recent research: poly(arylene)s (PAs), poly(arylene-vinylene)s (PAVs), and poly(arylene-ethynylene)s (PAEs). The first group is characterized by long chains of functionalized benzene or heteroaromatic rings. Poly(arylene-vinylene) polymers consist of aromatic or heteroaromatic rings connected by ethylene groups. The last group is made up of aromatic or heteraromatic rings connected by ethynylene groups. Initially, research was focused on the first type of polymers but recent studies have shown the versatility and viability of the second and third groups. Poly(arylene-vinylene) polymers were first discovered in 1990 to be electro luminescent and also undergo ultrafast photoinduced charge transfer.[8] These developments caused a large increase in their prevalence in research across the world. However, these molecules tend to have high energy LUMOs due to their predominately hole-type conductivity. The large energy gap between their HOMOs and LUMOs caused a large charge imbalance and a high barrier for charge injection, making these polymers only somewhat useful as organic semiconductors.[9]

Using ethynylene bridging molecules as is done in poly(arylene-ethynylene) polymers has also been a topic of study. These types of molecules possess LUMOs of lower energy due to, "enhanced electron affinity, which is ascribed to the electron-withdrawing nature of triple bonds" (Egbe, 2009). Because these molecules are so highly conjugated, many π-π interchain interactions occur, creating a large number of radiationless pathways by which the excited state electron can relax back down to the ground state. This tends to lower the fluorescent quantum yields of these molecules in solid and single-layer states because the π-π interchain interactions occur more easily. Conversely, in aggregated states the π-π interchain interactions become less significant, thus increasing the fluorescent quantum yields of these molecules.[9]

When the two types of polymers are combined into a poly(arylene-vinylene-ethynylene) system, several of the benefits of both types of molecules are present without several of the drawbacks. The less rigid vinylene segmets reduce the effects of the π-π interchain interactions in solid-state photoluminescence studies. Also, the effect of the ethynylene groups on the LUMO energy remains, causing these combination polymers to express relatively higher fluorescent quantum yields.[9] It is with these benefits in mind that the oligomers studied in this experiment contain both double and triple bonds.

Because of the electron donating central piece and the electron withdrawing end pieces, these molecules have a covalently bonded donor-acceptor relationship. When one of our oligomers absorbs a photon of light, we hypothesized that some amount of charge transfer would occur from the donor region of the central benzene to the electron withdrawing end pieces. This creates significant charge separation of the excited singlet state of the oligomer. The effects of this are taken into account in the experimental design section due to the implicit solvent effects that exist.

In this study, PAV-PAE oligomers were synthesized as opposed to polymers because of their ease of synthesis and processability as well as their more defined features such as molecular weight and structure. The insolubility and polydispersity, or wide range of molecular weights, of polymers make it very difficult to quantify their properties.[10] Often times, oligomer analogs are studied and their properties are extrapolated onto infinite chain lengths to predict the polymer properties. Studies have identified several drawbacks to this. First, it is impossible to correctly predict the band gap of a polymer by extrapolating as n goes to infinity because the band gaps of polymers exhibit convergence behavior. Similarly, it is impossible to determine reorganization energies, ionization potentials, polaron-bipolaron balances and disproportionation energies of polymers by studying their oligomer analogs.[10] It is for this reason, that conclusions draw in this study are not descriptive of all similar molecules, but indicated trends of electronic tuning that should be explored with further research.

iii. Photolysis:

The second process studied was that of the photo-uncaging of *o*-nitrobenzyl ester (NBE) protecting groups. Caged compounds are ones in which a covalently bonded protecting group can be removed photolytically.[3][11] Nitrobenzyl compounds were discovered to exhibit these characteristics as early as the 1960s.[3] The creation of a nitrobenzyl-caged compound has many applications in medicinal and biochemical research. Such a compound could be used to temporally and spatially control the release of molecules *in vivo*, which has applications in, for example, the release of hydrophobic drugs for the targeted delivery of therapeutics.[12] NBEs have many biological applications because of their compatibility with numerous functional groups and biological macromolecules.[11]

In order for these compounds to be biologically viable options, they must be water soluble, hydrolytically stable, biologically inert (both before photolysis as well as the cleaved protecting group must remain biologically inert), they must react quickly with a high quantum yield, and they must exhibit a bathochromatic shift in absorbance so as to penetrate deep tissues. [3] Perhaps the two most difficult of the preceding characteristics to obtain simultaneously are that the photouncaging process must occur quickly and without harmful effects on the biological system.[12]

Most of these caged compounds react when irradiated with UV light, which is detrimental to cells and DNA.[3] That is why it is important to shift the absorbance of these molecules to the red. Light in the visible and infrared range is much more efficient at penetrating into the deeper tissues of the body and is much less harmful to biological cells. Another method of reducing the harm of using UV light is to use two-photon absorption, which involves exciting the molecule with two photons of low energy light so the combined effect is a high-energy transition.[3] This phenomenon is not studied here, however, because the focus of this project is to induce a bathochromatic shift in absorbance using one-photon excitation. It is worth noting, however, that bathochromic shifts in one-photon absorbance could also lead to analogous shifts in two-photon absorbance.

Currently, the only NBEs with this potential are activated efficiently at wavelengths shorter then 350 nm. Light with wavelengths shorter then 350 nm does not penetrate tissue significantly, so these compounds are not good precursors to any sort of *in vivo* controlled molecules. The current paradigm for improving photolabile protecting groups centers on adding electron-donating groups to the aromatic ring in order to red shift the absorbance. This, however, has proven ineffective in terms of efficiency.[3] The hypothesis of this project is that conjugated, electron-withdrawing groups decrease the energy of the reactive excited state of NBE molecules, which leads to photouncaging upon irradiation with longer wavelengths of light. Several types of NBE derivatives were designed and their syntheses attempted. The same theoretical rationale used in the first portion of this study is used here: alkynes and electron withdrawing groups work together to lower the energy of the excited state π*-orbital. This decreases the energy gap of the π to π* transition as well as the n to π* transition, thus the molecule requires a lower energy (or red-shifted) photon to induce the electronic transition.

The mechanism by which the protecting group is removed from the substrate has been studied extensively.[3] The two lowest excited states, S_1 and S_2, of the NBE upon photon absorption result from the $n \rightarrow \pi^*$ transitions of the nitro group. The charge transfer excitation involves an excited state generated from the π-orbitals of the aromatic ring to the π*-orbitals of the nitro-group, shifting the molecule into its S_3 and S_4 states.[3] From these excited states, the molecule undergoes photoisomerization into the E or Z-aci-nitro state upon transfer of a proton from the alpha carbon to the nitro group. From here it can undergo inner-system crossing into the triplet state or again undergo photoisomerization. A five membered ring is formed with the benzylic carbon followed by a transfer of an oxygen atom from the nitro group to the benzylic carbon and release of the caged compound.[3] The studies done by Schaper et al were mainly focused on determining the rate-limiting step and rate of intersystem crossing of these reactions.

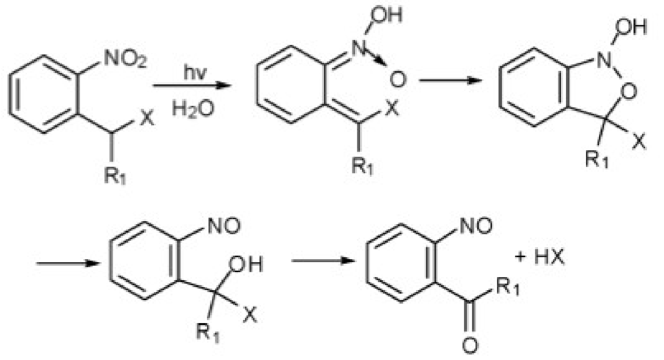

Figure 2: General mechanism for the photolysis of *o*-nitrobenzyl compounds.[13]

B. Electron Withdrawing Groups:

The use of electron withdrawing groups is the thread that connects both aspects of this project. The idea is that electron withdrawing groups change the energy of the π→π* and n→π* transitions, thus altering the energy required to photocleave the NBE derivatives and will effect the quantum yield and photophysical properties of the oligomers onto which they are attached. Electron withdrawing substituents lower the energy of π* orbitals, thus decreasing the energy of the π→π* and n→π* transitions. The lower energy required for these transitions will red-shift the light at which the NBE's will photolyse because a lower energy photon will be needed to induce the uncaging effect.[14]

The traditional electron withdrawing groups studied were 4-ethynyl-benzonitrile, 1-ethynyl-2,4-difluorobenzene, and 4-ethynyl trifluorotoluene. The first two groups are moderately electron withdrawing, while the third is strongly electron withdrawing.

Another substituent that was added to both systems was 2-ethynylthiophene. Thiophenes are five-membered aromatic rings that are often used in organic semiconductors.[15] Thiophene has slightly lower aromaticity than benzene,[15] and as a result its quinoid excited structure tends to be of lower energy than the benzene quinoid structure, thus reducing the energy of the photon required to induce the photouncaging.

The addition of all of these groups to the PAV-PAE oligomer is hypothesized to bathochromically shift the absorbance and fluorescence of the oligomers.

C. Solvent Effects:

Due to the large charge separation that is found in both the oligomer excited singlet state and the excited singlet and triplet states of the NBE, the solvent used during each of these experiments will have an effect on the results. In each case, the intermediate structures are much more polar due to the photon absorption and as a result will be stabilized by a more polar solvent. Stabilization of the intermediate structure will potentially lead to faster and more efficient reactions.

II. Methods:

A. π-Conjugated Oligomer Methodology:

Figure 3~~1~~: Scheme for the synthesis of the electron withdrawing addition groups.

Synthesizing π-conjugated oligomers:

The π-conjugated system studied in this experiment was first theorized and tested by graduate student, Robert Pawle, in the Thomas Lab. After it had shown considerable success under various other conditions, it was hypothesized that adding electron withdrawing groups would have interesting effects on the photophysical characteristics of the π-conjugated oligomer system.

Figure 4~~2~~: Scheme for the synthesis of the 2,4-difluoro methoxy oligomer.

The first oligomer base had the methoxy side chains on the central benzene ring. Several electron-withdrawing alkynes were added to this molecule to determine the effects on the photocharacteristics of the molecules. However, due to the extremely high polarity of these end molecules, they were very insoluble and were therefore nearly impossible to isolate using chromatography and recrystallization. Thiophene and 2,4-difluoro alkynes were both added to this central piece with varying success. The thiophene derivative was very difficult to isolate and after chromatography and several recrystallizations, we were still unable to purify the desired product. The difluoro (4a) derivative was equally as difficult to isolate, however, after several recrystallization attempts, the final product was found to be pure.

Figure 5~~3~~: Scheme for the synthesis of the octyloxy oligomers.

Facing the difficulties of the first oligomer piece, we decided to test a central piece with octyloxy side chains off of the central benzene instead. We hypothesized that this central piece would lead to much more soluble oligomers than the previous one. This was found to be correct for both the thiophene (6b) and nitrile (6a) adducts. 1-ethynyl-2,4-difluoro benzene was also added to this central piece with little purification success. Fluorinated compounds are very difficult to separate using flash chromatography, thus purification was quite difficult.

The relative fluorescent quantum yields of the oligomer molecules were tested using the methodology described by Fery-Forgues and Lavabre.[7] Using a standard, in this case Coumarin-6, the quantum yields of our new oligomers were determined relative to the known quantum yield of Coumarin-6. First, the absorbance of the sample was measured using a UV-Vis spectrophotometer. The absorbance of each sample was kept between 0.5 and 0.1 in order to maintain the proportionality between concentration and emission intensity. Using a PTI ASOC-10 Fluorimeter, the emission spectra of the standard and new molecule were recorded and the relative quantum yield was calculated using the following equation: , where Φ_F is the relative fluorescence quantum yield of the unknown, A is the absorbance at the excitation wavelength, F is the area under the corrected emission curve, n is the refractive index of the solvent used, and $\Phi_{F(S)}$ is the known fluorescence quantum yield of the standard. The subscripts x and s refer to the unknown and the standard, respectively.

The refractive indices of the solvents used must be taken into account because when light passes through a solvent, part of the beam is refracted by the solvent molecules. The refractive indices used in the calculations below were found in the Merck Index (12th edition).[16] Due to the solvent effects described above, three solvents were used in each other these experiments: dichloromethane, tetrahydrofuran, and acetonitrile.

B. Nitrobenzyl Ester Methodology:

Figure *6~~4~~*: Scheme for the synthesis of acetate standards.

Figure 7~~5~~: Scheme for the synthesis of 5-iodo-2-nitrobenzyl alcohol.

Figure 8~~6~~: Scheme for the synthesis of the electron withdrawing nitrobenzyl alcohol molecules.

Figure 9~~7~~: Scheme for the synthesis of the 5-(2-ethynyl thiophene)-2-nitrobenzyl acetate.

The general method of synthesis for the nitrobenzyl esters required first the syntheses of the necessary alkyne and 4-iodo nitrobenzyl alcohol, followed by a Sonogoshira reaction to replace the iodine in the meta position of the benzyl alcohol with the alkyne. Lastly, the acetate was formed using DCC coupling to give the final product.

The initial hypothesis of these experiments led to many synthetic attempts, not all of which were successful. At first, the direct addition of electron withdrawing benzene derivatives was attempted using boronic acid in a Suzuki coupling reaction. Penta~~e~~fluoro~~-~~boronic acid was the first attempt made in this fashion and it was quickly discovered that fluorinated boronic acids were very unreactive under~~to~~ those conditions. A second attempt was made using thiophene-2-boronoic acid with similar results. This methodology was quickly dropped in favor of using an alkyne ~~connecting~~ group, which was performed with considerably more success.

The two nitrobenzyl alcohols that were successfully synthesized had the thiophene and nitrile alkyne adducts attached in the meta position. Another group of molecules that was theorized to exhibit considerable effect on the photouncaging characteristics of these molecules were fluorinated benzene derivatives. Three such molecules were tested: 1-ethynyl-pentefluorobenzene, 1-ethynyl-2,4-difluorobenzene, and 4-ethynyl trifluorotoluene. The S~~s~~onogoshira coupling of TMS-acetylene groups to each of these molecules was found to be quite difficult, resulting in their commercial purchase for further experimentation.

Each of these fluorinated compounds exhibited substantially little reactivity with the nitrobenzyl alcohol under an array of conditions. For example, the S~~s~~onogoshira coupling of 4-iodo nitrobenzyl alcohol and 1-ethynyl-2,4-difluorobenzene went to about 50% completion after 48 hours a which point an attempt was made to isolate the desired product using flash chromatography and recrystallization, both of which were unsuccessful. The reaction mixture was reexposed to the reaction conditions at a different temperature with little variation in the results. Similar outcomes occurred with the other fluorinated compounds initially hypothesized to be unique additives.

The final step of the nitrobenzyl ester synthesis required creating the acetate from the alcohol. At first, the synthetic method used was similar to the one that had been successful in synthesizing 2-nitrobenzyl acetate. The nitrobenzyl alcohol was exposed to dimethylaminopyridine and triethylamine in order to add acetyl chloride to the alcohol to create the acetate. This method proved ineffective with both the thiophene-nitrobenzyl alcohol and the nitrile-nitrobenzyl alcohol. DCC coupling (dicyclohexylcarbodiimide) ended up being the synthetic method used and showed considerably more success than the previous one.

Testing NBE:

In order to determine the relative photouncaging efficiency of the synthesized NBE, we determined the photon flux of the mercury-xenon lamp used and then determined the efficiency of photouncaging of a standard; in this case we used 2-nitrobenzyl acetate. The rate of photouncaging of the thiophene NBE was determined relative to the known rate of 2-nitrobenzyl acetate. The solutions were placed in front of the mercury-xenon lamp in a cuvette for varying lengths of time. The rate of reaction was monitored by NMR spectroscopy. The calculations and results are shown in the discussion section below.

NMR analysis was done to determine the rate of reaction. Each trial began with an initial NMR to determine the ratio of the benzylic protons to any acetic acid protons. In all cases, the initial NMR spectrum showed that no acetic acid had yet been formed. This indicated that all of the molecules in the sample were starting material. After irradiation, another NMR spectrum was taken and the growth of the acetic acid peak was compared to the benzylic proton peak at around 5.33 ppm.

Due to several drawbacks of the experimental procedure, it was impossible to fully characterize the new thiophene acetate molecule. First, the only solvent used was chloroform-D. Several trials were attempted in Acetonitrile D-3, however, the acetic acid peak overlapped with the solvent peak, making it difficult to quantify the amount of acetic acid in the solution.

Another drawback was the lamp that was used. The Hg-Xe lamp did have a lense attached, however, the beam of light emitted was still quite large, leading to loss of efficiency and large error in the results. If the cuvette was not placed in exactly the same location, the results would likely be altered because the same number of photons would likely not enter the solution. This problem could be solved by using a laser or other smaller beam of light, however insufficient time and resources made those options impossible in this study.

C. Synthetic Methods:

1a. 4-[(trimethylsilyl)ethynyl]-benzonitrile: To a solution of $PdCl_2(PPh_3)_2$ (0.36 mmol, 0.036 eq), CuI (0.05 mmol, 0.005 eq) and 4-bromobenzonitrile (10 mmol, 1 eq) in 45 mL triethylamine was added trimethylsilylacetylene dropwise. After 18 hours at room temperature, the solution was filtered through a Celite pad and the collected filtrate was concentrated *in vacuo* to produce brown crystals. Flash chromatography (4:1, Hexanes:Dichloromethane) to produce iridescent white crystals. Yield: 1.19g (60%). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)= 7.61-7.53 (m, 4 H), 0.30 (s, 9 H).

1. 4-ethynyl-benzonitrile: A solution of 4-[(trimethylsilyl)ethynyl]-benzonitrile (1.5 mmol, 1 eq) and Na_2CO_3 (0.24 mmol, 0.16 eq) in 8 mL methanol was left at room temperature for 12 hours. The solvent was removed *in vacuo* and the subsequent solid was redissolved in 5% $NaHCO_3$.

The aqueous layer was extracted with dichloromethane (3x20mL). The combined organic layers were washed with brine and dried over Na_2SO_4, and recrystallized in 1:10 Dichloromethane: Hexanes. Yield: 0.31~~056~~g (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)= 7.65-7.57 (m, 4 H), 3.31 (s, 1 H).

2a. 2-[(trimethylsilyl)ethynyl]thiophene: To a solution of $PdCl_2[P(C_6H_5)_3]_4$ (0.16 mmol, 0.02 eq) and CuI (0.32 mmol, 0.04 eq) in dry THF, after sparging, was added 2-bromothiophene (8 mmol, 1 eq) and Triethylamine (30 mmol, 3.75 eq). Trimethylsilyl acetylene (16 mmol, 2 eq) was added dropwise to the initial solution. After 18 hours at room temperature, diethyl ether was added and the solution was filtered through a Celite pad. The solvent was removed *in vacuo* to produce a dark oil. Flash Chromatography (hexanes) yielded brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)= 7.25-7.22 (m, 2 H), 6.96-6.93 (m, 1 H), 0.270 (s, 9 H).

2. 2-ethynyl thiophene: To a flask charged with 2-[(trimethylsilyl)ethynyl]thiophene (5.5 mmol, 1 eq) was added KOH (11 mmol, 2 eq) dissolved in methanol (10 mL). After 18 hours at room temperature, the reaction mixture was poured over water. The aqueous layer was extracted with diethyl ether (3x 15mL). The combined organic layers were washed with brine and dried over $MgSO_4$ and concentrated *in vacuo*. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)= 7.30-7.25 (m, 2 H), 6.99-6.96 (m, 1 H), 3.36 (s, 1 H).

3a. 1,4-ditriethylphosphite-2,5-dimethoxybenzene: A solution of 1,4-dichloro-2,5-dimethoxybenzene (2.15 mmol, 1 eq) and triethyphosphite (5.75 mmol, 2.67 eq) was heated to 150° C for 18 hours. After cooling to room temperature, the mixture was dissolved in dichloromethane and washed with brine (1x15 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The solid product was washed with hexanes to produce a white solid. ^{1}H (300 MHz,

$CDCl_3$): δ (ppm)= 7.27 (s, 2 H), 4.07-3.98 (quintet, 8 H, J=7.2 Hz), 3.80 (s, 6 H), 3.22 (d, 4 H, J=20.4 Hz), 1.27-1.22 (t, 12 H, J=7.2 Hz).

3. Methoxy oligomer central piece: In flame-dried glassware: a solution of 1,4-ditriethylphosphite-2,5-dimethoxybenzene (1 mmol, 1 eq) and 4-iodobenzaldehyde (2 mmol, 2 eq) in dry THF (30 mL). Potassium *tert*-butoxide was added dropwise. After 2 hours, the reaction solution was filtered and the supernant was concentrated *in vacuo*. The crude product was recrystallized in chloroform/methanol. ^{1}H NMR (300 NMR, $CDCl_3$): δ (ppm)= 7.68 (d, 2 H, J=8.5 Hz), 7.49 (d, 1 H, J=16.2 Hz), 7.30 (d, 2 H, J=8.5), 7.12 (s, 1 H), 7.05 (d, 1 H, J=16.2 Hz), 3.93 (s, 3 H).

4. General Procedure to add electron-withdrawing alkyne to methoxy central piece: To a solution of **3** (0.134 mmol, 1 eq), Alkyne-adduct (0.3 mmol, 2.2 eq), $Pd[P(C_6H_5)_3]_4$ (0.0036 mmol, 0.27 eq), and CuI (0.012 mmol, 0.09 eq) dissolved in 1:1 (Triethylamine: dry THF) solution after sparing for 30 minutes. After 18 hours at 50° C, 9:1 (Methanol:H_2O) was added to precipitate the solid out of solution. After centrifuging the solution for 10 minutes (3500 rotations/min), the liquid was decanted and the solid was collected.

4a. 2,4-difluorobenzene methoxy oligomer: Purification: Flash Chromatography (1:1 Dichloromethane:Hexanes). Recrystallization (chloroform/methanol) and recrystallization (dichloromethane/ hexanes). Yield: 16 mg (62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)= 7.58-7.51 (m, 12 H), 7.17-7.12 (m, 4 H), 6.94-6.89 (m, 4 H), 3.97 (s, 6 H).

5a. 1,4-ditriethylphosphite-2,5-dioctyloxybenzene: A solution of 1,4-dichloro-2,5-dioctyloxybenzene (2.32 mmol, 1 eq) and triethylphosphite (17.2 mmol, 7.43 eq) was heated to 150° C for 18 hours. After cooling to room temperature, the mixture was dissolved in dichloromethane, washed with brine (2x30 mL), dried over $MgSO_4$ and concentrated *in vacuo*.

The crude product was recrystallized in hexanes. Yield: 1.27 g (86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)= 6.91 (s, 2 H), 4.03-3.90 (m, 12 H), 3.22 (d, 4 H, J=20 Hz), 1.77-1.74 (m, 4 H), 1.31-1.22 (m, 32 H), 0.89 (m, 6 H). ^{13}C (125 MHz, $CDCl_3$): δ (ppm)= 150.4, 119.5, 115.0, 69.1, 61.8, 31.8, 29.5, 29.4, 29.2, 26.8, 26.1, 25.7, 22.6, 16.4, 14.1.

5. Octyloxy oligomer central piece: In flame-dried glassware: a solution of 1,4-ditriethylphosphite-2,5-dioctyloxybenzene (1.50 mmol, 1 eq) and 4-iodobenzaldehyde (3.0 mmol, 2 eq) in dry THF (50 mL). Potassium *tert*-butoxide (3.0 mmol, 2 eq) was added dropwise, inducing a color change from yellow to dark green. After 3 hours at room temperature, THF was added to dissolve all products and the solution was filtered. The solvent was removed *in vacuo* to produce a yellow solid, which was recrystallized in Hexanes/Dichloromethane. Yield: 950 mg (79%). ^{1}H NMR (300 NMR, $CDCl_3$): δ (ppm)= 7.68 (d, 4 H, J=8 Hz), 7.47 (d, 2 H, J=16.5 Hz), 7.27 (d, 4 H, J=8 Hz), 7.06 (d, 4 H, J=16.5 Hz), 4.07-4.03 (t, 4 H, J=6.5 Hz), 1.92-1.83 (m, 4 H), 1.31 (s, 18 H), 0.90 (s, 8 H).

6. General procedure to add electron-withdrawing alkyne to octyloxy central unit: To a solution of octyloxy diiodide (0.0634 mmol, 1 eq), electron-withdrawing alkyne (0.1394 mmol, 2.2 eq), $Pd[P(C_6H_5)_3]_4$ (0.0017 mmol, 0.027 eq), and CuI (0.0057 mmol, 0.09 eq) in a 1:1 (diisopropyl amine: dry THF) solution after sparging for 30 minutes. After 18 hours at 50° C, the solvent was removed *in vacuo* and the solid product was redissolved in dichloromethane and 5% $NaHCO_3$. The aqueous layer was extracted with dichloromethane (3x20 mL). The combined organic layers were washed with brine (2x15 mL), dried over $MgSO_4$ and concentrated *in vacuo*.

6a. 4-ethynyl benzonitrile octyloxy oligomer: Purification: Flash Chromatography (1:1 hexanes:dichloromethane) to yield a yellow/orange solid. Yield: 37 mg (73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)= 7.67-7.61 (m, 8 H), 7.57-7.52 (m, 10 H), 7.16 (d, 4 H, J=14.7 Hz), 4.10-

4.06 (t, 4 H, J=6.5 Hz), 1.95-1.86 (m, 4 H), 1.40-1.23 (m, 18 H), 0.90-0.88 (m, 8 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm)= 151.5, 139.1, 132.4, 132.3, 132.2, 128.6, 128.3, 127.2, 126.8, 125.3, 121.1, 118.8, 111.7, 111.0, 94.4, 88.8, 69.8, 32.1, 29.7, 29.6, 29.5, 26.5, 22.9, 14.3.

6b. 2-ethynyl thiophene oxtyloxy oligomer: Purification: Flash Chromatography (1:1 Dichloromethane: Hexanes). Yield: 52 mg (73%). ^{1}H NMR (300 NMR, CDCl$_3$): δ (ppm)= 7.55-7.49 (m, 10 H), 7.32-7.30 (m, 4 H), 7.17-7.12 (m, 4 H), 7.05-7.02 (dd, 2 H, J=4 Hz, J=5 Hz), 4.10-4.05 (t, 4 H, J=6.6 Hz), 1.94-1.85 (m, 4 H), 1.40-1.26 (m, 18 H), 0.93-0.88 (m, 8 H).

7. 2-nitrobenzyl acetate: To a solution of 2-nitrobenzyl alcohol (4.0 mmol, 1 eq) and 4-dimethylaminopyridine (DMAP) (0.8 mmol, 0.2 eq) in dry dichloromethane (10 mL), were added triethylamine (TEA) (4.8 mmol, 1.2 eq). The solution was cooled to 0° C, and acetyl chloride (4.8 mmol, 1.2 eq) was added dropwise. After 24 hours at room temperature, 5% HCl (25 mL) was added and the aqueous layer was extracted with dichloromethane (3x15 mL). The combined organic layers were washed with brine and dried over MgSO$_4$. The crude product was recrystallized in hexanes to yield a pale yellow solid. Yield 0.20 g (27%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm)= 8.14 (d, 1 H, J=1.2 Hz), 7.70-7.61 (m, 2 H), 7.59-7.27 (m, 1 H), 5.53 (s, 2 H), 2.18 (s, 3 H).

8. 4,5-dimethoxy-2-nitrobenzyl acetate: To a solution of 4,5-dimethoxy-2-nitrobenzyl alcohol (2.5 mmol, 1 eq) and 4-dimethylaminopyridine (0.25mmol, 0.1 eq) in dry dichloromethane (25 mL), were added triethylamine (5 mmol, 2 eq) and acetyl chloride (2.75 mmol, 1.1 eq). After stirring for 18 hours at 25° C, 10% HCl was added (20 mL) and was extracted with dichloromethane (3x15mL). The combined organic layers were washed with 5% NaHCO$_3$ and brine, dried over MgSO$_4$. The crude product was recrystallized in ethanol/dichloromethane to yield pure desired product. Yield: 0.57 g (89%). ^{1}H (300 MHz, $CDCl_3$): δ (ppm)= 7.73 (s, 1 H), 7.01 (s, 1 H), 5.51 (s, 2 H), 3.98 (d, 2 H, J=8.7 Hz), 2.18 (s, 3 H).

9.a 5-iodo-2-nitrobenzoic acid: To a flask charged with Boron trifluoride etherate (18.5 mmol, 2.5 eq) cooled to -10° C were added dropwise: 5-amino-2-nitrobenzoic acid (7.4 mmol, 1 eq) dissolved in 20 mL dry THF and *tert*-butyl nitrite (19.2 mmol, 2.6 eq) dissolved in 5 mL dry THF. After the solution was warmed to room temperature and left for 40 min, cold diethyl ether was added (2x15 mL). Solid was collected by vacuum filtration and washed with cold diethyl ether (2x15mL). While solid was drying, KI (19.2 mmol, 2.6 eq)was added to 80 mL acetone to which the diazonium salt was added in small portions. The solution evolved gas bubbles (N_2) and darkened from yellow to dark red. After 18 hours at room temperature, the solvent was removed *in vacuo*. After adding diethyl ether, the organic layer was extracted with $NaHCO_s$ (3x15mL). The combined aqueous layers were acidified with 5% HCl to pH=1. The aqueous layer was extracted with diethyl ether (3x15mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo* to produce a yellow solid., which was recrystallized in 10% HCl. Yield: 1.7746 grams (82%). ^{1}H (300 MHz, Acetone-D6): δ (ppm)= 8.25 (d, 1 H, J=1.8 Hz), 8.21 (dd, 1 H, J=2.1 Hz and J=8.4 Hz), 7.78 (d, 1 H, J=8.4 Hz).

9. 5-iodo-2-nitrobenzyl alcohol: To a mixture of 5-iodo-nitrobenzoic acid (4.44 mmol, 1 eq) in 7 mL dry THF, cooled to 0° C, was added Borane/THF (5.9 mmol, 1.33 eq) dropwise. After the solution refluxed at 75° C for 18 hours saturated NH_4Cl was added to destroy excess borane. The aqueous layer was extracted with diethyl ether (3x15 mL). The combined organic layers were washed with Na_2CO_3 (2x10 mL), and dried over $MgSO_4$. Solvent was removed *in vacuo* to produce yellow solid. Yield: 1.05g (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)= 8.19 (s, 1 H), 7.84 (s, 2 H), 4.99 (s, 2 H), 2.43 (bs, 1 H).

10. General Procedure for the Sonogoshira reaction adding the electron withdrawing substituent to nitrobenzyl alcohol: To a solution of 5-iodo-2-nitrobenzyl alcohol (1.76 mmol, 1 eq) and CuI (0.0176 mmol, 0.01 eq) and $Pd[P(C_6H_5)_3]_4$ (0.106 mmol, 0.06 eq) and the electron withdrawing alkyne (1.76 mmol, 1 eq) cooled to 0° C was added diisopropyl amine (DIPA) (36 mmol, 30 eq) after sparging. After 18 hours NH_4Cl was added and the aqueous layer was extracted with diethyl ether (3x15 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo* to produce a solid product.

10a. 5-(4-ethynyl benzonitrile)-2-nitrobenzyl alcohol: Purification: Flash Chromatography (4:1 Dichloromethane: Hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)= 8.14 (d, 1 H, J=8.5 Hz), 7.98 (t, 1 H), 7.70-7.64 (m, 4 H), 7.62-7.60 (dd, 1 H, J=2 Hz and J=8.5 Hz), 5.05 (d, 2 H, J=6 Hz), 2.60-2.57 (t, 1 H, J=6 Hz).

10b. 5-(2-ethynyl thiophene)-2-nitrobenzyl alcohol: Purification: Flash Chromatography (Gradient from Hexanes to dichloromethane). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)= 8.13 (d, 1 H, J=8.5 Hz), 7.90 (s, 1 H), 7.58-7.56 (dd, 1 H, J=2 Hz and J=8.5 Hz), 7.40-7.37 (m, 2 H), 7.08-7.06 (dd, 1 H, J=4 Hz and J=5 Hz), 5.03 (d, 2 H, J=6.5 Hz), 2.49-2.26 (t, 1 H, J=6.5 Hz).

11. General Procedure for Nitro-Benzyl Acetate (DCC coupling): To a solution of nitrobenzyl alcohol (0.157 mmol, 1 eq) and dimethylaminopyridine (DMAP) (0.0157 mmol, 0.1 eq) in dry dichloromethane (10 mL) was added acetic acid (0.173 mmol, 1.1 eq) dropwise. Dicyclohexylcarbodiimide (DCC) (0.235 mmol, 1.5 eq) was dissolved in dichloromethane (5 mL) and added dropwise to the reaction flask. The mixture was r~~R~~efluxed for 18 hours at 50° C,~~.~~ After the reaction was cooled to room temperature, the solution was washed with 5% HCl, and the aqueous layer was extracted with dichloromethane (3x15 mL) and the combined organic layers were washed with 10%$NaHCO_3$. The aqueous layer was again extracted with dichloromethane (3x15 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*.

11b. 5-(2-ethynyl thiophene)-2-nitrobenzyl acetate: Purification: Flash Chromatography (dichloromethane). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)= 8.12 (d, 1 H, J=8.5 Hz), 7.70 (s, 1 H), 7.59-7.57 (dd, 1 H, J=1.5 Hz and J=8.5 Hz), 7.41-7.38 (m, 2 H), 7.08-7.06 (dd, 1 H, J=3.5 Hz and J=5 Hz), 5.52 (s, 2 H), 2.21 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm)= 170.4, 146.4, 133.5, 133.0, 131.6, 131.3, 129.4, 129.0, 127.6, 125.6, 122.1, 91.35, 88.1, 62.8, 21.0.

III. Results and Discussion

A. π-conjugated oligomers

Figure 10: Excitation and Emission spectra of the three oligomers in dichloromethane.

Figure 10 shows the emission and excitation spectra for all three oligomers that were synthesized and tested. As can be seen, the excitation spectra are all similar while the emission maxima are non-uniform, hence each oligomer shows a characteristic Stokes shift. This indicates that the addition of the electron withdrawing groups affected peak emission wavelengths differently. The oligomer with the highest energy emission was the octyloxy thiophene oligomer. The octyloxy nitrile oligomer had a slightly lower energy emission, while the difluoro methoxy oligomer had the lowest energy emission. It is unclear if the presence of the methoxy or octyloxy groups had tremendous effects on the absorbance and emission because it was difficult to synthesize and isolate both the methoxy and octyloxy oligomers with the same end electron-withdrawing groups. Thus it is unclear if the lower energy emission of the methoxy oligomer is due to the methoxy groups or the difluoro groups. It is likely that the cause is the difluoro end groups, which alter the electron distribution across the oligomer due to the high electronegativity of fluorine. The shapes of the emission peaks are also changed upon the addition of the various electron-withdrawing groups. It is unclear what the exact cause of this is, but is likely due to the variation in electron distribution across the various oligomers.

The more electron withdrawing of the two octyloxy oligomers, the nitrile oligomer, has lower energy emission than the thiophene oligomer. This is likely due to the effects of the thiophene on the aromaticity of the oligomer, as well as increased stabilization of the nitrile oligomer excited state by dichloromethane. In general, solvent effects are low: the Stokes shifts of all three oligomers are all between 60 and 70 nm in dichloromethane. Similar results were obtained in the tetrahydrofuran solvent, as can be seen in Figure 11.

Nitrile	λ_A (nm)	λ_{em} (nm)	ϕ_F
DCM	426	496	0.73 (±0.03)
THF	424	491	0.71 (0.01)
Acetonitrile	419	514	0.77 (±0.05)
Thiophene			
DCM	422	482	0.77 (±0.04)
THF	420	478	0.72 (±0.01)
Acetonitrile	417	481	0.75 (±0.01)
Difluoro			
DCM	418	477	0.79 (±0.02)
THF	418	473	0.77 (±0.02)
Acetonitrile	415	477	0.72 (±0.02)

Figure 11: Peak absorbance and emission wavelengths for all three conjugated oligomers. The third column represents the fluorescence quantum yield (Coumarin 6 standard).

The three oligomers have quite high fluorescence quantum yields. As shown in Figure 11, the quantum yields ranged from 71% to 79% with relatively little error. Again, fluorescence quantum yield measures the ratio of photons emitted to photons absorbed, thus high fluorescence quantum yields of these molecules indicate that they are efficient fluorescent emitters. These molecules tend to lose little energy by non-radiative pathways, for example as heat loss.

The solvents used showed different effects on each oligomer. The thiophene experienced little variation in the Stokes shift in the three solvents. Similarly, the fluorescence quantum yields of the thiophene oligomer in each solvent had a range of less than 10%. The difluoro experienced similar findings: the solvents seemed to have little effect on the quantum yield or Stokes shift. Each solvent stabilizes the ground and excited states of the oligomers differently, however, the narrow range in peak absorbance and emission wavelengths indicates that the solvents had little effect on these oligomers.

Figure 12: Emission spectra for the nitrile oligomer in both Acetonitrile and Tetrahydrofuran (THF).

The solvents did not affect the quantum yield of the nitrile oligomer any more than the other two, there is less than 10% variation in quantum yield in each solvent. However, the variation in solvents did show a solvochromatic shift in emission. Figure 12 shows that the peak emission was found at 491 nm in tetrahydrofuran and 514 nm in acetonitrile. The variation in solvent effects is most likely a result of the stabilization of the excited quinoid-like state by the more polar acetonitrile solvent. When the oligomer absorbs a photon, the electron is promoted into the excited electronic state and some higher vibrational state. Before the electron falls back to its ground electronic state, it must release vibrational energy until it rests in the lowest vibrational state of the excited electronic state, according to the Frank-Condon principle.[4] The solvochromatic shift implies that the lowest vibrational state of the excited electronic state has an overall lower energy in acetonitrile then in the other solvents. This is likely because the excited state is highly charge separated and is easily stabilized by acetonitrile. Nitrile groups are electron withdrawing in resonance forms because of the ability of the nitrogen to carry a charge and the presence of the triple bond.

Why this occurs in the nitrile oligomer as opposed to the thiophene or difluoro oligomers is not easily explained. As was mentioned earlier, thiophene molecules tend to be less aromatic than benzene. The loss of aromaticity could serve to reduce the charge separation of the excited state, thus reducing the effects of the solvent on stabilizing it. Similarly, in conjugated systems halides can act as electron donating groups because they have extra lone pairs of electrons. This could also reduce the charge separation of the excited state of the difluoro oligomer. Of the three electron withdrawing groups studied, only the nitrile group is electron withdrawing by resonance. The fluorine atoms are only electron withdrawing by induction and the thiophene by its lower aromaticity. This likely affects which oligomers are perceptible to changes in photophysical behavior in different solvents.

B. o-Nitrobenzyl Esters

	Rate of reaction (nmol/min)	λ_A (nm)	ε
Acetate	85.28 (±30.24)	262	11,154
Thiophene	30.5 (±6.16)	356	35,348

Figure 13: The rates of photouncaging and the peak absorbance wavelengths. The third column is the extinction coefficient.

The rates of reaction were monitored by NMR spectroscopy in the method described above. The rate of deprotection of the 2-nitrobenzyl acetate proceeded at 85.28 nmol/min while the thiophene acetate reacted at a rate of 30.5 nmol/min, as can be seen in Figure 13. The addition of the thiophene alkyne in the meta position of the nitrobenzyl acetate caused the reaction rate to decrease by 64%. This makes sense because electron-withdrawing groups tend to deactivate benzene rings and slow down their reactivity.[14] This effect most likely extends from the thiophene ring to the nitro group of the primary benzene, thus slowing down the uncaging reaction.

Figure 14: Graph of the peak absorbance of 2-nitrobenzyl acetate and 5-(2-ethynyl thiophene)-2-nitrobenzyl acetate.

As can be seen in Figures 13 and 14, the thiophene acetate absorbance peak is found at 356 nm and the 2-nitrobenzyl acetate absorbance peak is at 262 nm. This indicates a large red-shifting of the peak absorbance relative to the standard acetate. The bathochromatic shift observed shows that the addition of the thiophene alkyne in the meta position of the nitrobenzyl acetate did shift the peak absorbance by about 100 nm in the desired direction.

The extinction coefficients were calculated using the absorbances and concentrations of those in Figure 14. The concentrations of the two substances were not equal, however that was corrected in the calculation of the molar extinction coeffiencts, ε. The molar extinction coeffiencts for 2-nitrobenzyl acetate and the thiophene acetate are 11,154 $M^{-1}cm^{-1}$ and 35,348 $M^{-1}cm^{-1}$, respectively. The Beer-Lambert law states that absorption is directly proportional to concentration and path length: $A=\varepsilon cl$. The extinction coefficient measures the strength of absorption at a given wavelength.[5] In this case, the absorption of the thiophene acetate is much larger than the absorption of 2-nitrobenzyl acetate. Because both of these extinction coefficients were calculated at the molecules' respective peak absorbances, this is the maximum strength of absorption for each molecule. The calculated values show that the thiophene acetate absorbs more of the light at its peak absorbance than the standard.

Another interesting observation that was made during the synthetic process of these molecules is the presence of a perfectly split alcoholic proton in the NMR spectra of both 5-(4-

ethynyl benzonitrile)-2-nitrobenzyl alcohol and 5-(2-ethynyl thiophene)-2-nitrobenzyl alcohol (see Appendix 1). Normally, alcoholic protons show broad peaks anywhere from 1-5.5 ppm.[14] In both of the substituted nitrobenzyl alcohols, the alcoholic protons were perfectly split to the two benzylic protons on the alpha carbon. This suggests that these molecules have interesting structures and properties. The addition of the benzonitrile and thiophene substituents affects these molecules in interesting ways.

IV. Conclusions

We evaluated the effects of electron withdrawing groups on the photophysical behavior of highly conjugated systems. In the first study, the oligomers synthesized were shown to be efficient fluorescence emitters by their high fluorescence quantum yields. Only the nitrile oligomer experienced any strong solvent-effects when tested in acetonitrile. The oligomer experienced a solvochromatic shift of its peak absorbance by about 25 nm. This is most likely caused by the resonance electron-withdrawing effects of nitrile group, which are not present in the other two oligomers.

In the second project, we evaluated the *o*-nitrobenzyl ester construct for photolabile caged compounds using electron withdrawing adducts to red-shift the absorption using one-photon excitation. The NBE synthesized (5-(2-ethynyl thiophene)-2-nitrobenzyl acetate) showed a red-shift absorbance compared to the 2-nitrobenzyl acetate standard. The rate of photolysis of 5-(2-ethynyl thiophene)-2-nitrobenzyl acetate was considerably slower than that of 2-nitrobenzyl acetate, however the reaction did proceed. The addition of the electron withdrawing did not prevent the photouncaging of the protecting group.

In both instances, the goals of the projects were met. The goal to determine the photophysical characteristics of the electron withdrawing oligomers was achieved despite the setbacks experienced in the synthetic attempts. Similarly, the designed NBE derivative was found to be reactive under standard conditions and had a red-shifted absorbance. Despite the relative success of this research, both projects have ample opportunity for further study.

Future work:

Because of the broad range of applications of the molecules studied, both projects are precursors for future research. For example, further study should be conducted to see the effects of electron withdrawing groups on the photophysical characteristics of polymers with similar PAV-PAE structure. PAV-PAE polymers have been studied before[9], but combing the effects of thiophene polymers and these highly conjugated π-conjugated polymers likely will have interested effects on their photophysical characteristics. Similarly, further studies should be done to add other electron withdrawing groups. The high fluorescence quantum yields were maintained with the addition of all three groups in this study and it would be interesting to see if the trend continues with the addition of similar groups.

The photoquenching of PAV-PAE oligomers has been studied by graduate student, Robert Pawle in the Thomas lab. The oligomers synthesized here seem to be good precursors for similar quenching studies. Further testing of these oligomers would indicate their applicability in many industries, for instance in organic light emitting diodes.

During the nitrobenzyl ester portion of this project, we experienced relatively greater synthetic barriers. Of a total of eight hypothesized molecules, only one was successfully produced. Near the end of the time, several breakthroughs were experienced that have the potential to overcome some of the synthetic problems that occurred, especially for the synthesis of the benzonitrile NBE adduct. It would be interesting to see if a more electron-withdrawing group would have similar effects of the photouncaging characteristics of these molecules. In addition, other studies have used other ester linkages in order to test a wider range of applicability of these molecules.[11] Synthesis of a range of ester molecules would likely increase the knowledge and applicability of these molecules.

Due to several of the drawbacks of the experimental procedure discussed previously, it would be interesting to repeat the photouncaging procedure using other light sources, for example lasers. More precise actinometrical measurements can be done to determine the exact photon flux of the light source and from there the efficiency and rate of reaction can be determined more accurately. Also, this project did not test the photouncaging using two-photon excitation, but studies have shown some success with that type of reaction.[12] Testing the effectiveness of two-photon excitation would give a wider range of applications for these molecules in future studies.

Another drawback that was not solved in this study was the use of one study in the testing of the NBEs. Acetontrile did not work because of the problems mentioned before, however, no other solvents were tested. It would have been interesting to see if solvents affected the rate of reaction or the absorbance of the new NBE derivatives.

Both of these projects were only carried out in solid-state analysis. Especially in the case of the oligomers, solid-state analysis could show starkly different results from the ones described here. Further research needs to be conducted in order to know these effects.

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V. References

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