DIRECT THERMAL PATTERNING OF PI-CONJUGATED POLYMERS

by

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ABSTRACT

The focus of this work is to investigate a novel thermal patterning methodology involving near-infrared (NIR) 830 nm laser irradiation, by taking advantage of computer-to-plate imaging processes employed in the graphic arts industry and applying that methodology to functionalized derivatives of polythiophene and polyfluorene.

Poly(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) (PTHPET) was employed as the primary material in this proof-of-concept study, which involved the interaction of NIR laser light with a NIR absorbing dye doped in a π-conjugated polymer film. Thermal imaging of PTHPET using 830 nm laser irradiation was based on the observation that thermolytic cleavage and removal of the bulky THP group can be accomplished in the absence of acid. Exposure of NIR dye-doped polymer films to a NIR laser liberated the THP group, resulting in an insoluble, negative-tone pattern that was characterized using UV-vis spectroscopy, fluorescence spectroscopy and microscopy, TGA, variable temperature FT-IR and surface profilometry. PTHPET was patterned 10 μm resolution.

A second method for obtaining π-conjugated polymer patterns using NIR laser light was demonstrated, wherein, following deposition of a precursor π-conjugated polymer layer, a second, non-conjugated polymer film was deposited that contained the NIR absorbing dye. The top layer served as a sacrificial light-
to-heat conversion layer that absorbed the laser energy and heated the underlying \( \pi \)-conjugated polymer film. This method of patterning was demonstrated using a THP-functionalized polyfluorene-co-thiophene copolymer, which was found to retain its photoluminescent properties, \( \sim 86\% \) of the pristine quantum yield, and could be patterned with < 20 micron resolution. The generality of the technique was demonstrated with THP-functionalized polythiophene which was used to fabricate patterns of polymer with electrical conductivities similar to that of the parent polymers, and with a novel cross-linkable oxetane-functionalized polyfluorene.

**Keywords:** conjugated polymer; polythiophene; polyfluorene; laser patterning; laser imaging; fluorescence

**Subject Terms:** patterning conjugated polymers; thermal laser patterning polymers; microlithography – industrial applications; polymer thin films; fluorescent and conductive polymer microstructures
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<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>2PQ</td>
<td>2-phenylquinoline</td>
</tr>
<tr>
<td>A</td>
<td>absorbance</td>
</tr>
<tr>
<td>α</td>
<td>thermal diffusivity</td>
</tr>
<tr>
<td>β</td>
<td>absorption coefficient</td>
</tr>
<tr>
<td>b</td>
<td>pathlength</td>
</tr>
<tr>
<td>C</td>
<td>molar concentration</td>
</tr>
<tr>
<td>c</td>
<td>specific heat</td>
</tr>
<tr>
<td>C_p</td>
<td>heat capacity</td>
</tr>
<tr>
<td>CAD</td>
<td>computer aided drawing</td>
</tr>
<tr>
<td>CSA</td>
<td>camphorsulfonic acid</td>
</tr>
<tr>
<td>CtP</td>
<td>computer-to-plate</td>
</tr>
<tr>
<td>DHP</td>
<td>dihydropyran</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>ε</td>
<td>molar extinction coefficient</td>
</tr>
<tr>
<td>EHO - OPPE</td>
<td>poly(2,5-dialkoxy-(p)-phenylene ethylene) derivative</td>
</tr>
<tr>
<td>F8T2</td>
<td>poly(9,9'-dioctylfluorene-co-bithiophene)</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>h</td>
<td>height</td>
</tr>
<tr>
<td>l</td>
<td>light intensity</td>
</tr>
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</table>
\( I_o \) initial light intensity
\( I_v \) light intensity for vaporization
IR infrared
ITO indium tin oxide
k thermal conductivity
\( \lambda \) wavelength
L electrode length
LC liquid crystal
\( \mu \text{CP} \) microcontact printing
MEH-PPV poly(2-methoxy-5-2'-ethylhexyloxy)-(1,4-phenylene vinylene)
NIL nanoimprint lithography
NIR near-infrared
NMR nuclear magnetic resonance
\( \pi \text{CP} \) \( \pi \)-conjugated polymer
P laser power
\( \rho \) density
\( \rho_0 \) resistivity
P3HT poly(3-hexylthiophene)
P3AT poly(3-alkylthiophene)
PA poly(acetylene)
PAG photo acid generator
PCBM 3'-phenyl-3'H-cyclopropa[1,9][5,6]fullerene-\( C_{60} \)-I\(_r\)-3'-butanoic acid methyl ester
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>PDAF</td>
<td>poly(dialkylfluorene)</td>
</tr>
<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td>PE</td>
<td>poly(ethylene)</td>
</tr>
<tr>
<td>PEDOT</td>
<td>poly-3,4-ethylenedioxythiophene</td>
</tr>
<tr>
<td>PF</td>
<td>poly(fluorene)</td>
</tr>
<tr>
<td>PFET</td>
<td>polymer field-effect transistor</td>
</tr>
<tr>
<td>PFT-TT</td>
<td>poly(9,9'-dihexylfluorene-alt-2-(2-thiophene-3-ethoxy)tetrahydropyran)-co-(9,9'-dihexylfluorene-alt-bithiophene)</td>
</tr>
<tr>
<td>p(HEMA)</td>
<td>poly(2-hydroxyethyl methacrylate)</td>
</tr>
<tr>
<td>Φ&lt;sub&gt;PL&lt;/sub&gt;</td>
<td>quantum yield of photoluminescence</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>PLED</td>
<td>polymer light emitting device</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PPP</td>
<td>poly(p-phenylene)</td>
</tr>
<tr>
<td>PPV</td>
<td>poly(phenylene-vinylene)</td>
</tr>
<tr>
<td>PPy</td>
<td>polypyrrole</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PSS</td>
<td>polystyrenesulfonate</td>
</tr>
<tr>
<td>PT</td>
<td>poly(thiophene)</td>
</tr>
<tr>
<td>PTFE</td>
<td>poly(tetrafluorethylene)</td>
</tr>
<tr>
<td>PTHPET</td>
<td>poly(3-(2-(2-tetrahydropyranoxy)ethyl)thiophene)</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>q</td>
<td>heat flow</td>
</tr>
<tr>
<td>R</td>
<td>resistance</td>
</tr>
<tr>
<td>RGB</td>
<td>red-green-blue</td>
</tr>
<tr>
<td>s</td>
<td>conductivity probe distance</td>
</tr>
<tr>
<td>σ</td>
<td>conductivity</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>t₀</td>
<td>thickness</td>
</tr>
<tr>
<td>T₉</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>TAG</td>
<td>thermal acid generator</td>
</tr>
<tr>
<td>TGA</td>
<td>thermal gravimetric analysis</td>
</tr>
<tr>
<td>THP</td>
<td>tetrahydropyran(yl)</td>
</tr>
<tr>
<td>UHMW</td>
<td>ultra-high molecular weight</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>w</td>
<td>electrode channel width</td>
</tr>
</tbody>
</table>
CHAPTER 1: INTRODUCTION

1.1 What are $\pi$-Conjugated Polymers?

Historically, the concept of macromolecules was first developed by Hermann Staudinger in the early 1920’s, and a relatively short time later, the field of polymer chemistry exploded into a very diverse and interdisciplinary area of research comprising many aspects of chemistry from synthesis to catalysis to modelling and ultimately, wide spread application. In general, one-dimensional carbon-based polymeric materials can be broken up into two very broad categories of “saturated” and “unsaturated” macromolecular chains. The group of saturated materials consists of many of the more commonly known polymers such as teflon, nylon and polyester. The molecular structures of a small selection of saturated polymers, hereafter referred to as non-\(\pi\)-conjugated polymers, are shown in Figure 1.1.
From an industrial point of view, production and distribution of these plastic materials represent a multi-billion dollar a year business as they can find application in nearly every imaginable form, from simple grocery bags to very advanced technological applications where they perform as electronic insulators or dielectric materials in complex integrated microelectronic devices.

Despite the fact that the list of uses for non-\(\pi\)-conjugated polymers seems to be endless, from a modern and novel electronic device point of view, their uses are often limited to insulating applications. Thus, when compared to the
"unsaturated" polymers, hereafter referred to as \(\pi\)-conjugated polymers or \(\pi\)CPs, the non-\(\pi\)-conjugated materials are not electronically conducting, photo- or electro-luminescent, by virtue of their molecular and electronic structure, which typically consists of long chains of carbon atoms where all four valence electrons are involved in maintaining single covalent bonds (\(\sigma\)-bonds). On the other hand, \(\pi\)CPs consist of a series of alternating \(\sigma\)-bonds and double bonds (\(\pi\)-bonds). The delocalization of electrons is what gives \(\pi\)CPs their unique electrical and optical properties, which will be described in more detail in a following section.

Figure 1.2 shows schematically how localized molecular bonding \(\pi\)-orbitals and anti-bonding \(\pi^*\)-orbitals of small conjugated molecules become a continuum or band as more carbon centers are added to the molecular network and thus provide the \(\pi\)-electrons a greater opportunity to delocalize throughout a molecule.\[1, 2\] As electron delocalization increases along the polymer chain, the energy gap (Eg) between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) becomes more narrow. The Hückel approximation, i.e., the average energy between the HOMO and LUMO must decrease as the number of repeat units increases, and thus, predicts that as delocalization increases the band gap should approach that of metallic conductors and have, essentially, no band gap.\[3\] This is not the case. A band gap is observed as the number of repeat units increase as predicted by the Peierls distortion theory,\[4\] which states that there is an electronic instability in one-dimensional conjugated materials, which results in the formation of an
energy gap between the HOMO and LUMO. Typically, undoped \( \pi \)CPs have optical band gaps that are between 1240 to 354 nm (1.0 to 3.5 eV, respectively).

Figure 1.2: Schematic band diagram for the delocalization of \( \pi \)-electrons in \( \pi \)-conjugated molecules.

In the 1970's, the first pioneering work on conjugated polymers was reported by Alan MacDiarmid, Hideki Shriakawa and Alan Heeger, on their discovery and study of a conducting \( \pi \)CP, polyacetylene (PA), which, when doped with various oxidizing agents, became a metal-like conductor. They were awarded the Nobel Prize in Chemistry in 2000 for this work: "the discovery and development of electrically conductive polymers" in recognition of the overwhelming impact that their discovery had on the scientific community with respect to the emergence of novel applications and creation of a new
interdisciplinary scientific field joining chemistry and physics. A selection of common and intensely studied πCPs are shown in Figure 1.3.

![Molecular structures of various πCPs.](image)

Generally, π-conjugated polymers are inherently semiconductors, but different from traditional materials such as silicon, in that they do not become conducting unless doped with appropriate oxidizing or reducing agents.[5] The term “doping” used to describe oxidized or reduced conjugated polymers is taken from the inorganic semiconductor field but is actually a redox process that can be accomplished via chemical or electrochemical processes. Figure 1.4 is a diagram comparing the conductivities of various materials and highlights the
positions of various undoped and doped πCPs. Once oxidized (p-doped) or reduced (n-doped), the materials adopt a new electronic structure and new energy levels are introduced within the band gap of the polymer. Examples of energy levels introduced in p-doped and n-doped materials for traditional and polymer semiconductors are shown in Figure 1.5. The πCP used in this example is poly(p-phenylene). In the neutral, undoped form, the polymer is a stable aromatic chain consisting of a series of benzylic rings. Polymers of this type, i.e., those which have backbones with a similar structural conformation to cis-polyacetylene, have two non-degenerate ground states and can also exist in an unstable quinoid form as shown in Figure 1.5b.[6] Upon doping, oxidation in this example, the polymer chain becomes ionized with the removal of an electron forming a radical-cation which is stabilized by the extended π-conjugated system. The ionized entity in this form is called a polaron. Further oxidation removes more electrons from the valence band and produces more polarons where upon they pair up to form dication species, known as bipolarons, shown in Figure 1.5d.[6-8] These bipolaron states delocalize over several repeat units of the polymer main chain and hop between adjacent polymer chains.
Figure 1.4: Comparison of the conductivities of various materials.

Traditional Semiconductor Band Structure Diagrams

Traditional Semiconductor Polymeric Band Structure Diagrams (p-doping)

Figure 1.5: Band diagrams of a traditional semiconductor in the a) neutral, b) p-doped and c) n-doped state and a “p-doped” polymeric semiconductor.
A combination of narrowing the band gap, with an increasing number of polymer repeat units, and/or the introduction of dopants to these materials leads to numerous changes in the photo-physical and electrical properties. For example, in the neutral form, when πCPs absorb light with an energy equal to or greater than the energy of the band gap, electrons in the HOMO are excited into higher energy levels. This excitation process yields an electron-hole pair called an excition. Once excited, the electron can relax back to a ground state configuration by one of three pathways as shown in Figure 1.6. The first pathway is via a non-radiative decay path where the absorbed energy is released as heat in the form of vibrational or rotational motion. The second and third pathways involve relaxation of the excited electron via the release of energy in the form of light by either a fluorescence or phosphorescence relaxation. Fluorescence emission results from the relaxation of the electron from its excited singlet state back to the ground state whereas phosphorescence results when the electron crosses over from the excited singlet state to a degenerate triplet state followed by either non-radiative or radiative decay. When the same material is doped, as shown in Figure 1.5, the HOMO or LUMO will be of different energy from the pristine materials HOMO or LUMO, thus changing the polymer’s absorption properties. For example, when a πCP such as poly(3-hexylthiophene), a neutral-semiconducting material, is doped with an oxidant such as FeCl₃, the material changes from a red color (absorbing green light) to bluish-gray (absorbing yellow light). The change in color is due to the introduction of a new set of energy levels that are between the HOMO and
LUMO as shown in b) of Figure 1.5 and thus upon absorption of light, less energy is needed to excite valence electrons to an excited state.

![Diagram of Jablonski model showing electron excitation and resulting non-radiative decay, fluorescence and phosphorescence processes after absorption of light.]

Figure 1.6: Jablonski diagram depicting electron excitation and resulting non-radiative decay, fluorescence and phosphorescence processes after absorption of light.

1.2 Polythiophene, Polyfluorene and Their Derivatives

1.2.1 Polythiophenes

Poly(heterocycles) or conjugated polymers consisting of cyclic repeat units containing a heteroatom, such as nitrogen or sulphur, are an important and heavily studied class of \( \pi \text{CP} \). Figure 1.3 contains a few examples of some intensely studied poly(heterocycles). Analogous to the cis-form of polyacetylene and stabilized by the heteroatom, poly(heterocycles) have distinct structural and electronic differences from PA, such as non-degenerate ground states in their
aromatic and quinoid forms, a higher stability toward oxygen and light, and structural versatility which permits chemical modification of the monomer units and thus further control over the electronic and optical properties of the material.[9-12]

Poly thiophene and its derivatives are one of the most studied classes of poly(heterocycle)s because they are easily prepared and functionalized through a variety of chemical and electrochemical methods (some of which are described in section 1.3) and exhibit a wide range of interesting electronic and optical characteristics in the neutral and doped form. For example, because polythiophenes are electron-rich they tend to be easily (and reversibly) oxidized to form a highly conducting p-type material, with electrical conductivities reported as high as ~ 2000 S/cm.[9, 13]

In 1986, it was reported that chemical modification at the 3-position of the thiophene monomer unit with substituents such as straight chain alkyl groups, impart solubility to an otherwise insoluble polymer.[14, 15] Introduction of the side chain helps to prevent aggregation of the polymer main chains and thus hinders precipitation from solution during polymerization. Through careful choice of the synthetic method the final structural conformation of the poly(3-alkylthiophene) can be controlled. Further discussion of this aspect will be discussed in more detail in section 1.3. These structural changes, relative to unsubstituted polythiophene, do not appreciably change the oxidative properties of the monomer, thus allowing the continued use of electro-polymerization
methods, however, they may change considerably the electronic and optical properties of the material.

1.2.2 Polyfluorene

Another interesting class of π-conjugated polymer that has received considerable attention is polyfluorene and its derivatives because they have been shown to emit blue fluorescence in the solid-state, have good processability and can be synthesized using a wide variety of techniques.[16-18] Soluble poly(2,7-fluorene)s were first reported in 1989 by Yoshino and co-workers where they oxidatively polymerized 9,9'-dihexyl substituted fluorene using FeCl₃ (discussed in more detail in section 1.3.1).[19] However, this coupling method produced only low molecular weight polymers that were not regio-selective, in that, defect monomer linkages at sites other than the desired 2,7-positions were observed. In an effort to minimize these kinds of polymer defects and obtain higher molecular weight materials, transition-metal-catalyzed coupling reactions similar to those described by Suzuki,[20] Stille[21] and Yamamoto,[22] have been investigated. Today, polyfluorenes continue to be heavily investigated for their use in many devices, such as in optoelectronic applications where they serve as the active layer in polymer light emitting devices (PLEDs).

1.3 Preparation of Functionalized π-Conjugated Polymers

Materials scientists have an arsenal of synthetic methods at their disposal for the preparation of conjugated polymers. As will be discussed in sections 1.4 and 1.5, structural homogeneity of polymers is crucial for the intended patterning
and/or device applications. Thus, the choice of the synthetic pathway to the desired product is very important. Specifically, whether the chosen method yields a regio-regular or regio-random material, e.g., increasing or decreasing planarization of the \( \pi \)-system through structural defects. Often, the regularity of the final polymer is strongly dependant of the symmetry of the monomer unit or units, e.g., polymerization of a 3-alkyl thiophene versus a 3,4-dialkyl substituted thiophene.\[^{[9, 23]}\] The following section discusses a selection of polymerization methods which have been previously reported for the production of soluble, conductive and fluorescent polythiophene and polyfluorene derivatives that have found application in a variety of device applications. It should be noted that the aromatic nature of the thiophene and fluorene monomer unit share similar reactivities to the various polymerization methods that will be discussed in the following sections, thus in the given examples a synthesis involving either monomer unit could be applicable. Where possible, and for simplicity, examples will be given for the synthesis of the thiophene derivative rather than the fluorene.

### 1.3.1 Oxidative Coupling

A very simple oxidative coupling method for the polymerization of 3-alkyl thiophene in solution using FeCl\(_3\) was reported in the late 1980’s by Sugimoto \textit{et al.} and Leclerc \textit{et al.}\[^{[24]}\] The FeCl\(_3\) oxidizes the 3-alkylthiophene at the 2 and 5 positions forming radicals which react with other monomers which propagate to form the polymer, as shown as the inset in Figure 1.7. Reasonably high number average molecular weights (Mn) were obtained using this method, ranging from Mn = 30,000 to 300,000 Da, and high yields. Despite the ease of preparation
using this method, it is not without its problems. Molecular weights obtained from batch to batch, under identical reaction conditions, can be dissimilar ranging from $M_n = 54,000$ to $122,000$ Da and doping of the polymer with iron cannot be fully reversed. Also, due to the fact that radicals were formed at both the 2 (head position) and 5 position (tail position) of the thiophene ring, a range of couplings were observed in the final polymer as shown in Figure 1.7. This regio-random or irregular structure disrupts and twists the polymer, breaking the extended conjugation of the $\pi$-system.

![Figure 1.7: Oxidative coupling of 3AT with FeCl$_3$ and a selection of possible triad monomer couplings.](image)

1.3.2 The McCullough Method

The first synthesis of $\sim 100\%$ regio-regular ($\sim 100\%$ HT couplings) poly(3-alkylthiophene)s was reported by McCullough and Lowe in 1992.[25] The McCullough Method employed a 2-bromo-3-alkylthiophene which was selectively lithiated at the 5-position of the thiophene ring under cryogenic conditions, i.e.,
-40 °C. The lithiated intermediate was cooled further to -60 °C and was then treated with MgBr₂•Et₂O to generate a magnesiobromo Grignard reagent. Warming the reaction mixture slowly to room temperature in the presence of a nickel catalyst afforded a regio-regular poly(3-alkylthiophenes) (P3AT) via a metal catalyzed cross coupling reaction in moderate yields. Figure 1.8 contains the reaction scheme of the McCullough Method for the preparation of regio-regular P3ATs.

![Reaction Scheme of McCullough Method](image)

**Figure 1.8:** Regio-regular synthesis of P3ATs using the McCullough Method.

1.3.3 The GRIM Method

A short time later, a more simplified synthetic method for the preparation of regio-regular P3ATs was again reported by McCullough et al. which involved a magnesium-bromine exchange reaction, also known as a Grignard metathesis reaction (GRIM).[12, 26] In this method, a 2,5-dibromo substituted monomer was employed rather than the mono-brominated derivative. To a solution of 2,5-dibromo-3-alkylthiophene was added an alkylmagnesium bromide Grignard reagent to generate the Grignard species as shown in Figure 1.9. Surprisingly, it was discovered that during the formation of the Grignard species, a mixture of metalated intermediates were formed. Approximately 80% of the bromine
located at the 5-position of the thiophene were converted, leaving ~ 20 % 2-
position substitution, however, polymers with ~ 100 % HT couplings were
obtained after the addition of nickel catalyst. It was reported later that the isomer
selectivity of the nickel catalyst was responsible for the unexpected high HT
content. This method offered several advantages over the McCullough Method
in that the method did not require cryogenic temperatures and monomer
purification was easier, i.e., separation of isomers generated during the
bromination of alkylthiophene.

![Regio-regular synthesis of P3ATs using the GRIM method.](image)

**Figure 1.9: Regio-regular synthesis of P3ATs using the GRIM method.**

### 1.3.4 Yamamoto Coupling

Another coupling method has been described by Yamamoto et al. which
also involves the coupling of dibrominated monomers.[22] This method has been
shown to be very useful for coupling multiple kinds of monomers to produce
endless combinations of random copolymers. The reaction employs a relatively
large mole% of nickel “catalyst” (approximately 2 mol%) and is very sensitive to
ambient air and moisture making the method more cumbersome than some of
the other methods that are available. **Figure 1.10** contains an example of the Yamamoto coupling polymerization.

![Diagram of Yamamoto coupling reaction](image)

**Figure 1.10**: Yamamoto coupling reaction of 2,7-dibromo-9,9'-dioctylfluorene and 5,5'-dibromo-2,2'-bithiophene.

### 1.3.5 Suzuki Coupling

Another versatile method of polymer preparation has been reported by Suzuki *et al.* for the synthesis of new aryl bonds from diboronic acids and esters and dibromo reagents in the presence of a palladium catalyst, as shown in **Figure 1.11**.[20] This method of monomer coupling is well suited for the preparation of alternating copolymers, the reaction is not influenced by the presence of water and there are a wide variety of monomers commercially available.
1.3.6 Reactive Functional Groups

Unsubstituted polyfluorene (PF) and polythiophene (PT) are not soluble in common organic solvents, however, alkylation of the 9,9'-position of a fluorene unit or at the 3 or 4-position (or both) of a thiophene (if greater in length than 4 carbons) can render these materials soluble when polymerized.\textsuperscript{[9]} More importantly, these materials retain their interesting electronic and optical properties when functionalized and become solution processable. Today, the list of publications discussing the functionalization of polyfluorene and polythiophene derivatives is nearly endless because it has been found that the properties of the materials can be tuned or tailored to very specific uses by modifying the side chain(s). The following examples are a few of the functional groups or side chains that have been reported in the literature with an emphasis on polymer “patternability”.

There have been several functional groups discussed in the literature that have been shown to render a polymer insoluble (often due to cross-linking) in
common organic solvents after exposure to high intensity light. Two examples of photo-sensitive cross-linkable polymers are shown in Figure 1.12.\cite{27, 28}

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

Figure 1.12: Examples of cross-linkable polythiophenes.

Other functional groups have been studied that rely on the exposure of the patternable moiety to acid and/or the application of heat or light. For example, Scott et al. prepared thermally cross-linkable polyfluorenes where the polymer was end-capped with a 4-bromostyrene in a Yamamoto type coupling reaction as shown in Figure 1.13.\cite{29, 30} It was found that thermally cross-linking the polymers from the end of the chains decreased polymer chain mobility and decreased the aggregation of chains as well as change solubility. Polymers containing 9,9'-distyrylfluorene blocks (also shown in Figure 1.13) were also prepared, however, significant aggregation of the polymer main chains was observed, post thermal treatment, in photo and electroluminescent characterizations.
Another cross-linking functional group has been extensively studied by Meerholz and Müller that involves the photo-acid induced cationic reaction of oxetane side groups. Typically, the oxetane cross-linking reaction is initiated in a polymer film containing a photo-acid generator when exposed to UV light. The UV light is absorbed by the acid generator, which then decomposes into various products including a strong acid. Exposed films are then thermally annealed to promote the reaction of the acid throughout the exposed regions of the polymer thus facilitating cross-linking. The mechanism is shown in Figure 1.14. This group has studied the patterning with many versions of conjugated polymers containing this functional group and a selection of the materials are shown in Figure 1.15.
Figure 1.14: Photo-acid induced cross-linking of oxetane containing \( \pi \)CPs.

Figure 1.15: A selection of oxetane functionalized \( \pi \)CPs for use in PLEDs.

Holdcroft and co-workers demonstrated that polythiophenes, decorated with tetrahydropyranyl (THP) protected alcohol side chains, could be rendered insoluble via photolithographic and soft lithographic methods in the presence of a catalytic amount of an acid generator.[38-41] Upon the application of heat, dihydropyran is liberated from the film in the areas where acid reacted with the side chain, leaving a negative tone image of the polythiophene derivative after solvent development. The temperature at which deprotection of the polymer
occurred was approximately 100 °C lower in films containing acid compared to pristine films. The insoluble polymer becomes a hydrogen bonded network after deprotection of the alcohol. Copolymers containing varying amounts of monomers with a THP-protected thiophene derivative and 3-hexylthiophene were prepared and it was shown that insolubilization of the parent polymer was possible with as little as 20 % THP functionality.[39] Figure 1.16 contains the acid-catalyzed reaction scheme for the deprotection of the polythiophene derivative.

![Figure 1.16: The acid catalyzed deprotection of a tetrahydropyran-functionalized polythiophene derivative and liberation of dihydropyran.](image)

1.4 Characterization of π-Conjugated Polymers

There are many characterization techniques that are employed to measure a polymers properties once prepared, such as gel permeation chromatography (GPC) to measure the molecular weights, nuclear magnetic resonance (NMR) spectroscopy to determine structural connectivity, ultra-violet-visible (UV-vis) spectroscopy to measure the optical absorption and transmission properties. From an application point of view, photoluminescent (PL) and
conductive properties of conjugated polymers are also very important. The following sections will describe various techniques for measuring PL and electrical resistivity/conductivity of πCP films. For the sake of clarity, the more common laboratory characterization techniques such as GPC, NMR, UV-vis and infrared (IR) spectroscopy will not be described in this thesis.

1.4.1 Photoluminescent Quantum Yields (ΦPL)

As shown previously in Figure 1.6, energy absorption in πCPs are attributed to electronic excitation from a ground state singlet π-orbital to a singlet π*-orbital followed by relaxation of that excited state by one or more of the three conversion processes, internal conversion, fluorescence or phosphorescence. A lot of information about a polymer's electronic structure can be determined from its photoluminescent emission spectrum and thus quantitative analysis of the emission efficiency, i.e., photoluminescent quantum yield (ΦPL) is often measured for luminescent πCPs. The ΦPL can be measured in one of two ways, a relative method where the emission of a sample is compared with that of a known standard, such as 9,10-diphenylanthracene, or a direct method where emitted photons are collected and counted using an integrating sphere.[42, 43] The sphere is hollow with its inner surface coated with a reflective material and thus is capable of reflecting the emitted light of a sample to a fibre-optic cable directed toward a detector. Two spectra are required, one containing the excitation scan including the light from the excitation source without a sample present, as shown in as the black plot of Figure 1.17. This spectrum represents the incident
number of photons. The second spectrum, blue plot of Figure 1.17, contains emission from both lamp and exposed sample. A comparison of the excitation lines of the lamp from both spectra represents the number of photons absorbed and by integration of the area under the emission spectrum of the sample, the number of emitted photons from the sample can be determined. Thus, the ratio of photons emitted to photons absorbed, $\Phi_{PL}$, can be calculated.

![Photoluminescence emission spectrum](image)

Figure 1.17: An example of a photoluminescence emission spectrum for an excitation lamp and fluorescent sample in an integrating sphere spectrofluorimeter.

1.4.2 Thin Film Electric Conductivity: 4- and 2-Point Probes

The electrical conductivity of thin films and surfaces is typically obtained indirectly by measuring a sample resistivity ($\rho_0$) using a 4-point probe method.[44, 45] The higher a sample resistivity the lower the electrical
conductivity. Sharp metal probes, aligned in a linear fashion and spaced 1 mm apart (s), are brought into physical contact with a surface. An electrical current flows between the two outer most probes and an electrical potential is measured between the inner most probes, as shown in Figure 1.18. For a bulk sample, i.e., when the sample thickness (t) is much greater than the probe spacing, a different mathematical model is employed than for when the sample thickness is much smaller than the probe spacing, also shown in Figure 1.18.

![Figure 1.18: Schematic of a 4-point probe configuration and associated equations for the determination of surface resistivity.](image)

**Bulk Resistivity Measurements:**
\[ t \gg s \]
\[ \rho_o = 2\pi s (V / I) \]

**Thin Sheet Resistivity Measurements:**
\[ t \ll s \]
\[ \rho_o = \frac{\pi t}{\ln 2} \frac{V}{I} \]

Often, sample films are so thin or soft that the 4-point probe technique is incapable of making sufficient contact with the film material. Thus, resistivity can also be obtained using a 2-probe method where by contacts are made via two separated gold electrodes, often 20 – 60 µm apart.\[46\] The material to be measured is deposited on the electrode set-up such that a connection is made
between both electrodes either by spin coating, drop casting, evaporation or a Langmuir-Blodgett technique, as shown in Figure 1.19. A voltage is applied across the two electrodes and the current is sampled. Following Ohm’s Law the resistance (R) can be calculated. From the dimensions of the electrode set-up and film thickness the conductivity (σ) can be calculated according to the equation included in Figure 1.19.

![Figure 1.19: Schematic of a 2-point probe configuration and associated equation for the determination of conductivity.]

\[ \sigma = \frac{W}{RtL} \]

1.5 Electronic Applications of \( \pi \)-Conjugated Polymers

Device structures and performance based on electronically conducting and/or photo- or electroluminescent polymers have been intensely studied by both academic and industrial scientists.\([32, 35, 37, 47-60]\) This is because their application as the active layer material(s) in high-tech devices presents an increasingly interesting opportunity for researchers to continue to explore new synthetic strategies, material properties, novel patterning methodologies and device phenomena. A small selection of specific device applications will be
presented here, but these three examples are in no way an exhaustive list of the applications for conjugated polymers in a device driven industry. The following sections will describe the operation of three specific device structures, polymer field-effect transistors (PFETs),\cite{58, 61} polymer light emitting devices (PLEDs)\cite{50, 62} and polymer photovoltaics (PVs),\cite{59, 63} with an emphasis on the active layer properties, i.e., the $\pi$CP, followed by recent examples taken from the literature.

1.5.1 Polymer Field-Effect Transistors (PFET)

The world's first inorganic transistor was invented in 1947 by Shockley, Bardeen and Brattain and since then, this device has been the subject of intense study for nearly 60 years.\cite{64} The device was fabricated from inorganic semiconductor materials such as silicon and gallium arsenide. Almost 20 years later, the first polymer thin film transistor was reported by Tsumura, Koezuka and Ando.\cite{65} The active material was polythiophene (PT) and was chosen based on its ease of processability as it was electropolymerized directly on to the device structure, as shown in Figure 1.20. Charge is injected into the device from the source electrode and flows to the drain electrode across a channel of active material under a voltage that is applied between the gate and source electrode. Essentially, the gate electrode is responsible for switching the device into an on (current can flow) and off (current does not flow) state. The gate electrode accomplishes this task via an applied electric field that is established between itself and the source. Once established, this field induces a polarization in the insulating dielectric material which, when sufficiently polar, permits the injection
and flow of electric current between the source and drain via an induced conducting channel, as shown in Figure 1.21. Field-effect charge mobilities were measured to be $\sim 10^{-5} \text{ cm}^2/\text{Vs}$. An example of typically shaped organic FET current-voltage ($I$-$V$) curves are shown in Figure 1.22. As shown in Figure 1.22 at low gate voltage, below $-5 \text{ V}$, a very small amount of current can flow between the source and drain electrodes as indicated by the nearly flat I-V curve, however, when gate voltages greater than $-5 \text{ V}$ are applied, charge can be efficiently injected into the channel between the source and drain as indicated by the sharp increase of the curve. When the applied source-drain voltage is sufficiently large the injected current stops increasing and reaches what is called the saturation regime, i.e., the current is nearly constant at the given gate bias regardless of the applied source-drain bias. The slope in this area of the I-V curve is used to measure the field-effect mobility of the active layer material, in this example, pentacene.

Figure 1.20: Cross-sectional view of the first PFET fabricated from electropolymerized PT.
A more recent example of PFETs has been demonstrated by Friend and Sirringhaus using an alternating co-polymer of 9,9'-dioctylfluorene and bithiophene, F8T2, as the semiconducting device material. [67, 68] Conducting polymer electrodes of PEDOT-PSS were inkjet printed to define the source and drain of the device. The electrodes of the conducting polymer ink were isolated
from one another by pre-patterning the substrate surface via conventional photolithographic methods and photoresists. The active material was then deposited on top of the source and drain electrodes followed by deposition of the dielectric material, poly(vinylphenol). Finally, the gate electrode was printed in the same manner as the source and drain electrodes. A schematic diagram of the printed device is shown in Figure 1.23. Because F8T2 has a liquid crystalline (LC) phase, devices were investigated as is after spin casting and were annealed above its nematic LC phase temperature. Above this temperature the microcrystalline domains of the polymer film melt and the material becomes a nematic glass upon quenching. Devices that were annealed showed much higher charge carrier mobilities, between 0.009 – 0.02 cm$^2$/Vs, compared to < 0.001 cm$^2$/Vs for the devices that were not thermally treated. The crystallinity and orientation of active layer polymers in FET applications are incredibly important where the performance of the device is concerned.

Figure 1.23: Schematic diagram of a printed polymer FET.
1.5.2 Polymer Light Emitting Devices (PLED)

Since light emitting devices (LEDs) were first reported in Nature in 1990, polymer LEDs, or PLEDs, have been a topic of intense study.[69, 70] This early device consisted of a PPV active layer sandwiched between a high work-function material such as indium oxide as an anode and a low work-function material such as a very thin layer of aluminum or calcium for a cathode. External quantum device efficiencies as high as 0.05 % were reported, which is representative of the number of photons emitted per number of injected charge carriers. It was proposed that the electroluminescence was the result of a radiative recombination process similar to that observed in photoluminescent studies of the same conjugated polymer. The electroluminescent emission spectrum, which was of similar shape to that of the photoluminescent emission spectrum, was due to a singlet polaron excitation and relaxation, generated from the injection of electrons and holes from their respective electrodes, which migrate toward oppositely charged electrodes and eventually recombined, i.e., emitted light. A schematic of a working PLED showing the positive and negative charge injection, the migration of charge and exciton formation, i.e., association of the injected positive and negative charge, is shown in Figure 1.24.
A more recent example was reported by Friend et al. where they prepared a device consisting of a polymer field-effect transistor driven polymer light-emitting device.[7] The active materials employed for the PFET and PLED were P3HT and MEH-PPV, respectively. Figure 1.25 contains the schematic device structure and a photograph of the operating device. The device they presented was a huge step toward the realization of all-polymer optoelectronic integrated devices such as active-matrix LED displays.
Figure 1.25: a) Profile of the integrated polymer FET and LED. Upper left figure shows the devices position in an active-matrix display. The orientation of the P3HT layer, relative to the dielectric layer and sources are shown on the lower left. b) Photograph of the working device where one of the pixels are emitting. Reprinted with permission from AAAS [7]

1.5.3 Polymer Photovoltaic Devices (PV)

The fact that a solid material was capable of generating electricity upon exposure to sunlight was first realized in the latter half of the 19th century and was later studied in more depth by William Grylls Adams and his student Richard Evans Day.[71] Their experiments with selenium provided the starting point for future studies into this phenomenon, which today, is a huge area of study encompassing scientists from all branches of the physical sciences. By the 1920's, solar cells based on this material were fabricated but were very inefficient, converting only 0.5 % of the sun's light into usable electricity.[71]

Polymer solar cells have been aggressively studied over the last thirty years but the efficiencies of these materials cannot match that of their inorganic counterparts. Inorganic based devices have efficiencies of 10 – 20 % which is considerably higher than the 6 % recently reported by Carroll et al.[72] Despite
the differences in conversion efficiencies, organic based systems offer many advantages over their expensive inorganic counter parts such as: higher absorption coefficients, often $> 10^5$ cm$^{-1}$, which partially compensates for the lower charge mobilities of the organic materials as they can absorb more light, they can be easily processed into films they offer the possibility of structural modification through various synthetic strategies and can cost much less to fabricate.

Devices fabricated with organic active layers generate electricity upon exposure to light in the same manner as the inorganic versions. Generally, when light strikes the device, photoinduced electron transfer occurs in the active layer, followed by the formation of an electron-hole pair (exciton), followed by its dissociation into separate electrons and holes (negative and positive polarons, respectively) and eventual collection at the cathode and anode, respectively. In the first single layer devices,[71] see Figure 1.26a, charge separation only occurred in a very narrow region near the active layer – electrode interface and the devices showed poor conversion efficiencies, near 0.1 %. To increase device performance, bilayer devices were fabricated consisting of an electron donor layer, such as a P3AT[73] or MEH-PPV,[74, 75] and an acceptor layer, such as fullerene ($C_{60}$), see Figure 1.26b. Devices with this device structure showed much better conversion efficiencies, between 1 – 2 %,[71] over the single layer devices but still did not have the efficiencies of inorganic devices. The main problem with this particular device structure was that, as compared to that of the single-layer devices, the interface where charge separation was to
occur, between the donor and acceptor, was still very narrow. As a method to increase the effective surface area within the active layer where photoinduced excitation formation and charge dissociations could occur, films were prepared where there was a homogenous mix of both the donor and acceptor materials, as shown in Figure 1.26c. Upon casting, nanometer sized domains of phase separated donor and acceptor material are observed in the film, on the order of 10 to 20 nm, and facilitated the formation and diffusion of excitons. Thus far, devices with this configuration have shown the best performance using regio regular P3HT as the donor and a fullerene derivative, 3'-phenyl-3'H-cyclopropa[1,9][5,6]fullerene-C_{60}-1_h-3'-butanoic acid methyl ester (PCBM) as the electron acceptor.\[52, 76, 77] In this device structure, because the excitons can more easily dissociate, films can be made thicker and thus there can be more absorption of light, which leads to the increased opportunity for photoinduced electron transfer from P3HT matrix to the PCBM molecules.
Figure 1.26: Various photovoltaic solar cell configurations. a) Single active layer (inorganic or organic), b) bilayer donor-acceptor device and c) bulk heterojunction donor-acceptor blend. Positive and negative charge carriers are represented by (+) and (−), respectively. **Events where the excitation does not charge separate are denoted as "no dissociation".
1.6 Patterning Polymer Films

Present day micro-electronic and opto-electronic devices are heavily dependant on the fabrication method which often requires, at the very least, repeatable micron (\(\mu\text{m}\)) sized resolutions for the deposition of the active materials.[67, 78-90] Today, materials scientists and engineers have a vast selection of patterning techniques to choose from for the spatial deposition of \(\pi\)CPs, but the final choice depends on several material factors, for example, solubility, tolerance to ambient atmosphere, film morphology, post-patterning properties such as luminescence or electrical conductivity and finally, resolution. The actual methods of patterning generally fall into two very broad categories of additive and subtractive processes. Additive processes involve the deposition of an active material in only the areas where it is desired, \textit{i.e.}, inkjet printing,[91] where as a subtractive process involves the deposition of material over a large area followed by the removal of selected material in a given area, \textit{i.e.}, spin coating a film followed by direct laser patterning.[92, 93] As one may expect, an additive process might be more desirable from a conservation of material and cost point of view however, a subtractive process may be more desirable where high throughput is concerned. In conventional device fabrication, patterning is typically accomplished by photolithography, which is a method that uses masks and polymer photoresists, materials that are sensitive to light of very specific, high energy wavelengths, typically < 250 nm.[86] The resist is exposed to light through the masks and initiates a chemical reaction in the film. The chemical reactions change the resists solubility in various solvents. With proper choice of
resist and solvent both positive and negative tone images are possible post-development, as shown in Figure 1.27. However, when conventional photolithographies and photoresist technologies are employed for patterning πCPs, the electronic or optical properties of the conjugated polymer are often disrupted during the photolysis, e.g., photobleaching the πCP.[94] Thus, alternative methods of patterning need to be developed where the spatial deposition of πCPs are concerned.

![Figure 1.27: Positive and negative tone image formation in a photolithographic process.](image)

This section is broken up into four main parts describing a brief selection of patterning methods for πCPs. First, non-photolithographic, non-contact techniques such as inkjet printing[91] will be discussed, followed by non-photolithographic, contact processes such as micro-contact printing (μCP)[87, 95, 96] and nanoimprint lithography (NIL).[90, 96] Photolithographic methods involving chemically amplified photolithography,[97] cross-linking[28, 30] and
photobleaching will then be highlighted. The last section will describe thermal patterning of πCPs using laser light as the localized heating source in ablative and non-ablative processes.

1.6.1 Inkjet Printing π-Conjugated Polymers

The technique of inkjet printing of photo- and electro-active organic materials for electronic and visual display applications can be split up into two distinct categories, continuous mode and “drop-on-demand” mode. An inkjet printer operating in continuous mode pushes a constant flux of a solution of the material through a specially designed printer head where surface tension instabilities are generated in the fluid causing the material to separate into individual droplets. The droplets are directed toward a receiver substrate. Steering of the droplets is accomplished by first charging the droplets electrostatically during the break up and then deflected in a desired direction using a second applied electrostatic field. Drop-on-demand mode delivers droplets of material to a receiver substrate that are produced by pressure waves in the reservoir caused by the oscillation of a piezoelectric crystal positioned behind the orifice nozzle.

The inkjet printing process offers a number of advantages over other lithographic and manufacturing patterning process where the precise deposition of active layer materials are required for electronic and display applications. Some of these advantages are that the process is computer controlled (data driven) and therefore compatible with other technologies such as computer aided design (CAD) programs. Inkjet printing is an additive patterning process where
active material is only placed where it is desired, thereby minimizing product waste and cost. It is a non-contact technique thereby allowing material to be printed on flat and non-planar surfaces.

Inkjet printing has already been demonstrated to be a useful and versatile patterning method for organic based displays and devices. Yang et al. fabricated a series of PLED logos by inkjet printing an aqueous solution of a conducting polymer, PEDOT, on top of an ITO coated substrate.[91] The sandwich structured device was completed by spin casting a second polymer film, poly(2-methoxy-5-2’-ethylhexyloxy)-(1,4-phenylene vinylene) (MEH-PPV), on top of the patterned surface followed by evaporation of a calcium cathode, as shown in Figure 1.28. Only areas where the PEDOT is in contact with the MEH-PPV layer emit light.

![Figure 1.28: Schematic for the fabrication of a single color inkjet printed PLED.](image)

Despite the current level of success inkjet printing has demonstrated, there are some drawbacks to this method of patterning, the foremost problem being the resolution and the need for sub-µm feature sizes. Typically, resolutions obtained from inkjet printing range between 30 and 100 µm. As compared to the
other patterning techniques that will be discussed in the following sections, the factors which contribute to the relatively poor resolution of inkjet printing are variations in surface wetting, non-uniform solvent evaporation, non-uniformity of feature, or a need to "pre-pattern" the receiver substrate (chemical or structural) to contain the active material, as shown in the following example, Figure 1.29, reported by Friend et al. in 2007.[112] In this example the active layer material, poly(alkylfluorene-co-bithiophene), is inkjet printed into holes on a conductive substrate and capped with calcium and aluminum.

![Figure 1.29](image_url)

**Figure 1.29:** Photoluminescent and electroluminescent images of PLEDs prepared using inkjet printing. a) Photoluminescent image of an array of devices under blue-filtered illumination. b) Photoluminescent image under UV excitation. c) Electroluminescent emission from a completed device. Reprinted with permission from [112]. ©2007, American Institute of Physics.

### 1.6.2 Micro-Contact Printing (µCP)

It is desirable that simplified patterning methods are developed which take advantage of the solution processability and film forming properties that µCPs inherently posses and thus, contact techniques such as micro-contact printing have been realized.[84, 87, 95] This "soft lithographic" method offers the
advantages of selective transfer of material to a receiver substrate via the physical contact of an elastomer stamp, which in many cases, is prepared from polydimethylsiloxane (PDMS).

One of the first examples using a PDMS stamp, to selectively modify and pattern a surface, was reported by George Whitesides et al. in 1995.[113] Line patterns of electrochemically polymerized pyrrole were obtained on a gold electrode surface that was pre-patterned with alkanethiol self-assembled monolayers (SAMs) deposited by the μCP technique. As shown in Figure 1.30 the pattern generation occurs between the SAM blocking layers.

![Figure 1.30: Schematic for μCP of SAMs as a method to pattern polypyrrole on a gold surface.](image)

A more recent example of the direct micro-contact patterning of fluorescent conjugated polymers, which contain acid sensitive tetrahydropyran (THP) protected alcohol pendant groups, has been reported.[114, 115] An acidic ink is applied to the surface of a preformed polymer film using a PDMS stamp.
After application of the acidic ink, the films were heated at 185 °C for 15 seconds in air to thermally react the protecting group. Examples of these very luminescent and acid-sensitive polymers are shown in Figure 1.31. Post heating, the films were developed with a solvent mixture of THF and hexanes to remove polymer that had not been exposed to acid, resulting in a negative tone image of the πCP. The patterning and heating process did not destroy the photoluminescence of the polymers, as the emission properties were nearly identical to that of the pristine films.

![Figure 1.31: Examples of a THP functionalized polyfluorene and polyfluorene-co-thiophene.](image)

1.6.3 Nanoimprint Lithography (NIL)

Similar to μCP, nanoimprint lithography (NIL), first reported by Chou et al. in 1995, and offered a flexible, high throughput method of patterning that was hoped to be a solution to reduce the cost of manufacturing features in the micro- and nano-size range while circumventing the increasingly expensive costs of modern photolithographic techniques.[82, 90, 116] The method involves the physical contact of a master stamp onto a polymer film that is often held at a temperature slightly above the materials glass transition temperature (Tg). At
this temperature, the polymer is soft and malleable and thus, after removal of the master, the indented features or pattern of the master remain in the surface. A schematic diagram of the nanoimprinting process is shown in Figure 1.32.

While this seems to be a promising technique for the fabrication of low-cost nanostructures the method is plagued with many problems such as severe sticking of material to the master and a lack of adhesion of material to the substrate, non-uniform transport of the heated imprinted material between stamp features and thus an overall low quality pattern generation.

The aforementioned patterning techniques offer well defined resolutions and reasonably high throughput of patterned surfaces, however, they still do not have the high quality sub-micron resolution capabilities that other techniques can achieve or they partially rely on conventional photolithographic methods in at least one aspect of their patterning process, i.e., production of the master stamp. The following two sections will describe and discuss two methods that use only a conventional photolithographic process and will be explored in more detail.
1.6.4 Photolithography and Chemically Amplified Photolithography

Conventional photolithography is probably the oldest and most well studied method of patterning where photo-sensitive polymer films are patterned with light through a photo-mask.[38, 97] These materials have a specific role in that they are intended to protect the substrate from modification/damage in subsequent patterning/etching steps. Little regard is given to the polymer resist with respect to its electronic or luminescent properties and only the dissolution properties of the polymer are important, whereas the properties of patterned conjugated materials are of utmost importance.

A unique example of a maskless direct-write process for patterning πCPs using a laser assisted photolithographic technique has been reported by Holdcroft and co-workers in 1992 where structures of poly(3-hexylthiophene) were produced with a 442 nm laser.[92] Exposed regions of polymer were rendered insoluble via an intermolecular-radical coupling cross-linking reaction between α-carbons of the hexyl side chain in the presence of oxygen. Figure 1.33 contains a microscope image of the patterned polymer after development. Feature sizes of 4 μm in width could be resolved using this process. The bulk conductivity of patterned polymer was ~ 6 S/cm after oxidative doping with nitrosonium tetrafluoroborate.
Figure 1.33: Conductive patterns of P3HT obtained via a direct-write photolithographic process. The minimum feature size is 4 μm. Reprinted from [92], ©1992, with permission from Elsevier.

Chemically amplified photolithography is a modified version of the conventional photolithography process where the resist polymer has been modified, typically, to contain acid-labile or cross-linking functional groups. The solution of resist material usually contains a catalytic amount of a thermal- or photo-acid generator (TAG or PAG). Upon exposure to light, a photochemical event is initiated and cascades into other kinds of chemical reactions, e.g., cross-linking, deprotection and/or further acid generation.[117-119] Typically, a strong acid is generated by photo-degradation of the PAG and the polymers are converted from a solvent soluble derivative to an insoluble pattern during a post-exposure bake. Acid is further generated as a by-product of the reaction between the decomposed PAG and the resist functional groups. Thus, the reaction is considered to be catalytic with respect to acid generation. Many kinds
of reactions have been reported using this method of patterning such as structural modification, crosslinking, acid-doping/dedoping and photobleaching. Both positive and negative tone images are possible after development.

Chemically amplified photolithographic patterning of a \( \pi \)-conjugated polymer was first reported by Holdcroft \textit{et al.} in 1998, where they demonstrated that negative tone images of an acid-sensitive polythiophene derivative could be obtained with the inclusion of a catalytic amount of a PAG and exposure to 336 nm light through a shadow mask.\cite{38} After heating the film for 3 minutes at 120 \(^\circ\)C, images with features as small as 15 \( \mu \)m were obtained.

A more recent example of patterning conjugated polymers using chemically amplified photolithography has been reported by Meerholz \textit{et al.}, where they employed electroluminescent polyfluorene derivatives with photoresist properties. These can be photochemically cured to yield insoluble polymer patterns.\cite{35} The polymers are decorated with cross-linking oxetane pendant groups, which, when exposed to acid and mild heating, form a negative tone polymer image. Using this method of patterning, red-green-blue (RGB) LEDs have been fabricated with electroluminescence efficiencies on par with devices fabricated containing small-molecule emissive layers. \textbf{Figure 1.34} contains a photograph of an operating RGB device patterned using this chemically amplified photolithographic polymer system.
1.6.5 Photobleaching

Similar to the processes involved in the photolithography of photoresists, selective area photobleaching of polymer films through masks has been shown to be an effective and simple method for patterning negative and positive tone images for both conductive and light emitting applications. The method takes advantage of conjugated polymers tendency to photo-oxidatively bleach while exposed to light in the presence of oxygen.[120, 121] For an example that does not involve oxygen, cis-1,4-polybutadiene, an insulating and non-luminescent polymer was shown to undergo an 8 orders of magnitude change in conductivity, increasing from $10^{-13}$ to $\sim 10^{-5}$ S/cm, and became photoluminescent after exposure of UV-light through a photomask (photoinduced isomerisation – cis to trans) and subsequent treatment with $I_2$. Another example is reported by Weder et al. where they photobleached selected areas of a luminescent polymer film of a poly(2,5-dialk oxy-o-p-phenylene ethylene) derivative, EHO-OPPE, blended with
non-luminescent ultra-high molecular weight polyethylene (UHMW-PE), through a photomask. Luminescence from the irradiated areas decreased to < 9% of its original value. **Figure 1.35** contains a photoluminescent micrograph of an image obtained using this method of patterning.

![Image of Hermann Staudinger](image)

**Figure 1.35:** Photoluminescent image of the founder of macromolecular science, Hermann Staudinger, produced by selective area photobleaching of a EHO-OPPE/UHMW-PE polymer film. Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA. ©2001 [98]

### 1.6.6 Photothermal Lithography (ablative processes)

Many of the studies that have been conducted on the interactions of laser light and organic surfaces have been motivated, not by patterning, but because of its potential application in optical recording, *i.e.*, photographic films, photoresists, magneto-optic devices, *etc.*. Studies of this nature include translational fluid motion upon laser exposure,[122] laser-induced ablation and deposition of small molecules and πCPs,[103, 123, 124] and the calculations of
temperature changes during laser exposure.[125-128] For example Friend et al. demonstrated that thin films and photoluminescent gratings can be produced from ablated drop cast films of poly(p-phenylenvinylene) (PPV) and PPV precursors.[103] The absorption and photoluminescent characteristics of the ablated PPV films showed similar spectral profiles to the pristine, spin cast, PPV film indicating that the ablation process does not completely destroy the material as shown in Figure 1.36. Interestingly, the ablated films exhibited a blue shifted absorption profile relative to the pristine material indicating that the conjugation length has been shortened and yet the emission peaks remain at almost the same position as the spin cast films. They believe that this is due to a fraction of the longer conjugation segments that survive the ablation process, and that emission occurs from these longer segments. Further analysis of the films via FT-IR spectroscopy showed that the ablated material had a similar composition to the pristine PPV.

Figure 1.36: a) UV-vis absorption and b) photoluminescent spectra of ablated PPV, PPV precursor and spin cast films. Reprinted from [103], ©1999, with permission from Elsevier.
Photons directed toward the surface of a material are absorbed to a depth that is defined by the Beer-Lambert Law. The Beer-Lambert Law relates the absorbance, $A$, of a sample to its concentration, $C$, pathlength, $b$, and extinction coefficient, $\varepsilon$, according to $A = Cb\varepsilon$. In the case of thin films, the Beer-Lambert Law can also be expressed in terms of the intensity of light that passes ($I$) through a layer of sample with a given thickness ($t$) according to $I = I_0e^{(\beta t)}$, where $I_0$ is the initial light intensity and $\beta$ is the absorption coefficient. Thus, the depth of light penetration can be very shallow, i.e., a strongly absorbing material with a high value of $\varepsilon$ and $\beta$, or very deep penetration, i.e., a weakly absorbing material. How strongly a given material absorbs is dependant on the film thickness, wavelength of the exposing light and the absorption characteristics of the material, i.e., its band gap. Upon absorption of laser light at a specific wavelength, fluence and power, two events can occur. If UV light is employed the excitation process is typically electronic in nature and in the event of ablation the reaction is purely photochemical, i.e., ionization followed by decomposition. However, if the system undergoes an internal conversion process to an excited vibrational ground state then ablation is believed to occur via a purely thermal degradation process.[105] In this photothermal process laser photons are only considered as a source of thermal energy. Regardless of pathway, it is believed that the decomposition products are similar in both cases, i.e., whether an electronic decomposition or a thermal decomposition mechanism. An example of ablative laser patterning of polystyrene and polycarbonate substrates for use in miniaturized liquid-handling systems was reported by Girault et al.[129]
It is often necessary for ablative (and some nonablative) systems to incorporate a light sensitizing dye because a given material may not have a significant absorption profile at the wavelength of the exposure source. The interaction of laser light and dye-polymer systems has been investigated extensively over the last 40 years.\[105\] For example, polymer films of PMMA were molecularly doped with a porphyrin and were exposed to laser light through a copper wire mask. An irreversible swelling of the polymer was observed in the exposed areas at low laser dosage. Features were found to protrude from the surface at the lower dosages due to the release of trapped gases, however, at higher laser dosages ablation of material was observed, as grooves were generated in the polymer.\[130\]

1.6.7 Photothermal Lithography (non-ablative processes)

Examples of direct and non-ablative photothermal patterning of conjugated polymers are rare in the literature, often because of the proprietary nature of the work and organizations perusing the idea, despite the many advantages that thermal patterning offers such as compatibility with current printing technologies, multi-layer deposition and high throughput over wide areas with reasonable micron sized resolutions. Surprisingly, most of what is known about the laser induced heating, transfer or structural modification of organic films comes from the Print and Photographic industries in the study of computer-to-plate (CtP) transfer of graphics and data using thermal lasers (IR and NIR). Since the introduction of the first thermal plate in 1996, this method of printing has become the standard in the transfer of information from one medium to
another. The process is based on one fundamental principle, that one can induce lithographic changes in a given polymer film, such as solubility or hydrophilicity, by locally increasing the temperature of the system. The idea exploits a polymer’s inherent low thermal conductivity and inability to dissipate thermal energy quickly during laser heating.[131]

An example of indirect thermal patterning has been reported by Blanchet et al. where they describe a method for the transfer of pixels from a donor conjugated polymer film of polyaniline, containing single wall carbon nanotubes, to a flexible receiver substrate which are held in direct contact with each other via a vacuum.[132] A 780 nm IR laser is focused from the backside of the donor on to a very thin light absorbing layer of metal contained inside the donor layer and when heated with the laser, thermally decomposes surrounding organic material into gaseous products and thus, propel the conjugated polymer film forward onto the receiver substrate, as shown in Figure 1.37. The authors also demonstrate that multiple organic layers of active materials can be sequentially deposited using this technique in the fabrication of multilayer devices, however time consuming alignments of subsequent layers are necessary before patterning the next layer. Arrays of thermally printed transistors were prepared at a throughput of 1000 cm² / min with effective charge mobilities of 0.3 cm² / Vs and on/off ratios > 1000.
1.7 Laser Processing and Heat Generation

As briefly discussed in the previous sections concerning patterning conjugated polymers, upon absorption of laser light, an exposed surface can undergo either a localized temperature rise, ablation or a combination of both processes as shown in Figure 1.38. Heat-treatment of an exposed surface results when the intensity of the laser is below the vaporization threshold of the material being exposed, \( I < I_v \), as shown in Figure 1.38a. If the intensity of the light is above the threshold of vaporization then the process is often ablative in nature, \( I > I_v \), as discussed in the previous section. Similarly, a more detailed diagram has been reported by Lippert et al. where they propose a very
complicated qualitative mechanism route followed by laser exposed polymer-dye surfaces, as shown in Figure 1.39.[101] The diagram describes the possible phenomenon which can be observed in a given system, dependant on the absorption and thermal properties of the dopant and polymer matrix, wavelength of the laser, fluence, exposure time, etc.. Typically, laser processing (in non-ablative systems) of such materials is performed using infrared laser sources as the excitation energy that is generated is dissipated as heat and does so over a time scale that is very short, relative to the time scales of other excitation processes.[133] Laser induced processing of conjugated materials offers a single-step method for the direct patterning of a film, however, determination of the temperatures reached using such methods can be quite difficult.

Figure 1.38: Schematic for a) laser heating and b) laser ablation of a material surface.
Figure 1.39: Qualitative representation of the possible phenomenon in laser exposed dye-polymer films. Based on information presented in [101]

Quantitatively, the relationship between the flow of heat in a system \( (q) \) and the change in temperature of the system \( (T) \) can be expressed as **Equation 1-1**, where \( C_p \) is the heat capacity of the system at constant pressure.

\[
dq = C_p \, dT
\]

(eq. 1-1)

The heat capacity is characteristic of the given material and is proportional to the amount of material being heated. To remove this dependence on the quantity of material we can describe the heat capacity of one gram of the material, called the specific heat \( (c) \). The ability of a system to transmit or dissipate a sudden
increase in the amount of heat it experiences is dependant on several material properties such as density ($\rho$), thermal conductivity ($k$) and thermal diffusivity ($\alpha$) which can be obtained according to Equation 1-2.

$$\alpha = k / \rho C_p$$  
(eq. 1-2)

Thermal conductivity is a transport property and is a measure of how effectively heat can penetrate a material from an area of higher temperature to an area of lower temperature. Thermal diffusivity is a measure of how fast a given material can transmit heat to its immediate surroundings. For example, a high value for diffusivity indicates that a system can rapidly pass its heat to the surroundings, as shown in Figure 1.40. However, the most significant complicating factor in attempting to quantify the change in temperature of laser heated materials originates from the fact that all of the aforementioned material properties are temperature dependant, i.e., the thermal properties vary with the changing temperature!
1.8 Research Perspective and Thesis Outline

π-Conjugated polymers exhibit unique electrical and luminescent properties that make them attractive candidates as active materials in a wide variety of microelectronic and light-emitting devices. In all of these applications, the precise spatial deposition of the active material is crucial for the device performance. Also, after patterning and subsequent development, it is imperative that the πCP retains its chemical and structural properties. Moreover, it has been shown that current photolithographic and physical contact patterning methods have various limitations, for example damaging the πCP through photo-oxidation processes or the processes/techniques simply cannot achieve the
desired resolutions necessary in present day device fabrication. Advances through the synthesis of novel and patternable polymers, such as those reported by Holdcroft et al.[38, 39, 114, 134] and Meerholz et al.[34, 35, 135] have initiated the exploration of new avenues involving these materials while employing new methods of spatial deposition of conjugated polymers. It has been reported that these materials can be patterned using various techniques such as conventional photolithographic methods, as well as through less conventional methods such as μ-contact printing, while still retaining their emission properties as determined from their photo- and electro-luminescent spectra. Investigating these materials in novel patterning methods, such as direct thermal patterning, is warranted because the method offers a fast, reliable, high resolution and high-throughput printing method which is already implemented by the graphic arts industry, and thus, the technology need not be newly integrated into present day fabrication facilities.

This thesis explores a novel, direct patterning method for the spatial deposition of π-conjugated polymers using NIR laser light as a localized heating source and characterization of the material properties post processing. Previously studied polythiophene and polyfluorene derivatives containing THP protected alcohols and a novel crosslinking polyfluorene were prepared and employed as model polymers for this study due to their ease of processability, structural versatility, and interesting electrical and photo physical properties. Chapter Two of this thesis describes the proof-of-concept demonstration of thermal patterning of a polythiophene derivative using NIR laser light. The
patterning methodology presented in this chapter yielded polymer patterns with compromised optical properties, thus alternative methodologies were explored and are described and discussed in subsequent chapters. Chapters Three and Four describe thermal patterning of polyfluorene and polythiophene derivatives in bilayered polymer films with the emphasis on the material properties, i.e., fluorescence and conductivity, respectively, post-patterning and development. Chapter Five reports on the synthesis, characterization and patterning of a highly fluorescent novel polyfluorene containing pendant cross-linking functional groups, demonstrating that this variation of patterning, i.e., NIR direct thermal imaging, is versatile and not specific to only one type of functional group. Chapter Six summarizes this body of work and comments briefly on future opportunities and material considerations.
CHAPTER 2: DIRECT THERMAL PATTERNING OF SINGLE LAYER NIR DYE - \(\pi\)-CONJUGATED POLYMER FILMS

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Note: Synthetic portions were performed by Dr. Jianfei Yu.

2.1 Introduction

The advancement of high performance display technology is central to the growth of information technology, particularly in the electronic device sector. The next generation of displays must be thinner, more energy efficient, full color, high resolution, and less expensive. In this regard many research organizations are paying close attention to developments of \(\pi\)-conjugated polymers, \(\pi\)CPs, and are aggressively pursuing research programs aimed at speeding up their implementation. \(\pi\)CPs possess a number of important electronic properties that make them interesting. In the neutral form they are semiconductors and their conductivity can be reversibly modulated by application of an electric field - which makes them attractive candidates as active materials in organic field-effect transistors (OFETs).[61, 136, 137] Many \(\pi\)CPs are highly luminescent and are sought after as active materials in electroluminescent devices. In the oxidatively doped form, they are electronically conductive - thus potentially serving as
conductive films, transparent conductive coatings, or interconnects in novel electronic circuitry.

Organic semiconductors are different from conventional inorganic semiconductors: processing is simpler, e.g., spin coating, evaporation or printing;[67, 76, 138] there is good compatibility with substrates including flexible plastics; and there are excellent opportunities for structural diversity. Nevertheless, there are drawbacks. In the case of OFETs there is a need to improve charge mobility and reliability; in organic light emitting devices (OLEDs) the quest is for stable, highly electroluminescent materials with tunable emission; in electronic interconnects, higher stability of the oxidatively doped state is required. Rapid advances are being made in the development of materials particularly for OFETs and OLEDs with the expectation that wide commercial application of these devices may soon be realized. A critical, common concern in this technology, however, is device fabrication, requiring reproducible deposition of active material with micron (10 - 100 μm) resolution.

Techniques for patterning πCPs generally fall into either reactive or non-reactive categories. The former include area-selected electropolymerization on patterned self-assembled monolayers, direct writing using electrochemical scanning probe microscopy, or photochemical patterning such as photolithography, photo-ablation and photo-bleaching, which are based on the specific reactivity of a particular conjugated system. Non-reactive patterning methods include screen-printing, soft lithography and inkjet printing. The latter
are generic techniques that make use of preformed polymers and do not rely on a material’s reactivity.

Photolithography of πCPs differs from conventional lithography. In the latter there is usually no consideration of the intrinsic electronic property of the polymer resist because it usually plays no active role in device operation; in contrast, πCPs must retain their electronic and optical properties in order for them to function as intended. Since photolithography often involves direct irradiation of the conjugated polymer, the material’s photochemistry plays a pivotal role. Several reviews on the subject exist, and many different classes of polymer have been studied. These include polyacetylene, trans-1,4-polybutadiene, poly(p-phenylene sulfide), poly(p-phenylene vinylene), polyanilines, and polythiophenes. However, it has been shown that direct photopatterning frequently leads to photooxidation of the polymer. Photooxidation, however slight, has a deleterious effect on its properties, in particular, electroluminescence. πCPs have thus been designed to be more photosensitive, from the perspective of patterning, by attaching labile moieties to the main chain. A drawback however, is that πCPs are highly absorbing in the UV-vis region: a property that limits imaging to thin films.

It may be that photochemical patterning is too complex and too expensive in the short term for mass fabrication of polymer-based electronics and that a more desirable patterning methodology is needed that is technically simpler and more versatile. Indeed, many πCPs are aptly suited for simpler patterning techniques, such as screen printing, by virtue of their solubility. Thus reports of
all-polymer field effect transistors fabricated by printing techniques have generated considerable interest. [61, 141, 142] The current drawback of screen printing, however, appears to be lack of resolution and reproducibility. The desirable <10 μm resolution preferred for many devices is not easily achievable. Furthermore, since many conjugated polymers are not highly soluble, their solution viscosity may be too low. In a novel variation, micro-contact printing (μCP)[115, 143] has been used to deposit a soluble poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate conducting polymer complex (PEDOT-PSS) directly onto ITO and gold electrodes to yield conducting polymer lines with 100 μm features.[144] Another promising technique, inkjet printing, relies on the steering of material-containing droplets discharged from a nozzle and their contained impact and solidification onto substrates. The impinging droplet must rapidly wet the substrate, bind, and evaporate, before lateral displacement occurs.[67, 138] In order to restrict the spreading of droplets upon impact, and thus achieve higher resolution, substrates have been selectively patterned so as to possess hydrophobic and hydrophilic surface regions.

A variety of techniques are available for patterning π-conjugated polymers. The technique of choice depends on the material under consideration, the substrate, and the intended application. Both photolithographic and non-reactive techniques (covered in section 1.6) may be appropriate, although much has been speculated on the unique opportunity to pattern conjugated materials at low cost using the latter by virtue of the fact that solutions of the active material can be prepared. Pattern resolution generally increases on going from screen printing,
to inkjet printing, to soft lithographic techniques. All three techniques may or may
not be acceptable in the very near future in patterning mass-produced
components for light emitting devices, for example. Furthermore, it can be
argued that it is unlikely that non-reactive techniques can compete with
photolithographic techniques in terms of resolution or reproducibility; hence,
despite the apparent simplicity of printing techniques, photo-patterning
techniques should not be dismissed where the patterning of πCPs is concerned.

Notably, the technique used to mass-produce sub-10 μm pixels of organic
material is found in the graphic arts industry and uses the concept of direct
thermal imaging.[145] The fundamental concepts behind thermal patterning are
well documented,[146, 147] and have been perfected by several companies.
Currently, it involves the delivery of near infrared (NIR) light pulses from an
inorganic diode laser onto a polymer film containing a NIR-absorbing dye, as
shown in Figure 2.1. Typically, the polymer does not absorb the irradiation but
the dye, upon doing so, converts the NIR photons into heat by internal
conversion.[148, 149] The temperature of the irradiated regions rises rapidly
over a period of microseconds, which initiates a highly localized chemical or
physical change in the polymer. The local spot temperature can be controlled up
to several hundreds of degrees by control of the incident power and absorption
cross-section. Sophisticated optics deliver hundreds of NIR laser beams
simultaneously so that large formats may be scanned very rapidly. The
resolution of the image is typically 5 – 10 μm, and even smaller with more
sophisticated equipment. In current lithographic printing technology, printing
plates are composed of a thin layer of thermal or photosensitive hydrophobic polymer film and a hydrophilic substrate. The solubility of the polymer films changes in a region where the NIR pulse strikes and can be dissolved in a developing solution. The finished plate bears a hydrophobic image on a hydrophilic substrate. When ink is applied it adheres to the hydrophobic image. Transfer of the ink to paper or another suitable medium results in an image of photographic resolution. A type of thermal patterning of a πCP has already been reported wherein an organic donor film and acceptor substrate are brought into physical contact and a laser beam is directed at the backside of the donor film so as to propel the organic material toward the acceptor substrate.\footnote{132} After laser exposure is complete, the donor layer is removed, leaving a negative-tone pattern of organic material, as shown in Figure 1.37.

![Figure 2.1: A typical schematic for industrial direct thermal patterning.](image)

Previously, the photolithography of polythiophene derivatives was reported and that tetrahydropyranyl (THP) functionalized polymers could be catalytically
deprotected in the presence of acid in the solid state with close to 100% efficiency according to the reaction scheme shown in Figure 2.2.[39] The polymer, poly(3-(2-(2-tetrahydropyranoxy)ethyl)thiophene) (PTHPET), is thermally stable up to ~ 220 °C whereupon a 30% weight loss is observed between 220 and 275 °C attributed to the volatilization of dihydropyran (DHP). The weight loss is consistent with the deprotection scheme shown below in Figure 2.2. In conjunction with photoacid generators, chemically amplified photolithography of πCPs was also demonstrated.[39] In this chapter, thermal reaction of PTHPET induced by NIR irradiation is studied and direct thermal patterning of πCPs in which a soluble, thermally reactive polymer is converted to an insoluble polymer is demonstrated, as shown schematically in Figure 2.3.

*This is the first demonstration of patterning πCPs using this novel approach.* The necessity of incorporating a NIR dye to achieve local heating and the resulting properties of the polymers are described together with a discussion on the potential of direct thermal imaging as a high throughput method for patterning πCPs. The NIR dye used in this study is shown in Figure 2.4.

![Figure 2.2: Thermolytic reaction scheme of PTHPET](image)

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2.2 Results and Discussion

2.2.1 UV-vis Absorption Spectroscopy of PTHPET-NIR Dye Blends

The UV-vis-NIR absorption spectrum of an ~80 nm thick film of PTHPET is shown in Figure 2.5. While the optical density at $\lambda_{\text{max}}$ 463 nm is 0.42 (38% transmittance), the absorbance of the polymer at 830 nm is <0.02 which is equivalent to >95% transmittance. The absorbance of this polymer is negligible at wavelengths >650 nm and is therefore unlikely to undergo localized heating upon irradiation with 830 nm NIR irradiation - in fact, all attempts to thermally deprotect the neat polymer using 830 nm irradiation were unsuccessful.
In order to achieve local heating with a NIR laser, PTHPET was molecularly doped with an NIR dye so that the optical density of the dye at this wavelength provides a significant but uniform absorption cross section. The NIR dye was chosen based on its physical and chemical properties: the dye is soluble in both chloroform and methanol, has a strong absorption profile between 650 and 900 nm with absorption peaks at 750 nm and 850 nm ($\varepsilon = 250,000 \text{ M}^{-1}\text{cm}^{-1}$ at 830 nm in chloroform). An absorption spectrum of the NIR dye dissolved in a p(HEMA) film is shown in Figure 2.5. P(HEMA) was employed as a polymer support for the NIR dye solely for the purposes of obtaining a UV-vis-NIR absorption spectrum as the dye did not form uniform spin- or drop-cast films from solution. It should also be noted that the dye also exhibits a relatively weak absorption near 410 nm and 450 nm which overlaps with the absorption spectra of PTHPET.

The UV-vis-NIR absorption spectra of PTHPET/NIR dye blends (mole ratio 2:1 based on the thienyl unit) spin cast from a chloroform solution is shown in Figure 2.6. $\lambda_{\text{max}}$ associated with the polymer (~450 nm) is blue-shifted with respect to the pristine polymer by ~10 nm. Weak absorption peaks of the NIR dye are visible at ~410 nm and ~450 nm as shoulders.
Figure 2.5: UV-vis absorption spectra of a pristine p(HEMA) film, a p(HEMA)/NIR dye blend and pristine PTHPET.

Figure 2.6: UV-vis absorption spectra of PTHPET-NIR dye blends of varying thickness. Films contain ~ 32 mol% NIR dye.
2.2.2 Pre-Patterning Thermal Characteristics of PTHPET-NIR dye Films

Figure 2.7 shows thermogravimetric analysis curves for PTHPET (black plot) and PTHPET-NIR dye blends (red shaded plots). PTHPET was found to undergo a ~ 36% loss in total mass at ~ 225 °C. This is consistent with the expected weight loss (40%) of THP via the release of dihydropyran. In the presence of NIR dye (~ 39 mol%), PTHPET undergoes a thermal reaction at ~ 165 °C as observed from Figure 2.7 (pink line). The experimentally observed decrease in mass corresponding to loss of dihydropyran is 15%, which is consistent with the theoretical value of ~ 16%. The NIR dye itself thermally decomposes above 200 °C (green plot), hence, the dye does not prevent thermal reaction of the conjugated polymer, rather, it lowers the temperature of the reaction, possibly by increasing the free volume of the polymer.[39] To further investigate the presence of the NIR dye on the deprotection temperature of PTHPET, blends of polymer with varying amounts of NIR dye were prepared. The deprotection temperature of PTHPET was found to decrease substantially, from 225 °C to ~190 °C with only the addition of 4.6 mol% NIR dye, relative to the pristine polymer. Increasing the dye content further, from 4.6 mol% to 11.6 and 39.0 mol%, also shifted the deprotection temperatures to lower values, 180 °C and 165 °C, respectively, but not to the same extent as the 4.6 mol% dye content blend, as shown in Figure 2.8.
Figure 2.7: TGA thermograms of neat PTHPET (black), neat NIR dye (green) and PTHPET-NIR dye blends between 4.6 to 39.0 mol% NIR dye (red shaded plots) under ambient atmosphere. Heating rate 5 °C/min.

Figure 2.8: Change in deprotection temperature of PTHPET in the presence of varying amounts of NIR dye.
The thermal reaction of PTHPET was verified using variable temperature FT-IR and the corresponding spectra can be found in Figure 2.9a and b. The evolution of FT-IR spectra for PTHPET films with increasing temperature, correlates well with the information obtained from TGA experiments (see black plot in Figure 2.7) in that signals indicating the presence of OH groups (3400 – 3600 cm\(^{-1}\)) are absent at 190 °C but present upon heating the film to 240 °C. Also, C-H stretching signals found at \(\sim\) 2800 cm\(^{-1}\) are greatly diminished in intensity which is likely due to the loss of dihydropyran. FT-IR signals attributed to THP, found at 1200 cm\(^{-1}\), 1150 cm\(^{-1}\) (C–O–C antisymmetric stretch) and 650 cm\(^{-1}\) (O–C–O bending), also diminish in intensity at 240 °C, which also supports thermolysis of the polymer and loss of dihydropyran. Due to increased signal broadening in the finger-print region at 240 °C, precise assignments for signals attributed to THP are difficult to assign. In the presence of NIR dye, the emergence of a broad OH peak at \(\sim\) 3450 cm\(^{-1}\) at \(\sim\) 170 °C (Figure 2.9b) is consistent with the lower temperature of thermal reaction caused by the dye as observed in the thermogravimetric analysis discussed previously.
Figure 2.9: (a) Variable temperature FT-IR of PTHPET at 30 °C, 190 °C and 240 °C and (b) of a PTHPET-NIR Dye blend film at 30 °C, 150 °C and 175 °C. Under ambient atmosphere. NIR dye content was ~ 32 mol%.
2.2.3 Contact Angles of PTHPET Films

Neat films of PTHPET heated to 240 °C, and composite films of PTHPET-NIR dye heated to 180 °C are rendered completely insoluble in organic solvents, whereas the unheated films are readily re-dissolvable. The reason for the change in solubility has been described previously[39] and is due to the loss of the bulky THP group, the increased H-bonding between polymer chains as a result of the formation of side chain hydroxyl groups, and the length of the hydroxyethyl side chains which are too short to solubilize a 2,5-linked polythienyl main chain. The change in polarity of the films due to the presence of the hydroxyl groups following thermal reaction is confirmed by the change in contact angle of water droplets on the surface from 90.7 ± 2.9° for pristine PTHPET films to 44.9 ± 1.5° for a PTHPET film heated above its deprotection temperature.

2.2.4 Patterning Single Layer PTHPET-NIR Dye Films

With the knowledge that the presence of the NIR dye in the PTHPET film results in a significant absorbance at 830 nm, that the polymer undergoes thermal reaction at < 200 °C, and that resulting polymer films are rendered insoluble, films of PTHPET containing NIR dye were exposed to 830 nm irradiation from a portable 830 nm test laser and a Kodak NIR flat bed imaging laser scanner. Test films of PTHPET and NIR dye were prepared and examined to obtain a broad understanding of the laser patterning conditions using the portable laser with an average spot diameter size of 100 μm. The average laser power was 0.68 W and the average laser scan speed was 0.5 m/s. The combination of laser power and scan speed determined the dosage striking the
surface. The mass ratio of PTHPET to NIR dye in solution was held constant at 0.88 (w/w) and thin films were spin cast at the same rotation rate. Table 2.1 summarizes the experimental data and observations. As can be seen from Table 2.1, the optical density (OD) at 830 nm increases with increasing film thickness. Surface profiles were obtained for each polymer-dye film after laser exposure and before film development with methanol and THF, as shown in the blue shaded column of Table 2.1. As the films thickness and OD at 830 nm increased so too did the trench depth profiles measured along the surface of the exposed areas of films, increasing from ~25 nm at the lowest OD, of 0.458, to ~137 nm at the highest OD, of 1.376. The observed increasing trench depth is hypothesized to be the result of higher temperatures reached at the surface of the film during laser exposure due to the longer pathlength of the thicker films and thus, higher optical densities of NIR dye. Material removed from the surface is believed to be primarily thermally decomposed NIR dye based on the fact that a significant absorption decrease is observed for the NIR dye between 600 and 900 nm, however, very little change in absorption of PTHPET is observed near 460 nm, as shown in Figure 2.10. As mentioned in section 2.2.1, the overlap of NIR dye at shorter wavelengths, i.e., ~ 450 nm, makes a more precise assignment of the $\lambda_{\text{max}}$ of PTHPET difficult. Developing films with methanol removes NIR dye from the conjugated polymer film as indicated by the significant decrease in absorption between 600 and 900 nm, as shown in Table 2.1. Surface profiles of methanol developed films also exhibited evidence of trenches in the film, as shown in the red shaded column of Table 2.1, thus ablation of the
conjugated polymer cannot be ruled out. Developing the test films with THF removed unexposed polymer resulting in a negative tone image of \( \pi \)CP. Pattern heights of imaged polymer were measured and found to be of consistent height across a given film, except for Film 1, highlighted in green in Table 2.1. It is believed that the thickness and OD of this sample was insufficient to generate an adequate temperature rise in the film to facilitate thermal deprotection of the polymer. Pattern heights measured for Films 2 through 4 were found to be consistent and only varied slightly in height after THF development as indicated by the relatively low standard deviation in the pattern height measurement.

Table 2.1: Profilometric data for single layer PTHPET-NIR dye blends.

<table>
<thead>
<tr>
<th>Film</th>
<th>thickness / nm</th>
<th>abs: 830 nm</th>
<th>post exposure surface trench / nm</th>
<th>post methanol abs: 830 nm</th>
<th>post methanol surface trench / nm</th>
<th>pattern height / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>0.458</td>
<td>25 ± 2</td>
<td>0.024</td>
<td>n/a</td>
<td>13 ± 5</td>
</tr>
<tr>
<td>2</td>
<td>134</td>
<td>0.804</td>
<td>62 ± 4</td>
<td>0.034</td>
<td>22 ± 2</td>
<td>43 ± 1</td>
</tr>
<tr>
<td>3</td>
<td>174</td>
<td>1.053</td>
<td>95 ± 7</td>
<td>0.046</td>
<td>33 ± 2</td>
<td>51 ± 1</td>
</tr>
<tr>
<td>4</td>
<td>238</td>
<td>1.376</td>
<td>137 ± 3</td>
<td>0.072</td>
<td>43 ± 4</td>
<td>70 ± 2</td>
</tr>
</tbody>
</table>

1: Surface profiles, after methanol development, were not measured for this sample.
Figure 2.10: Absorption changes of the conjugated polymer and NIR dye in laser exposed films. Average laser dosage was 1468 mJ/cm².

Preliminary results for patterning THP-containing πCPs were successful and thus patterns of PTHPET were also obtained using a more sophisticated NIR flat bed imaging laser scanner with a spot size of ~5 μm in diameter. Laser power was varied between 12 and 20 W. The laser scan speed across the surface of a sample was varied between 0.3 m/s and 0.7 m/s. Irradiated films were developed by rinsing with methanol and THF. Figure 2.11a shows optical micrographs of developed films. Feature sizes range from 50 to 280 μm in length and 11 to 45 μm in width. Line spacings between patterned polymer are as small as 10 μm and were easily resolved. Figure 2.11b shows an enlargement of the image showing the quality of a 10 μm resolution pattern. Figure 2.11c shows pixilated patterns of varying density – such variations in density are the basis for
the formation of photographic quality images. The images illustrated were obtained with the laser operating at 20 W and a scan speed of 0.6 m/s, so that the incident laser energy was $\sim 600 \text{ mJ/cm}^2$. Line edge sharpness as well as corners with near-right angles are maintained when laser scan speeds are held constant at rates as high as 0.6 m/s. To put the rapidity of this image process in context, an area of letter sized sheet may be imaged with 10 $\mu$m resolution in 10 – 20 s. Limitations of the imaging process are as follows: While maintaining a constant laser power at 23 W and increasing laser scan speeds from 0.3 to 0.7 m/s, (corresponding laser dosages were 1617 to 693 mJ/cm$^2$), respectively, developed patterns became distorted (see Figure 2.12). Patterns of PTHPET were successfully obtained with laser dosages as low as 480 mJ/cm$^2$ however image quality was poor. In general, for the conditions and compositions described in this chapter, exposing the film to laser fluences below 500 mJ/cm$^2$ gave poor quality images presumably due to insufficient heating of the polymer. Successfully patterned films required a high NIR dye content with a dye absorbance between 0.7 [20% T] and 0.8 [16% T] at 830 nm.
Figure 2.11: Bright field micrographs of a patterned film of PTHPET and NIR dye (32 mol%). (a) Line and pixelated structures (Inset: surface profile), (b) higher magnification (c) 50 μm pixelated structures. Incident laser energy was ~ 600 mJ/cm².
A graph comparing vertically orientated line thicknesses, as shown in Figure 2.11a, to laser dosage is shown in Figure 2.13. Widths of the patterned lines correspond to the computer aided drafting (CAD) template and range between 10 to 50 μm. Vertical lines of PTHPET were obtained with a constant laser power (23 W) and varying laser scan speeds between 0.3 to 0.7 m/s. The corresponding laser dosages can be read from the x-axis of Figure 2.13. Patterned lines of PTHPET that were less than 15 μm wide exhibited poor pattern generation between laser dosages of 600 to 1000 mJ/cm² as the measured patterned heights were very low, < 40 nm, as compared to the pattern heights obtained where feature widths were > 15 μm. Pattern thicknesses that were measured for features with widths > 15 μm exhibited consistent heights.
within error, between 45 to 55 nm, across the given dosage range, 1000 to 1600 mJ/cm². At the lower laser dosages, 600 – 1000 mJ/cm², which corresponds to laser scan speeds between 0.7 to 0.5 m/s and a laser power of 23 W, it is possible that there was insufficient heating due to the reduced surface area, i.e., < 15 μm wide features, as compared to the wider features (> 15 μm in width), and therefore there was poor and inconsistent pattern generation in the polymer film. In other words, the wider the exposure area of a patterned feature the more consistent was the pattern transfer.

![Figure 2.13: PTHPET pattern widths and vertical line thicknesses are shown versus laser dosage. Pattern widths are based on the pre-selected CAD template feature sizes. Laser power was 23 W and laser scan speeds were 0.3 to 0.7 m/s. Polymer line structures (dark areas) are shown as insets.](image-url)

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**Figure 2.13:** PTHPET pattern widths and vertical line thicknesses are shown versus laser dosage. Pattern widths are based on the pre-selected CAD template feature sizes. Laser power was 23 W and laser scan speeds were 0.3 to 0.7 m/s. Polymer line structures (dark areas) are shown as insets.
2.2.5 Investigation of Acid Generation in NIR Dye Containing Films

A relevant question concerning these patterning studies is whether or not the thermal imaging reaction is acid catalyzed. Previous studies[115] have shown that > 5 mol% of acid (camphorsulfonic acid) is needed to adequately deprotect PTHPET. Thus, based on the amount of PTHPET employed in the direct thermal patterning experiments (~ 80 nm thick films), the minimum quantity of acid required for pattern transfer is ~ 2.5x10^{-6} mol. To investigate the possibility that acid was inadvertently introduced into the film upon addition of the NIR dye, an experiment was devised and carried out using an acid sensitive probe, 2-phenylquinoline (2PO), which, in the presence of acid, exhibits a strong UV-vis absorption increase at 344 nm.[150] UV-vis spectra of a solution of 2PO in the presence of various concentrations of CSA and composite films containing NIR dye, p(HEMA), PTHPET and 2PO, are shown in Figure 2.14 and Figure 2.15, respectively. As shown in Figure 2.14, as the acid concentration increases the absorption peak located at 344 nm also increases. In test films consisting of the probe and camphorsulfonic acid in a p(HEMA) matrix it was found that the lower detection limit for acid present in the system was 1.5x10^{-6} mol. Blended films containing only NIR dye and 2PO suspended in a p(HEMA) film, as well as films containing PTHPET, NIR dye and 2PO were prepared and exposed to 830 nm laser light. A decrease in absorbance in the NIR dye was observed between 600 and 900 nm indicating that laser light was absorbed by the NIR dye but an increase in absorbance at 344 nm, that would indicate the generation of acid and protonation of 2PO, was not observed. The absence of an absorption peak at 344 nm indicates that there is no acid is present or that if any acid was present or
was generated upon exposure with the 830 nm laser then it is of an amount that is below the limit of detection for this acid-sensitive probe employed here.

Figure 2.14: UV-vis absorption response of 2PQ to the concentration of H+ in methanol solution. Probe concentration was $1.6 \times 10^{-4}$ M.
2.2.6 Spectroscopic Properties of PTHPET-NIR Dye Films Post Laser Patterning

Figure 2.16 shows UV-vis-NIR absorption spectra of PTHPET-NIR dye films before and after patterning and development. An interesting feature of the spectra is that $\lambda_{\text{max}}$ of PTHPET prior to patterning and development is $\sim 450$ nm whereas after patterning it is $510$ nm. Previous studies have shown thermolysis of PTPET films led to a red shift of their UV-vis absorption properties,[39] which was attributed to planarization of the main chain backbone due to the removal of the bulky THP group, thus allowing further extension of the conjugation length of the polymer. The red-shift in the polymer observed in the present study is consistent with removal of the bulky THP group. Also of note is the absence of
NIR dye in the patterned polymer film indicating that the developing procedure successfully removes most of the NIR dye.

Figure 2.16: UV-vis-NIR absorption spectra of a pristine PTHPET/NIR dye film (green plot) and the patterned and developed film (red plot). Film thickness, ~80 nm. Pristine PTHPET is included for comparison (black plot).

Photoluminescent spectra of a pristine PTHPET film before and after heating in an oven for 30 minutes at 240 °C under an ambient atmosphere are shown in Figure 2.17. As expected, the absorbance spectrum red shifts, relative to the pristine material, to approximately 510 nm after heating, indicating deprotection of the polymer. The photoluminescent emission spectrum also changes considerably as compared to the pristine emission. Photoluminescent spectra were compared while keeping the excitation wavelength and emission detector slits constant. As compared to the pristine emission, the
photoluminescent emission for the heated film is nearly zero. This observed
decrease in emission is expected due to liberation of the bulky protecting group
and subsequent aggregation of the polymer main chains, which causes
quenching of the fluorescence.

![Emission spectra of PTHPET before and after heating.](image)

**Figure 2.17:** Emission spectra of PTHPET before and after heating. Film thickness was ~90 nm, $\lambda_{\text{ex}}$ 463 nm.

Photoluminescent spectra of a pure PTHPET film and of PTHPET films
containing dye before and after development are shown in **Figure 2.18** – the
latter film was not exposed to laser irradiation – it was only rinsed with methanol
to remove dye. Values of $\lambda_{\text{max}}$ (absorption) are 463, ~450, and 475 nm,
respectively. $\lambda_{\text{max}}$ corresponding to fluorescent emission from PTHPET is 605
nm. Quantum yields of fluorescence ($\Phi$) for PTHPET films, with and without dye,
are ~0.00 and ~0.10, respectively. Rinsing the NIR dye-containing film with
methanol, so as to remove the dye, partially restored the quantum yield of

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emission to ~ 0.04 (Figure 2.18c), indicating that even though a majority of the dye has been removed, as observed as a substantial decrease in dye absorption between 600 to 900 nm, residual NIR dye significantly quenches luminescence. The quantum yield of patterned and developed films of PTHPET was also lower than that of the pristine polymer films and is estimated to < 0.01. This value is low because of the increased coplanarity and hence π-stacking upon removal of the tetrahydropyranyl group. Also of note is that λ_{max} corresponding to the absorption of the PTHPET film red shifts by ~25 nm when rinsed with methanol. The shift in PTHPET absorbance is most likely due to the increase in the free volume of the polymer film upon removal of the NIR dye so as to permit the conjugated polymer to relax from a contorted conformation to a more planar conformation. An increase in coplanarity of the polythienyl in the solid state also contributes to the reduced quantum yield of fluorescence.[114]
Figure 2.18: Absorption and photoluminescence spectra of (a) pristine PTHPET, (b) and (c) PTHPET containing NIR dye before and after methanol development, respectively. $\lambda_{\text{ex}}$, 460 nm.

Despite the low photoluminescence of the patterned films, fluorescent images could still be obtained. Fluorescent images of the patterned PTHPET film (orange areas of Figure 2.19b and c) were obtained with a fluorescence microscope using a broad band excitation source filter to provide 380 – 420 nm light; photoluminescent emission was recorded for wavelengths > 430 nm. The photoluminescent emission intensity for PTHPET was low due to the poor overlap of the excitation energy (380 – 420 nm) with that of the patterned polymer ($\lambda_{\text{max}}$, 510 nm), and the thinness of the polymer pattern. Thus a high background emission from the underlying substrate is observed.
2.3 Conclusions

A novel method for the pixilation of π-conjugated polymers is presented. The technique, which employs novel chemistry and state-of-the-art reprographic instrumentation, has the potential for producing high resolution images with rapid throughput. Preliminary thermogravimetric analysis and variable temperature FT-IR experiments involving PTHPET and NIR dye showed that the presence of a NIR absorbing dye did not hinder the deprotection of the THP protected alcohol but rather it facilitated it, shifting the deprotection temperature to ~190 °C, ~50 degrees lower than the pristine material. Irradiation of the polymer-dye blend with 830 nm light results in localized heating, causing a thermal reaction to occur. Absorbance spectra of PTHPET films containing NIR dye exhibited a blue shift in
$\lambda_{\text{max}}$ attributed to twisting of the polymer main chain and shortening of the polymer conjugation length. Upon laser patterning and development of the material with methanol and THF, a red shift in the absorption is observed due to increased planarization of the polymer backbone, thus increasing the conjugation length, which is attributed to liberation of the bulky protecting group as dihydropyran as well as removal of the NIR dye from the film. Surface profiles of patterned PTHPET films prior to solvent development exhibited signs of ablation in exposed regions. The depth of the ablated feature depended on the optical density of the NIR dye, i.e., at higher dye contents deeper troughs were observed. Pixels of PTHPET are obtained with a resolution as small as 10 $\mu$m at laser scan speeds as fast as 0.7 m/s. The patterned material retains some of its fluorescence emission under direct excitation but the quantum yield of emission is approximately zero and is attributed to either the presence of residual NIR dye remaining in the film after development and/or coplanarization and chain aggregation after removal of the THP.

Although patterning PTHPET was successful using this novel technique, there still exists an opportunity to optimize the system with respect to the patterned materials’ optical properties, such as photoluminescence. For a proof-of-concept preliminary investigation, PTHPET was a good candidate to demonstrate this patterning process, however, its emission properties are poor after deprotection, regardless of the method employed for deprotection, i.e., bulk or laser heating. Also, directly incorporating the NIR dye in the $\pi$CP layer exhibited detrimental effects on the optical properties of the material even before
laser patterning and so alternative methods for incorporating the dye need to be investigated.

2.4 Experimental

Regio-regular PTHPET with a head-to-tail content of > 95%, as determined using NMR, was synthesized according to the general method described by McCullough et al.[39, 151] Molecular weights of PTHPET measured against polystyrene standards were determined using gel permeation chromatography (Waters model 510) equipped with μ-Styragel columns. PTHPET and polystyrene were eluted with THF at a flow rate of 1 mL/min and detected with a UV-vis spectrometer (Waters model 486) at 440 nm. The NIR dye employed in this study was 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,1,3-trimethyl-2H-benzo[e]-indol-2-ylidene-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,1,3-trimethyl-1-H-benzo[e] indolium 4-methylbenzene-sulfonate (FEW Chemicals) and the acid-sensitive molecular probe employed was 2-phenylquinoline (Aldrich) and was purified according to the literature procedure.[150]

Thermogravimetric analyses were performed on a Seiko Instruments Inc. TG/DTA 6300. Measurements were obtained at a heating rate of 5 °C/min on 5 – 8 mg polymer/dye samples under ambient atmosphere. Variable temperature FT-IR spectra of drop cast films on NaCl plates were recorded on a Nexus 670 series spectrometer coupled to a portable heater (Specac), temperature controller and sample holder. Samples were held for 20 minutes in air at a given temperature prior to recording a spectrum.
Polymer films were spin cast from chloroform for 30 seconds at 1500 RPM on 5 cm x 5 cm glass substrates (Corning). The thickness of the glass substrate was 0.95 mm. Patterns of PTHPET were obtained using a flat bed imaging laser scanner (Kodak Inc., Burnaby) which utilizes a NIR laser operating at a wavelength of 830 nm and a spot size of ~5 μm diameter. PTHPET patterns were typically obtained at a constant laser power of 23 W while varying the laser scan speed across the surface of the sample (0.3 m/s to 0.7 m/s). Patterns were also obtained using 20 – 12 W power and a constant laser scan speed of 0.6 m/s. Exposed PTHPET films were developed by rinsing with methanol followed by THF. UV-vis absorption spectra were obtained with a Varian Cary 300 Bio spectrometer. Film thicknesses were determined using an Alpha-Step IQ surface profiler. Visible and fluorescent micrographs were obtained with a Nikon 50i Eclipse series microscope equipped with a 100 W mercury lamp and Q Imaging Qi-Cam 1394 digital camera. A Nikon (V-2A) fluorescence filter cube was employed, consisting of a dichromic mirror that permitted excitation wavelengths in the range of 380 – 420 nm to pass and prevented wavelengths ≤ 450 nm from reaching the detector/camera. Photoluminescent spectra and quantum yield measurements were obtained on a Photon Technologies International Quantum Master model QM-4 equipped with an integrating sphere.

The determination of acid content in films containing NIR dye was performed by preparing test films of p(HEMA) containing the acid sensitive molecular probe, 2PO and varying amounts of CSA. The p(HEMA) and 2PO solution was prepared by dissolving 33.9 mg p(HEMA) and 32.3 mg 2PO
(1.6x10^{-4} \text{ mol}) in 3 \text{ mL} \text{ methanol}. To 500 \mu\text{L} \text{ aliquots of this polymer-probe solution was added} 250 \mu\text{L} \text{ aliquots of CSA stock solutions, with an acid concentration that ranged from 4.0x10^{-2} to 4.0x10^{-5} \text{ M} \text{ CSA}. The final solutions containing polymer, probe and acid were then spin cast at 1000 RPM for 30 seconds on quartz glass substrates. The UV-vis absorption spectra of the above films were then recorded.

Spin cast PTHPET films containing NIR dye and the acid sensitive probe were prepared by dissolving 4.0 mg of PTHPET (1.9x10^{-5} \text{ mol based on the polymer repeat unit}), 4.5 mg NIR dye (6.0x10^{-6} \text{ mol}) and 5.1 mg 2PQ (2.5x10^{-5} \text{ mol}) into 333 \mu\text{L} \text{ chloroform}. The solution was filtered through a 0.2 \mu\text{m} syringe tip filter and spin cast at 1500 RPM on quartz glass substrates. UV-vis absorption spectra were recorded before and after exposure to 830 nm laser light at energy dosages ranging from 1600 to 1200 mJ/cm^2.

P(HEMA) films containing 2PQ and varying amounts of NIR dye were prepared by dissolving ~2.6 mg of polymer, 4.5 mg 2PQ (2.2x10^{-5} \text{ mol}) and 1.5 mg or 14.4 mg NIR dye (2.0x10^{-6} or 2.0x10^{-5} \text{ mol respectively}) into 300 \mu\text{L} \text{ methanol}. Solutions were spin cast at 1500 RPM for 30 seconds on quartz glass substrates. UV-vis absorption spectra were obtained before and after patterning with 830 nm laser light at dosages ranging from 1200 to 1600 mJ/cm^2.
CHAPTER 3: DIRECT THERMAL PATTERNING OF FLUORESCENT \( \pi \)-CONJUGATED POLYMER MICROSTRUCTURES IN BILAYER POLYMER FILMS

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Note: Synthetic portions were performed by Dr. George Vamvounis.

3.1 Introduction

Patterning \( \pi \)-conjugated polymers (\( \pi \)CP) is crucial for their application in organic microelectronic devices. Within this class of polymer, polythiophene and polyfluorene derivatives are proven versatile materials as charge carriers in field effect transistors (OFETs)[7, 152] and photovoltaic applications.[59, 74] Furthermore, their mechanical flexibility and luminescent characteristics make them attractive candidates for flexible organic displays.[153-155] Standard lithographic techniques for patterning these materials requires dedicated equipment and can involve multiple elaborate steps of deposition, masking, aligning, exposure, baking, etching and developing: The process can be time-consuming, and the rate of throughput low.

Alternative techniques for spatially-controlling the deposition of polymeric semi-conductors with micron resolution are being investigated. The method
discussed in this chapter makes use of the thermal lability of functionalized polymers. For example, negative tone patterns of thiophene- and fluorene-based polymer films may be obtained by simply exposing selected areas of a tetrahydropyran (THP)-bearing polymer to trace quantities of catalytic acid, whereupon thermal cleavage of the THP group results in an intractable, hydrogen-bonded material.[39, 114] In Chapter 2 patterning THP-functionalized polymers with a 830 nm NIR laser beam was discussed wherein there was exposure of a film containing NIR absorbing dye, directly incorporated into a poly(3-(2-(2-tetrahydropyranoxy)ethyl)thiophene) (PTHPET) film, which resulted in localized heating leading to a homolytic deprotection reaction. The latent image formed in the πCP film was further developed with solvent to yield negative tone patterns of the polymer.[93] Direct thermal patterning of πCP films containing NIR dye offers the advantage of single step film preparation, rapid computer-to-plate direct patterning, and < 10 μm resolution imaging. However, the properties of the resulting polymer were significantly compromised, compared to the pristine parent polymer because the NIR absorbing dye was incorporated directly into the active polymer layer.[156] Thus, strategies have been devised wherein NIR dye is not incorporated into the film.

This chapter describes thermal imaging of a highly luminescent πCP in a similar manner to that described in Chapter 2 but using a novel bilayer approach, wherein a NIR dye is contained in a film of poly(2-hydroxyethylmethacrylate) (p(HEMA)) and spin cast on top of the πCP film. Using this bilayer film architecture the active conjugated polymer layer may be heated by exposure to
NIR irradiation while minimizing deleterious mixing of the polymer with the NIR dye that was described in the previous chapter. The NIR thermal patterning process for bilayered films is shown schematically in Figure 3.1.

![Figure 3.1: Direct thermal patterning scheme of PFT-TT in a bilayer film.](image)

The concept is demonstrated with PFT-TT (poly(9,9'-dihexylfluorene-alt-2-(2-thiophen-3-ethoxy)tetrahydropyran)-co-(9,9'-dihexylfluorene-alt-bithiophene)), which was chosen because it contains THP-functionality and is highly luminescent in the solid state by virtue of its donor-acceptor nature in which electronic excitation energy is transferred from the fluorene domains to isolated luminescent bithiophene groups via energy migration and transfer.\[134\] The inclusion of THP moieties in the polymer design provides an avenue for thermal patterning as discussed in Chapter 2. The molecular structure for PFT-TT and the thermolytic reaction scheme are shown in Figure 3.2. On the other hand, the concept of donor-acceptor systems is more often encountered in the blends of a
small molecule emitter dispersed in a non-emitting molecular matrix.\[157\] Adapting this concept of isolating emitter monomer units in a conjugated polymer donor-host results in highly fluorescent materials due to enhanced energy transfer from the absorbing host material to the emitting material. Also, this molecular blend minimizes aggregation of the emitting species. Aggregation is well known to introduce non-radiative decay pathways for luminescent materials, thus reducing the material’s solid-state emission efficiency. The donor-acceptor concept is described schematically in Figure 3.3 where the bulk fluorene-co-thiophene units absorb excitation energy and transfer the energy to the isolated bithiophene emitters.\[158\]

![Figure 3.3: Thermolytic reaction of PFT-TT.](image-url)

**Figure 3.2:** Thermolytic reaction of PFT-TT.
3.2 Results and Discussion

Characterization and thermal patterning of single layer films of PFT-TT containing NIR dye and conjugated polymer films where the NIR dye is contained in a top, non-conjugated polymer film, p(HEMA) was conducted. The following experiments investigate the UV-vis spectroscopic properties of the materials as well as the polymer thermal properties in the presence of NIR dye. Emphasis is placed on whether or not there are significant and measurable changes in the polymer properties, such as photoluminescent emission, while in the presence of NIR dye and before and after laser exposure.
3.2.1 PFT-TT UV-vis Absorption and Emission Properties

The absorption and emission properties of pristine PFT-TT in the solid-state are shown in Figure 3.4. PFT-TT exhibits a narrow $\lambda_{\text{max}}$ of absorption at 410 nm and a $\lambda_{\text{max em}}$ at 496 nm with shoulders at $\sim$ 525 and $\sim$ 580 nm. The quantum yield of emission for PFT-TT was measured using an excitation wavelength of 410 nm and was determined to be 0.22.

![Absorption and emission spectra of PFT-TT](image)

**Figure 3.4:** Solid-state absorption and photoluminescent emission spectra of PFT-TT. $\lambda_{\text{ex}}$ 410 nm, $\lambda_{\text{em}}$ 493 nm.

3.2.2 PFT-TT-NIR Dye Blends: TGA and FT-IR

**Figure 3.5** shows thermogravimetric analysis curves for pristine PFT-TT (black plot) and PFT-TT-NIR dye blends (red and blue plots). Neat PFT-TT was found to undergo a 14.8 % loss in total mass at $\sim$ 190 – 200 °C. This is consistent with the expect weight loss of 18 % of THP via the loss of
dihydropyran. In the presence of a NIR dye, (32.0 and 48.5 mol%), based on the THP-functionalized thienyl unit, the polymer was found to undergo thermal reaction at ~ 170 and ~ 160 °C, respectively. As shown in the single layer PTHPET-NIR dye systems (Chapter 2), the presence of NIR dye does not hinder the thermal reaction process, rather, it lowers the temperatures at which removal of THP occurs. The mol% of dye present, at this high level of loading in PFT-TT films, did not significantly change the observed deprotection temperature, i.e., 190 °C for the pristine material to, at best, 160 °C with nearly 50 mol% of dye present, whereas in the polythiophene based system there was a significant change in the deprotection temperature decreasing from 225 °C for the pristine material to ~ 190 °C with only ~ 5 mol% dye. The reason that there is less of a shift to lower deprotection temperatures for PFT-TT, as compared to the PTHPET temperature shift, could be related to the THP content of the polymer. For example, PFT-TT contains approximately 50% less THP character than PTHPET and a significant portion of the free volume in PFT-TT film is occupied by hexyl groups of the fluorene units, thus, interacting with dye. On the other hand, PTHPET films containing dye, the dye interacts with or is in the presence of THP-type functional group as described schematically in Figure 3.6.
Figure 3.5: TGA thermograms of neat PFT-TT (black) and polymer-NIR dye blends with 32.0 mol% (red plot) and 48.5 mol% NIR dye (blue plot). Heating rate 5 °C/min.

Figure 3.6: Proposed polymer-NIR dye blend interactions in thin films of PTHPET and PFT-TT and high NIR dye loading.
The thermal reaction of pristine PFT-TT and PFT-TT blended with NIR dye (~ 32 mol%) was further verified using variable temperature FT-IR and the corresponding spectra can be found in Figure 3.7. Thermal reaction of pristine PFT-TT is observed through the emergence of a broad peak near 3600 cm⁻¹ indicative of the presence of OH upon removal of THP at ~ 180 °C. Between 180 and 200 °C the signal intensity attributed to OH stretching becomes more intense indicating further deprotection of the polymer. Signals attributed to THP at ~ 1200 and 1100 cm⁻¹ corresponding to C-O-C antisymmetric stretching reduce in intensity at ~ 180 °C and are nearly unobservable by 240 °C indicating loss of dihydropyran. In PFT-TT-NIR dye blend films, the emergence of an OH stretching signal is more difficult to observe than in the pristine spectra and the peak is not observed until 180 °C which is surprising since the TGA thermogram of PFT-TT blended with NIR dye exhibits a change in mass, attributed to a loss of DHP, at ~ 160 °C. The reasons for these conflicting results are unclear but could be due to an unknown polymer-NIR dye phenomenon during heating.
Figure 3.7: (a) Variable temperature FTIR of PFT-TT at 25 °C, 180 °C, 200 °C and 240 °C and (b) of a PFT-TT-NIR Dye blend film at 25 °C, 180 °C, and 240 °C recorded the following day. NIR dye content was ~ 32 mol%.
3.2.3 Single Layer PFT-TT-NIR Dye Films: Patternning

Single layer films of PFT-TT containing varying amounts of NIR dye were prepared using the same method of solution and film preparation as described in Chapter 2 for PTHPET.[93] After laser exposure and solvent development, pattern transfer of PFT-TT was not observed for a range of laser dosages between 1700 to 1200 mJ/cm². One possible reason that this single layer system could not be patterned using the NIR laser is that the incorporation of high concentrations of NIR dye prevented the polymer from adhering to the glass substrate surface even after deprotection and so is removed upon development. The poor adhesion characteristics of PFT-TT were not observed in the single layer PTHPET polymer systems where dye was directly incorporated into the film. Another possibility that may explain why single layer films of PFT-TT containing NIR dye could not be successfully patterned is that PFT-TT consists of half the amount of THP along the polymer main chain, as compared to PTHPET which is considered to have 100% THP functionality, and thus solubility of the exposed/thermally reacted areas remains, at least, partially soluble, i.e., there is not enough of a solubility change in the polymer after deprotection and thus, remains soluble in developer.

Failure to thermally pattern single layers of PFT-TT was believed to be due to the direct incorporation of NIR dye in the film and so it was believed that exploring methods to keep the polymer in the presence of dye but not directly including it in the film was worthwhile and the results of that work is discussed in the following sections.
3.2.4 Bilayer PFT-TT-p(HEMA)/NIR Dye Films: UV-vis Absorption

Bilayer polymer films were prepared by spin casting a PFT-TT layer from chloroform solution onto a glass substrate, followed by spin casting a film of p(HEMA) containing NIR dye from methanol solution. The thickness of the PFT-TT layer was ~70 - 100 nm, determined by a profilometer scan across a mechanically applied scratch through the polymer film; the thickness of the p(HEMA)/NIR dye layer was varied from 180 to 300 nm. UV-vis absorption spectra of the components at various stages of the patterning process are shown in Figure 3.8 for initial PFT-TT and p(HEMA)/NIR dye thicknesses of 71 and 300 nm, respectively. The optical density of the PFT-TT film was ~ 0.8 at $\lambda_{\text{max}}$ 410 nm. Following deposition of the p(HEMA)/NIR dye layer a significant increase in absorption is observed between 600 and 900 nm. After exposure of the film to 830 nm NIR irradiation in the form of a series of lines ~80 μm wide spaced ~250 μm apart, and with an average power density of ~1300 mJ/cm$^2$, the absorption between 600 and 900 nm due to the NIR dye decreases by ~70% indicating that the NIR dye is either decomposed or ablated. Rinsing the NIR exposed film with methanol removed the remaining p(HEMA)/NIR dye layer as evidenced by the absence of absorption between 600 and 900 nm. A subsequent treatment of the film with THF, to remove PFT-TT originally lying under unexposed p(HEMA)/NIR dye regions provided a patterned structure possessing an optical density of ~0.2 at 423 nm, which is considerably lower in absorbance than the pristine material due to removal of the unexposed PFT-TT film. A small red shift in $\lambda_{\text{max}}$ of absorption for patterned PFT-TT, 10 – 15 nm, is observed after THF
development, as shown in Figure 3.9, which is attributed to the relaxation of the polymer main chain to a less twisted conformation after removal of the bulky THP group.[39]

Figure 3.8: UV-Vis absorption spectra of PFT-TT and p(HEMA)/NIR dye films at various stages of patterning and development. The pristine PFT-TT layer and p(HEMA)/NIR dye layer were 71 and 300 nm thick, respectively. The averaged NIR laser exposure dosage was ~1300 mJ/cm².
Figure 3.9: Solid state absorbance spectra of pristine and patterned PFT-TT.

3.2.5 Bilayer PFT-TT-p(HEMA)/NIR Dye Films: Surface Profiles

Following exposure of the bilayer film to 830 nm NIR laser irradiation, and prior to removal of the NIR dye layer with methanol, grooves were formed at the film's surface. Surface profiles of bilayered films, possessing a PFT-TT layer of $70 \pm 5$ nm, and p(HEMA)/NIR dye layer thickness of $184 \pm 26$, $252 \pm 20$, and $300 \pm 24$ nm, after exposure to a line scan from an 830 nm laser having a beam width of $\sim 80 \, \mu m$ and a power density of $\sim 1300 \, mJ/cm^2$, are shown in Figure 3.10. A trough is observed where the laser struck the surface. Much of this material has been physically transferred to the edge of the trough, although partial ablation of material cannot be ruled out. For p(HEMA)/NIR dye layer thicknesses of 184, 252, and 300 nm, the trough was $139 \pm 21$, $177 \pm 9$ and $222 \pm 11$ nm deep,
indicating ~ 76, 70, and 74 % of the film was lost during exposure. The optical densities (and percent transmission, %T) of the films at 830 nm prior to irradiation were 1.190 (6.5 %T), 1.853 (1.4 %T), and 2.025 (0.9 %T), so that the corresponding percentage of NIR irradiation absorbed was approximately 93.5 %, 98.6 %, and 99.1 %, respectively. Localized heating removes or partially ablates the p(HEMA)/NIR dye layer, but not before sufficient heat is transferred to the underlying πCP. Furthermore, the trough depth did not penetrate into the πCP layer. After removal of the remaining p(HEMA)/NIR dye layer with methanol, the underlying PFT-TT layer was found to be smooth and absent of troughs and ridges.

Figure 3.10: Surface profiles of bilayered PFT-TT films having varying p(HEMA)/NIR dye layer thicknesses. Laser dosage ~1300 mJ/cm². Inset shows a trend of increasing trough depth with increasing optical density at 830 nm.
3.2.6 Bilayer PFT-TT-p(HEMA)/NIR Dye Films: Photoluminescent Emission

Photoluminescence (PL) emission spectra were measured for fully developed PFT-TT films after NIR thermal patterning, using laser scan speeds between 0.3 and 0.9 m/s and varying laser power. Photoluminescent spectra for patterned polymer films with a varying optical density of NIR dye, at 830 nm, obtained using laser scan speeds of 0.3 to 0.9 m/s and laser powers of 13, 16, 19, and 22 W are shown in Figure 3.11 and Figure 3.12. The emission spectra of patterned PFT-TT are slightly different from that of the pristine material ($\lambda_{em}$ 496 nm), exhibiting an increase in the peak intensity at 532 nm and a broadening of the peak area between 550 and 700 nm. The relative peak height and broadening of the emission spectra do not vary significantly with laser power or dosage or optical density of NIR dye in the p(HEMA) layer. Commision Internationale de l'Eclairage (CIE)[159] values for PL emission from PFT-TT before and after direct thermal patterning are $x = 0.18$, $y = 0.52$ (green-blue color) and $x = 0.28$, $Y = 0.53$, i.e., the latter is richer in green-yellow. The changes in the emission spectra of polyfluorenes upon patterning/heating are fairly consistent for all sample films, as shown in Figure 3.13, and do not seem to be dependant on laser power, dosage or optical density of NIR dye. The changes in emission profile are reported to be due to either further aggregation of the polymer or formation of fluorenone at the 9,9'-position of the fluorene repeat unit after deprotection.[17, 160] In the present case, the change of emission color is believed to be due to aggregation of the polymer main chain following
removal of the bulky THP group\cite{17, 18, 161} and will be discussed in the following section.

Figure 3.11: Photoluminescent emission comparison at different patterning speeds (0.3 and 0.9 m/s). Optical density at 830 nm was 2.06. \(\lambda_{\text{ex}}\) 410 nm.

Figure 3.12: Photoluminescent emission comparison of patterned PFT-TT with varying optical densities of NIR dye in the top p(HEMA)/NIR dye layer. \(\lambda_{\text{ex}}\) 410 nm.
Photoluminescent quantum yields ($\Phi_{PL}$) were measured for PFT-TT films that were exposed to various laser powers (10 to 22 W) and scan speeds (0.3 to 0.9 m/s) corresponding to dosages between 703 to 1546 mJ/cm$^2$ at 0.3 m/s, 351 to 773 mJ/cm$^2$ at 0.6 m/s and 234 to 515 mJ/cm$^2$ at 0.9 m/s. Pristine PFT-TT exhibited a $\Phi_{PL}$ of ~ 0.22. Quantum yields of patterned PFT-TT are summarized in Figure 3.14a and Figure 3.14b. Figure 3.14a compares photoluminescent quantum yields of patterned and developed PFT-TT films obtained from bilayered films with varying amounts of NIR dye in the top polymer layer. As shown in Figure 3.14a, there is little difference in the quantum yield of patterned PFT-TT obtained from films with varying amounts of NIR dye at a given laser scan speed. For example, films patterned at 0.6 m/s (blue shaded squares in Figure 3.14a) with a dye optical density of 2.060 exhibited similar $\Phi_{PL}$ to films which contained a top polymer-dye layer with an optical density of 1.219. In fact, the quantum

Figure 3.13: CIE color stability in pristine and patterned PFT-TT films. Left plot contains $(x)$ and $(y)$ CIE values at varying laser dosage. Right plot contains a chromaticity coordinate diagram with pristine and patterned PFT-TT coordinates (averaged) plotted as black circles.
yields of patterned PFT-TT, obtained with a given laser scan speed, did not vary significantly across the employed laser dosage range. The quantum yield dependence on laser scan rate, rather than laser dosage, is best described by the section of Figure 3.14a where the plots over-lap near 750 mJ/cm$^2$. For example, films patterned at 0.3 m/s and lower laser dosage (blue and pink circles < 750 mJ/cm$^2$) exhibit a significantly lower $\Phi_{PL}$ than films patterned at 0.6 m/s and exposed to a higher laser dosage (dark blue and pink squares > 750 mJ/cm$^2$). This phenomenon is best described by comparing the quantum yields of patterned PFT-TT, obtained with a laser power of 16 W, while varying laser scanning rates from 0.3 m/s to 0.9 m/s as shown in Figure 3.14b. A linear trend is observed where the quantum yield of emission increases as laser scan speed increases. Thus, this polymer-dye system is more sensitive to laser scan speeds, which yield shorter dwell times of the laser beam striking the surface, than on the laser dosage and/or optical density of NIR dye.
After direct thermal patterning and development, quantum yield values ranged from 0.12 to as high as 0.19, depending on the laser scan speed. The highest values provided quantum yields that were 86% of the pristine polymer, indicating the suitability of the technique for patterning luminescent materials. For a given laser scan speed, the $\Phi_{\text{PL}}$ was relatively constant with laser power or dosage; but reducing the laser scan speed caused a loss in the photoluminescent efficiency as shown in Figure 3.15. Thus it appears that the dwell time of the laser at the film surface during exposure has more of an effect on $\Phi_{\text{PL}}$ than laser power. Longer dwell times lead to longer exposures and higher localized temperatures, which could translate to increased polymer aggregation after deprotection, which is well known to reduce photoluminescent quantum yield efficiency.[162-164]
3.2.7 Bilayer PFT-TT-p(HEMA)/NIR Dye Films: Fluorenone Analysis

A major drawback to employing polyfluorene and polyfluorene derivatives in photo and electroluminescent devices is its susceptibility to photo- and thermal-oxidation during patterning or device operation, resulting in unwanted changes to the emission spectra.[16, 18, 160, 165-167] The polymer’s photo and/or electroluminescent emission generally becomes more broad with a new low-energy peak centered near 525 nm and is often attributed to either main chain aggregation and/or fluorenone defects, thus, it was important to identify the origin of the color change in patterned PFT-TT films.

Figure 3.15: Photoluminescent quantum yields of patterned PFT-TT obtained at various laser dosages and laser scan speeds, $\lambda_{ex}$ 410 nm and $\lambda_{em}$ 420 – 780 nm.
Drop cast films of PFT-TT were prepared on NaCl substrates to investigate fluorenone formation using variable temperature fluorescence and variable temperature FT-IR. Fluorenone exhibits a very broad emission centered at 525 nm and a single, very sharp transmission peak which can be measured with FT-IR centered near ~1750 cm$^{-1}$. Emission and transmission spectra of drop cast PFT-TT films are shown in Figure 3.16. Films were heated in 25 degree intervals, under air and subdued light. Fluorescence and transmission spectra were obtained for each temperature, starting at 30 °C to a maximum of 250 °C. Unfortunately, prior to heating, the emission spectra exhibited a slightly more broad shape as compared to the spin cast films presented in a previous section, making identifying fluorenone formation using fluorescence emission more difficult. The difference in the emission shape profile is probably due to the method of film preparation and that there is a much greater tendency for polymers to aggregate from the drop cast solutions because of the slower evaporation process, as compared to the rapid evaporation process in spin cast films. Spin cast films were also prepared but were found to be too thin to provide sufficient IR absorption and thus IR signal intensity was very low. The shape of the emission profile stays constant until ~ 225 °C. At temperatures ≥ 225 °C the emission profile begins to broaden further and reduce in intensity, evidenced by the increased emission from 550 to 750 nm and increase in noise of the emission signal. According to thermograms obtained for PFT-TT using TGA, presented in section 3.2.2, the polymer begins to thermally degrade at temperatures > 250 °C, after thermal deprotection and liberation of THP. FT-IR spectra corresponding to
each of the emission spectra correlate well with the fact that the material is thermally stable at $< 200 \, ^\circ C$. At temperatures $\geq 200 \, ^\circ C$ the polymer undergoes thermal reaction, and liberation of dihydropyran from the film is inferred from a weak and broad transmission peak attributed to the formation of $-\text{OH}$ near 3600 cm$^{-1}$. A sharp FT-IR transmission signal between 1780 and 1720 cm$^{-1}$, which would indicate the presence and formation of a carbonyl, is absent at elevated temperatures.[167]

Figure 3.16: Variable temperature a) fluorescence emission and b) FT-IR spectra for PFT-TT obtained at various temperatures. $\lambda_{\text{ex}} 410 \, \text{nm}$ and $\lambda_{\text{em}} 420 - 780 \, \text{nm}$. 
3.2.8 Bilayer PFT-TT-p(HEMA)/NIR Dye Film Microscopy

Fluorescent images and pattern profiles were obtained for PFT-TT after NIR laser exposure and film development as shown in Figure 3.17 and Figure 3.18. Pixelated patterns (~43 μm square) of PFT-TT were produced at various laser scan speeds, 0.3, 0.6 and 0.9 m/s, using a laser power of 10 W. The pixels obtained at 0.3 m/s exhibit smeared corners and poorer resolution of adjacent squares, providing evidence of over-exposure and lateral thermal diffusion. At faster laser scan speeds, i.e., 0.6 and 0.9 m/s, patterned squares are resolved as a consequence of lower energy dosages. A series of PFT-TT lines were patterned diagonally, parallel and perpendicularly relative to the laser scan direction as shown in Figure 3.17. Features with widths > 30 μm were well resolved at scan speeds between 0.3 and 0.9 m/s and at laser powers between 10 to 22 W in all directions relative to the scanning laser, however, diagonal and parallel features of < 30 μm in width could not be completely resolved due to lateral diffusion of heat.
Figure 3.17: Fluorescent micrographs and surface profiles of patterned PFT-TT. $\lambda_{ex}$ 330 – 380 nm, $\lambda_{em} \geq 400$ nm. The surface profiles correspond to the different line widths as indicated by the arrows: a) 50, b) 30 and c) 20 $\mu$m lines. Laser power, 10 W. Scan speeds were 0.3, 0.6 and 0.9 m/s. The corresponding incident laser dosages were 703, 351 and 234 mJ/cm$^2$, respectively.

Figure 3.18: Fluorescent images of pixelated PFT-TT obtained with a laser power of 10 W and varying laser scan speed. Corresponding incident laser dosages are given.
3.3 Conclusions

Direct thermal patterning of PFT-TT has been demonstrated using a 830 nm NIR laser in bilayer structured films where the NIR dye was incorporated in the top, non-conjugated, polymer film, however, single layer films where the dye was incorporated directly in the πCP could not be successfully patterned. Failure to pattern the single films was believed to be due to the high NIR dye content and the resulting poor adhesion properties of the polymer during development.

It has also been shown that a fluorescent πCP containing a thermally labile functional group can be patterned using a bilayer film wherein a non-conjugated polymer film containing a NIR absorbing dye generates heat upon exposure to 830 nm laser light. After exposure and subsequent film development, a negative tone image of the πCP is obtained. A small red shift, between 10 – 15 nm, in the λ_max of PFT-TT is observed after patterning and development, possibly indicating that the polymer adopts a less twisted conformation after deprotection. PFT-TT retains its photoluminescent properties after patterning with an average Φ_{PL} ~0.17 or 86% of the original value. The photoluminescent properties of the polymer did not depend on the optical density of dye contained in the top layer or on the patterning laser power or dosage, but did depend on the laser scan speed, indicated by an increasing quantum yield of emission with increasing scan rate. This increase in quantum yield, relative to the films patterned at slower scan rates, is attributed to shorter dwell times of the laser on the surface and thus generating less of a temperature rise at the surface and within the exposed area of the film. Variable temperature fluorescence and
FT-IR spectroscopy was employed to investigate the possibility that broadening of the photoluminescent emission was due to introduction of fluorenone defects upon patterning, however, lack of a distinct carbonyl stretching peak near 1750 cm\(^{-1}\) indicates that broadening is probably due to main-chain aggregation after heating and insolubilization of the polymer. It should be noted that the “bulk heating” employed for this series of experiments investigating fluorenone does not mimic laser heating and that a more in-depth investigation could be the topic for a future project.

Patterns with 20 \(\mu m\) resolution were readily obtained at laser scan speeds as fast as 0.9 m/s and laser power and dosages as low as 10 W and 234 mJ/cm\(^2\), respectively. To put the speed of this patterning process into perspective, a letter-sized sheet can be completely pixelated with 20 \(\mu m\) resolution features in less than one minute.

### 3.4 Experimental

9,9-Dihexylfluorene-2,7-bis(trimethylenborate) (97%), potassium carbonate (99%), tetrakis(triphenylphosphine)palladium (99%), 5,5’-dibromo-2,2-bithiophene (99%) and poly(2-hydroxyethylmethacrylate) were purchased from Sigma Aldrich Canada Ltd. The NIR dye employed in this study was 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,1,3-trimethyl-2H-benzo[e]-indol-2-ylidene-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,1,3-trimethyl-1-H-benzo[e] indolium 4-methylbenzene-sulfonate (FEW Chemicals). Chemicals were used as received.
3.4.1 Synthesis of PFT-TT

The polymer employed in this body of work, PFT-TT, was synthesized by Dr. G. Vamvounis. The full characterization of this material has been reported in his Ph. D. thesis, 2004, Simon Fraser University, Burnaby BC.[158]

The synthesis of PFT-TT is briefly reported below: A solution, degassed with nitrogen, containing 2,5-dibromo-3-(2-(2-tetrahydropyranyl-2-oxo)ethyl)thiophene[114] (0.488g, 1.32 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (0.70g, 1.4 mmol), 5,5'-dibromo-2,2'-bithiophene (0.023g, 0.071 mmol) and a 3 mL aliquot of an aqueous solution of 2.4 M K₂CO₃ in THF (15 mL) was prepared and after mixing for several minutes 3 mol% of Pd(PPh₃)₄ (0.048g, 0.0042 mmol) was added to the vial and sealed. The solution was heated for 72 hours at 40 °C. The solution was diluted with CHCl₃ and washed twice with water. The organic phase was dried with MgSO₄ and a large portion of the solvent removed under reduced pressure. The remaining polymer solution (~2 mL) was precipitated into methanol to afford a bright yellow product. After filtration, 0.6 g of polymer was obtained (80% yield). Flash chromatography with CHCl₃ was performed to remove catalyst residue, followed by precipitation into methanol. ¹H NMR (ppm): 7.8 – 6.8 (m, 6H), 7.46 (s, 1H), 4.67 (m, 1H), 4.1 (m, 1H), 3.8 (m, 2H), 3.5 (m, 1H), 3.0 (br, s, 2H), 2.1 (s, 4H), 1.9 0.49 (m, 28H). Mw: 9400, PDI: 3.2.

3.4.2 General Procedures

¹H NMR spectra were recorded in CD₂Cl₂ solution on a 400 MHz Bruker AMX400 spectrometer, the chemical shifts are referenced to CH₂Cl₂ (δ = 5.36 for
Molecular weights of polymers were measured against polystyrene standards using gel permeation chromatography (Waters model 510) equipped with μ-Styrage columns. The conjugated polymers and polystyrene were eluted with THF at a flow rate of 1 mL/min and detected with a UV-vis spectrometer (Waters model 486) at 254 and 440 nm. UV-vis absorption spectra were obtained with a Varian Cary 300 Bio spectrometer. Thermogravimetric analyses were performed on a Seiko Instruments Inc. TG/DTA 6300. Variable temperature FT-IR spectra of drop cast films on NaCl plates were recorded on a Nexus 670 series spectrometer coupled to a portable heater (Specac), temperature controller and sample holder. Samples were held for 20 minutes in air at a given temperature prior to recording a spectrum. Film thicknesses were determined using an Alpha-Step IQ surface profiler. Optical and fluorescent micrographs were obtained with a Nikon 50i Eclipse series microscope equipped with a 100 W mercury lamp and Q Imaging Qi-Cam 1394 digital camera. A Nikon (UV-2B) fluorescence filter cube was employed, consisting of dichromatic mirrors that permitted excitation wavelengths in the range of 330 – 380 nm and prevented wavelengths ≤ 400 nm from reaching the detector/camera. Photoluminescent spectra and quantum yield measurements were obtained on a Photon Technologies International Quantum Master model QM-4 equipped with an integrating sphere. Bilayer films were prepared by spin casting polymer and p(HEMA)/dye solutions on glass or quartz substrates. π-Conjugated polymer solutions were prepared by dissolving ~ 15 mg of polymer in 1.00 mL chloroform. p(HEMA)/dye solutions were prepared by dissolving ~9.8 mg p(HEMA) and 30 –
50 mg NIR dye in 1.00 mL methanol. The π-conjugated polymer layer was spin cast on the substrate prior to the p(HEMA)/dye layer. Both films were spin cast at 1500 rpm for one minute. The thickness of the films, UV-vis absorbance and fluorescence spectra were recorded prior to and after deposition of the p(HEMA)/dye containing layer. Films were patterned using a Kodak flat bed 830 nm NIR laser scanner over a range of laser powers (10 – 22 W) at laser scan speeds of 0.3, 0.6 and 0.9 m/s. The corresponding laser dosage was 230 – 1700 mJ/cm$^2$ in the fixed-focus mode. The patterned films were first developed in methanol, followed by 30/70 (v/v) THF/hexanes.
CHAPTER 4: DIRECT THERMAL PATTERNING OF ELECTRONICALLY CONDUCTING $\pi$-CONJUGATED POLYMER MICROSTRUCTURES

Note: Synthetic portions were performed by Dr. Jianfei Yu and Ms. Xu Han.

4.1 Introduction

In Chapter 3, it was shown that fluorescent polymer structures could be successfully obtained using a direct thermal patterning method and a bilayered film architecture wherein an NIR absorbing dye was deposited as a second film on top of the $\pi$CP. In this chapter, the focus is on exploiting the electronic properties of the patterned materials, thus exploring the generality of the technique. This chapter also describes and discusses preliminary results from numerical modelling studies employed to estimate the temperature changes in laser exposed films.

As demonstrated in the previous chapter, the use of bilayered polymer films which consist of a top-layer, non-conjugated polymer film containing a NIR absorbing dye and an underlying layer of a fluorescent $\pi$CP functionalized with a thermally sensitive tetrahydropyran (THP) moiety can also be employed for patterning polymers.[168] Exposing the bilayer film to 830 nm laser irradiation thermally reacted the underlying polyfluorene layer and, after subsequent
development steps, was found to retain nearly all of its photoluminescent characteristics. Quantum yields of photoluminescence of the πCP were 86% of the pristine value of 0.22 and were obtained at scanning speeds as fast as 0.9 m/s at a laser dosage of 234 mJ/cm\(^2\). This bilayer method for patterning polymer films eliminates the need to incorporate the dye directly into the πCP film and therefore minimizes the exposure of the polymer to the detrimental quenching effects of the dye.[93] Some of the advantages that this patterning technique exploits are: simplicity of solution-based film preparation and uniform film coverage of substrates, there are no delamination/dissolution concerns for casting multilayer films and, there is the possibility for high throughput with micron size resolution.

A schematic for the thermal reaction of the polymers upon NIR laser exposure and subsequent heating that are investigated in this chapter and the πCPs and NIR absorbing dye employed are shown in Figure 4.1 and Figure 4.2.

Figure 4.1: Thermolytic deprotection reaction of a THP-functionalized πCP.
Using this bilayer film architecture and patterning method, as shown in Figure 4.3, the active $\pi$CP layer can still be heated via NIR laser exposure while minimizing the polymers exposure to the detrimental effects of the NIR dye that were observed when the NIR dye was incorporated directly in the $\pi$CP layer.[93]
This chapter describes the direct thermal patterning of bilayered polymer films containing the prototypical patternable polythiophene derivative, poly(3-(2-(2-tetrahydropyranlyoxy)ethyl)thiophene) (PTHPET) and a co-polymer of a THP-functionalized thiophene and 3-hexylthiophene (3HT), PTHPET-HT. The content of 3-hexylthiophene in the co-polymer is 25% and has a deprotection temperature of 200 °C.[39] These materials are analogues of poly(3-hexylthiophene). Films of the πCPs are coated with a second non-conjugated polymer film (poly(2-hydroxyethylmethacrylate)) (p(HEMA)) containing NIR absorbing dye and were then exposed to NIR laser irradiation at various laser dosages, as described in Chapter 3. Semiconductive and conductive conjugated polymer patterns obtained after the exposure of NIR laser light and subsequent development are demonstrated and described.

4.2 Results and Discussion

4.2.1 UV-vis Absorption Spectroscopy

The UV-vis absorption spectra of pristine spin cast P3HT, PTHPET and PTHPET-HT films are shown in Figure 4.4. P3HT was included for comparison purposes only. All of the spectra were relatively broad spanning a range of approximately 300 nm. The $\lambda_{\text{max}}$ for PTHPET is the most blue-shifted with respect to the other polymers with a maximum absorption at 463 nm. The $\lambda_{\text{max}}$ for PTHPET-HT is also blue-shifted with respect to P3HT, located at ~ 479 nm, but less than that of PTHPET. The differences in the $\lambda_{\text{max}}$ of these materials is attributed to the twisting that is induced upon the introduction of bulky THP
groups. As the amount of THP increases the extent of twisting of the polymer main chain also increases. The absence of a structured absorption profile for the polymers containing THP indicates that the presence of the protecting group disrupts the long-range ordering in the solid state making the films more amorphous relative to P3HT, however, x-ray diffraction studies reported by Yu et al. showed that the long range order was not completely suppressed indicated by a measured lamellar spacing of ~17 Å.[40]

Figure 4.4: UV-vis absorption spectra of pristine PTHPET and PTHPET spin cast films. P3HT is included for comparison.

4.2.2 Electrochemical Properties of THP-Functionalized Polythiophenes

The electrochemical p-doping potentials of PTHPET and PTHPET-HT films were measured by cyclic voltammetry versus a ferrocene/ferrocinium
(Fc/Fc\textsuperscript{+}) redox couple and are shown in Figure 4.5. For comparison purposes, the p-doping potentials of regio-regular poly(3-hexylthiophene) (P3HT) were also measured. The films were prepared by drop casting dilute polymer chloroform solutions directly onto the glassy carbon working electrode. It is well known that drop casting polymer films induces more order in a film, due to the slower evaporation of solvent relative to the faster evaporation rates observed in spin casting, thus, the structural order in the films employed for the electrochemical study will be different from those observed in the UV-vis spectra presented in the previous section. PTHPET and PTHPET-HT exhibited two weak and broad quasi-reversible p-doping/dedoping peaks and the shapes of the voltammograms were similar to that of P3HT. The first half-wave potentials, E\textsuperscript{1/2}, were measured for the \pi CPs and indicate that the homo-polymers, P3HT and PTHPET, are more easily oxidized than PTHPET-HT differing in potential by 118 and 83 mV, respectively, as shown in Table 4.1. This increase in oxidation potential could be due to increased twisting of the polymer main chain of PTHPET-HT as compared to P3HT and PTHPET due to the fact that the polymer consists of two different monomer units, which prevents well ordered packing in the solid-state via twisting of thienyl units and thus, reducing delocalization along the main chain. This is surprising since one may have expected PTHPET, which contains a higher content of bulky pendant THP groups than PTHPET-HT, to adopt a more twisted conformation and thus have the higher oxidation potential. Perhaps, due to the fact that PTHEPT is a homo-polymer and PTHPET-HT consists of two dissimilar monomer units, slow evaporation of solvent leads to higher degrees of
ordering and crystallinity in the homo-polymers. Introduction of the 3HT units appears to twist the polymer main chain to a less co-planar conformation, possibly through interaction of the alkyl chain and adjacent chains containing THP even though the amount of 3HT is only 25%.

The onset p-doping potentials were used to determine the highest occupied molecular orbitals (HOMO) using the equation, $E_{\text{HOMO}} = -e(E_{\text{onset}}^{\text{onset}} + 4.8\text{eV})$[169] in electron Volts (eV) and the band gap (Eg) was determined optically from the UV-vis absorption onset in solid-state films and are shown in Table 4.1. The lowest unoccupied molecular orbitals (LUMO) can then be estimated following the equation $E_{\text{LUMO}} = -e(E_{\text{HOMO}} - \text{Eg \text{eV}})$ in electron Volts.[169] The calculated $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ energy levels of PTHPET and PTHPET-HT are not significantly different from those of P3HT which has already been shown to be an excellent candidate as a donor material for polymer-fullerene bulk heterojunction solar cell applications.[71] More specifically, the $E_{\text{HOMO}}$ levels of PTHPET and PTHPET-HT are slightly higher than P3HT indicating that they have higher oxidative stability and thus could have higher open circuit voltages.[170]
Figure 4.5: Cyclic voltammograms of P3HT, PTHPET and PTHPET-HT films on glassy carbon in freshly distilled valeronitrile with tetrabutylammonium perchlorate (0.5 mol/L) as the supporting electrolyte. Potentials are versus a Fc/Fc+ redox couple. Scan rate: 50 mV/s.

Table 4.1: Electrochemical properties of πCP films.

<table>
<thead>
<tr>
<th>πCP</th>
<th>$E_g$ / nm, eV [a]</th>
<th>$E_{onset}^{ox}$ / V [b]</th>
<th>$E_{1/2}$ / V [c]</th>
<th>$E_{HOMO}$ / $E_{LUMO}$ / eV [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>655, 1.90</td>
<td>-0.046</td>
<td>-0.001</td>
<td>-4.75 / -2.85</td>
</tr>
<tr>
<td>PTHPET</td>
<td>570, 2.14</td>
<td>-0.025</td>
<td>0.034</td>
<td>-4.78 / -2.64</td>
</tr>
<tr>
<td>PTHPET-HT</td>
<td>601, 2.06</td>
<td>0.028</td>
<td>0.117</td>
<td>-4.83 / -2.77</td>
</tr>
</tbody>
</table>

[a] Determined from UV-vis absorption spectra onset. [b] Onset oxidation potential versus Fc/Fc+ redox couple. [c] Half wave potentials corresponding to p-doping/dedoping of πCP. [d] $E_{HOMO} = -e(E_{onset}^{ox} + 4.8 \text{ eV})$; $E_{LUMO} = -e(E_{HOMO} - E_g \text{ eV})$. [169]

4.2.3 UV-vis Absorption Before and After NIR Laser Patterning

Bilayered polymer structures were prepared where the underlying π-conjugated material was PTHPET or PTHPET-HT. A series of typical UV-vis
absorption spectra of PTHPET in a bilayered film is shown in Figure 4.6. Spectra that were obtained for PTHPET-HT films were similar to that of the PTHPET films. The film thickness of PTHPET was measured prior to spin casting the top p(HEMA)/NIR dye layer. The thickness of the underlying πCP layer was determined using profilometry to be 108 ± 1 nm. A p(HEMA)/NIR dye layer was spin cast on top of the PTHPET layer and the total film thicknesses was found to be 351 ± 22 nm. Thus the thickness of the top p(HEMA)/NIR dye layer was approximately 243 nm. The UV-vis absorption spectrum of PTHPET, before deposition of the p(HEMA)/NIR dye layer, shows a λ_max at 463 nm. After deposition of the dye containing layer, a large and broad absorption, 1.55 absorbance (2.82 %T) at 830 nm, is observed between 600 and 900 nm attributed to the NIR dye. A smaller absorption is also observed after dye deposition as a shoulder overlapping PTHPET absorption at approximately 420 nm. This film was then exposed to NIR laser irradiation as a series of lines ~ 89 μm wide spaced ~ 230 μm apart with an average dosage of 1300 mJ/cm². A substantial decrease in dye absorption was observed between 600 – 900 nm, i.e., the absorbance of dye at 830 nm decreased from ~ 1.5 to ~ 0.40 (~ 40 %T), before and after laser irradiation, respectively, as shown in the red plot of Figure 4.6. This decrease in absorption between 600 – 900 nm indicates that laser energy was absorbed by the dye and thermally decomposed or was ablated. The exposed film was rinsed with methanol, which removed the p(HEMA)/NIR dye layer as evidenced by the lack of absorption between 600 and 900 nm. Further development of the film with THF removes PTHPET originally underlying
the p(HEMA)/NIR dye layer that was not exposed to the NIR irradiation providing a pattern of insoluble \(\pi\)CP. The absorbance and \(\lambda_{\text{max}}\) of PTHPET decreased and red shifted significantly after patterning, \(\sim 0.1\) and \(\sim 510\) nm, respectively. The absorbance changes and shift in \(\lambda_{\text{max}}\) are attributed to removal of unexposed polymer during THF development and liberation of THP from the polymer and a relaxation of the main chain to a less twisted conformation permitting polymer aggregation, respectively.[40] Further evidence of aggregation in thermally reacted PTHPET by photoluminescent microscopy will be described in a following section.

![Graph showing UV-vis absorption spectra for a bilayer film of PTHPET and p(HEMA)/NIR dye at various stages of NIR laser patterning and development. The pristine PTHPET layer and p(HEMA)/NIR dye layer were 108 and 243 nm thick, respectively. The averaged NIR laser exposure dosage was \(\sim 1300\) mJ/cm\(^2\). Inset shows the sequence of the patterning and development process.](image)

**Figure 4.6:** UV-vis absorption spectra for a bilayer film of PTHPET and p(HEMA)/NIR dye at various stages of NIR laser patterning and development. The pristine PTHPET layer and p(HEMA)/NIR dye layer were 108 and 243 nm thick, respectively. The averaged NIR laser exposure dosage was \(\sim 1300\) mJ/cm\(^2\). Inset shows the sequence of the patterning and development process.
4.2.4 Post Laser Exposure Surface Profiles of Bilayer Polymer Films

Surface profiles of patterned lines were obtained from a bilayer PTHPET film prior to solvent development and are shown in Figure 4.7. The p(HEMA)/NIR dye layer thickness was \( \sim 243 \) nm and the absorbance of the dye at 830 nm was 1.55 (2.82 %T). The total film thickness, including an underlying \( \pi \text{CP} \) layer was \( \sim 351 \) nm. The exposure laser dosage was between 1130 and 1700 mJ/cm\(^2\) and line width was \( \sim 89 \) \( \mu \)m. Trough depth did not vary with laser dosage within error as indicated by the measured trough depths that ranged from 190 \( \pm 48 \) nm obtained at a laser dosage of 1130 mJ/cm\(^2\) to 234 \( \pm 20 \) nm obtained at a laser dosage of 1700 mJ/cm\(^2\). The rough surface of the p(HEMA)/NIR dye layer contributed to the large error in the measurement.

Figure 4.7: Surface profiles of a p(HEMA)/NIR dye layer in a bilayer PTHPET film that was exposed to various 830 nm laser dosages prior to development. Optical density of NIR dye at 830 nm was \( \sim 1.55 \) (\( \sim 2.82 \) %T).
UV-vis absorption spectra that were obtained after removal of the p(HEMA)/NIR dye layer with methanol (shown in Figure 4.6 (blue plot)) showed a small red shift in $\lambda_{\text{max}}$ of PTHPET from 463 to ~475 nm which is attributed to partial relaxation of the polymer main chain. A slight decrease in absorption was observed for patterned and methanol developed PTHPET, decreasing by ~11% of the pristine absorbance value of 0.53. The change in absorbance indicates that some PTHPET may have been removed during methanol development or that PTHEPT was partially ablated. Ablation of PTHPET is unlikely because the trench depths that were measured, prior to methanol development (see Figure 4.7) closely correspond to the film thickness measured for the p(HEMA)/NIR dye layer cast on top of the $\pi$CP. However, surface profiles that were obtained of the underlying conjugated polymer layer in the exposed areas did exhibit a trench similar to that observed in the dye containing layer, shown as the inset in Figure 4.10. Depths of the trenches in the $\pi$CP were consistent within error across the surface of the methanol developed film, ranging from $38 \pm 2$ nm at 1130 mJ/cm$^2$ to $43 \pm 4$ nm at 1700 mJ/cm$^2$ and so they do not appear to depend on laser dosage. This indicates that some of the underlying material was in fact removed upon methanol development but not during laser exposure. The ratio of the pristine PTHPET film thickness (108 nm) and trench depth measured after methanol development (~40 nm) account for approximately 38% of the initial film thickness.

To verify that the relative percentage of removed material after methanol development to the initial polymer film thickness was due to the loss of
dihydropyran (DHP), films containing polymers with varying amounts of THP were prepared and patterned. Bilayer films containing an underlying layer of PTHPET, 110 ± 4 nm thick, or PTHPET-HT, 116 ± 12 nm thick, a πCP with THP content 25% less than PTHPET, were prepared. P(HEMA)/Dye layers were deposited from methanol solutions on top of the πCP layers and exposed to NIR laser irradiation at dosages between 1130 and 1700 mJ/cm². UV-vis absorption spectra were collected for pristine and patterned films containing PTHPET and PTHPET-HT as described in section 4.2.3. Figure 4.8 contains the UV-vis absorption spectra for the materials. As shown by the substantial decrease in absorption between 600 and 900 nm, laser energy was absorbed by the NIR dye. A minimal change in the \( \lambda_{\text{max}} \) of absorption is observed for PTHPET after patterning and methanol development as discussed in the previous section. Surprisingly, the absorbance spectrum of PTHPET-HT after patterning and methanol development is very different from the pristine spectrum. The \( \lambda_{\text{max}} \) shifted considerably to longer wavelengths, changing from 479 nm to ~ 507 nm, and increased in absorption intensity, raising from 0.673 to 0.788. This observed increase in absorption could be due to a change in the absorption cross-section of the polymer main chains upon heating, deprotection and rinsing the film with methanol. Further development of the films with THF removed unexposed polymer leaving behind a negative tone image of the deprotected πCP. As expected, the resulting absorbance spectra of the fully developed films were found to be reduced in intensity and red shifted in their \( \lambda_{\text{max}} \) to 502 and 515 nm for PTHPET and PTHPET-HT, respectively, as shown in Figure 4.9.
Figure 4.8: UV-vis absorption spectra for bilayered films with PTHPET and PTHPET-HT as the underlying πCP layer at various stages of patterning and development.
Prior to THF development, patterned films of PTHPET and PTHPET-HT were examined for changes on the film surface, such as grooves or trenches. Profilometry scans of the polymer surfaces indicated that some of the πCP material was removed after methanol development. Plots showing the relative ratio of trench depth to initial πCP film thickness at various laser dosages after methanol development are shown in Figure 4.10. Trench depths did not vary with laser dosage for PTHPET or PTHPET-HT which exhibited average trench depths of 48 ± 2 nm and 36 ± 8 nm, respectively, over the given range of dosages. The volume of THP in the πCPs was modelled and estimated by calculating the solvent excluded volume of monomer units using standard 3D modelling software with a solvent probe radius of 1.0 and estimated to be
approximately 40% and 30% of the total volume of PTHPET and PTHPET-HT films, respectively. The ratios of trench depth to the initial film thickness for PTHPET and PTHPET-HT were calculated, 44 ± 2 % and 31 ± 8 %, respectively, and were found to correspond quite well to the change in the estimated theoretical volume ratios of monomer unit to DHP. Profiles of the PTHPET-HT trenches were rougher than those of PTHPET as shown in the inset of Figure 4.10, which contributes to the large error in the measurement. Roughness in the patterned areas of the PTHPET-HT films could be due to swelling during laser exposure/heating.[130] Examples of the molecular models employed for monomer units of PTHPET, de-PTHPET and the leaving group DHP are shown in Figure 4.11.

![Figure 4.10: Trench depths in PTHPET (blue plot) and PTHPET-HT (black plot) after thermal patterning and methanol development. Profiles of the trenches are shown as an inset for the πCPs.](image)
4.2.5 Fluorescence Microscopy of NIR Laser Patterned Polymer Films

Further evidence of patterned polymer aggregation after laser exposure is observed in bright-field/fluorescence microscopy images of methanol developed PTHPET films, as shown in Figure 4.12. The area of the film that was exposed to NIR irradiation is clearly more red-pink in color as compared to the color of the unexposed regions, i.e., the orange squares. Under excitation of 380 – 420 nm light (emission > 430 nm) unexposed regions of the film fluoresce red-orange light where as the patterned areas do not emit light, as expected because the quantum yield of emission of PTHPET after patterning was reported to be < 0.01 due to polymer aggregation after removal of THP.[171]
4.2.7 Electrical Conductivity of THP-Functionalized Polymers

As aggregation usually results in improved charge mobility,[163] the electrical conductivities (σ) of pristine and patterned spin cast films of P3HT, PTHPET and PTHPET-HT were measured under ambient conditions, doped with I₂ vapour on gold electrodes under an applied potential of 0.5 V using a 2-probe technique.[46] The gold electrodes, ~25 nm thick, were fabricated by evaporation of gold onto glass substrates and mechanically etched to produce a left and right electrode pad 40 to 60 µm apart. Pristine and unpatterned films of the πCPs were placed in a chamber of I₂ vapour and the change in resistance of the films was measured for 20 minutes. Following Equation 4-1,[45]
\[ \sigma = \frac{W}{R t L} \]  \hspace{1cm} \text{(eq. 4-1)}

where \( W \) is the channel width (cm), \( R \) is the measured resistance (\( \Omega \)), \( t \) is the film thickness (cm) and \( L \) is the electrode length (cm); the conductivities of the materials were calculated and plotted versus time as shown in Figure 4.13. Undoped, the electrical conductivities of the \( \pi \)CPs were low, ranging between \( 1 \times 10^{-6} \) to \( 1 \times 10^{-5} \) S/cm, however once introduced to the \( I_2 \) chamber, conductivities rose very quickly as indicated by the steep onsets of the curves after approximately 60 seconds and reached maximum conductivity by approximately 100 seconds, \( i.e. \), after 40 seconds inside the \( I_2 \) chamber. Doped, P3HT (\( \sim 70 \) nm thick) and PTHPET-HT (\( \sim 103 \) nm thick), exhibited similar conductivities, between \( 1 \times 10^1 - 1 \times 10^2 \) S/cm, with conductivities of \( 60 \pm 26 \) S/cm and \( 16 \pm 2 \) S/cm, respectively. The maximum conductivity for PTHPET (\( \sim 101 \) nm thick) was an order of magnitude lower than P3HT and PTHPET-HT, between \( 1 \times 10^0 \) and \( 1 \times 10^1 \) S/cm, \( 3 \pm 1 \) S/cm. The conductivities of the \( \pi \)CPs stabilized between 150 – 200 seconds and maintained a constant conductivity over the time scale of the measurement.

Bilayer polymer films containing underlying layers of, PTHPET and PTHPET-HT, respectively, were patterned with laser dosages between \( 1130 - 1280 \) mJ/cm\(^2\) and \( 1310 - 1510 \) mJ/cm\(^2\) on gold/glass electrodes followed by solvent development with methanol to remove the p(HEMA)/NIR dye layer and THF which removes unexposed \( \pi \)CP. The resulting patterns of PTHPET and PTHPET-HT was a series of polymer lines \( \sim 100 \) \( \mu \)m wide and 65 and 40 nm thick, respectively, which connected the left and right gold electrodes, fabricated
as described in the previous section. A diagram of the electrode setup with patterned polymer is shown in Figure 4.14. The number of polymer lines connecting the two electrodes is typically between 35 and 45 depending on the size of the gold/glass electrode employed thus $L$ varied between 350 to 450 $\mu$m, i.e., polymer line width multiplied by the number of polymer lines is equal to $L$ for patterned films. The undoped electrical conductivities of patterned and developed films of PTHPET and PTHPET-HT were similar to or higher than those of the pristine materials, between $1 \times 10^{-4} - 1 \times 10^{-6}$ S/cm, and in the doped form with conductivities between $1 \times 10^{0} - 1 \times 10^{1}$ S/cm and $1 \times 10^{1} - 1 \times 10^{2}$ S/cm, or $5 \pm 1$ S/cm and $11 \pm 1$ S/cm, respectively, as shown in Figure 4.13. The similarities in conductivities indicate that after laser exposure and subsequent thermal reaction, the materials still retain their electronic characteristics in the neutral and doped form which are similar to those measured for P3HT reported elsewhere[172] and so could be a useful patterning method where spatial deposition of electrically conducting polymers are concerned.
Figure 4.13: Conductivity of P3HT, PTHPET and PTHPET-HT films as a function of time after exposure to I₂ vapour under ambient temperature and atmosphere. Patterned films were exposed to an average laser dosage of ~1200 and ~1400 mJ/cm², respectively.

Figure 4.14: 2-Point probe electrode setup for measuring the electrical conductivities of pristine and patterned polythiophenes. Bright field microscope image of a portion of a patterned film of PTHPET is shown.
4.3 Conclusions

It was found that polythiophene derivatives bearing THP pendant moieties can be selectively thermally deposited on a surface using a NIR laser, direct-write patterning method in a bilayer polymer-NIR dye architecture. Polymer-NIR dye films that were exposed to NIR laser irradiation exhibited surface changes in irradiated areas. Profiles of the films showed evidence of ablation but the depth of the trench did not extend into the underlying conjugated polymer, nor did the depth depend on the laser dosage, which ranged between 1100 to 1700 mJ/cm². Profiles of the conjugated polymer surface after methanol development also exhibited a trough-like appearance, however these features were not due to an ablative process. The troughs were due to the thermal reaction of the THP side chain and loss of dihydropyran from the material, based on the relative thickness of pristine film and the measured ablated trough depth.

The electronic properties of PTHPET and PTHPET-HT, i.e., their electrical conductivities while oxidatively doped with I₂, were measured for pristine and patterned spin cast films using a 2-point probe method. Conductivities were found to remain unchanged for patterned polymer as compared to the pristine materials. Conductivities of the doped materials were similar to that of P3HT ~60 S/cm, which was used as a model conductive polymer, ranging between 3 - 5 S/cm and 11 - 16 S/cm for PTHPET and PTHPET-HT, respectively. The fact that NIR laser patterning these materials does not destroy the electronic properties could indicate that this method is appropriate for the spatial deposition of πCPs for electronic applications.
4.4 Experimental

The π-conjugated polymers employed in this study were prepared according to the reported literature procedures.[39] Molecular weights of polymers were measured against polystyrene standards and were determined using gel permeation chromatography (Waters model 510) equipped with μ-Styrage columns. The conjugated polymers and polystyrene were eluted with THF at a flow rate of 1 mL/min and detected with a UV-vis spectrometer (Waters model 486) at 254 and 440 nm. The NIR dye employed in these series of experiments was 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,1,3-trimethyl-2H-benzo[e]-indol-2-ylidene-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,1,3-trimethyl-1-H-benzo[e] indolium 4-methylbenzene-sulfonate (FEW Chemicals) and the poly(2-hydroxyethylmethacrylate) was obtained from Sigma-Aldrich and used without further purification. UV-vis absorption spectra were obtained with a Varian Cary 300 Bio spectrometer. Film thicknesses were determined using an Alpha-Step IQ surface profiler. Visible and fluorescent micrographs were obtained with a Nikon 50i Eclipse series microscope equipped with a 100 W mercury lamp and Q Imaging Qi-Cam 1394 digital camera. Nikon (UV-2B) and (V-2A) fluorescence filter cubes were employed, consisting of dichromatic mirrors that permitted excitation wavelengths in the range of 330 – 380 nm and 380 – 420 nm and prevented wavelengths ≤ 400 nm and ≤ 450 nm from reaching the detector/camera, respectively. Cyclic voltammetric measurements were performed on a 263A Potentiostat/Galvanostat (PAR) using a glassy carbon working electrode (3 mm diameter), platinum wire in 0.05 M tetrabutylammonium
iodine in acetonitrile, Pt wire counter electrode and ferrocene as an internal reference in freshly distilled valeronitrile with tetrabutylammonium perchlorate (0.5 mol/L) as the electrolyte. Molecular volume modelling was performed using ChemDraw 3D version 7.0 software. π-conjugated polymer solutions were prepared by dissolving ~10 mg of polymer in 1000 μL chloroform. p(HEMA)-dye solutions were prepared by dissolving ~9.8 mg p(HEMA) and between 30 and 50 mg NIR dye into 1000 μL methanol. The πCP layer was spin cast on the substrate prior to the p(HEMA)/dye layer. Both films were spin cast at 1500 RPM for 1 minute. Thickness of the films and UV-vis absorbance spectra were recorded prior to and after deposition of the p(HEMA)/dye containing layer. Polymer films were patterned using a 830 nm NIR laser at laser scan speeds between 0.3 to 0.6 m/s and laser dosages between 1100 to 1700 mJ/cm². Patterned films were first developed with several milliliters of methanol followed by several milliliters of THF. Electrical conductivities of the πCPs were measured on a Solartron SI 1287 for pristine drop and spin-cast films as well as NIR laser patterned films using two evaporated Au films as electrodes, ~25 nm thick, on glass substrates with a channel width between the electrodes 40 to 60 μm wide (2-probe technique) under ambient conditions. Films were exposed to iodine vapour during the conductivity measurement for 20 minutes.
CHAPTER 5: A PRELIMINARY INVESTIGATION OF PATTERNING A CROSS-LINKABLE AND HIGHLY FLUORESCENT POLYFLUORENE

5.1 Introduction

Precise and selective area deposition using additive or subtractive patterning methods for conjugated polymers is of utmost importance for present-day electroluminescent and microelectronic device fabrication. In order for these kinds of materials to be useful in these high-tech applications, the chemical stability of the active layer material is crucial. An example of one class of conjugated polymer that has received considerable attention in the literature with respect to its role as the active layer in many device applications are polyfluorenes and their derivatives.[79, 111, 114, 134, 173] As presented in Chapter 1, polyfluorene and its derivatives can be easily prepared using numerous synthetic procedures such as Yamamoto or Suzuki type coupling reactions,[20, 22] they have been demonstrated to be efficient blue emitters with solid state quantum yields > 0.50,[16-18] they have good thermal stability, and have been shown to be well suited as charge-transport materials in donor-acceptor polymer/polymer or polymer/small molecule blends. Functionalized derivatives of these materials have also been reported demonstrating that they can be patterned using various techniques such as conventional photolithographic and μ-contact printing (μCP) methods.[79] The polymers were functionalized with various reactive groups such as phenyl vinylene and
tetrahydropyran (THP) protected alcohols.[30, 114] Another patternable functional group that has received some attention in the literature has been reported by Meerholz et al. where cross-linkable oxetane functionalized alkoxyphenyl substituents have been shown to undergo acid-catalyzed cross-linking using photolithographic methods in the fabrication of LEDs.[35, 37] The cross-linking reaction is shown in Figure 5.1. An important feature of these kinds of materials is that, after insolubilization, via deprotection or cross-linking, successive active layer materials can be deposited, thus easily fabricating multilayer structures.

![Figure 5.1: An example of an acid catalyzed oxetane cross-linking reaction.](image)

More recent examples from the literature that demonstrate the usefulness and versatility of oxetane-functionalized materials have been reported by Nuyken and Meerholz where novel hole transporting polymers based on triarylamines were employed in PLEDs.[36] Examples of these materials are shown in Figure 5.2.
Figure 5.2: Examples of cross-linkable hole transport materials.

Surprisingly, these oxetane-functionalized materials have not been investigated in the literature using other methods of patterning, such as contact printing or thermal patterning. Thus, the application of an oxetane-functionalized polyfluorene, employed as a thermally patternable material, will be the primary focus of this chapter and used to demonstrate the generality and versatility of the direct thermal patterning method presented in this thesis.

Polyfluorene derivatives are not without drawbacks: in that after extended use in light-emitting applications or after prolonged heating, a low-energy green photoluminescent emission (between 2.2 to 2.4 eV or 564 to 516 nm, respectively) can emerge and is typically attributed to aggregation of polymer chains followed by excimer emission and/or the presence of fluorenone, shown in Figure 5.3.\[161\] It has been suggested that fluorenone could be introduced during monomer and polymer synthesis followed by subsequent photooxidation.\[173\] However, Heeger et al. have reported that fluorenone defects are generated via a photooxidative and/or thermal-oxidation processes.
Identifying the origin and formation mechanism of fluorenone defects in polyfluorenes is a very important first step before devising ways to reduce or prevent this green emission impurity.

![Figure 5.3: Photo-thermal oxidation of poly(alkylfluorene) and formation of fluorenone defects.](image)

Figure 5.3: Photo-thermal oxidation of poly(alkylfluorene) and formation of fluorenone defects.

Structural modifications to polyfluorenes have been proposed in the literature where by the 9,9' position of the fluorene unit is functionalized with alkoxyphenyl moieties (Figure 5.4) with the intention of suppressing the formation of fluorenone.[16, 17] The phenyl rings, orientated nearly perpendicular to the polymer main chain, are believed to help reduce aggregation by preventing \( \pi-\pi \) stacking as well as to sterically hindering the 9,9' carbon atom, thus helping to prevent attack by oxygen.[166] The effectiveness of this kind of substitution has been debated in the literature where Lee et al. showed that phenyl substituents do stabilize the polymer toward photo-thermal oxidation.[166] however, Inganäs and Andersson et al. have reported conflicting results, which show that the introduction of phenyl substituents at the 9,9'position do not make the polymer more resistant to photo-thermal oxidation.[18]
This preliminary study investigates whether direct thermal patterning is appropriate technique for patterning other types of functional groups, such as oxetane cross-linking moieties. The synthesis and contact printing ($\mu$CP) of a new oxetane-alkoxyphenyl functionalized polyfluorene is also described. Because of the thermal nature of this patterning technique, there is an opportunity to explore the thermal stability of a 9,9'-phenyl substituted polyfluorene, and thus, as a secondary focus, the thermal and oxidative stability of the material with respect to resistance to fluorenone defects in the polymer backbone will also be presented. Furthermore, a comparison in the patternability of the functionalized polymer using the two techniques previously mentioned, i.e., $\mu$CP and direct thermal patterning, will also be described.

5.2 Results and Discussion

5.2.1 The synthesis of poly(9,9'-bis([3-ethyl(oxetane-3-ethyloxy)-hexyl]-4-hydroxyphenyl)-fluorene) (XPF)

A new polyfluorene, poly(9,9'-bis([3-ethyl(oxetane-3-ethyloxy)-hexyl]-4-hydroxyphenyl])-fluorene), abbreviated XPF where "x" indicates that it is a cross-linking polyfluorene, was successfully synthesized in four steps as outlined in Figure 5.5. 2,7-dibromo-9,9'-bis-(4-hydroxyphenyl)-fluorene (2) was prepared by
Dr. Xiwen Chen, a research associate in the Holdcroft group. Compound (1) was prepared as reported in the literature,[36] purified via vacuum distillation and indentified by gas chromatography on the basis of its retention time as compared to the retention times of the starting materials, 1,6-dibromohexane and 3-hydroxymethyl-3-ethyloxetane. The structures of monomer compounds (2), (3) and XPF were confirmed by $^1$H NMR, as shown in Figures 5.6, 5.7 and 5.8.

![Synthetic scheme employed for Yamamoto polymerization of XPF.](image)

Figure 5.5: Synthetic scheme employed for Yamamoto polymerization of XPF.
Two sets of aromatic resonance peaks for compound (2) were observed between 6.7 to 6.9 ppm and 7.5 to 7.9 ppm corresponding to the hydroxyphenyl substituents and fluorene protons, respectively, as shown in **Figure 5.6**. A small broad peak was observed down field at 9.4 ppm attributed to the protons attached to the oxygen of the hydroxyphenyl moieties.

![Figure 5.6: 500 MHz $^1$H NMR spectrum 2,7-dibromo-9,9'-bis-(4-hydroxyphenyl)-fluorene (2).](image)

After the addition of the cross-linking moieties to compound (2), new peaks were observed for compound (3) up field, associated with compound (1). Aliphatic hydrogen resonance peaks were observed between 0.9 to 1.8 associated with the hexyl chain and terminal CH$_3$ of the oxetane moiety, as shown in **Figure 5.7**. Protons to either side of the four membered oxetane ring
exhibited slightly different chemical shifts, as observed by a quartet at 3.5 ppm, as these are also adjacent to the terminal CH$_3$, and a singlet peak shifted slightly down-field at 3.6 ppm due to its proximity to the ether oxygen. The two remaining peaks located between 4.3 to 4.4 ppm are attributed to the pair of oxetane CH$_2$ protons. Integrations for the proton peaks of compound (3) are slightly greater than expected probably due to impurity compounds carried through from the reaction of compound (1), i.e., the product of dibromohexane reacted with two 3-(hydroxymethyl)-3-ethyloxtane. Resonance peaks down field at approximately 9.4 ppm were absent for compound (3) indicating that all of the hydroxyphenyl moieties were reacted.

![Figure 5.7: 500 MHz ¹H NMR spectrum of 2,7-dibromo-9,9'-bis[[3-ethyl(oxetane-3-ethyloxy)-hexyl]-4-hydroxyphenyl]]-fluorene (3).](image-url)
The molecular structure of XPF was verified with $^1$H NMR. The characteristic signals between 3.4 to 4.4 ppm for the oxetane moiety, as described in the previous section, remained after the polymerization of (3). The NMR spectrum of XPF was nearly identical to that of (3) with the exception that the peaks were broader than those of the monomer.

Figure 5.8: 500 MHz $^1$H NMR spectrum of XPF.

5.2.2 Optical Properties of XPF

Spin cast films of XPF were prepared and the UV-vis and photoluminescent spectra recorded, and shown in Figure 5.9. The absorbance spectra were found to be very similar to 9-9'-dialkyl substituted polyfluorenes.
reported elsewhere,[18, 166] with a $\lambda_{\text{max}}$ of absorption located at 388 nm. Photoluminescent emission spectra of XPF thin films were obtained with an excitation wavelength of 388 nm and the emission profile showed $\lambda_{\text{max}}$ of emission at ~430 nm with a second peak at ~460 nm and a shoulder at 480 nm. Solid-state photoluminescent quantum yield ($\Phi_{\text{PL}}$) was measured and was similar to other 9,9'-alkylphenyl substituted polyfluorenes at 0.58. The high quantum yield is attributed to reduced aggregation of the polymer chains due to the presence and perpendicular orientation of phenyl rings at the 9,9' position, relative to the polymer main chain. Commision Internationale de l'Eclairage coordinate values for XPF were calculated and are $x = 0.17$ and $y = 0.16$ placing the color of the polymer emission in the blue part of the spectrum.

![Figure 5.9: Normalized UV-vis absorption and photoluminescent spectra of spin cast XPF. Excitation 388 nm. Film thickness ~55 nm.](image-url)
5.2.3 Thermal Properties of XPF

The thermal stability of XPF was investigated using TGA. Figure 5.10 shows thermograms obtained under air and under nitrogen atmosphere. As shown, the polymer heated under an ambient atmosphere exhibits a gradual decrease in mass after heating to ~ 225 °C possibly due to degradation of the polymer side chains. A gradual, rather than steep decrease in mass above 225 °C indicates that the side chains probably do not volatilize upon heating. Under a nitrogen atmosphere the polymer shows an improved thermal stability in that the decomposition temperature shifts to approximately 425 °C at which point a sharp decrease in mass is observed indicating thermal decomposition of the polymer.

DSC was employed to determine whether the polymer had a distinct glass transition temperature (Tg) before and after cross-linking, however heating-cooling curves ranging from 10 °C to 175 °C and 10 °C to 225 °C exhibited no distinct Tg.
Variable temperature FT-IR was employed to further investigate the thermal stability of XPF under ambient conditions in subdued light. Figure 5.11 shows the FT-IR spectra obtained at various temperatures for pristine XPF. As XPF is heated from room temperature to 200 °C, the height of a peak located at 980 cm\(^{-1}\), attributed to C-O-C stretching in the oxetane ring, diminishes at elevated temperatures. The change in oxetane C-O-C ring stretching at elevated temperatures is attributed to a thermally induced cross-linking reaction. Minor decreases in peak heights at 1110 and 1250 cm\(^{-1}\), attributed to anti-symmetric stretching in aliphatic C-O-C ethers, are also observed. Also of note, is the emergence of a broad peak at 1725 cm\(^{-1}\) indicating that fluorenone defects at the 9,9'-position of the fluorene unit are forming between 150 and 200 °C.[17] There
has been considerable debate in the literature as to whether or not phenyl substituents stabilize the 9,9' position inhibiting or preventing carbonyl formation upon thermal treatments under air.[18, 166] As shown here, for films heated under subdued light and ambient atmosphere, the incorporation of phenyl groups at the 9,9' position does not suppress carbonyl formation. Films of XPF were then thoroughly rinsed with organic solvents such as THF and chloroform to investigate if there was a change in the solubility of the polymer after heating and all films were found to be insoluble.

Figure 5.11: Variable temperature FT-IR spectra of pristine XPF under ambient atmosphere and subdued light.
Variable temperature FT-IR in conjunction with photoluminescent emission profiles obtained after heating was helpful in supporting the claims made by Inganäs and Andersson that phenyl substituents did not prevent fluorenone defects upon heating even under subdued light in ambient atmosphere. Figure 5.12 shows the emission spectra of a drop cast XPF film at various temperatures and the corresponding FT-IR spectra at various temperatures. A small peak is observed at ~1725 cm\(^{-1}\) in the FT-IR spectra after heating the film to 185 °C which is attributed to a carbonyl moiety. Below this temperature, the peak at 1725 cm\(^{-1}\) is not observed. This is a good indicator that fluorenone defects are forming in the film upon heating.[167] Emission spectra of the XPF films, after being heated and subsequently cooled, also exhibit characteristic evidence of the presence fluorenone in polyfluorenes. Below 185 °C, the shape of the emission spectra remain the same, however, above this temperature broadening of the emission to longer wavelengths is observed. The peak at 1725 cm\(^{-1}\) continued to increase in size heating the film to 200 °C and PL emission continued to broaden between 400 and 550 nm as shown in Figure 5.12a. The CIE color coordinates were calculated for heated films and found to be different from that of the pristine spin cast and drop cast polymer. The drop cast film was slightly green-shifted relative to the spin cast film, with CIE coordinates of x = 0.19, y = 0.22. After heating the film to 185 and 200 °C, the color coordinates shifted considerably to colors more rich in green color relative to the pristine drop cast film, as shown in Figure 5.13, changing to (0.20, 0.24) and (0.24, 0.27) for the x and y values, respectively.
Figure 5.12: Variable temperature a) fluorescence emission and b) the corresponding FT-IR spectra for XPF. $\lambda_{\text{ex}}$ 380 nm and $\lambda_{\text{em}}$ 390 – 750 nm.

Figure 5.13: Color shift CIE plot of spin and drop cast XPF films annealed at various temperatures under ambient atmosphere and subdued light.
To further investigate cross-linking in XPF films and in an attempt to suppress the formation of fluorenone, films were prepared containing camphor sulphonic acid (CSA), heated to various temperatures, and spectra were compared to the pristine material. The presence of acid was expected to lower the temperature and increase the rate at which cross-linking and insolublization of the material occurs.[37] XPF films containing ~1 mol% CSA were prepared and heated in small increments so as to measure the change in oxetane ring stretching at 980 cm$^{-1}$ as shown in Figure 5.14. The FT-IR spectrum associated with the XPF film when heated to 185 °C (pink plot) shows the beginning of a peak at 1725 cm$^{-1}$ that, at higher temperatures, is attributed to fluorenone defects. The presence of acid does not appear to facilitate crosslinking, as the absorption frequencies associated with oxetane symmetric and antisymmetric stretching and bending of aromatic and aliphatic ethers (1290, 1250, 1110 and 980 cm$^{-1}$) do not exhibit a significant decrease in intensity until ~180°C at this mol% of acid, which is also the temperature at which fluorenone begins to form. Also of note is the appearance of an –OH stretching peak at ~3500 cm$^{-1}$ at ~185 °C, shown in Figure 5.15. As shown in Figure 5.1, as oxetane cross-linking initiates, a terminal hydroxyl group is formed and can serve as a second indicator of a successful cross-linking reaction. Based on the relatively small increase in peak height of the OH stretching peak, as compared to the intensity of the characteristic oxetane peaks at 980 and 1110 cm$^{-1}$ which are considerably diminished, the cross-linking reaction is probably propagating more within the film rather than initiating new cross-linking sites.
Figure 5.14: Variable temperature FT-IR spectra of XPF in the presence of CSA.

Figure 5.15: Variable temperature FT-IR spectra following the evolution of –OH stretching peaks in an XPF film in the presence of CSA.
5.2.4 Patterning of XPF

Patternability of XPF is investigated using two different techniques, microcontact printing and direct thermal patterning. Microcontact printing involves physically delivering a molecular acid-ink to the polymer surface through contact with a flexible PDMS stamp, which, after several drying and heating steps results in a negative tone image of active material, where as DTP involves selective area NIR laser exposure and heating of the polymer through a NIR dye layer. Both processes will be highlighted in the following sections for patterning XPF.

5.2.4.1 μ-Contact Printing

Patterning oxetane baring polyfluorenes has been demonstrated by Meeholz et al. using standard photolithographic methods whereby cross-linking of the pendent groups is accomplished via photoinduced acid generation followed by subsequent annealing which results in insoluble polymer patterns in exposed areas. Microcontact patterning is also capable of spatially depositing acid on an acid-sensitive polymer surface as reported elsewhere.[39, 41, 114] Inking a PDMS stamp, with 400 x 400 μm features, with a 0.01 M CSA solution in a 50/50 mixture of THF/hexanes was accomplished by carefully dipping the stamp surface into the solution followed by slow drying under air. The surface of the PDMS stamp changed slightly in appearance from clear and smooth to slightly cloudy. The change in appearance is due to deposition of CSA after evaporation of solvent. Re-dipping and recoating the stamp with ink was repeated, if necessary, until the surface appeared to have uniform coverage of
acid, i.e., until no large particles were observable. The “inked” stamp was then brought into contact with a spin cast film of XPF for ~ 15 to 30 seconds. The length of time the stamp remained in contact with the polymer film appeared to affect image quality but was only investigated qualitatively using optical microscopy. Films with shorter contact times tended to yield patterns of poorer quality after development as compared to those patterns where the stamp was in contact with the surface for longer periods of time. After removal of the stamp, the films were heated in an oven under air for approximately two minutes to facilitate diffusion of the deposited acid into the film. As shown in Figure 5.1, acid is necessary for the cationic polymerization of the oxetane cross-linkers. Development conditions for printed XPF were determined by rinsing stamped films with solvent mixtures of THF and hexanes. Rinsing the films with 50/50 mixtures of THF/hexanes did not result in a patterned surface as shown in the fluorescence micrographs of Figure 5.16a. Areas of the film that were in contact with the PDMS stamp appear darker in color than the surrounding area which were not in contact with CSA. The changes in color are possibly due to thickness variations of the stamped areas versus the un-stamped areas, i.e., some of the un-stamped material may have been removed during the 50/50 rinsing step, or that the cross-linked film has slightly different absorption-emission properties than the pristine material. Also of note is the observed non-uniformity in the stamped area as the stamp surface may not have made even contact with the polymer surface resulting in uneven CSA deposition. Rinsing the patterned film with a solvent mixture of 70/30 THF/hexanes resulted in a negative tone
image of the PDMS stamp as shown in Figure 5.16b. Cross-linked patterned 400 x 400 μm features of XPF are easily resolved and residual, un-stamped, polymer was completely removed as shown by the dark areas around the features. Squares are very uniform in shape and the pattern heights were similar to the pristine film thickness, ~50 nm in height.

![Fluorescent micrographs of XPF patterned via μCP. a) Post-50/50 THF/hexanes development and b) post-70/30 THF/hexanes development. Excitation 380 – 420 nm and emission collected ≥430 nm.](image)

The resolution of this printing technique using XPF was investigated using PDMS stamps containing various spaced vertical lines and spaces as shown in Figure 5.17a. The stamp consisted of lines ranging in width of 5, 10, 50, 100 and 200 μm. The smallest features of the stamp were not resolved due to
defects in the PDMS stamp. Well resolved lines of printed XPF are shown in Figure 5.17b. Features wider than 50 μm exhibit good patterning quality in that the lines are straight and free of breaks or gaps. Even at 10 μm, the patterns of XPF are well defined although the lines appear more rough near the edges than the 50 and 100 μm features. Based on these images, it is possible that using a more carefully fabricated stamp, patterned polymer features with better than 10 μm resolution could be possible.

Figure 5.17: a) PDMS stamp profile of vertically orientated line features with various widths and spacing, b) fluorescent micrographs of a printed XPF spin cast film and the associated printed polymer line widths. Excitation 380 – 420 nm and emission collected ≥430 nm.
Patterns of XPF were also obtained using a PDMS stamp while pressing lightly on the stamp to increase contact with the polymer surface. The PDMS stamp profile and resulting XPF pattern are shown in Figure 5.18. The stamp profile is smooth and featureless however the polymer pattern, after heating and development, is very rough across the stamp-film contact area as shown in Figure 5.18b. Polymer is probably adhering slightly to the stamp and upon removal is pulling material upwards. Polymer appears to remain in only the stamped areas and does not bulge into the gaps between printed features as shown by the well defined edges of the patterned material.

Figure 5.18: a) PDMS stamp profile and b) XPF pattern profile obtained after lightly pressing the PDMS stamp onto the film surface. Inset is a fluorescent image of the patterned XPF areas. Excitation 380 – 420 nm and emission collected ≥430 nm.
5.2.4.2 Direct Thermal Patterning Pristine XPF Films

Oxetane cross-linking and patterning was investigated for neat XPF films in bilayered films using direct thermal patterning. Films of XPF were spin cast from chloroform solution onto glass substrates. Resulting films were 54 ± 4 nm thick and had an optical density of 0.322, as shown in Figure 5.19. A NIR dye and p(HEMA) layer was spin cast on top of the XPF layer from a methanol solution. The optical density of NIR dye at 830 nm and film thickness was measured and found to be 2.022 and 297 ± 24 nm, respectively. Films were exposed to an average laser dosage of ~1300 mJ/cm² and a significant decrease in the UV-vis absorption at 830 nm was observed, dropping from 2.022 to 0.918, as shown in the red plot of Figure 5.19. The change in the absorption profile after exposure indicates that laser energy was absorbed by the NIR dye layer, resulting in heat generation and possible ablation of top layer material. Profiles of the film surface, post exposure and pre-methanol development, did show evidence of ablation with troughs that averaged in depth ~ 200 nm. The films were rinsed with methanol to remove the p(HEMA)/NIR dye layer and profiles were recorded of the XPF surface. The absorbance of XPF after laser exposure and methanol development was nearly identical to the pre-patterning absorbance value ~0.320, suggesting that material was not removed during the exposure and methanol development. Surface profiles showed no signs of ablation, however, areas exposed to the laser beam exhibited upward protrusions of swelled XPF, similar in appearance to features described by Fukumura and Masuhara obtained after laser exposure of dye-doped PMMA.
Features of this type indicate heating of the lower polymer layer and evolution of trapped gasses in the films. After full development, upon visual inspection, it was found that nearly all of XPF was removed from the substrate surface and an accurate UV-vis absorbance spectrum could not be obtained.

Pattern transfer of XPF to the glass was poor and line quality was inconsistent across the surface. Figure 5.20 shows fluorescent microscopy images of one of these areas of the film after various stages of solvent development. After rinsing the film with methanol to remove p(HEMA)/NIR dye dark lines are observable where the laser exposed the surface. However, after development with a 50/50 mixture of THF/hexanes these dark features become

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**Figure 5.19:** UV-vis absorption spectra of XPF and p(HEMA)/NIR dye films at various stages of patterning and development. Pristine XPF and dye layers were 55 and 297 nm thick, respectively. The average laser dosage was \( \sim 1300 \text{ mJ/cm}^2 \).
faint and very difficult to see under fluorescent excitation. It is unclear at this time why the emission from polymer changes after 50/50 development. Rinsing the film with 70/30 THF/hexanes removed nearly all of the polymer from the substrate, however, random areas of patterned XPF were observed using fluorescence microscopy, as shown in Figure 5.20c. Profiles of the areas that exhibited evidence of partial patterning were obtained and the heights were found to be much smaller than that of the initial polymer film thickness (~ 55 nm), with pattern features ranging from 10 to 20 nm in height and only 30 μm in width. A possible reason for poor pattern transfer of XPF could be that during laser heating side chains are cleaved and removed from the polymer main chain with the formation of fluorenone defects. Cleavage of the side chains would prevent thermally induced cross-linking which is necessary for insolubilization and pattern generation of the polymer. A second possibility could be that applying only localized thermal energy to the polymer film is insufficient to induce cross-linking. These results for thermal patterning XPF are encouraging, in that, with optimized blends of polymer and an acid, pattern transfer using this technique may be improved. Thus, a second series of experiments were devised where films containing CSA were prepared and thermally patterned, the results of which are covered in a following section.
There are significant differences in patterning polymers containing THP versus those which contain oxetane cross-linking functional groups. To promote insolubility in the exposed regions of the THP materials, the protecting group is thermally removed followed by the formation H-bonds and polymer aggregation where as an oxetane undergoes a stepwise polymerization-type reaction which is dependant on the ability of an oxetane group to become protonated followed by association and interaction with another oxetane group. Thus, it is necessary to add an acid generator and a curing step, 60 to 150 °C, in the patterning process for oxetane-bearing materials, otherwise patterns will be of poor and inconsistent quality, as demonstrated previously (see Figure 5.20). The acid initiates the ring-opening of the oxetane moiety and a subsequent curing step promotes mobility of the oxetane moieties facilitating the cross-linking reaction. Extensive optimization of the solution compositions of polymer and acid as well as fine tuning the optical density of the NIR dye layer prior to patterning XPF using the

Figure 5.20: Fluorescent microscopy images of XPF at various stages of patterning and development. Excitation 380 – 420 nm and emission collected ≥430 nm.
direct thermal patterning method, as described in Chapters 3 and 4, is necessary, and are discussed below.

5.2.4.3 Direct Thermal Patterning of XPF in Bilayer Films Containing CSA

In was believed that thermal patterning of XPF may be possible if an acid was included to initiate the cationic-polymerization of the oxetane moiety, thus, films of XPF were prepared, ~ 200 nm thick and with an optical density of 1.134 at 386 nm, that included ~ 6x10^{-5} mol CSA (6.5x10^{-2} M) in the top p(HEMA)/NIR dye layer, having an optical density of 2.460 and a thickness of ~ 300 nm (500 nm total thickness). Films were prepared and patterned as described in Chapter 3, using a bilayer architecture. For this first model, it was believed that the light-to-heat conversion layer would serve as a form of “inked stamp” as demonstrated in the microcontact printing section and that the areas exposed with the laser would heat sufficiently to initiate cross-linking, as shown in Figure 5.21, in the same manner as applying the “acid ink” to the polymer surface using μCP. The bilayer film was patterned and a UV-vis spectrum was recorded at various stages of processing, as shown in Figure 5.22. A curing step was added to the procedure to facilitate oxetane ring-opening and cross-linking. The UV-vis absorbance spectra recorded for pristine and exposed XPF exhibited similar absorbance profiles as those for PFT-TT films discussed in Chapter 3, i.e., \( \lambda_{\text{max}} \) of the patterned and methanol-developed polymer did not shift from its pristine value of 386 nm. After the film was exposed to the laser, and before methanol development, it was heated for 2 minutes at 90 °C to facilitate cross-linking. The absorbance spectrum of the film before and after curing were identical as shown
in the red and aqua blue plots of Figure 5.22. Rinsing the film with methanol removed most of the remaining p(HEMA)/NIR dye and CSA layer from the polymer film but peaks attributed to the NIR dye were still present. Further development with methanol could not remove the residual dye layer. Further development of the film by rinsing with a 70/30 solution of THF/hexanes or chloroform could not develop the film further as indicated by UV-vis absorbance of the rinsed film, which exhibited only a minor decrease in polymer absorbance at 836 nm. Applying acid to the surface of XPF, as outlined in Figure 5.21, followed by subsequent curing, regardless of laser heating, cross-linked (or partially cross-linked) the entire polymer film.

Figure 5.21: Acid-assisted thermal patterning of XPF in a bilayered film.
Figure 5.22: UV-vis absorption spectra of XPF and a bilayer p(HEMA)/NIR dye film containing CSA at various stages of patterning and development. The average laser dosage was ~1300 mJ/cm².

A second system was examined, wherein CSA was replaced by a thermal acid generator (TAG), 4,4′-dimethyldiphenyliodonium hexafluorophosphate, IBPF, see Figure 5.23. This particular thermal acid generator was chosen because it is soluble in methanol and its acid generating properties have been well established in the literature.[117-119] However, when the p(HEMA)/NIR dye solution was prepared and the thermal acid was added, the solution solidified into an insoluble mixture of dye, TAG and p(HEMA). Adding the reagents to methanol in a different order, gentle heating and sonication could not redissolve the materials. Thus, a third method was devised and implemented, shown in Figure 5.24, wherein the TAG is mixed directly with XPF followed by deposition of the light-to-heat conversion layer, as described in the following section.
5.2.4.4 Direct Thermal Patterning XPF Films Containing a Thermal Acid Generator

The third model for the thermal patterning of XPF incorporated a thermal acid generator, IBPF, directly in the πCP layer, as shown in Figure 5.24. XPF solutions were prepared by dissolving the polymer and varying amounts of TAG, 34 and 52 wt%, respectively, in chloroform and spin cast into films on glass.
substrates. Polymer film thicknesses varied for the samples with different weight percents of TAG ranging between 250 and 300 nm and different optical densities, ranging from 1.327 to 0.939, for the polymer, however the $\lambda_{\text{max}}$ of the $\pi$CP were unchanged at 390 nm despite the high TAG content, as shown in Figure 5.25.

![Normalized Absorbance](image)

**Figure 5.25:** UV-vis absorption spectra of pristine XPF films containing 34 and 52 wt% IBPF.

The photoluminescent emission spectra were obtained for XPF films containing varying contents of TAG. Films were excited at 390 nm and the emission was collected between 400 to 750 nm, as shown in Figure 5.26. Pristine emission of XPF is included in Figure 5.26 for comparison. The XPF films containing TAG exhibited similar emission spectra with $\lambda_{\text{max}}$ of emission slightly blue-shifted at $\sim$ 425 nm relative to the pristine material, shifting by $\sim$ 5 nm. The shoulder at 460 nm observed for the pristine polymer shifts
considerably in the TAG containing films, blue-shifting by \( \sim 15 \) nm, and the emission is narrower than the pristine emission. The shoulder observed at \( \sim 480 \) nm in the pristine emission is absent in the TAG containing films. The reason for this substantial difference in the emission is probably due to the high TAG content in the film which prevents aggregation of the polymer main chains.[162-164, 174, 175]

![Photoluminescent emission spectra of pristine XPF films containing 34 and 52 wt% IBPF.](image)

Figure 5.26: Photoluminescent emission spectra of pristine XPF films containing 34 and 52 wt% IBPF.

A p(HEMA)/NIR dye layer was deposited on top of the \( \pi \)CP layer. The typical increase in absorbance between 600 to 900 nm and at \( \sim 475 \) nm, attributed to the NIR dye was observed, with optical densities at 830 nm of 2.79 and 2.34 for the 34 and 52 wt% films, respectively. Bilayer films were exposed to 830 nm laser irradiation, with an average dosage of \( \sim 1300 \) mJ/cm\(^2\), and the
resulting spectra are shown in Figure 5.27. For clarity, the absorption spectrum of the 34 wt% TAG film is not shown. Patterned films were cured under air and subdued light at 90 °C for 2 minutes to promote cross-linking of the oxetane moieties before methanol development. A test film of pristine XFP containing 34 wt% TAG was prepared and cured with the patterned samples. Subsequent development of the films with 70/30 THF/hexanes solution removed unexposed XPF and all of the cured test polymer film, unlike cured films of XPF in the presence of CSA, where cross-linking was initiated throughout the entire film. The UV-vis absorbance of the fully developed and patterned material was measurable and are shown in Figure 5.28. The $\lambda_{\text{max}}$ for the developed and patterned XPF films containing TAG were similar to pristine values at ~ 392 nm. The resulting patterns were characterized using UV-vis and photoluminescent spectroscopy and surface profiles were obtained where possible and are described in the following section.
Figure 5.27: UV-vis absorption spectra of XPF with 54 wt% IBPF and p(HEMA)/NIR dye films at various stages of patterning and development. The average laser exposure dosage was \( \sim 1300 \) mJ/cm\(^2\).

Figure 5.28: UV-vis absorption spectra of patterned and fully developed XPF that contained 34 wt% and 54 wt% IBPF. The average laser exposure dosage was \( \sim 1300 \) mJ/cm\(^2\).
Photoluminescent emission spectra and quantum yields of thermally patterned XPF were obtained and are shown in Figure 5.29. After development and patterning the emission spectra adopted a profile similar to that of the pristine polymer with emission peaks located at ~ 430 and ~ 460 nm, as well as a shoulder located at 480 nm. This suggests that the patterned material retains its pristine emission characteristics and that the formation of fluorenone is an unlikely reason for patterning failures, due to the fact that a broad emission peak is absent between 500 to 600.[18] This result is surprising because variable temperature FT-IR indicated that, under ambient atmosphere and elevated temperatures, fluorenone defects emerge in the polymer film at temperatures above 185 °C. At this optical density of NIR dye, i.e., ~ 2.5 at 830 nm, and laser dosages, i.e., ~1300 mJ/cm², patterning XPF in the presence of a TAG is possible. Quantum yields of photoluminescent emission were measured for patterned films and found to be approximately the same, with $\Phi_{PL}$ values of 0.25 and 0.23 for the 34 wt% and 52 wt% films, respectively. These values are approximately half of the pristine XPF value of 0.58.
Figure 5.29: Photoluminescent emission spectra of patterned and fully developed XPF that contained 34 wt% and 54 wt% IBPF. The average laser exposure dosage was ~1300 mJ/cm².

With the knowledge that XPF was successfully transferred to the glass substrate using the NIR 830 nm laser, based on the spectroscopic results presented above, fluorescent microscopy and surface profilometry were employed to characterize the polymer structures. Figure 5.30 contains microscope images and surface profiles of the patterned polymer. As shown qualitatively in the fluorescence microscopy images, both films containing varying weight percents of TAG, generated, at least partially, well-developed polymer structures. Figure 5.30a shows a patterned polymer grid of XPF. A profile scan length is indicated by the red line of the microscopy images in Figure 5.30. Pattern heights for the XPF film containing 34 wt% TAG were, on average, lower than the pattern heights measured for the film containing 52 wt% TAG, thus the
amount of acid present in the pristine, pre-patterned film may be an important parameter for successful laser patterning XPF. Despite the fact that the results presented in this chapter are preliminary, including Figure 5.30, thermally patterning an oxetane-functionalized material is demonstrated and that improved patterning of this material can be achieved through modifications to the polymer structure, i.e., removing patternable functional groups from “weak points” such as the 9,9’-position of the fluorene unit, adjusting the thermal acid generator : polymer ratio, as well as through a more systematic study of the curing times post-laser exposure. Work related to this project is promising.

Figure 5.30: Fluorescent micrographs and surface profiles of patterned and developed XPF a) from a film containing 34 wt% IBPF and b) from a film containing 52 wt% IBPF. Average laser dosage was ~ 1300 mJ/cm².
5.3 Conclusions

A new and highly photoluminescent blue emitting polyfluorene has been synthesized using standard a Yamamoto polymerization method. The 9,9'-position of the fluorene unit was substituted with alkoxyphenyl pendent groups terminated with cross-linkable oxetane functional groups. Based on the results presented here, the orientation of the phenyl substituents enhances the photoluminescent efficiency of the material by reducing polymer main chain aggregation, supported by the very high quantum yield, 0.58, which has also been demonstrated by other groups.

Patterning XPF using μ-contact printing methods was an effective method of depositing a πCP with resolutions as low as 10 μm, however, stamping conditions need to be better optimized in order to improve the pattern quality and uniformity. Thermal patterning of XPF was possible using the bilayered film architecture introduced in Chapter 3 and without the need for an acid generator as shown in Figure 5.20c, however, the pattern quality was poor and low pattern heights, < 20 nm, were observed. Including a curing time to the developing process and a thermal acid generator, such as 4,4'-dimethylidiphenyliodonium hexafluorophosphate, improved polymer pattern formation of XPF yielding polymer patterns as high as 60 nm. The polymer retained its absorption and luminescent properties and the photoluminescent quantum yield of emission was calculated and determined to be approximately 50% of the pristine material. In short, the results indicate that a more extensive optimization of the solution
formulation containing XPF and the thermal acid, as well as a more in depth study into the curing-developing stage need to be explored.

The presence and role of the phenyl substitution at the 9,9'-position of the fluorene unit has been argued in the literature. Some believe that the groups promote thermal and photo-oxidative stability, preventing the formation of fluorenone defects in the polymer main chain. Others believe that the incorporation of the phenyl groups do not confer thermal stability to the polymer. The variable temperature fluorescence and FT-IR results presented in this chapter however, support the findings reported by Andersson et al., that the phenyl functionality do not increase the thermal stability of fluorenone units to the formation of fluorenone defects. However, in the preliminary work presented here, thermal laser patterning does not appear to introduce fluorenone defects in the polymer main chain based on the emission spectra of patterned films and on the absence of a broad emission band between 500 and 600 nm.

5.4 Experimental

5.4.1 Synthesis of 3-(6-bromohexyloxymethyl)-3-ethyloxetane (1)

Compound (1) was prepared according to the procedure reported by Wen et al.[36] A two-neck flask equipped with a water condenser was charged with 11.62 g (0.100 mol) 3-(hydroxymethyl)-3-ethyloxetane and 73.19 g (0.300 mol) 1,6-dibromohexane in 400 mL hexanes. An aqueous solution (100 mL) of sodium hydroxide (45 wt%) and 1.61 g (5.00 mmol) tetrabutylammonium bromide
(TBAB) was then added to the hexanes solution under stirring. The mixture was then stirred over night at room temperature then refluxed for 2 hours. The solution was cooled to room temperature and diluted with water. The organic layer was extracted with hexanes and washed several times with water until neutral. The organic layer was then separated and dried with MgSO₄. Excess solvent was removed in vacuo and the compound (1) was purified via distillation at reduced pressure. The target product was obtained as a clear colorless liquid in approximately 78 % yield. Purity was determined by gas chromatography to be ~90 % and used without further purification.

5.4.2 Synthesis of 2,7-dibromo-9,9'-bis-(4-hydroxyphenyl)-fluorene (2)

The synthesis of 2,7-dibromo-9,9'-bis-(4-hydroxyphenyl)-fluorene was performed according to the procedure reported previously by Lindgren et al. [18]. To a 2 necked flask equipped with a condenser and magnetic stirrer was added 6.54 g (69.5 mmol) phenol and 2.35 g (6.95 mmol) 2,7-dibromofluoren-9-one. The flask was evacuated then the mixture was heated to 50 °C under argon, at which point the mixture became orange in color. Methanesulfonic acid (10 mL) and 28.6 mg (0.27 mmol) mercaptopropionic acid were then added and the reaction mixture was permitted to react over night. The resulting red suspension was poured into 250 mL water then filtered and rinsed with hot water several times. Compound (1) was obtained after precipitation from ethylacetate into petroleum ether. The compound was filtered and dried in vacuo in 98.5 % yield.

\[ ^1H \text{ NMR (DMSO-D}_6\text{): } \delta 6.67(\text{m, 4.00H}), 6.88(\text{m, 4.09H}), 7.49(\text{d, 1.97H}), 7.59(\text{dd, 2.03H}), 7.89(\text{d, 2.02H}), 9.42(\text{OH, 1.49H}). \]
5.4.3 Synthesis of 2,7-dibromo-9,9'-bis[[3-ethyl(oxetane-3-ethyloxy)-hexyl]-4-hydroxyphenyl]-fluorene (3)

A 50 mL round bottom flask was charged with 2.29 g (4.48 mmol) of 2,7-dibromo-9,9'-bis-(4-hydroxyphenyl)-fluorene (2) in 25 mL DMSO under argon atmosphere. While stirring the above solution, 5.19 g of 3-(6-bromohexyloxymethyl)-3-ethyloxetane (1) (17.9 mmol) was added and the solution was degassed several times. Finely ground potassium hydroxide (1.18 g, 18 mmol) was added and the reaction mixture turned from purple in color to green and was then heated to 60 °C over night. After approximately 1 hour the solution color changed from green to orange-brown. The solution was then permitted to cool to room temperature, diluted with 45 mL water and the organic layer was extracted with diethyl ether. The ether layers were collected, washed with water and dried over MgS04. The monomer was purified by silica-gel column chromatography using ethyl acetate/hexanes (1:5) as eluent. Product (3) was obtained as a sticky, viscous, colorless oil in 30 % yield. 1H NMR (acetone-D6): δ 0.90(m, 6.75H), 1.50(m, 9.23H), 1.63 – 1.79(m, 13.72H), 3.51(q, 4.56H), 3.56(s, 4.53H), 4.00(t, 4.00H), 4.27 – 4.35(m, 8.99H), 6.88(d, 4.07H), 7.13(d, 3.94H), 7.60(d, 3.87H), 7.90(d, 1.96H).

5.4.4 Synthesis of Poly(9,9'-bis[[3-ethyl(oxetane-3-ethyloxy)-hexyl]-4-hydroxyphenyl]]-fluorene) (XPF)

XPF was synthesized according to the Yamamoto polymerization method described elsewhere.[22] In a glove box, a 50 mL long-necked round bottom flask was charged with 290.6 mg (1 mmol) bis-(1,5-cyclooctadiene)nickel(0) and 156.2 mg (1 mmol) 2,2'-dipyridyl and sealed with a rubber stopper. Under argon
atmosphere, 0.12 mL (1 mmol) 1,5-cyclooctadiene and 4 mL of freshly dried and distilled DMF were added under stirring. The solution became dark blue-purple in color immediately and was permitted to react for several hours under subdued light. A degassed solution of 402.7 mg (0.445 mmol) 2,7-dibromo-9,9'-bis[[3-ethyl(oxetane-3-ethyloxy)-hexyl]-4-hydroxyphenyl]-fluorene (3) in 15 mL of freshly distilled toluene was then added via syringe. The solution was heated to 85 °C for 5 days. On the 5th day, a degassed aliquot of 0.1 mL of 1-bromo-4-t-butylbenzene was added and the reaction permitted to continue for another 24 hours to end-cap the polymer. The reaction mixture was cooled to room temperature and diluted with THF. The solution was filtered through an alumina column to remove catalyst with THF as eluent. The organic phase was collected and THF was removed at reduced pressure. The polymer was further purified via precipitation in stirred methanol. The pale yellow solids were collected and dried at reduced pressure in 57% yield. Mn: 21800 Da Mw: 75000 Da. ^1H NMR (CD2Cl2): δ 0.82 (m, 6.30H), 1.40 (m, 9.32H), 1.66 – 1.72 (m, 8.28H), 3.41 – 3.46 (m, 9.76H), 3.87 (t, 3.94H), 4.27 – 4.35 (m, 8.56H), 6.72 (d, 2.01H), 7.12 (d, 2.10H), 7.56 (d, 1.86H), 7.78 (d, 1.00H).

5.4.5 General Procedures

All materials were provided from Sigma-Aldrich and used as received unless otherwise noted. 4,4'-dimethylidiphenyliodonium hexafluorophosphate (IBPF) was provided by Creo Inc. (now Kodak Inc.) and used under dark-room conditions as received. The molecular weight of XPF was measured against polystyrene standards using gel permeation chromatography (Waters model 510).
equipped with μ-Styrargel columns. The conjugated polymer and polystyrene were eluted with THF at a flow rate of 1 mL/min and detected with a UV-vis spectrometer (Waters model 486) at 254 and 440 nm. UV-vis absorption spectra were obtained with a Varian Cary 300 Bio spectrometer. Thermogravimetric analyses were performed on a Shimadzu TGA-50. Measurements were obtained at a heating rate of 5 °C/min on 5 – 8 mg polymer samples under ambient and N₂ atmosphere. Differential scanning calorimetry was performed using a Perkin Elmer DSC 7 coupled to a Perkin Elmer thermal analysis controller (TAC 7/DX) at a heating rate of 5 °C/min under a nitrogen atmosphere. Variable temperature FT-IR spectra of drop cast films on NaCl plates were recorded on a ABB FTLA2000 series spectrometer coupled with a portable heater (Specac), temperature controller and sample holder. Samples were held for 20 minutes in air at a given temperature prior to recording a spectrum. Film thicknesses were determined using an Alpha-Step IQ surface profiler. Visible and fluorescent micrographs were obtained with a Nikon 50i Eclipse series microscope equipped with a 100 W mercury lamp and Q Imaging Qi-Cam 1394 digital camera. Nikon (UV-2B) and (V-2A) fluorescence filter cubes were employed, consisting of dichromic mirrors that permitted excitation wavelengths in the range of 330 – 380 nm and 380 – 420 nm and prevented wavelengths ≤ 400 nm and ≤ 450 nm from reaching the detector/camera respectively. Photoluminescent spectra and quantum yield measurements were obtained on a Photon Technologies International Quantum Master model QM-4 equipped with an integrating sphere.
5.4.6 μ-Contact Printing of XPF

An acid solution with a concentration of 0.01 M camphorsulfonic acid (CSA) dissolved in a solvent mixture 50/50 THF and hexanes (v/v) was prepared as the acidic ink. PDMS stamps containing 400 μm x 400 μm squares with 100 μm spaces and various lines widths and spaces between 5 and 250 μm were placed in the acidic ink for ~ 3 seconds, removed from the solution and permitted to air dry for 30 seconds before being brought into contact with a polymer film. The stamp was applied to the surface of the polymer film for ~ 15 seconds. The polymer film was placed in a pre-heated oven at 110 °C under ambient atmosphere and subdued light for 2 minutes. The film was developed first with several milliliters of a 50/50 THF/hexanes solvent mixture followed by dipping into a second developing solution containing 70/30 THF and hexanes, respectively.

5.4.7 Direct Thermal Patterning of XPF100

Individual bilayer films were prepared by spin casting polymer from chloroform and the top p(HEMA)/NIR dye layer from methanol solutions on glass. π-conjugated polymer solutions were prepared by dissolving 5.0 to 9.0 mg of the conjugated polymer in 400 to 600 μL chloroform. p(HEMA)/NIR dye containing solutions were prepared by dissolving 3.0 mg p(HEMA) and between 8.0 and 16.0 mg NIR dye (FEW Chemicals) into 300 μL methanol. Weight percents of IBPF were based on the total mass of XPF and IBPF. The π-conjugated polymer layer was spin cast on the substrate prior to the p(HEMA)/NIR dye layer. Both
films were spin cast at 1500 RPM for 1 minute. Thickness of the films, UV-vis absorbance and fluorescence spectra were recorded prior to and after deposition of the p(HEMA)/NIR dye containing layer. Films were patterned using an 830 nm NIR laser over a range of laser dosages (1700 – 900 mJ/cm²). Etching profiles of the films surface were recorded before and after methanol and THF/hexanes (50/50 or 70/30 (v/v)) development steps. Pattern heights and widths of the patterned films were measured after the final development step.
CHAPTER 6: THESIS SUMMARY AND FUTURE WORK

6.1 Summary

A novel method for patterning tetrahydropyran (THP) -functionalized π-conjugated polymers has been presented in this thesis. As a proof-of-concept, a thermally sensitive polythiophene derivative, PTHPET, was successfully imaged using an 830 nm thermal laser. In order to achieve thermal patterning of the polymer it was necessary to incorporate a NIR absorbing dye. It was shown that resolutions of patterned polymer features, as small as 10 μm, were achievable using laser dosages of ~ 600 mJ/cm² and laser scan speeds of 0.6 m/s. However, it was also shown that direct incorporation of NIR dye in the polymer film compromised the optical properties of the πCP.

An alternative method for thermally patterning THP-functionalized πCPs was investigated which alleviated the necessity of incorporating the NIR dye directly in the πCP. The approach involved depositing a second, methanol-soluble, non-conjugated polymer and NIR dye layer on top of the πCP layer. The πCP employed was a highly photoluminescent, THP-functionalized, polyfluorene-co-thiophene derivative, PFT-TT. The top dye-containing layer served as a sacrificial light-to-heat conversion layer that permitted heating of the underlying πCP layer without the need for direct incorporation of NIR dye. The photoluminescent properties of the πCP were nearly identical to that of the parent
polymer, retaining 86% of the original quantum yield. The resolution of patterned polymer features were also similar to that formed using single layer polymer architectures, with feature widths as small as 20 μm.

The generality of this patterning method was explored. First, the electrical conductivity of thermally patterned THP-functionalized polythiophene derivatives was evaluated using a 2-point probe technique. The resulting conductivities for patterned polymer, oxidized using I₂ vapour, were similar to that of the oxidized pristine material. Secondly, a novel cross-linking oxetane-functionalized polyfluorene was synthesized and investigated for use in micro-contact printing and direct thermal patterning. Thermally cross-linked and patterned polymer films were obtained using the bilayer approach, demonstrating that this patterning method is suitable for use with materials other than those containing thermally labile functional groups, such as tetrahydroxyran.

6.2 Material Considerations for use in Direct Thermal Patterning

The implementation of thermal lasers to deposit polymeric active materials could have a dramatic impact on the fabrication of organic microelectronic devices. The method discussed in this thesis has been shown to rapidly pattern polymers with ~ 10 μm resolutions over large areas and that the optical properties, such as absorption or fluorescence, and electronic properties, such as electrical conductivity, remain nearly identical to that of the pristine materials. From a material point of view, the biggest challenge will be in the synthesis of novel, high performance materials that retain 100% of their pristine properties.
such as crystallinity or film morphology, electron/hole mobilities or light emitting properties while still possessing the structural qualities that make direct thermal patterning (DTP) possible.

Polyfluorenes have been shown to be a very well-suited class of polymers in electroluminescent applications and by virtue of their synthetic versatility libraries of materials are possible in a relatively short amount of time. Thus, preliminary results for the laser patterning of varieties of THP-functionalized polyfluorenes, substituted at the 9,9'-position with and without phenyl functionality, has been attempted and has seen various degrees of success. A challenge arises from the fact that a patternable functionality is centralized on a weak point (arguably) in the fluorene monomer unit, the 9,9' carbon atom. For materials to have a greater chance of success in thermal patterning process, the patternable functional group should be located on some other part of the monomer unit or a copolymer or block design should be considered. Thiophene based polymers appear to have the best patterning characteristics, where image quality is concerned, and show the best thermal stability; however, they are not well suited for light-emitting applications.

**6.3 Direct Thermal Patterning and Device Fabrication**

Thermally patterning functionalized polymers using NIR lasers has been demonstrated using a variety of thiophene and fluorene based materials to varying degrees of success. The properties of the materials have been shown to be similar to that of the pristine polymers and so a logical next step would be employing the method in the fabrication of simple devices such as thin film
transistors. Device architecture would not need to be complicated and special materials are not required. The process would involve deposition and patterning of the active material on a silicon substrate coated with an arbitrary dielectric layer, such as silicon oxide, followed by deposition of the source-drain electrodes via metal evaporation through an appropriate mask. Measurements of the devices properties would be conducted using conventional FET testing methods.
APPENDIX 1 – PORTABLE 830 NM LASER OPERATION

A1.1 Laser Focusing

A simplified schematic of the portable 830 nm laser is shown in Figure A.1.

Figure A.1: A basic schematic of the portable 830 nm NIR laser. (1) Power switches and controls for disc rotation speed, laser scanning rate and laser power. (2) Rotating disc where samples are mounted for patterning. (3) Laser housing with protective cover (cover not shown). (4) Laser focusing micrometer.

Focusing of the laser spot is accomplished by directing the unfocused beam toward a piece of paper that is covered lightly with pencil lead. The pencil lead serves as the laser light absorbing medium. The paper is mounted on a substrate that is of similar height to that of the sample to be patterned so as to have a similar focusing distance from the laser source. For example, if a material
is patterned on a glass substrate of a particular thickness mount the focusing paper on a glass substrate should be the same thickness. When the is switched on, it is brought into focus with slow adjustments of the focusing micrometer knob. As the beam is brought into focus, the laser spot becomes smaller and eventually produces a spark at the surface of the paper. The spark should get brighter as the laser spot becomes more focused on the piece of paper. The laser was refocused when different laser powers were selected.

A1.2 Sample Mounting

Figure A.2 illustrates mounting of a sample film and the zone of laser exposure relative to the center of the rotating disc sample stage. Samples are mounted on the rotating disc opposite the laser, shown as the orange substrate in Figure A.1. Once mounted, the sample can be rotated in the path of the laser beam at a predetermined rate. The rate of rotation determines the dwell time and energy dosage of the incident beam on the surface of the sample. Samples are mounted on the disc within the first 2 to 2.5 cm of the circumference which means that areas of the film that are exposed to laser light between 55 and 40 mm from the center of the disc.
After a sample has been exposed the film consists of a series of arcs across the surface. Each arc has an associated distance from the center of the rotating disc and thus laser dosage can be calculated for each arc. In a given sample, however, the number of arcs could be between 70 and 100 and so the exposed films are typically divided up into 4 or 5 sections where the dosages and surface features are calculated. The radii employed for the individual sections are typically 55, 50, 45 and 40 mm which corresponds to laser dosages ranging from 1230, 1350, 1510 and 1700 mJ/cm², respectively.

**A1.3 Calculations**

**Disc Speed (m/s)**

The speed at which a sample is exposed is dependant on the samples’ distance from the center of the rotating disc in mm (R) and the rotation rate in
RPM (S) of the rotating disc. The disc speed can be calculated using **Equation A-1**.

\[
\frac{\pi SR}{3 \times 10^4} = \text{disc speed}
\]  

(A-1)

**Dwell Time (\mu s)**

The dwell time of the laser beam on the surface of a sample is dependant on the spot height of the laser (H) (2 \mu m nominal), the samples’ distance from the center of the rotating disc in mm (R) and the rotation rate in RPM (S) of the rotating disc. The dwell time can be calculated using **Equation A-2**.

\[
\frac{H \times 3 \times 10^4}{\pi SR} = \text{dwell time}
\]  

(A-2)

**Energy Density (mJ/cm}^2\)**

The energy density of the laser is dependant on the laser power in mW (P), laser spot width (W) (100 \mu m nominal), the samples distance from the center of the rotating disc in mm (R) and the rotation rate in RPM (S) of the rotating disc. The energy density can be calculated using **Equation A-3**.

\[
\frac{3 \times 10^6 \times P}{\pi SWR} = \text{energy density}
\]  

(A-3)
REFERENCES


