DIFFERENT CHAIN LENGTH CONJUGATED POLYMERS: PHOTOPHYSICAL STUDIES AND DYE-SENSITIZED SOLAR CELL APPLICATIONS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2015
To my parents
ACKNOWLEDGMENTS

I want to give my sincere appreciation to all those who helped and supported me in the past five years at the University of Florida. First of all, I want to express my deepest thanks to my principal investigator, Dr. Kirk S. Schanze, for his guidance, encouragement and support through my PhD study. It has been a privilege for me to work with him whose wisdom is everlasting and passion for science fuels our research. Without his help, this work would not be possible.

I would like to give my heartfelt thanks to my committee members, Dr. Ronald K. Castellano, Dr. Stephen A. Miller, Dr. Nicolas C. Polfer and Dr. Jiangeng Xue, for their help, support and valuable time. I also want to thank Dr. John R. Reynolds, Dr. John M. Papanikolas, Dr. Franky So and Dr. Omar F. Mohammed Abdelsaboor for their advice and suggestions. Their expertise and wisdom inspire the work in this dissertation.

I have been lucky to work with many great colleagues who are also my friends. Dr. Zhen Fang passed valuable DSSC fabrication and characterization technics to me. Dr. Fude Feng taught the tricks of running reactions and doing work-ups and shared with me numerous research ideas. Dr. Gyu Leem and I spent days and months on improving DSSC performance together. Dr. Galyna Dubinina and I worked on research proposals and initiative works on many challenging projects. Dr. Jan-Moritz Koenen and I worked on polyelectrolyte project and hanged out a lot. The discussion topics between Dr. Dustin Jenkins and I went beyond just chemistry. Dr. Coralie Richard and Dr. Dan Patel, from the Reynolds group, are amazing collaborators and friends to me as well. Mr. Robert J. Dillon and Ms. Amani Alsam also contributed a lot to my research projects.
There are a lot of great fellow graduate students in the Schanze groups I want to thank. Dr. Dongping Xie, Dr. Zhuo Chen, Dr. Danlu Wu, Dr. Xuzhi Zhu and Dr. Jie Yang helped me a lot settle down in Gainesville and are always willing to give me assistance without hesitation whenever I need it. Dr. Hsien-Yi Hus, Russell W. Winkle, Subhadip Goswami and I joined the Schanze group at the same year and had lots of fun working together. I also want to thank Dr. Randi S. Price, Junlin Jiang, Shanshan Wang, Yun Huang, Jiliang Wang, Yajing Yang, Ethan D. Holt and Bethy Kim for their valuable advice and friendship. I want to give special thanks to my Turkish friends Dr. Ali Şenol Gündoğan and Seda Çekli for the happy time we had together and their suggestions on my research.

Last, but not least, I want to thank my parents for their love, support and encouragement through my entire life. This dissertation is dedicated to them.
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<td>A</td>
<td>Acceptor</td>
</tr>
<tr>
<td>ADMET</td>
<td>Acyclic Diene Metathesis</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>BHJ</td>
<td>Bulk-Heterojunction Solar Cell</td>
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<tr>
<td>CM</td>
<td>Cross-Metathesis</td>
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<tr>
<td>CP</td>
<td>Conjugated Polymer</td>
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<tr>
<td>CPE</td>
<td>Conjugated Polyelectrolyte</td>
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<tr>
<td>D</td>
<td>Donor</td>
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<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
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<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of Polymerization</td>
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<td>DSSC</td>
<td>Dye-Sensitized Solar Cells</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>FMO</td>
<td>Frontier Molecule Orbitals</td>
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<tr>
<td>GPC</td>
<td>Gel permeation Chromotography</td>
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<tr>
<td>HCP</td>
<td>Hyperbranched Conjugated Polymers</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident Photon to Current Efficiency</td>
</tr>
<tr>
<td>Jsc</td>
<td>Short Circuit Current Density</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diodes</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<td>MEH-PPV</td>
<td>Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene]</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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<tr>
<td>Mn</td>
<td>Number Average Molecular Weight</td>
</tr>
<tr>
<td>MV</td>
<td>Methyl Viologen</td>
</tr>
<tr>
<td>NDI</td>
<td>Naphthalene Diimide</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic Thin Film Transistor</td>
</tr>
<tr>
<td>OPE</td>
<td>Oligo(phenylene-ethynylene)</td>
</tr>
<tr>
<td>PA</td>
<td>Polyacetylene</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity Index</td>
</tr>
<tr>
<td>PFO</td>
<td>Poly(9,9-dioctylfluorenyl-2,7-diyl)</td>
</tr>
<tr>
<td>PIF</td>
<td>Polyindenofluorene</td>
</tr>
<tr>
<td>PMII</td>
<td>1-Methyl-3-(n-propyl)imidazolium Iodide</td>
</tr>
<tr>
<td>PPE</td>
<td>Poly(p-phenylene-ethynylene)</td>
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<tr>
<td>PPV</td>
<td>Poly(phenylene vinylene)</td>
</tr>
<tr>
<td>PT</td>
<td>Polythiophene</td>
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<td>RCM</td>
<td>Ring-closing Metathesis</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>ROM</td>
<td>Ring-opening Metathesis</td>
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<td>SDS</td>
<td>Sodium Dodecyl Sulfate</td>
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<td>TA</td>
<td>Transient Absorption</td>
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<tr>
<td>TBAF</td>
<td>Tributylammonium Fluoride</td>
</tr>
<tr>
<td>TBAT</td>
<td>Tetrabutylammonium Difluorotriphenylsilicate</td>
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<tr>
<td>TBP</td>
<td>4-Tert-butyl-pyridine</td>
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<tr>
<td>TBT</td>
<td>4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole</td>
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<tr>
<td>TCO</td>
<td>Transparent Conducting Optical Glasses</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>TiO2</td>
<td>Titanium Dioxide</td>
</tr>
<tr>
<td>TMSA</td>
<td>Trimethylsilyl Acetylene</td>
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<tr>
<td>Voc</td>
<td>Open Circuit Potential</td>
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Conjugated polymers have drawn significant attention from the science community due to their interesting photophysical and optoelectronic properties. The polymer structure-property relationships have been well studied; however, the molecular weight effects on polymer properties have been less explored. In this dissertation, we focus on the synthesis of different molecular weight conjugated polymers using the end-capping strategy, and the investigation of the energy/electron transfer behavior and applications in dye-sensitized solar cells (DSSCs).

First, two families of conjugated polyelectrolytes (CPEs) featuring the same backbone but with different side chain linkages were synthesized and applied as active materials for DSSCs. CPEs bearing oxygen linkages (-O-) are more likely to aggregate in solution, and the aggregation status depends strongly on the molecular weight. In contrast, there is no obvious evidence showing that CPEs with methylene (-CH₂-) linkages aggregate in solution. The oxygen linkage family shows strong chain length dependence on cell performance, while little difference can be observed in the methylene linkage family.
Second, a series of poly(p-phenylene-ethynylene)s (PPEs) having different chain length and naphthalene diimide derivative as end-caps were synthesized and their photophysical properties were investigated. The overall quenching efficiency increases with decreasing polymer chain length as evidenced by fluorescence quantum yields. In addition, the charge recombination rate was investigated by ultra-fast transient absorption. The charge recombination rate also depends strongly on the chain length: as the chain length increases, the charge recombination rate decreases.

Third, a series of PPEs with different chain length and 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (TBT) end-caps were synthesized. Under light irradiation, energy transfer from the PPE to TBT occurs via the Forster Resonance Energy Transfer (FRET) mechanism. The overall energy transfer efficiency increases with decreasing molecular weight. Ultra-fast transient absorption studies showed that the energy transfer happens in the pico-second time scale for all the polymers, and the lowest molecular weight polymer has fastest transfer rate.

Last, a series of “through-space” conjugated polymers with different chain length and [2.2]paracyclophane moiety end-caps with TBT were synthesized. Despite the fact that conjugation is interrupted, very efficient energy transfer can still be observed and the overall energy transfer efficiency also depends on the molecular weight.
Conjugated Polymers

Conjugated polymers (CPs) feature polymer backbones with connected π-orbitals, in which electrons are delocalized within many repeat units. The delocalization of electrons narrows the band-gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and, therefore, lowers the energy required to promote one electron to the conducting band and improves the conductivity of CPs.

Iodine-doped polyacetylene with high conductivity was discovered by Nobel laureates Alan J. Heeger, Alan MacDiamid and Hideki Shirakawa in 1977. Since then, this research area has received significant attention from the science and engineering communities. Research has mainly focused on the synthesis, functionalization and application of new materials. Many synthetic strategies have been applied to tune the properties of CPs, such as changing the polymer backbone architectures and incorporating donor-acceptor units into the backbones. These strategies help researchers alter the band-gap, molar extinction efficient, electron/ hole mobility, thermo/ photo stability, etc. The resulting polymers find applications in the fields of dye-sensitized solar cells (DSSCs), bulk-heterojunction solar cells (BHJs), light emitting diodes (LEDs), organic thin film transistors (OFETs), fixed p-n junctions, chemo- and biosensors, cell imaging, antimicrobials, diagnosis, therapy, etc.
**Linear Conjugated Polymers**

Common types of conjugated polymers have linear backbones with fully conjugated double bonds, triple bonds or aromatic rings. Some classic examples of linear conjugated polymers are shown in Figure 1-1. The relative synthetic ease makes them more readily accessible, and their properties can feasibly be tuned by controlling the molecular weight, solubility, etc.

![Examples of linear conjugated polymers](image.png)

Figure 1-1. Examples of linear conjugated polymers. Figure was reprinted from Heeger with permission. Copyright 2010 The Royal Society of Chemistry.

In linear of conjugated polymers, such as polyacetylene (PA), polythiophene (PT) and poly(phenylene acetylene) (PPE), the linear polymer backbone provides the light harvesting properties. Since the entire backbone is connected by conjugated \( \pi \)-bonds, one may assume that the conjugation length will be equal to the chain length. However, the \( \pi \)-conjugation is actually broken into smaller segments with different conjugation
lengths due to conformational disorder which limits the exciton migration length to ~ 10 nm.\textsuperscript{27-30} But, very efficient intra-/inter-chain energy/electron transfer can still happen via a hopping mechanism.

**Conjugated Dendrimers and Hyperbranched Conjugated Polymers**

Dendrimers are highly branched organic macromolecules with well-defined molecular structures featuring a central core, different degree of interior branches and functional groups on the surface. Dendrimers can be categorized by generation (i.e. the number of branching) (Figure 1-2).\textsuperscript{31} Dendrimers are monodispersed and can only be synthesized stepwise. Therefore, synthetic difficulty becomes one of the major drawbacks of dendritic systems. The photophysical properties of conjugated dendrimers largely depend on the conjugated core, however, other properties, like solubility and self-assembly, are dominated by the surface functional groups.

![Figure 1-2](https://example.com/figure.png)

Figure 1-2. Examples of conjugated dendrimers. Figure was reprinted from Schanze et al with permission.\textsuperscript{31} Copyright 2012 American Chemical Society.

Hyperbranched conjugated polymers (HCPs) have three-dimensional dendritic structures which are π-conjugated. Compared to dendrimers, the structures of HCPs are less well-defined, but are easier to synthesize, which increases their accessibility. While the degree of branching of HCPs can not be well controlled, the accuracy of
branching is difficult to be predicted. Like dendrimers, the optoelectronic properties are largely controlled by the conjugated backbones, but other properties are provided by terminal functional groups.

**Polymers with Interrupted Conjugation**

Although, much attention has been paid to the investigation of fully conjugated systems, polymers with interrupted conjugation can be very interesting as well. There are two common methods to construct such a system: one is to break the conjugation of back-bones into smaller segments with non-conjugated groups/linkages\(^{32-34}\) and another way is to graft π-conjugated chromophores onto non-conjugated polymer backbones.\(^{35-37}\)

The photophysical properties of fully conjugated polymers depend strongly on the conjugation length.\(^{38,39}\) In interrupted conjugation systems, conjugation is limited to each aromatic segment; therefore, the polymers inherit most of the optoelectronic properties of the chromophores. However, due to the fact that all the chromophores are in the vicinity of each other, they can still have very strong photophysical interaction among polymer chains. For example (Figure 1-3), when oligo(phenylene-ethynylene) (OPE, energy donor) and thiophene-benzothiadiazole (TBT, energy acceptor) are grafted onto the polymer chain at the same time, ultra-fast energy transfer can occur from donors to acceptors. And the overall energy transfer efficiency depends on the donor/acceptor ratio.\(^{37}\)

At the same time, conjugation-interrupted polymers also show some advantages over small molecules because of their polymer properties, like stronger tendency to form films, superior mechanical properties, et al. These polymers have already found applications in the fields of transistors,\(^4^0\) OLEDs,\(^4^1\) DSSCs,\(^3^6\) and so forth.
Figure 1-3. Structures of conjugated small molecules and conjugated interrupted polymers. Figure was reprinted from Chen et al with permission.© Copyright 2012 American Chemical Society.

**Synthesis of Conjugated Polymers and Control of Molecular Weights**

Many synthetic methodologies have been applied to boost the facile synthesis of conjugated polymers, such as electropolymerization, alkylene/alkene metathesis and transition metal catalyzed cross-coupling reactions.

**Electropolymerization**

In the 1970s, when electropolymerization was first discovered, the application of this technique was very limited, because the media used for this reaction was water, which is a poor solvent for most aromatic molecules. It was Diaz and co-workers who used acetonitrile (1% aqueous) which contained 0.1 M Et₄NBF₄ electrolyte as the solvent for the electropolymerization of pyrrole in 1979 that opened the gate for mass application of this polymerization method. Since then, many conducting polymers have been synthesized in this way, such as polythiophene, poly(p-phenylene), polypyrrene, polyindole, polyazulene, polyfluorene, etc.

In a typical electropolymerization, three steps are involved (Figure 1-4 (A)).

At the applied voltage, a molecule (RH₂) is oxidized to its radical cation [RH₂⁺] efficiently.
when it approaches the electrode surface. Because the electro-chemical reaction is very fast, a large number of radical cations accumulate around the electrode. 2) Two monomer radical cations \([\text{RH}_2^{+}]\) can form a dimer dication \([\text{H}_2\text{R-RH}_2^{2+}]\) through a coupling reaction and then lose two protons to yield a dimer \([\text{HR-RH}]\). 3) The newly formed dimer \([\text{HR-RH}]\) can undergo electrooxidation to generate a dimer radical \((\text{HR-RH}^{+})\), which reacts with a monomer radical cation \([\text{RH}_2^{+}]\) to create a new dication \([\text{HR-RH-RH}_2^{2+}]\), followed by losing two protons to produce a neutral trimer. The overall reaction is repeated to generate polymers.

\[
\begin{align*}
1) \quad & \text{RH}_2 \quad \stackrel{-\text{e}^-}{\longrightarrow} \quad \text{RH}_2^{+} \\
2) \quad & 2 \text{RH}_2^{+} \quad \longrightarrow \quad [\text{H}_2\text{R-RH}_2]^{2+} \quad -2\text{H}^+ \quad \longrightarrow \quad \text{HR-RH} \\
3) \quad & \text{HR-RH} \quad \stackrel{-\text{e}^-}{\longrightarrow} \quad [\text{HR-RH}]^{+} \quad \text{RH}_2^{+} \quad \longrightarrow \quad [\text{HR-RH-RH}_2]^{2+} \quad -2\text{H}^+ \quad \longrightarrow \quad \text{HR-R-RH} \\
\text{overall reaction} \quad & (X+2) \text{RH}_2 \quad \stackrel{\text{Epa}}{\longrightarrow} \quad \text{HR-(R)}_x\text{-RH} \quad + \quad (2X+2) \text{H}^+ \quad + \quad (2X+2) \text{e}^- \\
\end{align*}
\]

Figure 1-4. Electropolymerization A) General procedures for electropolymerization; B) Electropolymerization of polythiophene.

Depending on the stability of the radical cations, many other reactions can occur.

When the radical has a long lifetime (i.e. the radical is fairly stable), it can diffuse far away from the electrode into the solution and react with other molecules to form byproducts. However, when radicals are short-lived, they often react with solvent molecules or other nearby molecules immediately after being generated. In order to
have the desired dimerization or polymerization reactions, radicals need to have suitable stability, which depends strongly on the nature of the molecules. In addition, there are many other factors that can affect the overall electrochemical reactions and, therefore, the polymer molecular weight as well. These factors include, but are not limited to, electrode materials, solvent, electrolytes and temperature.  

**Alkene and Alkyne Metathesis**

Alkene and alkyne metathesis has captured the attention of the polymer synthesis community for a long time. Since its discovery, the application of this method has gone way beyond the industrial manufacturing of polyolefins, and several distinguishable processes have been identified: cross-metathesis (CM), ring-opening metathesis (ROM), ring-closing metathesis (RCM) and acyclic diene metathesis (ADMET) (Figure 1-5). A large variety of catalysts have been developed, most of which are based on tungsten (W), molybdenum (Mo) or ruthenium (Ru) complexes. Compared to the more water and air sensitive W and Mo catalysts (Shrock types), Ru-based catalysts (Grubbs type) have more tolerance towards air, water and reaction substrates, making them more useful in the construction of functional materials. Because of their pioneering work in developing the synthetic methodology and various catalysts, Grubbs, Schrock and Chauvin shared the Nobel Prize in Chemistry in the year of 2005.

Besides being employed in the synthesis of non-conjugated polymers, alkene metathesis has also been extensively used to synthesize poly(arylene-vinylene)s (PPVs) (Figure 1-6). The polymerization reaction follows a typical step-growth mechanism: At the beginning of the reaction, the monomer conversion rate is high, and large amount of oligomer formation is observed. Subsequently, polymer molecular
weights grow with time with the decrease in low molecular weight molecules. The expected polydispersity index (PDI) is around 2 (Flory-Schulz distribution). However, there are examples that polymers synthesized by the metathesis show narrow PDI, although, the overall molecular weight is relatively low.\textsuperscript{54,55} By performing the polymerization at optimized conditions (e.g., the right combination of catalyst, solvent, temperature and monomer concentration), high molecular weight polymers can be obtained.\textsuperscript{56,57}

Figure 1-5. Alkene and alkyne metathesis A) Schematic representation of a general alkene metathesis reaction; B) examples of W, Mo and Ru based catalysts. Figure was reprinted from Bunz et al with permission.\textsuperscript{43} Copyright 2012 John Wiley & Sons.

In contrast to the application of alkene metathesis to build PPVs, there are fewer reports concerning the synthesis of poly(phenylene ethynylene)s (PPEs) via alkyne
metathesis. However, compared to other synthetic methodologies, alkyne metathesis can give very high molecular weight polymers.\textsuperscript{58}

Figure 1-6. Examples of poly(arylene-ethynylene)s synthesized by alkene metathesis. Figure was reprinted from Bunz et al with permission.\textsuperscript{43} Copyright 2012 John Wiley & Sons.

**Pd Catalyzed Cross-coupling Reactions**

The development of cross-coupling reactions, especially palladium-catalyzed carbon-carbon bond formation reactions, facilitates the synthesis of CPs. Compared to catalysts used in metathesis polymerization, most Pd catalysts have relatively higher tolerance to different functional groups and reaction conditions, and they are less sensitive to water, making them more popular choices for the synthesis of CPs. Due to their significant contribution to the development of Pd-catalyzed reactions, Heck, Negishi and Suzuki were awarded the Nobel Prize in Chemistry in 2010.

There are several milestone name reactions using Pd-catalysts and they are listed in Table 1-1. Although, these reactions involve different catalytic systems and substrates and have different application scopes, they share very similar catalytic cycles (Figure 1-7). The catalytic cycle usually starts with oxidative addition of organic halides (Reactant B, Ar-X, X= Cl, Br or I) onto the Pd catalyst to form a new complex, followed
by a transmetallation reaction of activated Reactant A (Nu') with the newly generated complex to put Nu on the same catalytic center. Then, trans-cis isomerization will take place to put Ar and Nu at cis position. The final step is the production of the desired coupling compound along with the regeneration of the catalyst by reductive elimination.

Table 1-1. Name reactions using palladium catalysts

<table>
<thead>
<tr>
<th>Name Reaction</th>
<th>Reactant A Substrate</th>
<th>Reactant A Hybridization</th>
<th>Reactant B Substrate</th>
<th>Reactant B Hybridization</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heck</td>
<td>Alkene</td>
<td>sp²</td>
<td>R-X</td>
<td>sp²</td>
<td>Pd</td>
</tr>
<tr>
<td>Negishi</td>
<td>R-Zn-X</td>
<td>sp, sp², sp³</td>
<td>R-X</td>
<td>sp², sp³</td>
<td>Pd or Ni</td>
</tr>
<tr>
<td>Suzuki</td>
<td>R-B(OR)₂</td>
<td>sp²</td>
<td>R-X</td>
<td>sp², sp³</td>
<td>Pd</td>
</tr>
<tr>
<td>Stille</td>
<td>R-SnR₃</td>
<td>sp, sp², sp³</td>
<td>R-X</td>
<td>sp², sp³</td>
<td>Pd</td>
</tr>
<tr>
<td>Sonogashira</td>
<td>Alkyne</td>
<td>sp</td>
<td>R-X</td>
<td>sp², sp³</td>
<td>Pd and Cu(I)</td>
</tr>
</tbody>
</table>

Figure 1-7. Schematic representation of catalytic cycle of Pd-catalyzed cross-coupling reactions. Figure was reprinted from Amatore and Jutand with permission. Copyright 2000 American Chemical Society.

Because the catalyst can dissociate from the reactant, the reaction has no living polymerization characteristics. In fact, cross-coupling polymerizations are typical step-
growth reactions with PDI around 2. Furthermore, it’s possible to obtain high molecular weight polymers by using 1:1 ratio of Reactant A and Reactant B. The molecular weight is determined by degree of polymerization (DP), is given by:

$$DP = \frac{1}{1-p},$$
where p is the extent of reaction

Polymer molecular weight can be tuned via the control of DPs by introducing a stoichiometric imbalance of functional groups of Reactant A to that of Reactant B. The resulted DP is given by:

$$DP = \frac{1+r}{1+r-2rp},$$
where r is stoichiometric imbalance ratio.\(^{60}\)

If the stoichiometric imbalance is caused by the addition of a mono-functioned end-cap, the polymer molecular weight can be controlled, and the end-group function can be introduced at the same time. This strategy has been successfully applied by many research groups to synthesize CPs with different molecular weight with end-group functionality.\(^{61-64}\)

More recently, several groups developed a chain-growth process for controlled synthesis of polythiophenes,\(^{65}\) polyfluorenes,\(^{66,67}\) polyphenylenes,\(^{68}\) and poly(phenylene ethylene)s.\(^{69}\) The chain-growth reactions still undergo the same catalytic cycle as the step-growth mechanism reactions – oxidative addition, \textit{trans}-metalation, \textit{trans-cis} isomerization and reductive elimination. However, the oxidation addition happens in an intra-chain manner due to the nature of the new catalytic systems, giving the polymerization living characteristics. Due to the living polymerization nature, this method can be used to control molecular weight, build di-block polymers and synthesize grafting polymers using the “grafting-from” approach.
Photophysical Process of Conjugated Polymers

Conjugated molecules can interact with a large region of the solar spectrum, from near-UV to near-IR, since the degree of π-conjugation differs in different conjugated systems. Despite the difference in absorption wavelength, the absorption process of all the molecules follows the same principle, the Stark-Einstein law, which says that each absorbed photon will cause only one primary chemical or physical change. The Stark-Einstein law is also called the photochemical equivalence law, for it can be rephrased as: for every mole of quanta of light absorbed, one mole of substance will react. The formula is given by:

$$\Delta E_{\text{mol}} = N_A h \nu$$, where $N_A$ is Avogadro's number.\(^\text{70}\)

Molecules that can absorb light are called chromophores and they are responsible for the colors of molecules. When light irradiates the molecule, a certain wavelength of light is absorbed and the molecule shows the complementary color which is not absorbed. If all the visible light is absorbed by a substance, it will appear to be black. After light is absorbed, many interesting photophysical process can happen.

Excitation, Fluorescence and Phosphorescence

During the photoexcitation process, an electron is excited from the ground state to an excited state and will remain in the excited states until the relaxation or transfer process occurs. A schematic diagram, named in honor of Aleksander Jablonski, has often been used to illustrate the photophysical process, as shown in Figure 1-8. A Jablonski diagram portrays the relative electronic and vibrational energy levels of the ground and excited states without any attempt to depict the nuclear and electronic geometries.
When a molecule absorbs a photon with appropriate energy, an electron is promoted to a vibronically excited level of electronic singlet state, $S_1$, from the lowest vibronic level of the electronic ground state, $S_0$. This process is called ground state excitation and occurs on the time scale of $10^{-16} – 10^{-14}$ s. There are many vibrational levels within the $S_1$ state, and the chance of an electron being promoted to a specific energy level depends on the energy overlapping. However, the molecule will relax to the lowest vibronic level of electronic state $S_1$, because the extra energy is transferred to solvent or lost due to molecule reorganization. The relaxation usually takes about $10^{-14} – 10^{-11}$ s. When a proper light source is applied (e.g. a high energy laser), it's possible that the molecules will be promoted to higher energy electronic singlet states, $S_2 – S_n$.

Without external interactions, two possible follow-up conversions can occur for the singlet excited state: decay to $S_0$ or transfer to first excited triplet state, $T_1$. There are two possible pathways to decay to $S_0$: radiative decay and non-radiative decay. In the
radiative decay, a photon is emitted to give fluorescence and the energy of the emitted photon depends on the energy difference between $S_1$ and $S_0$. There is usually a shift, called Stokes shift, to longer wavelength, between the absorption wavelength maximum and emission wavelength maximum due to the energy difference between photon absorbed and photon emitted. Radiative decay mostly happens in the time range of $10^{-9}$ – $10^{-7}$ s. On the other hand, the singlet excited state can relax to ground state without emitting photons. Instead, the energy will be lost in the form of heat.

Alternatively, the excited state can undergo intersystem crossing (ISC) from singlet excited state to triplet excited state. The intersystem crossing rate depends strongly on the system and can vary in a large range. After intersystem crossing, the system relaxes to the lowest triplet excited state, $T_1$. Similar to the process in the singlet excited state, the molecule will eventually decay to the ground state via either radiative decay which produces phosphorescence or non-radiative decay which generates heat. However, in the singlet state, the electron spins are still paired the same as the electrons pairs in the ground state. In contrast, in the triplet state, the electrons spins are parallel (Figure 1-9). Because of the difference in electron spin orientation in the ground state and triplet state, direct excitation of electrons from ground state to the triplet state is quantum mechanically forbidden. An electron must be excited to its singlet excited and undergo ISC to convert to the triplet excited state. For the same reason, the radiative decay rate (from $T_1$ to $S_0$ (phosphorescence, usually $10^3$ - $10^2$ s$^{-1}$) is considerably slower compared to the rate of singlet emission (fluorescence, $10^9$ - $10^7$ s$^{-1}$).
Figure 1-9. Schematic representation of electron spin in ground, singlet excited and triplet excited state.

**Energy and Electron Transfer**

When a photo-excited molecule interacts with another substance, the excited state molecule can be quenched. There are two distinct pathways for the quenching: energy transfer when excited electron transfers its energy to interacting molecules and returns back the ground state; electron transfer if the electron hops to the interacting molecules. For each pathway, the molecule that gives energy or electron is called donor (D) while the molecule that accepts energy or electron is called acceptor (A). The donor has higher excited-state energy than the acceptor. The interaction mechanisms for energy and electron transfer differ significantly and are discussed below.

**Energy transfer**

Energy transfer can occur via either a radiative or non-radiative process. In a radiative energy transfer process, the excited donor molecules (D*) emit photons which are directly absorbed by acceptors (A). Apparently, this requires that the emission spectrum of D* must have some overlap with the absorption spectrum of A. The overall energy transfer efficiency depends on the quantum yield of the donor molecules, the overlap integral (J) of the emission and absorption spectra, the concentration of acceptor and the molar extinction coefficient. In general, the radiative energy transfer efficiency is not very high.
On the other hand, non-radiative energy transfer, which does not involve the emission and absorption of photons, but only energy can be very efficient. The energy transfer is a two-step process: photoexcitation of the donor molecule Equation 1-1 and energy transfer from donor to acceptor Equation 1-2.

\[
D + h\gamma \rightarrow D^*  \tag{1-1}
\]

\[
D^* + A \rightarrow D + A^*  \tag{1-2}
\]

There are two different mechanisms for the energy transfer step: Förster energy transfer which occurs via a dipole-dipole interaction and Dexter energy transfer which involves an electron exchange interaction (Figure 1-10).

Figure 1-10. Schematic presentation of the mechanism of energy transfer. A) Dexter energy transfer; B) Förster energy transfer.\textsuperscript{72} Figures are adapted with modification.

In Förster energy transfer, the driving force is the electronic coupling interaction between the dipole moments of the excited donor and the acceptor (dipole-dipole interaction). During Förster energy transfer, the energy of the excited electron in the lowest unoccupied molecular orbital (LUMO) of the donor (D*) is transferred to the acceptor (A) via a Columbic interaction, and the electron relaxes to the highest occupied
molecular orbital (HOMO). At the same time, the acceptor acquires the energy and one of its electrons is promoted from the HOMO to LUMO. This mechanism does not involve the exchange of electrons and can occur over a long distance (30-100 Å).

The electrostatic interaction energy \( E \) between the two interacting dipoles is directly proportional to the strength of both transition dipoles \( \mu_D \) and \( \mu_A \) and inversely proportional to the cube of the distance between the donor and acceptor.

\[
E(\text{dipole} - \text{dipole}) \propto \frac{\mu_D \mu_A}{R_{DA}^3} \tag{1-3}
\]

The energy transfer rate \( k_{ET} \) can be derived from equation 1-3 and is proportional to the square of the electrostatic interaction energy \( E \).

\[
k_{ET}(\text{dipole} - \text{dipole}) \propto E^2 \approx \left( \frac{\mu_D \mu_A}{R_{DA}^3} \right)^2 = \frac{\mu_D^2 \mu_A^2}{R_{DA}^6} \tag{1-4}
\]

Energy transfer efficiency increases with the magnitude of dipole moments and decreases significantly with increasing donor-acceptor separation, since the rate is proportional to the inverse sixth power of the distance between donor and acceptor.\(^{72}\)

In Dexter energy transfer, there is direct electron exchange between the donor and acceptor via the overlapping orbitals of \( D^* \) and \( A \). The excited electron in the LUMO of \( D^* \) hops to the LUMO of \( A \) and one electron in the HOMO of \( A \) is transferred to the HOMO of \( D^* \). Another key difference between Dexter and Förster energy transfer is that both singlet-singlet and triplet-triplet energy transfer can take place in via Dexter energy transfer while Förster theory can be applied in triplet-triplet energy transfer.

The energy transfer rate in the Dexter mechanism is given by:

\[
k_{ET} (\text{exchange}) = K \exp \left( \frac{-2R_{DA}}{R_{DA}^0} \right) \tag{1-6}
\]
Where $K$ is a parameter related to specific orbital interactions, $J$ is the spectral overlap integral, $R_{DA}^0$ is the separation of D* and A when they are in van der Waals contact and $R_{DA}$ is the distance between D and A. Because the transfer rate is exponential dependent of the distance of D and A ($R_{DA}$), energy transfer is efficient only when D and A are very close to each other (5-10 Å).

**Electron transfer**

Electron transfer is a very important reaction in many biological processes\textsuperscript{73,74} and photo-electronic devices.\textsuperscript{75,76} Unlike energy transfer, electron transfer involves actual electron transfers from a donor to an acceptor, which produces a charge separated state (Figure 1-11). In photoinduced electron transfer, one electron in the donor is excited to its LUMO and then transferred to the LUMO of the acceptor. As a result, the donor is oxidized to $D^+$, while the acceptor is simultaneously reduced to $A^-$. The electron transfer produces a charge separated state which may be deactivated to the ground state by charge recombination or may undergo follow-up reactions if the charge separated state is long-lived.

![Figure 1-11. Schematic representation of electron transfer.](image)

Rudolph A. Marcus developed a theory to explain electron transfer which treated the electron transfer process as a transition state. In the Marcus theory the excited donor and acceptor pair (DA*) and the charge separation state (D$^+$A$^-$) are treated as the reactant and product, respectively (Figure 1-12).\textsuperscript{77}
Figure 1-12. Potential energy surface diagram for electron transfer process. In the figure, DA, DA*, TS and D+ A- stand for the grand state, excited state, transition state and charge separation state, respectively; \( \Delta G^0 \) and \( \lambda \) are Gibbs free energy change and reorganization energy, respectively. Figure is adapted with modification.\(^{72}\)

The electron transfer rate can be derived from the theory:

\[
k_{if} = \frac{2\pi}{\hbar} |V_{if}|^2 \sqrt{\frac{1}{4\pi k_B T \lambda}} \exp\left[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}\right]
\]

where, \( V_{if} \) is the electronic coupling matrix element, \( \lambda \) is the reorganization energy induced by the electron transfer and \( \Delta G^0 \) is the Gibbs free energy variation during the reaction. The electron transfer rate is controlled by two parameters: 1) the electronic matrix element and 2) the reorganization energy. In order to have high electron transfer rate, the electronic coupling needs to be maximized while the reorganization energy should be minimized.

The electronic coupling can be understood as the tendency of the donor to transfer an electron to the acceptor, and therefore, transfer integral can be assigned to quantify the electron coupling matrix. The overall transfer integral depends on both the interacting Frontier Molecule Orbitals (FMOs) of the donor and acceptor and the relative positions of the interacting molecules. One method to estimate the transfer integral is to
apply Koopman’s theory, which use half the splitting of the HOMO to calculate the hole transfer integral and half the splitting of the LUMO to calculate the electron transfer integral (Figure 1-13). In general, the HOMO splitting is systematically larger than LUMO splitting, because, the FMOs of the HOMO feature bonding characters while the FMOs of the LUMO are mostly anti-bonding. When two molecules approach each other, the FMOs start to interact with each other, splitting the HOMO and LUMO into two energy levels. The splitting creates anti-bonding characters in HOMO and some bonding in the LUMO and. The anti-bonding character greatly increases the energy level of HOMO and, therefore, enlarges the magnitude of HOMO splitting. Because the original LUMO has anti-bonding characters, the significance of the splitting is smaller. In fact, most organic materials have higher hole mobility than electron mobility due to larger HOMO splitting.

![Energy diagram to illustrate splitting.](image)

The relative position of the interacting molecules also affects the electronic coupling. For example, co-facial displacement of the two molecules usually provides the largest electronic interaction. However, lateral displacement can cause the splitting of the LUMO even larger than that of the HOMO.
The reorganization energy is the sum of the inner and outer contribution. Upon electron gain/loss, the geometry of the donor/acceptor changes, and the energy variation associated with the change is the inner reorganization energy. The polarization, relaxation and stabilization effects of the surrounding environment on the donor/acceptor also cause an energy change, which is assigned as the outer reorganization energy. In many cases, the magnitudes of the inner and outer reorganization energy are of the same order.

Figure 1-14. Potential energy surface diagram for illustration of reorganization energy.

A potential energy surface diagram can be used to illustrate the electron transfer process (Figure 1-14). During an electron transfer reaction, the donor (D) is oxidized to D+ and the acceptor (A) is reduced to A- simultaneously. This step does not involve any geometry change. The following step is the relaxation of the product nuclear geometries. The energy required to overcome the barrier for the transition is provided by photon irradiation in the case of photo-induced electron transfer (See Figure 1-12). The reorganization energy greatly affects the overall electron transfer efficiency since the electron transfer rate is exponentially proportional to the sum of reorganization energy and Gibbs free energy change.
Energy and Electron Transfer in Conjugated Polymers

Compared to small molecules and oligomers, energy and electron migration is very efficient in conjugated polymers due to the molecular wire effect which is proposed by Swager and co-workers (Figure 1-15).\(^8\) The conjugated polymer chains resemble molecular wires along which the exciton can delocalize and migrate along the wire efficiently. This effect contributes to the fact that the quenching efficiency of conjugated polymers is several order of magnitude higher compared to small molecules. For example, Zhou and Swager prepared a water-soluble conjugated polymer featuring PPE backbone with a crown-ether side chain on each repeat unit (Figure 1-16).\(^8\) In solution, the polymer shows strong emission which can be quenched by methyl viologen (MV\(^{2+}\)) about 50-100 fold greater efficiency compared to an oligomer with only three benzene rings bearing the same crown-ether group. In the case of small molecules, each quencher can quench the fluorescence of only one small molecule. In contrast, in polymer emission quenching, all excitons generated by different chromophore units on a polymer chain can be quenched, as long as they can migrate to the quenching site and encounter a quencher. The molecule wire effect acts as an amplifier and greatly enhances the quenching efficiency. Based on this strategy, many conjugated polymer sensors have been developed.\(^{18,81}\)

However, the photophysical process in conjugated polymers is very complicated. In polymer assemblies, there can be both interchain and intrachain energy and/or electron transfer competing with each other. Intrachain transfer refers to energy/electron migration along a single polymer chain while interchain process means the exciton hops among multiple polymer chains. The conformation and assembly status of polymers depends on the solvent and temperature, which affect the energy and charge transfer
processes. Numerous researchers have continued to resolve the complexity and understand the mechanisms and kinetics of energy/electron transfer in CPs.

Figure 1-15. Schematic representation of molecular wire effect. Figure was reprinted from Zhou and Swager with permission. \(^{80}\) Copyright 1995 American Chemical Society.

**Monomeric Chemosensor:** Sensitivity determined by the equilibrium constant

Figure 1-16. Comparison of polymer and small molecule fluorescence sensors. Green color indicates the molecule is emissive and grey color means the fluorescence is quenched. Figure was reprinted from Zhou and Swager with permission. \(^{80}\) Copyright 1995 American Chemical Society.

Swager and co-workers contributed significantly in this area. \(^{82}\) They demonstrated that, in a pure rigid-rod system, like PPEs, the exciton hop along the
polymer backbone follows a 1D random-walk model. The exciton migration does not have a preferred direction and will pass a certain portion of the polymer chain multiple times when it travels back-and-forth. The exciton can be effectively quenched as long as it reaches the quenching site before decaying to the ground state. The effective migration length depends on the product of lifetime of excitation (τ) and transfer rate (v). In order to determine the effective excitation migration length, Zhou and Swager synthesized a series of PPEs with different chain lengths. In the quenching experiments, they noticed that the quenching efficiency stopped increasing after the number of repeating units reached ~ 140. Therefore, they concluded that in solution the effective exciton migration length of PPEs is about 140 (Ph-CC-) units. Based on the conclusion, they calculated the total exciton travel distance is about 20,000 phenylethynyl units. However, one thing that needs to be pointed out here is that PPEs are not perfectly rigid-rods and the persistence length is about 15 nm.

Wrighton and Swager reported energy transfer study in a system containing PPEs with anthracene substitution (PPEAn) at the polymer chain ends (Figure 1-17). The polymer backbone harvests energy and creates excitons which transfer to anthracene, due to the fact that anthracene has a lower LUMO energy and acts as an acceptor. Compared to PPEs without anthracene substitution, the emission of PPEAn shows two distinct bands in solution (Figure 1-17). The higher energy band at 478 nm comes from the polymer backbone while the lower energy band at 510 nm is assigned to anthracene emission. The intensity ratio of the higher energy band to the lower band is about 2:1, indicating fairly efficient energy transfer. However, in a PPEAn film, there is only one emission peak, and the emission from the PPE backbone is completed.
quenched indicating the energy transfer efficiency is enhanced (Figure 1-17). The authors stated that in solution, energy migration is only one-dimensional (e.g. the exciton can only travel along the polymer chain). In contrast, polymer chains are closer to each other in films making interchain energy hopping possible, making energy transfer three-dimensions.

Figure 1-17. Chemical structure of PPEAn and emission spectra of PPEAn in solution and film. Figure was reprinted from Swager. Copyright 2011 John Wiley & Sons.

The effective conjugation length is also believed to affect the energy transfer rate. Swager investigated the energy migration rate of PPEs containing iptycene units (PPEIp) in liquid crystalline (LC) solvents. The effective conjugation length of PPE type polymers in solution (like tetrahydrofuran (THF) or dichloromethane (DCM)) is limited to around 9-10 repeating units. But, when the polymers are dissolved in a liquid crystalline solvent (e.g. 1-(trans-4-hexylcyclohexyl)-4-isothiocyianatobenzene, 6CHBT),
both absorption and emission spectra show significant bathochromic shifts indicating increasing conjugation length in polymer (Figure 1-18 A & B). In addition, the fluoresce anisotropy increases from ~0.3 in DCM to ~0.72 in 6CHBT (Figure 1-18 D). The possible reason is that the polymer chains are better aligned along the liquid crystalline direction. As a result, the authors observed improved energy transfer efficiency and they attributed it to increased conjugation length and better alignment.

![Figure 1-18. Photophysical properties of PPEIp. A) UV-vis absorption and B) emission of PPEIp in DCM, film and LC solution; C) schematic representation of extended polymer chain model; D) polarized emission spectra of PPEIp. Figure was reprinted from Swager. Copyright 2005 American Chemical Society.](image)

Mullen and Breda’s work helped explain the details of energy/electron transfer in conjugated polymers. They studied the energy transfer in a donor-acceptor system.
featuring a polyindenoﬂuorene (PIF) backbone (donor) and perylene derivatives as end-groups (acceptor) (Figure 1-19A). They stated that energy transfer in solution, which does not involve much interchain interaction, can be viewed as a two-step process: exciton migration along the backbone and energy transfer to the acceptor. The effective conjugation length is shorter than the total polymer chain length, and the polymer chain is “divided” into several conjugated segments. After excitation, the exciton hops among these segments, which is a slow process due to the weak dipole coupling between chain segments. Hopping means the exciton jumps to a nearby segment which is a homomolecular self-exchange process and does not involve energy change. Once the exciton reaches the segment which has close contact with the acceptor, ultrafast energy transfer takes place, and the energy transfer rate is determined by the reorganization energy and electronic coupling matrix (see previous section). Energy migration is more efficient in rigid rods compared to flexible chains, due to smaller reorganization energy loss, and the electronic coupling matrix is calculated to decrease with increasing D-A distance (Figure 1-19B). Thus, the hopping process becomes the key step in determining the overall transfer rate.

In films, the polymer chains stack together, and this favors interchain energy transfer from the conjugated segments of one chain to the perylene unit in another chain. As a result, the energy transfer efficiency is about 10 times higher in films compared to in solution.
Energy and electron transfer in more flexible conjugated polymers are even more complicated. Scholes, Tobert and Schwartz studied the energy transfer in poly[2-methy-oxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) in solution and in a restricted matrix. MEH-PPV chain is more flexible compared to PPEs, and has both tightly coiled and open chain conformations in solution (Figure 1-20 A). In the tightly coiled conformation zone, conformational subunits (chain segments within which the repeating units are conjugated) are close to each other, facilitating interchain energy transfer. In the open chain conformation region, conformational subunits are in the extended chain mode, which favors intrachain energy transfer. In a confined silica composite matrix, where the polymer chain conformation is confined, most polymer chains adapt the extended conformation (Figure 1-20 B). Interchain energy transfer is inhibited and the energy transfer prefers to occur through the intrachain hopping mechanism. Thus, the overall energy transfer efficiency is lower in films compared to in solution.
Conjugated Polyelectrolytes and Dye-sensitized Solar Cells

Conjugated polyelectrolytes (CPEs) are \( \pi \)-conjugated polymers with ionic pendant chains. They inherit the interesting electronic and optical properties of organic \( \pi \)-conjugated backbones and are soluble in polar solvents, such as water, ethanol, etc. Many ionic side chains have been proven to endow this solubility to CPs, including sulfonate (-SO\(_3\)), carboxylate (-CO\(_2\)), phosphonate (-PO\(_3^2\)) and quaternary ammonium (-NR\(_3^+\)) groups (Figure 1-21). The charged side groups can interact with many species, such as metal ions, metal oxides, polyelectrolytes, proteins, oligo and polynucleic acids, making CPEs outstanding platforms for a variety of applications.\(^{89,90}\) Charges also allow direct deposition of CPEs on top of neutral semiconductor surface, making CPEs applicable in device fabrications.\(^{91,92}\) In addition, the use of some polar solvents, like methanol and water, to make CPE-based devices is more environmentally friendly, as these solvents are regarded as green solvents.
Selective Applications of CPEs

Chemo and bio-sensing are very important applications of CPEs. The working principles of sensors are based on fluorescence quenching and/or recovery. There are two quenching pathways, dynamic quenching and static quenching, which are shown in the simplified Jablonski diagram (Figure 1-22). In a quenching process, a ground state fluorophore (F) first absorbs light and is excited to the singlet excited state (F*). When F* returns to the ground state via photon emission, it produces fluorescence. However, quenching occurs when F* interacts with a species which causes the fluorescence intensity or lifetime be reduced. In fact, quenching is a subcategory of energy/electron transfer (refer to section 1.3.2) and the molecular wire effect makes CPEs superior candidates for sensing applications compared to small dyes (see section 1.3.3).

One of the early CPE-based sensors exploiting the amplified quenching mechanism was reported by Whitten and co-workers (Figure 1-23). Biotin-functionalized viologens quench the emission of MPS-PPV very efficiently in aqueous solution. But, the fluorescence is recovered by addition of avidins to the solution. Avidins can bind very strongly with biotins and prevent the viologen quenchers to approach the MPS-PPV chain. Therefore, the quenching is stopped which induces the recovery of CPE emission. This system exhibits high sensitivity for the detection of avidins.
Polymer conformation change provides another useful mechanism for sensing applications. Schanze and co-workers studied the $\text{Ca}^{2+}$-induced aggregation of $\text{PPE-CO}_2^-$ and the quenching behavior by methyl viologen ($\text{MV}^{2+}$). $\text{Divalent cation CA}^{2+}$ serves as a bridge between negatively charged polymers and causes the polymer chains to aggregate. In the aggregated state, the overall quantum yields of CPEs decreases. Quenching is more efficient, probably because the diffusion of the exciton is three-dimensional within the aggregates, which increases the probability of quenching.

Another important application of CPEs is in antimicrobials. For several decades, quinolones, glycopeptides, and streptogramins, which were introduced in the mid-20th
century, were the only options for antimicrobial applications. One serious crisis can arise due to the bacterial resistance which limits the usefulness of these drugs. Therefore, new antibacterial materials are needed to resolve the crisis. Photo-dynamic inactivation of bacteria, which was first introduced more than a century ago, is an alternative (Figure 1-24).\(^5\) Singlet oxygen (\(1^1O_2\)) is believed to be the active species that causes cell damage or death, because it degrades cell walls, lipid membranes, enzymes and nucleic acids in photodynamic inactivation.\(^6\)

![Figure 1-24. Mechanism of biocidal action. (i) Reversible bacteria adhesion to the particles. (ii) Photoexcitation of CPE. (iii) Singlet oxygen generation. (iv) Killing bacteria by oxygen. (v) Aggregation of particles. Figure was reprinted from Whitten.\(^7\) Copyright 2008 American Chemical Society.](image)

When irradiated, CPEs can generate singlet excited states which can undergo intersystem crossing to produce triplet excitons. The energy of the triplet exciton is can be used to convert ground state dioxygen (\(3^3O_2\)) to excited state singlet oxygen \(1^1O_2\). Since CPEs can bind closely to the bacteria, the \(1^1O_2\) only has to travel a short diffusion pathway to reach the bacteria which will reduce its toxic effect.\(^8\) Based on that, the Whitten and Schanze groups developed several CPE-based antimicrobials (e.g. CPEs grafted silica particles).\(^7,9\) Silane functionalized iodobenzene was first grafted onto silica particles which then reacted with 1,4-diiodobenzene and 1,4-diethynylbenzene in
solution to give polymer coatings. When exposed to light, bacteria which were accompanying or in the vicinity of the particles were killed effectively.

CPEs are also outstanding candidates for drug and gene delivery, because the fluorescence change can be used to monitor the release process \textit{in vivo}.\textsuperscript{21,25} Wang and co-workers designed several drug delivery systems and one example is shown in Figure 1-25.\textsuperscript{100} Positively charged poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) forms a complex with anionic poly(L-glutamic acid) which is conjugated with an anticancer drug through electrostatic interaction. The PFO alone shows very strong fluorescence, but upon interaction with drugs, the fluorescence is quenched by the drug via an electron-transfer mechanism. However, upon hydrolysis of the poly(L-glutamic acid), the drug is released, thereby stopping the electron-transfer process and recovering the fluorescence of the PFO. The quenching and recovery of fluorescence make it very convenient for monitoring drug release.
Dye-Sensitized Solar Cells (DSSCs)

Because of the increasing demand for energy, the depletion of fossil fuels and the environmental impact associated with the use of non-renewable energy resources, “green” energy technology has drawn significant attention recently. Dye-sensitized solar cells (DSSCs) are among the most important emerging photovoltaic devices which can be alternatives to traditional inorganic solid state solar cells. A typical DSSC structure is shown schematically in Figure 1-26. It is made of a transparent nanoporous semiconductor electrode on a transparent conducting optical glass (TCO), a thin layer of light-harvesting materials on the surface of the semiconductor electrode (usually titanium dioxide, TiO\textsubscript{2}), a counter electrode, and redox electrolyte solution (I\textsuperscript{-}/I\textsubscript{3}-, for example) filling the pores. Under working conditions, the light harvesting materials (dyes) absorb sunlight and promote ground state electrons to the excited state. The excited state electrons are injected into the conduction band of TiO\textsubscript{2}, leaving the oxidized dyes behind. The electrons go through the circuit to deliver work. After losing energy, electrons can reduce I\textsubscript{3} to I\textsuperscript{-}. The oxidized dyes are reduced by I\textsuperscript{-} and the same process is repeated.\textsuperscript{101}

Operational principles of DSSCs

Under working conditions, many photo/electro-chemical reactions occur as shown in a simplified energy diagram (Figure 1-27 (a)) with different time constant (Figure 1-27 (b)). There are both desired reactions, such as reactions 0, 2, 3, 4 and 7, and undesired reactions, listed as 1, 5 and 6, which need to be hindered.
Processes 1 and 2: Charge Injection vs Decay. In order to have the cell working properly, the charge injection time constant (reaction 2) should be shorter than that of exciton decay (reaction 1). Depending on the nature of dyes, the lifetime of some dyes can be as long as $10^{-6}$ s while some other dyes are very short lived with lifetime as short as $10^{-9}$ s. The short excited state life-time increases the chance of that electron will not be injected into the conducting band of TiO$_2$, and decay to the ground state will occur instead. The mechanism of charge injection is still not very clear, but it is well accepted that the charge injection is an ultrafast process with a femtosecond component. However, very slow injection was also observed in a DSSC device whose time scale is around 150 ps. Such a slow injection process greatly reduces the charge collection efficiency and reduces the cell performance. The overall injection process has been an important research topic and is greatly influenced by additives in electrolyte solutions, the Fermi energy level of TiO$_2$, the dye binding model and the distance between the dye molecules and TiO$_2$ particles, etc. For example, the addition of 4-tert-butyl-pyridine (TBP) into the electrolyte solution
increases the energy level of conduction band edge and increases the energy overlap of the excited state dyes and the TiO$_2$ conducting band (Figure 1-28).$^{75}$

Figure 1-27. Reactions in DSSCs. A) Energy diagram; B) time constant. Figures were reprinted from Hagfeld.$^{101}$ Copyright 2010 American Chemical Society.

Figure 1-28. Energy level change with and without TBP. Figures were reprinted from Hagfeld.$^{101}$ Copyright 2010 American Chemical Society.

**Reactions 3 & 7: Regeneration of Dyes and Redox Couples.** In order to have the cell working in a continuous manner, the oxidized dye has to be reduced to the ground state (regeneration of dyes, reaction 3). The time constant in this reaction is limited by the diffusion of the redox couple. For example, in a non-viscous solvent, like dimethylformamide (DMF), the diffusion rate constant is around $10^9-10^{10}$ M$^{-1}$s$^{-1}$ and the time constant of regeneration is about 1-10 ns with normal redox couple concentrations ($\sim 0.1$ M). Iodide/triiodide ($I^-/I_3^-$) is a common redox couple with iodide as the reductant
and triiodide as the oxidant and the reaction mechanism is proposed as follows (Figure 1-29). The first step is the one-electron transfer reaction between oxidized dye and iodide, followed by the addition of a second iodide. After reduction of oxidized dyes, iodide is converted to diiodide ($I_2^-$), which subsequently undergoes a disproportionation reaction and converts to triiodide and iodide. The last step is the reduction of triiodide back to iodide at the cathode interface (reaction 7). Other redox mediators have been applied in DSSCs as well, such as $\text{Br}^-/\text{Br}_3^-$ and Cobalt complex.  

\[
\begin{align*}
S^+ + I^- & \rightarrow (S\cdots I) \\
(S\cdots I) + I^- & \rightarrow (S\cdots I_2^-) \\
(S\cdots I_2^-) & \rightarrow S + I_2^- \\
2I_2^- & \rightarrow I_3^- + I^- \\
I_3^- + 2e^- & \rightarrow 3I^-
\end{align*}
\]

Figure 1-29. Regeneration of dyes and redox couples

**Reaction 4, 5 and 6: Charge Transport and Recombination.** After injection from excited dye molecules to the conduction band of TiO$_2$, charges will travel through the network of TiO$_2$ particles to the outside load (reaction 4). The charge density is higher at the surface of TiO$_2$ films compared to the bulk conducting substrate and charge transport occurs by diffusion, driven by the charge density. Once charges reach the conducting substrate, the current can be detected. But, there are traps located inside the bulk TiO$_2$ particles, at the grain boundaries and at the interface of TiO$_2$ and electrolytes, which reduce the charge collection efficiency.
Moreover, charge recombination with either oxidized dye or a redox couple is another process which reduces charge collection efficiency. There are still debates on the driving force of recombination. Some results show that, like charge transport, charge recombination is also controlled by diffusion; i.e., the collision of electrons with oxidized dyes or redox molecules.\textsuperscript{108} However, there are also studies showing that recombination kinetics lies in the inverted Marcus region, where the driving force ($\Delta G$) is smaller than the reorganization energy ($\lambda$) and an increase in driving force will decrease the recombination rate (Equation 1-7).\textsuperscript{109} Redox couples have been found to have a huge impact on charge recombination in DSSCs. One way to characterize recombination is to determine the lifetime of electrons which can be obtained using transient absorption technique. It has been found that the electron lifetime in a system with iodide/triiodide is longer compared to most other systems which makes iodide/triiodide a very successful redox couple in DSSCs.\textsuperscript{110}

**Solar cell characterization**

There are several common parameters to characterize cell performance. The incident photon-to-current efficiency (IPCE) indicates the efficiency of a device converting photons to electricity at a certain wavelength, which is given by:

$$IPCE(\lambda) = \frac{n_{electrons}}{n_{photons}} = \frac{I/e}{P/h\nu} = \frac{I}{P} \times \frac{1240}{\lambda(nm)}$$

Where $I$ is the photocurrent measured in A/m\textsuperscript{2}, $P$ is the incident light power with unit of W/m\textsuperscript{2} and $\lambda$ is the incident wavelength in nm. However, it is important to note that the actual number of photons absorbed is almost impossible to measure due to light scattering and transmission in the device. So the number calculated in the above equation represents the lower limit.
The photocurrent density-voltage behavior (J-V) is another important criterion to characterize solar cells (Figure 1-30). Short-circuit current density (J_{sc}) is the current for unit area under short-circuit condition. The open-circuit potential (V_{oc}) is the maximum potential that can be obtained when a cell is under open circuit conditions. It is also the energy difference between the Fermi level of the semiconductor electrode under working conditions and the Nernst potential of the redox couple. The fill factor (FF) is the ratio of the maximum output, J_{opt}V_{opt}, to J_{sc}V_{oc} (FF=(J_{opt}V_{opt})/(J_{sc}V_{oc})) and is affected by many factors, such as internal resistance. Overall cell efficiency (\eta) is the ratio of the maximum output to the incident light energy (\eta=(J_{opt}V_{opt})/P_{in}).

Figure 1-30. A typical DSSC J-V curve. Figure was reprinted from Huang et al. Copyright 2007 Bentham Science Publishers Ltd.

Materials used in DSSCs

Metal Oxide Anode. The use of mesoporous TiO_2 as anode is one of the most important reasons for the high efficiency of DSSCs. In nature, there are three types of TiO_2 crystals: rutile, anatase and brookite. Although rutile is the most thermodynamically stable form, anatase is the most used structure in DSSCs, due to larger bandgap and higher conduction band edge, E_c, which increases the Fermi energy level and V_{oc}. In
DSSC applications, mesoporous TiO$_2$ is used instead of single crystals, because mesoporous materials have larger surface area, which increases the amount of dyes absorbed. For better cell performance, many improvements have been made on the architectures of the TiO$_2$ layer. A typical high performance DSSC device usually employs multiple TiO$_2$ layers, and each layer has a different thickness and the size of TiO$_2$ in each layer may vary. First, a blocking layer (~50 nm thick) is coated on the TCO substrate to prevent direct contact of the redox couple with the substrate and reduce charge recombination. Second, an active dye absorbing layer (~10-20 µm thick) is deposited onto of the blocking layer. This layer utilizes mesoporous TiO$_2$ with diameter of ~20 nm, and offers a large surface area for efficient dye uptake. Third, a light scattering layer (~3 µm thick) consisting of ~400 nm TiO$_2$ particles is deposited to give effective scattering and to increase the chance of incident light being harvested by dyes. Last, the entire structure is treated with aqueous TiCl$_4$ to obtain an ultrapure TiO$_2$ shell coating, which increase electron lifetime and lower the energy barrier for charge injection.

In addition, TiO$_2$ nanostructures with well-defined morphology, such as nanorods, nanotubes and nanowires, have been developed to improve the charge transport efficiency.$^{112}$ The highly oriented nanostructures are expected to better allow electrons to reach the TCO-electrode surface. Some other materials are also used as DSSC electrode materials, such as zinc oxide (ZnO), tin(II) dioxide (SnO$_2$) and niobium pentoxide (Nb$_2$O$_5$). Zinc oxide was initially used in DSSC and has gained significant attention recently. Its bandgap and conduction band edge are similar to those of TiO$_2$. 
and electron mobility is higher. However, the chemical stability hinders its application, since ZnO decomposes under both acidic and basic condition.

Figure 1-31. Examples of TiO$_2$ nanostructures. A) nano tubes, B) nano particles, C) nano rods, D) nano wires. Figure was reprinted from Chen et al.$^{112}$ Copyright 2007 American Chemical Society.

**Dyes.** Development of novel dyes has been crucial in achieving high performance DSSC and the number of publications concerning this topic increases each year. The characteristics of ideal dyes should meet several requirements: (1) Dyes should have high molar extinction coeﬃciency and broad absorption in the visible and near-infrared (NIR) region to ensure efficient photon harvesting. (2) They have to be able to bind strongly with the metal oxide electrode and usually this is achieved by functionalizing the molecules with anchoring groups, such as -CO$_2$H, -H$_2$PO$_3$ or -CN. (3) Dyes must have suitable energy levels: the excited state energy level should be higher
than the conduction band edge of electrodes for electron injection purposes, and the reduction potential of the oxidized dye has to be more positive than that of the redox couple for dye regeneration. (4) The dyes need to be both photochemically and thermally stable for long term applications. (5) The binding and aggregation behaviors also need to be optimized to boost cell performance.

Organometallic compounds, especially ruthenium (Ru(II)) complexes (Figure 1-32), have found great success in DSSC applications due to their superb properties: broad absorption spectra, high extinction coefficient, suitable energy levels, long-lived excited state, fast electron injection and good stability. The light harvesting properties are largely attributed to the absorption in the visible region due to a metal-to-ligand charge transfer (MLCT). Therefore, the electronic interaction between d orbitals of the central metal and π* ligands (d(π)→π*) is the key to tune the absorption spectra. Ruthenium compounds are dπ6 coordinated, which means the MLCT absorption can be tuned by changing the substituents on the ligands or controlling the d(π)→π* back-bonding donation.113 Anchoring groups are necessary to ensure strong binding of dyes onto the TiO2 surface and efficient charge injection.

![Figure 1-32. Examples of Ruthenium dyes.](image)

Compared to organometallic compounds, pure organic dyes have many advantages and are emerging as a class of competing materials for DSSC.
applications. In general, organic dyes have higher molar extinction coefficient than metal complexes, leading to increased light harvesting efficiency and reducing the amount of dyes needed in the cell. In addition, the donor-acceptor structure can be easily modified and the absorption spectra are easily tuned. With the development of computational chemistry, the photophysical properties and energy levels of new dyes can be more accurately predicted. Furthermore, the cost of organic dyes is less than that of organometallics and the supply is abundant. One approach for dye design is to construct donor-acceptor (D-A) structures and the charge transfer from donor to acceptor accounts for the absorption in the long wavelength region. The absorption spectra can be tuned by changing the relative strength of the donor/acceptor (i.e. stronger D-A interaction will lead to more red-shifted absorption). Traditionally, organic dyes have the disadvantage of having sharp absorption peaks instead of a broad absorption across a large spectral region, decreasing light absorbing ability. However, upon careful design of the D-A structure, black dyes which have strong absorption across the entire visible region can be synthesized. Co-absorbing is another approach to overcome the shortcomings of organic dyes. Mixtures of two or more dyes with complementary absorption spectra are co-adsorbed onto TiO₂, thereby broadening the overall absorption spectrum.

**Electrolyte Solution.** A typical electrolyte solution is made of a solvent, redox couples and additives. Iodide/triiodide was the first redox couple used in DSSCs and is still the most common redox couple. Iodide/triiodide couple has a suitable redox potential, high diffusion co-efficiency and can undergo fast redox reaction. Research on this combination is mainly focused on the effects of different cation on cell performance.
For example, it has been found that the $V_{oc}$ increases with cation size in the alkali metal family: $\text{Li}^+<\text{Na}^+<\text{K}^+<\text{Rb}^+<\text{Cs}^+$. However, the photochemical stability issue and corrosive nature of iodide/triiodide triggered the search for alternative redox couples. One approach is the use of pseudohalogenes, such as SCN$^−$/($\text{SCN})_3^−$ and SeCN$^−$/(SeCN)$_3^−$, which can generate similar $V_{oc}$, but they still have stability issue. Another approach is to use transition metal mediators, such as $\text{Co}^{2+/3+}$ systems, which undergo rapid redox reactions but have the problem of increasing the probability of charge recombination reactions.\textsuperscript{118}

In the early days of DSSC development, liquid electrolyte solutions were exclusively used. The general requirements of electrolyte solution are: (1) a good solvent for the redox couple and other additives; (2) chemical stability to maintain reasonable cell lifetimes; (3) low viscosity to facilitate efficient materials transport and electrochemical reactions; (4) no tendency to hydrolyze dyes or dissolve metal oxide electrodes. For the purpose of sealing the cell, the electrolyte solution should be compatible with sealing materials (i.e. not capable of dissolving the sealing materials, otherwise solution leakage can be a problem). Polar organic solvents with high boiling points have been the major choices, such as nitriles, DMF, carbonate, etc. There are also attempts to use gels or polymers as the electrolytes. But, in general, cells applying gel or polymer electrolytes show lower efficiency due to the lower mobility of the redox couple in those matrixes.

Additives have been a key component in increasing the cell efficiency, but their specific function is usually not clear. In most cases, the effects have been attributed to suppressing of charge recombination or shifting of the conduction band edge. For
example, 4-tert-butylpyridine (TBT) has been widely used in DSSCs which usually increases $V_{oc}$ significantly. Some investigation showed that TBP suppressed the dark current on the TiO$_2$ surface and improved the photovoltage,$^{119}$ while others claimed that TBP with the presence of lithium cations can increase the band edge of the TiO$_2$ electrode.$^{120}$

**Scope of Present Study**

The purposes of present study are to design and synthesize variable chain length poly(phenylene ethynylene)s with end-caps, investigate their aggregation properties in solution and ultrafast energy/electron transfer and apply these materials in dye-sensitized solar cells.

Chapter 2 describes the synthesis of two families of conjugated polyelectrolytes (CPEs) featuring the same backbone but different side chain linkages and demonstrates their application as active materials for dye-sensitized solar cells (DSSCs). It is found that CPEs bearing an oxygen linkage (-O-) are more likely to form aggregates in solution, and that the aggregation status depends strongly on the molecular weights. In contrast, there is no obvious evidence showing that CPEs with methylene (-CH$_2$-) linkages aggregate in solution. In addition, the two families of polymers show different trends in adsorbing onto mesoporous TiO$_2$ films and different overall cell efficiencies. The oxygen linkage family shows strong chain length dependence on film adsorption and, therefore, the cell performance. In contrast, little difference can be observed in the methylene linkage family.

In Chapter 3, a series of different chain length poly(p-phenylene-ethynylene)s (PPEs) with naphthalene diimide derivative end-caps were synthesized. When polymers are photoexcited, the electron will transfer from the PPE backbones to naphthalene
dimide, thereby quenching the polymer fluorescence. The overall quenching efficiency increases with decreasing polymer chain length, as evidenced by fluorescence quantum yield measurement. And the charge recombination rate was investigated by ultra-fast transient absorption spectroscopy. The charge recombination rate also depends strongly on the chain length: as the chain length increases, the charge recombination rate decreases.

In Chapter 4, a series of different chain length poly(p-phenylene-ethynylene)s (PPEs) with 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (TBT) end-caps were synthesized. Under light irradiation, energy transfer from the PPE backbone to the TBT end-groups occurs via the Forster Resonance Energy Transfer (FRET) mechanism. The overall energy transfer efficiency increases with decreasing molecular weight while the fluorescence lifetime remains almost the same. Ultra-fast transient absorption study shows that the energy transfer happens in pico-second time scale for all the polymers and the lower molecular weight samples show faster decay in the initial stage.

In Chapter 5, a series of different chain length “through-space” conjugated polymers with [2.2]paracylophane moiety end-capped with TBT were synthesized. Despite the fact that the conjugation is interrupted, very efficient energy transfer can still be observed and the overall energy transfer efficiency also depends on the molecular weight. Fluorescence lifetime study reveals that there is a rising time in the energy transfer process for the sample with longest chain length, which indicates there is distance limitation on exciton hopping.
CHAPTER 2
CONJUGATED POLYELECTROLYTE SENSITIZED TiO$_2$ SOLAR CELLS: CHAIN LENGTH AND AGGREGATION EFFECTS ON EFFICIENCY

Background

Dye-sensitized solar cells (DSSCs) are one of the most important low-cost alternatives to conventional silicon based inorganic solar cells.$^{101,121}$ Since the first report of the technology, it has drawn significant attention from the scientific community.$^{122}$ A great deal of effort has been made to understand the fundamental problems, improve the overall cell efficiency, and explore the possibility for commercialization. And there are several advantages of the DSSC format compared to the traditional solar cells, which include the use of low-cost materials, mechanical flexibility and possibility of large scale manufacture. Originally, metal-organics, in particular ruthenium and metal-porphyrin complexes, have been utilized as the sensitizers and demonstrated power conversion efficiency (PCE) as high as 13% and incident photon to current efficiency (IPCE) higher than 85%.$^{123}$ Meanwhile, donor-$\pi$-bridge-acceptor (D-$\pi$-A) type organic dyes are emerging as a new class of sensitizers and upon careful structure design, they can also attain efficiencies matching that of inorganic dyes.$^{124,125}$ More recently, highly effective hybrid perovskite cells have been made, achieving efficiency as high as 19.3%.$^{126}$

Conjugated polyelectrolytes (CPEs) are $\pi$-conjugated polymers with ionic pendant chains. Some of the key advantages of CPEs are strong absorption in the visible region, tunable bandgap, and processability from green solvents.$^{90,92}$ Despite the advantages, the application of CPEs as sensitizers in DSSCs has not been well studied. Schanze and Reynold’s groups have conducted innovative research in CPE based DSSCs.$^{127-130}$ In most cases, the work has been focused on the design of novel D-A
structure CPEs, which are believed to facilitate intramolecular charge transfer (ICT) from donor to acceptor resulting in lower bandgap. Such polymers show broad absorption and large extinction coefficients, both of which are crucial to efficient light harvesting. However, recently both Schanze and Ramakrishna groups noticed that polymer chain length can also have a significant impact on the overall cell performance when CPEs were used as the sensitizers for DSSCs.\textsuperscript{131,132} The authors attributed the decreasing of cell efficiency of large molecular weight polymers to the fact they have larger size which reduces the penetration ability into the TiO\textsubscript{2} layers and total amount of sensitizers absorbed. Very similar phenomenon has also been found in case of dendrimers where overall cell efficiency decreases with increasing dendrimer size.\textsuperscript{133,134}

In this work, we study the relationship between overall cell efficiency and molecular weight of two series of CPEs which feature the same conjugated backbone with alternating (1,4-phenylene) and (2,5-thienylene ethynylene) repeating units, but different linkages between the backbone and carboxylic side chains, namely oxy-methylene (-O-CH\textsubscript{2}-) (P1-O-n) and methylene (-CH\textsubscript{2}-) (P2-C-n), respectively. In addition, a model compound was synthesized to compare its properties with the polymers. The polymer backbone structure was chosen mainly due to the ease of synthesizing building blocks and convenience of controlling molecular weight via the end-capping strategy. The carboxylic side chains help the polymers adsorb onto the surface of TiO\textsubscript{2} films and ensure that polymers are in close proximity to the TiO\textsubscript{2} film, which facilitates charge injection. Steady state absorption and emission spectra of polymers were taken to compare photophysical properties and dynamic light scattering was applied to investigate polymer aggregation in solution. When used in DSSCs, the efficiencies of
P1-O series showed a strong dependence on molecular weight, while that of P2-C series did not change regardless of chain length. The results showed here clearly demonstrated that slight change in side chain could have a huge impact on the aggregation behaviors of polymers and solar cell performance.

Results and Discussion

Synthesis

In this study, two families of polymers, P1-O and P2-C, were synthesized which feature the same conjugated backbone with alternating (1,4-phenylene) and (2,5-thienylene ethynylene) repeating units, but have different linkages between the backbone and side chains, namely oxy-methylene (-O-CH$_2$-) and methylene (-CH$_2$-), respectively. For comparison, a model oligomer which has similar structure to the polymers was also prepared. The structures of the polymers and oligomer are shown in Figure 2-1. All the samples feature carboxylic acid side groups which help improve polymer solubility in solution and serve as anchoring groups for film adsorption.

![Figure 2-1. Structure of P1-O-n, P2-C-n and the Model compound](image-url)
Figure 2-2. Synthesis of polymers.

Polymers were synthesized via the “precursor route” in which the carboxy groups were protected as esters. The ester protected polymers were hydrolyzed and then acidified to obtain the carboxylic acid substituted polymers. Due the fact that 2,5-diethynyl-thiophene is not stable, 2,5-bis((trimethylsilyl)ethynyl)thiophene was used in the polymerization reaction and trimethylsilyl groups were deprotected \textit{in situ} with tetrabutylammonium difluorotriphenylsilicate (TBAT). Polymerization between 3 and 1 or 2 afforded polymer P1-O-DP-n and P2-C-DP-n, respectively. The polymer chain length was controlled by applying the “end-capping” strategy in polymerization by adding mono-functioned end-cap to the reaction. Once end-caps react with polymer chains,
polymerization process is terminated. Polymer molecular weight decreases with increasing molar ratio of end-caps in the reaction. The molecular weights and degree of polymerization (DP) of polymers were characterized by GPC using dodecyl ester protected polymer precursors.

Figure 2-3. GPC analysis of polymers. A) P1-O-ester-7 (black square, $M_n=5000$, PDI=1.55), P1-O-ester-9 (red circle, $M_n=6600$, PDI=1.53), P1-O-ester-14 (blue triangle, $M_n=9900$, PDI=1.74); B) P2-C-ester: P2-C-7-ester (black square, $M_n=5100$, PDI=1.87), P2-C-12-ester (red circle, $M_n=8400$, PDI=2.00), P2-C-18-ester (blue triangle, $M_n=13000$, PDI=1.98).

Proton NMR is also used to calculate the number of repeating units and characterize the molecular weight. Chemical shift of the aromatic protons of 1-iodo-4-(trifluoromethyl)-benzene appear at around 7.64 ppm while the thiophene aromatic protons are at around 6.96 ppm in P1-O-esters polymers. Chemical shifts of tert-butyl protons are at around 1.45 ppm while the methylene protons are at around 1.25 ppm in P2-C-ester polymers. Proton signal integrations are used to calculate the molar ratio of functional groups and the number of repeating units is derived from the calculation. The results obtained by both methods are quite comparable and listed in Table 2-1.
Figure 2-4. $^1$H-NMR characterization of polymers. A) $^1$H-NMR of P1-O-n-ester at the aromatic region; B) $^1$H-NMR of P2-C-n-ester at the alkane region.

Table 2-1. Molecular weight table of P1-O, P2-C and Model compound

<table>
<thead>
<tr>
<th></th>
<th>Mn(g/mol)$^a$</th>
<th>Mw(g/mol)$^a$</th>
<th>PDI</th>
<th>DP(GPC)$^b$</th>
<th>DP(NMR)$^c$</th>
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</thead>
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<tr>
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<td>6</td>
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<tr>
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<tr>
<td>P2-C-18-ester</td>
<td>13000</td>
<td>26000</td>
<td>1.98</td>
<td>18</td>
<td>17</td>
</tr>
</tbody>
</table>

$^a$ Narrow-dispersed polystyrenes were used as the standard. $^b$ Degree of polymerization was calculated using Mn obtained by GPC. $^c$ Degree of polymerization was calculated using signal intensity integration ratio from $^1$H-NMR.

The model compound was synthesized in a stepwise route (Figure 2-5). Reaction of compound 4 with trimethylsilyl acetylene (TMSA), followed by deprotection, yielded compound 5. And, compound 5 was reacted with 2,4-diiodothiophene to give compound 6, which was used to couple with compound 7 to get compound 8 (ester protected model compound, Model-ester). Finally, compound 8 was hydrolyzed under basic condition and acidified to afford the model compound.
DLS Characterization

Dynamic Light Scattering (DLS) has been widely used for the characterization of polyelectrolyte samples.\textsuperscript{135,136} In this work, DLS measurements were performed to study the size of the polymer chains in DMF and the concentration was set at 0.1 mg/mL which was the same used for adsorption on TiO\textsubscript{2} films. As shown in Figure 2-6, the model compound has smaller size (about 2 nm) compared to polymer samples. And, the sizes of the P2-C series remain fairly the same (about 7 nm). It is well known that the radius of gyration of polyelectrolytes stays constant in a wide range of different molecular weight which explains the trend for the P2-C series.\textsuperscript{137,138} In contrast, the particle size of P1-O increases (from ~6 nm for P1-O-7, ~12 nm for P1-O-9, to ~13 nm for P1-O-14) with increasing molecular weight. The increasing particle size for P1-O
series might be caused by aggregation. Higher molecular weight polymers are more likely to form bigger aggregates, therefore, the average polymer size increases significantly as well.\textsuperscript{62}

![Graph showing DLS characterization of samples in DMF (solution concentration=0.1 mg/ml).](image)

Figure 2-6. DLS characterization of samples in DMF (solution concentration=0.1 mg/ml).

Previous work from our lab show that despite the similarities in the backbone structures, the side chain linkages can make a difference in the aggregation state of polymers in solution.\textsuperscript{21,139,140} While polymers with \(-\text{O-CH}_2\) linkages aggregate in solution, polymers which have \(-\text{CH}_2\) linkage show surprisingly reduced tendency of aggregation in solution. The difference might be caused by the electronic effect of the oxygen atoms or the oxygen substituents being able to stabilize the stacked polymer chains.\textsuperscript{139} It has been reported that P2-C series adopt ellipsoidal conformation instead of rigid-worm like chains in solution.\textsuperscript{21} Our previous AFM results showed that the diameter of the ellipsoidal polymer chain is about 47±3 Å. The DLS particle size of the P2-C series is in good agreement with previous atomic force microscopy (AFM) result (7 nm vs 5 nm). Therefore, P2-C series are more like to be monomeric in solution while the P1-O series are aggregated. Although the end-caps are different in the two series of polymers, they do not affect the aggregation status.\textsuperscript{62,139,141}
Optical Properties in Solution

Steady-state UV-visible absorption and emission spectra of the samples were measured in dimethylformamide (DMF) (Figure 2-7), and the concentration of the samples was adjusted to 50 µg/ml (based on repeat units). Molar extinction coefficient and fluorescence quantum yield are listed in Table 2-2. As shown in Figure 2-7 a and c, the absorption spectra are similar for both series and the absorption maximum is red-shifted as the molecular weight increases, because of the increasing in the conjugation length (424 nm, 425 nm and 432 nm for P1-O-7, P1-O-9, P1-O-14, respectively; 388 nm, 398 nm and 407 nm for P2-C-7, P2-C-12 and P2-C-18, respectively). The absorption spectra of the P1-O series red-shift about 25 nm compared to the P2-C series, due to the fact that oxy-methylene is a stronger donor than the methylene group, which increases the HOMO energy level. Finally, the absorption maximum of the model compound is blue-shifted about 20 nm compared to P1-O series, due to the significant decrease in conjugation length.

Table 2-2. GPC results and photophysical data

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<tr>
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<th>Mn²</th>
<th>PDI</th>
<th>DP</th>
<th>λabs(nm)</th>
<th>ε(10⁴ cm⁻¹ M⁻¹)</th>
<th>λem(nm)</th>
<th>φflb</th>
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<td>424</td>
<td>3.1</td>
<td>528</td>
<td>0.14</td>
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<td>P1-O-9</td>
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<td>470</td>
<td>0.39</td>
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<td>388</td>
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<td>398</td>
<td>5.5</td>
<td>456</td>
<td>0.12</td>
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<tr>
<td>P2-C-18</td>
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<td>18</td>
<td>407</td>
<td>5.9</td>
<td>457</td>
<td>0.13</td>
</tr>
</tbody>
</table>

²narrow dispersed polystyrene was used as the standard. bmeasurement was done in pH=8 water with the P1-O-n-salt and P2-C-n-salt samples, and Quinine Sulfate in 0.1 M H₂SO₄ as standard, φfl=0.545.
Figure 2-7. The ground state absorption and emission spectra. A) UV-vis absorption and B) emission spectra of P1-O-7 (black square), P1-O-9 (red circle), P1-O-14 (blue up triangle) and model compound (dark cyan down triangle); C) UV-vis absorption and D) emission spectra of P2-C-7 (black square), P2-C-12 (red circle) and P2-C-18 (blue triangle).

Figure 2-7 b and d show the fluorescence emission of P1-O and P2-C series respectively. Despite the increasing chain length, the emission peak shows only a slight change for the P2-C series with emission maximum at around 456 nm. In comparison, the emission maximum of P1-O-14 is red-shifted 10 nm compared to P1-O-9 which indicates the formation of aggregates of P1-O-14. In addition, P2-C series show more structured emission compared to the P1-O series; this should also be due to the fact that P2-C is more likely to be monomeric in solution. Moreover, the emission intensity of the vibrational band of the P2-Cs increases with molecular weight. Finally, the model compound has more blue shifted and narrower emission band compared to P1-O-n.
polymers. The aggregation status has a significant effect on the overall fluorescence quantum yields as well. The fluorescence quantum yields of P1-O-n polymers decrease with increasing molecular weight. The quantum yield of P1-O-7 is as high as 14% while that of P1-O-14 decreases to 7.1%. In contrast, P2-C-n polymers show almost the same quantum yield (~12-13%) regardless the molecular weights and the model has a quantum yield of 39%.

**TiO₂ Film Characterization, Polymer Adsorption and Charge Injection**

The detailed information for making nanocrystalline TiO₂ colloids and DSSC cell fabrication are provided in the experimental section. It is worth noting that in most literature reports, the size of TiO₂ particle used varies from 20 nm to 30 nm to achieve high efficiency and most researchers have applied a three-layer TiO₂ film: a blocking layer, an active layer and a scattering layer. However, it was not our goal to produce high performance cells, only a single layer TiO₂ was used to facilitate photophysical characterization of films. Because, the single layer film is more transparent than multi-layer films and makes UV-vis absorption and transient absorption measurements easier. The TiO₂ particle has an average size of 20 nm and the film thickness is around 13 µm, according to the scanning electron microscope (SEM) images (Figure 2-8).

![Figure 2-8. SEM characterization of TiO₂ films. A) Top view of the film and B) side view of the film intersection.](image)
UV-visible absorption spectroscopy was used to monitor the adsorption of the P1-O-n and P2-C-n polymers. All the bare TiO$_2$ films have little absorption beyond 380 nm due to light scattering and all the films have very similar thickness according to SEM images. For film adsorption, a solution of 0.1 mg/mL of polymer in DMF was stirred for 24 h before the TiO$_2$ electrodes were immersed into it and soaked for 36 h. The UV-vis absorption of the resulting polymer coated film was measured and the film absorptance, (which can be calculated as absorptance $= 1 - 10^{-A}$, where A is the film absorption), was plotted in Figure 2-9. It's interesting that the peak absorptance of P1-O-n sensitized films increases with decreasing molecular weight while the P2-C-n sensitized films show almost identical peak absorptance.

![Figure 2-9](image)

Figure 2-9. Absorptance of polymer sensitized films. A) Absorptance of P1-O-n films and the time dependent absorption (inserted plot): P1-O-7 (black square), P1-O-9 (red circle) and P1-O-14 (blue triangle); B) Absorptance of P2-C-n films: P2-C-7 (black square), P2-C-12 (red circle) and P2-C-18 (blue triangle).

The absorptance is direct proportional to the amount of polymers adsorbed, because each polymer within a polymer series has very similar molar extinction coefficient and the amount of polymers adsorbed is only fact that changes the absorptance. For the P1-O-n polymers, lower molecular weight samples form smaller aggregates and are more
likely to penetrate deep into the TiO$_2$ films, which increase the amount of materials absorbed onto the TiO$_2$ films.$^{131}$ In contrast, the P2-C-n polymers do not aggregate and have essentially the same size in solution, therefore, show very similar adsorption behaviors. In addition, the absorptance curves resemble the absorption spectra, with higher molecular weight polymers show more red-shifted curves.

In order to further characterize the film absorption properties of P1-O-n series, time-dependent film absorption measurements were performed. TiO$_2$ films with same film thickness were contained in polymer solution with same concentration for various amounts of time and the film absorption was measured. The absorption values at 440 nm were recorded and the calculated absorptance was plotted in Figure 2-9, inset figure. Absorptance of all films increases with time with the first 15 h showing the most significant enhancement. Then, it reaches a plateau after 30 h, indicating that the adsorption is almost saturated and the final absorptance is consistent with film absorptance data. In addition, at any given time, absorption intensity increases with decreasing molecular weight (P1-O-7 > P1-O-9 > P1-O-14).

Figure 2-10. Calculated surface coverage of polymer sensitized films.
The amount of polymers adsorbed can also be characterized by surface coverage ($\Gamma$, based on polymer repeat units), which can be calculated as:

$$\Gamma = \frac{A}{\varepsilon}$$

where $A$ is the film absorption and $\varepsilon$ is the molar extinction coefficient. In the calculation, there are two assumptions upon polymer adsorption onto TiO$_2$ films: 1) the polymer molar extinction coefficient does not change and 2) the changing of UV-vis absorption spectrum of polymer is negligible. The unit of $\varepsilon$ is converted to cm$^2$/mol and $\Gamma$ has the unit of mol/cm$^2$. The P1-O-7 has the largest surface coverage in the P1-O-n polymers while the P2-C-n polymers are almost the same, which is consistent with the film absorptance results. The amount of polymers adsorbed is about $1.5 \times 10^{16}$ cm$^{-2}$, which is lower compared to small metal-organic or organic dyes ($5\sim20 \times 10^{16}$ cm$^{-2}$).

![AFM images of dye-sensitized TiO$_2$ films.](image)

Figure 2-11. AFM images of dye-sensitized TiO$_2$ films. AFM images of A) P2-C-18 sensitized TiO$_2$ film; B) P1-0-14 sensitized TiO$_2$ film; C) bare TiO$_2$ film. Root mean square values (RMS) of P2-C-18, P1-0-14, and bare TiO$_2$ are 18.6 nm, 20.5 nm and 17.4 nm, respectively.

The surface morphology of TiO$_2$ films was characterized by AFM (Figure 2-11). Upon dye deposition on top of TiO$_2$ films, morphology will change which can be characterized by the root mean square (RMS) roughness of the surface. Compared to
the RMS value of bare TiO$_2$ (17.4 nm), that of P2-C-18 sensitized film increased slightly (from 17.4 nm to 18.6 nm), indicating that P2-C-18 polymers successfully absorbed onto the film and there is no obvious aggregation on the film surface. However, the RMS value of film sensitized with P1-O-14 (20.5 nm) is significantly higher than that of bare TiO$_2$ which was caused by adsorbing of aggregated polymer particles. It has been reported that dye aggregation reduced electron lifetime and lowered overall cell performance.$^{144, 145}$ Considering the fact that P2-O-n series show lower absorptance which means fewer materials absorbed (Figure 2-9), it’s proposed that the aggregated P1-O-n polymers will cover the film surface and prevent more materials from penetrating into the inside layer. It’s clear that the aggregation status determines the film morphology and affect the total amount of materials can be absorbed which ultimately affect the cell performance significantly.

![Figure 2-12. Film transient absorption and kinetics of dye-sensitized TiO$_2$ films. A) Transient Absorption spectra after initial 15 ns camera delay of P1-O-7 (black square), P1-O-9 (red circle), P1-O-14 (blue up triangle) and model compound (dark cyan down triangle) sensitized films; B) kinetic decay of P1-O-DP and Model compound sensitized TiO$_2$ films: P1-O-7 (black), P1-O-9 (red), P1-O-14 (blue) and model compound (dark cyan).]
Film transient absorption (TA) measurements (Figure 2-12) were performed on P1-O-n sensitized films to have insight information on charge injection and regeneration. Polymer sensitized films were contained in sealed cuvettes containing 0.1 M LiClO$_4$ in acetonitrile and degassed for 30 min before measurements. Immediately after subjection to 355 nm laser excitation pulses, strong transient absorption of polymer radical cation was observed. Polymers became radical cations after losing electrons due to charge injection to TiO$_2$ conducting bands. The spectra of all investigated films are very similar with the radical cation signal rises from approximately 500 nm and the peak is around 675 nm. The signal intensity of P1-O polymers decreases with molecular weight, which is consistent with the trend of the film absorptance. Charge recombination occurs between the polymer cations and the TiO$_2$ conducting band electrons and the signal decay kinetics were measured at 650 nm and plotted in Figure 2-12 B. The lifetime of polymers is about several hundred microseconds, which is generally shorter than organic-metal complexes.$^{146,147}$ However, a strong electronic coupling between the polymer sensitizers and the TiO$_2$ conducting band can facilitate the ultrafast electron injection.$^{148}$ All the sensitizers have very similar average lifetime ($\sim$200 μs), except P1-O-14 which has the largest aggregation size (Table 2-3). The decreasing lifetime of the excited electrons can decrease the overall cell performance.$^{149}$

<table>
<thead>
<tr>
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<th>$A_1$</th>
<th>$\tau_1$ (μs)</th>
<th>$A_2$</th>
<th>$\tau_2$ (μs)</th>
<th>$A_3$</th>
<th>$\tau_3$ (μs)</th>
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<td>203</td>
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</tbody>
</table>

$^a$ Exponential decay 2 or 3 was used for fitting and $\tau_{ave}$ was calculated using $\tau = \sum A_n \times \tau_n$. 

80
Polymer Sensitized Solar Cells

The scope of this work is to understand the effects of polymer molecular weight and aggregation on DSSCs performance rather than achieving high cell efficiency, therefore, all the cells were fabricated and characterized under the same condition without seeking to optimize overall performance (varying electrolyte, etc.). The active areas of cells are 0.2 cm$^2$. Three different batches of devices were prepared for each sample and the results were consistent for all.

Figure 2-13. IPCE and current-voltage (J-V) characters of polymer cells. A) IPCE and B) J-V curves of P1-O-n and model compound: P1-O-7 (black square), P1-O-9 (red circle), P1-O-14 (blue up triangle) and model compound (magenta down triangle); C) IPCE and D) J-V curves of P2-C-n: P2-C-7 (black square), P2-C-12 (red circle) and P2-C-18 (blue triangle).
Incident photon to current efficiency (IPCE) of both P1-O-n and P2-C-n series were plotted in Figure 2-13. A significant difference in the photovoltaic performance is observed for the P1-O series while the P2-C-n polymers show little change despite the difference in molecular weight (Figure 2-11 A). In the P1-O-n polymers, P1-O-7, which has the lowest molecular weight polymer, shows the highest peak IPCE value (~50%) and the IPCE value decreases with increasing molecular weight. The IPCE of P1-O-14 is only about half of P1-O-7 (~25%), indicating that the charge injection efficiency will also be lower. In contrast, all P2-C-n polymers show very high peak IPCE (~48%), indicating that photoinduced charge injection will be quite efficient at short-circuit conditions. The trend in peak IPCE value is consistent with the film absorptance (Figure 2-9). The difference in current density of devices is also due to change in total amount of polymers adsorbed. Although, the model compound shows highest peak IPCE value, the IPCE response region is narrower.

The same trend can be observed in the J-V curve of the P1-O series (Figure 2-13 B & D), where P1-O-7 shows the highest open-circuit voltage value ($V_{oc}$, 0.49 V) and short-circuit current ($J_{sc}$, 2.70 mA/cm$^2$), and P1-O-14 has the lowest $V_{oc}$ (0.45 V) and $J_{sc}$ (1.56 mA/cm$^2$). This may also be caused by polymer aggregation which affects surface coverage: less aggregated samples can better cover the TiO$_2$ surface which will reduce the charge recombination rate between electrons in the conducting band of TiO$_2$ and I$^-$/I$_3^-$ electrolytes or dye cations at the interface of TiO$_2$ particle, and increase the open-circuit voltage and short-circuit current.$^{150,151}$ The P2-C-n polymers all have the same $V_{oc}$ and $J_{sc}$, but have decreased $V_{oc}$ and $J_{sc}$ compared to P1-O-7, which are probably due to lower LUMO energy level and narrower photo response region, respectively.$^{123}$
Although the model compound does not aggregate, the surface coverage is less efficient than P1-O-n polymers and a slightly lower $V_{oc}$ is observed. The absorbed light to photon to current efficiency was calculated and the trend is also consistent with film absorption.

**Table 2-4. Summary of cell performance**

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<th></th>
<th>$V_{oc}$(V)</th>
<th>$J_{sc}$(mA/cm$^2$)</th>
<th>FF(%)</th>
<th>IPCE$_{max}$ (%)</th>
<th>APCE$_{max}$ (%)</th>
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<td>62.6</td>
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<td>P2-C-18</td>
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<td>50.1</td>
<td>47.4</td>
<td>65.2</td>
<td>0.49</td>
</tr>
</tbody>
</table>

$^a$ Three cells for each polymer were made and the all the number reported were the average values; $^b$ was calculated using $APCE = IPCE_{max}/Absorptance$.

**Summary**

Two series of conjugated polyelectrolytes featuring the same alternating (1,4-phenylene) and (2,5-thienylene ethynylene) repeating units, but with different molecular weight, were synthesized and utilized as light harvesting materials in DSSCs. DLS and steady state photophysical studies showed that P1-O series which had oxy-methylene (-O-CH$_2$-) linkage between the backbone and carboxylic acid group were aggregated in solution while P2-C series which had methylene (-CH$_2$-) instead were in the monomeric state in solution. The aggregation state determines the film morphology and affects the total amount of materials can be absorbed. As a result, the cell efficiency of P1-O series decreased with increasing molecular weight while cell performance of P2-C series was independent of molecular weight. Although, the fact causing the difference between alkyl and oxygen substituents are still not very clear, the results still provide us with
guidance of designing molecular structure and controlling molecular weight in achieving high efficiency DSSCs.

Experiments and Materials

Materials

Unless specified, all compounds and solvents were purchased from commercial sources (Aldrich, Acros, Strem Chemicals, et al) and used without further purification. For all palladium-catalyzed reactions, the solvents were carefully degassed with argon for at least 30 min. $^1$H and $^{13}$C-NMR spectra were recorded on either Inova2 (500 MHz) or Varian Gemini-300 spectrometer (300 MHz). The chemical shifts (δ) are reported in parts per million (ppm) using the residual solvent signals as internal standards.

Instrumentation

$^1$H and $^{13}$C NMR spectra were measured on Varian Mercury 300, Gemini 300, or Inova 500 spectrometers. Chemical shifts were referenced to the residual solvent peaks. High resolution mass spectrometry was performed on a Bruker APEX II 4.7 T Fourier Transform Ion Cyclotron Resonance mass spectrometer (Bruker Daltonics, MA). Gel Permeation Chromatography (GPC) data was collected on a system composed of a Shimadzu LC-6D pump, an Agilent mixed-D column, and a Shimadzu SPD-20A photodiode array (PDA) detector, with THF as eluent at 1 ml/min flow rate. The system was calibrated against linear narrow dispersed polystyrene standards in THF.

UV–visible absorption measurements were carried out on a Shimadzu UV-1800 dual beam absorption spectrophotometer. Photoluminescence spectra were recorded on a spectrofluorimeter from Photon Technology International (PTI). Photoluminescence lifetimes were obtained by time-correlated single photon counting.
(TCSPC) using a Fluo Time 100 (Picoquant), and excitation was provided using a PDL 800-B Picosecond Pulsed Diode Laser (375 nm).

Dynamic light scattering (DLS) characterization was performed on a Zetasizer Nano (Malvern Instruments, Worcestershire, United Kingdom) at 25°C. The concentration of the samples was adjusted to 0.1 mg/ml for this measurement. Three measurement cycles were run for each sample. The data were averaged from 10 light scattering periods of 10 s for each cycle. Average diameter values were calculated using the Malvern Instruments DTS software.

Film transient absorption measurements were conducted on a home-built apparatus. The excitation wavelength was generated by a Continuum Surelite OPO Plus pumped with the third harmonic (355 nm) of a Continuum Surelite II-10 Nd:YAG laser. Xenon arc lamp was used as a probe source. Triax 180 Monochromator and Si amplified photodetector from Thorlabs (PDA8A) were used for detection at single wavelength. Films were merged in sealed cuvettes containing 0.1 M LiClO$_4$ in acetonitrile and degassed with Ar for 30 min before measurements. Kinetic trace was measured at a wavelength of 650 nm. Exponential decay 2 or 3 was used for fitting $y = y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2}$ or $y = y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} + A_3 e^{-x/\tau_3}$ and the average lifetime was calculated as $\tau = \sum A_n \tau_n$.

AFM images of polymer-coated TiO$_2$ films and bare TiO$_2$ films were obtained using Digital Instruments (Vecco) in ambient atmosphere equipped with Nanoscope controller (Bruker). Tapping mode by an integrated tip/cantilever (125 µm in length with 325 kHz resonant frequency, Mikromasch USA) was used at a scan rate of 1.2 µm/s.
and 0.1 µm/s with a range of 3µm × 3µm and 0.5 µm × 0.5 µm, respectively, at room temperature in air.

**TiO_2 Sol Preparation**

The nanocrystalline titanium dioxide (TiO_2) electrode and platinum counter-electrode were prepared according to literature with modifications.\(^{152}\) Detailed information is provided as below. Titanium isopropoxide (35.52 g) was added to a separatory funnel containing 10 mL isopropanol. The Ti(i-OPr)_4/isopropanol solution was then added dropwise to acetic acid/H_2O (80 mL acetic acid, 250 mL deionized H_2O) that had been pre-chilled to 0°C and was stirred rapidly. Ti(i-OPr)_4/isopropanol was added over a period of ~20-30 minutes. The reaction solution was then heated to 80°C using and rapidly stirred the entire time. Upon heating to this temperature, the reaction solution becomes a thick gel and then later becomes a loose, white colloidal solution. The reaction solution was heated at 80°C for 8 hours and stirred the entire time.

At the end of the 8 hours, the reaction solution was cooled to room temperature and ultrasonicated (70% power, pulse on for 1 sec, off for 0.5 sec) for five minutes to break up TiO_2 aggregates. Upon ultrasonication, the colloidal solution becomes clearer with hints of blue color. The total volume of the colloidal solution was measured at this time to determine the amount of TiO_2 per unit volume. A portion of the colloidal solution was then placed in a Teflon cup which in turn was placed in an acid digestion bomb and autoclaved for 13 h at 420°C (ramp rate = 5°C/minute). After cooling the bomb to room temperature, the TiO_2 colloid (white solid + colloidal solution) was transferred to a clean 100 mL beaker for ultrasonicating (5 minutes, see above conditions). The resulting white solution was then concentrate the TiO_2 to a final concentration of 12 wt%. For example, if 80 mL out of a total 370 mL TiO_2 colloid is autoclaved, it gives 2.16 g/80 mL
TiO$_2$ post-autoclave. It is preferable to concentrate beyond then add deionized water to give a final weight. It is important to minimize the amount of TiO$_2$ that is “lost” along the way. It is also important to avoid rotovapping to dryness or partial dryness (i.e. allowing a significant amount of TiO$_2$ to precipitate out of solution); this seems to significantly affect DSSC performance.

After acquiring a 12 wt% colloidal solution, hydroxypropylcellulose (HPC) was added slowly over ~1 minute to a rapidly stirred solution. The HPC concentration is 6 wt% (with respect to total weight of solution) and 50 wt% (with respect to TiO$_2$ weight). The solution is stirred well for 12-24 hours and then stirred less rapidly for 3-5 days (stir rate is lowered to avoid “frothy” pastes that are difficult to make thin films with). The TiO$_2$ paste is stored in a brown amber vial until use and stirred continuously. The paste appears as a semi-viscous white fluid.

**Device Fabrication**

FTO substrates are cleaned by sonication in pH=13 water containing 2 wt% sodium dodecyl sulfate (SDS), followed by isopropanol and acetone (20 minutes each). For depositing thin films, tape-casting is performed using 50 μm scotch tape. The thickness of the film depends on the number of tape stripes used on either side of the exposed substrate surface. For example, two layers of tape stripes will give a TiO$_2$ film thickness of about 15 μm. TiO$_2$ paste is applied to the substrate by pipette and spread using a razor blade. The thin film is allowed to air dry at room temperature for 10-20 minutes; the films should be crack-free and fairly transparent. The films are then sintered by slowly heating the films at a rate of 5 °C/min to a final temperature of 450 °C and maintaining this temperature for 30 minutes. The films are then cooled at a rate of 10 °C/min.
And, two holes were drilled at the Pt cathode. A solution of 0.1 mg/ml of polymer in DMF was stirred for 24 h before the TiO_2 electrodes were immersed into it. After 36 h of absorption, the electrodes were rinsed with dry DMF and acetone to remove the unabsorbed dyes, and then placed under vacuum for 2 h for further drying. The platinum cathode and TiO_2 anode were sealed together with surlyn (Solaronix Meltonix 1170-25). Electrolyte solution containing 0.05 M I\textsubscript{2}, 0.1 M LiI, 0.6 M 1-methyl-3-(n-propyl)imidazolium iodide (PMII), and 0.5 M 4-tert-butylpyridine (TBP) in butyronitrile was injected into the sealed device from the holes on the platinum cathode. For incident photon to current efficiency (IPCE) characterization, an Oriel Cornerstone monochromator was used as light source, and the device current response was recorded under short circuit conditions at 10 nm intervals using a Keithley 2400 source meter. The light intensity at each wavelength was calibrated with an energy meter (S350, UDT Instruments). The current-voltage characteristics of the cells were measured with a Keithley 2400 source meter under AM1.5 (100 mW/cm\textsuperscript{2}) solar simulator. The active area of the TiO_2 film is 0.5 cm * 0.5 cm for IPCE and current-voltage measurements.

**Synthetic Procedures**

Tert-butyl 2-(4-iodophenyl)acetate\textsuperscript{140} and Compound 1,\textsuperscript{141} 2,\textsuperscript{141} 3,\textsuperscript{139} 4\textsuperscript{153} and 7\textsuperscript{141} were synthesized according to reported method in literature.

**Compound 5.** Compound 4 (2.00 g, 6.90 mmol) was dissolved in a mixed solvent of THF (20 ml) and (i-Pr)\textsubscript{2}NH (10 ml) in a round bottom flask and degased for 30 min. Then, Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (28 mg, 0.4 mmol) and Cul (7.5 mg, 0.4 mmol) were added the flask and degassed for another 30 min. Afterwards, trimethylsilylacetylene (0.75 g, 7.65 mmol) was injected into the solution and reacted at room temperature for
overnight. The solvent was evaporated and the residue was purified with a flash column. The eluent was evaporated under vacuum and the solid was dissolved in THF (10 ml) and TBAF (7 ml, 1 M in THF) was added to the solution. After two hours, 10 ml water was added and the solution was extracted with dichloromethane. The organic layer was washed with saturated ammonium chloride, water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by silica chromatography to yield compound 5 (1.17 g, 90%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.23 (t, 3H), 3.06 (s, 1H), 3.61 (s, 2H), 4.14 (q, 2H), 7.24 (d, 2H), 7.46 (d, 2H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\), 14.30, 41.44, 61.16, 77.38, 83.55, 121.04, 129.42, 132.43, 135.07, 171.23. MS (ESI) m/z ([M + H]\(^+\)), calculated 189.092; found 189.0910.

**Compound 6.** Compound 5 (1.00 g, 5.32 mmol) and 2, 5-diiodothiophene (1.79 g, 5.32 mmol) were dissolved in a mixed solvent of THF (15 ml) and (i-Pr)\(_2\)NH (10 ml) and degased for 30 min. Then, Pd(PPh\(_3\))\(_2\)Cl\(_2\) (28 mg, 0.4 mmol) and CuI (7.5 mg, 0.4 mmol) were added and the reaction was run for 12 h under argon protection. After the reaction, the solvent was removed under vacuum and solid was purified with silica chromatography to give compound 6 (0.93 g, 44%). \(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 1.23 (t, 3H), 3.62 (s, 2H), 4.14 (q, 2H), 6.95 (d, 1H), 7.18 (d, 1H), 7.27 (d, 2H), 7.49 (d, 2H). \(^13\)C NMR (75 MHz, CD\(_2\)Cl\(_2\)) \(\delta\), 15.87, 43.02, 62.86, 76.55, 83.19, 96.46, 123.01, 131.28, 131.42, 133.30, 135.21, 137.21, 139.23, 172.82. MS (ESI) m/z ([M + NH\(_4\)]\(^+\)), calculated 414.001; found 414.002.

**Compound 8.** Compound 6 (0.50 g, 1.26 mmol) and compound 7 (0.39 g, 0.63 mmol) were added into flask containing THF (15 ml) and (i-Pr)\(_2\)NH (10 ml) and the
solution was degased for 30 min. Then, Pd(PPh$_3$)$_2$Cl$_2$ (14 mg, 0.2 mmol) and Cul (3.75 mg, 0.2 mmol) were added. After reaction overnight, the solvent was removed under vacuum and the solid was purified by silica chromatography to give compound 8 (0.60 g, 92%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ 0.87 (t, 6H), 1.26 (m, 42H), 1.67 (m, 4H), 3.63 (s, 4H), 4.14 (q, 4H), 4.22 (t, 4H), 4.72 (s, 4H). 6.97 (s, 2H), 7.20 (d, 2H), 7.23 (d, 2H), 7.29 (d, 4H), 7.50 (d, 4H). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 13.85, 13.94, 22.67, 25.82, 29.34, 29.50, 29.58, 29.63, 29.64, 31.91, 41.13, 60.91, 65.57, 66.70, 82.07, 88.48, 89.82, 94.15, 113.97, 117.27, 121.12, 124.11, 125.26, 129.50, 131.45, 132.03, 132.46, 135.35, 153.05, 168.35, 170.84. MS (MALDI) m/z ([M + H]$^+$), calculated 1146.53; found 1146.51.

**Model compound.** Compound 8 (0.20 g, 0.17 mmol) was dissolved in THF (5 ml) which was added NaOH solution (2 ml, 1M) dropwise and heated at 45 °C. After 6 h, THF was removed under vacuum and 5 ml water was added to the flask and the solution was stirred for another 6 h. Then, the solution was concentrated and added to acetone. The precipitate was collected and re-dissolved in 2 ml water and HCl (2M, 5 ml) was added. Then, the precipitate was collected and washed several times with water. Last, the solid was dried under vacuum to give the model compound (90 mg, 70%). $^1$H NMR (500 MHz, DMSO-d$_6$) δ 3.67 (s, 4H), 4.87 (s, 4H), 7.18 (s, 2H), 7.37 (d, 4H), 7.45 (dd, 4H), 7.56 (d, 4H). $^{13}$C NMR (125 MHz, DMSO-d$_6$) δ 40.43, 65.84, 82.23, 88.16, 91.31, 94.93, 112.86, 120.05, 123.93, 124.45, 130.31, 130.59, 131.55, 131.82, 133.77, 137.03, 152.83, 170.35, 172.71. MS (APCI) m/z ([M - 2H + Na]$^+$), calculated 776.092; found 775.071.
General method for polymerization. Monomer 2 (45.0mg, 0.163mmol) was dissolved in 15ml dry THF in a round bottom flask at room temperature and the solution was degased for 30min. Then, Tetrabutylammonium difluorotriphenylsilicate (264mg, 0.489mmol) was added into the flask under argon protection. After 6 hours, monomer 1 or 3 (0.163mmol), a different amount of 1-iodo-4-(trifluoromethyl)benzene or tert-butyl 2-(4-iodophenyl)acetate (10%, 20% or 30%, molar ratio) and 15ml dry (i-Pr)₂NH were added. The solution was degased for another 30min before 16.2 mg (0.014 mmol) Pd(PPh₃)₄ and 5.0 mg (0.026 mmol) of Cul were added. The resulted reaction mixture was heated to 40 °C for 24 hr. The yellow solution was flashed through a silica gel column and the eluent was collected and concentrated. The concentrated solution was poured into 100ml of methanol and the polymer precipitated out immediately. This process was repeated twice. Last, the precipitate was collected and dried under vacuum. Typical yield of this reaction is 50%-70%.

P1-O-ester-7. GPC (THF, polystyrene standard): Mₜₜ=7700, Mₙ=5000, PDI=1.55. ¹H NMR (300 MHz, CDCl₃) δ 7.64 (br, 4H), 7.56 (br, 4H), 7.21 (br, 12H), 6.96 (br, 12H), 4.71 (br, 24H), 4.23 (br, 24H), 1.67 (br, 24H), 1.31-1.25 (br, 216H), 0.87 (br, 36H).

P1-O-ester-9. GPC (THF, polystyrene standard): Mₜₜ=10200, Mₙ=6600, PDI=1.53. ¹H NMR (300 MHz, CDCl₃) δ 7.64 (br, 4H), 7.56 (br, 4H), 7.21 (br, 16H), 6.96 (br, 16H), 4.71 (br, 32H), 4.23 (br, 32H), 1.67 (br, 32H), 1.31-1.25 (br, 288H), 0.87 (br, 48H).

P1-O-ester-14. GPC (THF, polystyrene standard): Mₜₜ=17200, Mₙ=9900, PDI=1.74. ¹H NMR (300 MHz, CDCl₃) δ 7.64 (br, 4H), 7.56 (br, 4H), 7.21 (br, 26H), 6.96
P2-C-ester-7. GPC (THF, polystyrene standard): $M_w=9500$, $M_n=5100$, PDI=1.87.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.49 (br, 14H), 7.18 (br, 14H), 4.12 (br, 28H), 3.83 (br, 28H), 1.61 (br, 28H), 1.40 (s, 18H), 1.31-1.25 (br, 252H), 0.87 (br, 42H).

P2-C-ester-12. GPC (THF, polystyrene standard): $M_w=17000$, $M_n=8400$, PDI=2.00. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.49 (br, 22H), 7.18 (br, 22H), 4.12 (br, 44H), 3.83 (br, 44H), 1.61 (br, 44H), 1.40 (s, 18H), 1.31-1.25 (br, 396H), 0.87 (br, 66H).

P2-C-ester-18. GPC (THF, polystyrene standard): $M_w=26000$, $M_n=13000$, PDI=1.98. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.49 (br, 34H), 7.18 (br, 34H), 4.12 (br, 68H), 3.83 (br, 68H), 1.61 (br, 68H), 1.40 (s, 18H), 1.31-1.25 (br, 612H), 0.87 (br, 102H).

**General method for hydrolysis.** To 100 mg of P1-O-ester polymer was in 30 mL of THF and 5 eq. of NaOH, pre-dissolved in 5 ml di-water, was added drop wisely. The reaction mixture was stirred at 45 °C overnight. Then THF was removed under vacuum and another 5ml of di-water was added. The reaction mixture was heated at 45 °C for another 6 hr. The solution was concentrated and the product was precipitated from a mixture of acetone/methanol (95:5 volume ratio). The precipitate was collected and dissolved in basic water (pH=8), followed by filtration with a dialysis filter (D=0.45µm). Finally, the solution was dialyzed for two days and freeze-dried.

To 100 mg of P2-C-ester was dissolved in 20 mL chloroform in a flask and 5 mL trifluoreacetic acid was added dropwise over 10 min. The mixture was stirred for 2 h under R.T. and all the solvent was removed under vacuum. The residual solid was dissolved in 30 mL of THF and 5 eq. of NaOH, pre-dissolved in 5 ml di-water, was
added dropwise. The reaction mixture was stirred at 45 °C overnight. Then THF was removed under vacuum and another 5ml of di-water was added. The reaction mixture was heated at 45 °C for another 6 hr. The solution was concentrated and the product was precipitated from a mixture of acetone/methanol (95:5 volume ratio). The precipitate was collected and dissolved in basic water (pH=8), followed by filtration with a dialysis filter (D=0.45 µm). Finally, the solution was dialyzed for two days and freeze-dried.

P1-O-7 \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 7.24\) (br, 2H), 6.85 (br, 2H), 4.59 (br, 4H).

P1-O-9 \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 7.24\) (br, 2H), 6.85 (br, 2H), 4.59 (br, 4H).

P1-O-14. \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 7.24\) (br, 2H), 6.85 (br, 2H), 4.59 (br, 4H).

P2-C-7 \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 7.23\) (br, 2H), 6.80 (br, 2H), 3.64 (br, 4H)

P2-C-12 \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 7.23\) (br, 2H), 6.80 (br, 2H), 3.64 (br, 4H)

P2-C-18 \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 7.23\) (br, 2H), 6.80 (br, 2H), 3.64 (br, 4H)

**General method for acidification.** A 20mg sample of hydrolyzed polymer was dissolved in 5ml basic water (pH=8) and 5 ml of pH=1 hydrochloric acid was added to the solution dropwise. The mixture was stirred for 2 hr and centrifuged. The solid at the bottom of centrifuge tube was collected and dried under vacuum. No other purification was performed before use as a sensitizer for DSSCs.
CHAPTER 3
CHARGE SEPARATION IN DIFFERENT CHAIN LENGTH CONJUGATED POLYMERS

Background

Since their discovery, conjugated chromophores have been outstanding candidates for many artificial electronic device applications, such as solar cells, light emitting diodes, field effect transistors, etc.\textsuperscript{8,10,14,15} Compared to small organic molecules, conjugated polymers have many advantages, such as being more stable, easier to synthesize and more feasible for device processing. Charge transport plays an important role in these devices. For example, in bulk heterojunction solar cells, it is crucial to have fast charge separation and long-lived charge separated states in order to build high performance devices. Further, it has been proved that molecular weight can significantly affect device performance and quenching efficiency.\textsuperscript{62,154-156} Many works have already furthered the understanding of the effect of the molecular weight on charge transport behavior while charge recombination receives less attention.

To the knowledge of authors, most of the charge recombination studies have been focused on systems containing small molecular weight molecules, due to the fact that small molecules have well-defined structures and molecular weight is monodispersed. Otsubo and co-workers reported charge separation and recombination studies in systems of oligothiophene-fullerene dyads.\textsuperscript{157,158} In a system consisting of tetrathiophene-fullerene, the charge separation rate was faster in highly polar solvents (on the order of $10^{10}\text{s}^{-1}$), such as THF and benzonitrile, and decreased in less polar solvents (on the order of $10^{9}\text{s}^{-1}$), such as anisole and toluene. And, the charge separation state was not observed in non-polar benzene. The chain length effect of oligothiophene on charge separation and recombination rate was also investigated.
With increasing chain length, from octathiophene-fullerene to dodecathiophene-fullerene, the charge separation rate increased while the charge recombination rate decreased. And, in charge recombination, there were both fast processes which originated from direct charge recombination and slow processes which were due to indirect charge recombination after charge migration. Albinsson and collaborators investigated charge separation and recombination in donor-bridge-acceptor systems where donors and acceptors were porphyrin compounds.\textsuperscript{159,160} It was interesting that, in a system with a broken conjugation bridge, the singlet excited state of the donor was quenched via a singlet energy transfer mechanism and the quenching rate was independent of solvent. In contrast, when the bridge was π-conjugated, the quenching occurred via an electron transfer mechanism. Both charge separation and recombination rate in π-conjugated bridge systems decreased with increasing bridge length and the charge separation rate decreased more rapidly compared to that of charge recombination.

In this work, we reported the synthesis of a series of polymers (PPE-NDI-n) featuring a poly-(phenylene ethynylene) (PPE) (donor) backbone and naphthalene diimide derivative (NDI, acceptor) end-caps, and charge recombination studies on the polymers. The polymer structure was chosen due the fact that there is no overlap of the emission spectra of PPE and absorption of NDI. Further, the NDI is almost non-fluorescent which minimize of energy transfer. The polymer chain length was varied to study the effect polymer molecular weight on charge transfer and recombination behaviors. Femtosecond (fs) time-resolved transient absorption (TA) spectroscopy was applied to investigate charge recombination kinetics and the long-lived charge
separation state was also studied by nanosecond TA. The results of this work provide insight about the charge recombination kinetics and charge separated state.

**Results and Discussion**

**Synthesis and Characterization**

In this study, a series of polymers, PPE-NDI-n, were synthesized which feature the same conjugated poly(phenylene ethynylene) backbone and naphthalene diimide derivative end-group substitution, but different molecular weight. The synthetic procedure was outlined in Figure 3-1.

![Synthesis scheme of PPE-NDI-n.](image)

The synthesis of monomer started with the reaction of 1,4-dichlorobenzene with n-bromohexane under Kumada coupling reaction conditions to give compound 1. Then,
A typical iodination reaction was performed on compound 1 to get compound 2, which was further reacted with ethynyltrimethylsilane under Sonogashira reaction conditions to obtain compound 3. Deprotection of the trimethylsilyl group by strong base generated compound 4. The synthesis of end-groups started with reacting naphthalene diimide with one equivalent of octan-1-amine to afford compound 5. Due the possibility of having both mono and di-substitution products and tough work-up, the yield was very low. Compound 5 was further reacted with 4-iodoaniline to generate compound 6 with decent yield. Reaction of compound 6 with ethynyltrimethylsilane under Sonogashira reaction conditions produced compound 7 which was deprotected by tributylammonium fluoride (TBAF) to get compound 8. In this step, strong base was not used to avoid hydrolyzing the imide functional groups.

The polymers were synthesized under Sonogashira polycondensation reaction conditions and molecular weight was controlled using the “end-capping” strategy during polymerization reactions. In a typical reaction, compound 2 and 4 (1:1 molar ratio) and various amounts of compound 6 were added into flask. Without the presence of mono-functionalized compound 6, the polymer chain will keep growing. However, the addition of compound 6 changed the stoichiometric balance of the functional groups and lowered the overall molecular weight. Compound 8 was added at the end of polymerization to ensure efficient end-capping at both chain ends. In addition, one PPE polymer without electron acceptor was synthesized as a model compound. The synthesis of OPE-8 was reported by Mr. Junling Jiang from the Schanze group (unpublished results).

Polymer molecular weights were characterized by both GPC and $^1$H-NMR (Figure 3-2). The GPC trace shows a clear decrease in the retention time with
increasing polymer molecular weight (Mn (PPE-NDI-8) < Mn (PPE-NDI-14) < Mn (PPE-NDI-22) < Mn (PPE-NDI-39)). In the $^1$H-NMR spectrum, both proton signals from the naphthalene diimide and polymer backbone appear. Chemical shift at 8.82 ppm was assigned to the aromatic protons on the naphthalene rings and shifts at 7.73 ppm and 6.98 ppm came from the phenyl ring next to the naphthalene unit. Aromatic protons of the PPE backbone occur at 7.38 ppm and the methylene unit which was directly connected to the phenyl ring had a chemical shift at around 2.84 ppm. Signal integration of naphthalene protons and methylene protons were used to calculate the molar ratio of naphthalene units to phenyl rings. Assuming there are two naphthalene groups on each polymer chain, the number of phenyl rings and repeat units can be determined by calculating the ratio of the signal integration at 7.38 ppm and 2.84 ppm.

The number of repeat units calculated from NMR differs significantly from the that derived from GPC when molecular weight is high (Table 3-1). And, the reason might be a) that as the molecular weight gets too large, conjugated polymers tend to form $\pi-\pi$
stacking and aggregate in solution, shielding the NMR signal; or b) high molecular weight polymers were obtained using a reduced amount of end-caps in the reaction systems, which resulted in a decreased $^1$H-NMR signal of the end-cap protons and cause more error in signal integration.

### Table 3-1. Molecular weight characterization of PPE-NDI-n and PPE

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<th>GPC$^a$</th>
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<tr>
<td></td>
<td>Mn (g/mol)</td>
<td>Mw (g/mol)</td>
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<tr>
<td>PPE-NDI-8</td>
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<td>1610</td>
</tr>
<tr>
<td>PPE-NDI-39</td>
<td>11700</td>
<td>23800</td>
</tr>
<tr>
<td>PPE</td>
<td>5400</td>
<td>8200</td>
</tr>
</tbody>
</table>

$^a$ Narrow dispersed polystyrene was used as the standard. $^b$ Degree of polymerization was calculated using Mn obtained by GPC. $^c$ Degree of polymerization was calculated using signal intensity integration ratio from $^1$H-NMR. $^d$ Calculated using the $^1$H-NMR integration of the t-butyl and PPE backbone signals.

### Energetics and Optical Properties

The objective of this project is to investigate the charge recombination in conjugated polymers. It is essential to have the redox state information, in order to understand the excited and charge-separated state energies. The singlet excited state energy of PPE-NDI-n polymers is available from the fluorescence emission spectra. The reduction and oxidation potentials of the NDI end-caps and PPE backbone are obtained from cyclic voltammetry (CV), and the charge separated-state energy is calculated from the difference in the PPE backbone oxidation and NDI reduction potentials. Cyclic voltammetry was performed on all polymers, but reasonable results were obtained only on the shortest chain length polymer, namely, PPE-NDI-8 (Figure 3-3), due to the intrinsic difficulty of performing CV on high molecular weight polymers. However, the energetics of other PPE-NDI-n polymers should be very similar to that of PPE-NDI-8,
because they have the same polymer structure and almost identical absorption and emission (Figure 3-4).

**Figure 3-3.** A) Energetics and B) CV of PPE-NDI-8. Cyclic voltammogram of PPE-NDI-8 in methylene chloride with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as electrolyte, vs. SCE.

The cyclic voltammogram of PPE-NDI-8 shows two quasi-reversible reduction peaks with $E_{\text{red}} = -0.61$ V and $E_{\text{red}} = -1.01$ V, along with a single irreversible oxidation peak with $E_{\text{ox}} = 1.49$ V and onset at 1.22 V (potentials vs. SCE). One thing needs to be pointed out here is that each reduction wave on the CV very likely corresponds to one electron transfer to both NDI end-caps which is supported by previous studies.\(^ {161,162}\)

The charge-separated state energy is calculated using $E_{\text{cs}} = E_{\text{ox}} - E_{\text{red}} - 14.4/\varepsilon R_{\text{DA}}$, where $E_{\text{ox}}$ is the oxidation potential of the PPE backbone, $E_{\text{red}}$ is the first reduction potential of the NDI end-caps, $\varepsilon$ is the dielectric constant and $R_{\text{DA}}$ is the distance between the donor and acceptor units. The $14.4/\varepsilon R_{\text{DA}}$ term is the Coulombic stabilization energy in the charge-separated state and is estimated to be 0.05 eV for PPE-NDI-8 in DCM, assuming the average distance between the positive charge and the NDI is about the length of 4 repeat units. In the case of PPE-NDI-8, the charge-separated state energy ($E_{\text{cs}}$) is calculated to be $\sim 1.90$ eV and the singlet energy is
~2.94 eV. In PPE type conjugated polymers, the triplet state energy is found to be 0.7 ± 0.1 eV below the singlet state. Thus, the triplet state energy level in PPE-NDI-n polymers is about 2.1 ± 0.1 eV, which is within the range of reported value for PPE type polymers (1.95 – 2.26 eV). The triplet energy level of the NDI compound has been estimated to be 2.03 eV, using the phosphorus emission unset wavelength (λ = 610 nm).

Table 3-2. Table of energetics

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{singlet}}$/eV (^c)</th>
<th>$E_{\text{red}}$/V (^d)</th>
<th>$E_{\text{ox}}$/V (^d)</th>
<th>$E_{\text{cs}}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPE8(^a)</td>
<td>2.99</td>
<td>N.A.</td>
<td>1.31</td>
<td>2.14</td>
</tr>
<tr>
<td>NDI-H(^b)</td>
<td>3.21</td>
<td>N.A.</td>
<td>-0.53</td>
<td>N.A.</td>
</tr>
<tr>
<td>PPE-NDI-8</td>
<td>2.94</td>
<td>-0.65</td>
<td>1.27(^e)</td>
<td>2.14</td>
</tr>
</tbody>
</table>

\(^a\) Taken from our group’s unpublished results. \(^b\) Taken from Ref 162. \(^c\) Estimated from fluorescence emission. \(^d\) Value reported vs. SCE. \(^e\) Calculated using the average number of $E_{\text{ox}}$(OPE8) and the onset of PPE-NDI-8 oxidation potential.

UV-visible absorption and emission spectra of the samples were measured in THF, and the concentration of the samples was adjusted to 50 µM (based on repeating unit for polymers) (Figure 3-4). The NDI has two major absorption peaks at 358 nm and 378 nm. The PPE backbone has a broad absorption from 300 nm to 425 nm, with the absorption maximum at 377 nm. Although, the PPE and NDI absorption spectra have a large overlap (300-395 nm), the absorption of the PPE-NDI-n polymers is still dominated by the PPE backbone because the absorption coefficient of the PPE backbone (8.8*10^6 for PPE-NDI-39) is significantly higher than that of the NDI end-caps (≈5*10^5 for NDI). The NDI does not have any absorption beyond 395 nm while the emission of the PPE backbone starts near 390 nm. The mismatch of the PPE emission and NDI absorption ensures that the energy transfer in the PPE-NDI system is minimized. In addition, the NDI is almost non-emissive in solution compared to the PPE polymer, with a quantum
yield of $\varphi=0.18\%$, while the quantum yield of the PPE is about 76%. Therefore, the emission of PPE-NDI-n polymers mostly comes from the PPE backbone.

Figure 3-4. UV-vis absorption and emission spectra in THF. A) UV-vis absorption of the PPE (black) and NDI (red), normalized according to the absorption coefficient. B) Fluorescence emission of the PPE (black) and NDI (red), normalized according to fluorescence quantum yields. C) UV-vis absorption and D) emission of PPE-NDI-8 (black square), PPE-BDI-14 (red circle), PPE-NDI-22 (blue up-triangle) and PPE-NDI-39 (dark cyan down-triangle), and the signals are normalized according to the quantum yields. The excitation wavelength for all samples is 375 nm. Absorption spectra in C are offset for clarity.

In the absorption spectra of PPE-NDI-n polymers, the NDI absorption band at 362 nm can be easily identified in PPE-NDI-8 and this feature becomes less pronounced as the polymer molecular weight increases. However, despite overlapping with the PPE backbone absorbance, the NDI absorption band at 379 nm can clearly be distinguished even in longest chain length polymer. Meanwhile, the PPE backbone absorption becomes stronger as molecular weight increases, due to the fact that the
molar extinction coefficient increases with molecular weight.\textsuperscript{140} The overall absorption spectra increasingly resemble the PPE model polymer as the molecular weight increases due to the increased contribution of the PPE backbone. Despite the changing molecular weight, the absorption maximum remains essentially the same (at 379 nm), indicating the conjugation length is saturated for all polymer samples. In many donor-acceptor molecule systems, besides the $\pi-\pi^*$ transition band, a charge transfer absorption band can also be observed. However, it was not the case for PPE-NDI-n polymers, due to weak electronic coupling.

Table 3-3. Summary of the photophysical properties.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>NDI Content (molar %)</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\varepsilon$ ($10^4$ cm$^{-1}$ M$^{-1}$)</th>
<th>Lifetime at 420 nm (ns)</th>
<th>Quantum Yield$^a$</th>
<th>e-transfer Efficiency %$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE-NDI-39</td>
<td>4.9</td>
<td>379</td>
<td>422</td>
<td>2.25</td>
<td>0.18</td>
<td>0.15</td>
<td>80.5</td>
</tr>
<tr>
<td>PPE-NDI-22</td>
<td>8.3</td>
<td>379</td>
<td>422</td>
<td>2.14</td>
<td>0.15</td>
<td>0.093</td>
<td>87.9</td>
</tr>
<tr>
<td>PPE-NDI-14</td>
<td>12.5</td>
<td>379</td>
<td>422</td>
<td>2.16</td>
<td>0.15</td>
<td>0.044</td>
<td>94.3</td>
</tr>
<tr>
<td>PPE-NDI-8</td>
<td>20</td>
<td>379</td>
<td>422</td>
<td>2.24</td>
<td>0.13</td>
<td>0.013</td>
<td>98.3</td>
</tr>
<tr>
<td>PPE</td>
<td>0</td>
<td>380</td>
<td>422</td>
<td>2.12</td>
<td>0.38</td>
<td>0.77</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

$^a$With anthrathene as quantum yield standard, $\varphi$ =0.27 in ethanol at room temperature. $^b$Energy transfer efficiencies ($\eta$) were calculated as $\eta = 1 - \varphi$(PPE380-525nm)/$\varphi$(PPE), in which $\varphi$(PPE) was the fluorescence quantum yield of donor-only polymer PPE.

All polymers have almost identical emission spectra with emission maxima at 422 nm which is the same as the PPE model polymer. However, the emission intensity is significantly weaker compared PPE model due to charge transfer. Although there is only 5% NDI (molar ratio) in PPE-NDI-39, more than 80% of the emission of polymer backbone is quenched. Further, the quenching is more efficient in PPE-NDI-22 and this trend continues as NDI content increases (Table 3-3). The overall energy transfer efficiency was calculated using the ratio of PPE-NDI-n polymer fluorescence quantum yields to the PPE model polymer quantum yield, and the trend is clear that charge transfer efficiency decreases with increasing $M_n$. 

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**Charge Recombination Study**

Femtosecond (fs) transient absorption (TA) spectroscopy was used to characterize the intrachain charge recombination kinetics in PPE-NDI-n polymers. Figure 3-5 compares the transient spectrum of the PPE and PPE-NDI-8. The transient spectrum of PPE has negative signals (bleach) from 420 nm to 510 nm which are the combination of ground state bleaching and stimulated emission. An intense excited state absorption also is observed for $\lambda > 510$ nm. The transient spectrum of PPE-NDI-n is very different compared to that of PPE. The spectrum is dominated by three strong absorption bands with one at around 480 nm, which is attributed to the absorption of naphthalene diimide radical anion (NDI$^-$), and a broad band from about 570 nm to 650 nm, which is attributed to a combination of NDI radical anion and PPE radical cation (PPE$^{**}$) absorptions.$^{161,166}$ The appearance of the 480 nm band clearly indicates the formation of NDI radical anion which is generated by one electron transfer from the PPE backbone to the NDI end group. In the spectrum of PPE-NDI-8, the bleaching from 420 nm to 510 nm, observed in the spectrum of the PPE, is completely covered by the NDI$^-$ absorption.

Figure 3-5. Transient spectra of the PPE and PPE-NDI-8 in DCM after 100 ps.
The time dependent transient absorption spectrum of PPE-NDI-n polymers is plotted in Figure 3-6. As the molecular weight increases, the feature of NDI$^\ast$ peak at ~480 nm becomes less structured due to the fact that the NDI content decreases with increasing molecular weight and the NDI$^\ast$ signal intensity, which is proportional to the NDI content, decreases as well. In addition, charge transfer is less efficient in high molecular weight polymer and the bleaching signal from the PPE backbone becomes more significant. The broad peak from ~550 to 650 nm also starts to blend with the PPE excited state absorption as molecular weight increases. Another interesting finding is that absorption signals for PPE-NDI-8 and PPE-NDI-14 decay to zero after ~5 ns while there are still signals at ~480 nm in the spectra of PPE-NDI-22 and PPE-NDI-39 which means the NDI$^\ast$ lives longer in high molecular weight polymers.

![Figure 3-6. Time-resolved transient absorption spectra of PPE-NDI-n polymers.](image-url)
Detailed information of charge transfer kinetics can be obtained by monitoring signals at specific wavelengths. Because the signal at 480 nm is dominated by NDI$^-$ absorption, this wavelength was exclusively used to probe the charge separated state. In the TA spectrum, a rise in absorbance was not observed due to polymer relaxation and reorganization and therefore, the charge transfer dynamics can not be resolved.\textsuperscript{167,168} In general, the decay kinetics has two components: fast component (with $\tau \approx 100$ ps) which is attributed to polymer structure relaxation and reorganization and a relatively slow component (with $\tau$ on the order of several hundred ps) reflecting the process of charge recombination. More careful review of the charge recombination process shows that there is an increasing contribution from the slow recombination process as the molecular weight increases (Table 3-4). One explanation is that the holes generated by electron transfer from PPE to NDI end-groups can delocalize along the conjugated backbone and become further removed from the end NDI$^-$ as the polymer chain length increases. The charge recombination is driven by the Coulomb
interaction between the cation and anion radicals, and the strength of which follows Coulomb’s law which is proportional to the inverse square of the distance between the interacting charges. The distance between the cation and anion radicals increases with molecular weight as the hole delocalized further away from the NDI end-caps. Therefore, Coulombic interactions decrease dramatically. The residue signals in the kinetic trace increase with molecular weight which is also consistent with the transient absorption spectrum.

**Table 3-4. Charge recombination kinetics**

<table>
<thead>
<tr>
<th></th>
<th>t₁ (ps)</th>
<th>A₁</th>
<th>t₂ (ps)</th>
<th>A₂</th>
<th>y₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE-NDI-8</td>
<td>100.00</td>
<td>0.65</td>
<td>436.00</td>
<td>0.27</td>
<td>0.05</td>
</tr>
<tr>
<td>PPE-NDI-14</td>
<td>64.00</td>
<td>0.41</td>
<td>414.00</td>
<td>0.36</td>
<td>0.10</td>
</tr>
<tr>
<td>PPE-NDI-22</td>
<td>155.00</td>
<td>0.57</td>
<td>764.00</td>
<td>0.24</td>
<td>0.13</td>
</tr>
<tr>
<td>PPE-NDI-39</td>
<td>121.00</td>
<td>0.37</td>
<td>676.00</td>
<td>0.30</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Equation \( y = A₁ \times e^{-\frac{x}{t₁}} + A₂ \times e^{-\frac{x}{t₂}} + y₀ \) was used for fitting.

**Figure 3-8.** Transient kinetics from \( \lambda=480 \) nm.

Nano-second (ns) TA spectroscopy was used to further investigate the long-lived charge-separated state of PPE-NDI-n polymers in THF (Figure 3-9). However, no PPE
radical cation or NDI radical anion signal is detected after an initial 15 ns camera delay, because the lifetimes of the radicals are shorter than 15 ns. But interestingly, intense PPE triplet absorption is detected.

Figure 3-9. Nasosecond TA spectra of PPE-NDI-n, PPE and NDI in THF. The optical density of all samples at 355 nm is adjusted to 0.6.

The triplet excited states can be generated by either intersystem crossing from the singlet excited state or induced by charge recombination.\textsuperscript{169,170} Considering the fact that more than 80% of the fluorescence is quenched in PPE-NDI-n polymers, charge recombination should be the major contribution to induced triplet formation. However, more careful investigation is needed for better understanding of the triplet formation. In addition, the absorption intensity increases with molecular weight across the polymer
series. The PPE-NDI-8 does not show any PPE triplet absorption while that of the PPE-NDI-39 is almost the same as the PPE model polymer.

**Summary and Future Work**

A series of polymers (PPE-NDI-n) with different molecular weight were synthesized which featured the same poly-(phenylene ethynylene) (PPE) conjugated backbone and naphthalene diimide derivative (NDI) substitution at the polymer chain ends. The energetics of polymers were investigated by cyclic voltammetry and steady state absorption and emission spectroscopy. Despite the increasing of molecular weight, all PPE-NDI-n polymers show similar energy levels. But, the fluorescence emission quantum yield measurements indicate very efficient electron transfer from the PPE backbone to the NDI end-groups, and the transfer efficiency increases with decreasing molecular weight. Femtosecond transient absorption (fsTA) analysis showed that charge recombination rate also increased with decreasing chain length. Nanosecond TA (nsTA) results shows the formation of the PPE triplet excited state and more careful investigation is needed to understand this phenomenon.

**Experiments and Materials**

**Materials**

Unless specified, all compounds and solvents were purchased from commercial sources (Aldrich, Acros, Strem Chemicals, et al) and used without further purification. For all palladium-catalyzed reactions, the solvents were carefully degassed with argon for at least 30 min. $^1$H and $^{13}$C-NMR spectra were recorded on either Inova2 (500 MHz) or Varian Gemini-300 spectrometer (300 MHz). The chemical shifts (δ) are reported in parts per million (ppm) using the residual solvent signals as internal standards.
Instrumentation

$^1\text{H}$ and $^{13}\text{C}$ NMR spectra were measured on a Mercury 300, a Gemini 300, or an Inova 500. Chemical shifts were referenced to the residual solvent peaks. High resolution mass spectrometry was performed on a Bruker APEX II 4.7 T Fourier Transform Ion Cyclotron Resonance mass spectrometer (Bruker Daltonics, MA). Gel Permeation Chromatography (GPC) data was collected on a system composed of a Shimadzu LC-6D pump, an Agilent mixed-D column, and a Shimadzu SPD-20A photodiode array (PDA) detector, with THF as eluent at 1 ml/min flow rate. The system was calibrated against linear narrow dispersed polystyrene standards in THF.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed in a dry methylene chloride ($\text{CH}_2\text{Cl}_2$) solution containing 0.1 M tetra-$n$-butylammonium hexafluorophosphate (TBAH). The three-electrode setup consisted of a platinum microdisk (2 mm$^2$) working electrode, a platinum wire auxiliary electrode, and a silver wire reference electrode. Solutions were degassed with argon flow prior to measurements, and positive argon pressure was maintained during the measurements. The concentration of PPE-NDI-8 in the solutions was 0.5 mM. A 100 mV/s scan rate was used. All potentials were calibrated by using a ferrocene internal standard ($E(\text{Fc}/\text{Fc}^+) = 0.43$ V vs SCE in $\text{CH}_2\text{Cl}_2$), and potentials are reported vs SCE.

UV–visible absorption measurements were carried out on a Shimadzu UV-1800 dual beam absorption spectrophotometer. Photoluminescence spectra were recorded on a spectrofluorimeter from Photon Technology International (PTI). Photoluminescence lifetimes were obtained by time-correlated single photon counting (TCSPC) using a Fluo Time 100 (Picoquant), and excitation was provided using a PDL 800-B Picosecond Pulsed Diode Laser (375 nm).
Nanosecond triplet-triplet transient absorption measurements were acquired with excitation at 355 nm (10 mJ/pulse) using the third harmonic of a Continuum Surelite II-10 Nd:YAG laser. Perkin-Elmer LS1130-3 pulsed xenon lamp was used as a probe source and the transient absorption signal was detected with a gated–intensified CCD mounted on a 0.18 M spectrograph (Princetor PiMax/Acton Pro 180). Samples were prepared to an optical density of 0.6 at the excitation wavelength in a continuously circulating 1 cm pathlength flow cell (volume = 10 mL).

Ultrafast pump–probe experiment were performed with femtosecond (fs) transient absorption spectroscopy with broadband capabilities. Detailed information of the experimental setup can be found elsewhere. Briefly, Ultrafast Systems Helios femtosecond transient absorption spectrometer equipped with UV-Vis and near-IR detectors was used to measure the samples in this study. White-light-continuum probe pulse was generated in a 2 mm thick sapphire plate in an Ultrafast System LLC spectrometer using a few μJ pulse energy of the fundamental output of a Ti:sapphire fs regenerative amplifier operating at 800 nm with 35 fs pulses and a repetition rate of 1 kHz. The pump pulses at 355 nm were created from fs pulses generated in an optical parametric amplifier (Newport Spectra-Physics). The sample solution was constantly stirred to avoid photodegradation in scanned volume. The pump and probe beams were overlapped both spatially and temporally on the sample solution, and the transmitted probe light from the samples was collected on the broad-band UV-visible-near-IR detectors to record the time-resolved excitation-induced difference spectra.

**Synthetic Procedures**

Tert-butyl 2-(4-ethynylphenyl)acetate and tert-butyl 2-(4-iodophenyl)acetate were synthesized according to literature.
**1,4-Dihexylbenzene (Compound 1).** To a solution of hexylmagnesiumbromide [prepared from magnesium (1.375 g, 75 mmol) and n-bromohexane (10.5 mL, 75 mmol)] and NiCl$_2$·dppp (50 mg, 200 µmol) in 50 mL anhydrous Et$_2$O was added dropwise 1,4-dichlorobenzene (5 g, 34 mmol) in 50 mL anhydrous Et$_2$O. The solution was refluxed for 12 h. After cooling to R.T., the mixture was hydrolyzed with HCl under ice bath and extracted with Et$_2$O (50 mL, 3 times). The organic layers were combined, dried with Na$_2$SO$_4$ and evaporated under vacuum. The residue oil was distilled to afford compound 1 as colorless oil (13.3 g, 80%). $^1$H-NMR (300 MHz, CDCl$_3$) δ 7.08 (s, 4 H), 2.57 (t, 4 H), 1.60 (m, 4 H), 1.42-1.24 (m, 12 H), 0.88 (t, 6 H).

**1,4-Dihexyl-2,5-diiodobenzene (compound 2).** Compound 1 (5 g, 20 mmol), I$_2$ (5.6 g, 22 mmol) and HIO$_3$ (1.76 g, 10 mmol) were dissolved in a mixture solvent of HOAC (100 mL), H$_2$SO$_4$ (5 mL) and water (2 mL) and refluxed for 8 h at 120 °C. After the mixture was cooled to R.T., it was poured into ice water (200 mL). The mixture was then extracted with chloroform (100 mL, 3 times) and the organic layers were collected, washed with water and tried with Na$_2$SO$_4$. All the solvent was removed under vacuum and the crude product was purified by column with hexane as the eluent to give compound 2 (8 g, 86%). $^1$H-NMR (300 MHz, CDCl$_3$) δ 7.59 (s, 2 H), 2.59 (t, 4 H), 1.52 (m, 4 H), 1.38-1.28 (m, 12 H), 0.89 (t, 6 H).

**((2,5-di hexyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (compound 3).** Compound 2 (4 g, 8 mmol) was dissolved in a mixed solvent of THF and diisopropylamine and degased was argon for 30 min. PdCl$_2$(PPh$_3$)$_2$ (100 mg, 0.14 mmol) and Cul (50 mg, 0.26 mmol) were added under argon protection. The mixture was degased for another 30 min before TMSA (2 g, 20 mmol) was added. The reaction
was stirred at R.T. for overnight. The mixture was filtered and the solution was evaporated under vacuum. The solid was purified by column with hexane as eluent to yield compound 3 (3.3 g, 95%). \(^{1}\text{H-NMR (300 MHz, CDCl}_3\) \(\delta\) 7.24 (s, 2 H), 2.68 (t, 4 H), 1.58 (m, 4 H), 1.40-1.25 (m, 12 H), 0.89 (t, 6 H), 0.25 (s, 18 H).

1,4-diethynyl-2,5-dihexylbenzene (compound 4). Compound 3 (2 g, 4.56 mmol) was dissolved in a mixed solvent of THF/MeOH (2:1 ratio, 120 mL) and degases with argon for 30 min. Anhydrous K\(_2\)CO\(_3\) (6.9 g, 50 mmol) was added to the mixture and stirred for 4 h. The mixture was filter and extracted with DCM and the organic layer was washed with water and brine. Then, the solvent was evaporated under vacuum and the residue solid was passed through a short column with hexane as the eluent to yield compound 3 (1.2 g, 94%). \(^{1}\text{H-NMR (300 MHz, CDCl}_3\) \(\delta\) 7.30 (s, 2 H), 3.28 (s, 2 H), 2.71 (t, 4 H), 1.60 (m, 4 H), 1.40-1.26 (m, 12 H), 0.89 (t, 6H).

7-Octyl-1H-isochromeno[6,5,4-def]isoquinoline-1,3,6,8(7H)-tetraone (compound 5). 1,4,5,8-Naphthalenetetracarboxylic acid dianhydride (10 g, 37.3 mmol) was dissolved in anhydrous DMF at 120 °C. 1-Aminoctane (4.82 g, 37.3 mmol) in 20 mL of anhydrous DMF was added to the mixture dropwise over 5 min. The reaction was fluxed for 15 h. After reaction, solvent was removed under vacuum. The crude product was purified by column with DCM to yield compound 5 (3.1 g, 22%). \(^{1}\text{H-NMR (300 MHz, CDCl}_3\) \(\delta\) 8.82 (s, 4 H), 4.20 (t, 4 H), 1.44-1.28 (m, 12 H), 0.88 (t, 3 H).

N-octyl-N’-(4’-iodophenyl)naphthalene-1,4,5,8-tetracarboxylic acid bisimide (compound 6). Compound 5 (1 g, 2.68 mmol) dissolved in 50 mL anhydrous DMF at 120 °C. 4-idoaniline (0.88 g, 4 mmol) in 5 mL of anhydrous DMF was added to the mixture dropwise over 5 min. The reaction was fluxed for 15 h. After reaction, solvent
was removed under vacuum. The crude product was purified by column with DCM to yield compound 6 (1 g, 65%). $^1$H-NMR (300 MHz, CDCl$_3$) δ 8.79 (s, 4 H), 7.91 (d, 2H) 7.09 (d, 2 H), 4.20 (t, 2 H), 1.75 (m, 2 H), 1.44 (m, 2 H), 1.37 (m, 2 H), 1.35-1.25 (m, 6 H), 0.88 (t, 3 H).

**N-octyl-N’-(4’-trimethylsilyl ethynylphenyl)naphtalene-1,4,5,8-tetracarboxylic acid bisimide (compound 7).** Compound 6 (1 g, 1.74 mmol) was dissolved in a mixed solvent of THF and diisopropylamine and degased was argon for 30 min. PdCl$_2$(PPh$_3$)$_2$ (100 mg, 0.14 mmol) and Cul (50 mg, 0.26 mmol) were added under argon protection. The mixture was degased for another 30 min before TMSA (0.26 g, 2.6 mmol) was added. The reaction was stirred at R.T. for overnight. The mixture was filtered and the solution was evaporated under vacuum. The solid was purified by column with DCM as eluent to yield compound 7 (766 mg, 80%). $^1$H-NMR (300 MHz, CDCl$_3$) δ 8.79 (s, 4 H), 7.65 (d, 2 H), 7.26 (d, 2 H), 4.21 (m, 2 H), 1.76 (m, 2 H), 1.42 (m, 2 H), 1.40-1.23 (m, 6 H), 0.88 (t, 3 H), 0.28 (s, 9 H).

**N-octyl-N’-(4’-ethynyl phenyl)naphthalene-1,4,5,8-tetracarboxylic acid bisimide (compound 8).** Compound 7 (600 mg, 1.1 mmol) was dissolved in 15 mL chloroform and degased under argon for 30 min. TBAF (1.65 mL, 1 M solution in THF) was added into the solution and the mixture was stirred for 2 h at room temperature. The reaction mixture was washed with water and dried with Na$_2$SO$_4$ and the solvent was removed under vacuum. The residue solid was purified by column with DCM as the eluent to yield compound 8 (473 mg, 90%). $^1$H-NMR (300 MHz, CDCl$_3$) δ 8.78 (s, 4 H), 7.68 (d, 2 H), 7.30 (d, 2 H), 4.14 (m, 2 H), 3.17 (s, 1 H), 1.75 (m, 2 H), 1.41 (m, 2 H), 1.39-1.23 (m, 8H), 0.87 (t, 3 H).
**General method for polymerization of PPE-NDI-n.** Compound 2 (84.7 mg, 0.17 mmol), compound 4 (50 mg, 0.17 mmol) and various amount of compound 6 (0.1-0.6 equivalent) were added to a mixed solvent of 20 mL THF and 10 mL piperidine and the mixture was degased for 30 min. The solution was degased for another 30min before 16.2 mg (0.014 mmol) Pd(PPh$_3$)$_4$ and 5.0 mg (0.026 mmol) of CuI were added. The resulted reaction mixture was heated to 40 °C for 24 hr. Then, various amount of compound 8 (0.1-0.6 equivalent) was added to the mixture and the solution was stirred at 40 °C for another 6 h. The pale yellow solution was flashed through a silica gel column and the eluent was collected and concentrated. The concentrated solution was poured into 100ml of methanol and the polymer precipitated out immediately. This process was repeated twice. Last, the precipitate was collected and dried under vacuum. Typical yield of this reaction is 50%-70%.

**PPE-NDI-8.** GPC (THF, polystyrene standard): Mn= 3.1 kDa, Mw=4.8 kDa, PDI=1.51. $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.82 (s, 8 H), 7.73(d, 4 H), 7.38 (b, 20 H), 4.22 (b, 2 H), 2.84 (b, 32 H), 1.8-1.2 (b, 128 H), 0.89 (b, 48 H).

**PPE-NDI-14.** GPC (THF, polystyrene standard): Mn= 4.8 kDa, Mw=9.0 kDa, PDI=1.87. $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.82 (s, 8 H), 7.73(d, 4 H), 7.38 (b, 40 H), 4.22 (b, 2 H), 2.84 (b, 76 H), 1.8-1.2 (b, 304 H), 0.89 (b, 114 H).

**PPE-NDI-22.** GPC (THF, polystyrene standard): Mn= 7.3 kDa, Mw=16.1 kDa, PDI=2.21. $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.82 (s, 8 H), 7.73(d, 4 H), 7.38 (b, 59 H), 4.22 (b, 2 H), 2.84 (b, 116 H), 1.8-1.2 (b, 442 H), 0.89 (b, 128 H).
**PPE-NDI-39.** GPC (THF, polystyrene standard): Mn= 11.7 kDa, Mw=23.8 kDa, PDI=2.03. \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.82 (s, 8 H), 7.73(d, 4 H), 7.38 (b, 120 H), 4.22 (b, 2 H), 2.84 (b, 240 H), 1.8-1.2 (b, 930 H), 0.89 (b, 341 H).

**PPE.** Compound 2 (84.7 mg, 0.17 mmol), compound 4 (50 mg, 0.17 mmol) and tert-butyl 2-(4-iodophenyl)acetate (16 mg, 0.05 mmol) were added to a mixed solvent of 20 mL THF and 10 mL piperidine and the mixture was degased for 30 min. The solution was degased for another 30min before 16.2 mg (0.014 mmol) Pd(PPh\(_3\))\(_4\) and 5.0 mg (0.026 mmol) of Cul were added. The resulted reaction mixture was heated to 40 °C for 24 hr. Then, tert-butyl 2-(4-ethynylphenyl)acetate (10.8 mg, 0.05 mmol) was added to the mixture and the solution was stirred at 40 °C for another 6 h. The pale yellow solution was flashed through a silica gel column and the eluent was collected and concentrated. The concentrated solution was poured into 100ml of methanol and the polymer precipitated out immediately. This process was repeated twice. Last, the precipitate was collected and dried under vacuum. Typical yield of this reaction is 50%-70%.

**PPE.** GPC (THF, polystyrene standard): Mn= 5.4 kDa, Mw=9.2 kDa, PDI=1.40. \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, 4H), 7.38 (br, 22H), 7.28 (d, 4H), 3.55 (s, 4H), 2.84 (br, 44H), 1.45 (br, 64H), 1.34 (br, 90H), 0.89 (br, 66H).
CHAPTER 4
ULTRAFAST ENERGY TRANSFER IN VARIABLE CHAIN LENGTH CONJUGATED POLYMERS WITH ENERGY ACCEPTOR END-CAPS

Background

Since the discovery, conjugated polymers (CPs) have found numerous applications, such as organic light emitting diodes (OLEDs), bulk-heterojunction solar cells (BHJs), chemo-/biosensors, cell imaging and etc. Compared to small organic dyes, CPs have higher extinction coefficient, better stability and superior processing properties. The synthetic ease of alternating the building blocks for the construction of conjugated polymers makes it convenient to change polymer architectures, modify functional groups and tune optical properties, such as the HOMO and LUMO energy levels. More interestingly, ultrafast energy transfer in conjugated polymer systems has been discovered, which is essential for the development of highly efficient sensors, electroluminescent devices and photovoltaics. However, energy transfer is very complicated in conjugated systems, in which both intrachain and interchain energy migration processes can take place and the dominant process depends strongly on the nature of the systems. In order to resolve the complexity, many systems have been designed to investigate the energy transfer process. One approach is to synthesize energy acceptor-capped CPs which incorporate chromophores with low LUMO energy level (acceptors) onto the end of polymer backbone with high LUMO (donor). In such a system, after selective excitation of the donor chromophores, energy will transfer from the donors to the acceptors.

Swager and Wrighton reported studies investigating energy transfer in polymers with poly-(phenylene ethynylene) (PPE) (donor) backbone and anthracene (acceptor) substitution (PPEAn) at the polymer chain ends. In solution, the energy transfer from
the PPE backbone to the anthracene moieties is only modestly efficient, because anthracene is not a strong acceptor and there is a mismatch of the PPE emission and anthracene absorption spectra. Müllen and Brédas compared interchain and intrachain energy transfer in acceptor-capped conjugated polymers.\textsuperscript{84,85} They found that electronic matrix elements, which affects the energy transfer rate, decreased with increasing donor-acceptor distance in both interchain and intrachain energy transfer. In addition, the energy transfer was more efficient in film than in solution. Recently, we reported very efficient energy transfer along flexible polymer chain with conjugated oligo(phenylene ethynlene) (OPE) donor and thiophene-benzothiadiazole (TBT) acceptor side pendants.\textsuperscript{37} The energy transfer rate varies from 0.02-0.5 ps\textsuperscript{−1} depending on the distance between the acceptors and the initially formed donor excitons.

In this chapter, we present energy transfer study in a series of conjugated polymers featuring PPE backbones end-capped with TBT. This system is chosen because of the perfect match of the emission spectrum of the PPE with the absorption spectrum of the TBT. The quantum yields of both the PPE and TBT moieties are reasonably high. The intrachain energy transfer is very efficient, with dynamic and overall efficiency comparable to similar systems.\textsuperscript{84,85} Femtosecond (fs) time-resolved transient absorption (TA) spectroscopy is applied to investigate the rate of energy transfer which provides insight information about the energy transfer kinetics. The results of this work help us better understand the intramolecular energy transfer processes in conjugated polymers and that the transfer rate depends on the D-A distance in conjugated polymers.
Results and Discussion

Structures, Synthesis and Characterization

The structures of polymers investigated in this study all feature the PPE backbone and are shown in Figure 4-1. The PPE-TBT-n polymers are all end-capped with TBT units while the PPE polymer has phenyl end groups (the same polymer in Chapter 3). The PPE backbone adopts a rod-like conformation in solution and there is minimal structure distortion along the backbone. In diluted solution, the interchain energy transfer is eliminated, which makes the intrachain energy transfer process easier to investigate.\textsuperscript{82,86}

Figure 4-1. Molecular structures.

In comparison, poly(p-phenylene vinylene) (PPV), whose chain is more flexible, has both tightly coiled conformation and open chain conformation in solution. And, interchain energy transfer dominates in the tightly coiled conformation zone while intrachain energy transfer is favored in open chain conformation regain.\textsuperscript{87,88} In addition, the PPE backbone and TBT moieties have distinct singlet excited state energy level: the singlet energy level of the PPE backbone is relatively higher (~3.01 eV) which makes it a good donor and the TBT serves as an acceptor which has lower singlet energy level (~2.07 eV). The emission spectrum of the PPE matches well with the absorption of the TBT.
which facilitates the energy transfer. And the overlap of the PPE and TBT absorption is minimal which allows selective photoexcitation of the PPE backbone. Moreover, both PPE and TBT have high fluorescence quantum yields, which allows quantification of energy transfer efficiency. In summary, polymers studied in this work are perfect candidates for intramolecular energy transfer investigation and the molecular weights of polymers are varied to study the chain length dependent behaviors.

Figure 4-2. Synthesis scheme of polymers.

The general synthesis route for the preparation of polymers is outlined in Figure 4-2. Palladium (Pd) catalyzed Sonogashira cross-coupling polymerization was applied for the synthesis of polymers. Cross-coupling polymerization is a typical polycondensation reaction which proceeds via the step-growth mechanism. The molecular weights of resulting polymers are determined by the degree of polymerization (DP), which is given by $\text{DP} = 1/(1-p)$ (where $p$ is the extent of reaction and assuming stoichiometric balance of the reacting functional groups). Polymer molecular weight can be tuned via the control of DPs by introducing stoichiometric imbalance ratio of
functional groups and DP is given by \( DP = \frac{1+r}{1+r-2rp} \) (where \( r \) is stoichiometric imbalance ratio).\(^6\) Adding variable amount of mono-functionalized end groups to the reaction mixture at the beginning has been widely applied to introduce stoichiometric imbalance and end-group functionality.\(^6\) At the beginning of reaction, reactants 1 and 2 (1:1 molar ratio) and different amount of A1 (0.1-0.3 molar ratio) or B1 (0.3 molar ratio) were added to the flask. After 24 h, certain amount of extra end groups A2 (0.1-0.3 molar ratio) or B2 (0.3 molar ratio) were added and the reaction continued for another 12 h in order to make sure polymers were end capped at both chain ends.\(^6\)

Figure 4-3. Synthesis of OPE-TBT model compound.

The OPE-TBT model compound was synthesized stepwise. Reaction of 1,4-diodobenzene with 1 equivalent trimethylsilyl acetylene (TMSA) and 1 equivalent triisopropylsilyl acetylene (TIPSA) afforded compound 3. Deprotection reaction was performed on compound 3 with potassium carbonate to yield compound 4, which was further reacted with compound 1 to make compound 5. Under Sonagashira reaction conditions, the coupling of compound 5 with compound A1 yields compound 6. Deprotection of the triisopropylsilyl group on compound 6 produces compound 7 with high yield. The last step is to couple compound 7 with compound 5. The reaction yields
of compound 3 and 5 are relatively low due to the possibility of creating both di- and mono-substituted products.

The polymer molecular weights and structure were characterized by gel permeation chromatography (GPC) and $^1$H-NMR. It is known that GPC usually overestimates the molecular weight of conjugated polymers, but it is still a well-accepted method for relative molecular weight characterization in this field. The number average molecular weights ($M_n$) of polymers vary from 5.7 to 14 kDa which correspond to 19 to 50 repeating units. Polymers are named after the number of repeating units, PPE-TBT-19, PPE-TBT-30, PPE-TBT-37 and PPE-TBT-50, respectively. The PPE polymer has a molecular weight of 5.4 kDa, which is comparable to the shortest chain length TBT end-capped polymer, namely PPE-TBT-19.

![Figure 4-4. GPC traces of PPE-TBT-n. PPE-TBT-19 (black squares, Mn=5.7 kDa, PDI=2.24), PPE-TBT-30 (red circle, Mn=8.7 kDa, PDI=2.57), PPE-TBT-37 (blue up triangle, Mn=10.6 kDa, PDI=2.55), PPE-TBT-50 (dark cyan down triangle, Mn=14.0 kDa, PDI=2.87) and PPE (left triangle magenta, Mn=5.4 kDa, PDI=1.70).](image-url)
$^1$H-NMR was used to confirm the chemical structure and molecular weight. Resonances at $\delta = 8.15$ ppm (labeled as T) belong to benzothiadiazole protons and the resonance at $\delta = 2.85$ ppm (labeled as M) is assigned to the methylene protons (-CH$_2$-) next to phenyl groups on the conjugated backbone (Figure 4-5). And, since there are two TBT units on each polymer chain, the number of methylene groups can be determined using the ratio of the peak integrations of T to M. Each repeat unit has methylene groups and, therefore, the number of repeat is determined. However, as molecular increases, the NMR signal integration method becomes less accurate.$^{62}$

Figure 4-5. $^1$H-NMR spectra of PPE-TBT-n and PEE. A) Zoomed in area and B) whole spectra.

**Optical Properties in Solution**

The absorption and fluorescence spectra of the TBT-TIPS, OPE-TBT and PPE polymer were measured in THF solutions and they are plotted in Figure 4-6. The PPE polymer features a broad single absorption band at around 387 nm while the OPE-TBT and TBT-TIPS have both π-π* transition and charge transfer absorption bands (Figure
Compared to TBT-TIPS, both absorption bands of OPE-TBT are red-shifted due to increasing HOMO energy level.

Figure 4-6. Steady state photophysical properties in THF solutions. A) Normalized UV-vis absorption and B) fluorescence emission spectra of PPE(black), TBT-TIPS (red) and OPE-TBT (blue); C) normalized UV-vis absorption of and D) emission spectra of PPE-TBT-19 (black squares), PPE-TBT-30 (red circle), PPE-TBT-37 (blue up triangle), PPE-TBT-50 (dark cyan down triangle) and PPE (left triangle magenta); emission spectra were normalized according to the quantum yield. Inset plot in Figure C is the zoom in area of 425-600 nm. Inset plot in figure D shows the energy transfer efficiency. The excitation wavelength is 370 nm for all samples.

The PPE backbone and TBT moiety have a great mismatch in absorption spectra, which allows selectively excitation of the PPE chromophore and study of the energy transfer efficiency. The PPE backbone and TBT moiety also show distinct emissions with the PPE emitting at 420 nm and the TBT featuring a broad emission peak at 590
nm (Figure 4-6 B). But, both chromophores have fairly high quantum yield ($\phi_{\text{PPE}} = 0.92$ and $\phi_{\text{TBT-TIPS}} = 0.73$). The OPE-TBT shows little donor emission due to very efficient energy transfer (> 99.5%) and the acceptor emission also red-shifts compared to that of TBT-TIPS.

The steady state absorption of PPE-TBT-$n$ polymers was measured in THF and the concentration is 50 $\mu$M (based on repeat units). And, the spectra were plotted in Figure 4-6 (C) and normalized at absorption maximum (~390 nm). The PPE, which doesn’t have TBT end-caps, has no absorption beyond 430 nm. But, an additional absorption band, from 470 nm to 550 nm, shows up in the spectra of TBT-PPE polymers, which is attributed to the TBT absorption. The intensity of the TBT absorption increases with decreasing molecular weight, indicating increasing TBT content. But, compared to the dominating absorption band 390 nm, which is attributed to the PPE backbone absorption, the TBT absorption is still less intense. Since the effective conjugation length of PPE type polymers in isotropic solvent (like THF or DCM) is limited to be around 9-10 repeat units, the absorption maximum of PPE backbone remains essentially the same.$^{64}$

Steady state emission spectra of polymers (PPE-TBT-$n$ and PPE) at the same concentration (50 $\mu$M, based on repeating units) were plotted in Figure 4-6 (D) and normalized according to their quantum yield. The PPE shows a single peak at around 420 nm and the PPE-TBT-$n$ polymers have an additional band at about 600 nm, which is attributed to the TBT emission. The emission intensity of the 420 nm peak decreases with increasing TBT content while the 600 nm peak increases, which indicates more energy transfer from the PPE backbone to the end TBT acceptors. Compared to the
PPE, more than 60% of the donor emission (420 nm) in PPE-TBT-50 is quenched and the quenching is more significant in PPE-TBT-37 with efficiency reaching 70%. This trend continues as the molecular weight of polymers decreases as evidenced in the PPE emission fluorescence quantum yield (Table 4-1). The overall energy transfer efficiency was calculated using the quantum yield of emission from 380 nm to 525 nm (the donor emission) in PPE-TBT-n polymers over the quantum yield of PPE. The trend is clear that energy transfer efficiency decreases with TBT content. The trend is supported by the changing of fluorescence lifetime at 420 nm which decreases with molecular weight: the average lifetime at 420 nm is about 357 ps, 299 ps, 290 ps and 222 ps for PPE-TBT-50, PPE-TBT-37, PPE-TBT-30 and PPE-TBT-19, respectively. The decreasing in donor lifetime indicates more efficient quenching, which is caused by energy transfer to the acceptors.

Table 4-1. Photophysical Properties of Polymer Samples

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ_{abs} (nm)</th>
<th>λ_{em} (nm)</th>
<th>Lifetime at 420 nm (ps)^a</th>
<th>Lifetime at 600 nm (ns)^a</th>
<th>PPE (380 nm-525 nm)</th>
<th>TBT (525 nm-750 nm)</th>
<th>Overall (380 nm-750 nm)</th>
<th>Energy Transfer Efficiency %^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBT-PPE-19</td>
<td>389</td>
<td>423</td>
<td>222</td>
<td>4.45</td>
<td>0.082</td>
<td>0.52</td>
<td>0.6</td>
<td>91.1</td>
</tr>
<tr>
<td>TBT-PPE-30</td>
<td>393</td>
<td>423</td>
<td>290</td>
<td>4.45</td>
<td>0.16</td>
<td>0.55</td>
<td>0.71</td>
<td>82.6</td>
</tr>
<tr>
<td>TBT-PPE-37</td>
<td>393</td>
<td>423</td>
<td>299</td>
<td>4.45</td>
<td>0.27</td>
<td>0.4</td>
<td>0.67</td>
<td>70.7</td>
</tr>
<tr>
<td>TBT-PPE-50</td>
<td>396</td>
<td>423</td>
<td>357</td>
<td>4.45</td>
<td>0.34</td>
<td>0.39</td>
<td>0.72</td>
<td>63.0</td>
</tr>
<tr>
<td>PPE</td>
<td>397</td>
<td>423</td>
<td>462</td>
<td>N.A.</td>
<td>0.92</td>
<td>N.A.</td>
<td>0.92</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

^a Data was collected on a streak camera.  ^b With anthrathene as quantum yield standard, φ =0.27 in ethanol at room temperature.  ^c Energy transfer efficiency (η) were calculated as η = 1 − φ(PPE(380-525nm))/φ(PPE), in which φ(PPE) was the fluorescence quantum yield of donor-only polymer PPE.

**Fluorescence Polarization Investigation**

Fluorescence polarization studies of polymers (PPE-TBT-n and PPE) were performed at room temperature using THF as the solvent while the anisotropy of OPE-TBT was measured in glycerin (Figure 4-7). A 380 nm excitation wavelength was
chosen to selectively excite the PPE chromophore. The fluorescence emission polarization, which can be characterized by anisotropy \( r \), is calculated from the emission intensity through a polarizer using equation:

\[
    r = \frac{I_{VV} - I_{VH}}{I_{VV} + 2I_{VH}} \tag{4-1}
\]

where \( I_{VV} \) and \( I_{VH} \) are the intensity observed when the emission polarizer is parallel and perpendicular to the direction of the polarized excitation respectively.

Figure 4-7. Anisotropy characterization and simplified representation of polymer chain conformation. A) Anisotropy of PPE-TBT-19 (black), PPE-TBT-30 (red), PPE-TBT-37 (blue), PPE-TBT-50 (dark cyan) and PPE (magenta); B) anisotropy of PPE-TBT-19 in DCB (filled black square) and THF (hollow black square) and PPE-TBT-50 in DCE (filled blue circle) and THF (hollow blue circle); C) anisotropy of PPE (black), PPE-TBT-19 (red) and OPE-TBT (blue); D) simplified representation of polymer chain conformation and dipoles. Polymers are dissolved in THF while the OPE-TBT is dissolved in glycerin.
Two interesting trends can be observed in the emission anisotropy of PPE-TBT-n polymers: 1) the emission polarization of PPE backbone (400-500 nm) increases with decreasing molecular weight; 2) the donor emission (400-500 nm) polarization of the OPE-TBT is higher than that of polymers and the acceptor emission (550-700 nm) polarization is almost zero and 3) the acceptor emission polarization of the OPE-TBT is lower compared to the polymers.

The emission anisotropy reveals the angular displacement of the polymers that occur between absorption and emission of a photon, which depends strongly upon the relative time scales of fluorescence emission lifetime and rotation diffusion of polymers. When the time scales of the two are on the same order, an increase of emission lifetime or decreasing of rotation diffusion rate will result a decreasing anisotropy.\textsuperscript{71} The lifetime of PPE emission increases with molecular weight (Table 4-1), but, it should not be the cause here. Because the model PPE polymer and PPE-TBT-19 have similar molecular weights and they show very similar anisotropy value as well, despite the fact the lifetime of the PPE is two-time longer compared to that of PPE-TBT-19. An increasing of molecular weight will lower the rotation diffusion rate and increase the anisotropy, which is the opposite of the observation. But, in order to rule out the possibility that the change in anisotropy is caused by the changing of either fluorescence emission lifetime or rotation diffusion, anisotropy of PPE-TBT-19 and PPE-TBT-50 were measured in ortho-dichlorobenzene (DCB), which is a more viscous solvent and can slow down the polymer rotation diffusion rate. It is obvious that the emission anisotropy does not change with solvent, which demonstrates that the emission lifetime is way shorter compared to the rotation diffusion rate. Therefore, the change of emission anisotropy
should not be caused by the changing of fluorescence lifetime or rotation diffusion, which leads to the speculation that the change of PPE backbone emission anisotropy is caused by the polymer chain conformation variation.

The anisotropy can be calculated according equation:

$$r(\beta) = \frac{2}{5} \left( \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right)$$

(4-2)

In which (\(\beta\)) is the angle between the absorption and emission dipole moments. The anisotropy is 0.4 when the dipoles are aligned with each other (\(\beta = 0\)) and a misalignment reduces the overall anisotropy. And, the emission anisotropy of the polymer backbone in PPE-T-n polymers is significantly lower than 0.4 and decreases with increasing molecular weight. It has been demonstrated that in isotropic solutions, PPEs adopt “worm-like” conformation and the polymer chains are broken into smaller segments with different conjugation lengths, which have different segment orientation (Figure 4-7 D). The “worm-like” conformation results in angular displacement variation along the polymer backbones. After photoexcitation, the exciton migrates along the polymer backbone before emitting and the migration follows a “random-walk” model. There are more possible dipole orientations in longer chain-length polymers and a greater possibility that the emission dipole is misaligned with the original excitation polymerization direction. As a result, the anisotropy of the PPE backbone emission is lower in high molecular polymers.

The anisotropy of the OPE-TBT donor emission is significantly higher, because the structure of the OPE-TBT is more rigid and there is less conformation variation. After energy transfer, the anisotropy of the TBT emission is almost zero, which is due to the angular displacement between the OPE and the TBT dipoles. The molecular
structure of the OPE-TBT was simulated using DFT calculations (detailed information can be found in the experimental part) and the result is shown in Figure 4-8. The dipole angle is calculated by using the unit vectors, given in the output of a Gaussian 09 geometry optimization, and setting them in a right triangle. This triangle has the overall dipole vector (0.4147 Debye) as the hypotenuse, and the unit vectors as the other sides of the triangle. The x-vector (0.2521 Debye) runs along the oligo-phenylacetylide axis, while the y-vector (0.3278 Debye) lies perpendicular, but still in the aromatic plane. The acute dipole angle relative to the oligo-phenylacetylide axis is found by calculating the angle using \( \sin^{-1}(\frac{y\text{-vector}}{\text{overall dipole}}) = \sin^{-1}(0.3278/0.4147) = \sin^{-1}(0.7905) = 52.2 \) degrees. The anisotropy is calculated to be 0.024 (Equation 4-2). And, the measured anisotropy of the OPE-TBT acceptor emission is about 0.038 which agrees well with the calculated result.

![Figure 4-8. Structure simulation and calculated dipole of OPE-TBT.](image)

The anisotropy of TBT emission in the polymer is significantly higher compared to OPE-TBT compound, which is also very likely due to the polymer chain conformation variation. In polymers, the conjugated segments have different orientation, which increases the chance that the absorption and emission dipoles of TBT are aligned with each other and increases the overall anisotropy. And the average angle, \( \beta \), can also be determined using the average anisotropy values according to equation 4-2 and are listed in Table 4-2.
The energy transfer efficiency in conjugated polymers is affected by polymer chain conformation. The less planarized polymer chains lead to less efficient exciton migration due to reduced alignment of transition dipole moments. Therefore, the change of energy transfer efficient in different chain-length polymers can be the results of two factors: the increased distance between the effective donor and acceptors and reduced exciton migration efficiency, which is caused by conformation disorder.

Table 4-2. Average Anisotropy and Angle Displacement

<table>
<thead>
<tr>
<th></th>
<th>( r_{\text{ave}}(400-500 \text{ nm}) )</th>
<th>( r_{\text{ave}}(550-700 \text{ nm}) )</th>
<th>( \beta(\circ)^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE-TBT-19</td>
<td>0.265</td>
<td>0.099</td>
<td>45.1</td>
</tr>
<tr>
<td>PPE-TBT-30</td>
<td>0.251</td>
<td>0.100</td>
<td>45.0</td>
</tr>
<tr>
<td>PPE-TBT-37</td>
<td>0.236</td>
<td>0.106</td>
<td>44.5</td>
</tr>
<tr>
<td>PPE-TBT-50</td>
<td>0.212</td>
<td>0.113</td>
<td>43.8</td>
</tr>
<tr>
<td>PPE</td>
<td>0.249</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>OPE-TBT</td>
<td>0.346</td>
<td>0.038</td>
<td>50.8</td>
</tr>
</tbody>
</table>

\(^a\) Calculated using \( r_{\text{ave}}(550 - 700 \text{ nm}) = \frac{2}{5} \left( \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right) \)

Energy Transfer Kinetics

Time resolved fluorescence lifetime of the PPE-TBT-\( n \) polymers and PPE were investigated to understand the relative long-time energy transfer behaviors, using the streak camera. Figure 4-9 A compares the lifetime of the donor emission (PPE, 420 nm) of the PPE-TBT-\( n \) polymers and the PPE. The fluorescence of the PPE-TBT-\( n \) polymers decays faster than that the PPE, indicating that the energy transfer is still occurring even at long-time scale. The decay rate depends on the chain length, with the shortest chain decaying fastest (Table 4-1). The PPE decays slower and has a rising time. In contrast, the fluorescence lifetime of the acceptor emission (TBT, 600 nm) remains the same for the PPE-TBT-\( n \) polymers regardless of the chain length. But the life-time is shorter compared to the TBT-TIPS compound and the reason should be that the conjugation system of the TBT is disturbed in the PPE-TBT-\( n \) polymers. Close analysis
of early time fluorescence decays reveals that the majority of the energy transfer must happen within the instrument response of the camera (~15 ps), since there is no evidence of signal “growing in” (Figure 4-9 B, inset plot).

Figure 4-9. Fluorescence lifetime characterization in THF with streak camera. A) Donor emission lifetime (420 nm) of PPE-TBT-19 (black), PPE-TBT-30 (red), PPE-TBT-37 (blue), PPE-TBT-50 (dark cyan) and PPE (magenta); B) acceptor emission lifetime (600 nm) of PPE-TBT-19 (black), PPE-TBT-50 (dark cyan) and TBT-TIPS (magenta). Inset figure shows the early time of PPE-TBT-19 and PPE-TBT-50 decay.

In order to further investigate the fast component of the energy transfer dynamics, ultrafast transient absorption measurements were performed on polymers.
Figure 4-10 compares the transient absorption spectra of the PPE and PPE-TBT-30 at \( t = 100 \) ps. The transient spectrum of the PPE (black line) shows negative band (bleach) from 350 nm to 520 nm, which is the result of a combination of ground state bleaching and stimulated emission. There are also indication of polymer relaxation in the spectrum, evidenced by the subtle red-shift of stimulated emission (420 nm and 450 nm) compared to the steady state fluorescence emission (Figure 4-6). Both the transient absorption spectra of the PPE and the PPE-TBT-30 also feature a strong broad induced absorption band starting from 520 nm.

Figure 4-11. Time-resolved ultrafast transient absorption spectra. A) PPE and B) PPE-TBT-30.

The time-resolved ultrafast transient absorption spectra provide more evidence on polymer relaxation, since the induced absorption is shifting to lower energy and broadening as well (Figure 4-11 A). The ultrafast transient absorption spectrum of the PPE-TBT-30 mostly resembles that of the PPE, indicating that laser pulse predominantly excite the PPE backbone. But, there are additional peaks in the spectrum, which indicates the energy transfer feature. The negative signal at 480 nm corresponds to the bleaching of the TBT end-caps while the stimulated TBT emission...
(negative signal, ~600 nm) is overlapping with the induced absorption of the PPE and the TBT. The stimulated emission of TBT can be observed after 1 ns (Figure 4-11 B). These features arise due to energy transfer from the PPE backbone to the TBT end-caps, since only the PPE backbone is excited.

The energy transfer dynamics was examined at the wavelength of 428 nm and plotted in Figure 4-12 A. The wavelength was chosen because it has the least contribution from the TBT-related spectral features as well as minimal effects from the PPE relaxation. This wavelength is also between the two PPE stimulated emission peaks (~420 nm and ~440 nm), so the spectrum shifting does not have a significant effect. The signal from the PPE polymer evolves slower and there is a slight growth at the beginning of the decay, which is also observed in the time-resolved fluorescence lifetime. The PPE-TBT-19 polymer decays much faster compared to the PPE and the decay kinetics of the PPE-TBT-n polymers begin to resemble the PPE polymer as the polymer chain gets longer.

![Figure 4-12. TA decay kinetics. A) Kinetic trace and B) early time decay of PPE-TBT-19 (black), PPE-TBT-30 (red), PPE-TBT-37 (blue), PPE-TBT-50 (dark cyan) and PPE (magenta).](image-url)
A careful examination of the decay kinetics reveals that there are ultrafast components (< 2 ps) in the energy transfer process, which are attributed to the rapid energy transfer from the excited PPE segments that are close to the TBT end-caps (Figure 4-12 B). Therefore, the PPE-TBT-19 has greater amplitude to the fast time component, since the chance of having an excited PPE segment close to the TBT end-caps is higher. There are also relatively slow component in the energy transfer process, which is attributed to the exciton hopping along the polymer backbone. For longer chain-length polymer, the possibility of creating an exciton which is far away from the acceptor is higher, thus, the exciton hopping is more likely to happen before the energy transfer.

Figure 4-13. Schematic representation of the energy transfer processes in conjugated polymers. A) Direct energy transfer and B) exciton hopping and energy transfer.

A comparison of the time-resolved fluorescence data and ultrafast TA data shows that these two data sets match up very well and they are plotted on top of each other in Figure 4-14. The fluorescence experiment completely misses the ultrafast component for the decay kinetics due to the instrument limitation. There are other
noticeable differences in the two, probably due to the fluorescence decay being the integrated decay over the whole emission spectrum, whereas the ultrafast TA decay is solely the signal of one wavelength. The calculated lifetime is listed in Table 4-3. The lifetime for the “slow” components $t_2$ and $t_3$ were taken from fits to the time-resolved fluorescence. The ultrafast components for the PPE-TBT-19, PPE-TBT-30 and PPE-TBT-37 polymers are within 1 ps and the amplitude decreases with increasing polymer chain-length. The PPE-TBT-50 has negative component (signal rising time) due to the contribution of the PPE backbone fluorescence. The calculated average lifetime clearly shows that the energy transfer rate decreases with increasing polymer chain-length.

![Graph](image)

**Figure 4-14.** Comparison of ultrafast TA decay kinetics (circles) and time-resolved fluorescence (lines) data. PPE-TBT-19 (black), PPE-TBT-30 (red), PPE-TBT-37 (blue), PPE-TBT-50 (dark cyan) and PPE (magenta).

**Table 4-3.** Summary of lifetime measurements.

<table>
<thead>
<tr>
<th></th>
<th>$a_1$</th>
<th>$t_1$ (ps)</th>
<th>$a_2$</th>
<th>$t_2$ (ps)$^a$</th>
<th>$a_3$</th>
<th>$t_3$ (ps)$^a$</th>
<th>$t_{\text{ave}}$ (ps)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE-TBT-19</td>
<td>0.4</td>
<td>0.47</td>
<td>0.31</td>
<td>55</td>
<td>0.29</td>
<td>348</td>
<td>117</td>
</tr>
<tr>
<td>PPE-TBT-30</td>
<td>0.25</td>
<td>0.46</td>
<td>0.29</td>
<td>73</td>
<td>0.46</td>
<td>374</td>
<td>193.4</td>
</tr>
<tr>
<td>PPE-TBT-37</td>
<td>0.15</td>
<td>0.64</td>
<td>0.31</td>
<td>78</td>
<td>0.53</td>
<td>378</td>
<td>225.7</td>
</tr>
<tr>
<td>PPE-TBT-50</td>
<td>-0.19</td>
<td>42.5</td>
<td>0.52</td>
<td>154</td>
<td>0.68</td>
<td>420</td>
<td>355.4</td>
</tr>
</tbody>
</table>

$^a$ Data taken from the fluorescence lifetime obtained via the steak camera. $^b$ Calculated as $t = \sum a_n t_n$.  

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Summary

Energy transfer in conjugated donor-acceptor polymers was studied in a system consisting of poly-(phenylene ethynylene) (PPE) end-capped with thiophene-benzothiadiazole (TBT). A series of polymers with different chain length were synthesized by applying the “end-capping” strategy via Palladium catalyzed Sonogashira polycondensation reaction. Highly efficient energy transfer from PPE donor to TBT acceptor was observed by fluorescence emission measurements and the overall energy transfer efficiency decreases with increasing polymer molecular weights, with the lowest molecular weight polymer achieving an overall of more than 90% energy transfer efficiency. The decreased energy transfer efficiency is most likely due to longer distance between the donor and the acceptor, which has been observed in many FRET energy transfer systems. Fluorescence emission anisotropy demonstrates that polymers adopt “worm-like” conformation in isotopic solutions, which lower the energy migration rate and the energy transfer efficiency. Ultrafast transient absorption and time-resolved fluorescence lifetime investigations confirm that most of the energy transfer happens with the first 10-20 ps and the energy transfer rate decreases with increasing polymer chain-length. In addition, there is evidence showing energy transfer is also occurring on long-time scale (~ns).

Experiments and Materials

Materials

Unless specified, all compounds and solvents were purchased from commercial sources (Aldrich, Acros or Strem Chemicals) and used without further purification. For all palladium-catalyzed reactions, the solvents were carefully degassed with argon for at least 30 min.
**Instrumentation**

$^1$H and $^{13}$C-NMR spectra were recorded on either Varian Inova2 (500 MHz) or Gemini-300 spectrometer (300 MHz). The chemical shifts ($\delta$) are reported in parts per million (ppm) using the residual solvent signals as internal standards. High resolution mass spectrometry was performed on a Bruker APEX II 4.7 T Fourier Transform Ion Cyclotron Resonance mass spectrometer (Bruker Daltonics, MA). Gel Permeation Chromatography (GPC) data was collected on a system composed of a Shimadzu LC-6D pump, an Agilent mixed-D column, and a Shimadzu SPD-20A photodiode array (PDA) detector, with THF as eluent at 1 ml/min flow rate. The system was calibrated against linear narrow dispersed polystyrene standards in THF.

UV−visible absorption measurements were carried out on a Shimadzu UV-1800 dual beam absorption spectrophotometer. Photoluminescence spectra were recorded on a spectrofluorimeter from Photon Technology International (PTI).

Computational calculation was carried out using DFT as implemented in Gaussian 091 Rev. C.02. The geometry was optimized using the B3LYP functional along with the 6-31G(d) basis set for all atoms. Silicon isopropyl groups and solubilizing hexyl moieties were replaced with methyl groups for computational efficiency. This model is designated by the addition of a prime (’) to its name, thus the model for OPE-TBT is termed as OPE-TBT’. The optimization was started from an idealized geometry, without symmetry constraints. The optimized structure was characterized by a vibrational frequency calculation and was shown to be at a minimum by the absence of imaginary frequencies.

Spectroscopy carried out at UNC-Chapel Hill by Robert J. Dillon. In the photoluminescence lifetimes experiments, light emanating from the sample is re-collected by
the objective, transmitted through a dichroic beam splitter (Semrock: FF670), and focused onto the entrance slit of a streak camera (Hamamatsu: Streakscope). The instrument response of the streak camera is approximately 17 ps. For transient absorption spectroscopy, samples were dissolved in THF to an OD of between 0.4 and 0.5 in a 2 mm cuvette. Femtosecond pulses were derived from a Clark-MXR CPA 2210 Ti: Sapphire laser which produces ~ 150 fs pulses centered at 775 nm with a 1 kHz repetition rate. A portion of the output was frequency doubled (to 388 nm) in a BBO and used for photoexcitation of the donor. Low fluences (25 µJ/cm²) were necessary to achieve linear behavior of the transients. Kinetics were monitored by a weak continuum probe pulse generated by focusing a small portion of the 775 nm fundamental into a translating CaF₂ window. Spectra were collected at a rate of 1 kHz with pump on and pump off spectra interleaved by mechanical chopping, are chirp corrected for delay times Δt < 20 ps, and are each the average of 8000 individual pump on and pump off spectra.

**Synthetic Procedures**

Tetrakis(triphenyl phosphine) palladium (Pd(PPh₃)₄) was from Strem Chemical and triisopropylsilyl acetylene (TIPSA) was from TCI. Copper (I) iodide (CuI), diisopropylamine ((i-Pr)₂NH), tetrahydrofuran (THF) and all other chemicals were purchased from either Sigma-Aldrich or Fisher Chemicals. All reagents were used without further purification unless specified.

1,4-dihexyl-2,5-diiodobenzene (1), 1,4-diethynyl-2,5-dihexylbenzene (2) and PPE were synthesized following the procedures detailed in the previous chapter. 4-(5-ethynylthiophen-2-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (A1), 4-(5-iodothiophen-2-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (A2), tert-butyl 2-(4-
ethynylphenyl)acetate (B1)\textsuperscript{140} and tert-butyl 2-(4-iodophenyl)acetate (B2)\textsuperscript{140} were synthesized according to published procedures.

**General Procedure for Polymerization.** Monomer 1 (84.6 mg, 0.17 mmol), 2 (50.0 mg, 0.17 mmol) and A1 (0.1-0.3 molar ratio) were dissolved in a solution of 20 mL dry THF and 10 mL (i-Pr)\textsubscript{2}NH in a round bottom flask at room temperature. The solution was degassed for 30 min before 16.2 mg (0.014 mmol) Pd(PPh\textsubscript{3})\textsubscript{4} and 5.0 mg (0.026 mmol) of Cul were added. The resulting reaction mixture was heated to 45 °C for 24 hr. Then, A2 (0.1-0.3 molar ratio) was added to the solution and the reaction was allowed for another 12 h. The solution was flashed through a silica gel column and the eluent was collected and concentrated. The concentrated solution was poured into 100 mL of methanol and the polymer precipitated out immediately. This process was repeated twice. Last, the precipitate was collected and dried under vacuum. Typical yield of this reaction is 50-70%.

**PPE-TBT-19.** GPC (THF, polystyrene standard): M\textsubscript{n} = 5.7 kDa, M\textsubscript{w} = 12.9 kDa, PDI = 2.24. \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) \textdelta 8.15 (d, 2H), 8.05 (d, 2H), 7.90 (s, 4H), 7.69 (dd, 2H), 7.38 (br. 28H), 7.36 (d, 2H), 7.24 (dd, 2H), 2.85 (t, 56H), 1.73 (m, 56H), 1.43 (m, 56H), 1.34 (br, 112H), 0.89 (t, 84H).

**PPE-TBT-30.** GPC (THF, polystyrene standard): M\textsubscript{n} = 8.7 kDa, M\textsubscript{w} = 22.5 kDa, PDI = 2.57. \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) \textdelta 8.15 (d, 2H), 8.05 (d, 2H), 7.90 (s, 4H), 7.69 (dd, 2H), 7.38 (br. 40H), 7.36 (d, 2H), 7.24 (dd, 2H), 2.85 (br, 80H), 1.73 (br, 80H), 1.43 (br, 80H), 1.34 (br, 160H), 0.89 (br, 120H).

**PPE-TBT-37.** GPC (THF, polystyrene standard): M\textsubscript{n} = 10.6 kDa, M\textsubscript{w} = 27.2 kDa, PDI = 2.55. \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) \textdelta 8.15 (d, 2H), 8.05 (d, 2H), 7.90 (s, 4H), 7.69
(dd, 2H), 7.38 (br. 52H), 7.36 (d, 2H), 7.24 (dd, 2H), 2.85 (br, 104H), 1.73 (br, 104H), 1.43 (br, 104H), 1.34 (br, 208H), 0.89 (br, 156H).

**PPE-TBT-50.** GPC (THF, polystyrene standard): $M_n = 14.0$ kDa, $M_w = 40.3$ kDa, PDI = 2.87. $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.15 (d, 2H), 8.05 (d, 2H), 7.90 (s, 4H), 7.69 (dd, 2H), 7.38 (br. 60H), 7.36 (d, 2H), 7.24 (dd, 2H), 2.85 (br, 120H), 1.73 (br, 120H), 1.43 (br, 120H), 1.34 (br, 240H), 0.89 (br, 180H).

**Compound 3.** 1,4-Diiodobenzene (5 g, 15.2 mmol) was dissolved in a mixed solvent of THF (40 mL) and (i-Pr)$_2$NH (40 mL) and the solution was degassed for 30 min before 150 mg (0.13 mmol) Pd(PPh$_3$)$_4$ and 50 mg (0.26 mmol) of CuI were added. Then, trimethylsilyl acetylene (1.49 g, 15.2 mmol) and triisopropylsilyl acetylene (2.76 g, 15.2 mmol) were added. The resulting mixture was stirred under Ar protection at R.T. for 4 h. After the reaction, the solvent was removed under vacuum and the residue solid was purified by column with hexane as the eluent to yield compound 3 (2.26 g, 42%).

$^1$H-NMR (500 MHz, CDCl$_3$) δ 7.39 (s, 4H), 1.12 (s, 21H), 0.25 (s, 9H).

**Compound 4.** Compound 3 (2 g, 5.6 mmol) was dissolved in a mixed solvent of THF (40 mL) and MeOH (10 mL). Potassium carbonate (1.5 g, 11.3 mmol), which was dissolved in 5 mL of water, was added to the mixture and the resulting mixture was stirred at R.T. for 2 h. After the reaction, the mixture was extracted with DCM (3 x 20 mL) and the organic layers were combined. After removing the solvent under vacuum, the residual solid was purified with a flash column with hexane as the eluent to yield compound 4 (1.50 g, 95%). $^1$H-NMR (500 MHz, CDCl$_3$) δ 7.42 (s, 4H), 3.16 (s, 1H), 1.13 (s, 21H).
**Compound 5.** Compound 4 (1 g, 3.5 mmol) and compound 1 (1.77 g, 3.5 mmol) were dissolved in a solution of 20 ml dry THF and 10 ml (i-Pr)_2NH in a round bottom flask at room temperature. The solution was degassed for 30 min before 16.2 mg (0.014 mmol) Pd(PPh_3)_4 and 5.0 mg (0.026 mmol) of Cul were added. The resulting reaction mixture was stirred at R.T. for 24 hr. After the reaction, the solvent was removed under vacuum and the residue solid was purified by silica column with 1:1 ratio of hexane and DCM as the eluent to yield compound 5 (0.93 g, 40%). ^1H-NMR (500 MHz, CDCl_3) δ 7.67 (s, 1H), 7.44 (dd, 4H), 7.30 (s, 1H), 2.73 (t, 2H), 2.65 (t, 2H), 1.69-1.55 (m, 4H), 1.43-1.27 (m, 12H), 1.14 (s, 21H), 0.89 (m, 6H).

**Compound 6.** Compound 5 (0.8 g, 1.2 mmol) and compound A1 (0.4 g, 1.2 mmol) were dissolved in a solution of 20 ml dry THF and 10 ml (i-Pr)_2NH in a round bottom flask at room temperature. The solution was degassed for 30 min before 16.2 mg (0.014 mmol) Pd(PPh_3)_4 and 5.0 mg (0.026 mmol) of Cul were added. The resulting reaction mixture was stirred at R.T. for 24 hr. After the reaction, the solvent was removed under vacuum and the residue solid was purified by column with 1:1 ratio of hexane and DCM as the eluent to yield compound 6 (0.92 g, 88%). ^1H-NMR (500 MHz, CDCl_3) δ 8.14 (d, 1H), 8.02 (d, 1H), 7.86 (dd, 2H), 7.46 (dd, 4H), 7.37 (s, 2H), 7.34 (d, 1H), 7.22 (d, 1H), 2.81 (t, 4H), 1.72 (m, 4H), 1.49-1.21 (m, 4H), 1.15 (s, 21H), 0.90 (m, 6H). ^13C-NMR (125 MHz, CDCl_3) δ 152.72, 152.62, 142.51, 142.36, 140.85, 139.40, 132.69, 132.51, 132.21, 132.15, 131.36, 128.21, 127.87, 127.47, 127.19, 126.57, 125.83, 125.79, 125.36, 124.91, 123.50, 123.45, 122.72, 122.51, 106.83, 94.43, 94.02, 93.02, 90.46, 87.72, 34.33, 34.31, 31.93, 31.90, 30.84, 30.78, 29.42, 29.40, 22.84, 22.78, 18.83, 14.33, 14.27, 11.48.
**Compound 7.** Compound 6 (0.8 g, 0.94 mmol) was dissolved in chloroform (15 mL) and degassed for 30 min. Then, 1 mL TBAF in THF (1 M) was added and the solution was stirred for 4 h at R.T. After the reaction, the solution was washed with water and extracted with DCM (3 x 15 mL) and the organic layer was collected and dried with anhydrous sodium sulfate (Na$_2$SO$_4$). The solvent was removed under vacuum and the solid was purified by column with 1:1 ratio of hexane and DCM as the eluent to yield compound 7 (0.59 g, 91%). $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.14 (d, 1H), 8.02 (d, 1H), 7.86 (dd, 2H), 7.37 (s, 2H), 7.34 (d, 1H), 7.22 (d, 1H), 3.21 (s, 1H), 2.81 (t, 4H), 1.72 (m, 4H), 1.49-1.21 (m, 4H), 0.90 (m, 6H). $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 152.69, 152.59, 142.53, 142.37, 140.87, 139.39, 132.69, 132.53, 132.25, 132.21, 131.46, 128.19, 127.87, 127.45, 127.16, 126.55, 125.79, 125.74, 125.32, 124.88, 124.09, 122.63, 122.60, 122.04, 94.40, 93.73, 90.66, 87.79, 83.45, 79.09, 34.33, 34.29, 31.92, 31.91, 30.82, 30.76, 29.42, 29.39, 22.84, 22.77, 14.32, 14.25.

**OPE-TBT.** Compound 7 (0.4 g, 0.57 mmol) and compound 5 (0.38 g, 0.57 mmol) were dissolved in a solution of 20 ml dry THF and 10 ml (i-Pr)$_2$NH in a round bottom flask at room temperature. The solution was degased for 30 min before 16.2 mg (0.014 mmol) Pd(PPh$_3$)$_4$ and 5.0 mg (0.026 mmol) of CuI were added. The resulting reaction mixture was stirred at R.T. for 24 hr. After the reaction, the solvent was removed under vacuum and the residue solid was purified by column with 1:1 ratio of hexane and DCM as the eluent to yield compound OPE-TBT (0.36 g, 72%). $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.13 (d, 1H), 8.01 (d, 1H), 7.85 (dd, 2H), 7.52 (s, 4H), 7.46 (m, 5H), 7.38 (d, 4H), 7.34 (d, 1H), 7.20 (m, 3H), 2.82 (t, 8H), 1.72 (m, 8H), 1.49-1.21 (m, 8H), 1.15 (s, 21H), 0.90 (m, 12H). $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 152.68, 152.58, 142.51, 142.49, 142.36,
140.85, 139.38, 132.69, 132.50, 132.20, 132.15, 131.57, 131.35, 128.20, 127.86,
127.45, 127.17, 126.53, 125.80, 125.76, 125.32, 124.88, 123.48, 123.42, 122.70,
122.67, 122.64, 122.54, 106.82, 94.43, 94.07, 93.93, 93.01, 90.60, 90.43, 87.77, 34.34,
34.31, 31.93, 31.92, 31.90, 30.84, 30.80, 29.44, 29.40, 22.85, 22.79, 22.78, 18.82,
14.34, 14.27, 11.47. MS (MALDI) m/z ([M + H]^+), calculated 1216.623, found 1216.621.
CHAPTER 5
ENERGY TRANSFER IN “THROUGH-SPACE” CONJUGATED POLYMERS

Background

Light harvesting polymers, which can convert solar energy to either electrical energy or chemical energy, have drawn a lot of attention from the science community. They also show very interesting light/electro-response activities which help them find applications in areas such as light emitting diodes, optical data storage and optical limiting. Both fundamental study and application of light harvesting polymers have been focused on materials with conjugated backbones. However, polymers with interrupted conjugated backbone or conjugated side chains can be very interesting as well. They inherit many typical polymer properties, such as high mechanical strength and better stability, but their photo-optical properties resemble individual chromophores.

The [2,2]paracyclophane moiety brings two phenyl rings in close proximity to each other and enforces a cofacial overlap, which causes partial overlap of the two phenyl π-electrons. And, when incorporated into conjugated structures, interesting photophysical properties have been discovered. The main contribution of absorption comes from the “monomer state” (the structure mimics stilbenes). The emission can come from two different excited states: the “phane state” whose conjugation has contribution from the entire [2,2]cyclophane unit and the “monomer state” which only involves the stilbene structure. In [2,2]cyclophane containing oligomers and polymers, the conjugation length increases with number of repeating units, but, the conjugation is less efficient compared to fully conjugated polymers with similar structure. This special conjugation behavior has been termed “through-space” conjugation. The
[2,2]cyclophane containing polymers can be viewed as a series of stacked \( \pi \)-electron systems and is valuable for intermolecular interaction study. Traditionally, intermolecular interaction study was performed on bulk materials, such as polymer films. However, spectroscopic measurements on bulk materials do not really reveal the average status of molecules, rather the lowest energy state. In dilute solution, intermolecular interaction is minimized which is very difficult to probe.

In this chapter, a series of “through-space” conjugated polymers containing [2,2]cyclophane moieties backbone and 4,7-di(thien-2-yl)benzo[c][1,2,5]thiadiazole (TBT) end-caps were synthesized. This system is chosen because of the perfect match of the emission spectrum of polymer backbone with the absorption spectrum of the TBT and high quantum yield of both the backbone and the TBT end-caps. Energy transfer is very efficient, with dynamic and overall efficiency comparable to fully conjugated systems which proves that this type of polymers can serve as molecular wires.

Results and Discussion

Synthesis and Characterization

The molecular structures and synthesis route are outlined in Figure 5-1. 4,16-Diethynyl[2,2]paracyclophane (Monomer 1) was synthesized in three steps, starting with reaction of [2,2]paracyclophane with concentrated bromine. The resulting compound 1 was further converted to 4,16-bis[(trimethylsilyl)ethynyl][2,2]-paracyclophane (compound 2) under typical Sonogashira reaction conditions. Deprotection of compound 2 with TBAF in chloroform gave monomer 1 with high yield. Reaction of hydroquinone with n-bromooctane under basic conditions yields compound 3 which was easily converted to monomer 2 under typical iodination reaction conditions.
Figure 5.1. Molecular structures and synthesis procedures.
The same “end-capping” strategy, which was discussed in detail in Chapter 4, was applied for the synthesis of polymers and controlling the molecular weight. In order to determine the absorption and emission states of [2,2]paracyclophane containing polymers (P1-n), a fully conjugated polymer (PPE) and a model compound (OPE) have been synthesized and the detail synthetic information can be found in experimental section. The molecular weights of P1-n polymers vary from 5.8 kDa to 10.6 kDa and 23.5 kDa which corresponds to 9, 19 and 39 repeat units, respectively. The molecular weights of the P0 and the PPE are 12 kDa and 61.2 kDa, respectively, which correspond to 20 and 136 repeat units. All polymers should reach saturated conjugation, for the maximum conjugation length of [2,2]paracyclophane containing polymers is 9 repeating units while that of PPE is about 9-10.\textsuperscript{191}

![Increasing molecular weight](image)

Figure 5-2. GPC trace of polymers. P1-9 (black square), P1-19 (red circle), P1-39 (blue triangle) and P0 (dark cyan down-triangle).

**Optical Properties in Solution**

The absorption and emission spectra of the P0, PPE and OPE were plotted in Figure 5-3. The main absorption band of P0 is at 385 nm which is about 30 nm blue-shifted compared to that of PPE (417 nm), indicating the effective conjugation length is
shorter in P0 and the “through-space” conjugation is less efficient than the completely delocalized π-electrons in fully conjugated systems. However, the partially overlapped π-electron in [2,2]paracyclophane unit does contribute to the conjugation, for the absorption maximum of P0 is about 20 nm red-shifted compared to the OPE model compound, whose absorption maximum is at 364 nm. The emission maximum of P0 resembles that of OPE, probably due to the fact that the state containing cyclophane core has higher energy. Thus, the emission does not involve the “phane state” which is consistent with literature report.\(^{191}\)

Figure 5-3. Steady state optical properties of P0, PPE and OPE in THF. A) Absorption and B) emission spectra of P0, PPE and OPE. P0 (black square), PPE (red circle) and OPE (blue triangle). Excitation wavelength has been set at the absorption maximum for each sample.

The steady state absorption spectra of P1-n and P0 at the same concentration (50 µM, based on repeat units) were plotted in Figure 5-3 (A) and normalized at absorption maximum (~387 nm). P0, which does not contain the TBT moiety, has no absorption beyond 425 nm. An absorption band centered at 470 nm shows up in the spectra of P1-n series and increases with decreasing molecular weight, which is consistent with TBT content (Table 5-1). But, compared to the dominating absorption
band 387 nm which is attributed to backbone absorption, the 470 nm band is still less intense. Since the effective conjugation length of [2,2]paracyclophane containing polymers in solution is limited to be around 9 repeating units, the absorption maximum of the backbone remains essentially the same.\textsuperscript{191}

![Figure 5-4. Steady state absorption and emission of P1-n and P0. A) Absorption and B) emission spectra of P1-9 (black square), P1-19 (red circle), P1-39 (blue triangle) and P0 (dark cyan down-triangle).]

Steady state emission spectra of P1-n polymers (50 μM, based on repeat units) are plotted in Figure 5-4 (B) and normalized according to their quantum yield, respectively. In addition to the polymer backbone emission (~420 nm), the P1-n polymers have an additional peak at about 600 nm which is attributed to the TBT emission. The intensity of the backbone emission (~420 nm) decreases with increasing polymer chain-length while the 600 nm peak increases, which indicates more efficient energy transfer from the polymer backbone to the end TBT acceptors. Compared to the P0 polymer, more than 80% of the donor emission (420 nm) in the P1-39 is quenched and the quenching efficiency of P1-19 is slightly higher than P1-39. However, the quenching efficiency reaches ~95% in the P1-9 polymer. The overall energy transfer efficiency was calculated using the quantum yield of emission
from 380 nm to 525 nm (the donor emission) over that of the P0 and the trend is clear that energy transfer efficiency decreases with increasing polymer chain-length.

The trend of changing energy transfer efficiency is compared with the changing of fluorescence lifetime at 420 nm which decreases with molecular weight: average lifetime at 420 nm is about 910 ps, 491 ps, 308 ps and 163 ps for P0, P1-39, P1-19 and P1-9, respectively. The decreasing in donor lifetime indicates more efficient quenching which is caused by energy transfer to the acceptors. Compared to the fully conjugated systems discussed in the Chapter 4, the presence of acceptors has a more significant impact on the lifetime of donors. At the same time, the lifetime of acceptor remains untouched.

<table>
<thead>
<tr>
<th>TBT content mol%</th>
<th>Lifetime at 420 nm (ps)</th>
<th>Lifetime at 600 nm (ns)</th>
<th>Fluorescence QY % a</th>
<th>Energy transfer efficiency b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Donor (400-525 nm)</td>
<td>Acceptor (525-700 nm)</td>
</tr>
<tr>
<td>P1-9</td>
<td>18.2</td>
<td>163</td>
<td>3.08</td>
<td>4.41</td>
</tr>
<tr>
<td>P1-19</td>
<td>9.5</td>
<td>308</td>
<td>3.20</td>
<td>11.9</td>
</tr>
<tr>
<td>P1-39</td>
<td>4.9</td>
<td>491</td>
<td>3.22</td>
<td>14.3</td>
</tr>
<tr>
<td>P0</td>
<td>0</td>
<td>910</td>
<td>N.A.</td>
<td>72.6</td>
</tr>
</tbody>
</table>

a With anthracene as quantum yield standard, $\varphi = 0.27$ in ethanol at room temperature. b Energy transfer efficiencies ($\eta$) were calculated as: $\eta = 1 - \varphi(P1-n 400-525nm)/\varphi(P0)$, in which $\varphi(P0)$ was the fluorescence quantum yield of donor-only polymer.

Summary and Future Work

A series of “through-space” conjugated polymers were synthesized and the energy transfer properties were investigated. Polymers feature backbones containing the [2,2]paracyclophane moieties, which serve the energy donor, and the TBT end-caps, which serve as the energy acceptors. Polymers have different chain length which were synthesized by applying the “end-capping” strategy in Palladium catalyzed Sonogashira polycondensation reactions. Energy transfer from donor to acceptor was
investigated by fluorescence emission and time-correlated single photon counting (TCSPC). Although the system does not have a completely delocalized π-system along the polymer backbone, very efficient energy transfer was still observed. In order to further investigate the energy transfer kinetics, ultrafast transient absorption study will be conducted on the polymers.

Experiments and Materials

Materials

Unless specified, all compounds and solvents were purchased from commercial sources (Aldrich, Acros, Strem Chemicals, et al) and used without further purification. For all palladium-catalyzed reactions, the solvents were carefully degassed with argon for at least 30 min. $^1$H and $^{13}$C-NMR spectra were recorded on either Inova2 (500 MHz) or Varian Gemini-300 spectrometer (300 MHz). The chemical shifts (δ) are reported in parts per million (ppm) using the residual solvent signals as internal standards.

Instrumentation

$^1$H and $^{13}$C NMR spectra were measured on a Mercury 300, a Gemini 300, or an Inova 500. Chemical shifts were referenced to the residual solvent peaks. High resolution mass spectrometry was performed on a Bruker APEX II 4.7 T Fourier Transform Ion Cyclotron Resonance mass spectrometer (Bruker Daltonics, MA). Gel Permeation Chromatography (GPC) data was collected on a system composed of a Shimadzu LC-6D pump, an Agilent mixed-D column, and a Shimadzu SPD-20A photodiode array (PDA) detector, with THF as eluent at 1 ml/min flow rate. The system was calibrated against linear narrow dispersed polystyrene standards in THF.

UV-visible absorption measurements were carried out on a Shimadzu UV-1800 dual beam absorption spectrophotometer. Photoluminescence spectra were recorded
on a spectrofluorimeter from Photon Technology International (PTI). Photoluminescence lifetimes were obtained by time-correlated single photon counting (TCSPC) using a Fluo Time 100 (Picoquant), and excitation was provided using a PDL 800-B Picosecond Pulsed Diode Laser (375 nm).

**Synthetic Procedures**

Tetrakis(triphenyl phosphine) palladium (Pd(PPh₃)₄) was from Strem Chemical and triisopropylsilyl acetylene (TIPSA) was from TCI. Copper (I) iodide (CuI), diisopropylamine ((i-Pr)₂NH), tetrahydrofuran (THF) and all other chemicals were purchased from either Sigma-Aldrich or Fisher Chemicals. All reagents were used without further purification unless specified.

4-(5-ethynylthiophen-2-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (A₁), 4-(5-iodothiophen-2-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (A₂), 4,16-diethynyl[2,2]paracyclophane (Monomer 1) and 1,4-diiodo-2,5-dioctylbenzene (Monomer 2) were synthesized according to literature. Iodobenzene and ethynylbenzene were purchased from Sigma.

**General Procedure for the synthesis of P1-n.** Monomer 1 (84.6 mg, 0.17 mmol), Monomer 2 (50.0 mg, 0.17 mmol) and A₁ (0.1-0.3 molar ratio) were dissolved in a solution of 20 mL dry THF and 10 mL piperidine in a round bottom flask at room temperature. The solution was degassed for 30 min before 16.2 mg (0.014 mmol) Pd(PPh₃)₄ and 5.0 mg (0.026 mmol) of CuI were added. The resulting reaction mixture was heated to 45 °C for 24 hr. Then, A₂ (0.1-0.3 molar ratio) was added to the solution and the reaction was allowed for another 12 h. The solution was passed through a short silica gel column and the eluent was collected and concentrated. The concentrated solution was poured into 100 mL of methanol and the polymer precipitated out.
immediately. This process was repeated twice. Last, the precipitate was collected and
dried under vacuum. Typical yield of this reaction is 50-70%.

**P1-9.** GPC (THF, polystyrene standard): $M_n = 5.8$ kDa, $M_w = 9.2$ kDa, PDI = 1.59.
$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 8.15 (d), 8.05 (d), 7.90 (s), 7.49 (d), 7.38 (d), 7.23 (m),
7.16-7.06 (m, 4H), 6.65 (m, 4H), 6.54 (m, 4H), 4.14 (br, 4H), 3.82 (br, 2H), 3.35 (br, 2H),
3.05-2.93 (br, 4H), 1.96 (br, 4H), 1.61-1.25 (br, 40H), 0.88 (br, 6H).

**P1-19.** GPC (THF, polystyrene standard): $M_n = 10.6$ kDa, $M_w = 21.0$ kDa, PDI = 1.97.
$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 8.15 (d), 8.05 (d), 7.90 (s), 7.49 (d), 7.38 (d), 7.23
(m), 7.16-7.06 (m, 4H), 6.65 (m, 4H), 6.54 (m, 4H), 4.14 (br, 4H), 3.82 (br, 2H), 3.35 (br,
2H), 3.05-2.93 (br, 4H), 1.96 (br, 4H), 1.61-1.25 (br, 40H), 0.88 (br, 6H).

**P1-39.** GPC (THF, polystyrene standard): $M_n = 23.5$ kDa, $M_w = 53.0$ kDa, PDI = 2.25.
$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 8.15 (d), 8.05 (d), 7.90 (s), 7.49 (d), 7.38 (d), 7.23
(m), 7.16-7.06 (m, 4H), 6.65 (m, 4H), 6.54 (m, 4H), 4.14 (br, 4H), 3.82 (br, 2H), 3.35 (br,
2H), 3.05-2.93 (br, 4H), 1.96 (br, 4H), 1.61-1.25 (br, 40H), 0.88 (br, 6H).

**P0. Monomer 1** (84.6 mg, 0.17 mmol), **Monomer 2** (50.0 mg, 0.17 mmol) and
**B1** (1.7 mg, 0.017 mmol) were dissolved in a solution of 20 mL dry THF and 10 mL
piperidine in a round bottom flask at room temperature. The solution was degased for
30 min before 16.2 mg (0.014 mmol) Pd(PPh$_3$)$_4$ and 5.0 mg (0.026 mmol) of Cul were
added. The resulting reaction mixture was heated to 45 °C for 24 hr. Then, **B2** (3.4 mg,
0.017 mmol) were added to the solution and the reaction was allowed for another 12 h.
The solution was flashed through a silica gel column and the eluent was collected and
concentrated. The concentrated solution was poured into 100 mL of methanol and the
polymer precipitated out immediately. This process was repeated twice. Last, the precipitate was collected and dried under vacuum. Typical yield of this reaction is 65%

**P0.** GPC (THF, polystyrene standard): $M_n = 12.2$ kDa, $M_w = 23.4$ kDa, PDI = 1.83. $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.16-7.06 (m, 4H), 6.65 (m, 4H), 6.54 (m, 4H), 4.14 (br, 4H), 3.82 (br, 2H), 3.35 (br, 2H), 3.05-2.93 (br, 4H), 1.96 (br, 4H), 1.61-1.25 (br, 40H), 0.88 (br, 6H).

**PPE.** 1,4-Diethynylbenzene (21.4 mg, 0.17 mmol) and **Monomer 2** (50.0 mg, 0.17 mmol) were dissolved in a solution of 20 mL dry THF and 10 mL piperidine in a round bottom flask at room temperature. The solution was degassed for 30 min before 16.2 mg (0.014 mmol) Pd(PPh$_3$)$_4$ and 5.0 mg (0.026 mmol) of CuI were added. The resulted reaction mixture was heated to 45 °C for 24 hr. The solution was flashed through a silica gel column and the eluent was collected and concentrated. The concentrated solution was poured into 100 ml of methanol, and the polymer precipitated out immediately. This process was repeated twice. Last, the precipitate was collected and dried under vacuum. Typical yield of this reaction is 80%.

**PPE.** GPC (THF, polystyrene standard): $M_n = 61.2$ kDa, $M_w = 126$ kDa, PDI = 2.06 $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.51 (br, 4H), 7.02 (br, 2H), 4.04 (br, 4H), 1.86 (br, 4H), 1.55 (br, 4H), 1.20-1.42 (m, 16H), 0.88 (br, 6H).

**OPE.** Ethynylbenzene (34.7 mg, 0.34 mmol) and **Monomer 2** (50.0 mg, 0.17 mmol) were dissolved in a solution of 20 mL dry THF and 10 mL piperidine in a round bottom flask at room temperature. The solution was degassed for 30 min before 16.2 mg (0.014 mmol) Pd(PPh$_3$)$_4$ and 5.0 mg (0.026 mmol) of CuI were added. The resulting reaction mixture was heated to 45 °C for 24 hr. after the reaction, the solvent was
removed under vacuum and the residual solid was purified by column chromatography to yield OPE (79.8 mg, 88%). $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.54 (d, 4H), 7.35 (m, 6H), 7.02 (s, 2H), 4.04 (t, 4H), 1.85 (m, 4H), 1.53 (m, 4H), 1.22-1.45 (m, 16H), 0.87 (t, 6H).

$^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$ 153.61, 131.58, 128.30, 128.24, 123.50, 117.02, 114.02, 94.83, 85.98, 69.69, 31.84, 29.42, 29.40, 29.33, 26.11, 22.69, 14.10.
CHAPTER 6
CONCLUSION

Conjugated polymers are among the most promising materials for applications in fields of organic photoelectronic devices. The investigation of this category of materials attracts a lot of attention from the science community. The studies detailed in this dissertation focus on the investigation of molecular weight effects on energy/electron transfer efficiency in conjugated polymers and the application in dye-sensitized solar cells.

In Chapter 2, two families of conjugated polyelectrolytes (CPEs) featuring the same backbone but different side chain linkages were synthesized and their application as light harvesting materials for dye-sensitized solar cells (DSSCs) was investigated. CPEs bearing an oxygen linkage (-O-) (P1-O-n) are more likely to aggregate in solution and, the aggregate status depends strongly on the molecular weights. In contrast, there is no obvious evidence showing that CPEs with methylene (-CH\textsubscript{2}-) (P2-C-n) linkage aggregate in solution. In addition, the two families of polymer also show different behaviors in adsorbing onto mesoporous TiO\textsubscript{2} films. The resulting films show different overall cell efficiency when applied in DSSCs. The P1-O-n TiO\textsubscript{2} films show strong chain length dependence in the absorption and, therefore, the cell performance. In contrast, little difference can be observed in the P2-C-n TiO\textsubscript{2} films. Once the aggregated P1-O-n polymers adsorbed onto the surface of TiO\textsubscript{2} films, they block the pores in the film and prevent more materials from penetrating into the inside layer. As a result, it slows down the kinetics of dye-adsorbing and total amount of dyes that are absorbed which ultimately lowers the overall cell efficiency.
In Chapter 3, a series of different chain length poly(p-phenylene-ethynylene)s (PPEs) end-capped by naphthalene diimide derivatives were synthesized. When polymers are excited, electrons transfer from the PPE backbones to the naphthalene diimide end-caps, and the polymer fluorescence is quenched. The overall quenching efficiency increases with decreasing polymer chain length as evidenced by fluorescence quantum yield measurements. And, the charge recombination rate is investigated by femtosecond transient absorption. The charge recombination rate also depends strongly on the chain length: as the chain length increases, the charge recombination rate decreases. In addition, the formation of the PPE triplet absorption was detected in the polymers. The overall triplet absorption intensity increases with molecular weights. More careful investigation is needed to understand the origin of the triplet formation.

In Chapter 4, a series of different chain length poly(p-phenylene-ethynylene)s (PPEs) end-capped by 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (TBT) were synthesized. Under light irradiation, energy transfer from the PPE to TBT occurs mainly via the Forster Resonance Energy Transfer (FRET) mechanism. The overall energy transfer efficiency increases with decreasing molecular weight. The overall lifetime of PPE backbones, which is the donor, decreases with molecular weight while the lifetime of acceptors, which are TBT, remains constant. Ultra-fast transient absorption study shows that the energy transfer happens in pico-second time scale for all the polymers and the lower molecular weight samples show faster decay in the initial stage. An interesting trend in steady state fluorescence anisotropy was also discovered that fluorescence anisotropy in the donor emission is significantly higher than that of acceptors. It has been proposed that polymers are not perfect rigid-rods, but are “worm-
like” structures in solution which consist different rigid conjugation segments. The segments can have some degree of free rotation which slows down the energy transfer processes.

In Chapter 5, a series of different chain length “through-space” conjugated polymers with [2.2]paracylophane moieties end-caped with TBT were synthesized. Despite the fact that the conjugation is partially interrupted, very efficient energy transfer was observed and the overall energy transfer efficiency decreased with increasing molecular weight.
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BIOGRAPHICAL SKETCH

Zhenxing Pan was born in 1987 in Sihong, Jiangsu, China, where he grew up and finished junior high school. At the age of 15, he went to Nanjing and stayed there for 3 years for senior high school. Then, at the age of 18, he attended Soochow University and received a bachelor of engineering degree in material science and engineering in the year of 2010. Immediately after graduation, he continued his graduate school work at the University of Florida, pursuing a Doctor of Philosophy degree in chemistry. Under the supervision of Dr. Kirk S. Schanze, he focused his research on conjugated polymers and optoelectronic devices. After his graduation, he will go back to China and pursue a career in chemical industry.