Optically Active and Stimuli-Responsive Macromolecules: Photophysics, Morphology and Sensor Applications

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Clemson University

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OPTICALLY ACTIVE AND STIMULI-RESPONSIVE MACROMOLECULES: PHOTOPHYSICS, MORPHOLOGY AND SENSOR APPLICATIONS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Ashley A. Buelt
May 2014

Accepted by:
Dr. Rhett C. Smith, Committee Chair
Dr. Karl Dieter
Dr. Jason McNeill
Dr. Stephen Foulger
Conjugated polymers are of particular interest for many device applications, especially those involving optoelectronics. Not only is there a potential for π-conjugated organic materials to replace inorganic materials in applications such as solar cells and light emitting diodes, but there is also the possibility for these materials to serve as key components of cheaper, more environmentally-friendly, lighter and more flexible materials. For over thirty years, researchers have been striving to understand the morphology, electrochemical and photophysical properties of this new class of organic materials. The work presented herein advances the field through synthetic design and morphological studies. In addition, several novel materials for metal ion and nitroorganic detection have been discovered.

The work delineated in Chapter 2 reveals the utility of the \( m \)-terphenyl unit to provide steric control of intra- and interchain interactions. A charge transfer band and a FRET effect were observed from materials prepared via simple post-polymerization modification. In Chapter 3, the detection of nitro-organics using several new polymers is discussed, with an extensive comparison to the literature. Steric, electronic, media polarity, and aggregation effects proved influential in the polymer-analyte interaction.

In Chapter 4 work is outlined wherein the morphology of polymers in solution and the solid state is further examined. The study revealed a correlation between aggregation in solution and eventual nanomorphology of films derived from the solutions. Chapter 5 expands upon the work in Chapter 2 with an exploration of six new polymers that were generated via post-polymerization of two parent polymers via
Sonogashira coupling. The new polymers were examined for use in metal ion and nitroorganic fluorescence response. The metal ion studies revealed the polymers to be tunable based on the donor or acceptor character of the spacer unit. From the detection of 2,4-dinitrotoluene, one polymer was found to have a comparable ultimate quenching efficiency to those discussed in Chapter 3.
DEDICATION

I would like to dedicate my dissertation to my parents, Ken Buelt and Susan Jensen-Kuehn and grandmother, LaVon M. Jensen who have always believed in me and never let me give up. I would also like to thank my friends for their continuous support and of course Professor Smith for being an amazing advisor.
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LIST OF ABBREVIATIONS

$\lambda_{em}$: wavelength of emission

$\lambda_{max}$: wavelength of absorption

$\Phi$: Photoluminescence quantum yield

CDCl$_3$: deuterated chloroform

CH$_2$Cl$_2$: dichloromethane

CH$_3$CN: acetonitrile

CP: conjugated polymer

D-A: donor-acceptor

DFT: density functional theory

DSC: differential scanning calorimetry

EA: electron affinity

EtOH: ethanol

GPC: gel permeation chromatography

HOMO: highest occupied molecular orbital

HRMS: high resolution mass spectroscopy

IP: ionization potential

KOrBu: potassium $t$-butoxide

LUMO: lowest unoccupied molecular orbital

MEH-PPV: poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene]

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<td>methanol</td>
</tr>
<tr>
<td>$M_n$</td>
<td>number average molar mass</td>
</tr>
<tr>
<td>$M_w$</td>
<td>weight average molar mass</td>
</tr>
<tr>
<td>$n$BuLi</td>
<td>$n$-butyllithium</td>
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<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>(O)LED</td>
<td>(organic) light emitting diode</td>
</tr>
<tr>
<td>PDI</td>
<td>polydispersity index</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>PPE</td>
<td>poly ($p$-phenyleneethynylene)</td>
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<td>PPV</td>
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<td>$T_m$</td>
<td>crystalline melting temperature</td>
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<td>TGA</td>
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<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<tr>
<td>UV-vis</td>
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Light is an astounding aspect of nature, one that provides energy and life. It is a mysterious concept that scientists and mathematicians struggled for centuries to understand and even today the scientific community is being surprised by new levels of understanding. Several prominent scientists such as Thomas Young, James Maxwell and Sir Isaac Newton realized light had wave-like and particle-like behaviour but had not yet recognized the duality of light. It wasn’t until Albert Einstein in 1905 that wave-particle duality was first embraced but it was still not fully understood. Max Planck’s description of energy in light as small packets, or bundles called photons sprung a new level of understanding. Neils Bohr redefined the atomic model incorporating Planck’s theories and described electrons existing in discrete orbits and when an electron falls to a lower orbital, energy is given off in the form of a photon.

In 1924, French quantum physicist Louis de Broglie introduced his wave-particle duality theory whereby he improved Einstein’s equation:

\[ E = mc^2 \]

by incorporating Planck’s constant to give:

\[ E = h\nu \]
and thus luminescence could finally be explained. Fluorescence and phosphorescence had been observed for quite some time prior to this and now energy could be related to frequency and wavelength, which is the foundation for understanding photoluminescence.

![Jablonski diagram illustrating radiative and non-radiative decay processes](image)

**Figure 1.1:** Jablonski diagram illustrating radiative and non-radiative decay processes

Most molecules exist in the ground electronic state at room temperature and upon absorption of light (photons) they become excited to the first or second excited state ($S_1$, $S_2$, respectively) depending on the amount of energy absorbed, as depicted in Figure 1.1.
An electron can get promoted to any singlet excited state ($S_n$) if enough energy is obtained but the simple diagram illustrated in Figure 1.1 only shows the first and second. A molecule in the excited state is energetically unstable and will return to the ground electronic state ($S_0$); however, this can transpire by either a radiative or non-radiative decay process. A molecule that absorbs light is known as a chromophore and a chromophore that fluoresces is known as a fluorophore.

These processes are illustrated by a Jablonski diagram as shown in Figure 1.1. Non-radiative decay processes are far more common than radiative. The energy absorbed can be given off as heat to the surroundings or can be transferred to other molecules via quenching via collisions or distance energy transfer. Some types of molecules such as π-conjugated materials are known for their radiative decay. The most common radiative decay is fluorescence. Fluorescence occurs by the molecule relaxing from an excited state to the ground state and a photon is given off as a result. In order for phosphorescence to occur, intersystem crossing must take place from a singlet excited state to a triplet excited state, which is a spin-forbidden process. Then another forbidden process must occur whereby a photon is given off from relaxing from a triplet excited state to the singlet ground state. Triplet states are also energetically unstable and non-radiate decay can result instead of phosphorescence thus making it the least common relaxation process.

When a molecule is excited the atoms vibrate or rotate from the excitation. The relation of energy to the distance between two atoms is given by the Morse curve Figure 1.2. The vibrational energy that occurs from excitation is periodic and anharmonic. When an atom moves from its equilibrium position electronic energy is produced. As two atoms
get closer to one another, their repulsive forces increase, and thus the energy between them also increases. As the atoms move farther from the equilibrium distance attractive forces are enacted to regain equilibrium and again energy increases. This occurs until the atoms are displaced beyond a certain distance and there are no longer any attractive forces thus reaching a plateau and anharmonic in nature.

The emission of a molecule is always at a lower energy than absorption and therefore the wavelength of emission is always greater than absorption because of the inverse relation. The difference between emission and absorption is known as the Stokes shift and was first observed by Stokes in 1852. The Stokes shift is affected by the fluorophores structure and the environment or rather, the solvent in which it is dissolved.

The rigidity of a molecule is a factor of absorption and emission. It controls the distance the atoms move from their equilibrium position, when excited and consequently affects the energy. A more rigid molecule will have less displacement of the atoms than a less rigid molecule and this can be seen in Figure 1.2. Ultimately these factors affect a molecules absorption and emission profile and consequently are of great interest for device applications.
Figure 1.3: Morse curve illustrating more rigid A) and less rigid B) molecules
In 2000, the Nobel Prize in Chemistry was awarded to Alan MacDiarmid, Alan J. Heeger, and Hideki Shirakawa for their discovery of semi-conductive \(\pi\)-conjugated polymers. The work these pioneers were awarded for began decades prior to 2000, the first polymer to be discovered with conductive capability was polyacetylene (PA), Figure 1.3, in the 1970s where it was doped with \(\text{Br}_2\) and found that the conductivity significantly increased from that of un-doped PA. Prior to this, conjugated polymers were utilized in applications like metallic-insulators, photoresistors, and insulators for the plastics industry. Upon unearthing conjugated polymers semi-conductive nature, the application possibilities were limitless and changed the direction of research.

This was the first time that any polymer was found to have conductivity on the

![Figure 1.3: Conjugated Polymers](image)

\(\pi\)-Conjugated Polymers

### Polyacetylene

\[
\left(\begin{array}{c}
\text{R} \\
\text{ } \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\end{array}\right)
\]

### Poly(p-phenylenevinylene)

\[
\left(\begin{array}{c}
\text{R} \\
\text{ } \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\end{array}\right)
\]

### Polythiophene

\[
\left(\begin{array}{c}
\text{S} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\end{array}\right)
\]

### Poly(p-phenyleneethynylene)

\[
\left(\begin{array}{c}
\text{R} \\
\text{R} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\end{array}\right)
\]

### Polyaniline

\[
\left(\begin{array}{c}
\text{H} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\end{array}\right)
\]

### Polypyrrole

\[
\left(\begin{array}{c}
\text{N} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\end{array}\right)
\]

### Poly(fluorene)

\[
\left(\begin{array}{c}
\text{R} \\
\text{R} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\text{\textit{n}} \\
\end{array}\right)
\]
order of metallic compounds.²,⁴ As a result of this discovery π-conjugated materials came to the forefront of research for applications such as photovoltaics, organic light emitting diodes, sensors, and many other facets due to the inherent electronic properties of their π-conjugated backbone. The first reported use of a conjugated polymer in an organic light emitting diode (OLED) was in 1987.⁵ By the 1990’s, the research had progressed beyond polyacetylene to other polymers such poly(p-phenylenevinylene), polythiophene, polyfluorene and others shown in Figure 1.3.⁶

Since the 1970s, there has been extensive research of various types of conjugated polymers both fully conjugated and some with intentional breaks in conjugation of traditional organic polymers as well as organometallic polymers. The conductive properties of some conjugated polymers have been close to that of metals, proving their validity in electronics. These studies have rendered such polymers as exciting materials for electronic applications due to their ease of processing, thin film flexibility, and low cost. Research has also revealed the versatility of functionalization which allows specific tuning for various device applications.
Applications

The electronic properties of π-conjugated polymers arrive from the delocalized electron density along the backbone of the polymer. This occurs because the conjugated π-bonds create a delocalized electron cloud through which electrons can flow freely. There are two types of orbitals involved with π-conjugated polymers; bonding and non-bonding. Within bonding orbitals there are two types σ, π and each of these also has an anti-bonding orbital σ*, π*. These are depicted in Figure 1.4.

![Energy orbital diagram illustrating bonding, non-bonding and anti-bonding](image)

**Figure 1.4**: Energy orbital diagram illustrating bonding, non-bonding and anti-bonding

The advantage of π-conjugated polymers is that their electronic properties can be tuned for the particular device application. There are also several ways this can be achieved through various monomer units, effective conjugation length, molecular geometry and spatial orientation. These types of adjustments affect the band gap of the
polymer. The band gap is comprised of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels as shown in Figure 1.5.7,8

![Diagram of Band Gap with A) classic conductance/valence band in relation to HOMO/LUMO level and B) HOMO/LUMO in relation to the vacuum level.](Figure 1.5)

Classical discussion of conductors involves a valence band and a conductance band and there is zero band gap. The electrons flow freely from the valence band which is the highest band with electrons to the conductance band which is the next highest band and contains holes or an absence of electrons. For an insulator there is an energy difference so large between the valence band and the conductance band that the electrons
cannot flow. Semi-conductors, have a smaller band gap between the two bands that electrons can still flow but there is some hinderance.\textsuperscript{9}

When discussing $\pi$-conjugated materials molecular orbital theory is utilized. Here the valence band is known as the HOMO and the conductance band is the LUMO. The band gap is calculated by the distance between the ionization energy and the electron affinity as depicted in Figure 1.5. The band gap energy level correlates to wavelength. The lower the band gap the longer the wavelength and vice versa.

Conductivity as well as photochemical characteristics can also be affected by creating a donor-acceptor model. A donor is an electron rich species and an acceptor is an electron deficient species. Combining these types of units encourages charge transfer where the electron moves from the HOMO of the donor to the LUMO of the acceptor. If a charge transfer occurs it is observed in the absorption spectra. Fluorescence resonance energy transfer is another phenomenon that can happen in $\pi$-conjugated materials. Here the fluorescence that is produced by one part of the molecule excites another part of the molecule and consequently an additional fluorescence band is observed. This can also be achieved by synthetic design and used for tuning the materials for specific devices.

Of the many applications that semi-conducting conjugated polymers can be employed, there are three that are prominent for the research herein; solar cells, OLEDs, and sensors. Solar cells exploit sunlight and convert it into electrical energy. Organic light emitting diodes convert electrical energy into light and sensors utilize chemical or physical stimulus which changes photophysical or electrical properties inviting detection.
Solar Cells

Solar cells have long been dominated by inorganic species previously including silicon, cadmium, tellurium, indium and selenium; however conjugated polymers have the potential to outperform inorganic materials, most notably for their flexible nature in addition to their conductivity. All solar cells contain an electron donor and an electron acceptor material. The electro-active component can be incorporated as two separate polymers, although there is the ability for one polymer to contain both a donor and an acceptor piece.

Figure 1.6: Schematic of how a solar cell works
Solar cells work by the donor polymer or part of the material absorbing a photon and then transferring the excited electron to the acceptor polymer or portion of the conjugated polymer via inter or intrachain processes. More specifically, the excited electron, or exciton, relaxes from the LUMO of the donor to the LUMO of the acceptor in a charge transfer fashion as depicted in Figure 1.6. Excitons, have a short life time and as discussed earlier can be subject to several non-radiative processes. In order to maximize efficiency, π-conjugated polymers containing a donor and acceptor piece are most attractive and this type of cell is known as a bulk heterojunction cell (Figure 1.7).\textsuperscript{11,12} During the charge transfer process, two charges are created in the conjugated system, a

\textbf{Figure 1.7:} A simplistic example of a bulk heterojunction solar cell
positive on the donor and a negative on the acceptor. Once the electrical current is applied, these charges move to either the anode or the cathode of the solar cell. Indium tin oxide is a typical anode due to high work function and cathodes consist of metals like aluminum, calcium or manganese.

There are a few materials that have come to light since the quest for competitive polymers over metals began. Most notably are those such as MEH-PPV, P3HT (Figure 1.8) and (PCBM Figure 1.7). Poly(3-hexylthiophene) and MEH-PPV are good electron donating conjugated polymers due to their electron rich backbone. Electron accepting materials like, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) a C60 derivative, are able to stabilize electrons well and can collect up to 6 electrons they also have lower

![Figure 1.8: Notable electron donating materials](image)

13
LUMO energy levels which helps encourage electron transfer.\textsuperscript{11,12}

Power conversion efficiencies (PCE) of organic photovoltaics (OPV) are less than ten percent and are currently around 5%.\textsuperscript{11,12} Theoretical calculations indicate that 10% conversion efficiency is possible with OPVs. In order to achieve this PCE level several things need to be optimized. The molar absorptivity of the molecule, band gap, lifetime, and charge transfer are a few of these characteristics and then the material needs to be cost-effective on an industrial scale. The environmental benefits as well as the potential for flexible materials have been the driving force to overcome these monumental challenges.

**Organic Light Emitting Diodes**

Light emitting diodes are possible because of electroluminescence. Electroluminescence is the process whereby light is generated by passing an electrical current through a material, in the case of OLEDs a π-conjugated polymer. An OLED works much like a solar cell where the conducting material is positioned between two electrodes and a material combining a donor and an acceptor is again desirable for efficiency. Much like solar cells inorganic materials have dominated LEDs. The first observed electroluminescence was in 1963 from anthracene crystals.\textsuperscript{8} Since then LEDs employing GaAs are common; however, in 1990 the first reported organic semiconductor material, poly(\textit{p}-phenylenevinylene), was reported in a OLED.\textsuperscript{13-15} This obviously sparked the quest for better organic materials with properties like tunability, processability, and again flexibility being the driving forces for the research in OLEDs.
Figure 1.9: Simple schematic of an OLED
Sensors

A chemosensor is a molecule that detects an analyte from a chemical reaction. This type of sensor is illustrated in Figure 1.10. In order for a chemosensor to be a good detector it must consist of a receptor and an indicator. Chromophores or fluorophores are typically employed in organic chemosensors for their convenient detection due to their optical properties. Several types of mechanisms can result from receptor binding but commonly utilized are: pH changes, photo induced electron transfer, and fluorescence resonance energy transfer (FRET). These are generally employed because when their optical properties are altered these can be easily detected in the field by the eye due to their absorbance or photoluminescence profiles and are fast detectors in time sensitive situations. Again due to the tunability of π-conjugated polymers, selectivity and sensitivity can be achieved. Current sensing work will be discussed in the following sections.

**Figure 1.10**: Simplistic schematic of fluorescent sensor
Sterically Encumbered Units

Each device application has specific requirements that a CP must possess. In order to amplify the polymer’s inherent characteristics which lend it towards a certain application, competing interactions must be controlled or eliminated. As mentioned previously, non-radiative processes can be very competitive. Inter and intrachain interactions can sometimes be competing but they can also be beneficiary. Interchain interactions occur when the exciton transfers from the LUMO of one chain to the HOMO of another. Intrachain processes are when the exciton transfers from the LUMO of a donor unit to the LUMO of an acceptor unit. Both types of interactions can be advantageous or detrimental. In order to make conjugated polymers tailorable for specific applications it’s extremely important to understand how to control these interactions. In addition to attempting to optimize lifetime via exciton confinement, steric control can be extremely useful for either enforcing or preventing these interactions. Steric scaffolds affect the geometry and orientation of chromophores which ultimately controls the interactions. These interactions then determine fluorescence quantum yields, charge transfer, and charge carrier mobility.\(^{18}\)

To date there have been several types of steric protecting scaffolds studied. Some of the most effective are \(2,2\)/paracyclophane, covalently linked polymer chains, and xanthenes. These types of materials are illustrated in Figure 1.11. Swager’s group has studied macrocycles with both a single polymer chain in an effort to prevent interchain interactions and two different polymers to prevent and enforce interchain interactions.
Figure 1.11: Sterically encumbered conjugated polymers relevant to discussion
The length of alkyl chains as covalent linkers has also been studied to optimize geometry and distance as a means of control.¹⁹,²⁰

Bulky sidechains or units have also been used to prevent the formation of aggregates in the solid state. Yang and Swager utilized pentiptycene units for this purpose and were found to be very effective.²¹ Not only are steric units excellent for the aforementioned reasons but they can also create porous regions, or free space, in the solid state which are necessary for analytes to travel through the material.

Another type of steric protecting group is the \( m \)-terphenyl unit and some examples can be seen in Figure 1.12. Some of the examples in Figure 1.12 (A, B, C), contain a 2,6-dimesitylphenyl unit which is a derivative of the \( m \)-terphenyl. Terphenyls have been used in small molecule models to examine their affect in low molecular weight compounds,²² and they have been shown to effectively eliminate extraneous interchain interactions.²³, ²⁴ Similar utility is noted for conducting metallopolymers where they control unwanted metal-induced cross-linking.²⁵,²⁶ Such \( m \)-phenylene units also promote exciton confinement due to conjugation disruption.²⁷ Hyperbranched luminescent polymers that are functionalizable post-polymerization have also been explored.²⁸
Figure 1.12: Some $m$-terphenyl protecting groups
Metal Ion Detection by $\pi$-Conjugated Polymers

Conjugated polymers have come to the forefront of research for metal ion detection due to their sensitivity, tunability and optical characteristics. Fluorescence detection is the main method for detection. It is one of the most powerful methods for chemosensors because it doesn’t consume analytes and several spectroscopic techniques have been developed for field use in addition to laser fiber optics. Fluorescence is also a sensitive method allowing for detection of single molecules and thus is most viable for industrial, environmental and biological applications. Most commonly targeted metals are transition metals including but not limited to: $\text{Ag}^{2+}$, $\text{Cd}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$, $\text{Fe}^{2+}$, $\text{Hg}^{2+}$, $\text{Mn}^{2+}$, $\text{Mo}^{2+}$, $\text{Ni}^{2+}$, and $\text{Zn}^{2+}$. There is also a field of research for static binding incorporating metals like rhenium, ruthenium, platinum, palladium, iridium and osmium; however that is outside the scope of this introductory chapter for metal sensing. Static binding is intended for metallopolymers where the metal being incorporated is bound covalently and irreversibly during or after polymer synthesis, either in the backbone of the polymer or as a tethered side chain. Many platinum, palladium, and ruthenium metallopolymers are done in this manner. Dynamic binding usually occurs after synthesis of the polymer and is not bound covalently rather via non-covalent coordination interactions and can be reversible. Dynamic binding can lead to the detection of multiple ions or can be selective. Most of the polymers discussed in this introduction are dynamic binding as they are more advantageous for metal sensing.
Fluorescent sensors signal chemical presence by a change in the fluorescent spectral properties. This can occur either through a change in the intensity, a blue or red shift or an entirely new wavelength. There are also several mechanisms by which these changes can occur. The types of mechanisms that are most common are photoinduced charge and electron transfer (PCT, PET, respectively), paramagnetic quenching, fluorescence resonance energy transfer, and excimer or exciplex formation.

Some common types of ligands that are effective fluorophores for ion sensing are: anthraquinone, xanthone, acridinone, rhodamine, fluorescein, quinoline, naphthalimide, dansyl and many others. The fluorophore can be incorporated into any conjugated polymer for use in ion detection; however, polyamines, polyethers, polysulfides, PPVs and PPEs are common and macrocycles are often included. The specific combination of fluorophore and conjugated polymer directly correlates to the ion being tested and thus it is essential to continue work in this area of research.

Metal ion detection by CPs has been reviewed previously\textsuperscript{14,29}, most recently by Holliday’s group for lanthanide metals;\textsuperscript{31} however earlier notable polymers are delineated below. Some dynamic metallopolymers from the literature have been illustrated in Figure 1.13. With dynamic binding it is important to recognize that the metal center is directly involved in the conjugation system and thus can have a profound effect on the conductivity, and photophysical properties.

Reynolds and coworkers examined the use of Schiff-base ligand in polymer B of Figure 1.13, for their high coordination affinity, and robust chemical nature. From their studies they found that zinc, copper, nickel and cobalt ions bound to the ligand.\textsuperscript{32-33} They
Figure 1.13: Some relevant metal ion sensing polymers from the literature
also found that the electrochemical properties of the polythiophene backbone were altered by the metal centers inductively.\textsuperscript{33,34} Pizzoferrato and coworkers found that a porphyrin based polymer (Figure 1.13.D) can exhibit near IR emission upon coordination with a lanthanide element erbium. The emission was centered at 1530 nm from the resulting metallopolymer. Terpyridine containing ligands like that of the polymer in Figure 1.13.C have also been found to be excellent binding moieties for metals.

In 2010, Hirao’s group published a poly(aniline sulfonic acid) based polymer for the detection of transition metals in regards to water contamination.\textsuperscript{35} They found that upon addition of (copper II) acetate to the aqueous solution there was a morphological change from an extended coil to a compact coil and can be detected by a colorometric transition metal sensor due to a yellow to green color change upon conformational change.

Work in our own research group for metal ion detection has included the incorporation of 2,2’bipyridyl (bipy) units primarily. These bipy units have been employed in polyelectrolyte conjugated polymers, PPE’s and PPV’s as can be seen in Figure 1.14.\textsuperscript{25,26,36} Most notably we found that the redox properties from particular metals can enhance the polymer’s properties while still keeping the qualities of the CP. We also found that the bipy units can eliminate undesirable crosslinking/network formation, and leave a cleft of free space for analytes. This can also allow for different ligand-to-ligand distances.\textsuperscript{36} Independent nanomorphology of polymer films was also demonstrated on different substrates. My contribution to our group’s ongoing interests to this area will be discussed in Chapter 5.
Figure 1.14: Some relevant metallopolymers and metal sensing polymer from the Smith group
Nitroorganic Detection by π-Conjugated Polymers

Nitro-organic or explosive detection is another important area of research for CPs. This type of research is extremely relevant for landmine detection, and other chemical warfare. Trinitrotoluene (TNT), dinitrotoluene (DNT) and the taggant 2,3-dimethyl-2,3-dinitrobutane (DMDNB) are common nitro-organics that are used in explosive materials. Dinitrotoluene and DMDNB have higher vapor pressures than that of TNT and are thus often used as the analyte in these studies. TNT has a high electron affinity and thus engages in electron transfer quenching mechanisms. The necessary polymer characteristics (electronic makeup, morphology and film thickness) in addition to small molecule properties (binding strength, vapor pressure, quenching level, and diffusion rate through films) must be explored thoroughly in order to create state-of-the-art materials. Nitroaromatic detection by CPs has been reviewed previously, most recently Swager’s group. Some notable reports up to that time are delineated below.

Some of the best conjugated polymers for explosive detection were also those discovered early on. The latest review in 2013 by Rochat and Swager reported that Yang and Swager developed a series of poly(p-phenyleneethynylene) moieties that incorporated rigid iptycene units into the polymer backbone Figure 1.14. As previously discussed pentiptycenes are excellent bulky groups that generate free space and minimize aggregation in thin films giving rise to solution-like optical properties by prevention of undesirable interchain interactions. These moieties also give rise to size exclusion characteristics. These polymers exhibit high fluorescent quantum yields,
high stabilities and low detection levels in times applicable in the field. Polymer 5 was found to detect TNT at 10 ppb after a few seconds of exposure.\textsuperscript{40} Due to these impressive capabilities, it has been employed in the detection of roadside bombs, buried landmines, suspected bomb makers, and other homeland security-related tasks.\textsuperscript{42}

In 2008, this work was expanded to the excitation of polymer 6 (slightly modified version of polymer X) using multiphoton irradiation.\textsuperscript{43} Multiphoton excitation is advantageous for explosive detection because it safer since it uses infrared radiation, and can be used from a farther distance (remote sensing) due to its higher depth penetration. Infrared irradiation also allows for a minimization of absorbance from the medium and decreases scattering effects. The polymer was found to be on par qualitatively with single-photon excitation responses for similar polymers.

Pyrene-containing polymers (9, 10, 11 in Figure 1.15) as thin films were studied in aqueous media and significant emission quenching was observed from low concentrations of TNT. The proposed mechanism was formation of non-fluorescent complexes between the polymer and TNT as a result of matching orbital energies. Selectivity was also achieved over other nitroaromatics: DNT, nitrobenzene and trinitrophenol.

PPE polymers were found to be generally more responsive than their PPV counterparts due to their enhanced rigidity which promotes exciton transport. PPV polymer 4 also exhibited a large two-photon cross-section and thus could be utilized for multiphoton detection of TNT like polymer 6 mentioned previously.\textsuperscript{43}
Silicon-based $\pi$-conjugated polymers have also been extensively studied. Polysiloles are effective explosive sensors due to their low LUMO energy levels as a result of $\pi^*$ and $\sigma^*$ orbital mixing. This mixing often lends delocalized electronic states.\(^{44-46}\) Polymer 7 had a less selective response to several nitro-organics due to its open scaffold and had a detection limit of 200 pg cm\(^{-2}\) for Tetryl (i.e., 2,4,6-trinitrophenylmethylnitramine).

Since the last review of this field, some progress has been made and one report that bears mentioning was by Pablos and coworkers. They discovered colorometric sensors (the material changed color (RGB) by naked eye) for the detection of TNT upon addition of polymer membranes or coated fibers in solution containing TNT.\(^{47}\) Here fluorescence isn’t needed and can be analogous to a simple pH test using pH paper. They found the intensity of the color depended on the concentration of TNT. Low concentrations ($1 \times 10^{-5}$ M) were barely visible and detection times were around 25-30 min which is far longer than that of the solid state fluorescence detectors; however, one did have a detection time of 2 min.

Work in our own research group in the area of nitro-organic detection has included polyfluorene PPVs, cyclophane PPEs, $m$-terphenyl PPVs and others. We concluded from our recent study that there is a lack of correlation between solution and solid state quenching efficiencies.\(^{48}\) From this study the sensitivity and selectivity of several conjugated polymers with nitro-organics was outlined. My contribution to our group’s ongoing interests to this area will be discussed in Chapters 3 and 5.
**Figure 1.16**: Conjugated polymers for nitroaromatic detection generated by Smith group
Techniques

Absorbance Spectroscopy

Absorbance spectroscopy is one technique used to characterize a material’s photophysical properties. This is necessary for applications such as solar cells or light emitting diodes. From UV-Visible spectroscopy (UV-vis) not only can the regions where the material absorbs light be determined but also charge-transfer bands can be seen as discussed earlier.

Absorbance spectroscopy assesses ultraviolet and visible wavelengths (200 – 800 nm) of the electromagnetic spectrum. A simple diagram of the typical components of a spectrometer can be seen in Figure 1.17. A beam of light from a visible (tungsten) and/or UV (deuterium) light source is separated into components via a prism or grating monochromometer. In the diagram below the monochromatic wavelength is sent through the material and the portion of light that is not absorbed is then sent to the detector. In a

![Figure 1.17: Simplistic schematic of UV-Vis single beam spectrometer](image-url)

Figure 1.17: Simplistic schematic of UV-Vis single beam spectrometer
simple UV-vis spectrometer like the one in Figure 1.17 a reference sample (the transparent solvent the material is dissolved in) must be taken prior to running the sample. Some spectrometers run a reference and the sample at the same time but this requires a more elaborate design. The intensity of the initial beam of light is defined as $I_0$, and the intensity beam that is from the sample is defined as $I$. Absorbance may be presented as transmittance where $T = I/I_0$ or more commonly as absorbance where $A = \log I_0/I$.

Molar absorptivity is a corrected absorption value of the material in a dilute transparent solvent. Molar absorptivity is a parameter used for comparison because the absorbance of a sample is proportional to its molar concentration in the sample cuvette. Molar absorptivity ($\varepsilon$) is defined as $\varepsilon = A/cl$, where $A$ is absorbance, $c$ is the concentration of the sample and $l$ is the path length of the cuvette. Large molar absorptivities are seen for strongly absorbing units and very small absorptivities for weak absorption. This is a particularly useful tool when comparing the relative strength of chromophores (light absorbing units) in different compounds.
Photoluminescence Spectroscopy

Photoluminescence (PL) or fluorescence spectroscopy is another useful technique used for organic small molecules and polymers. Like UV-vis, this technique is also used to characterize a material’s photophysical properties and is again necessary for applications such as solar cells and organic light emitting diodes.

Once the absorbance profile for a material is determined the PL is generally taken. Most often a material is excited at the $\lambda_{\text{max}}$ from the UV-vis spectrum and from this the emission profile can be collected. A simple schematic of a fluorescence spectrometer is delineated in Figure 1.18. All fluorescence spectrometers contain a light source, a sample holder and a detector. In modern spectrometers the wavelength of incident radiation is selectable and the signal from the detector is manipulated and presented from a computer.

**Figure 1.18:** Simple schematic of a single beam fluorescence spectrometer
In simple spectrometers, a filter is utilized for both the excitation and emission wavelengths and in more sophisticated spectrometers a monochrometer is used. Commercial fluorescence spectrometers utilize photomultiplier tubes or charge-coupled device cameras as detectors. The optical paths of the excitation and emission wavelengths are orthogonal to one another, which allows for a minimization of excitation wavelength to be passed onto the detector.

There are a few types of light sources that can be employed. The first of which was a tungsten/halogen lamp and then mercury lamps were later employed. Mercury lamps depend on the pressure of a filter gas where medium and high pressures give rise to an output over the whole UV-vis spectral region. Mercury lamps are commonly employed in line sources. Line sources provide a series of discrete lines and while this is often adequate a more superior source is a continuum of energy and this can be attained from a xenon arc lamp. Xenon arc lamps provide relatively uniform intensity over a broad spectral range from ultraviolet to near infrared; however they are more unstable long term than discharge sources and thus a method to correct drift is necessary.

As previously discussed, fluorescence is a result of radiative relaxation from an excited state (Figure 1.1). Not only can a PL spectrometer measure fluorescence but it can also deduce phosphorescence, FRET, and some can also provide lifetime and polarization data. Lifetime and polarization measurements require a more elaborate design than the one displayed in Figure 1.18.
Thermal Analysis

A polymer’s thermal properties are essential to know for device applications. The temperature at which a polymer decomposes is relevant for applications such as solar cells for example. There are two common techniques used to assess the thermal characteristics; thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). From thermal analysis (TA), the decomposition temperature ($T_d$), glass transition temperature ($T_g$), the crystalline melting ($T_m$) and crystallization temperature ($T_c$), as well as other characteristics can be determined. Typically thermal analysis is run under inert conditions (nitrogen, argon) but can be run under air or oxygen.

Differential Scanning Calorimetry

DSC measures the heat energy per unit of time, or power, differential between a reference and the material being analyzed. Generally, a hermetically sealed aluminum or platinum pan is utilized. This technique is commonly used to determine the $T_m$, $T_g$, and $T_c$, (Figure 1.19) as well as the heat of fusion of a polymer. Kinetics of chemical reactions (oxidation and decomposition) can also be determined from DSC.

There are several factors that can affect the DSC curve such as heating rate, sample history (prehistory), atmosphere, sample size and reference. Only prehistory and heating rate will be discussed here. Generally, it is advantageous to destroy the prehistory of a sample in order to generate a reproducible curve. To accomplish this, the sample is heated above the crystalline melting temperature, or if unknown in many cases below the decomposition temperature, in an inert atmosphere and then cooled back to the start temperature. This should be repeated until the curve is consistent. The prehistory should
be studied, however, if determining how a particular process, i.e. aging, film or fiber processing affects a compound. The heating rate can be adjusted in order to achieve the best representation. Typical heating rates are between 10-20 °C/min because the ratio of single to noise is dependent on the heating rate. As the temperature increases the thermal lag between the sensor and the sample also increases and therefore decreases resolution.
of transitions. Although, the amplitude of $\Delta T$ signal increases with heating rate, but it also increases the signal to noise ratio.

**Thermal Gravimetric Analysis**

The $T_d$ of a polymer is usually determined from TGA. The necessary components of a TGA are a precision microbalance, a furnace, a program controller, and a data acquisition system (Figure 1.20). TGA records the mass loss versus the temperature. This is done by weighing the sample overtime as temperature increases under a controlled atmosphere. The loss of mass can be due to several things: volatilization of a solvent,
decomposition of the material resulting in gases given off and there is generally a small percentage of material remaining known as ash.

In order for a material to be properly analyzed by TGA, mass and temperature are the two most important factors that must be determined accurately. In Table 1.1, the influences on mass and temperature are given. Most of the factors affecting mass can be dealt with by proper maintenance of the equipment and choice of atmosphere. Buoyancy problems occur when the sample is in a lighter gas environment. This is often negligible; however, can be corrected via instrumental and software adjustments. Atmosphere turbulence depends on the gas, flow rate, direction of flow and pressure. Electrostatic and magnetic forces arise from low humidity of the surroundings and the purge gas. These conditions can cause the sample holder to be attracted to the closest wall. Electronic drift is generally only a problem for experiments lasting several hours but some instruments are sensitive to vibration in which case precaution to minimize this should be taken.

Temperature accuracy is a greater problem in TGA than mass. The geometry of the sample, furnace and the sample are the largest contributors to temperature inaccuracy.

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<th>Mass</th>
<th>Temperature</th>
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<tbody>
<tr>
<td>Buoyancy</td>
<td>Heating Rate</td>
</tr>
<tr>
<td>Atmospheric turbulence</td>
<td>Enthalpy of the process</td>
</tr>
<tr>
<td>Electrostatic and magnetic forces</td>
<td>Sample, furnace and sensor arrangement</td>
</tr>
<tr>
<td>Electronic drift</td>
<td>Electronic drift</td>
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</table>

*Table 1.1: Factors that affect thermogravimetry*
The placement of the sample holder should be as close to the heat source, thermocouple, as possible without affecting the mass of the sample. Overtime the thermocouple can become corroded by previous sample degradation and affect the accuracy. There are also mass and temperature calibrations via standards utilizing a background correction.
Present Work

The research herein examines how polymeric design affects photonic properties and the morphology of \(\pi\)-conjugated polymers. Primarily, the polymers designed here were intended for use in organic light emitting diodes or solar cells. Polyelectrolyte studies have been incorporated for insight into the benefits of their photophysical and morphology properties when made in layer-by-layer films.

Chapter 2\(^a\): Two poly\((p\text{-phenylenevinylene})\) derivative alternating copolymers (P1-I and P2-I) have been prepared featuring iodo substituents and \(m\)-phenylene units to periodically disrupt conjugation. P1-I was derivatized with various chromophores to yield P1a-f. In P1a-f, the chromophores were positioned within a sterically protected pocket shielding them from interchain interactions so that intrachain interactions between polymer segments could be observed. Solution and film properties of polymers have been examined. Post-polymerization chromophore modification leads to new photophysical properties such as intramolecular charge transfer and fluorescent resonance energy transfer processes in some cases.

Chapter 3\(^b\): A series of eight poly\((p\text{-phenylenevinylene})\) (PPV) and poly\((p\text{-phenyleneethynylene})\) (PPE) (P1-P8) derivatives were tested for their ability to detect the nitroaromatic explosive 2,4,6-trinitrotoluene (TNT) and its model compound 2,6-dinitrotoluene (DNT). The polymers P1-P8 represent five structural classes that have not been examined for nitroaromatic sensing. These new motifs include PPE derivatives with

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\(^b\) License obtained for permission, see Appendix
a main chain $m$-terphenyl unit (P1) or oxacyclophane canopy-like structure (P2); and PPV derivatives with 2,6-mesitylenephénylene repeats (P3 and P4), 9,9-dialkyl-1,4-fluorenylene repeats (P5 and P6) or $m$-phenylene units that periodically disrupt $\pi$-conjugation along the backbone of the polymer (P7 and P8). The time-dependent photoluminescent response of films to and DNT, as well as solution-phase Stern-Volmer quenching constants for both TNT and DNT were determined. Results are rationalized in terms of side chain steric and $\pi$-system electronics, and are discussed relative to known conjugated polymers.

Chapter 4: The synthesis of two $\pi$-conjugated polymers whose structures include $m$-pyridyl linkages that create regularly-spaced bends and disrupt $\pi$-conjugation along the polymer backbones is described. The $\pi$-conjugated segments in the two polymers were comprised of $p$-(2,5-dialkoxyphenylene)vinylene, $p$-phenylenevinylene and 2,7-carbazole subunits. Additionally, each $m$-pyridylene unit is enshrouded within a steric cleft provided by 2,6-diaryl substitution of the pyridyl ring, thus minimizing inter-chain interactions about these sites. The concentration-dependence of photophysical characteristics along with small angle neutron scattering (SANS) were employed to resolve solution aggregation properties and atomic force microscopy was employed to assess surface morphology of polymer films.

Chapter 5: Two $\pi$-conjugated polymers featuring main chain $m$-phenylene linkers as well as iodo-substituents were initially prepared. The presence of the iodo

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functionality allowed for the preparation of six additional polymers from the initial two iodo-substituted polymers via facile post-polymerization modification using Sonogashira type coupling chemistry. The post-polymerization modification led to crosslinking, incorporation of a pyridyl-bearing functionality for potential use as a ligand for transition metals or to the introduction of a ferrocenyl substituent as a possible redox-active unit. The m-phenylene units were incorporated into the polymer main chain structure in order to periodically disrupt conjugation, and thus allow for more uniformity in the effective conjugation length and thus absorption and emission profiles. The thermal stability and photophysical properties of all eight polymers are reported, as well as the stimuli-responsiveness of relevant materials to nitroaromatics and metal ions.

d) Submitted to Polymer Chemistry, March #, 2014.
References


CHAPTER TWO

POLY(P-PHENYLENEVINYLENE) DERIVATIVES WITH DEFINED CONJUGATION SEGMENTS AND POST POLYMERIZATION MODIFICATION WITH STERICALLY-ENSHROUDED CHROMOPHORES

Introduction

The rapid evolution of conjugated polymer (CP) research from the initial discovery of their metallic conductivity in the doped state in the 1970s\textsuperscript{1-4} to the utility of CPs in commercial devices has been one of the great success stories in materials science over the last half century. Ongoing interest in improving such systems has lead to an ever-increasing sophistication of polymer structures and nano/molecular architectures being explored.\textsuperscript{5} These studies are driven in part by the widespread recognition that application of CPs in technologically viable contexts requires careful control of the

\textbf{Chart 2.1:} \textit{M-terphenyl motif}

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interchain interactions that dictate energy and charge transfer (CT)/mobility processes.\textsuperscript{6–9} These processes can be decidedly influenced by the presence of defects resulting from a particular synthetic methodology, the manner in which polymer films are formed, and other subtle considerations.\textsuperscript{10–17} Disruption of conjugation by incorporating functionalities that twist the $\pi$-system from coplanarity is one strategy that facilitates exciton confinement.\textsuperscript{15} Another strategy towards tuning CP photophysical profiles is to prepare hyperbranched luminescent polymers that bear functionalities that allow them to be functionalized post-polymerization,\textsuperscript{18} thus affording a remarkable platform for tailored application and property acquisition.

In the current work, we have prepared $\pi$-conjugated polymers featuring both periodic disruptions of conjugation in the form of $m$-phenylene units, and iodo substituents for post-polymerization elaboration with various chromophores. The introduction of periodic conjugation disruption yields materials in which the effective conjugation length is well defined. One goal of the current project was to scaffold intrachain interactions between these well-defined conjugation segments and appended small molecule chromophores. It was envisioned that this goal could be accomplished if the sites for post-polymerization modification were positioned within a sterically enshrouded pocket that would allow close contact of the appended chromophore with adjacent segments, but which shielded the chromophore from extraneous interchain interactions (Figure 1D). The $m$-terphenyl unit has been selected to provide the desired steric cleft. Such $m$-terphenyl units have found increasing utility as steric protecting groups\textsuperscript{19–21} to shield chromophores from extraneous inter-$\pi$-system interactions in CPs.
(Figure 1A$^{22}$ and B$^{23}$) and in ligand-modified scaffolds for conducting metallopolymer
(Figure 1C)$^{24}$ as a means of providing steric coordination control against metal-induced
cross-linking.$^{25}$
Figure 2.1: Some conjugated materials featuring \( m \)-terphenyl subunits (A–C) and schematic design of materials described in the current work (D).
Results and Discussion

Synthesis

Horner-Wittig condensation is a preferred method for the preparation of PPV derivatives because it yields near exclusive formation of E-olefinic linkages, and has a lower incidence of defects than alternative routes such as Heck coupling or Gilch condensation. Target materials were thus designed to serve as monomers for Horner-Wittig condensation polymerization as the preferred route to the post-polymerization-modifiable polymer bearing $m$-phenylene segments.

The convenient preparation of $m$-terphenyl 1 in ca. 20 g batches lead to its selection as an initial precursor comprising both the $m$-phenylene segments and the iodo substituent required for post-polymerization modification. Radical bromination of 1 following the reported procedure led to 2, which was conveniently transformed to monomer 3 by a Michaelis-Arbuzov reaction (Scheme 1A). Terephthaldialdehyde derivative 4 and the $\alpha,\omega$-diformyl mesogen (5) were selected for copolymerization with 3 (Scheme 1A). The incorporation of hexyloxy substituents on 4 and 5 was chosen with the aim of improving the solubility of the derived polymers in common organic solvents.

Polymers P1-I and P2-I were prepared by Horner-Wittig condensation polymerization of 3 with the requisite dialdehyde in tetrahydrofuran (THF) employing KO'Bu as the base. The preparation of P1-I was carried out under fairly concentrated conditions in an effort to disfavor the formation of cyclic structures that sometimes diminish the molecular weight of CPs incorporating $m$-phenylene units in their
Scheme 2.1: Synthesis of monomers and iodo-substituted polymers (A) and post-polymerization modification of P1-I (B).
backbones. The number average molecular weights ($M_n$) of P1-I and P2-I determined by gel permeation chromatography (GPC) suggest reasonable success in suppression of cyclic structure formation, although polydispersity indices of 2.3 and 2.9, respectively, are somewhat higher than the ideal value of 2 for a condensation polymerization, and the ($M_n$) of 6600 for P1-I is lower than expected if cyclic structures were completely suppressed.

P1-I was selected for post-polymerization modification with chromophores. Sonogashira coupling was found to be a convenient attachment strategy that allowed us to employ a variety of commercially available terminal alkynes as coupling partners as shown in Scheme 1B. The relative number of iodo sites that were successfully modified in each case was estimated by GPC and NMR spectroscopy. GPC data indicate a $M_n$ increase of between 1000 and 2000 Da for each polymer after functionalization (Table 1), reflecting the expected change in hydrodynamic radius of polymer chains as iodo substituents are replaced by arylethyne units. GPC analysis of CPs can have a wide margin of error, reported to be up to 40% in some cases, so elemental microanalysis is a more reliable measure of percent functionalization of iodo sites. The percentage of iodo substituents replaced in P1a-f determined by micro-analysis range from 56 to 100% (about 16%, Table 1).
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<td></td>
<td>(3.96)</td>
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<tr>
<td>P1f</td>
<td>7 100</td>
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</table>

Table 2.1: Select physical data for polymers a) PDI will not change upon derivatization of P1-I to give P1a-P1f; b) $\lambda_{excit} = 405$ nm for series P1 and 456 nm for P2-I; c) Indicates the percentage of iodo substituents replaced in the functionalization step, as determined by elemental microanalysis; d) Two bands were observed; e) The numbers in parentheses refer to the absorbance assigned as a charge transfer band.
Photophysical Characterization

The photophysical data for all polymers are provided in Table 1, and spectra are provided in Figure 2. Visually, P1-I is neon yellow ($\lambda_{\text{max}} = 402$ nm in dichloromethane) and P2-I, featuring longer effective conjugation segments, is bright orange-red ($\lambda_{\text{max}} = 456$ nm in dichloromethane). An interesting, yet unsurprising, divergence in the behavior of P1-I versus that of P2-I is that the absorption and emission maxima for P1-I exhibit notable bathochromic shifts in the solid state compared to solutions, while hypsochromic shifts are observed for P2-I. Bathochromic shifts are typical for CPs that agglomerate in some way in the solid state, and in the case of P1-I, the fact that both the emission and absorption maxima shift suggests that there is some solid state inter- or intrachain interaction in both the ground (i.e., aggregation) and excited states (i.e., excimer formation) that are not present in solution. CPs exhibiting hypsochromic shifts like that observed for P2-I in the solid state are less common, but can occur when there is a twisting of $\pi$-systems in the solid state to shorten the effective conjugation length. In the case of P2-I, the tri(phenylenevinylene) spacer between $m$-terphenyl units has a greater persistence length than the single phenylene vinylene spacer in P1-I. The formation of twisted structures such as loops or helices in the solid state would not be unexpected for a polymer such as P2-I, in which bent segments have been intentionally incorporated, and would explain the hypsochromic shift of both absorption and emission maxima.

Some interesting features resulted from the incorporation of ethynylaryl sidechains in the post-polymerization modification of P1-I. As can be seen in Table 1, most of the emission and absorption maxima are similar before and after modification.
This would be expected on the basis of the greater contribution of the polymer than the relatively small and predominantly UV-absorbing chromophores incorporated post-polymerization. The quantum yields, however, vary substantially from 0.31 to 0.66. This variation indicates that the modifications influence the rigidity, chain conformation and persistence length in solution and thus alter the efficiency of radiative versus nonradiative...

Figure 2.2: Absorption spectra for dichloromethane solutions (A), the inset shows the additional charge transfer band present in P1e) and films (B), and photoluminescence spectra for dichloromethane solutions (C) and films (D). Excitation was provided at the $\lambda_{\text{max}}$ of the solution sample in all cases.
decay processes. Although solid state quantum yields were not determined, solid state luminescence is apparently weaker than that of solutions, as reflected by the noisy spectra in Figure 2D.

Particularly noteworthy changes in the photophysical properties occurred when P1-I was modified to form P1d and P1e. The absorption spectrum of polymer P1d showed two bands, one attributable to the polymer-centered $\pi$-$\pi^*$ observed in the parent polymer, and one attributable to the biphenylethynyl-containing chromophore added to the polymer in the modification step (Figure 2A and Table 1). The wavelength of excitation was altered, and it was found that excitation into the biphenylethynyl-centered band still leads to efficient polymer-centered emission. This observation confirms that the biphenylethynyl-containing chromophore is able to transfer its excited state energy to the polymer’s $\pi$-system in an intrachain FRET effect.

Perhaps not surprisingly, a CT band was observed in the absorption spectrum of 4-fluorophenylethynyl-derivatized P1e at 615 nm with log $\varepsilon$ of 3.14 (Table 1). The interaction of fluorinated arenes with electron rich arenes in CPs is well known, and the CT band in P1e is similarly attributable to the interaction of the fluoroaryl chromophore with the electron rich, hexyloxy-substituted segments of the polymer in an intrachain fashion.
Conclusion

Poly($p$-phenylenevinylene) derivatives incorporating periodic disruption of conjugation by $m$-phenylene units have been prepared that also feature iodo substituents for post-polymerization modification. The inclusion of bent $m$-phenylene spacers lead to significant differences between solution and solid state absorption and emission features, and to potential supramolecular structure formation in the iodo-substituted polymers. Modification of iodo-derivatized P1-1 by Sonogashira coupling lead to six new chromophore-derivatized materials. The strategic placement of these post-polymerization appended chromophores within the steric cleft of a $m$-terphenyl subunit lead to them being shielded from significant interchain interactions, and only intrachain interaction was observed in the form of FRET (P1d) and CT (P1e). These results suggest that a similar post-polymerization modification strategy may prove useful for tailoring materials for specific applications with minimal competing interchain processes at the appended chromophores.
Experimental

General Considerations

Air sensitive manipulations were carried out in a dry box under an atmosphere of N$_2$ or with standard Schlenk techniques. Toluene and THF were purified and made anhydrous/anaerobic by utilizing an MBraun solvent purification system, in which the solvent was passed through alumina columns under a N$_2$ atmosphere. Anhydrous diisopropylamine was purchased from Sigma Aldrich and used without further purification. Other reagents were used as received without further purification from Alfa Aesar, Acros, and TCI America. The 2,6-bis(4-methylphenyl)iodobenzene (1) and 2,6-bis(4-bromomethylphenyl)iodobenzene (2),$^{26}$ 4,$^{28}$ and 5$^{29}$ were prepared as previously reported.$^{26}$ All NMR spectra were recorded on a Bruker Avance 300 spectrometer which operated at 300 MHz for proton, 75 MHz for carbon and 121.47 MHz for phosphorous. Chemical shifts were reported in parts per million (δ ppm). Carbon-13 and $^1$H NMR spectra were internally referenced to residual solvent signals, and $^{31}$P NMR spectra were referenced to 85% phosphoric acid.

General Spectroscopic Methods

A Varian Cary 50 Bio absorption spectrophotometer was used to record all absorption spectra. Photoluminescence (PL) spectra were obtained using a Varian Cary Eclipse fluorescence spectrophotometer. All samples for absorbance and PL spectra used dichloromethane as a solvent in Spectrosil quartz cuvettes with a path length of 1 cm. Prior to analysis, the initial solutions were filtered through 0.2μm syringe filters. PL
quantum yields were measured relative to quinine bisulfate in 0.1 M H$_2$SO$_4$(aq) ($\Phi = 0.546$).$^{36}$

**Preparation of 2,6-bis-(4-(diethoxyphosphorylmethyl)- phenyl)-iodobenzene (3)** A 3.00 g (5.54 mmol) sample of 2 was combined with 2.20 g (13.2 mmol) of triethylphosphite and heated at 175 °C for 24 h. The resulting dark brown solution was then vacuum distilled to remove the excess triethylphosphite followed by the addition of 25 mL of pentane to give a brown solid. The solid was then filtered and recrystallized from a saturated toluene solution at −25 °C to afford 0.832 g of the pure product as off-white crystals (22.9%).$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.28 (t, 12H, $J = 7.0$ Hz), 3.24 (d, 4H, $J = 21.5$ Hz), 4.00–4.12 (m, 8H), 7.26 (d, 2H, $J = 7.5$ Hz), 7.33 (d, 4H, $J = 8$ Hz), 7.38–7.43 (m, 5H).$^{13}$C{1H} NMR (75.4 MHz, CDCl$_3$): $\delta$ 16.4 ($J_{CP} = 6$ Hz), 33.7 ($J_{CP} = 137$ Hz), 62.3 ($J_{CP} = 7$ Hz), 103.7, 127.6, 128.7, 129.3, 129.4, 129.6, 129.6, 131.0 ($J_{CP} = 9.0$ Hz), 144.2, 147.7 ppm.$^{31}$P{1H} NMR (121.5 MHz, CDCl$_3$): $\delta$ 26.8 (s). HRMS calcd. for C$_{28}$H$_{36}$IO$_6$P$_2$ (M + H), 657.1032; found 657.1028.

**Preparation of P1-I.** To a mixture of 3 (1.27 g, 1.93 mmol) and 4 (650 mg, 1.93 mmol) in THF (80 mL) was added KO'Bu (598 mg, 5.80 mmol) portionwise with stirring. After stirring for 17 h, an additional aliquot of 4 was added (65.6 mg, 0.195 mmol). The reaction vessel was heated for 4 h and then stirred at room temperature for an additional 24.5 h. After stirring, an additional aliquot of 4 (90 mg, 0.267 mmol) and KO'Bu (50mg, 4.85mmol) was added and heated to 60 °C for 13.5 h. After heating, the solution was added to methanol (50 mL). Residual polymer was rinsed from the reaction vessel with chloroform. Precipitated polymer was filtered from the methanol, added to chloroform,
and stirred for 1 h. The solution was then rinsed three times with water to remove impurities and the organic layer was poured into methanol and extracted with dichloromethane and water. The organic layer was concentrated by rotary evaporation. This process yielded a total of 919 mg of P1-I (69.8%). 

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.80–1.01 (m, 8H), 1.27–1.43 (m, 45H), 1.87–1.92 (m, 2H), 3.49–3.52 (m, 0.5H), 4.08–4.10 (m, 2H), 5.34–5.36 (m, 1H), 6.93–7.64 (m, 39H). Anal. calcd. for monomer formula C$_{40}$H$_{43}$IO$_2$: C, 70.40; H, 6.40; I, 18.59; Found: C, 70.82; H, 6.52; I, 17.97.

**General Procedure for the Preparation of P1a-f**

To a solution of 80 mg (0.118 mmol) P1 in anhydrous toluene (4 mL); the Pd(PPh$_3$)$_4$ (6.0 mg, 0.0052 mmol) and CuI (1.0 mg, 0.0052 mmol) were added and resultant mixture was stirred for 10 min. The requisite alkyne was dissolved in diisopropylamine and added dropwise. The reactions were stirred for 16 h and then heated to 90 °C for 24 h. After heating, the reaction mixture was combined with 25 mL dichloromethane. The organics were extracted sequentially with water (4 x 25 mL), 10% HCl(aq) (25 mL) then again with water (25 mL). The organic layers were concentrated by rotary evaporation and dried in vacuo. The crude polymer was stirred in methanol overnight, followed by filtration, and drying in vacuo to give polymers P1a-f in the yields indicated below.

**P1a.** 53.1 mg (58.0%). 

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.02–0.29 (m, 6H) 0.85–2.19 (m, 22H, overlaps water peak) 3.98–4.12 (m, 4H) 6.93–7.72 (m, 17H, overlaps CHCl3 peak). Anal. calcd. for monomer formula C$_{40}$H$_{52}$O$_2$Si: C, 82.77; H, 8.03; I, 0.00; Found: C, 76.27; H, 7.52; I, 0.45. Calculated numbers refer to 100% substitution of iodo.
substituents. Actual substitution percentages given in Table 1 are based on iodine analysis.

P1b. 38.0 mg (40.9%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 0.77–2.19 (m, 31H, overlaps water peak) 4.12–4.14 (m, 4H) 7.02–7.91 (m, 21H, overlaps CHCl\textsubscript{3} peak). Anal. calcd. for monomer formula C\textsubscript{52}H\textsubscript{56}O\textsubscript{2}: C, 87.60; H, 7.92; I, 0.00; Found: C, 83.36; H, 8.05; I, 0.57. Calculated numbers refer to 100% substitution of iodo substituents. Actual substitution percentages given in Table 1 are based on iodine analysis.

P1c. 39.0 mg (42.6%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 0.75–2.44 (m, 22H, overlaps water peak) 3.93–4.11 (m, 4H) 7.04–7.89 (m, 22H, overlaps CHCl\textsubscript{3} peak). Anal. calcd. for monomer formula C\textsubscript{48}H\textsubscript{48}O\textsubscript{2}: C, 82.77; H, 8.03; I, 0.00; Found: C, 80.51; H, 6.65; I, 8.15. Calculated numbers refer to 100% substitution of iodo substituents. Actual percentages given in Table 1 are based on iodine analysis.

P1d. 83.2 mg (82.4%) \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 0.88–1.96 (m, 22H, overlaps water peak) 4.09–4.13 (m, 4H) 7.08–7.68 (m, 26H, overlaps CHCl\textsubscript{3} peak). Anal. calcd. for monomer formula C\textsubscript{54}H\textsubscript{52}O\textsubscript{2}: C, 88.48; H, 7.15; I, 0.00; Found: C, 85.05; H, 6.81; I, 0.00. Calculated numbers refer to 100% substitution of iodo substituents. Actual percentages in Table 1 are based on iodine analysis.

P1e. 42.0 mg (44.7%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 0.85–2.06 (m, 22H, overlaps water peak) 3.98–4.10 (m, 4H) 7.28–7.72 m, 21H, overlaps CHCl\textsubscript{3} peak). Anal. calcd. for monomer formula C\textsubscript{48}H\textsubscript{47}FO\textsubscript{2}: C, 85.42; H, 7.02; I, 0.00; Found: C, 84.45; H, 6.91; I, 6.59. Calculated numbers refer to 100% substitution of iodo substituents. Actual percentages in Table 1 are based on iodine analysis.
**P1f.** 55.4 mg (55.4%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.85–2.06 (m, 22H, overlaps water peak) 4.09–4.11 (m, 4H) 7.19–7.72 m; 21H, overlaps CHCl\(_3\) peak. Anal. calcd. for monomer formula C\(_{49}\)H\(_{47}\)F\(_3\)O\(_2\): C, 81.19; H, 6.95; I, 0.00; Found: C, 74.62; H, 6.53; I, 5.93. Calculated numbers refer to 100% substitution of iodo substituents. Actual percentages in Table 1 are based on iodine analysis.

**Preparation of P2-I**

To a mixture of 5 (815 mg, 0.0873 mmol) and 3 (578 mg, 0.0873 mmol) in THF (5 mL) was added KO\(_{t}\)Bu (27.0 mg, 0.262 mmol) portion wise with stirring. After stirring for 3 h at room temperature the reaction mixture was heated to 65 °C for 25 h. After the reaction was done heating the contents were poured into methanol (5 mL) and shaken vigorously for 5 min. The reaction mixture was then mixed with 25mL of dichloromethane. The organics were then extracted sequentially with water (3 x 25 mL). The organic layers were then concentrated by rotary evaporation and dried in vacuo to yield 98.2 mg of **P2-I** (87.4%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.86–1.91 (m, presumed to be 66H, overlap water peak) 4.09 (m, 12H) 7.20–7.63 m, presumed to be 25H, overlap CHCl\(_3\) peak). Anal. calcd. For monomer formula C\(_{80}\)H\(_{103}\)IO\(_6\): C, 74.63; H, 8.06; Found: C, 70.82; H, 7.80.
References


CHAPTER THREE

CONJUGATED POLYMERS FOR THE FLUORESCENT DETECTION OF NITROAROMATICS: INFLUENCE OF SIDECHAIN STERICS AND \( \pi \)-SYSTEM ELECTRONICS

Introduction

Conjugated polymers (CPs) are premier materials for fluorescent sensing of analytes ranging from neurotransmitters\(^1\) and metal ions\(^2,3\) to chemical warfare agents\(^4,5\) and explosives.\(^6,7\) Some of these sensing mechanisms rely on modification of the CP backbone or sidechains to include specific recognition elements, while others rely on nonspecific Coulombic attraction between charged CP components with oppositely-charged dipoles or ionic moieties on target analytes.\(^8\) A sensing mechanism that has attracted particular interest for the detection of nitroorganic explosives is the formation of a complex, generally between the electron-rich \( \pi \)-system of a fluorescent CP and the electron deficient \( \pi \)-system of a nitroaromatic analyte. The attendant loss of fluorescence intensity can then be measured to assess the presence or concentration of the analyte. This sensing paradigm distinguishes itself in that it has proven useful for the detection of explosives such as 2,4,6-trinitrotoluene (TNT) or taggants such as 2,3-dimethyl-2,3-dinitrobutane (DMDNB).\(^9\) Commercial explosives such as tritonol, pentolite and RDX also contain some 2,6-dinitrotoluene (DNT) as a contaminant.\(^7\) Because DNT is present in so many common explosives and is notably more volatile and thus easier to detect in

\(^9\)Reprinted and adapted with permission, license in Appendix
vapor phase, DNT is often a prime target for sensing systems as well. Sensing systems capable of detecting such nefarious agents are of prime contemporary interest as tools to provide safety and security against improvised explosive devices (IEDs) and landmines, for example.

Ideally, a sensing material will bind the target analyte strongly and with a high signal modulation such that the sensor will be very sensitive. This is especially pertinent for detection of TNT and DNT, not remarkably volatile materials, in the vapor phase. In order to develop a better understanding of what polymer structures could exhibit high sensitivity to nitroaromatics, we thus surveyed the literature to find polymer-based fluorescent sensors for which the Stern Volmer quenching constant ($K_{SV}$) has been reported for either DNT or TNT (Chart 1). These materials will serve as points of comparison for the newly-tested polymers in the current report.

It is notable that the materials in Chart 1 are all comprised of a central $\sigma$-conjugated or $\pi$-conjugated system serving as the fluorophore, often flanked by sterically encumbered sidechains. The benefits endowed by such bulky sidechains derive from an increase in porosity of the material, which allows more facile analyte vapor entry, or possibly by simply providing the requisite pockets of free space for the analyte to occupy adjacent to the sensor $\pi$-system, allowing the $\pi$-complex to form. Dendritic$^{10}$ and microporous$^{11}$ molecular architectures have also been explored to provide favorable geometries for nitroaromatic-sensor interaction. Although a large portion of the work in the $\pi$-conjugated polymer area has employed iptycene
Chart 3.1: Structures of reference molecules R1-R18 from the literature for which Stern-Volmer quenching constants ($K_{SV}$) have been reported. The $K_{SV}$ values for DNT and TNT are summarized in Table 1.
derivatives as the bulky sidechains (i.e., R10-11 and R15 in Chart 1), there have been several reports exploring other structural motifs as well, and it would be instructive to examine some more recently-reported polymer architectures with the aim of understanding and optimizing the response of these sensors.

CPs have garner such significant attention in fluorescent sensing because they can purportedly exhibit significantly heightened responses to analyte versus small molecules by virtue of the extended electronic communication along the polymer’s backbone. Polymers often are also easily fabricated into devices as thin films, making them good candidates for sensors that can be used in field work. One insightful report revealed that small molecular sensors can exhibit sensitivity to nitroaromatics on par with those observed using CP sensors provided that a high association constant exists between the sensor and the analyte.\textsuperscript{12} One benefit of using such sensitive small molecules is that they have well-defined conjugation lengths and generally sharper spectroscopic signatures than CPs. They can also be incorporated into an appropriate host polymer such as polyurethane\textsuperscript{12} for use in solid state or thin film sensors. There are consequently many small molecular sensors for nitroaromatics that could prove to be practically applicable. For the current discussion, however, we will limit the scope to $\pi$-conjugated CPs. However, in order to further reveal whether extended electronic communication is essential, we include a $\pi$-conjugated polymer with periodic disruption of conjugation in this study as well.

In the current work, we examine how the fluorescence quenching extent and kinetics are influenced by the electronic and steric properties of sidechains, as well as by
sidechain attachment geometry in some polymers. Both fully $\pi$-conjugated polymers and polymers featuring fluorophore segments of defined $\pi$-conjugation length within their backbones are examined.
Experimental

Reagents and General Methods

Polymers P1,13 P2,14 P3-4,15 P5-6 and P7-816 were prepared as previously reported and their $K_{SV}$ values were determined for the current work by analysis of spectroscopic titrations as described below. The $K_{SV}$ values in Table 1 for R1 and R4-7;17 R2-3 and R8-10;18 R11 and R15,10 R12-14;19 R16,20 and R17-1821 are provided as they have been previously reported and were not independently confirmed for this work.

General Spectroscopic Methods

Photoluminescence (PL) spectra were acquired on a Varian Cary Eclipse fluorescence spectrophotometer. Absorption spectra were recorded on a Varian Cary 50 Bio absorption spectrophotometer. Samples for all absorbance and PL spectra used anhydrous tetrahydrofuran (THF) or toluene. Samples were measured in Spectrosil quartz cuvettes having a path length of 1 cm. Solutions for PL analysis were filtered through a PTFE syringe filter (0.1 μm) prior to analysis. The THF solvent for all optical measurements was purified and made anhydrous/anaerobic by passage through alumina columns under a N₂ atmosphere employing an MBraun solvent purification system. Photoluminescence quantum yields were measured relative to quinine bisulfate ($\Phi = 0.564$) in 0.1 N aqueous sulfuric acid.22 Polymer concentrations are reported as moles of repeat unit per L.

Response of Polymer and Molecule films to Nitro-Organics (DMDNB, DNT, TNT)
Films were made by drop casting onto a quartz substrate and allowed to dry in a desiccator overnight prior to analysis. The film was sealed in a quartz cuvette and placed at a 45 ° angle from the excitation source. An initial photoluminescence spectrum was acquired, then a sample of either DNT or TNT was added to the bottom of the cuvette without touching the film. The cuvette was sealed and an initial scan was taken. Additional scans were taken over the times reported in Table 2 to monitor change in photoluminescence.

**Titrations of Polymers and M1 with Nitroaromatics**

A 3.0 mL solution (1.0 x 10⁻⁶ M in THF) of the corresponding polymer or small molecule was added to a cuvette and the initial photoluminescence spectrum was acquired. Aliquots (10 μL) of the nitro-organic solutions in THF (or toluene in one of the trials for P2) were added to the solution. After each addition, the cuvette was sealed, the contents were mixed by flipping the cuvette, and another photoluminescence spectrum was acquired. This was repeated until sufficient quenching took place to show a leveling off of the linear Stern-Volmer plot.
Results and Discussion

Polymer Selection

Chart 1 provides a representative set of polymers from the literature for which the Stern-Volmer quenching constants have been reported. For the current work, small molecule-based sensors, as well as microporous network and dendrimer-based sensors have been excluded from the list, and instead more conventional linear polymers have been selected. Chart 2 provides the structures of the polymers for which we have measured the fluorescent response characteristics upon exposure to DNT and TNT for the current report.

In selecting the new polymers for this study, one goal was to maintain some similarity of the π-conjugated backbone present in the newly-screened and previously-tested polymers, thus allowing for clearer interpretation of the influence exerted by specific sidechains. The π-conjugated units of the newly-screened polymers are thus comprised by phenyleneethynylene (P1-2, Chart 2) or phenylenevinylene (P3-8, Chart 2) segments.

Polymers P1-8 also incorporate several different sidechain architectures that have not yet been explored in nitroorganic detection. For example, the m-terphenyl unit in PPE derivative P1 and PPV derivatives P3-4 was selected because it provides a region of free space in the vicinity of the π-conjugated backbone, reminiscent of the space provided by iptycene derivatives present in successful nitroaromatic sensors R10-11 and R15. Alternatively, the terphenyl-based oxacyclophane canopy in P2 provides a rigid spacer
Chart 3.2: Structures for polymers P1-P8 from the literature. Stern-Volmer quenching constants for DNT and TNT are provided in Table 3.1.
that is expected to increase the average interchain spacing and thus may increase the permeability of a film of this polymer to analyte vapour. The 9,9-dialkyl substituents in the 1,4-fluorenylene units of P5-6 are likewise expected to provide some space between polymer chains by virtue of their orthogonality to the π-conjugated backbone. Finally, periodic m-phenylene units in the backbones of P7-8 not only provide periodic disruption to π-conjugation, but also lead to V-shaped kinks that may lead to some helical or foldamer-type geometries that would be expected to create some porosity in the resultant films.

In addition to the availability of free space around a polymer’s backbone and resultant porosity of a polymer film, the electronics of the π-conjugated backbone will also influence the magnitude of association between the nitroaromatic and the sensor π-system. A comparison of P3 to P4 illustrates the expected outcome of tuning electronics. The presence of more electron-releasing alkoxy substituents in P3 versus P4 would be expected to increase its interaction with an electron-deficient TNT or DNT molecule. Likewise, P5 and P6 both include 9,9-dialkyl-1,4-fluorenylene subunits, but P5 also has subunits with electron-releasing alkoxy substituents. P7 differs from P8 in that there is a longer 2,5-dialkoxyphenylenevinylene spacer between bends in the polymer chain, possibly providing a larger electron-rich π-system surface area for interaction with an electron-deficient nitroaromatic. Caution must be exercised when making such simplistic arguments, however, because chain conformation and aggregation of chains in solution will also exert a significant influence on the analyte-polymer interaction.

Stern-Volmer Quenching by DNT and TNT in Solution
Measurements of Stern-Volmer quenching constants ($K_{SV}$) in solution are a convenient way to measure relative affinities between a fluorophore and a quenching agent. In the current context, it will allow for the evaluation of inherent TNT or DNT affinity to the polymer chains without interference from permeability and film thickness influences that are expected to influence the rate and magnitude of response to the nitroorganics in the solid state.

One important consideration in evaluating these data is that the solvent has a notable influence on the $K_{SV}$. The type of dipole-dipole interactions that are in play between a nitroaromatic and an electron-rich π-system will be significantly diminished in polar solvents where the polar molecules can be stabilized by solvation. The data in Table 1 illustrate this effect to some extent; the $K_{SV}$ values measured in chloroform are lower than for similar systems measured in toluene. As a result, most researchers have used toluene for the measurements reported in Table 1. In the current study, it was therefore desired to follow suit by using toluene in measurements involving P1-8. Quite disappointingly, many of the polymers P1-8 were not soluble in toluene, but they were all soluble in THF. To overcome this hurdle, toluene-soluble P2 was measured in both toluene and THF, while the other members of the series were only measured in THF. This course of action allowed direct comparison of toluene soluble P2 to other polymer measurements in toluene listed in Table 1. Furthermore, since all polymers P1-8 were measured in THF, they can be ranked relative to one another. In this way, P2 can be thought of as a “secondary standard” to correlate data for polymers in THF to those in
toluene. The data for P2 allow us to estimate that the $K_{SV}$ is ~1.7 times greater in toluene than in THF for either DNT or TNT.

The medium effect is accentuated when quenching constants for films are included (R12-14 and R17-18). In these cases solvent is absent and the polymer-analyte interaction may thus be considerably higher than is observed in solution. This expectation is borne out by the exceedingly high $K_{SV}$ values reported for the films relative to the solution values in Table 1.

The $K_{SV}$ values provide some insight into structure-quenching correlation. P1 and P2, for example, share a PPE-type backbone comprised by alternating 2,5-dialkoxyphenyleneethynylene and a m-terphenyleneethynylene unit. The fact that the m-terphenyl unit in P2 is disposed as an oxacyclophane “canopy”, whereas the m-terphenyl in P1 is not wrapped into a macrocycle does not influence the $K_{SV}$ values with either DNT ($K_{SV} = 190 \text{ M}^{-1}$ vs. $180 \text{ M}^{-1}$) or TNT ($K_{SV} = 430 \text{ M}^{-1}$ vs. $420 \text{ M}^{-1}$) to any great extent in THF. Iptycene-substituted R10 also has a PPE-derivative backbone that should be electronically very similar to that in P1 and P2. The $K_{SV}$ of R10 in toluene ($1170 \text{ M}^{-1}$) is about 70% higher than the value for P2 in toluene ($700 \text{ M}^{-1}$). This difference is an indication that the rigidity of the iptycene unit may offer benefits regarding either chain conformation or simple free space around the backbone for analyte interaction, reinforcing the hypothesis that both steric and electronic influences are important.
<table>
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<th>$K_{sv}$ (1/M)</th>
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</tr>
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</tr>
<tr>
<td>P2</td>
<td>THF</td>
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</tr>
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<td>CH$_3$Ph</td>
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Table 3.1: Stern-Volmer quenching constants ($K_{sv}$) for polymers shown in Charts 1-2
Data for P2 and P4 provide an opportunity to gauge the difference between PPE and PPV backbones with very similar substituents. In this case, PPV-derivative P4 has a $K_{SV}$ 2.9- and 2.3-times that of P1 for DNT and TNT, respectively, in THF. P4 can also be compared to P3, which has two additional electron-releasing alkoxy substituents per repeat unit. Despite the electronic differences, the two polymers differ by only 10-20% for DNT or TNT in THF, a difference too small to justify definitive interpretation. Other PPV derivatives P5 and P6, which incorporate the 1,4-fluorenylene unit, generally exhibit somewhat lower $K_{SV}$ values compared to P3 and P4, though the more electron-rich P5 has a $K_{SV}$ for TNT similar to that for P3, reflecting the improved affinity of the more electron-rich backbone for interaction with TNT. Conversely, R15 and R16 lack any electron-releasing substituents attached to their PPV backbones and have very low quenching constants.

The final pair of polymers examined in the current study is P7-8. These polymers feature short π-conjugated segments with periodic disruptions of conjugation at each $m$-phenylene linker. Recent studies involving small-angle neutron scattering (SANS) have revealed that such PPV derivatives with periodic $m$-arylene units form unilamellar discs in THF.\textsuperscript{23} Unlike other common polymer chain conformations, unilamellar discs have a large accessible surface area for analyte binding, making these polymers intriguing candidates. P8 has a larger electron-rich π-system between $m$-phenylene conjugation-disrupting units and exhibits notably higher quenching efficiency than P7. Indeed, P8 has the highest $K_{SV}$ of any of the polymers examined in THF, and compares well to PPE and PPV derivatives measured in toluene if a 1.7-fold improvement in toluene versus THF is
assumed on the basis of data for P2. If, however, it is the aggregation to form high surface-area unilamellar discs that provides P8 with some of its enhanced quenching, then this aggregation may also change in a different solvent. These data suggest that a thorough evaluation of media effects and aggregation processes, coupled with evaluation of the extent to which these factors influence analyte-polymer interactions could provide an important advance in the rational design of polymer-based sensing strategies. Another conclusion that one can draw from the high performance of P8 is that, as suggested by other studies, the extended conjugation along a polymer backbone is not a prerequisite for high analyte sensitivity.

**Quenching of Film Fluorescence by DNT**

From a practical standpoint, film-based sensing is a more convenient means of analyte detection than having to prepare solutions for testing. This is especially true in the current context where detection of nitroaromatics in a vapor may be desired to detect a hidden IED or landmine. On the basis of these considerations, films of P1-8 were prepared on a quartz substrate in a sealed vessel with 140 ppb DNT vapor and the films’ photoluminescence intensity was monitored over time. DNT was selected instead of TNT due to its higher vapor pressure. The luminescence of films was monitored either until it leveled off, or after a maximum time of 90 minutes. Table 2 summarizes data from these tests. One conclusion that is immediately evident from these data is that there is no particular correlation between the $K_{SV}$ values reported in Table 1 and the ability of DNT to quench a polymer film’s luminescence. It appears that both the time required to reach maximum luminescence quenching ($t_q$) and the extent of quenching ($I/I_0$) is dictated to
large extent by the films porosity to DNT. This is most evident by noting that R10, with rigid iptycene sidechains, and P2, with the rigid m-terphenyl canopy, both >80% quenching in only 0.5 min, whereas none of the other polymers attained greater than 63% quenching even after 90 minutes.

<table>
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<th>$t_{\text{max}}$ (min)</th>
<th>$I/I_0$</th>
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<tr>
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<tr>
<td>P2</td>
<td>0.5</td>
<td>17%</td>
<td>14</td>
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<tr>
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</tr>
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<td>P4</td>
<td>10</td>
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<td>P5</td>
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<td>90</td>
<td>78%</td>
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<td>R10</td>
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Table 3.2: Relative DNT quenching time and efficiency
Conclusions

The solution quenching constants for DNT and TNT as well as thin film fluorescence response to DNT have been determined for eight polymers. The polymers examined were representatives of five structural architectures that have not previously been employed in nitroaromatic sensing. Solution studies confirm that both electronic and steric influences are important to the relative binding affinities. The decided influence of media polarity and the role of polymer aggregation in solution also appears to play an important role in the polymer-analyte interaction. Film studies reveal a lack of correlation between the solution quenching constants and the ultimate quenching efficiency in the solid state. This implies that film porosity and the availability of free space around the π-system fluorescent reporter is the most critical consideration for thin film sensor design.
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CHAPTER FOUR

CONJUGATED POLYMERS WITH \textit{m}-PYRIDINE LINKAGES: SYNTHESIS, PHOTOPHYSICS, SOLUTION STRUCTURE AND FILM MORPHOLOGY

Introduction

Organic electronics employing organic conjugated polymers (OCPs) have come to the forefront of research aimed at their evolution to commercial status in applications such as photovoltaics, \textsuperscript{1} organic light emitting diodes, \textsuperscript{2} electrochemical supercapacitors \textsuperscript{3} and sensors. \textsuperscript{4, 5} One of the most attractive features of using organic polymers rather than metals or inorganic semiconductor materials is that organic polymer processing can be comparatively efficient and inexpensive when thin films are prepared using existing roll-to-roll printing techniques, for example. The tantalizing promise held by such facile scalability for organic electronics has remained predominantly unfulfilled due to several challenges that have yet to be solved. One challenge to researchers has been an inability to fully understand or reliably predict how a material’s molecular properties such as absorption and emission profile, band gap, ionization potential and electron affinity, etc. will translate to the solid state such as in the thin films that would be used in devices. Furthermore, because interchain interactions play a crucial role in dictating everything from energy and charge transfer to bulk conductivity, exciton migration/confinement, and electroluminescence quantum efficiencies, \textsuperscript{6-8, 9} it is

\textsuperscript{9}Submitted for publication to Journal of Materials Chemistry C, February 27, 214
Chart 4.1: Some polymers relevant to the current discussion
critical to understand how OCP chains aggregate and assemble when a solution is concentrated as solvent evaporates to produce a film that will ultimately comprise a key component of an optoelectronic device.

Several strategies have been developed to control interchain interactions in OCPs from a structural standpoint to exert control at the synthetic level. One approach has been to incorporate sterically-encumbered sidechains in an effort to minimize inter-π-system interactions (Chart 1A).\textsuperscript{10,11,12,13} Another area of active research is to guide ordered assembly through supramolecular interactions (Chart 1B).\textsuperscript{14,15} Metal ion coordination can also be used to transform ligand-appended OCPs into ordered networks.\textsuperscript{16}

In addition to the synthesis-centred strategies, a variety of calculations\textsuperscript{17,18,19} and analytical techniques such as near field scanning optical microscopy,\textsuperscript{20} atomic force microscopy (AFM),\textsuperscript{21,22} and small angle neutron scattering (SANS)\textsuperscript{23} have been applied in an effort to reveal how some of the more promising OCPs might assemble in the solid state and how such assembly is related to the opto/electronic properties most critical to device function.

One fundamental barrier to all of the aforementioned efforts has been that the polydispersity of OCP chain lengths in a sample makes it difficult to completely elucidate the applicable structure-property relationships: in a given sample there will be several molecularly different entities from which optoelectronic properties are derived. For example, there may exist crystalline domains or other regions of chain aggregation that exhibit different photophysical signatures than the amorphous regions of the material.\textsuperscript{24,25} Even along a single chain there may be twisting of the π-system of one segment out of
coplanarity with respect to an adjacent segment such that on-chain electronic communication (exciton migration, etc.) is interrupted, leading to different effective conjugation lengths with concomitant broadening of spectroscopic signatures.\textsuperscript{26} For all of these complicating reasons, researchers have often turned to monodisperse oligomers of variable length as a more convenient sample set to elucidate how properties vary with increasing conjugation length, with the aim of extrapolating their findings to make predictions concerning polymer properties.\textsuperscript{27,28, 29} Our group has adopted the strategy of studying polyelectrolytes\textsuperscript{30, 31} or OCPs\textsuperscript{26} that contain periodic disruptors of conjugation such as \textit{m}-phenylene units (Chart 1C) to exploit the predictability of the well-defined chromophores in combination with the advantageous processability and film-forming ability typical of many organic polymers.

\textbf{P1-I} and its post-polymerization derivatives \textbf{P1-R} (Chart 1C)\textsuperscript{26} feature periodic disruption of the \(\pi\)-system such that each polymer maintains the absorption and photoluminescence of the parent even after modification with other chromophores that are orthogonal to the main-chain \(\pi\)-system. Furthermore, chromophores R can be selected to facilitate interaction between the sidechain chromophore and the main chain polymer-centred \(\pi\)-system to yield FRET (R = anthrylethynylene) or charge transfer (R = \textit{4}-fluorophenylethynylene) effects. Work is underway to elucidate solid-state properties of cross-linked, redox-active and stimuli-responsive polymers built on the \textbf{P1-I} platform.

For the current report, the focus is on polymers \textbf{BHP} and \textbf{CP} (Scheme 2), which are structurally similar to \textbf{P1-I}. Both \textbf{BHP} and \textbf{CP} feature a \textit{m}-pyridylene unit as the conjugation-disrupting unit instead of the \textit{m}-phenylene moiety of \textbf{P1-I}. Periodic
disruption and steric shielding will remain intact in CP and BHP, with the added benefits that pyridine might offer for controlling and tuning the polymer properties on an electronic and photophysical level. For example, pyridylene is more electron-deficient than phenylene, and thus electron/hole mobility would be predicted to change. In LED applications, for example, pyridylene-bearing materials have proven beneficial due to improved electron-injection and often improved electroluminescence quantum efficiency.\textsuperscript{32} Furthermore, pyridylene has the potential to undergo protonation or bind metal ions, offering additional prospects for stimuli-responsiveness. Although polymers that are structurally very similar to CP and BHP are known\textsuperscript{33,32} (Chart 1D), there does not appear to have been a study on the solution aggregation and film morphology behaviour of such materials. Herein, the focus is on further elucidating the aggregation and film morphology of the polymers by analysis of small angle neutron scattering, atomic force microscopy and concentration-dependent/film photophysical data.
Experimental

General Considerations

Air sensitive manipulations were carried out in a dry box under an atmosphere of N\textsubscript{2} or with standard Schlenk techniques. Toluene and THF were purified and made anhydrous/anaerobic by utilizing an MBraun solvent purification system, in which the solvent was passed through alumina columns under a N\textsubscript{2} atmosphere. Anhydrous diisopropylamine was purchased from Sigma Aldrich and used without further purification. Other reagents were used as received without further purification. The 1,4-diformyl-2,5-bis(hexyloxy)benzene was prepared as previously reported.\textsuperscript{34} All NMR spectra were recorded on a Jeol ECX-300 or Bruker 300 spectrometer which operated at 300 MHz for proton, 75 MHz for carbon and 121.47 MHz for phosphorous. Chemical shifts are reported in parts per million (δ ppm). Carbon-13 and \textsuperscript{1}H NMR spectra were internally referenced to residual solvent signals, and \textsuperscript{31}P NMR spectra were referenced to 85% phosphoric acid.

General Spectroscopic Methods

A Varian Cary 50 Bio absorption spectrophotometer was used to record all absorption spectra and a Jobin Yvon spectrophotometer was employed to obtain all photoluminescence (PL) spectra. All samples for absorbance and PL spectra used chlorobenzene and tetrahydrofuran as a solvent in Spectrosil quartz cuvettes with a path length of 1 cm. Prior to analysis, the initial solutions for absorbance and PL spectra were filtered through 0.2 mm PTFE syringe filters. PL quantum yields were measured relative to 9,10-diphenylanthracene in cyclohexane.
**Preparation of NMe.** This procedure is analogous to that reported by Cave and Raston.\(^{35}\) In a mortar, \(p\)-tert-butylbenzaldehyde (4.89 mL, 29.3 mmol) \(p\)-methylacetophenone (7.81 mL, 58.5 mmol) and NaOH (2.37 g, 58.5 mmol) were ground vigorously with a pestle for 10 minutes. The reaction mixture changed colour from clear to bright yellow and finally to a cream colour. The mixture also thickened to a tacky substance. An aliquot was taken for \(^1\)H NMR analysis to confirm that the reaction to intermediate 1 was complete. The solid was then transferred without purification to a suspension of ammonium acetate (16.5 g, 0.214 mol) and glacial acetic acid (75 mL). The reaction mixture was refluxed for 32 h. The reaction was quenched by adding 30 mL of water, leading to the precipitation of a yellowish solid. The precipitate was washed with water and ethanol and dried. The resultant mustard-yellow solid was then recrystallized by vapour-phase diffusion of pentane into a CHCl\(_3\) solution of the crude solid. A light cream coloured precipitate was observed and collected by vacuum filtration. The solid was then stirred with methanol, vacuum filtered and dried in vacuo to afford the pure product as a cream solid (2.511 g, 21.9 %). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.41 (s, 9 H) 2.45 (s, 6 H), 7.34 (d, 2 H, \(J = 7.95\) Hz), 7.57 (d, 2 H, \(J = 8.25\) Hz), 7.71 (d, 2 H, \(J = 8.40\) Hz), 7.86 (s, 2 H), 8.12 (d, 2 H, \(J = 8.25\) Hz). \(^{13}\)C\{\(^1\)H\} NMR (75.4 MHz, CDCl\(_3\)): \(\delta\) 21.47, 31.45, 34.85, 116.54, 126.16, 126.98, 127.11, 129.53, 136.41, 137.05, 139.03, 149.98, 152.27, 157.42. Anal. calcd. for monomer formula C\(_{29}\)H\(_{29}\)N: C, 88.96; H, 7.47; N, 3.58; Found: C, 89.01; H, 7.47; N, 3.53.

**Preparation of NdiBr.** Samples of NMe (1.18 g, 3.01 mmol), \(N\)-bromosuccinimide (NBS, 1.34 g, 7.53 mmol), and BPO (0.073 g, 0.30 mmol) were
dissolved in 80 mL of CHCl₃ and the solution was heated to reflux for 12 h. At this point an additional 18 equiv (9.65 g) of NBS were added and reflux was continued for an additional 12 h. The reaction mixture was a reddish-brown colour with a precipitate. The solution was decanted and the precipitate was rinsed with sodium carbonate. The solution was extracted once with saturated sodium carbonate (200 mL), once with saturated sodium sulphate (200 mL), and three times with water (200 mL). The volatiles were removed from the combined soluble portion of the reaction by rotary evaporation. The material so isolated was a white powder (1.92 g) existing as a mixture of bromomethylated and dibromomethylated species (see main text) that was taken as the crude product for conversion to \( \text{NBr} \) without further purification. \(^1\text{H} \) NMR (300 MHz, CDCl₃): \( \delta \) (for main isomers present) 1.40 (s, 9 H) 6.73 (s, 1 H), 7.27 (s, 2 H), 7.60 (m, 2 H), 7.72 (m, 2 H), 7.95 (m, 2 H), 8.19 (m, 2 H). The spectrum is provided in Figure S3 of the Electronic Supplementary Information.

**Preparation of NBr.** A flask containing 25 mL of anhydrous THF and \( \text{NdiBr} \) (1.92 g, 3.00 mmol) was placed under an atmosphere of dry nitrogen on a Schlenk line and cooled to 0 °C in an ice bath. Diethyl phosphite (2.49 g, 18.0 mmol) and ethyldiisopropylamine (2.33 g, 18.0 mmol) were added dropwise. The reaction was allowed to slowly warm to room temperature as the ice bath melted and warmed under ambient conditions, followed by stirring at room temperature for 20 h. At this point the solution had changed to a dark brown mixture. Water (125 mL) was added and the mixture changed to a creamy light brown colour. The solution was extracted three times with ether (80 mL each). The organic layers were then combined and rinsed with brine...
(60 mL) and H₂O (60 mL), collected and dried over sodium sulphate. Volatiles were then removed from the combined organics under reduced pressure via rotary evaporation. The resulting yellow compound was passed through a fritted funnel containing silica gel employing CHCl₃ as the eluent. Volatiles were then removed from the resultant yellow solution under reduced pressure via rotary evaporation to give the product as a yellow solid (0.587 g, 35.6%). ¹H NMR (300 MHz, CDCl₃): δ 1.39 (s, 9 H), 4.58 (s, 4 H), 7.55 (m, 2 H), 7.67 (d, 2 H, J = 8.58 Hz), 7.88 (s, 2 H), 8.15 (d, 2 H, J = 8.25 Hz). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 31.41, 33.38, 34.88, 117.39, 126.26, 126.96, 127.48, 127.67, 129.58, 135.91, 138.70, 139.67, 150.38, 152.60, 156.83. HRMS (m/z): calcd for C₂₉H₂₈NBr₂ (M + H)⁺, 548.0588; found, 548.0582.

**Preparation of NPhos.** A sample of NBr (0.564 g, 1.02 mmol) and triethylphosphite (1.023 g, 6.16 mmol) were combined in a flask in the glovebox, followed by refluxing for 3 hours under an atmosphere of dry nitrogen. After cooling the solution to room temperature, excess triethylphosphite was removed by vacuum distillation to yield the crude product as a dark yellow viscous liquid. The crude product was recursively triturated with pentane to yield a pale tan solid, which was subsequently collected by vacuum filtration and dried in vacuo to afford 0.581 g (90.1%) of the target. ¹H NMR (300 MHz, CDCl₃): δ 1.25 (t, 12 H, J = 5.52), 1.62 (s, 4 H), 3.23 (d, 4 H J = 21.63), 4.05 (quint., 8 H, J₁ = 7.20, J₂ = 7.23), 7.46 (m, 4 H), 7.57 (d, 2 H, J = 8.25 Hz), 7.68 (d, 2 H, J = 8.40 Hz), 7.87 (s, 2 H), 8.14 (d, 4 H, J = 7.53 Hz). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 16.49, 31.35, 32.81, 34.64, 34.78, 62.29, 116.88, 126.14, 126.87, 127.28, 130.22, 132.68, 136.03, 138.24, 152.35, 157.01 ppm. ³¹P NMR (121.47 MHz,
CDCl₃): δ 26.75. HRMS (m/z): calcd for C₃₇H₄₈NO₆P₂ (M + H)+, 664.2957; found, 664.2966.

**Preparation of BHP.** Samples of NPhos (0.081 g, 0.128 mmol), 1,4-diformyl-2,5-bis(hexyloxy)benzene (0.043 g, 0.128 mmol), and KOtBu (0.043 g, 0.384 mmol) were combined in THF (25 mL) in a pressure flask and stirred at room temperature for 24 hours in the dry box. The sealed tube, which contained a yellow solution, was then removed from the dry box and heated at 55 °C for 12 h. Proton NMR analysis of the product at this stage revealed that monomers were still present, so an additional aliquot of KOtBu (0.042 g) was added in dry THF and the solution was left to stir at room temperature for 24 h. The flask was removed from the glove box and heated at 50 °C for another 24 hours. Methanol (10 mL) was added. The THF layer was concentrated to yield a solid, which was recursively washed with ethanol to yield the final product (39 mg, 44.3%). ¹H NMR (300 MHz, C₆D₆): δ (integration reported per repeat unit) 0.73-1.80 (m, 29 H), 3.44-3.90 (m, 8 H), 6.81-8.40 (m, 16 H), 10.88 (s, 6 H). FT-IR (cm⁻¹): 2953.1, 2921.7, 2852.8, 1690.0, 1661.3, 1631.9, 1569.9, 1260.6, 816.8.

**Preparation of CP.** A mixture of NPhos (0.083 g, 0.131 mmol), 9-(2-ethylhexyl)-carbazole-3,6-dicarboxaldehyde (0.043 g, 0.131 mmol) and KOtBu (0.044 g, 0.393 mmol) were combined in a glovebox with anhydrous THF (24 mL) and stirred for 14 h. Then the reaction was heated to 55 °C and continued stirring for 24 h. Methanol (5 mL) was added during work up and stirring led to precipitation of a yellow solid. The mixture was centrifuged and the supernatant was decanted from the resultant yellow solid. The yellow solid was dried in vacuo to give 52 mg (58%) of the polymer. ¹H NMR
(300 MHz, CDCl₃): δ (integration calculated per repeat unit) 0.60-2.10 (m, 25 H), 3.80-4.25 (m, 5 H), 6.90-8.70 (m, 20 H), 10.1 (m, 6 H). FT-IR (cm⁻¹): 2956, 2928, 2870, 1685, 1571, 824.

**Small Angle Neutron Scattering (SANS)**

The experiments were carried out in the Centre for Neutron Research at the National Institute of Standards and Technology on NG3 30-m SANS instrument. Solutions of 0.5 and 1wt% BHP and CP polymers were dissolved in d₈-tetrahydrofuran purchased from Cambridge Isotopes Laboratories, Inc. The solutions were placed in 2 mm path length cells. A neutron beam of wavelength, λ, of 6.0 Å with wavelength spread of Δλ/λ ≈ 10%, was used for all measurements. Experiments were carried out at three sample-to-detector distances of 1.3 m, 4.0 m and 13.1 m to cover a broad scattering vector range, q (where q = (4π/λ) sinθ and 2θ is the scattering angle) of 0.003Å⁻¹ to 0.4 Å⁻¹. A two dimensional (2D) detector was used. The intensity was integrated over the 2D detector to form plots of I versus q. The data were normalized to background and transmission of the samples. Finally the scattering of the solvent was subtracted. In dilute solution, the intensity measured is given by (1):³⁸

\[ I(q) = \phi V_p \Delta \rho^2 P(q) \]

where \( \phi \) is the particle volume fraction, \( \Delta \rho \) is the difference between scattering length density (SLD) of the scattering particle (\( \rho_p \)) and that of the solvent (\( \rho_s \)). SLD is calculated by summing the coherent scattering length, a measure of neutron and the nuclei interaction, of all atoms over the sample volume, \( \rho_i = \sum b_j N/V_m \) where \( b_j \) is the scattering length of atom j, \( V_m \) is molar volume and \( N \) is Avogadro number. The
calculated neutron SLDs are $1.23 \times 10^{-6} \, \text{Å}^{-2}$ for BHP, $1.41 \times 10^{-6} \, \text{Å}^{-2}$ for CP and $6.35 \times 10^{-6} \, \text{Å}^{-2}$ for $d_8$-tetrahydrofuran.

**SANS data analysis:**

The SAS Fit program\textsuperscript{39} was used to analyse the SANS data. Initial analysis was carried out using Guinier\textsuperscript{40} approximation at low q, which is given by the equation 2 for a spherical particle, where $R_g$ is the radius of gyration.

$$I(q) \approx \rho^2 V^2 \exp \left( -\frac{1}{3} q^2 R_g^2 \right)$$  \hspace{1cm} (2)

At intermediate q range, where the transform of a single object is expressed in the scattering data the intensity scales exponentially with the momentum transfer vector q as shown in equation 3.

$$I(q) \propto q^{-\alpha}$$  \hspace{1cm} (3)

In this q range, the exponent, $\alpha$, extracted from the slope of $\log(I)$ versus $\log(q)$ plot, is the signature of the shape of the scattering objects.\textsuperscript{41}

A full analysis of the scattering patterns was carried out by fitting the curves to full form factors. A conjunction of form factors are used to capture the scattering from the entire q range. A unilamellar disc-like aggregate of homogeneous scattering cross section\textsuperscript{42} given in equation 4 was used for most of the q range.

$$I = \pi^2 R^4 \Delta \eta^4 L^2 \frac{2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right) \left( \frac{\sin(qL/2)}{qL/2} \right)^2$$  \hspace{1cm} (4)

$R$ is radius of disc, $L$ is layer thickness, $J_1$ is a first order Bessel function, and $\Delta \eta$ is scattering contrast. The scattering from large aggregates at low q regime was analysed using Beaucage model\textsuperscript{43} where the intensity is given by equation 5:
\( I(q) = \sum_{i=1}^{n} G_i \exp\left(-\frac{q^2 R_i^2}{3}\right) + B_i \exp\left(-\frac{q^2 R_{i+1}^2}{3}\right) \left[\text{erf}\left(\frac{q k_i R_{i+1}}{\sqrt{6}}\right)\right]^{1/6} \)

\( G_i \) is Guinier pre factor, \( B_i \) is a pre-factor to power-law scattering and \( P_i \) is a scaling exponent for larger particles. The first term in equation 5 describes the size of large aggregates and second term describes characteristic sizes of smaller units present in the large aggregates.

**AFM Imaging**

AFM images were obtained using a NanoScope IIIa (Digital Instrument, Japan) operating in tapping mode. A Si\textsubscript{3}N\textsubscript{4} cantilever with a spring constant of about 12-103 N/m was used. Samples were prepared by drop-casting from polymer solutions onto the silicon wafer. The silicon substrates were cleaned by soaking in a mixture of conc. H\textsubscript{2}SO\textsubscript{4} and 30\% H\textsubscript{2}O\textsubscript{2} (7:3, v/v) at 80 °C for 1 h. The substrates were rinsed with distilled water several times and dried with N\textsubscript{2} gas.
Results and Discussion

Synthesis

The requisite monomers for the preparation of BHP and CP were prepared according to the sequence outlined in Scheme 1. Monomers that could undergo Horner-Wittig reaction with readily-available aldehyde comonomers were targeted for the current study.\textsuperscript{34} Horner-Wittig condensation is preferred over the Gilch or Heck methods because it minimizes defects and has high stereoselectivity for E-olefinic linkages.\textsuperscript{44}

Precursor NMe was prepared using a novel route to terpyridines and 2,6-diarylpyridines that employs a mechanochemical step.\textsuperscript{35} Simply grinding solvent-free 4-\textit{tert}-butylbenzaldehyde and 4-methylacetophenone with NaOH led to intermediate 1 (observed by $^1$H NMR spectrometry but not isolated) and subsequent refluxing with ammonium acetate yielded NMe.

Radical bromination of NMe using N-bromosuccinimide (NBS) did not cleanly produce the desired bis(bromomethyl) species NBr. Instead, contamination by species containing dibromomethyl units was observed by $^1$H NMR analysis of reaction aliquots even early in the reaction progress. It was thus found to be more convenient to add excess NBS to NMe to yield crude bis(dibromomethyl) derivative NdiBr. The dibromomethyl sites in NdiBr underwent ready monodebromination by diethylphosphite in the presence of Hüning’s Base to give NBr.\textsuperscript{45} The NBr so produced then underwent reaction with triethylphosphite via a Michaelis-Arbuzov reaction to yield monomer NPhos.
Scheme 4.1: Preparation of monomers. Conditions: i. excess N-bromosuccinimide, catalytic benzoyl peroxide, reflux in CHCl₃ (90.6%); ii. HP(O)(OC₂H₅)₂, ethyldiisopropylamine, 0-20 °C, 20 h (35.6%); iii. P(OC₂H₅)₃, 130 °C, 3 h (90.1%). Ar = 4-t-butylphenyl.
Scheme 4.2: Preparation of polymers
NPhos was employed in polymer preparation according to the process outlined in Scheme 2. Horner Wittig condensation polymerization of NPhos with either 1,4-diformyl-2,5-bis-(hexyloxy)benzene or 9-(2-Ethylhexyl)carbazole-3,6-dicarboxaldehyde cleanly produced CP and BHP, respectively. Proton NMR end group analysis readily allowed calculation of the degree of polymerization ($X_n$) and number average molecular weight ($M_n$) for BHP ($X_n = 33$, $M_n = 49,200$ Da) and CP ($X_n = 16$, $M_n = 11,500$ Da).

One of the important considerations when relating conjugated polymer structure to properties is the extent to which adjacent π-conjugated subunits may be coplanar. A polymer that exhibits coplanarity of two adjacent π-conjugated segments has the ability to engage in extended electronic communication across the coplanar section of the backbone, whereas if two π-conjugated segments are orthogonal to one another this represents a break in conjugation and shortens the average effective conjugation length of the material. Although photophysical measurements (see next section) and calculations can provide some insight into the issue of conjugation extent, solid state packing influences can also exert a decided influence on the effective conjugation length of the material. In the current case, the interface between the $m$-pyridyl unit with adjacent phenylene rings that comprise a portion of the backbone in each polymer, is of particular interest. Steric interactions can lead to deflection from coplanarity of attached aryl rings. The classic example of this effect is biphenyl, which is well-known to exhibit a dihedral angle of 40° in the ground state, whereas coplanarity is attained in the excited state.46
In light of the importance of substructure geometry, small molecule model NMe was selected for investigation by single crystal X-ray diffraction with the hope of obtaining some insight into the accessible geometry of the 2,6-diarylpyridyl unit present in CP and BHP. The ORTEP drawing obtained from the data refinement is provided in Figure 1. Refinement parameters are summarized in Table S1 in the ESI. Perhaps surprisingly, the dihedral angles between p-tolyl substituents at the pyridyl 2- and 6-positions and the pyridyl ring to which they are attached are only 14.2° in the crystal structure. The dihedral angle between the 4-t-butylphenyl substituent and the pyridyl ring is also smaller than might be anticipated, at 17.9°. These measurements suggest that near
coplanarity of adjacent \( \pi \)-systems might be possible at this repeat unit in the polymer chain. It should be noted, however, that \( \pi \)-conjugation through *multiple* repeat units is not possible by virtue of the *meta*-disposition of attachment to the pyridine unit.

**Photophysical Properties**

The absorption and photoluminescence data for BHP and CP are summarized in Table 1. Both CPs demonstrate \( \lambda_{\text{max}} \) and \( \lambda_{\text{em}} \) properties in dilute solution which are typical for polymers of with similar structures.\(^{47,7,48,49}\) Not surprisingly, CP has a greater Stokes shift than BHP, most likely owing to the donor-acceptor nature of the dihexyloxyphenylene/\( m \)-pyridylene backbone.\(^{50}\)

<table>
<thead>
<tr>
<th></th>
<th>BHP</th>
<th>CP</th>
</tr>
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<tbody>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>410</td>
<td>481</td>
</tr>
<tr>
<td>( \lambda_{\text{em}} ) (nm)</td>
<td>479</td>
<td>557</td>
</tr>
<tr>
<td>Stokes’ Shift (nm)</td>
<td>69</td>
<td>79</td>
</tr>
<tr>
<td>( \Phi ) (%)(^b)</td>
<td>0.48</td>
<td>0.18</td>
</tr>
<tr>
<td>Ionization Energy (eV)</td>
<td>5.43</td>
<td>5.46</td>
</tr>
<tr>
<td>Electron Affinity (eV)</td>
<td>2.60</td>
<td>2.50</td>
</tr>
<tr>
<td>( E_g ) (eV)</td>
<td>2.83</td>
<td>2.95</td>
</tr>
</tbody>
</table>

*Table 4.1:* Select electrochemical and photophysical properties of BHP and CP in chlorobenzene.
One interesting photophysical observation is that for both polymers the photoluminescence undergoes a progressive bathochromic shift as the concentration increases from very dilute to 1 wt% (Figure 2). This behaviour is often an indication of aggregation, and has been noted previously for \textit{m}-terphenyl-bearing PPV derivatives.\textsuperscript{26} Poly(phenylene)vinylene polymers are known to exhibit a greater bathochromic shift

\textbf{Figure 4.2:} Concentration-dependent Fluorescence of BHP (A) and CP (B) in THF. The lowest concentration is \textasciitilde{}0.1 μM and the highest concentration is 1 wt% in each case studies done in chlorobenzene.
with greater persistence length.\textsuperscript{51,50} Similarly, as concentration increases one would expect an increase in red shifting due to more interchain interactions.

**Small Angle Neutron Scattering (SANS)**

SANS experiments were conducted in order to determine the structure of aggregates formed in solutions of BHP and CP observed in the photoluminescence studies described in Figure 2. The patterns of both polymer solutions at two concentrations are shown in Figure 3. Qualitatively, all patterns clearly show crossover from that of a large structure at low q to a well-defined aggregate at intermediate q range. The low q range provides insight into the chain conformation within the aggregates. The three linear lines marked on the patterns schematically depict these regimes where the overall scattering function is a convolution of the contributions of all scattering objects. This complexity of the patterns is a clear indication of presence of scattering objects of different sizes and shapes.

At low q values scattering is dominated by bigger aggregates as noted by the upturn of the patterns. A Guinier analysis of patterns of BHP, provides \( R_g \) values of ca. 555 Å and ca. 493 Å for 0.5 wt% and 1 wt% respectively. Similarly, from the spectra of CP polymer, Guinier analysis provides radii of gyrations of ca. 410 Å and 399 Å at 0.5 wt% and 1 wt% respectively. At intermediate q values, the patterns are scaled with \( \sim q^{-2} \) for both polymers at both concentrations. This result suggests the presence of a disc-like structures with a thickness of approximately one molecule, are common to both polymers. At high q values, where scattering is dominated by the internal structure of the scatters, the scattering intensity of BHP polymer scales with \( \sim q^{-1} \) at both concentrations.
This scaling subjects that within the aggregates the polymer molecules are rather starched out. Surprisingly though, the high q scattering of CP polymer at both concentrations scales with $\sim q^{-4}$. These scaling exponents at high q values show the relatively smooth interface of CP polymer aggregates with solvent compare with that of the BHP.

This Guinier analysis at low q region resolved the presence of large aggregates. The scaling exponents at intermediate q indicate the presence of disc-like structures. A sum of form factors given in equations 4 and 5 was used to analyse the entire pattern. The results are given in Table 2, including the thickness of the disc, diameter of the disc, radius of gyration of larger aggregates, the radius of the gyration of smaller aggregates and the scaling exponent extracted from the fit.

The thickness and the diameter of the unilamellar disc remains roughly the same as a function of concentrations for both the polymers. The radius of gyration of the smaller unit obtained from the fit is roughly the same with the calculated value of the $R_g$ obtained from the thickness and the diameter of the disc using the relationship shown in equation 6.

\begin{equation}
R_g^2 = \frac{\nu^2}{12} + \frac{d^2}{8}
\end{equation}

where $d$ is the diameter of the disc.
Figure 4.3: SANS patterns of solutions (a) BHP (b) CP in deuterated THF at the indicated concentrations. The symbols correspond to the experimental data and the solid lines correspond to the model described in the text. The solid lines under the patterns schematically present the different q regimes where from left to right they correspond to the Guinier region, intermediate q and high q range.
### Unilamellar disc of homogeneous scattering cross section

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thickness (Å)</th>
<th>Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHP- 0.5wt%</td>
<td>17.4 ± 0.8</td>
<td>113.9 ± 2.3</td>
</tr>
<tr>
<td>BHP- 1wt%</td>
<td>19.1 ± 0.0</td>
<td>116.6 ± 0.0</td>
</tr>
<tr>
<td>CP- 0.5wt%</td>
<td>15.3 ± 0.3</td>
<td>97.3 ± 3.6</td>
</tr>
<tr>
<td>CP- 1wt%</td>
<td>16.9 ± 0.0</td>
<td>100.2 ± 0.0</td>
</tr>
</tbody>
</table>

### Beaçauge exponential scaling law

<table>
<thead>
<tr>
<th>Samples</th>
<th>R_{g,i} (Å)</th>
<th>R_{g,i+1} (Å)</th>
<th>Power Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHP- 0.5wt%</td>
<td>551.7 ± 3.9</td>
<td>52.5 ± 0.0</td>
<td>3.2</td>
</tr>
<tr>
<td>BHP- 1wt%</td>
<td>519.2 ± 1.2</td>
<td>48.4 ± 1.3</td>
<td>3.5</td>
</tr>
<tr>
<td>CP- 0.5wt%</td>
<td>451.6 ± 0.9</td>
<td>34.0 ± 2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>CP- 1wt%</td>
<td>426.5 ± 0.5</td>
<td>38.5 ± 0.7</td>
<td>2.5</td>
</tr>
</tbody>
</table>

**Table 4.2:** Parameters obtained from the sum model fit of SANS data
Overall, the pattern is consistent with large aggregates that consist of a network of smaller disc-like structures each of which is approximately one molecule thick. The radius of gyration obtained from the Guinier approximation calculations yield roughly the same values as the $R_g$ of the bigger aggregates obtained from the full analysis. The $R_g$ of those bigger aggregates is larger for lower concentration than at higher concentration for both polymers. This larger value at lower concentrations is commonly attributable to swelling of the polymer aggregate as a result of solvent inclusion in the matrix.

**Atomic Force Microscopy (AFM) of Polymer Films**

Having employed SANS to elucidate some aspects of polymer aggregation as a solution becomes more concentrated, the next point of interest was to evaluate the morphology of films prepared from the aggregate-bearing solutions. BHP and CP films were thus cast from THF solutions of different concentrations and analysed by atomic force microscopy (AFM). Figure 4 shows the AFM topography images of polymer films. Thin films of BHP cast from a 0.5 wt% solution exhibit spherical structures with an average diameter of about $46.7 \pm 6.9$ nm as well as smaller approximately circular features with diameters of about $15.5 \pm 2.3$ nm (Figure 4a). The dimension of these features decrease in BHP films cast from 1 wt% (Figure 4b). The average feature size decreases to about $34.9 \pm 10.9$ nm and $13.4 \pm 2.2$ nm for the larger features and smaller features, respectively.

AFM images of CP films reveal that these films follow the same trends as observed for BHP. When the thin films are prepared from 0.5 wt% CP solutions,
nanoscale features are observed as shown in Figure 4c, with average feature diameters of about 33.7 ± 6.0 nm and 12.7 ± 2.0 nm. Films cast from the 1 wt% CP solution show slightly smaller feature sizes, similar to those observed in films cast from BHP solution of the same concentration.

Figure 4.4: AFM topography images of conjugated polymer thin films on silicon wafer prepared by drop casting from polymer solutions in THF. The samples are (a) 0.5 wt% BHP, (b) 1 wt% BHP, (c) 0.5 wt% CP and (d) 1 wt% CP.
Interestingly, the size of the features observed by AFM in the thin films are consistent with the aggregate sizes determined from SANS measurements of solutions of the same concentration. The larger features in the films of BHP cast from the 0.5 wt% solution, with a diameter of about 47 nm compare well with the $R_g$ (~52-55 nm) of the larger aggregates revealed by SANS. Likewise, the smaller features in the film, with a diameter of ~15 nm, are consistent with the diameter of unilamellar discs calculated from SANS data (~11 nm). Similarly, the larger features in CP films (diameter 34.9 ± 10.9 nm) compare well with the large aggregate $R_g$ of ~ 43-45 nm, while small film features (diameter ~ 13 nm) again correlate with the diameter of unilamellar discs (~10 nm) calculated from SANS data for the CP solution from which the film was cast.
Conclusion

Two polymers having regularly-spaced $m$-pyridylene conjugation disruptors were prepared. Photoluminescence studies indicated that aggregation of polymer chains occurs to progressively greater extent as the solution concentration is increased and that this aggregation is manifest photophysically as a bathochromic shift of photoluminescence. Aggregate dimension and shape in solution were revealed by SANS. Correlation between SANS-derived aggregate dimensions and the feature size of nanoscale features in thin films was observed through comparison of SANS and AFM data. Future efforts will probe the effect on aggregation, film morphology and photophysics as a result of metal ion coordination to the pyridyl moieties and other structural variation of the polymers.
References


(5) *Handbook of Conducting Polymers*, CRC Press, New York, **2007**.


Figure S4.1. Proton NMR (300 MHz, CDCl₃) of NMe (the structure is shown as an inset).
Figure S4.2. Carbon NMR (75 MHz, CDCl$_3$) of NMe.
Figure S4.3. Proton NMR (300 MHz, CDCl$_3$) of NdiBr (the structure is shown as an inset).
**Figure S4.4.** Proton NMR (300 MHz, CDCl$_3$) of NBr (the structure is shown as an inset).
Figure S4.5. Carbon NMR (75 MHz, CDCl₃) of NBr.
Figure S4.6. Proton NMR (300 MHz, CDCl₃) of NPhos (the structure is shown as an inset).
Figure S4.7. Carbon NMR (75 MHz, CDCl$_3$) of NPhos.
**Figure S4.8.** Phosphorous NMR (121.47 MHz, CDCl$_3$) of NPhos.
Figure S4.9. Proton NMR (300 MHz, C₆D₆) of BHP (the structure is shown as an inset).
Figure S4.10. Proton NMR (300 MHz, CDCl₃) of CP (the structure is shown as an inset).
Figure S4.11. Infrared Spectrum of BHP.
Figure S4.12. Infrared Spectrum of CP.
CHAPTER FIVE

CONJUGATED POLYMERS WITH $m$-PYRIDINE LINKAGES: SYNTHESIS, PHOTOPHYSICS, SOLUTION STRUCTURE AND FILM MORPHOLOGY

Introduction

Conjugated polymers (CPs) have generated a significant interest in the optoelectronic materials field not only for their potential as semiconductors but also due to their processability and scalability by existing technologies. The flexibility of organic polymers also portends the utility of organic semiconductors for a variety of applications for which rigid and brittle inorganic materials would not be applicable. Some applications that have attracted particular attention are thin-film photovoltaics, organic light emitting diodes (OLEDs), superconductors, supercapacitors, field effect transistors and in printable batteries and circuits. The ongoing quest to deduce rational structure-property relationships in CPs thus remains a critical research thrust. Chemists have long probed structure-property relationships in small molecules by undertaking systematic and methodical changes in the individual structural elements of the molecule and then carefully probing the resultant effect on properties. Likewise, biochemists routinely utilize site-specific mutagenesis wherein a single amino acid in a peptide sequence can be altered to assess the resultant influence on an enzyme or other protein’s structure and function. In contrast to small molecules and monodisperse biomacromolecules such

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Chart 5.1: Polymers with \( m \)-pyridylene (A) or \( m \)-phenylene (B) bends in polymer main chains.
as proteins, however, CPs and other organic polymers are polydisperse. In light of
the fact that the average molecular weight and polydispersity of a polymer has a
notable influence on its properties,\textsuperscript{14-20} the variability of a polymer’s properties
even from batch to batch can significantly complicate efforts to reveal
straightforward structure-property relationships that would subsequently facilitate
rational design of materials. The photophysical signatures of CPs are of particular
interest when considering their application in device settings mentioned above.
Photophysical properties are dramatically influenced not only by molecular weight
and polydispersity, but also on the type of inter/intra-chain interactions present in a
film of the material,\textsuperscript{21-23} and the distribution of effective conjugation lengths of the
\(\pi\)-conjugated segments of the polymer. The effective conjugation length of the \(\pi\)-
conjugated segments in the backbone will have an average value, but twisting of
adjacent \(\pi\)-conjugated segments from coplanarity at various points along the
backbone will also give rise to some distribution of effective conjugation lengths
about the average value. This lack of uniformity in effective conjugation length in
turn leads to a broadening of electrochemical and photophysical characteristics of
the bulk material.

A variety of techniques have been applied in an attempt to elucidate how
each of the aforementioned complicating features could contribute to a polymer’s
properties. In order to screen out interchain interactions, for example, a multitude
of CPs with sterically encumbered substituents have been prepared and studied.\textsuperscript{21, 22, 24-32} Examples include the polymers in Chart 1, Chart 2B-D, and Chart 3B,D.
Alternatively, specific inter-\(\pi\)-system interactions have been intentionally enforced through the use of rigid structural elements to provide the desired distance and orientation between adjacent \(\pi\)-systems.\(^{33-42}\)

The issue of variable effective conjugation lengths has also been tackled by tedious preparation of extensive series of oligomeric model compounds\(^{43}\) of increasing length in the hopes of extrapolating the property trends to predict the properties of a polymeric analogue. This approach has been only somewhat effective because properties do not scale linearly with the length of the molecule.\(^{23}\) There has also been some recent work to incorporate small segments of poly(\(p\)-phenylene vinylene) (PPV)\(^{23, 44}\) and poly(\(p\)-phenylene ethynylene) (PPE)\(^{45}\) into polymers with periodic disruption of conjugation in an effort to combine the predictability of small molecule-based chromophores with the processability of polymers. Some examples of these materials include the neutral polymers shown in Chart 1\(^{23, 44}\) and Chart 3A\(^{46}\) and the ionic polymer in Chart 3C.\(^{47}\) The latter efforts could be thought of as a “linked oligomer” approach to optical materials.

The molecular weight and polydispersity influence on polymer properties can be alleviated to some extent by utilizing a single parent polymer of known molecular weight and polydispersity and altering its structure through post-polymerization modification. This has been done with success for a wide range of organic polymers, including CPs such as hyperbranched PPEs\(^{47}\) and some PPVs\(^{23}\) in which the conjugation is periodically disrupted by \(m\)-phenylene units. Derivatives of P1-I in which the iodo substituent is replaced by small molecule
chromophores have shown low incidence of inter-chain interactions while enforcing intra-chain interactions between the backbone π-system and the small molecule chromophore, leading to intramolecular charge transfer and fluorescence resonance energy transfer (FRET).\textsuperscript{23, 45, 48}
Chart 5.2: Materials with representative sterically-encumbered sidechains which have also demonstrated success for detection of nitroaromatic vapors
Herein, the readily-prepared P1-I and P2-I (Chart 1) were chosen as the basis for further investigation because they possesses both periodic disruption of π-conjugation that will lead to more uniform photophysical characteristics and an iodo-substituent for facile post-polymerization modification. Specifically, two sets of polymers each containing a cross-linking, a potentially metal ion-responsive or a redox-active unit, were targeted for study (Scheme 1).

Post-polymerization crosslinking was hypothesized to provide a potentially rigid open-pore structure that might be advantageous for detection of volatile organic compounds (VOCs). For example, there is a need for fast and simple detection of nitroaromatics.49,50 The interest in detecting nitroaromatics stems from the fact that nitroaromatics are found in explosives that are often employed in landmines or improvised explosive devices (IEDs). Some of the most commonly-used nitroaromatics found in explosives are 2,4,6-trinitrotoluene (TNT) 2,6-dinitrotoluene (DNT) or taggants such as 2,3-dimethyl-2,3-dinitrobutane (DMDNB). DNT is present in most commercial explosive preparations either as an additive or as an impurity and it also has a considerably higher vapor pressure than TNT, and so it is often the actual target of fluorescent sensing strategies. Both small molecules (i.e., Chart 2A) and polymers (Chart 2 B-D) have proven useful for fluorescence-based detection of nitroaromatics.26,51-56 In each of these cases the bulky side chains such as iptycenés (Chart 2A-B),57-59 cyclophane-containing “canopy” (Chart 2C)48 and m-terphenyls (Chart 2 D)45,60-62 provide free volume around a π-conjugated fluorophore for analyte occupancy. Crosslinked conjugated
microporous polymer networks likewise provide the free volumes necessary for efficient nitroaromatic entry and detection.\textsuperscript{63}

The incorporation of pyridine substituents into a CP (Chart 3) is another strategy to enhance its ability to sense analytes, in this case metal ions.\textsuperscript{26,64,65} Metal ion detection is of interest for a variety of applications ranging from monitoring toxic heavy metal content in the environment\textsuperscript{66-72} to tracking metal ion concentration and translocation in biological systems.\textsuperscript{68,73-83} Hybrid organic/inorganic materials such as conjugated metallopolymers resulting from metal ion binding to a ligand-modified CP can also exhibit a synergistic combination of CP optical properties with the redox properties available to metal complexes to yield materials for use in thin films in OLEDs and solar cells.\textsuperscript{84,85} The incorporation of metal-binding units within a sterically-shielded cleft can eliminate undesirable crosslinking/network formation\textsuperscript{86} and thus are excellent candidates for soluble metal ion detection applications.\textsuperscript{87,13,28-31}
Chart 5.3: Metal ion-responsive polymers that contain main chain pyridyl substituents
Scheme 5.1 Polymer Synthesis

\[ X = \text{CL} \quad \text{P1-CL, P2-CL} \]
\[ N \quad \text{P1-N, P2-N} \]
\[ \text{Fe} \quad \text{P1-Fe, P2-Fe} \]
Results and Discussions

Synthesis

The preparation of 2,5-bis-(hexyloxy)-1,4-dibenzaldehyde used in this study proceeded in good yield via a known protocol (Scheme 1). The first step was bromomethylation of 1,4-bis(hexyloxy)benzene, which afforded 1 in 71% yield. Quantitative conversion of 1 to the diacetate 2 was followed by ready reduction to 3. Finally, oxidation via pyridinium chlorochromate gave 4 in a good yield of 67.9%. The other dialdehyde monomer 5 is commercially-available. Bis(phosphonate ester) 6 was prepared as previously reported.

Horner-Wittig condensation polymerization was then utilized to carry out polymerization of 6 with either 4 for P1-I or 5 for P2-I (Scheme 2). Horner-Wittig condensation was chosen for polymerization over Heck and Gilch routes because it leads to nearly complete E-olefinic linkages.

The three ethyne derivatives employed in post-polymerization modification (Scheme 1) were commercially available, allowing for facile replacement of the iodo substituents of parents P1-I and P2-I via Sonogashira coupling without additional synthetic effort. The percentage of iodo groups that were successfully replaced by the arylethynyl moieties was readily assessed by elemental microanalysis for C, H, N and I. Replacement efficiency was relatively high, ranging from 63-100%, a range matching the previously-reported substitution efficiency of P1-I.
The decomposition temperatures \((T_d)\), glass transition temperatures \((T_g)\) and melting temperatures \((T_m)\) for the polymers obtained from thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are provided in Table 1 (See also SI figures S15, S16, S19, respectively). One notable observation is that these polymers had significant char yield (65-77 %) even after heating to 800 °C with formation of glassy carbon. The potential utility of these polymers to prepare high-carbon materials will be explored and reported separately. Nonetheless, all of the polymers exhibit high thermal stability, with decomposition temperatures above 300 °C.
Scheme 5.2: Synthetic route to monomer 4 and polymers P1-I and P2-I
Photophysical Characterization

A summary of photophysical data is provided in Table 1. The UV-visible absorption and photoluminescence spectra for both films and dilute solutions are provided in Figures 1 and 2. The parent polymers have notable differences. First, P1-I is neon yellow powder and has a $\lambda_{\text{max}}$ of 402 nm whereas P2-I is a pale yellow powder with a $\lambda_{\text{max}}$ of 368 nm. This observation is attributable to the more blue absorbance and photoluminescence typical of carbazole-bearing $\pi$-systems\textsuperscript{91,92} compared to those of dialkoxyphenylene-bearing $\pi$-systems.\textsuperscript{93}

Several interesting photophysical property changes were evident upon post-polymerization modification of the parent polymers. A charge transfer (CT) band was observed at 415 nm in the UV-vis absorption of P1-N in solution. This is not surprising due to the proximity of the electron-rich dialkoxyphenylene polymer backbone moiety to the electron-deficient ethynylpyridine unit. A similar CT band was previously observed between a dialkoxyphenylene unit and a 2-(4-fluorophenyl)ethynyl substituent in this same geometry.\textsuperscript{89} For several of the polymers, there is a hypsochromic shift in absorption upon going from solution to film, similar to that in P1-I. Also interestingly P2-N exhibits an additional band in the solid state fluorescence spectra (Figure 2) likely due to an intrachain FRET effect between the polymer backbone and the appended side chain. Incorporation of the crosslinking unit also leads to severely diminished photoluminescence quantum efficiency. This is likely a result of internal absorption due to the closer proximity of chains enforced by the rigid crosslinking unit (Figure 3).
Figure 5.1: Calculated optimized geometry for a small segment of P1-CL illustrating pockets of free space around cross-linked sites. The hexyloxy groups have been truncated to methoxy groups and H atoms are excluded for clarity.
Figure 5.2: Normalised photophysical properties for the P1 series. Solution UV-vis absorption (A) and photoluminescence (B) spectra compared to UV-vis absorption (C) and photoluminescence (D) spectra of thin films. Solid black lines = P1-I, dotted lines = P1-CL, solid grey lines = P1-N, dashed lines = P1-Fe. The intensity of film photoluminescence for P1-Fe was negligible.

Figure 5.3: Photophysical properties for the P2 series. Solution UV-vis absorption (A) and photoluminescence (B) spectra compared to UV-vis absorption (C) and photoluminescence (D) spectra of thin films. Solid black lines = P2-I, dotted lines = P2-CL, solid grey lines = P2-N, dashed lines = P2-Fe. The intensity of film photoluminescence for P2-Fe was negligible.
For P1 series $\lambda_{\text{excit}} = 405$ nm, for P2 series $\lambda_{\text{excit}} = 368$ nm.

determined by elemental analysis.

CT band.

FRET band

no $T_m$ observed prior to decomposition. Dichloromethane was the solvent used.

Table 5.1: Select physical characteristics.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Film</th>
<th>Functionalization</th>
<th>Thermal (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{abs}}$</td>
<td>$\lambda_{\text{emit}}^a$</td>
<td>$\Phi_F$</td>
</tr>
<tr>
<td>P1-I</td>
<td>402</td>
<td>465</td>
<td>0.31 ± 0.02</td>
</tr>
<tr>
<td>P1-CL</td>
<td>330</td>
<td>456</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>P1-N</td>
<td>286</td>
<td>471 (415)$^c$</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>P1-Fe</td>
<td>300</td>
<td>463</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>P2-I</td>
<td>368</td>
<td>406 (424)</td>
<td>0.62 ± 0.02</td>
</tr>
<tr>
<td>P2-CL</td>
<td>342</td>
<td>427</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>P2-N</td>
<td>327</td>
<td>525</td>
<td>0.58 ± 0.02</td>
</tr>
<tr>
<td>P2-Fe</td>
<td>331</td>
<td>540</td>
<td>0.88 ± 0.02</td>
</tr>
</tbody>
</table>

$^a$ For P1 series $\lambda_{\text{excit}} = 405$ nm, for P2 series $\lambda_{\text{excit}} = 368$ nm. $^b$ determined by elemental analysis. $^c$ CT band. $^d$ FRET band $^e$ no $T_m$ observed prior to decomposition. Dichloromethane was the solvent used.
Photoluminescence Response of Films to DNT Vapor

One benefit of the m-terphenyl unit is the large volumes of free space that can be created between around or between polymer chains. The free space created at the crosslink sites in P1-CL (Figure 3), for example, is evident from the optimized geometry obtained from Density Functional Theory calculations at the B3LYP/6-31G* level for a small model segment of P1-CL. The availability of free space within the polymer network has been identified as a key requirement for efficient detection of volatile organic compound (VOC) vapors because free volume facilitates analyte entry and diffusion to the chromophore/fluorophore sites responsible for signal transduction. DNT was selected for the current study due to its role in detection of explosives (vide supra) and its higher vapor pressure than TNT. The DNT was added to a sealed quartz vessel with a thin film of polymer and the fluorescence was measured over 120 min or until there was no additional change in PL. P1-CL demonstrated the most rapid response with nearly half of the initial fluorescence quenched within 30 sec. The combined rapid response time and significant reduction of photoluminescence for films of P1-CL result from a combination of the rigid network structure imparted by crosslinking with the electron-rich dialkoxy-derivatized fluorophore of the polymer backbone. These are the two “optimal” design features of a nitroaromatic detection material. Although P2-CL would be expected to have a similarly open pore structure, the lower electron density of the carbazole-bearing fluorophore would be expected to have a significantly diminished affinity for interaction with the electron-deficient π-
system of DNT, so there is a significantly slower response time. Carbazole-bearing 
P2-I did show the greatest eventual quenching efficiency, but with a response time 
that was over two orders of magnitude slower than that of P1-CL.
Figure 5.4: Time-dependence of photoluminescence following exposure of polymer thin films to 140 ppb DNT vapor
Photoluminescence Response of P1-N and P2-N to Metal Ions

The incorporation of ethynylpyridine within the steric cleft provided by the m-terphenyl pocket was undertaken with the aim of creating a well-defined metal-binding site. The distance between the backbone of the polymer and the metal enforces intra-chain interactions, as manifest by the CT band in P1-N. The potential for intrachain inter-π-system interaction between the fluorophore and the metal-binding unit was anticipated to enhance fluorescence changes upon metal ion coordination. Upon metal ion addition, the λ_max of the polymers absorption spectra exhibited bathochromic shifts (See ESI, Figure S-21). Upon addition of Zn^{2+} to a solution of P1-N, a new charge transfer band was also observed at 686 nm.

The coordination-induced photoluminescence responses can be seen from the spectra shown in Figure 5. By altering the spacer in the backbone of the polymer, the quantum yield can be tuned. The more electron rich backbone of P1-N generated a lower Φ_F than P2-N because of the difference in energy matching. The LUMO of the ligand is likely in between the HOMO and LUMO of the polymer backbone effectively quenching the fluorescence. Whereas, the ligand π* orbital is likely higher than the LUMO of the polymer backbone for P2-N allowing for fluorescence decay. When the various metals are bound a turn-on, turn-off sensor can in effect be created.

The relative intensity of metals bound to P1-N increase in all cases except Zn^{2+}. This is due to lowering the π* energy level for the ligand below or at the same level of
the HOMO for the backbone. This allows for an increase of the fluorescence given off resulting in a turn on type mechanism. The more electron deficient polymer, P2-N, exhibited all quenching or the same intensity with the metal ions because upon addition the π* orbital or the metal is lowered in between the HOMO and LUMO of the polymer’s energy levels. For P2-N only Zn^{2+}, Cd^{2+}, and Hg^{2+} ions quench the fluorescence. This is because they are diamagnetic and have a closed-shell d(10) electron configuration. This follows the trend that the more electron deficient the polymer the greater the quenching effect as seen previously.\textsuperscript{45}
Figure 5.5: Photoluminescence response of P1-N (upper) and P2-N (lower) upon addition of metal ions in dichloromethane.
**Experimental**

### General Considerations

Air sensitive manipulations were carried out in a dry box under an atmosphere of N$_2$ or with standard Schlenk techniques. Toluene and THF were purified and made anhydrous/anaerobic by utilizing an MBraun solvent purification system, in which the solvent was passed through alumina columns under a N$_2$ atmosphere. Anhydrous diisopropylamine was purchased from Sigma Aldrich and used without further purification. Other reagents were used as received without further purification from Alfa Aesar, Acros, and TCI America. The 2,6-bis(4-methylphenyl)iodobenzene, 2,6-bis(4-bromomethylphenyl)iodobenzene, 2,6-bis-(4-(diethoxyphosphorylmethyl)-phenyl)iodobenzene, and $\text{P1-I}^{23}$ were prepared as previously reported. All NMR spectra were recorded on a Joel ECX-300 spectrometer which operated at 300 MHz for proton, 75 MHz for carbon and 121.47 MHz for phosphorous. Chemical shifts were reported in parts per million (δ ppm). Carbon$^{13}$ and $^1$H NMR spectra were internally referenced to residual solvent signals, and $^{31}$P NMR spectra were referenced to 85% phosphoric acid.

### Instrumentation

A Varian Cary 50 Bio absorption spectrophotometer was used to record all absorption spectra. Photoluminescence (PL) spectra were obtained using a Jobin Yvon fluorescence spectrophotometer. All samples for absorbance and PL spectra used dichloromethane as a solvent in Spectrosil quartz cuvettes with a path length
of 1 cm. Prior to analysis, the initial solutions for absorbance and PL spectra were filtered through 0.2 mm PTFE syringe filters. PL quantum yields were measured relative to 9,10-diphenylanthracene in cyclohexane (Φ_F = 0.90).  

Differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were performed on a TA Discovery Series instrument and TA Hi-Res TGA Q5000 instrument, respectively.

**Detection of DNT**

Using a quartz cell with an optical path length of 1 cm, a thin film of the polymer was cast on one side. DNT was then placed in the cuvette whilst not touching the film and capped. Photoluminescence changes were measured over 120 minutes.

**Metal Ion Detection**

A quartz cell with an optical path length of 1 cm was utilized and a 3.0 mL aliquot of each polymer in dichloromethane was added. Excess metal ions (10 or more equiv.) were added to the polymer solution. Absorbance and PL changes were measured. The metal salts used were CaCO_3, Cd(NO_3)_2, Co(NO_3)_2·6H_2O, CuCl_2, Hg(OAc)_2, MgSO_4, NiSO_4·6H_2O, ZnCl_2.

**Preparation of P2**

To a mixture of 2,6-bis-(4-(diethoxyphosphorylmethyl)phenyl)-iodobenzene  
^{23} (0.250 g, 0.381 mmol) and 9-(2-ethylhexyl)-carbazole-3,6-dicarboxaldehyde (0.128 g, 0.381 mmol) in THF (30 mL) was added KO'Bu (0.118 g, 1.14 mmol) portionwise with stirring. After stirring for 17 h, the reaction
was heated at 55 °C for 24.5 h. After heating, the solution was added to methanol (50 mL). Precipitated polymer was filtered from the methanol, Soxhlet extracted using chloroform for 48 h. The solid was then dried in vacuo. This process yielded a total of 97 mg of **P2-I** (35.7%). Anal. calcd. for monomer formula C_{44}H_{44}IN: C, 74.04; H, 6.21; I, 17.78; N, 1.96; Found: C, 70.64; H, 5.82; I, 11.93; N, 2.05.

**General Procedure for the Preparation of P1 and P2 series**

To a solution of 80 mg (0.118 mmol) **P1-I** in anhydrous toluene (4 mL); the Pd(PPh$_3$)$_4$ (6.8 mg, 0.0059 mmol) and CuI (1.1 mg, 0.0059 mmol) were added and resultant mixture was stirred for 10 min. The requisite alkyne was dissolved in diisopropylamine and added dropwise. The reactions were stirred for 48 h and then heated to 90 °C for 24 h. After heating, the reaction mixture was combined with 25 mL dichloromethane. The organics were extracted sequentially with water (4 x 25 mL), 10% vol. HCl(aq) (25 mL) then again with water (25 mL), except **P1-N** and **P2-N** were not washed with HCl due to potential protonation of the nitrogen. The organic layers were concentrated by rotary evaporation and dried in vacuo. The crude polymer was stirred in methanol overnight, followed by filtration. The polymers were then washed with acetone and diethyl ether and dried in vacuo.

**P1-CL. Yield** was 50.0 mg (62.7 %). Anal. calcd. for monomer formula C$_{50}$H$_{46}$O$_2$: C, 88.45; H, 6.83; I, 0.00; Found: C, 81.71; H, 5.79; I, 37.0. Calculated numbers refer to 100% substitution of iodo substituents. Actual substitution percentages provided in Table 1 are based on iodine analysis.
P1-N. Yield was 36.0 mg (46.7 %). Anal. calcd. for monomer formula C_{47}H_{45}NO_2: C, 86.06; H, 6.92; N, 2.13; I, 0.00; Found: C, 46.10; H, 3.90; N, 3.31; I, N/A. Calculated numbers refer to 100% substitution of iodo substituents. Actual substitution percentages given in Table 1 are based on iodine analysis.

P1-Fe. Yield was 80.0 mg (89.2 %). Anal. calcd. for monomer formula C_{52}H_{50}FeO_2: C, 81.87; H, 6.61; I, 0.00; Found: C, 56.16; H, 4.39; I, 2.30. Calculated numbers refer to 100% substitution of iodo substituents. Actual substitution percentages given in Table 1 are based on iodine analysis.

P2-CL. Yield was 65.0 mg (85.8 %): Anal. calcd. for monomer formula C_{54}H_{49}N: C, 91.17; H, 6.94; N, 1.97; I, 0.00; Found: C, 78.38; H, 6.03; N, 2.02; I, 8.00. Calculated numbers refer to 100% substitution of iodo substituents. Actual substitution percentages given in Table 1 are based on iodine analysis.

P2-N. Yield was 40.0 mg (51.8 %): Anal. calcd. for monomer formula C_{51}H_{48}N_2: C, 88.98; H, 7.03; N, 4.07; I, 0.00; Found: C, 59.39; H, 4.48; N, 5.27; I, 2.81. Calculated numbers refer to 100% substitution of iodo substituents. Actual substitution percentages given in Table 1 are based on iodine analysis.

P2-Fe. Yield was 21.0 mg (23.5 %): Anal. calcd. for monomer formula C_{56}H_{53}NFe: C, 84.56; H, 6.72; N, 1.76; I, 0.00; Found: C, 76.71; H, 6.09; N, 1.61; I, 0.00. Calculated numbers refer to 100% substitution of iodo substituents. Actual substitution percentages given in Table 1 are based on iodine analysis.
Conclusion

Seven new conjugated polymers were synthesized and their photophysics were examined. A few interesting things were observed, a charge transfer band, vibronic transitions, and FRET effect all attributable to polymer design. Through judicious monomer design electronic transitions were engineered in an intrachain fashion and interchain interactions were eliminated. One polymer was highly successful for nitroaromatic detection, quenching a notable degree of fluorescence in a time frame useful in the field. Excess metal ions were added to both \( \text{P1-N} \) and \( \text{P2-N} \) and binding was observed via bathochromic shifts upon addition. A MLCT was observed in \( \text{P1-N} \) with \( \text{Zn}^{2+} \) due to the electron rich polymer system and electron deficient metal center. Zinc metal ions quenched both polymers but \( \text{P1-N} \) exhibited an increase in intensity for all other metal ions in varying degrees, whereas \( \text{P2-N} \) was quenched by only diamagnetic metal ions. This was determined to be a result of energy matching in a “turn on” / “turn off” type mechanism.
References


Figure S5.1: Proton NMR (300 MHz, CDCl₃) of 1
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CHAPTER SIX
CONCLUSION AND FUTURE DIRECTIONS

The focus of the research herein was to synthesize novel conjugated polymers with potential for use in sensing, OLEDs and solar cells. Of particular interest was to further elucidate the impact of incorporating a \textit{m}-phenylene or \textit{m}-pyridylene unit within the backbone of the polymer.

Several novel polymers were generated in Chapter 2 as the foundation for the rest of the work presented herein. From this work it was confirmed that the terphenyl unit both enforces intrachain interactions while eliminating competing interchain interactions. Notably, charge transfer or FRET effects can be built into the polymer by simply altering the appended side chain.

In Chapter 4 a pyridine derivative of the terphenyl unit was also examined. The morphology of the materials was extensively studied in order to probe their possible utility for thin film applications. These polymers were also tested for their ability to exhibit a fluorescence change upon exposure to nitroorganic compounds such as those found in explosives. Chapter 3 was entirely directed towards nitroorganic detection and the major finding was that an effective thin film nitroorganic-detecting polymer must feature both an electron-rich pi-system and a vapor-permeable film morphology typified by the presence of bulky sidechains.

Finally, Chapter 5 examined several new polymers using the same technique employed in Chapter 2. This time the polymers were tested for both nitr-organic and
metal ion sensing. One of the polymers generated was reasonably efficient at detecting DNT and compared nicely with the polymers in Chapter 3.

Several modifications could be carried out for future work. Some of the possibilities are to alter the donor and/or acceptor groups for further understanding of the tunable quality of CPs. Similarly other polymer chains could be covalently linked to tune the properties. Other metal sensing ligands could be incorporated in conjunction with the terphenyl, either in the backbone of the polymer or attached as an appendage added in a post-polymerization modification step. Direct comparison of materials with bipyridyl or terpyridyl units would be feasible from the previous work in our (vida supra).
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