

***Photo-chemically induced dissolution of charged poly(thiophene)
multilayer films***

A Thesis

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by

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I. Introduction

Over the past thirty years, electrically conducting organic polymers and small molecules have emerged as promising materials in popular technologies including, but not limited to, sensors, displays, microelectronics, and photovoltaic devices.^{[1],[2]} This class of compounds has most notably gained attention as revolutionary components in the development and production of the next generation of electronic devices.^[3] Substantial interest in organic semi-conductors over the decades has coalesced into the thriving field of research known as organic electronics.^{[4],[5]} Organic semi-conductors have become a highly valued component in emerging large-area, low-cost electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic (OPV) devices.^[6]

Conjugated polymers (CPs, Figure 1) are of specific interest when designing modern organic, electrically conducting materials because they combine the appealing opto-electronic properties of inorganic semiconductors,

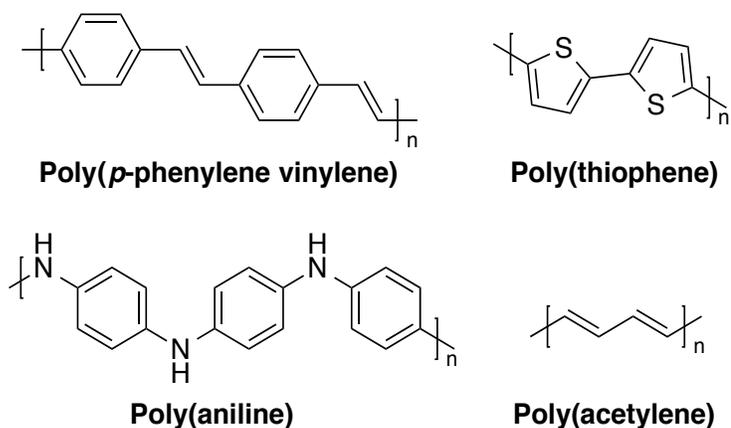


Figure 1. Several examples of conjugated polymers. The delocalized pi system resulting from the sp^2 nature of each carbon in the backbone promotes electron mobility.

such as charge carrier mobility and conductivity, with the synthetic variety and versatility enabled by organic chemistry.^[7] Currently, the performance of CPs in commercial applications does not match that of more traditional inorganic semiconductors. For example, silicon at room temperature has an electron mobility around $1400 \text{ cm}^2/(\text{V}\cdot\text{s})$,^[8] while organic semiconductors have achieved limited mobilities ranging from $5\text{--}10 \text{ cm}^2/(\text{V}\cdot\text{s})$.^[9] A material's conductivity (an extremely important quality when designing electronics) is proportional to the product of mobility and carrier concentration. Despite the relatively low conductivities of CPs, investigation into organic semi-conductors has exposed several distinct advantages that set them apart from their inorganic counterparts: CPs offer the potential for inexpensive solution-based processing over large areas,^[10] require simpler equipment for processing, and are in general less expensive. While CP-based materials are not imagined to replace traditional inorganic materials, they have been envisioned to be the introduction of low-cost, large-area electronics such as solar panels and displays.^[11]

The design of improved semi-conductor materials is critical to the improvement of organic electronics and electronics as a whole.^[6] Advances specific to the field of organic electronics in the last decade have concerned the investigation of novel materials, device design, film deposition procedures, and device performance and stability.^[12] Our laboratory focuses on exploiting modern understanding of physical organic chemistry in order to rationally design and understand the properties of new organic materials with photo-responsive

characteristics. The aim of the research described in this thesis was to synthesize photo-responsive thiophene-based CPs for integration into poly(electrolyte) multilayer films using layer-by-layer self assembly. Synthesis of the photo-responsive CP involved the incorporation of the *o*-nitrobenzyl photo-labile moiety into the polymer side chain. The side chain was further additionally modified by alkylation with a quaternary amine to ultimately yield a photo-responsive poly(cation). The charged polymers (Figure 2) could then be assembled into thin films using layer-by-layer (LbL) self-assembly, a deposition technique that takes advantage of non-covalent interactions such as ion-ion interactions or hydrogen bonding to build multilayer films.^[31]

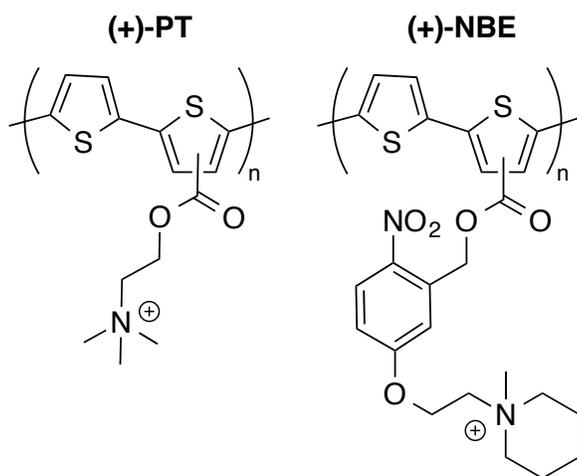


Figure 2. Two poly(cation)s were synthesized for incorporation into PEM films: 1) the photo-inert poly(cation) (+)-PT (left) was used in control experiments, 2) the poly(cation) with the photo-reactive *o*-nitrobenzyl moiety (+)-NBE (right) was designed to produce PEM CP films with photo-responsive behavior.

Integrating a photo-cleavable group into the polymeric structure allows for light to be used to disrupt intermolecular electrostatic interactions, enabling control over the film's solubility. The fabrication of photo-responsive poly(thiophene)-based films is sought after in hopes of creating an economical

organic semiconductor that is capable of acting as a positive photoresist (Figure 3) and is thus patternable using photochemical processing such as photolithography.

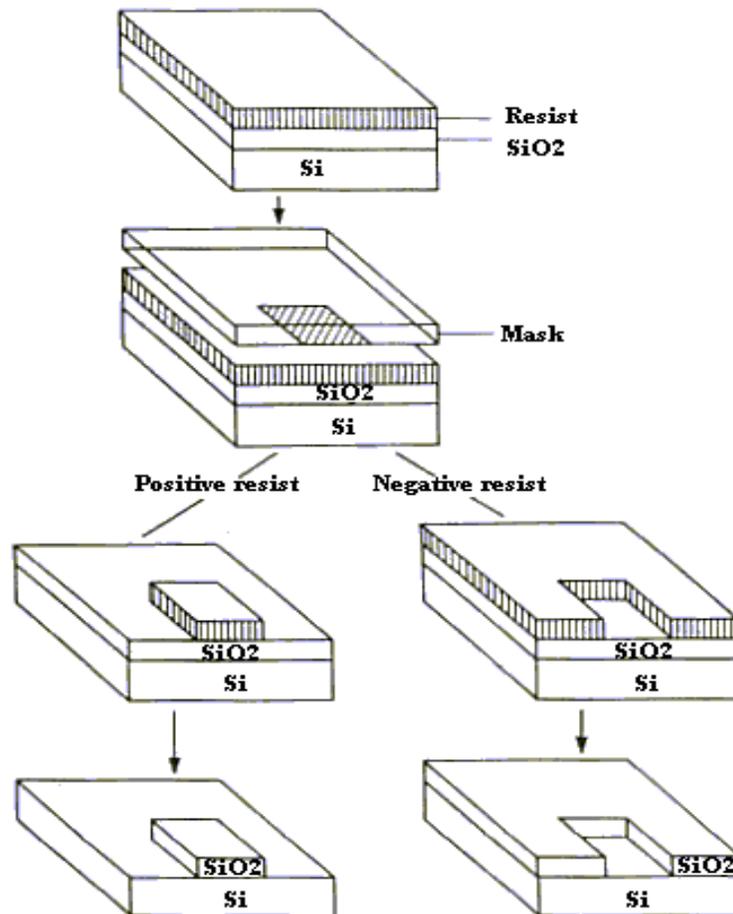


Figure 3. An illustration^[25] of how a photoresist works to enable photochemical patterning of traditional semiconductor materials (SiO₂) using photochemical techniques such as photolithography. Photoresists can act in one of two ways: a negative photoresist becomes soluble and can be washed after irradiation, while a positive photoresist becomes insoluble after irradiation. Chemical etching is then used to pattern the exposed material (silicon in this illustration). The creation of a photo-patternable conjugated polymer system circumvents the need of an additional material to act as a photoresist during processing.

II. Background

The synthesis and design of PT-based photo-responsive PEM films exploits well-understood techniques and methods with precedence in the literature.^{[18],[24]} These include the use of stimuli-responsive materials and the incorporation of photo-labile moieties, organic synthesis and polymer synthesis, and the assembly of charged poly(electrolyte)s into thin films using layer-by-layer self-assembly.

A. Stimuli-responsive materials

Stimuli-responsive materials are materials that exhibit reversible or irreversible changes in their chemical structure and physical properties in response to changes in their external environment. The stimulus that induces a change in the material (Figure 4) can range from pH, temperature, ionic strength, light irradiation, and mechanical forces to electric, magnetic, and acoustic fields.^[13] The most attractive feature of stimuli-responsive materials is the exquisite control gained over physical properties such as solubility.^[13] The “response” of a stimuli-responsive small molecule or polymer can be defined in a several ways. Responsive polymers are typically classified as those that change their solubility, individual chain dimensions, or the degree of intermolecular associations upon interaction of the external stimulus.^[14] Control over solubility and conformation is imperative to the patterning and construction of smart

organic devices, and a large amount of work has already been dedicated to engineering new materials that are stimuli-responsive.^[14]

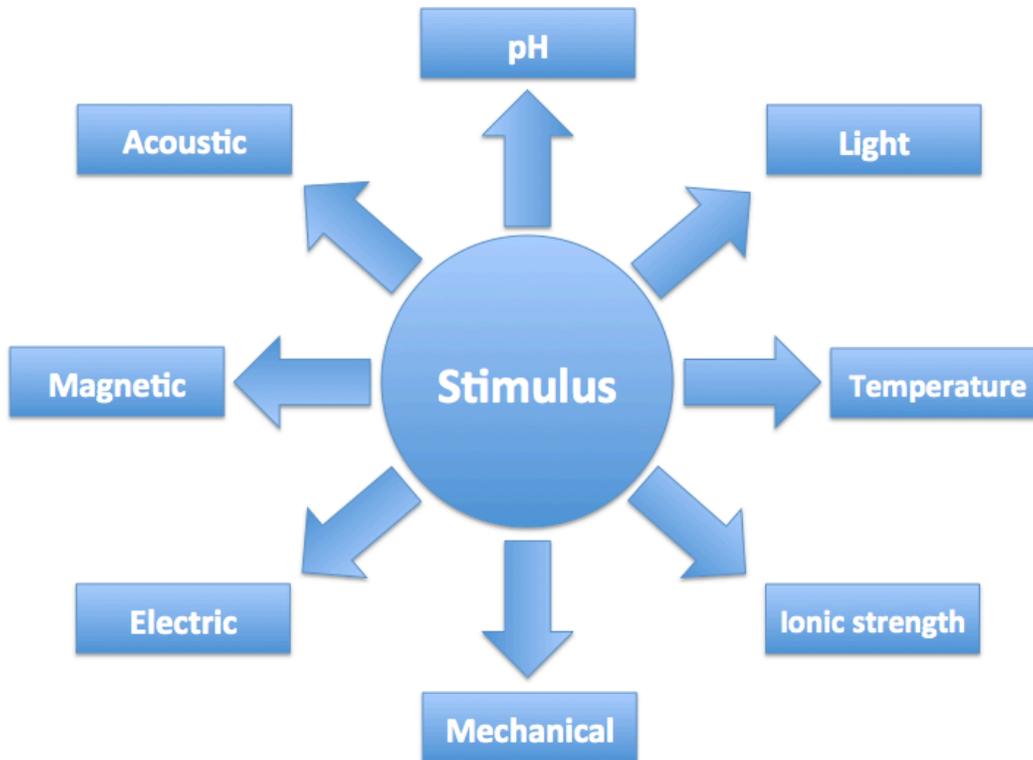


Figure 4. The stimuli that induce a change in stimuli-responsive materials can range from pH, temperature, ionic strength, light and mechanical forces to electric, magnetic, and acoustic fields.^[13]

Light is an exceptional stimulus for use in stimuli-responsive materials because it offers distinct advantages over other available stimuli. These include spatiotemporal control (control over where and when light irradiates the material), stoichiometry (through combination of power and time of irradiation), and energy (through control over wavelength of light).^[7] Additionally, light is capable of penetrating certain solid-state materials, such as quartz and other optically transparent solids, simplifying the delivery of the stimulus in comparison to other

stimuli like pH.^[7] Light-responsive, or photo-responsive, polymers have gained considerable attention in the field of organic electronics because of their potential application in common photochemical processing techniques that are critical steps in the fabrication of microprocessors in electronic devices such as photolithography.^[7] The incorporation of a structural unit that is susceptible to cleavage upon irradiation with light, also known as a photo-labile moiety, is required in the synthesis of a photo-responsive conjugated polymer.

There are a number of well-studied photo-labile moieties to choose from when designing a photo-responsive polymer.^{[15],[16]} Among them, the *ortho*-nitrobenzyl (ONB) group offers several advantages: it is easily prepared and modified, it is applicable to a variety of “caged” functional groups including amines, carboxylic acids, and alcohols, and it retains its photochemical reactivity

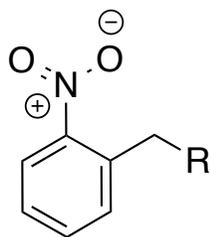
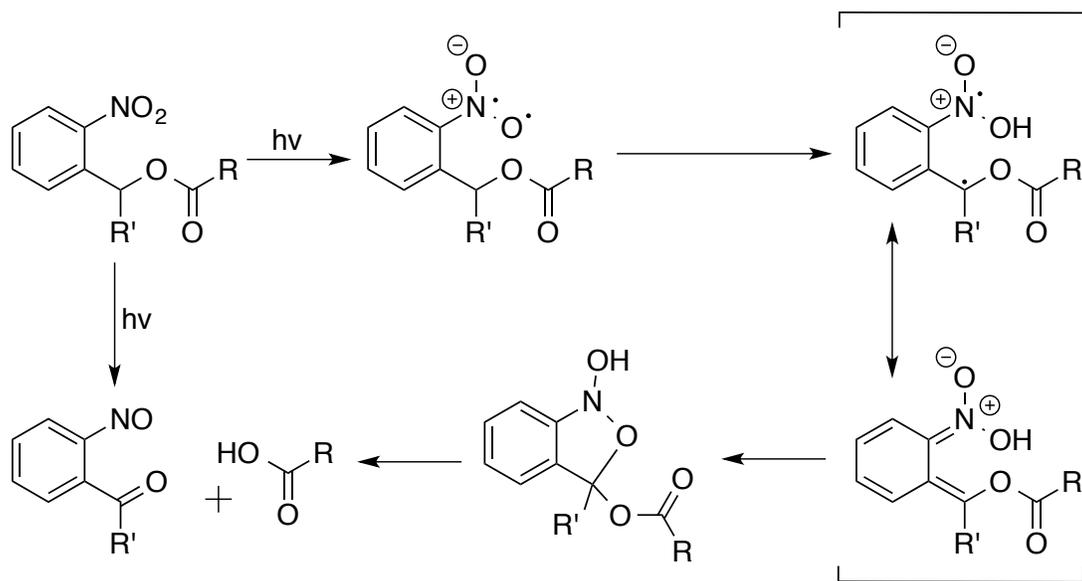


Figure 5. The *ortho*-nitrobenzyl (ONB) group, a common photo-labile moiety, was incorporated into polymer (+)-NBE.

in many solvents and in the solid state.^{[7],[17]} The ONB group (Figure 5) has already found its place in an array of disciplines, ranging from biochemistry to materials science, because integration of the ONB group results in a new approach to thin film photo-patterning with applications in protein patterning, microfluidics, and organic electronics.^[7]



Scheme 1. Photo-isomerization of *o*-nitrobenzyl derivatives into *o*-nitrosobenzaldehyde, releasing a free carboxylic acid.^[17]

The mechanism that allows for photo-cleavage of the ONB moiety is a photo-induced rearrangement^[17] of an *o*-nitrobenzyl alcohol derivative into an *o*-nitrosobenzaldehyde and free carboxylic acid upon irradiation with UV light (Scheme 1). Coughlin *et al.* found that linkers and protecting groups based on ONB chemistry can exhibit cleavage in minutes when exposed to 365 nm light with high intensity. Times varied from several hours with a low power density of 1.3 mW/cm² using a 365 nm source to 5 minutes or less when applying greater light intensities of 20 to 40 mW/cm².^[17] Photo-cleavage efficiency improves when wavelengths near 300 nm are used because the ONB moiety exhibits an absorption maximum near this wavelength.^[17]

o-Nitrobenzyl esters (NBEs) undergo photolysis when subjected to irradiation with ultraviolet (UV) light.^[18] Exciting the organic chromophore leads

to the formation of a highly reactive di-radical species (Scheme 1). Hydrogen abstraction in the γ -position is particularly common among all of the plausible reaction pathways, and was recognized early on by Ronald G.W. Norrish. This type of photo-isomerization for carbonyl compounds is now commonly described as a Norrish-type II reaction.^[15] In the Norrish-type II reaction, nitrobenzyl carbamates, carbonates, and esters are converted into an acetal derivative that readily collapses into an aldehyde or ketone and the liberated fragment (i.e. carboxylic acid). In the case of the ester, this spontaneous collapse leads to the formation of a carboxylic acid and *o*-nitrosobenzaldehyde.^{[7],[15]}

B. Thiophene and poly(thiophene)

An assortment of conjugated polymers and small molecules can be used to build organic electrically conducting devices. Thiophene is an aromatic sulfur heterocycle among this class that is chemically stable and especially easy to process.^[12] The use of thiophene in commercial applications has already been investigated extensively over the years. Its investigation has spread from early dye chemistry^[19] to modern drug design^[20] and conductivity-based sensory devices,^{[21],[22]} as well as electronic and optoelectronic devices.^[23] More recently, scientists and engineers are heavily investigating thiophene oligomers and polymers because of their luminescence and opto-electronic properties.^[12] Thiophene is a suitable candidate for the fabrication of novel materials with interesting opto-electronic properties because thiophene chemistry is remarkably adaptable, allowing for a wide variety of thiophene-based chemical structures and

the fine-tuning of physical properties. The heterocycle can be functionalized in positions α and β to sulfur or on the sulfur atom itself.^[12] The continuous creation of new thiophene-based compounds in a variety of disciplines is driven by this ability to fine-tune its desirable properties and improve insight to their structure-property relationships.^[12]

Poly(thiophene)s (PTs; Figure 1), are among the most popular of conjugated polymers being investigated in the field of organic electronics. The conductivity and stability of PT derivatives has stimulated considerable interest in the use of PT as an active electronic element in a myriad of thin film devices and sensors.^[24] PTs demonstrate exceptional photo-oxidative stability and show relatively red-shifted absorbance when compared to other classes of conjugated materials used in organic opto-electronic devices.^[10] Resistance to photo-oxidation is important when developing a photo-patternable conjugated material because photo-oxidation will decrease conjugation length and have a negative effect on the material's conductivity. PT's overall stability makes it a preferable candidate for the fabrication of photo-patternable opto-electronic CP devices. The major drawback of PT is that un-substituted poly(thiophene) is intrinsically insoluble.^[26] Substitution using organic synthesis can impart solubility, but may perturb the delocalized pi system of the polymer backbone, potentially decreasing the conductivity of the material. Since its discovery, a great deal of work has focused on synthesizing substituted poly(thiophene)s that are amenable to solution-based processing and able to retain relatively high conductivities.

C. Layer-by-layer (LbL) self-assembly

The synthesis of *charged* poly(thiophene)s yields polymers suitable for layer-by-layer (LbL) self-assembly. LbL self-assembly is a film deposition technique that builds thin multilayer films one layer at a time through the sequential adsorption of oppositely charged materials in solution onto a substrate (Figure 6). Non-covalent, electrostatically favorable charge-charge interactions between sequentially-deposited oppositely-charged poly(electrolyte)s drive the formation of poly(electrolyte) multilayer (PEM) films. An enthalpic gain due to ion-ion interactions and additional entropic factors such as the release of solvent (i.e. H₂O) and counter-ions contribute to the spontaneous assembly of the polymers.^[30] An LbL approach to the assembly of PEM films offers several advantages including the ability to coat irregularly shaped surfaces, nanoscale control over film thickness and control over surface chemistry, and easy solution-based processing.^[18] LbL self-assembly has already been applied in innovative technologies such as antibacterial surfaces, sensors, and drug encapsulation.^[18]

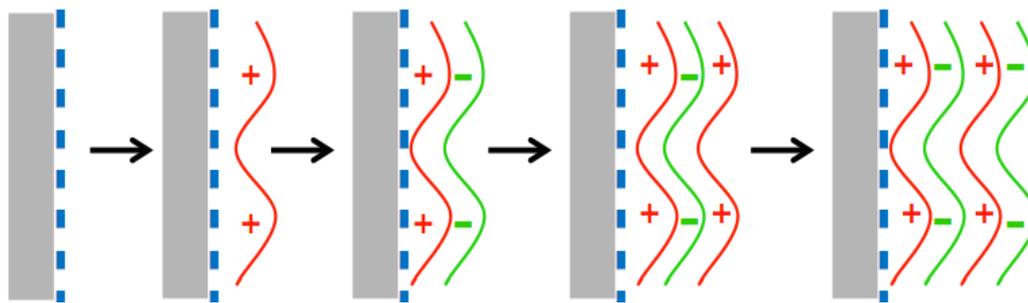


Figure 6. Electrostatic interactions between poly(cation)s and poly(anion)s leads to self-assembly of polymer films.

The incorporation of a photo-labile moiety into the poly(electrolyte) side chain of one of the poly(electrolyte)s produces a photo-responsive PEM film. It was hypothesized that light could be used to cause dissolution of the film by affecting the charge-charge interactions holding the film together. Photochemically inducing a switch in charge in one of the poly(electrolyte) side chains will cause disruption of attractive ion-ion interactions through introducing repulsive interactions, triggering dissolution of the film in the irradiated area. Thus, the incorporation of a photo-labile moiety gives control over solubility of the film. Hydrolysis, pH, and temperature are external stimuli that have been demonstrated to be effective in triggering the disassembly of LbL films^[18] but, as discussed above, light has found obvious utility in surface patterning and offers real-time control over distribution, stoichiometry, and energy and is thus the preferred external stimulus to promote CP dissolution in this design.^{[7],[18]}

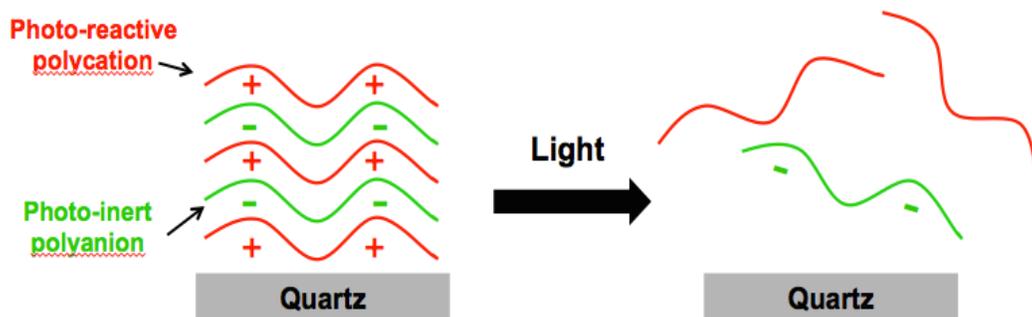
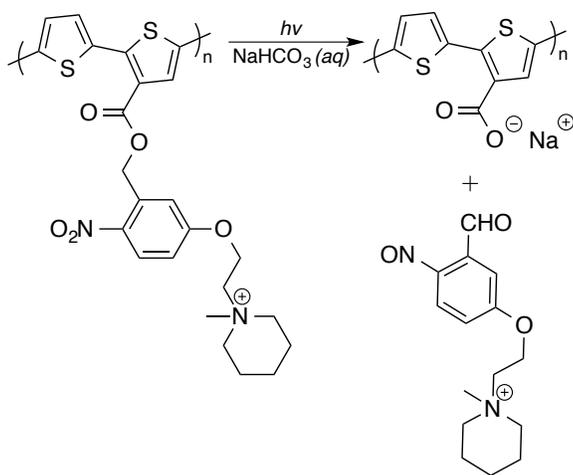


Figure 7. Cleavage of a photo-cleavable moiety on the poly(cation) followed by deprotonation reverses the charge and causes dissolution of the film.

Our design was based on well-understood technologies that have been successfully applied in similar polymer systems. The formation of photo-inert PEM films using charged PTs was described by McCullough *et al.*^[24] The incorporation of the ONB moiety into PEM films of non-conjugated polymers was previously demonstrated in our laboratory.^[18] Our design combines both techniques by linking the ONB moiety to thiophene and functionalizing the ONB side chain to give a monomer a formal positive charge. Polymerization of this compound yields a photo-responsive poly(cation) suitable for LbL self-assembly with any commercially available poly(anion). Upon irradiating the assembled film with UV light, the covalent linkage between the ONB moiety and the polymer backbone is broken, yielding a polymer with a carboxylic acid on each repeat unit. Once the sample is exposed to mild aqueous base such as aqueous sodium bicarbonate (NaHCO₃), the anionic carboxylate is generated (Scheme 2). Hence, photo-cleavage of the side chains on the polymer and subsequent deprotonation switches the formal charge of the poly(electrolyte) from positive to negative, causing repulsive electrostatic interactions that lead to dissolution of the film.



Scheme 2. Irradiation of the poly(cation) assembled in PEM films causes a reversal of formal charge. This produces repulsive electrostatic interactions between the poly(cation) and poly(anion), leading to film dissolution.

III. Experimentation and Methods

General Considerations: All chemicals were purchased and used as received from commercial sources. Dry solvent was obtained from Innovative Technologies PureSolv 400 solvent purifier. Silica gel (230-400 mesh) was used as the stationary phase for flash chromatography.

NMR spectra were obtained on a Bruker DPX-300 or Bruker Avance III 500 spectrometer. Chemical shifts are reported relative to the solvent used (7.26 ppm for CHCl₃, 2.54 ppm for DMSO). ¹H NMR spectra of the synthesized monomers and polymers can be viewed in Supporting Information.

A. Materials and synthetic methods

Poly(sodium 4-styrenesulfonate) (**PSS**; MW = 70 000 g/mol) was purchased from Sigma Aldrich and used as received. Quartz slides were purchased from Advalue Technology. All other materials were synthesized in the laboratory using standard inert atmosphere synthetic techniques with magnetic stirring.

Synthesis of the photo-inert PT poly(cation) for control experiments was performed under the following conditions:

2,5-dibromothiophene-3-carboxylic acid (1): A 250-mL 3-neck round bottom flask with a magnetic stir bar was charged with 3-thiophene carboxylic acid (1.00 g, 7.80 mmol) and *N*-bromosuccinimide (3.06 g, 17.2 mmol). The flask was

evacuated and refilled with argon three times. Under argon flow, 15 mL of dry dimethylformamide (DMF) were added. The mixture was left to stir overnight at 50 °C. The reaction mixture was then poured into approximately 500 mL of brine where an off-white solid precipitated. The solid was collected by removing solvent using vacuum filtration, which gave a pure product as an off-white solid (1.708 g, 76.6%). ¹H NMR (CDCl₃, 500 MHz): δ 7.40 (s, 1H).

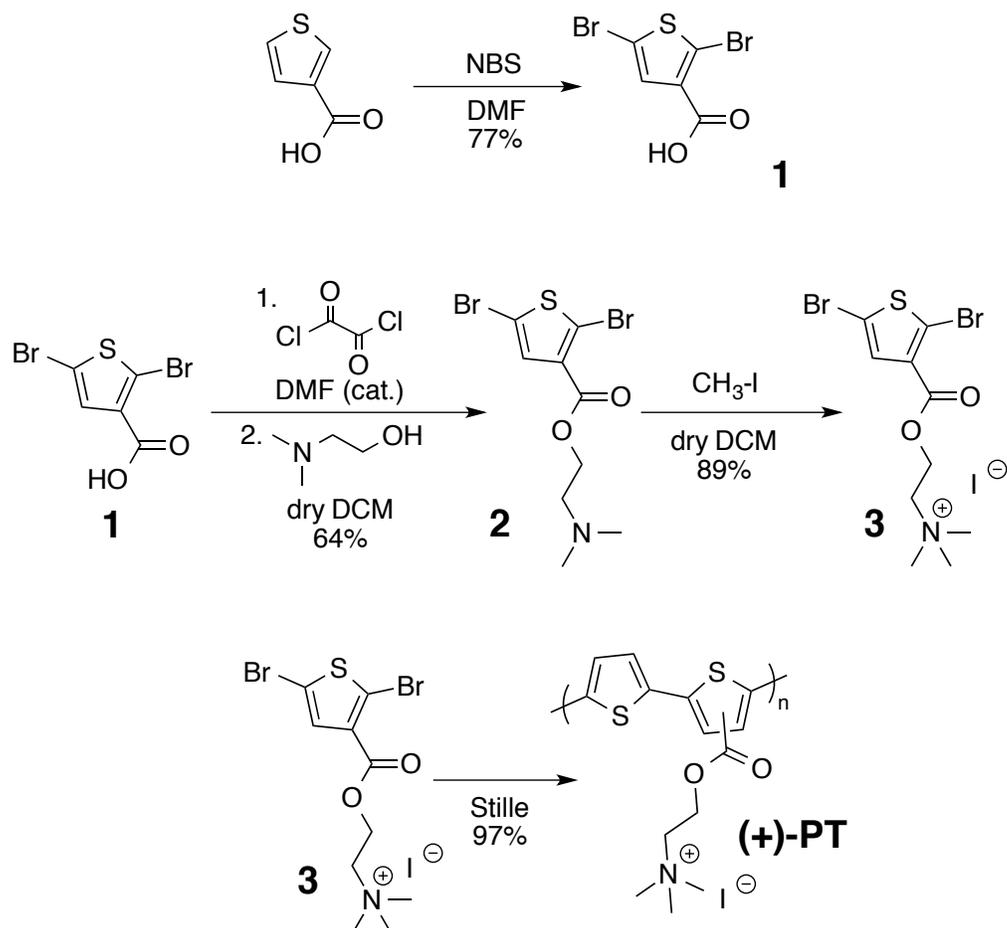
2-(dimethylamino)ethyl-2,5-dibromothiophene-3-carboxylate (2): A round bottom flask with a magnetic stir bar was charged with **1** (1.50 g, 5.27 mmol). The flask was evacuated and refilled with argon three times. Under argon flow, 50 mL of dry dichloromethane (DCM) were added at room temperature, along with approximately 50 drops of anhydrous DMF. The reaction vessel was then placed into a water-ice bath and cooled to 0 °C. Oxalyl chloride (0.5 mL, 5.8 mmol) was added drop-wise to the reaction mixture via syringe. The reaction was left to run for three hours and allowed to warm to room temperature. The formation of the acid chloride was monitored using thin-layer chromatography (solvent: DCM). After three hours, 1-(2-dimethylamino)ethanol (1.58 mL, 15.8 mmol) was added to the reaction mixture and left to run overnight. Upon completion, the reaction mixture was washed twice with 5% NaOH(aq) (100 mL), once with deionized water (H₂O, 100 mL), and once with brine (100 mL), then dried over magnesium sulfate. Solvent was removed *in vacuo* to yield the crude product. The product was purified using flash chromatography (solvent: ethyl acetate, EtOAc), giving a pure product as an off-white crystalline solid (1.20 g, 63.6%). ¹H NMR (CDCl₃,

500 MHz): δ 7.35 (s, 1H), 4.38 (t, 2H, 6 Hz), 2.70 (s, 2H), 2.33 (s, 6H).

2-(trimethylamino)ethyl-2,5-dibromothiophene-3-carboxylate (3): A 100-mL 2-neck round bottom flask with a magnetic stir bar was evacuated and refilled with argon three times. Under argon flow, a solution of **2** (0.897 g, 2.51 mmol) dissolved in 25 mL of anhydrous DCM and methyl iodide (6.25 mL, 100. mmol) were added. The reaction was left to run overnight. Upon completion, solvent and excess CH₃I were removed *in vacuo* to yield **3** as a pale yellow solid (1.12 g, 89.1%). ¹H NMR (DMSO, 500 MHz): δ 7.61 (s, 1H), 4.70 (s, 2H), 3.80 (t, 2H, 4 Hz), 3.20 (s, 9H).

Stille polymerization: Polymer (+)-PT: A 100-mL 2-neck round bottom flask with a magnetic stir bar was charged with **4** (0.150 g, 0.474 mmol), tri(*o*-tolyl)phosphine (72 mg, 0.48 mmol), 2,5-bis(trimethylstannyl)thiophene (194 mg, 0.48 mmol), and tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] (22 mg, 0.024 mmol). The flask was evacuated and refilled with argon three times followed by addition of 25 mL deoxygenated anhydrous DMF. The reaction mixture was left to run at 95 °C for 72 hours. Upon completion, the reaction mixture was added drop-wise to hexanes to precipitate and purify the polymer. After centrifugation, the supernatant was carefully removed and the polymer was collected as a dark metallic red solid (0.136 g, 97%). ¹H NMR spectrum can be observed in Supporting Information (Figure S2).

Scheme 3. Synthesis of photo-inert control polymer (+)-PT



"Stille": Pd catalyst, 2,5-bis(trimethylstannyl)thiophene, tri-(*o*-tolyl)phosphine

Synthesis of the photo-reactive poly(thiophene) poly(cation) for use in photo-responsive PEM films was performed under the following conditions:

5-(2-piperidine-1-ethoxy)-2-nitrobenzaldehyde (5): A flamed-dried 3-neck 500-mL round bottom flask was charged with 5-hydroxy-2-nitrobenzaldehyde (5.00 g, 30 mmol), 1-(2-chloroethyl)-piperidine hydrochloride (8.28 g, 45 mmol), and K₂CO₃ (12.5 g, 90 mmol). The flask was evacuated and refilled with argon three times. Under argon flow, anhydrous DMF was added, and the resulting mixture was heated at 45 °C and stirred for 48 hours. The mixture was poured into 1 M NaOH (5 mL), extracted with Et₂O (3 x 20 mL), washed with sat. NaHCO₃(aq) (10 mL), H₂O (10 mL), and brine (10 mL), and dried over magnesium sulfate to afford the pure product as a yellow oil (4.05 g, 48.6%). ¹H NMR (CDCl₃, 300 MHz): δ 10.45 (s, 1H), 8.13 (d, 1H, 9 Hz), 7.31 (d, 1H, 3 Hz), 7.14 (dd, 1H, 3 Hz, 9 Hz), 4.21 (t, 2H, 6 Hz), 2.78 (t, 2H, 6 Hz), 2.48 (t, 4H, 4.8 Hz), 1.58 (q, 4H, 5.4 Hz), 1.45 (multiplet, 2H).

2-nitro-5-(2-piperidin-1-ylethoxy)benzyl alcohol (6): A 50-mL 2-neck round bottom flask with a magnetic stir bar was evacuated and refilled with argon three times, then placed into an ice-water bath. Under argon flow, **5** (0.22 g, 0.80 mmol) dissolved in 10 mL methanol was added at 0°C. Sodium borohydride (45 mg, 1.2 mmol) was added and the ice-water bath was removed. The reaction was stirred at room temperature overnight. Upon completion, the reaction mixture was concentrated *in vacuo*. The yellow oil was then re-dissolved in ethyl acetate, washed with DI H₂O and brine, and dried over MgSO₄. Solvent was removed *in*

vacuo to afford **6** (0.156 g, 70%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃): δ 8.13 (1H, d, J = 9 Hz), 7.24 (d, 1H, J = 3 Hz), 6.88 (dd, 1H, J = 3 Hz, 9 Hz), 4.98 (s, 2H), 4.40 (s, br -OH, 1H), 4.21 (t, 2H, 6 Hz), 2.80 (t, 2H, 6 Hz), 2.50 (t, 4H, 4.8 Hz), 1.60 (q, 4H, 5.4 Hz), 1.46 (multiplet, 2H).

2-nitro-5-(2-piperidin-1-ylethoxy)benzyl-2,5-dibromothiophene-3-

carboxylate (7): A round bottom flask with a magnetic stir bar was charged with **6** (0.156 g, 0.55 mmol), **1** (0.141 g, 0.5 mmol), and dimethylaminopyridine (DMAP; 6 mg, 0.05 mmol). The flask was evacuated and refilled with argon three times. Under argon flow, *N,N'*-dicyclohexylcarbodiimide (DCC; 0.114 g, 0.55 mmol) dissolved in 15 mL of anhydrous DCM was added. The reaction was left to reflux at 40 °C overnight. The reaction mixture was washed with saturated NaHCO₃, DI water, and brine. Drying over magnesium sulfate and removal of solvent *in vacuo* gave the crude product as a yellow solid. Flash chromatography on silica using 5% MeOH:DCM as eluent followed by syringe filtration to remove insoluble DCU by-product gave the product **7** (0.719 g, 65%) as a yellow solid. ¹H NMR (CDCl₃, 500 MHz): δ 8.21 (d, 1H, J = 9 Hz), 7.41 (s, 1H), 7.13 (d, 1H, J = 3 Hz), 6.925 (dd, 1H, J = 3 Hz, 9 Hz), 5.75 (s, 2H), 4.18 (t, 2H, J = 6 Hz), 2.78 (t, 2H, J = 6 Hz), 2.49 (s, 4H), 1.60, (q, 4H, J = 5.4 Hz), 1.45 (multiplet, 2H).

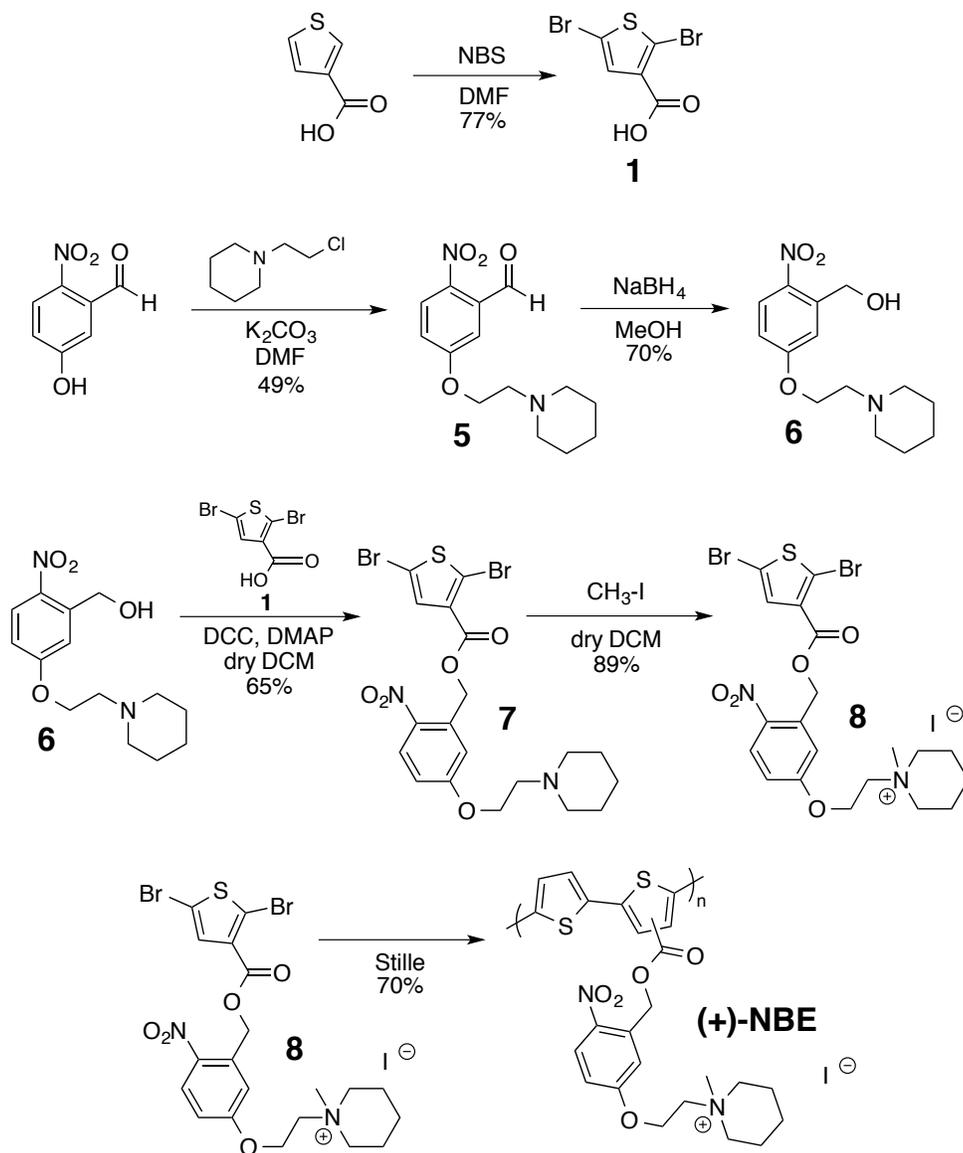
2-nitro-5-(2-piperidin-1-methylethoxy)benzyl-2,5-dibromothiophene-3-

carboxylate (8): A 100-mL 2-neck round bottom flask was evacuated and refilled with argon three times. The flask was then charged with **7** (2.143 g, 3.91 mmol) dissolved in 10 mL of dry CH₂Cl₂. Methyl iodide (9.74 mL, 156 mmol) was

added to the reaction mixture, which was then stirred overnight at room temperature. Upon completion, the solvent and excess CH₃I was removed *in vacuo* and the crude product was washed with DCM to yield **8** as a crystalline, off-white solid (2.400 g, 88.9%). ¹H NMR (DMSO, 300 MHz): δ 8.31 (d, 1H, J = 9 Hz), 7.59 (d, 1H, J = 1.5 Hz), 7.37 (s, 1H), 7.265 (d, 1H, J = 9 Hz), 5.71 (s, 2H), 4.69 (s, 2H), 3.91 (s, 2H), 3.48 (s, 4H), 3.18 (s, 3H), 1.87 (s, 4H), 1.60 (s, 2H).

Stille Polymerization: Polymer (+)-NBE: A round bottom flask with a magnetic stir bar was charged with **8** (2.400 g, 4.26 mmol), tri(*o*-tolyl)phosphine (648 mg, 2.13 mmol), 2,5-bis(trimethylstanny)thiophene (1.746 g, 4.26 mmol), and Pd₂(dba)₃ (195 mg, 0.213 mmol). The flask was evacuated and refilled with argon three times and followed by the addition of 200 mL of deoxygenated anhydrous DMF. The reaction mixture was left to run at 95 °C for 72 hours. Upon completion, the reaction mixture was added drop-wise to hexanes to precipitate the polymer. After centrifugation, the supernatant was removed and the polymer was collected and dried to give the product as a dark red metallic solid (1.589 g, 70.1%). ¹H NMR spectrum can be observed in Supporting Information (Figure S2).

Scheme 4. Synthesis of photo-reactive poly(cation) (+)-NBE.



"Stille": Pd catalyst, 2,5-bis(trimethylstannyl)thiophene, tri-(*o*-tolyl)phosphine

B. Film deposition on quartz using layer-by-layer self-assembly

A poly(styrene) sulfonate (**PSS**) solution at a concentration of 0.2% (w/v) was prepared in 0.1 M NaCl(aq) and used as a photo-inert poly(anion) for LbL self-assembly. **(+)-PT** (control polymer) and **(+)-NBE** were each separately dissolved in DMF at 0.2% (w/v) to produce photo-inert and photo-responsive poly(cation) solutions, respectively. Before layer deposition, quartz slides (Advalue Technology) were cleaned in air plasma for 3 minutes using a Harrick Plasma Cleaner (PDC-32G). Multilayer films were assembled using a dipping method facilitated by an EMD Millipore Midas III automated slide stainer. Samples were mounted and exposed to the poly(cation) [**(+)-PT** or **(+)-NBE**, 0.2% w/v] solution for 10 minutes, then rinsed with deionized water for 5 minutes. Then, samples were exposed to the poly(anion) (**PSS**, 0.2% w/v in 0.1 M NaCl) solution for 10 minutes and subsequently rinsed with deionized water for 5 minutes. This procedure resulted in the formation of one bilayer, and repeated until the desired number of bilayers was added.

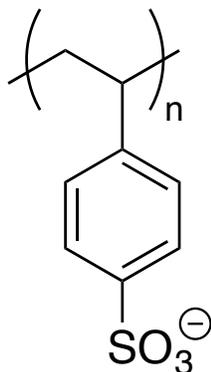


Figure 8. Poly(styrene) sulfonate, the commercially available photo-inert poly(anion) used in the assembly of PEM films.

C. Photolysis of PEM films: Instrumentation and measurements

Electronic absorbance spectra were acquired using a Varian Cary-100 instrument in double-beam mode with a baseline correction. Plasma-cleaned quartz slides were used for background subtraction spectra with solid-state samples. Irradiation of the films was performed with a 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water filter, electronic shutter, and a 295 nm high-pass filter in the light path. Samples were placed approximately 10 cm in front of the 200W Hg/Xe lamp with a 295 nm cut-on filter for 10-minute intervals. UV/Vis absorbance spectra of the films were obtained before washing with mild aqueous base. The slides were then immersed in 30-50 mL of 0.1 M NaHCO₃ (*aq*) for 5 minutes. The samples were carefully rinsed with DI H₂O and dried with gentle airflow. UV/Vis absorbance spectra of the films were then acquired and compared to the spectrum before irradiation and before the wash with 0.1 M NaHCO₃ (*aq*).

IV. Results and Discussion

The objective of this work was to synthesize charged, photo-responsive poly(thiophene)-based poly(electrolyte)s and assemble them in layer-by-layer (LbL) films where, upon irradiation, photochemical cleavage followed by deprotonation would cause disruptive electrostatic interactions between the poly(electrolyte) layers and trigger the dissolution of the film. A large amount of the work done to realize this goal involved the synthesis of photo-reactive and photo-inert PT-based poly(electrolyte)s. The synthetic design for each of the desired polymers, (+)-PT and (+)-NBE, started with commercially available 3-thiophenecarboxylic acid.

The carboxylic acid was brominated at the 2- and 5- positions in preparation for Stille polymerization later in the synthetic route (Scheme 3 and 4) where the C-Br bonds were replaced with C-C bonds to form the polymer. Bromination of thiophene with *N*-bromosuccinimide (NBS) was the best available method for preparing 2,5-dibromo-3-thiophene carboxylic acid.^[27] NBS

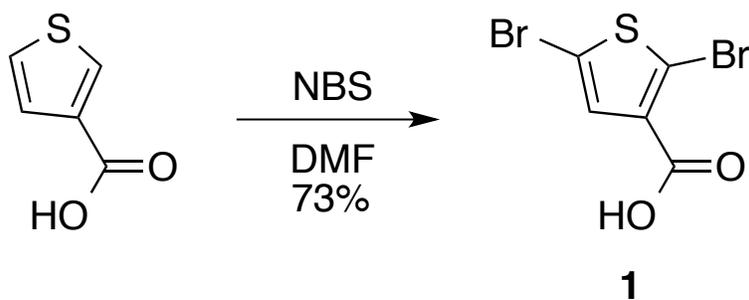


Figure 9. NBS bromination of thiophene-3-carboxylic acid.

bromination in dry DMF proceeded in good yield and required no further purification (Figure 10). The di-brominated carboxylic acid was used as a precursor in the synthesis of both polymers.

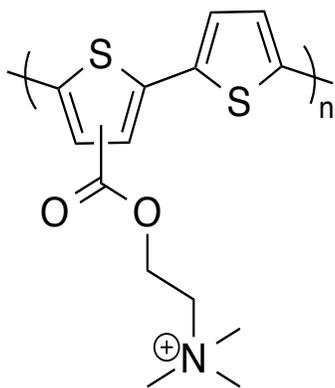


Figure 10. Polymer (+)-PT lacks a photo-cleavable moiety and should therefore preserve its positive charge and remain insoluble after irradiation and subsequent exposure to 0.1 M $\text{NaHCO}_3(\text{aq})$. A PEM film comprising (+)-PT/PSS was shown to remain insoluble upon irradiation followed by rinsing with 0.1 M $\text{NaHCO}_3(\text{aq})$.

The photo-inert, poly(cation)ic control polymer (+)-PT was synthesized to confirm that photolysis of the photo-cleavable nitrobenzyl group incorporated in the photo-reactive poly(cation) (+)-NBE is required to enable dissolution of the PEM film. The logic behind this was that (+)-PT, which lacks the photo-labile moiety, would show no decrease in film thickness (monitored using absorbance) after irradiation since the structure and thus electrostatic interactions between the poly(electrolyte) multilayers should remain unchanged (Figure 10).

The synthesis of (+)-PT (Scheme 3) began with the common precursor 2,5-dibromo-3-carboxylic acid thiophene described above. Our initial approach to the esterification of the precursor with 2-(dimethylamino)ethanol utilized the *N,N'*-dicyclohexylcarbodiimide (DCC)-mediated esterification of 2,5-dibromothiophene-3-carboxylic acid. This reaction resulted in unsatisfactory yields and excess unwanted by-products, shifting our focus to acid chloride formation.

Oxalyl chloride was reacted with the carboxylic acid to form the reactive acid chloride. Next, an amino alcohol, 1-(2-dimethylamino)ethanol was added to the reaction mixture to undergo acyl substitution in a one-pot reaction, forming the ester **2** (Scheme 3). This reaction proceeded in adequate yield, but required purification using flash chromatography (EtOAc).

The final step in the synthesis of the photo-inert monomer was methylation of the amino- side chain to give a formal positive charge to the monomer for facilitation of PEM film assembly using LbL self-assembly after polymerization. Methylation using methyl iodide proceeded with nearly quantitative yields and required no purification since any remaining solvent and unreacted CH₃I was removed *in vacuo*. The resulting monomer **3** was amenable to step-growth polymerization with 2,5-di(trimethylstannyl)thiophene under Stille coupling conditions with Pd₂(dba)₃/P(*o*-tolyl)₃ to yield (+)-**PT**. The polymerization was run using both DMF and dry toluene as solvents—DMF was found to be the preferred solvent.

PEM films of (+)-**PT** (Figure 10) and **PSS** (Figure 8) were assembled by LbL self-assembly using the following conditions: plasma-cleaned quartz slides were mounted and repeatedly dipped in the poly(electrolyte) solutions, alternating dipping between poly(cation) and poly(anion) solutions. Quartz was used as the substrate because of its optical transparency. Plasma cleaning was required to clean the quartz surface by oxidizing unwanted contaminants and activates the surface by exposing Si-OH/Si-O⁻ (pKa=2-4)^[28] groups on the surface to

participate in electrostatic interactions necessary for the assembly of PEM films during LbL self-assembly.

Each 10-minute exposure to a poly(electrolyte) solution was followed by rinsing with deionized water for five minutes at 500 mL/min to remove weakly bound material, leaving only material participating in strong electrostatic interactions. A secondary 5-minute rinse was employed for poly(electrolyte)s dissolved in solvent other than water, such as DMF. This required rinsing the sample in its corresponding solvent (DMF) for 5 minutes before rinsing with water, ensuring that any material insoluble in water not participating in strong electrostatic interactions was removed from the sample surface. The poly(anion) used in every PEM film assembled was the photo-inert poly(anion) **PSS** due to its orthogonal absorbance to the PT backbone in the UV region (~225 nm). The time required to create one bilayer (one cycle), or one layer of poly(cation) bound to poly(anion), ranged from 30-40 minutes depending on the solvents involved and whether or not additional rinses were necessary. It should be noted that aqueous solutions of the synthesized poly(cation)s were preferred but currently only DMF solutions have been suitable for LbL assembly. However, after several weeks in H₂O, polymers (+)-**NBE** and (+)-**PT** have been found to be slightly soluble.

Photolysis experiments were performed on the (+)-**PT/PSS** films to demonstrate that the photo-labile moiety must be present to facilitate dissolution. Again, it was hypothesized that without the photo-cleavage of the nitrobenzyl group, photolysis would not create the free carboxylic acid for deprotonation to

the carboxylate anion—the formation of the carboxylate anion is necessary to impart solubility. Samples were irradiated with light at a distance of 10 cm from a Hg/Xe lamp with a 295 nm cut-on filter and a power density of 22 mW/cm². Absorbance spectra of the samples as a function of irradiation time were collected to monitor film thickness.

The results shown in Figure 11 demonstrate that the film thickness of PEM films of (+)-PT/PSS was not affected by light irradiation or exposure to mild aqueous base NaHCO₃(aq). The initial absorbance spectrum at zero minutes

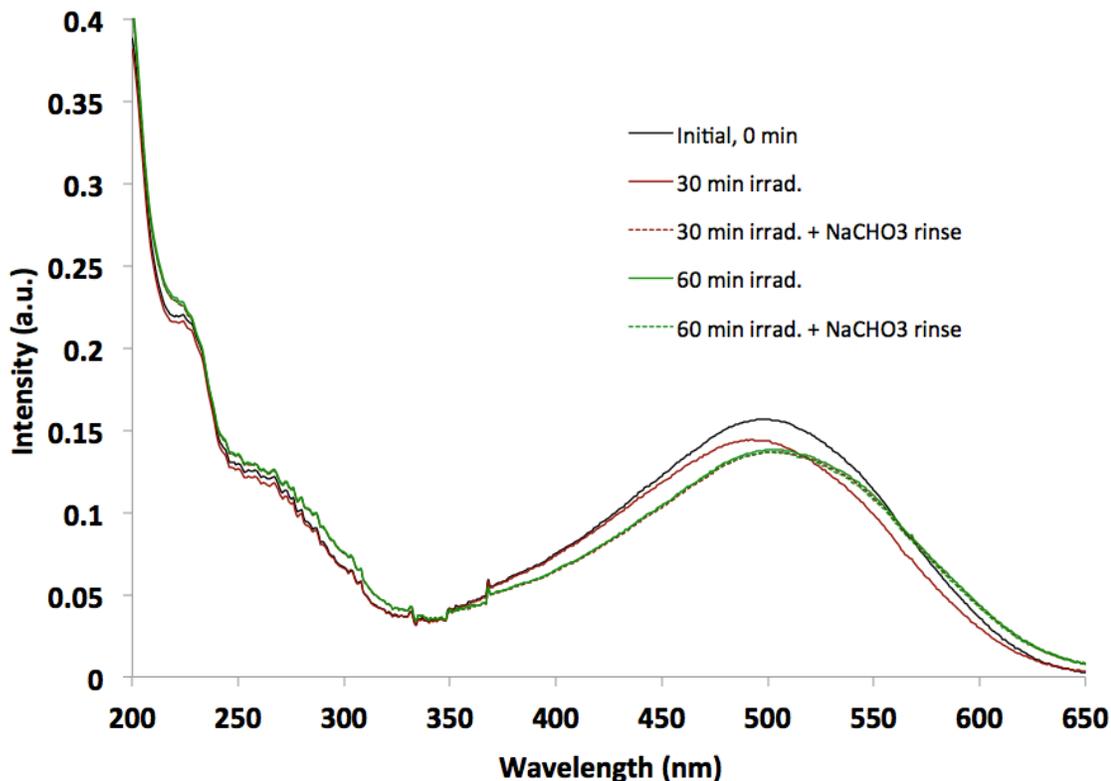


Figure 11. PEM films comprising (+)-PT/PSS did not show any distinguishable decrease in film thickness after irradiation and interaction with mild aqueous base NaHCO₃(aq). Film thickness was monitored by observing changes in the absorbance band corresponding to PSS (230 nm).

(Figure 10) corresponds to the absorbance of 10 bilayers in the PEM film and showed features attributable to PSS (230 nm), and the thiophene polymer backbone (500 nm).

Upon irradiation for 60 minutes, two key observations were made. First, the decrease in absorbance around 500 nm and band broadening suggested that photo-oxidation of the poly(thiophene) backbone was occurring during irradiation. Photo-oxidation upon irradiation of our system does not hinder the results or the integrity of the design because the major application of the designed materials is in photochemical processing and patterning, where the film acts as a *positive* photoresist. A useful description of how a positive photoresist works is “what shows goes”. This type of photoresist becomes soluble when exposed to light, while the unexposed portions remain insoluble. Thus, any photo-oxidized polymer will become soluble and be washed away.

Second, it was observed that the absorbance band corresponding to **PSS** remained unchanged after irradiation. The small discrepancies in absorbance were attributed to error due to positioning of the sample when collecting the spectra. This was evidence that film thickness did not change as a result of irradiation and subsequent exposure to mild aqueous base. Photolysis experiments with the photo-inert (+)-**PT** supported the hypothesis that the incorporation of a photo-labile moiety in the PEM films is necessary to enable solubility.

Successful results from the control experiments with the photo-inert polymer (+)-**PT** motivated the synthesis of the photo-reactive polymer (+)-**NBE**. The synthetic design of (+)-**NBE** (Scheme 4) consisted of the *N,N'*-dicarbodiimide mediated coupling of the aforementioned 2,5-dibromothiophene-3-carboxylic acid **1** and an *o*-nitrobenzyl alcohol **8** alkylated at the 5- phenolic position with a piperidine to give a tertiary amine. Alkylation of commercially available 5-hydroxy-2-nitrobenzaldehyde with 1-(2-chloroethyl)piperidine hydrochloride in anhydrous DMF under typical Williamson ether synthesis conditions yielded the alkylated nitrobenzaldehyde **5**, which NaBH₄ reduced to yield the nitrobenzyl alcohol **6** (Scheme 4). The ester was then coupled to **1** using DCC-mediated coupling to yield **7**, which was methylated using methyl iodide to give charged monomer **8** in near quantitative yield. The monomer was amenable to Stille coupling, and upon palladium-catalyzed cross-coupling with 2,5-(trimethylstannyl)-thiophene under Stille conditions gave the polymer (+)-**NBE**.

PEM films of (+)-**NBE/PSS** were assembled using the same methodology that applied to the assembly of (+)-**PT/PSS** films described above. Films consisting of 10 bilayers of were (+)-**NBE/PSS** constructed to perform additional control experiments that involved the photo-labile ONB moiety. These control experiments were performed to observe and test the photo-cleavage said to be responsible for enabling dissolution of the films.

First, the effect of prolonged exposure to mild aqueous base on PEM films comprising the photo-reactive poly(cation) in the absence of irradiation was evaluated. (+)-NBE/PSS films were submerged in 0.1 M $\text{NaHCO}_3(aq)$ for five minute increments. Absorbance measurements were taken after each rinse. After a total of 15 minutes of interaction with $\text{NaHCO}_3(aq)$, no noticeable changes in absorbances corresponding to the nitrobenzyl unit (305 nm), PSS (230 nm) or the thiophene backbone (500 nm) were observed (Figure 12). At no point were the films irradiated with UV light. This suggested that the photo-reactive nitrobenzyl ester moiety was stable in mild aqueous base under ambient conditions, and that irradiation was necessary to enable dissolution of the film.

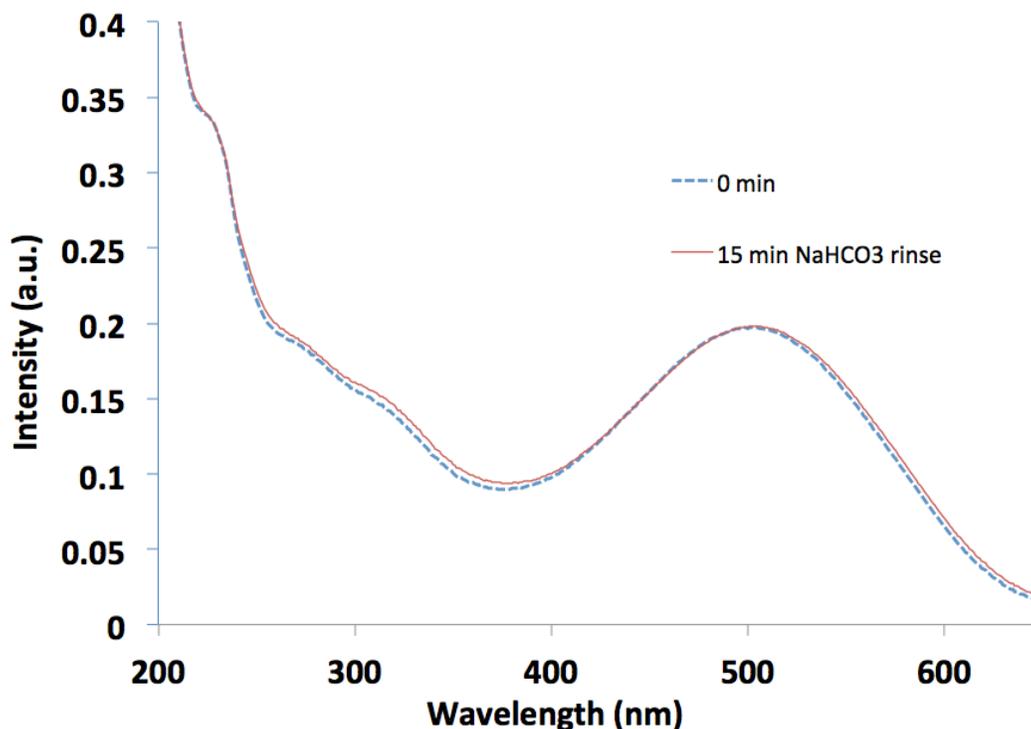


Figure 12. PEM films comprising (+)-NBE/PSS did not show any decrease in absorbance as a result of only prolonged interaction with mild aqueous base $\text{NaHCO}_3(aq)$. This indicated that irradiation is a necessary step to inducing solubility of the film.

Our hypothesis was that film thickness would decrease after irradiation only if the samples were exposed to mild aqueous base for deprotonation. Only after deprotonation of the newly-formed carboxylic acid would the negative charge on the carboxylate moiety be able to cause disruptive electrostatic interactions with the poly(anion). Irradiation conditions identical to the ones previously described were used in the absence of $\text{NaHCO}_3(\text{aq})$ as a second control experiment. Figure 13 shows the results of this photolysis experiment.

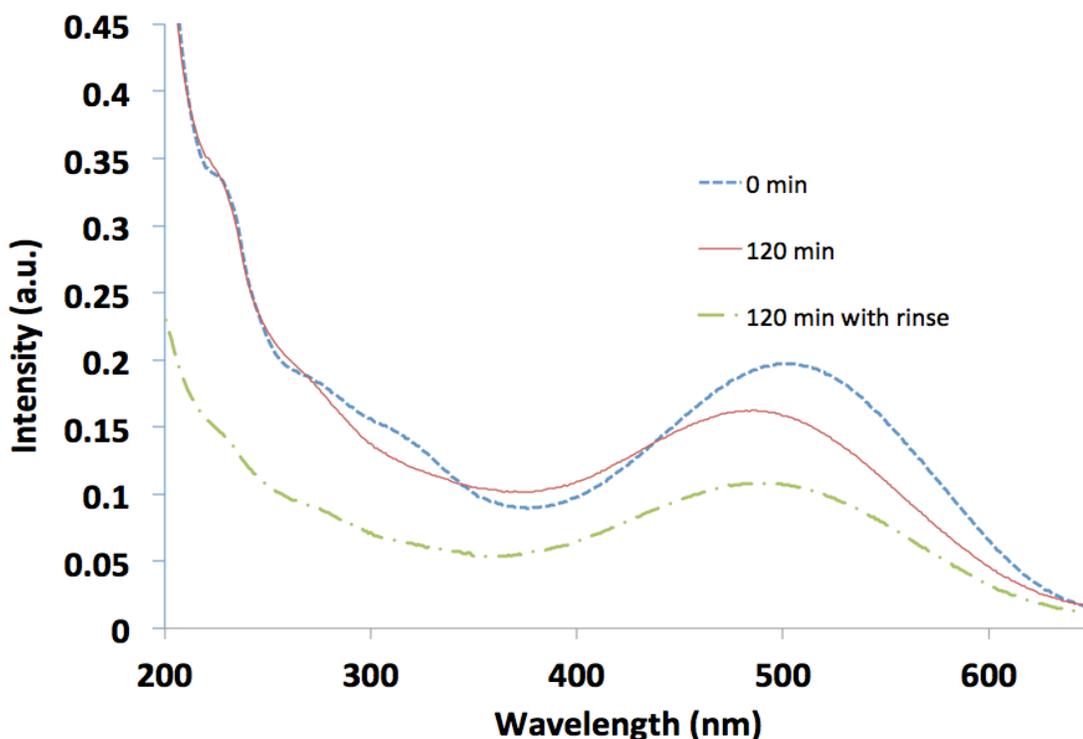


Figure 13. Irradiation of (+)-NBE/PSS films in the absence of a subsequent mild aqueous base rinse does not affect the film thickness. Only after deprotonation using mild base does dissolution occur due to the disruptive electrostatic interactions that are introduced.

The initial absorbance spectrum showed features attributable to PSS (230 nm), the nitro-aromatic *o*-nitrobenzyl unit (305 nm), and the poly(thiophene)

backbone (500 nm). Irradiation of the film with a 200W Hg/Xe lamp at wavelengths greater than 295 nm for 120 minutes at a distance of 10 cm caused a decrease in intensity and a hypsochromic shift in the thiophene absorbance band, consistent with photo-oxidation. The ONB absorbance band also shows a slight decrease. However, the absorbance band corresponding to **PSS** *remained unchanged*. Only after a 5 minute rinse with 0.1 M $\text{NaHCO}_3(\text{aq})$ did the absorbance of PSS decrease significantly. These observations validated the necessity of the mild aqueous base for deprotonation to impart solubility after the photo-cleavage has occurred.

This collection of control experiments supported photo-cleavage occurring in the photo-reactive PT-based PEM films and subsequent deprotonation causing film dissolution. As a result, additional photolysis experiments were performed to completion in order to evaluate the efficiency of the design. Irradiation of the film with a 200 W Hg/Xe lamp at wavelengths greater than 295 nm for as long as 6 hours did not result in complete photo-isomerization and cleavage of the nitrobenzyl esters as determined by the disappearance of the absorbance band at 203 nm corresponding to PSS, and to a lesser degree the intensity the absorbance of the thiophene backbone (~500 nm). Only after an irradiation time of up to 8 hours did the absorbance band attributable to PSS drop below an intensity of 0.05, corresponding to a decrease of approximately 95% in film thickness (Figure 14).

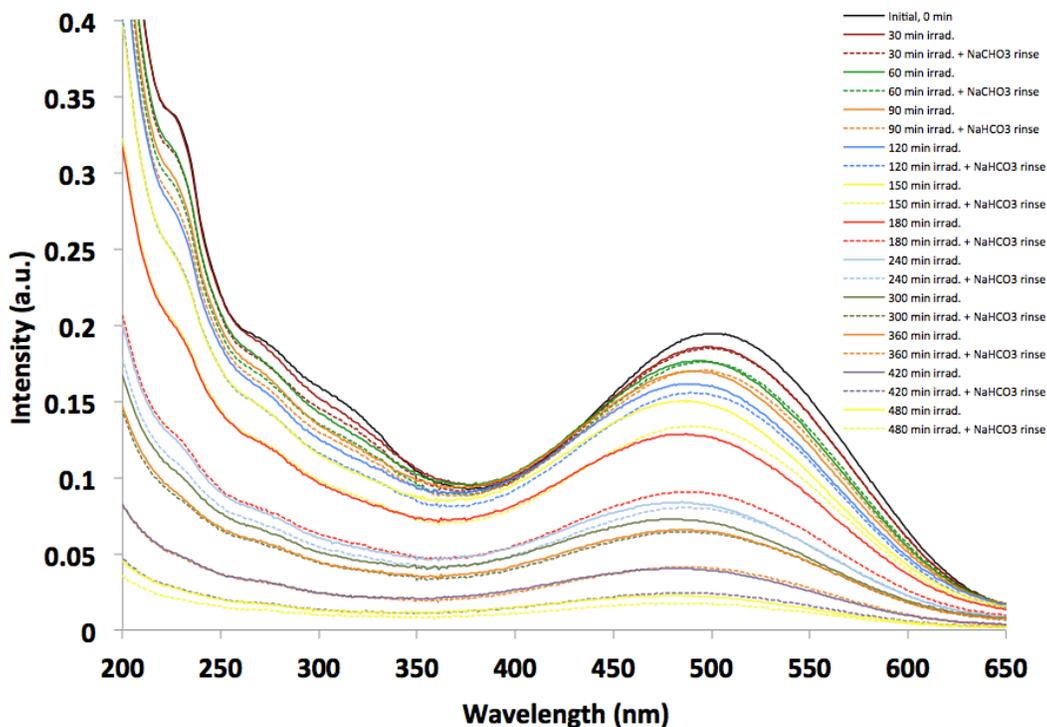


Figure 13. The dissolution of PEM films comprising (+)-NBE/PSS upon irradiation and subsequent rinse with mild aqueous base NaHCO_3 . Complete dissolution of a film consisting of ten bi-layers requires more than 8 hours of irradiation time.

The observed trends in the decrease of absorbance are consistent with UV irradiation forming the free carboxylic acid, and subsequent deprotonation causing dissolution of the (+)-NBE/PSS. Based on this collection of experimental observations, we concluded that repulsive electrostatic interactions between anionic PSS and the anionic polymeric photoproduct of (+)-NBE cause dissolution of the PEM films, and that we are able to effectively control the solubility of the constructed photo-responsive PEM films using light as a stimulus.

V. Conclusion

In conclusion, we have developed a new method for inducing dissolution of thiophene-based PEM films by photo-chemically disrupting the attractive intermolecular electrostatic forces between the layers in the film. Our system complements previously reported approaches to the stimuli-responsive polymers while combining the advantages of photochemical reactions, such as precise control over the delivery of the stimulus, and LbL self-assembly, such as nanoscale control of film thickness. Using the synthetic versatility of organic synthesis, we incorporated a formal positive charge through a photo-cleavable linker on poly(thiophene)-based conjugated materials, yielding a photo-responsive poly(cation). We demonstrated that upon irradiation and subsequent deprotonation of thin films comprising this poly(cation), the formal charge on the polymer chain can be reversed. However, films of photo-responsive poly(thiophene)s resist dissolution upon photolysis alone. Deprotonation with a mild aqueous base is necessary to form the anionic carboxylate. Photo-cleavage of the linker enables control over the formal charge of the polymer in PEM films and therefore allows control over solubility in the solid-state, such as in thin films. We predict the potential application of this design to be in the fabrication of electrically conducting photo-patternable thin films.

VI. Future Work

While our design produced promising results, it was concluded that there was room for improvement. In particular, the time required to completely dissolve the photo-reactive PEM films exceeded 8 hours. This observation clearly indicated that the quantum efficiency of the photochemical reaction in (+)-NBE was low and did not meet the standards put forth by our laboratory. The quantum efficiency of the material, in this case, was described as the ratio of induced photochemical reactions to the number of photons of given energy delivered to the material. Altering the nitrobenzyl side chains in order to stabilize the radical intermediate generated during the Norrish Type II photoreaction can increase the quantum efficiency of the photo-cleavage reaction. This increased efficiency can be obtained by either methylating the benzylic position of the side chain or by using a nitrobenzyl ether side chain.^[29]

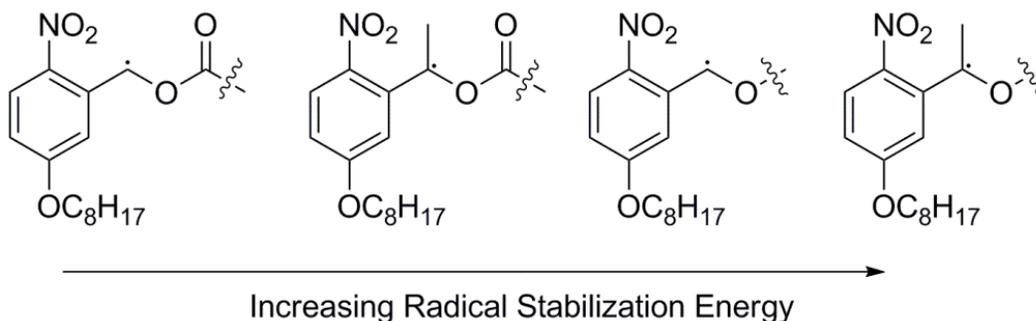


Figure 12. Altering the nitrobenzyl side chains in order to stabilize the radical intermediate generated during the photoreaction can increase the quantum efficiency of the reaction.^[29]

Our new goals are to synthesize and characterize thiophene-based poly(cation)s that incorporate ether linkages to the nitrobenzyl moiety rather than ester linkages. These ether-based polymers will include both the methylated and un-methylated nitrobenzyl groups. In turn, we hope to optimize the quantum efficiency of the photochemical reaction that enables solubility in order to obtain faster dissolution times.

Moving to an ether-based system offers a handful of advantages. Ether linkages are not susceptible to hydrolysis and are thus suitable for Suzuki chemistry. Suzuki couplings are preferable to Stille couplings because Suzuki chemistry involves mild reagents with significantly lower toxicities. Stille polymerization requires the use of hazardous stannyl reagents that can act as neurotoxins. In addition, the yields of Suzuki couplings are generally higher, and there is a larger selection of commercially available monomers prepared for Suzuki chemistry. The availability of these monomers opens doors to new synthetic routes that incorporate electron-deficient (*p*-type) and electron-rich (*n*-type) co-monomers in the polymerization. Semiconductor doping such as this has the potential to increase the conductivity of the assembled PEM films.

Finally, we hope to characterize the charge carrier mobilities of the PEM films once the photochemical reactivity and patterning ability of the system have been optimized. This will include conductivity measurements to evaluate the commercial viability of these materials in thin film electronic devices.

VI. References

- [1] Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324.
- [2] Swager, T. M.; Thomas, S. W.; Joly, G. D. *Chem. Rev.* **2007**, *107*, 1339.
- [3] Wang, C.; Dong, H.; Hu, W.; Liu, Y. *Chem. Rev.* **2012**, *112*, 2208-2267.
- [4] Muccini, M. *Nat. Mat.* **2006**, *5*, 605.
- [5] Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99-117.
- [6] Arias, A.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3-24.
- [7] Thomas, S.W. *Macromol. Chem. Phys.* **2012**, *213*, 2443-2449.
- [8] <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/Si/electric.html>, Accessed December 14, 2013
- [9] Sirringhaus, H. *Adv. Mater.* **2005**, *17*, 2411-2425.
- [10] Smith, Z. C.; Pawle, R. H.; Thomas, S.W. *ACS Macro Lett.* **2012**, *1*, 825-829.
- [11] Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Bredas, J. *Chem. Rev.* **2007**, *107*, 926.
- [12] Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581-1593.
- [13] Hu, J.; Liu, S. *Macromolecules* **2010**, *43*, 8315-8330.
- [14] Roy, D.; Cambre, J. N.; Sumerlin, B. S. *Prog. Polym. Sci.* **2010**, *35*, 278-301.
- [15] Bochet, C. *J. Chem. Soc. Perkin Trans. 1* **2002**, 125-142.
- [16] Barltrop, J. A.; Schofield, P. *J. Chem. Soc.* **1964**, 4758.
- [17] Zhao, H.; Sterner, E. S.; Coughlin, E. B.; Theato, P. *Macromolecules* **2012**, *45*, 1723-1736.
- [18] Koylu, D.; Thapa, M.; Gumbley, P.; Thomas, S.W. *Adv. Mater.* **2012**, *24*, 1451-1454.
- [19] King, W.J.; Nord, F.F.; *J. Org. Chem.* **1949**, *14*, 638.
- [20] Wu, C.; Decker, E.R.; Blok, N.; Bui, H.; You, T.J.; Wang, J.; Bourgoyne, A.R.; Knowles, V.; Berens, K.L.; Holland, G.W.; Brock, T.A.; Dixon, R.A.F. *J. Med. Chem.* **2004**, *47*, 1969
- [21] Vriezema, D.M.; Hoogboom, J.; Velonia, K.; Takazawa, K; Nolte, R.J.M. *Angew. Chem. Int. Ed.* **2003**, *42*, 772.

- [22] Yu, H.; Pullen, A.E.; Buschel, M.G.; Swager, T.M. *Angew. Chem. Int. Ed.* **2004**, *43*, 3700.
- [23] Halik, M.; Klauk, H.; Zschieschang, U.; Schmid, G.; Ponomarenko, S.; Kirchmeyer, S.; Weber, W. *Adv. Mater.* **2003**, *15*, 917.
- [24] Zhai, L.; McCullough, R. D. *Adv. Mater.* **2002**, *14*, 901-905.
- [25] Positive and Negative Photoresists,
(<http://www.ece.gatech.edu/research/labs/vc/theory/PosNegRes.html>,
accessed April 14, 2014).
- [26] Roncali, J. *Chem. Rev.* **1992**, *92*, 711
- [27] Gronowitz, S.; *The Chemistry of Heterocyclic Compounds, Thiophene and Its Derivatives*, Wiley-Interscience 1985.
- [28] Parks, G. A. *Chem. Rev.* 1965, *65*, 177-198
- [29] Solomek, T.; Mercier, S.; Bally, T.; Bochet, C. G. *Photobiol. Sci.* **2012**, *11*, 548
- [30] Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319-348.
- [31] Ariga, K.; Hill, J. P.; Ji, Q. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2319-2340.

VII. Appendix

This appendix contains the NMR spectra obtained in the characterization of the synthesized monomers and polymers:

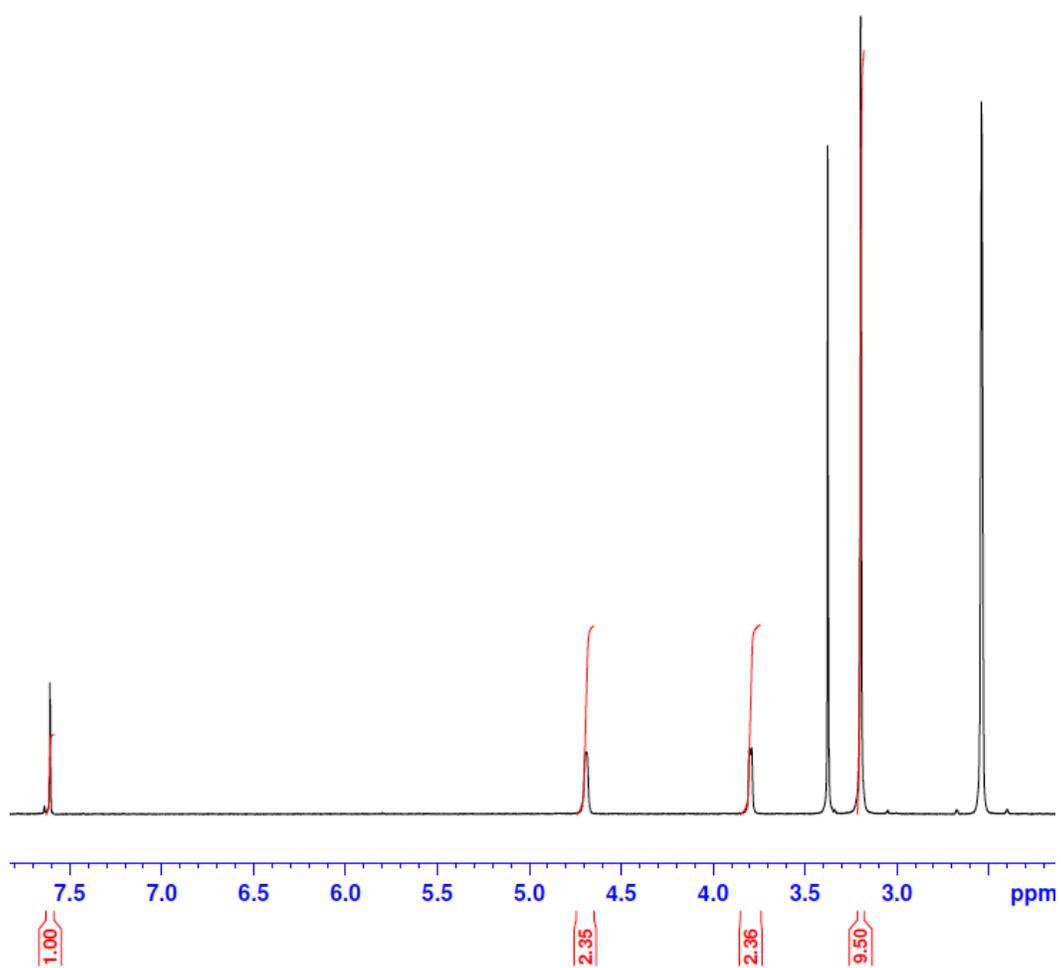


Figure S1. ^1H NMR spectrum of photo-inert monomer **3** in $d\text{-DMSO}$.

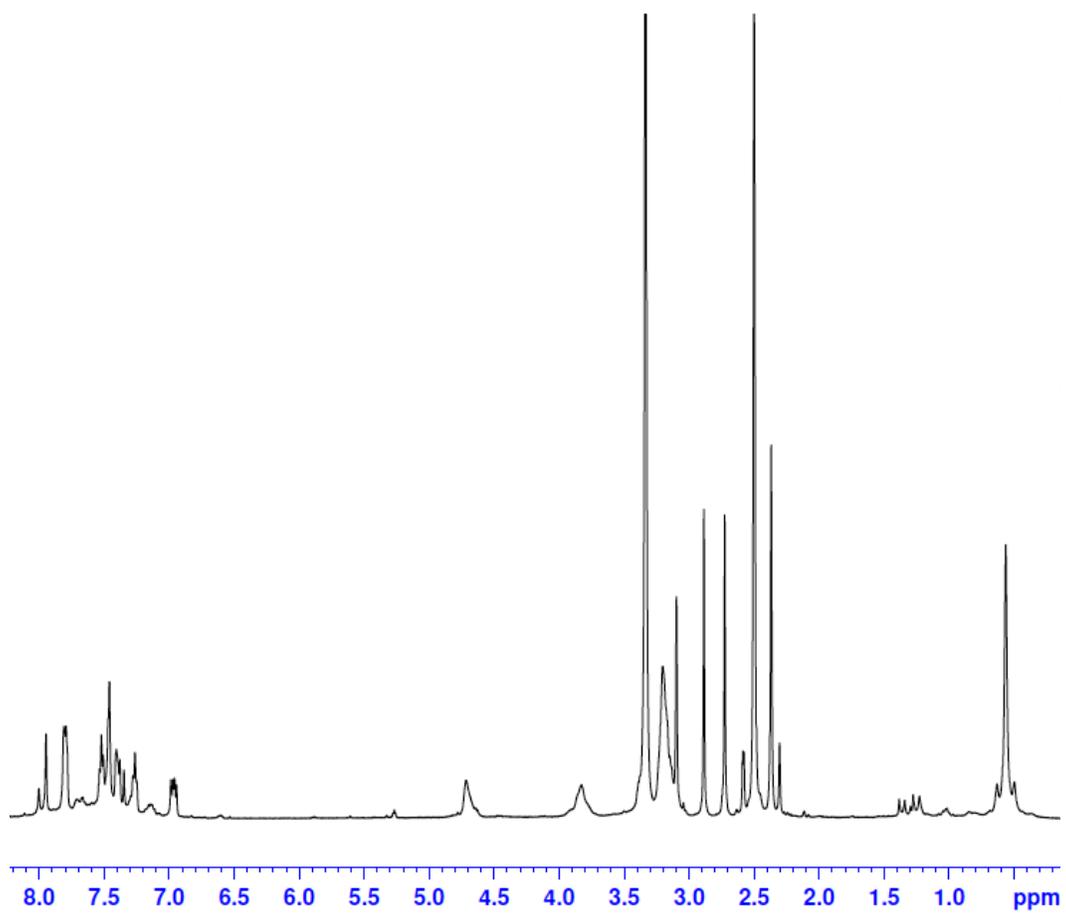


Figure S2. ^1H NMR spectrum of photo-inert poly(cation) (+)-PT in d-DMSO.

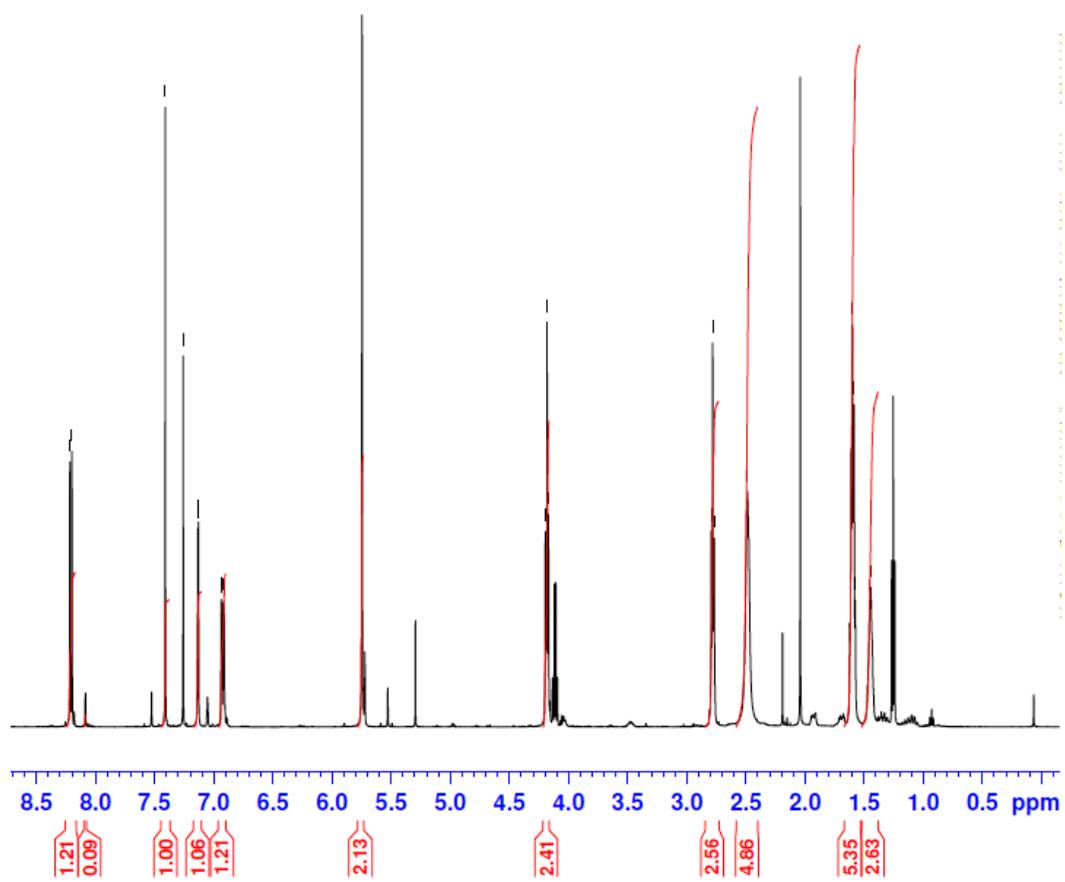


Figure S3. ^1H NMR spectrum of photo-reactive monomer **9** in $d\text{-DMSO}$.

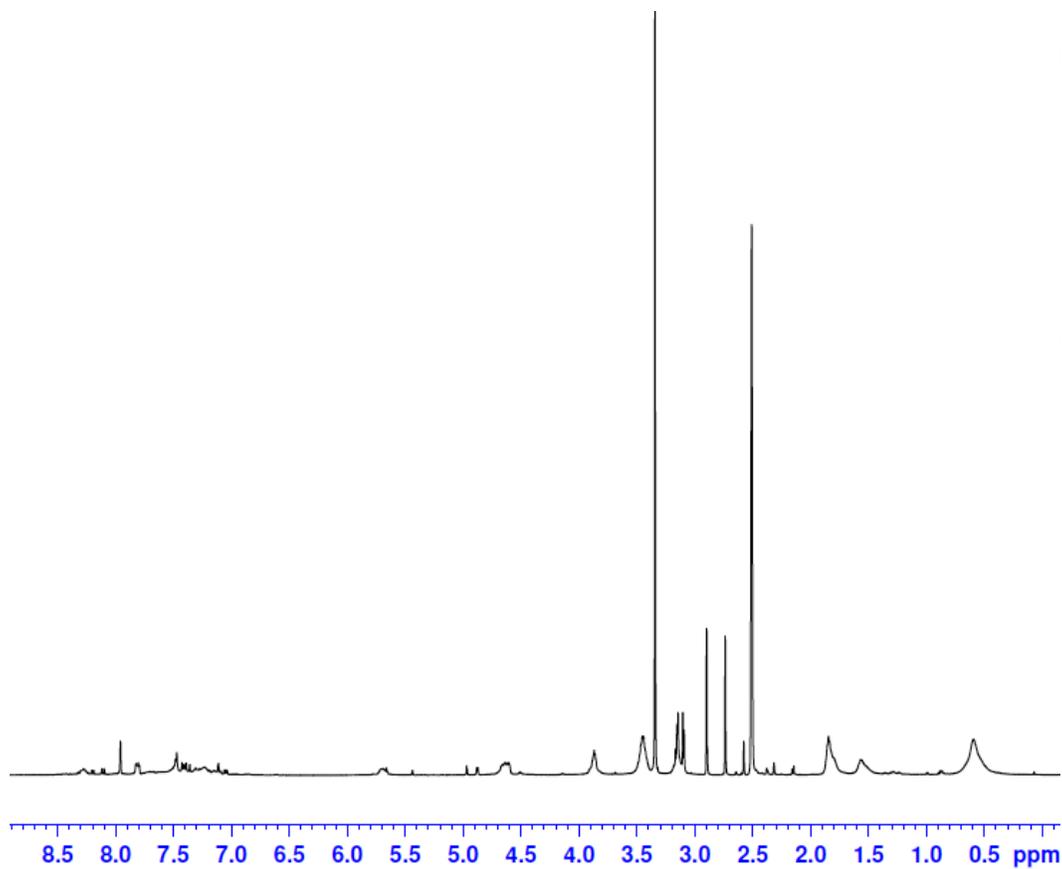


Figure S3. ^1H NMR spectrum of photo-reactive poly(cation) (+)-NBE in d-DMSO.