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Breaking the Barriers of All-Polymer Solar Cells: Solving Electron Transporter And Morphology Problems

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BREAKING THE BARRIERS OF ALL-POLYMER SOLAR CELLS: 
SOLVING ELECTRON TRANSPORTER AND MORPHOLOGY PROBLEMS

A Dissertation Presented

by

NAGARJUNA GAVVALAPALLI

Submitted to the Graduate School of the 
University of Massachusetts Amherst in partial fulfillment 
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DEDICATION

To my parents, brother and my beloved wife Nagamani
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A Ph.D. program is a long journey that requires a strong commitment, perseverance, hard work and self-motivation to succeed. This journey would not have been successful without the support and encouragement from many people. I would like to take this opportunity to express my sincere gratitude and recognize those who have helped and inspired me to come this far.

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First and foremost, I wish to express my sincere respect and gratitude to my advisor Prof. D. Venkataraman for making me realize the true meaning of Ph. D. and turning my Ph. D. into a meaningful one instead of just another degree. His dedication, passion and excitement towards science are always an inspiration to me. He taught me how to pick the right problem, how to foresee a problem and the importance of quality over quantity in science. He worked with me to improve my communication and presentation skills. He gave the freedom to design and pursue new projects. He nurtured me to evolve into an independent scientist over my Ph. D. career. His unwavering support and guidance both in research and other professional decisions has been immensely helpful and I greatly appreciate it.

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ABSTRACT

BREAKING THE BARRIERS OF ALL-POLYMER SOLAR CELLS:
SOLVING ELECTRON TRANSPORTER AND MORPHOLOGY PROBLEMS

SEPTEMBER 2012

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All-polymer solar cells (APSC) are a class of organic solar cells in which hole and electron transporting phases are made of conjugated polymers. Unlike polymer/fullerene solar cell, photoactive material of APSC can be designed to have hole and electron transporting polymers with complementary absorption range and proper frontier energy level offset. However, the highest reported PCE of APSC is 5 times less than that of polymer/fullerene solar cell. The low PCE of APSC is mainly due to: i) low charge separation efficiency; and ii) lack of optimal morphology to facilitate charge transfer and transport; and iii) lack of control over the exciton and charge transport in each phase. My research work is focused towards addressing these issues.

The charge separation efficiency of APSC can be enhanced by designing novel electron transporting polymers with: i) broad absorption range; ii) high electron mobility; and iii) high dielectric constant. In addition to with the above parameters chemical and electronic structure of the repeating unit of conjugated polymer also plays a role in charge separation efficiency. So far only three classes of electron transporting polymers, CN substituted PPV, 2,1,3-benzothiadiazole derived polymers and rylene diimide derived
polymers, are used in APSC. Thus to enhance the charge separation efficiency new
classes of electron transporting polymers with the above characteristics need to be
synthesized. I have developed a new straightforward synthetic strategy to rapidly
generate new classes of electron transporting polymers with different chemical and
electronic structure, broad absorption range, and high electron mobility from readily
available electron deficient monomers.

In APSCs due to low entropy of mixing, polymers tend to micro-phase segregate
rather than forming the more useful nano-phase segregation. Optimizing the polymer
blend morphology to obtain nano-phase segregation is specific to the system under study,
time consuming, and not trivial. Thus to avoid micro-phase segregation, nanoparticles of
hole and electron transporters are synthesized and blended. But the PCE of nanoparticle
blends are far less than those of polymer blends. This is mainly due to the: i) lack of
optimal assembly of nanoparticles to facilitate charge transfer and transport processes;
and ii) lack of control over the exciton and charge transport properties within the
nanoparticles. Polymer packing within the nanoparticle controls the optoelectronic and
charge transport properties of the nanoparticle. In this work I have shown that the solvent
used to synthesize nanoparticles plays a crucial role in determining the assembly of
polymer chains inside the nanoparticle there by affecting its exciton and charge transport
processes. To obtain the optimal morphology for better charge transfer and transport, we
have also synthesized nanoparticles of different radius with surfactants of opposite
charge. We propose that depending on the radius and/or Coulombic interactions these
nanoparticles can be assembled into mineral structure-types that are useful for
photovoltaic devices.
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A.4 Long time PL decay and power law fits for nanoparticles made from 0.5 wt% P3HT in a) CHCl₃; b) toluene; c) toluene/CHCl₃ (1:4) and d) 0.05 wt% P3HT in toluene/CHCl₃ (1:4). ................................................................. 183

A.5 Size correlated fluorescence polarization anisotropy of P3HT nanoparticles with 440 nm laser excitation. (a) PL image (2 seconds exposure), and (b) corresponding surface height image of the same region, indicating significant heterogeneity in particle size. (c) Excitation polarization anisotropy trace for selected particles, I, II, and III highlighted in (a) and (b). (d) Shows a scatter plot correlating linear excitation anisotropy parameter, M, with particle size. ......................... 185

A.6 Fluorescence emission spectra of P3HT nanoparticles made from P3HT 0.5 wt% and 1mM SDS in a)CHCl₃; b)Toluene; c) toluene/CHCl₃ (4:1); and d) P3HT 0.05 wt% and 1mM SDS in toluene/CHCl₃ (4:1) under 440 nm excitation. Inset: steady state polarization anisotropy of the same sample. ................................................................. 186
CHAPTER 1

INTRODUCTION TO ALL-POLYMER SOLAR CELLS AND REASONS FOR THEIR LOW POWER CONVERSION EFFICIENCY

1.1 Introduction

There has been a surge in global energy demand with the advancement in technology, economic growth, and increasing growth in population. Harvesting solar energy is one of the cleaner ways to meet the world’s energy demand. Solar energy received by the earth in one hour from the Sun is more than the total energy consumption across the planet in one year.\(^1\)\(^-\)\(^4\) Solar cells convert light into electricity and it is one of the ways to harvest solar energy. Depending on the active material used to harvest light, solar cells can be classified into two types - inorganic and organic solar cells. Most of the inorganic solar cells are either Silicon based and they dominate the solar cell market.\(^5\) The efficiency of multijunction inorganic solar cells in lab-scale devices is as high as 43% and the efficiency of commercially available Silicon based solar cell is 16-20%.\(^5\)\(^,\)\(^6\) Compared to inorganic solar cells, organic solar cells are flexible, low-cost and easily solution processable; making large-scale device fabrication easier and economical compared to inorganic solar cells. Moreover, the physical and chemical properties of organic polymeric materials can be tailored to meet the desired needs.\(^7\)\(^-\)\(^{12}\) Although organic solar cells have several interesting features compared to inorganic solar cells, the efficiency of organic solar cells is lower than inorganic solar cells. A lot of research over the past two decades is focused to enhance the efficiency of organic solar cells by synthesizing new active materials and employing new active layer fabrication
**Figure 1.1** Energy level diagram of an organic heterojunction under illumination. IP(D) and EA(A) denote the ionization potential (HOMO level energy) of the hole transporter (HT) layer and electron affinity (LUMO level energy) of the electron transporter (ET) layer, respectively. Absorption of photons with average photon energy larger than the optical band gap on either side of the heterojunction (step 1) is followed by thermalization and the formation of excitons (step 2). Excitons diffuse to the heterojunction (step 3) where they dissociate and transfer an electron (hole) into the ET (HT) layer (step 4). The difference between IP (D) and EA (A) determines the maximum open circuit voltage (Voc) under illumination. The arrows denote the energy offsets between the HOMO (LUMO) energies (Reprinted from reference 10 with permission from Royal Society of Chemistry).

Techniques. The active material of organic solar cells comprises of hole and electron transporters to generate and move the charges. Depending on the type of hole and electron transporting materials, organic solar cells can be subdivided into three types: (i) polymer/fullerene; (ii) small molecule/small molecule; and (iii) polymer/polymer solar cells. In the same order, the highest power conversion efficiency (PCE) reported for each type of solar cells is 10%, 7%, and 2.3% respectively. Thanks to the enormous
amount of active research that has been carried out in polymer/fullerene solar cells, their PCEs in lab-scale devices are now over 10%. But in order to compete with the inorganic solar cells and for successful commercialization of organic solar cells, the PCE of organic solar cells has to be increased further and should be reproducible in large scale devices.⁷

The working principle of an organic solar cell is depicted in Figure 1.1. When the active material of an organic solar cell absorbs sunlight it creates an exciton, a bound electron-hole pair. These electron-hole pairs (excitons) either recombine to emit light or heat or, in a more useful process, dissociate and move to their respective electrodes to generate photovoltaic current. In order to achieve higher efficiency in solar cells, the absorption spectrum of the active material(s) should overlap with the solar emission spectrum (AM 1.5) and the following requirements have to be met: (a) hole and electron transporters with optimal frontier energy levels should be assembled into structures such that heterojunctions should exist at lengths scales of a few nanometers for efficient charge separation, (b) continuous phases of charge-carrier transporters should exist for efficient charge transport, and (c) the active medium (i.e., the thickness of the OPV device) should have a characteristic length scale of micrometers to match the typical photon capture distance.¹⁰ In polymer/fullerene solar cells, the polymer plays a key role in absorbing sunlight as well as transporting holes while fullerene transports electrons. Thus the challenge in polymer/fullerene solar cells is to develop a polymeric hole transporting material that has broad absorption in the solar spectrum with appropriate frontier orbital energy levels for optimal charge transfer with respect to fullerene. Although the polymer is critical to absorb light and generate charges, the success of polymer/fullerene solar cells can be mainly attributed to fullerene. Fullerene and its
derivatives have: i) high electron mobility, ii) multidimensional charge transport; and iii) high dielectric constant for efficient charge separation; iv) can diffuse into grain boundaries and amorphous regions of hole transporter domain; and v) aggregate into nanocrystalline domains for better electron transport.

The hole transporter in polymer/fullerene solar cells should meet these stringent requirements for high PCE: i) hole transporting polymers should have \( \sim 0.4 \) eV LUMO energy level offset with fullerene for efficient charge transfer; energy offset lower than 0.4 eV hinders charge separation while higher LUMO energy offset decreases PCE; and ii) the energy difference between HOMO of hole transporter and LUMO of electron transporter should be high for high open circuit voltage and PCE (along with maintaining the required LUMO energy level offset). Moreover since fullerene has a very narrow absorption range, the hole transporting polymer should have broad absorption range. Thus, designing new hole transporting materials that meet all these stringent requirements is difficult and the number of hole transporting materials that satisfy all these requirements are scarce.

![Chemical structures of hole transporters discussed in this chapter.](image.png)

**Figure 1.2** Chemical structures of hole transporters discussed in this chapter.
In polymer/polymer solar cells an electron transporting polymer is used instead of fullerene in the active layer, hence the name all-polymer solar cells (APSCs). Compared to polymer/fullerene solar cells, APSCs have several advantages such as: i) hole and electron transporting polymers with complementary absorption range can be used to achieve broad absorption range; ii) electron transporting polymer with suitable energy levels offset to that of hole transporter can be selected to obtain efficient charge transfer.

Figure 1.3 Chemical structures of electron transporters discussed in this chapter.
Table 1.1 Type of hole and electron transporting polymers, absorption range, difference in frontier energy levels and photovoltaic metrics of various all-polymer solar cells.

<table>
<thead>
<tr>
<th>HT-Polymer:</th>
<th>Type of HT Polymer</th>
<th>Type of ET Polymer</th>
<th>Device Type</th>
<th>HT+ET absorption range</th>
<th>Band gap</th>
<th>$^1\Delta$</th>
<th>$^2\Delta$</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
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*indicates derivative polymers; HT = hole transporter; ET = electron transporter; $^1\Delta = \text{LUMO}_{ET} - \text{HOMO}_{HT}$; $^2\Delta = \text{LUMO}_{HT} - \text{LUMO}_{ET}$. 
Table 1.1 continued

<table>
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<tr>
<th>HT-Polymer: ET-Polymer</th>
<th>Type of HT Polymer</th>
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*indicates derivative polymers; HT = hole transporter; ET = electron transporter; $^1\Delta = \text{LUMO}^\text{ET} - \text{HOMO}^\text{HT}$; $^2\Delta = \text{LUMO}^\text{HT} - \text{LUMO}^\text{ET}$. 


Table 1.1 continued

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<td>300 - 650</td>
<td>1.91</td>
<td>1.41</td>
<td>0.88</td>
<td>0.1</td>
<td>0.71</td>
<td>0.27</td>
<td>0.02</td>
<td>ref&lt;sup&gt;36&lt;/sup&gt;</td>
</tr>
<tr>
<td>P2:DOCN-PPV</td>
<td>PT1</td>
<td>CN-PPV</td>
<td>Blend</td>
<td>300 - 650</td>
<td>1.91</td>
<td>1.33</td>
<td>0.72</td>
<td>0.53</td>
<td>0.98</td>
<td>0.29</td>
<td>0.15</td>
<td>ref&lt;sup&gt;36&lt;/sup&gt;</td>
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<tr>
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<td>CN-PPV</td>
<td>Blend</td>
<td>300 - 650</td>
<td>1.91</td>
<td>1.31</td>
<td>0.69</td>
<td>1.78</td>
<td>0.85</td>
<td>0.29</td>
<td>0.44</td>
<td>ref&lt;sup&gt;36&lt;/sup&gt;</td>
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<tr>
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<td>PPV</td>
<td>CN-PPV</td>
<td>Blend</td>
<td>300 - 610</td>
<td>2.03</td>
<td>1.81</td>
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<td>1.3</td>
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<td>0.75</td>
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<tr>
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<td>P3AT</td>
<td>NDI</td>
<td>Blend</td>
<td>300 -1050</td>
<td>1.18</td>
<td>---</td>
<td>---</td>
<td>2.43</td>
<td>0.63</td>
<td>0.7</td>
<td>1.1</td>
<td>ref&lt;sup&gt;31&lt;/sup&gt;</td>
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<tr>
<td>M3EH-PPV:CN-ether-PPV</td>
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<td>CN-PPV</td>
<td>Bilayer</td>
<td>300 - 650</td>
<td>1.91</td>
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<td>3.12</td>
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<td>CN-PPV</td>
<td>Blend</td>
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<td>CN-PPV</td>
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<td>Bilayer</td>
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<td>Bilayer</td>
<td>300 - 850</td>
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<td>0.9</td>
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<td>0.17</td>
<td>ref&lt;sup&gt;40&lt;/sup&gt;</td>
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<tr>
<td>PQT-OP:CN-PPV</td>
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<td>CN-PPV</td>
<td>Bilayer</td>
<td>---</td>
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<td>---</td>
<td>2.43</td>
<td>1.18</td>
<td>0.39</td>
<td>1.12</td>
<td>ref&lt;sup&gt;40&lt;/sup&gt;</td>
</tr>
<tr>
<td>PQT-DD:CN-PPV</td>
<td>P3AT</td>
<td>CN-PPV</td>
<td>Bilayer</td>
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<td>---</td>
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<td>1.2</td>
<td>0.38</td>
<td>0.69</td>
<td>ref&lt;sup&gt;40&lt;/sup&gt;</td>
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</table>

*indicates derivative polymers; HT = hole transporter; ET = electron transporter; $^1\Delta$ = LUMO<sup>ET</sup>-HOMO<sup>HT</sup>; $^2\Delta$ = LUMO<sup>HT</sup>-LUMO<sup>ET</sup>. 
separation, high open circuit voltage and PCE. In APSC, unlike fullerene in polymer/fullerene blend, since both hole and electron transporting polymers absorb light for efficient charge generation, the electron transporting polymer should also form nanodomains. The active research in the area of polymer/fullerene solar cells in the past two decades has mainly focused on developing low band gap hole transporting polymers and much less attention has been paid on developing electron transporting polymers. Thus, there are only a few reports on the design rules and synthesis of electron transporting polymers. Knowledge generated by studying the photovoltaic metrics, charge transport and photophysics properties of known APSC devices fabricated from various electron transporting polymers has been useful to understand the: i) required characteristics for electron transporting polymers for efficient PCE; and ii) the optimal morphology for efficient APSC. Based on these learning’s, a novel and apt approach can be designed to synthesize and assemble the electron transporting polymers for efficient APSC. PCE of APSCs reported so far in the literature is shown in Figure 1.4 and the values are tabulated in Table 1.1. Chemical structures of the polymers discussed in this

![Figure 1.4](image.png)

**Figure 1.4** Power conversion efficiencies (PCE) of all-polymer solar cells reported in literature a) based on the type of electron transporting polymer; b) based on the type of hole and electron transporting polymer.
chapter are shown in Figure 1.2 and Figure 1.3.

1.2 Charge Transfer, Separation and Transport

1.2.1 Importance of High Charge Transport

The efficiency of APSCs is mainly limited by charge separation and collection.\textsuperscript{17, 24, 25} There is a linear dependence of PCE on the short circuit current density in APSC (Figure 1.5). The efficiency of charge carrier extraction depends on the charge carrier mobility of polymers.\textsuperscript{24, 25, 28} The importance of high electron mobility can be clearly evidenced by comparing the electron mobilities of MDMO-PPV/PCBM blend with MDMO-PPV/PCNEPV blend.\textsuperscript{42, 43} The optimized photoconversion efficiency of MDMO-PPV/PCNEPV and MDMO-PPV/PCBM blend are 0.75% and 2.5%, respectively. Even though MDMO-PPV/PCNEPV blend exhibited large absorption range in solar spectrum, required LUMO offset (0.5 eV) for electron transfer and high open circuit voltage (1.3-1.5 V) its efficiency is lower than MDMO-PPV/PCBM blend. To understand the reason for the observed higher efficiency of MDMO-PPV/PCBM blend compared to MDMO-PPV/PCNEPV blend, the photogeneration and charge transport mechanism in MDMO-PPV/PCNEPV blend are studied. The hole and electron mobilities for MDMO-
PPV/PCBM blend are 1.4x10^{-8} \text{ m}^2/\text{Vs} and 2.0x10^{-7} \text{ m}^2/\text{Vs} and for MDMO-PPV/PCNEPV blend are 5x10^{-10} \text{ m}^2/\text{Vs} and 6x10^{-11} \text{ m}^2/\text{Vs}, respectively. The electron mobility of MDMO-PPV/PCBM blend is 4 orders of magnitude higher than MDMO-PPV/PCNEPV blend. The high electron mobility of PCBM domains in the blend enhances the initial separation distance between charges by delocalizing and moving the charges quickly, leading to higher PCE. Whereas in MDMO-PPV/PCNEPV blend, the geminate recombination of bound electron-hole pair is high due to low as well as trap-limited electron mobility leading to low PCE.

Enhancement in PCE due to increase in hole mobility is also known. For example, PCE of P3HT/F8TBT blend could be enhanced from 0.14% to 1.2% by annealing the blend \(^{44}\) (see Figure 1.7 for F8TBT chemical structure). The enhancement in PCE is attributed to the increase in hole mobility in P3HT phase due to annealing. The charge mobility studies on the blend before and after annealing indicated an order of magnitude increase in hole mobility of P3HT post annealing. The hole mobility of P3HT in the blend before and after annealing is 1.8x10^{-6} and 1.7x10^{-5} \text{ cm}^2/\text{Vs}, respectively. The hole mobility of annealed P3HT/F8TBT blend is comparable to that of as spun pristine P3HT films, indicating that the order of P3HT in the blend is similar to that of as spun P3HT pristine films. In general the order in P3HT thin films is reflected in the optical absorption spectrum of thin film. The vibronic features in the absorption spectrum of P3HT are representative of the order in thin films. The thin film absorption spectrum of annealed blend, unlike as spun blend, exhibits vibronic features similar to that of pristine P3HT, indicating that P3HT chains in the annealed blend are of same order as pristine P3HT. Unlike P3HT, F8TBT is amorphous and showed no enhancement in mobility with
annealing. Moreover, the enhancement in both fill factor and charge collection efficiency in P3HT/F8TBT blend after annealing is an indicative of the increase in geminate pair separation efficiency due to enhancement in mobility.

In general rylene diimide derived small molecules exhibit high electron mobilities, however their absorption range is not broad and it is difficult to make thin films of small molecules for solar cell applications. Thus to enhance the PCE of APSCs rylene diimide is copolymerized with many donor monomers to generate donor-acceptor alternating copolymers with broad absorption and high electron mobility. Rylene diimide based electron transporting polymers can be classified into two types: i) perylene diimide (PDI) containing polymers; and ii) naphthalene diimide (NDI) containing polymers. Of these, perylene diimide containing donor-acceptor alternating copolymers are widely employed in APSC. Polymer P, a conjugated alternating copolymer of perylenediimide and phenylene vinylene, has broad absorption (300-750 nm) and high electron mobility (0.8x10^{-2} cm^{2}/Vs) and is used as an electron transporter in APSC. An APSC made of as spun PPHT and polymer P exhibited 1.67% PCE. After annealing, the PCE increased to record high 2.32%, which is the highest reported PCE for an APSC till date. The hole mobility of PPHT is enhanced by two orders of magnitude upon annealing, while no change is observed in the electron mobility. The hole mobilities of PPHT before and after annealing are 2.6x 10^{-6} cm^{2}/Vs and 8.3x10^{-4} cm^{2}/Vs, respectively. Thus, the enhancement in PCE upon annealing is attributed to the improvement in hole mobility.
1.2.2 Importance of Balance in Charge Transport

NDI containing donor-acceptor alternating copolymers, in general, have low band gap and high electron mobility compared to PDI containing D-A polymers.\textsuperscript{24,31,32} Thus, to generate more efficient APSCs, NDI based electron transporting polymer, P(NDI2OD-T2), is blended with P3HT.\textsuperscript{24} The PCE of P3HT/P(NDI2OD-T2) blend is optimized by: i) changing the weight ratio between P3HT and P(NDI2OD-T2); and ii) optimizing the thin film morphology by casting the polymer blend from different solvent compositions. The PCE achieved at 1:2 weight ratio of P3HT and P(NDI2OD-T2) ((PCE=0.16%) is twice that of 1:1 weight ratio (PCE=0.09%) in both chlorobenzene and ortho-dichlorobenzene. The PCE of 1:2 weight ratio was further enhanced to 0.62% by casting the films from xylene. Even though the PCE of P3HT/P(NDI2OD-T2) blend is lower than that of many APSCs consisting of PDI derived electron transporting polymers, the fill factor (FF) is very high (0.67) and is close to fullerene containing solar cells. Charge transport measurements on P3HT/P(NDI2OD-T2) blend indicated that the blend has similar hole and electron mobilities.\textsuperscript{46} The hole and electron mobility of the blend are $2 \times 10^{-3}$ and $4 \times 10^{-3} \text{ cm}^2/\text{Vs}$ respectively. The balance in charge transport (hole and electron mobilities) indicates that continuous pathways are available for the transfer of both charges (hole and electron) in the active layer. To further enhance the efficiency, thin films of the blend were casted from mixture of p-xylene and chloronapthalene and PCE of 1.4% was achieved at 1:1 solvent ratio.\textsuperscript{31} The enhancement in PCE is mainly due to the increase in short circuit current density. The use of aromatic polarizable solvents suppresses the pre-aggregate formation of P(NDI2OD-T2) in solution and avoids microphase segregation of polymers in thin films.
1.2.3 Importance of Optimal Frontier Energy Levels

P3HT/P(NDI2OD-T2) blend exhibits high and balanced charge transport, and has red shifted absorption compared to the PDI derived electron transporting polymers.\(^{31}\) But the PCE is still lower than the PDI containing APSCs.\(^ {16, 27}\)

P3HT/P(NDI2OD-T2) blend has very high FF and moderate Jsc, but low Voc. Low Voc is mainly due to the low lying LUMO in NDI derived polymers compared to PDI derived polymers. Voc depends on the difference in energy of HOMO of hole transporter and LUMO of electron transporter see the Figure 1.6. Thus to enhance Voc, the LUMO of NDI derived electron transporting polymers has to be pushed up. In D-A polymers, the frontier energy levels are the resultant of mixing D and A frontier energy levels.\(^ {11, 12}\) Thus to push the LUMO of NDI derived polymer high and to localize the LUMO charge density on NDI moiety, NDI was copolymerized with more sterically hindered fluorine unit (PF-NDI) instead of bithiophene spacer.\(^ {32}\) As expected, the LUMO of PF-NDI (-3.6 eV) is 0.4 eV higher than the LUMO of P(NDI2OD-T2) (-4.0 eV). Thin films of P3HT/PF-NDI blend were cast from mixture of chlorobenzene (solvent) and diiodoocatane (additive). The PCE of P3HT/PF-NDI blend (1.63%) is higher than that of

![Figure 1.6](image)

Figure 1.6 Dependence of open circuit voltage (Voc) on energy gap between LUMO of electron transporter and HOMO of hole transporter.
P3HT/P(NDI2OD-T2) blend (1.4%). The FF and Jsc for P3HT/PF-NDI blend are same as P3HT/P(NDI2OD-T2) blend, but Voc of the former as expected enhanced from 0.56 V to 0.68 V leading to an increased PCE. The PCE recorded for P3HT/PF-NDI blend (1.63%) is the highest recorded till date for APSCs employing NDI derived electron transporting polymers and/or P3HT as a hole transporter.

From the above discussion, it is clear that Voc depends on the energy gap between the HOMO of hole transporter and LUMO of electron transporter and this energy gap should be high for attaining high Voc (See the Figure 1.6, the data is taken from several reported APSC). In APSCs, both hole and electron transporting polymers contribute towards generating photocurrent, therefore there should be enough LUMO (and HOMO) energy offset (~0.4 eV) between the hole and electron transporting material to separate the bound electro-hole pair. Complementing the frontier energy levels of hole and electron transporting polymers is necessary to achieve high PCE. Frontier energy levels of rylene diimde containing electron transporting D-A alternating conjugated copolymers can be varied by changing the donor moiety.24, 26, 27, 32 This methodology provides an opportunity to alter the frontier energy levels of electron transporting materials and complement the plethora of existing hole transporting materials. Thus to broaden the available frontier energy level range for PDI containing polymers, PDI was copolymerized with several donor moieties.26, 27 The range of frontier energy levels obtained for various PDI-based D-A polymers is -5.3 to -6.0 eV for HOMO and -4.0 to -3.6 eV for LUMO. Of these PDI-based D-A polymers, PC-PDI exhibited highest PCE of 2.23% reported till date for a PDI derived electron transporting polymer.27 Thin film of PT1/PC-PDI blend was cast from a mixture of toluene and chloroform and the
corresponding device also showed the highest Jsc (6.35 mA/cm\(^2\)) recorded till date for an APSC.\(^{27}\)

1.3 Need for New Electron Transporting Polymers

Even though copolymerization with various donor moieties is widely employed to alter the frontier energy levels of rylene diimide derived electron transporting polymers, this methodology has few limitations. The range of LUMO energy levels that can be obtained are within 0.4 eV.\(^{26, 27}\) Also, the direction and magnitude of change in frontier energy levels cannot be predicted beforehand. With some donor moieties, the LUMO energy level did not change indicating that rylene diimide unit dominates LUMO energy level.\(^{28}\) Some donor moieties introduced into the D-A alternating copolymers have adverse effect on the electron mobility of rylene diimide polymers. For example, PDI copolymerized with bithiophene carbazole compared to bithiophene has an order of magnitude lower mobility (Figure 1.7).\(^{28}\) Similar effect is also observed in 2,1,3-benzothiadiazole derived D-A polymers. For example, F8TBT\(^{30}\) (\(\mu_e=10^{-5}\) cm\(^2\)/Vs)
compared to F8BT\textsuperscript{47} ($\mu_e=10^{-3}$ cm\textsuperscript{2}/Vs) has two additional thiophene repeating units as spacer and shows two orders of magnitude lower electron mobility compared to F8BT (Figure 1.7). Thus it is clear that even though copolymerization of D-A strategy is a good approach to alter the frontier energy levels and broaden the absorption range, it has no predictability on the direction and magnitude of frontier energy level change and in some cases it can impede the electron mobility of the resulting D-A copolymers. The effect of incorporating donor moieties along the back bone of high electron affinity moieties on charge separation and intra-chain transport is also yet to be studied and understood.

Dielectric constant ($\varepsilon$) of the polymer backbone also plays a crucial role in charge separation and therefore in PCE. Low charge separation efficiency in APSC compared to the polymer/fullerene is also attributed to the low dielectric constant of the polymer backbone ($\varepsilon \sim 3$) compared to fullerene and its derivatives ($\varepsilon \sim 4$).\textsuperscript{16, 40, 42, 43, 48, 49} Thus, electron transporting polymers with high dielectric constant need to be synthesized for high charge separation and PCE. The differences in the chemical and electronic structure of polymer backbone also impact the PCE and charge separation. For example, photoefficiency of a silole containing polymer

\textbf{Figure 1.8} Change in the photocurrent-potential dependence based on the chemical and electronic structure of the polymer backbone (Reprinted from ref.50 with permission from Elsevier).
(P(MeTTST:BT)) is 5 times that of a polymer without silole (PBT) (Figure 1.8).\textsuperscript{50} The reason for the enhanced photoefficiency in the former is attributed to the $\sigma^*-\pi^*$ conjugation between $\sigma$ bonds on silicon and $\pi^*$ orbitals on butadiene, which provides low-lying LUMO and very good electron accepting and transporting properties. Similarly, in polymer/fullerene blends it is known that a fluorinated backbone enhances the PCE compared to the non-fluorinated polymer.\textsuperscript{51, 52} In polymer/fullerene solar cells several classes of hole transporting polymers with different chemical and electronic structure are synthesized for high PCE, but only few polymers are successful in showing PCE higher than 5%. In APSC, so far only three classes of polymers, CN substituted PPV, 2,1,3 benzothiadiazole derived polymers, and rylene diimide (NDI and PDI) derived polymers, are used as electron transporting polymers (Figure 1.4 and Table 1.1). To further enhance the PCE of APSC, new classes of electron transporting polymers with high dielectric constant, high electron mobility, broad absorption range and different chemical and electronic structure have to be synthesized. A library of electron transporting polymers with broad range of frontier energy levels also helps us to pick the best complementary electron transporter for the desired hole transporting polymer for efficient charge separation and high Voc. This will also provide an opportunity to study and understand the structure-property relations such as the effect of chemical and electronic structure on charge separation, intra and inter charge transport properties.

1.4 Morphology

1.4.1 Bilayer Structure for Efficient APSC and the Importance of Polymer Conformation at the Interface
Similar to polymer/fullerene organic solar cells, controlling the active layer morphology in an APSC is critical to achieve high PCE. In general, APSCs are fabricated as either bilayer or blend morphology. An advantage of bilayer structure is that the dissociated excitons are efficiently converted into free charges at 4 nm away from the bilayer interface. However, charge separation depends on the domain size for the blend.

Unlike polymer/fullerene solar cells, some of the best PCEs are achieved in bilayer structure for APSCs (See the Figure 1.9 for the PCE achieved in bilayer and blend APSCs). For example, POPT/MEH-CNPPV bilayer structure shows a PCE of 2.0%. Surprisingly, even though the electron mobility of CNPPV (~10^{-5} cm^2/Vs) is low and the combined absorption range of POPT and CNPPV is smaller than most of the rylene-dimide derived electron transporting polymers, the PCE of POPT/MEH-CNPPV bilayer system is one of the best. Polymer conformation at the hole and electron transporter domain interface is crucial in determining PCE. For example, when P3HT was used as hole transporting layer instead of POPT, the efficiency of the system reduced
to 0.93%. With the help of computational and PDS spectroscopic studies the observed decrease in PCE from POPT to P3HT was explained based on the energetics of charge transfer state. In POPT/MEH-CNPPV, the spacing between hole and electron transporting polymers backbone is enhanced due to sterically hindered phenyl side chains which in turn reduce the Coulombic interaction between bound electron-hole pair. This destabilizes the geminate pair and enhances the energy of charge transfer state making it

**Figure 1.10** a) Cartoon showing enhanced polymer backbone separation at the interface due to bulky side chain; b) energy diagram indicating that increased polymer backbone separation destabilizes the geminate pair; c) comparison of current voltage curves of P3HT/CNPPV and POPT/CNPPV systems; d) chemical structures of P3HT and POPT (Reprinted from ref.40 with permission from American Chemical Society).
easier for charge separation (Figure 1.10). Similar decrease in PCE is also observed when P3HT is used instead of POPT along with the NDI derived electron transporting polymer (N2200). This confirms the importance of polymer conformation at the interface for efficient charge separation. Quantum chemical calculations also showed that electronic character of interfacial excited state is dependent upon the polymer geometrical configuration at the interface.

1.4.2 Bilayer vs Blend

In bilayer structure, excitons that are generated at the interface and 20 nm (diffusion length of excitons) away from the interface are converted into free charges. In general, the thickness of the active layer is ~100 nm to match the typical photon capture distance. But the exciton can travel only upto < 20 nm, thus most of the excitons generated in bilayer structure are futile. Hence by increasing the interfacial area, more excitons can be converted into free charges. However the charge collection efficiency will be impeded.

Figure 1.11 Three examples of morphologies generated by minimization of the Ising Hamiltonian with decrease in interfacial area between hole (light phase) and electron transporter (dark phase) from a) to c); d) Plots of the exciton dissociation efficiency (dotted line), charge collection efficiency (dashed line), and internal quantum efficiency (solid line) vs interfacial area (Reprinted from ref.53 with permission from American Chemical Society).
due to increased number of available recombination sites. The evolution of morphology of a blend with decreasing interfacial area is simulated and the corresponding exciton dissociation, charge collection and internal quantum efficiencies are also calculated and the results are summarized in Figure 1.11. From Figure it is clear that IQE at extremities of the blend morphology (a) and (c) is very low. Moderate IQE is found at the intermediate morphology that resembles BHJ structure with optimal domain size and continuous phases of charge-carrier transporters.

Since BHJ structure increases the interface for efficient charge separation and provides percolation pathway for charge carriers many APSCs are fabricated as blends. The efficiency of M3EH-PPV/CN-ether-PPV blend is higher than that of bilayer. The PCEs for the blend and bilayer are 1.7% and 1.3% respectively. The enhanced PCE in blend is because of the vertically composition graded structure of active material which enhances the charge collection. Hole collecting electrode (ITO) and active layer interface is rich in hole transporter (M3EH-PPV) and electron collecting electrode (Ca/Al) active material interface is rich in electron transporter (CN-Ether-PPV) (Figure 1.12). Thus the blend, compared to bilayer, has more interfaces for exciton dissociation and charge separation and the necessary percolation pathway for charge transport and collection is provided by the vertically

Figure 1.12 Vertical composition gradient of M3EH-PPV/CN-ether-PPV blend (Reprinted from ref.38 with permission from American Chemical Society).
composition graded structure. Vertically composition graded structure is mainly due to the difference in solubility of M3EH-PPV and CN-Ether-PPV in chlorobenzene. Finding the proper solvent to obtain vertical composition graded structure for chosen polymer blend is difficult. In some cases unfavorable vertically composition graded structure may impede the PCE. For instance, the PCE of P3HT/ F8TBT blend annealed before depositing Al electrode (PCE =0.19%) is lower than that of annealed after depositing Al electrode (PCE =1.2%).\textsuperscript{44} The enhancement in PCE is mainly due to the alteration of the composition of the active layer near the electrodes. For the device that is annealed before depositing Al electrode, both top and bottom electrode interface is enriched with P3HT impeding the electron collection at Al electrode. But when the sample was annealed after the deposition of Al electrode, the composition of F8TBT was enhanced at the interface of top (Al) electrode thus increasing the charge collection efficiency. Thus to obtain the optimal morphology of polymer blend, the solvent and annealing temperature have to be optimized.

1.4.3 Employing the Optimization Conditions Known for Polymer/Fullerene Blends to APSCs

Even though the number of APSCs developed is fewer than polymer/fullerene cells, almost all the optimization techniques that are employed in polymer/fullerene cells are applied to optimize the morphology of polymer/polymer blend. The weight ratio between the hole and electron transporting polymers is optimized to enhance the PCE.\textsuperscript{25} By changing the weight ratio from 1:2 to 3:1, the PCE of P4/P2 blend is enhanced from 0.8\% to 1.48\%. The solvent used to cast film is also varied to enhance the PCE.\textsuperscript{24} For example, P(NDI2OD-T2)/P3HT blend casted from xylenes (PCE= 0.62\%) showed
enhanced PCE compared to the blend casted from chlorobenzene (PCE=0.16%). The mixture of solvents used for spin coating the blend is also varied to enhance PCE.\textsuperscript{27} PCE obtained for PT1/PC-PDI blend is enhanced from 1.85% to 2.23% by using a mixture of toluene/chloroform (9:1 v/v) instead of pure toluene. This is one of the highest PCEs observed for APSCs containing PDI derived electron transporting polymer. Additives are also used to enhance the PCE of APSC.\textsuperscript{32} The PCE of P3HT/PF-NDI blend casted from chlorobenzene without DIO is 0.76%. PCE enhanced to 1.63% by using DIO (1%) as an additive, this is the highest PCE obtained for APSCs containing NDI derived electron transporting polymer and/or P3HT hole transporter.

The morphology of the polymer blend can be optimized by varying different fabrication conditions as discussed above. Since there are several parameters in fabrication of APSCs that can potentially influence the morphology of polymer blend, finding the right parameter to optimize the morphology is difficult, tedious and time consuming. Moreover the optimization conditions that work well for one polymer/polymer blend are not guaranteed to be applicable for another polymer/polymer blend. This is mainly because the strength of intermolecular interactions between hole and electron transporter polymers, and between solvent and each of the transporter polymer vary from polymer to polymer. In some cases the solvent suitable for one polymer may impede the optoelectronic properties of other polymer. For example P3HT/P(NDI2OD-T2) blend casted from p-xylene showed low PCE (0.2%) and this is mainly attributed to the formation of large aggregates of P(NDI2OD-T2) in thin film due to its low solubility in p-xylene.\textsuperscript{31} But when blend was casted from a mixture of p-xylene and chloronapthalene (1:1 v/v), a good solvent for solubilizing P(NDI2OD-T2), the
efficiency enhanced to 1.4%. Although the solvent mixture is good for solubilizing P(NDI2OD-T2) it hampers the P3HT chain assembly. This was confirmed based on the suppression of 0-0 transition and pronounced 0-2 transition in the absorption spectrum of blend film casted from mixture of solvents. Crystalline P3HT aggregates and the corresponding 0-0 transition in the absorption spectrum are observed in P3HT/PCBM blends exhibiting high PCE.\textsuperscript{7} The relative intensity of 0-0 transition compared to other vibronic transition is correlated with mobility and crystallinity of P3HT in thin films. Thus finding a solvent that is suitable for both the acceptor and donor polymers and provides thin film blend morphology that has interconnected polymer (hole and electron transporting) domains of suitable size (<20 nm) is crucial to generate high efficiency APSCs.

1.4.4 Fabricating Pre-aggregates for Optimal Morphology

The problem of optimizing the blend morphology via annealing, adding additives and changing the solvent to obtain nano-aggregates of polymer has been overcome by pre-aggregating polymer into nanofibers.\textsuperscript{33} The PCE of as spun P3HT/F8BT blend is 0.008%, but the PCE increased to 0.045% after annealing. Annealing the blend helps polymers to form crystalline nanodomains that are suitable for efficient exciton dissociation. Alternatively, device fabricated by blending P3HT nanofibers and F8BT gave 0.055% PCE without annealing.\textsuperscript{33} The aspect ratio of P3HT nanofibers is suitable for efficient exciton dissociation and charge transport across the thin film. Pre-aggregation of polymer into nanofibers is one of the best way to obtain the required morphology for APSC, but it has some limitations; i) every polymer cannot be pre-aggregated into nanofibers,\textsuperscript{7} ii) since both the polymers absorb and generate excitons in
APSCs, the fate of excitons that are generated in non-nanofiber polymer domains is unclear, and iii) from poly (3-alkylthiophene)/PCBM blend,\textsuperscript{7} it is known that the aspect ratio of nanofibers, and processing and annealing conditions of nanofiber/PCBM blend also need to be optimized for better PCE.

To avoid the problem of optimizing the aspect ratio of aggregates and finding a suitable solvent for processing pre-aggregates and their blends, nanoparticles of polymers are made.\textsuperscript{7, 54} The advantage of fabricating nanoparticles is that nanoparticles of any polymer that is: i) insoluble in water; ii) soluble in an organic solvent that is immiscible with water; and iii) turns into solid state when the solvent is evaporated can be prepared. Thus, stable nanoparticle dispersions of both hole and electron transporting polymer can be prepared individually in water. Size of the nanoparticles can be controlled by changing the concentration of either surfactant or polymer; thus nanoparticles offer a straightforward way to control the domain size of transporters. To prove that PCE of the blend of nanoparticles depend only on the size of nanoparticles, nanoparticles of PFB and

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure13.png}
\caption{Plots of the exciton dissociation efficiency (dotted line), charge collection efficiency (dashed line), and internal quantum efficiency (solid line) vs interfacial area for checkered morphology (Reprinted from ref.40 with permission from American Chemical Society).}
\end{figure}
F8BT of diameter 49 and 53 nm are prepared from both chloroform and xylene. The external quantum efficiency (EQE) of the device fabricated from these nanoparticles blend is found to be 1.7% and the EQE is unchanged with respect to the solvent used to make the nanoparticles. Contrarily, the EQE of PFB/F8BT polymer blend spin-coated from chloroform is different (higher, EQE=4%) than that of xylenes (EQE=1.5%). This indicates that efficiency of the devices fabricated from nanoparticle blend depends on the size and assembly of nanoparticles in thin film, but not on the organic solvent used to make the nanoparticles. Calculations on the efficiency of exciton dissociation, charge collection and IQE for highly ordered checkered morphology with nano-size domains is shown in Figure 1.13. From the calculation it is clear that IQE of such a checkered morphology (IQE=80%) is higher than that of random blend morphology (IQE=50%). Fabrication of photovoltaic devices from polymer nanoparticle blend is a reliable approach to obtain high PCE and reproducible device metrics. But the PCE are far less than the polymer blend. This is mainly because: i) lack of optimal assembly of nanoparticles to facilitate charge transfer and transport processes; and ii) lack of control over the exciton and charge transport properties within the nanoparticles. Thus, before realizing the complete potential of nanoparticle approach these challenges should be addressed.

1.5 Summary

In APSCs, an electron transporting conjugated polymer with complementary absorption to that of hole transporting polymer and desired energy level offset can be used to enhance the absorption range in solar spectrum and open circuit voltage. Thus, it has several advantages over the polymer/fullerene and small molecule/fullerene solar
cells and ideally should have very high PCE. However, the current state of art of APSCs PCE is 5 times less than that of polymer/fullerene solar cell and 3.5 times less than that of small molecule/fullerene solar cell. This is mainly due to: i) only three classes of polymers, –CN substituted PPV, 2,1,3 benzothiadiazole derived polymers, and rylene diimide (NDI and PDI) derived polymers, are synthesized and tested as electron transporting polymers; ii) limited number of electron transporting polymers with broad absorption range and high electron mobility to complement the frontier energy levels of plethora of hole transporting materials; iii) dielectric constant of the polymers are low compared to fullerene and its derivatives; and iv) difficulty to control the polymer/polymer blend morphology compared to polymer/fullerene blend.

Due to low entropy of mixing the polymers, polymer/polymer blend tend to micro-phase segregate. But in APSC both hole and electron transporting polymers absorb sunlight and generate excitons. Thus unlike polymer/fullerene solar cells, in APSC both hole and electron transporting polymers should form domains of sizes closer to the exciton diffusion range for efficient geminate pair dissociation. And also, there should be continuous network of these domains for the separated charges to reach electrode with high efficiency. Controlling the morphology of polymer/polymer blend is more challenging than polymer/fullerene blend. Thus, to optimize the morphology of polymer/polymer blend many optimization techniques such as annealing, changing solvent, using mixture of solvent, and adding additives are employed. However, the PCE of APSCs is still only as high as 2.3%. Pre-aggregating the polymers into nanofibers or nanoparticles is a novel approach to control the domain size and morphology. Synthesizing nanofibers of every polymer is not trivial. On the contrary, nanoparticles of
most of the conjugated polymers can be readily synthesized. However, several major challenges such as i) how to attain the percolation network of hole and electron transporting nanoparticles in the thin film?; ii) how to control the exciton and charge transport properties within the nanoparticles?; and iii) what is the effect of size of the nanoparticle, organic solvent and surfactant used to make the nanoparticle on polymer packing inside the particle, optoelectronic and charge transport properties of the nanoparticle are yet to be addressed.

1.6 Scope of This Dissertation

A major part of my research and this dissertation focuses on the design and synthesis of new classes of electron transporting polymers with different chemical and electronic structure with: i) high electron mobility; ii) broad absorption range; and iii) good solution processability. Designing new electron deficient monomers with different chemical and electronic structure and polymerizing them is one approach to synthesize new classes of electron transporting polymers. However, this approach is time consuming. The focus of the synthetic methodology developed by me (discussed in chapter 3) is that it provides a straightforward synthetic strategy to generate a library of electron transporting conjugated polymers with different chemical and electronic structures from readily available monomers. A library of electron transporting polymers generated using this methodology would provide electron transporting polymers with wide range of frontier energy levels to complement the existing plethora of hole transporting polymers. This will also provide an opportunity to study and understand the structure-property relations such as the effect of chemical and electronic structure on charge separation, and intra and inter charge transport properties. Chapter 2 focuses on generating electron
transporting polymers by appending an electron deficient heterocyclic compound onto the electron rich thiophene backbone.

Chapter 4 focuses on optimizing the synthesis of conjugated polymer nanoparticles in the view of: i) controlling the size of nanoparticles; ii) controlling polymer packing inside the nanoparticle; ii) controlling optoelectronic and charge transport properties; and iii) designing strategies towards directing the assembly of nanoparticles in thin films. The effect of surfactant and polymer concentration on the size of nanoparticles and the effect of organic solvent and surfactant used to make the nanoparticle on optical, optoelectronic, charge transport properties of nanoparticle thin films and on polymer packing inside the nanoparticle are studied. P3HT is employed for the above studies. The charge transport properties of PBTDV2 (an electron transporting polymer synthesized by me) nanoparticles, P3HT/PCBM nanoparticle blend and P3HT/PBTDV2 nanoparticle blend are also discussed.

Chapter 5 focuses on investigating the effect of dipolar side chains (1,2,3-triazole) and polymer packing in thin films on polymer sensory response towards nitroaromatics. The side chains on the polymer backbone were modified to control polymer packing and energy transfer in thin films to enhance sensory response. Chapter 6 focuses on elucidating the reason for the observed alteration in melting point of n-alkanes: Is it intermolecular interaction energy or entropy? We have used PIXEL, a computational program that calculates the intermolecular interaction energies, to gain insights on the observed alteration in melting point of n-alkanes.

1.7 References


36. Sang, G. Y.; Zhou, E. J.; Huang, Y.; Zou, Y. P.; Zhao, G. J.; Li, Y. F., Incorporation of Thiénylenevinylene and Triphenylamine Moieties into


CHAPTER 2

IMPACT OF PENDANT 1,2,3-TRIAZOLE ON THE SYNTHESIS, OPTICAL
AND CHARGE TRANSPORT PROPERTIES OF THIOPHENE-BASED
POLYMERS

2.1 Introduction

Charge transport properties of a polymer depend on the electronic nature of the repeating unit and self-assembly of the polymer in thin films.\textsuperscript{1-6} A conjugated polymer made of an electron deficient moiety will have high electron affinity and will be electron transporting in nature.\textsuperscript{7-10} The magnitude of charge mobility depends on the nature of polymer assembly in thin films; crystalline polymers generally exhibit high mobility compared to the amorphous polymers.\textsuperscript{1-3} Regioregular alkyl substituted polythiophenes self-assemble into ordered structures in thin films and in general exhibit high charge transport properties than non-regioregular polythiophenes.\textsuperscript{11, 12} But most of the alkyl-substituted polythiophenes are hole transporting due to the high ionization potential of electron rich polythiophene backbone. Nonetheless, by incorporating electron deficient moieties either into the polymer backbone or as a side chain, the electron affinity of the polymer can be increased. Thus, to generate low band gap and electron deficient polymers based on thiophene, we appended 1,2,3-triazole directly onto the polythiophene backbone (Figure 2.1). We hypothesized that 1,2,3-triazole will act as an electron withdrawing substituent and enhances the electron affinity of the polythiophene backbone. We chose 1,2,3-triazole because: i) it can be easily synthesized using established 1,3-dipolar cycloaddition, also known as click chemistry,\textsuperscript{13} ii) it can be further functionalized to modulate the electronic nature of the polythiophene backbone;
and iii) it is shown that 1,2,4-triazole, a regio-isomer of 1,2,3-triazole, acts as an electron acceptor moiety in donor-acceptor polymers of thiophene and 1,2,4-triazole.\textsuperscript{14, 15} We chose to append 1,2,3-triazole directly onto the polythiophene backbone rather than incorporating into the main chain because: i) conjugated polymers containing acceptor moieties as side chains have better photovoltaic metrics compared to the main chain donor-acceptor polymers; ii) conjugated polymers with conjugated side chains (here 1,2,3-triazole) have broad absorption range in the solar spectrum;\textsuperscript{16-25} and iii) regioregular 1,2,3-triazole substituted polythiophenes are expected to exhibit ordered self-assembled structures in thin film and they can be easily synthesized using Grignard metathesis (GRIM) polymerization. In this work we have studied the impact of 1,2,3-triazole on the GRIM polymerization mechanism of thiophene and elucidated the electronic nature of 1,2,3-triazole on polythiophene backbone.

2.2 Results and Discussion

1,2,3-triazole appended polythiophenes can be synthesized by either post functionalization of alkyne substituted polythiophenes or polymerizing the 1,2,3-triazole appended thiophene monomer. Since post functionalization of alkyne-substituted polythiophene would allow us to rapidly generate 1,2,3-triazole appended polythiophenes with wide variety of side chains, we chose this as our synthetic route (Figure 2.2). Polythiophene can be generated either by oxidation polymerization using FeCl\textsubscript{3} or Grignard metathesis (GRIM)\textsuperscript{36, 27} polymerization conditions. We have attempted both the polymerization conditions on
corresponding monomers to generate 3-alkyne substituted polythiophene (Scheme 1). Alkyne substituted thiophene (M1) was synthesized via Sonagashira coupling of 3-
bromothiophene with TMS acetylene. Oxidation polymerization of M1 using FeCl₃ did not yield polymer. Thus, we changed to GRIM polymerization synthetic route. GRIM polymerization requires a 2,5 dihalogen (Br or I) substituted thiophene as a monomer. Standard dibromination conditions on M1 did not generate the required monomer. This might be because of the alteration in electronics of the thiophene monomer due to conjugated alkyne at the 3rd position. By changing the synthetic route and starting from 3-iodothiophene (Scheme 1), 2,5-dibromo 3-alkyne substituted thiophene monomer (M2) was successfully synthesized. However, M2 did not undergo polymerization under standard GRIM conditions. Since, 3-alkyne substituted thiophene did not undergo polymerization, we have synthesized 1,2,3-triazole substituted thiophene (M3) and 2,5-dibromo 3-(1,2,3-triazole) substituted thiophene (M4). Unfortunately, attempted oxidation polymerization conditions on M3 and GRIM polymerization conditions on M4 were not successful. Attempted GRIM polymerization condition on M4 at elevated temperature was also not successful.

To probe if M4 undergoes Grignard metathesis or not, M4 was reacted with tBuMgCl for 3 h and the reaction mixture was quenched with H₂O (Figure 2.4). The organic components were extracted with diethyl ether and the solvent was removed under reduced pressure. The ¹H NMR of residue showed that starting material to product ratio was 17:83. For peaks attributable to the product, each peak between δ 7.4 - 7.6 integrated to one proton consistent with a single component with 3 aromatic protons. Based on precedence, the peaks around δ 7.4 - 7.6 were assigned to protons on thiophene and the peak at δ 7.4 was assigned to the triazole proton. The coupling constant, J, of the peaks between δ 7.4 - 7.6 was found to be 1.6 Hz consistent with a ‘meta’ coupling. We
Figure 2.3 Synthesis of monomer and polymer.

Figure 2.4 Quenching studies for monomers M4 and M5.
therefore concluded that the Grignard metathesis occurred with –Br group at the 2\textsuperscript{nd} position, ortho to the triazole moiety (Figure 2.4). The driving force for the formation of Grignard at this position may be due to the coordination of the triazole nitrogen and the monomer acting as a chelating ligand for Mg\textsuperscript{2+}. Although there are few reports indicating that the Grignard metathesis at the 2\textsuperscript{nd} position does result in polymerization\textsuperscript{29, 30} our result is consistent with earlier studies\textsuperscript{31, 32} with 5-bromo-2-iodo-3-hexylthiophene, which have shown that the metal-halogen exchange at 2\textsuperscript{nd} position does not result in polymerization. It has been argued that if the Grignard metathesis occurs at 2\textsuperscript{nd} position on the thiophene ring, then the Ni(0) does not insert in the carbon-bromine bond at the 5\textsuperscript{th}.

![NMR spectra](image)

**Figure 2.5** NMR of products obtained after reacting (a) M5 and (b) M4 with Grignard and then quenching with water.
position bond purportedly due to lack of stabilization from the alkyl chain at the 3\textsuperscript{rd} position. We believe that in our case, the chelating ability of the triazole moiety stabilizes the Grignard or the nickel complex that results from the Grignard and prevents further reaction.

To direct the Grignard metathesis at the 5\textsuperscript{th} position of the thiophene, we designed \textbf{M5} with iodine at the 5\textsuperscript{th} position and bromine at the 2\textsuperscript{nd} position (Figure 2.3). Since it is known that Grignard metathesis occurs faster with a C-I than a C-Br bond, we expected that the Grignard reagent should preferentially react at the 5\textsuperscript{th} position. The synthesis of \textbf{M5} is shown in Scheme 1. We screened a variety of iodination conditions and found that NIS/\text{CF}_3\text{SO}_3\text{H} provided the iodinated compound in excellent yields. \textbf{M5} was reacted with \textit{t}-\text{BuMgCl} and the reaction mixture was quenched with water. The coupling constant in the peaks between $\delta$ 7.3 and $\delta$ 7.7 was found to be 5.7 Hz, consistent with the coupling expected between the protons at the 4\textsuperscript{th} and 5\textsuperscript{th} position; this observation is consistent with the metathesis happening at the 5\textsuperscript{th} position (Figure 2.4 and Figure 2.5).\textsuperscript{28} We were gratified to note that \textbf{M5} polymerized under GRIM conditions. The polymer (\textbf{P3TzT}) is soluble in chloroform at room temperature and in DMF at elevated temperature. Polymer GPC trace is shown in Figure 2.6.
What is the impact of triazole on the electronic structure of the conjugated polymer backbone? In the literature, it has been shown that 1,2,3-triazole can act as an electron donor\textsuperscript{33} or as an electron acceptor\textsuperscript{34}. If triazole acts as electron donor, then we expect that the HOMO levels will be affected whereas if triazole acts as an acceptor, LUMO levels of the conjugated polymer backbone will be affected.\textsuperscript{35-38} The resonance and inductive effects of triazole will also depend on the orientation of the triazole ring with respect to the backbone. Therefore the question is what is the impact of triazole on the electronic structure of the conjugated polymer backbone and on the frontier energy levels? The UV-Vis absorption and fluorescence spectra of the polymer solution and thin film are shown in Figure 2.7. Solution state UV-Vis and fluorescence spectra were recorded using a solution of the polymer in chloroform. Thin films for solid state measurements were cast from chloroform onto a glass slide and the UV-Vis and fluorescence spectra were recorded before and after thermal annealing at 100 °C for 30 minutes. There was no substantial change in absorption and emission spectra before and
after thermal annealing, indicating that no substantial changes occurred in the packing of molecules upon annealing. The absorption $\lambda_{\text{max}}$ in solution is 415 nm and in thin film is 506 nm with a red shift of 91 nm in thin films. In comparison, P3HT has a red shift of 115 nm in thin films. Crystal structures of M4 and terthiophene (7) bearing the triazole moiety show that the triazole is twisted with respect to the thiophene backbone with a dihedral angle of 35° and 45° respectively (Figure 2.8). Powder X-ray diffraction analysis of the polymer thin film shows peaks at 2.75 nm, 1.52 nm, 0.5 nm, and 0.38 nm, indicating that the polymer is crystalline (Figure 2.8). Even though the crystal structures indicate that the triazole moiety may not be coplanar with thiophene backbone, the non-coplanarity seems to not hinder the packing of the polymer in thin films.

In order to understand the placement effect of triazole in side chain compared to main chain, we compared P3TzT with the polymer reported in the literature, 4RTaz/Th$^{14, 15}$ We find that in solution, $\lambda_{\text{max}}$ of P3TzT absorption is red shifted by 62 nm compared to $\lambda_{\text{max}}$ of 4RTaz/Th. The red shift in the solution absorption $\lambda_{\text{max}}$ of P3TzT compared to 4RTaz/Th indicates that the conjugation length has increased and the band gap of P3TzT
Table 2.1 Optical and electrochemical data of polymers.\(^a\)

<table>
<thead>
<tr>
<th>polymer</th>
<th>(\lambda_{\text{max}}^{\text{sol}}) [nm]</th>
<th>(\lambda_{\text{max}}) [nm]</th>
<th>(E_{\text{g}}^{\text{opt}}) [eV]</th>
<th>HOMO [eV]</th>
<th>LUMO(^{\text{opt}}) [eV]</th>
<th>LUMO(^{\text{elec}}) [eV]</th>
<th>(E_{\text{g}}^{\text{elec}}) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>449</td>
<td>564</td>
<td>1.83</td>
<td>-5.12</td>
<td>-3.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P3TzT</td>
<td>415</td>
<td>506</td>
<td>1.90</td>
<td>-5.10</td>
<td>-3.14</td>
<td>-3.07</td>
<td>2.03</td>
</tr>
<tr>
<td>P3TzT+TF</td>
<td>395</td>
<td>-</td>
<td>-5.15</td>
<td>-</td>
<td>-2.91</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>Atom</td>
<td>353</td>
<td>375</td>
<td>2.61</td>
<td>-5.37</td>
<td>-2.76</td>
<td>-2.80</td>
<td>2.57</td>
</tr>
<tr>
<td>4RTaz/Th</td>
<td>460</td>
<td>492</td>
<td>1.98</td>
<td>-5.46</td>
<td>-3.45</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2D-PT</td>
<td></td>
<td></td>
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</tbody>
</table>

\(^a\)\(E_{\text{g}}^{\text{opt}}\) calculated from the intersection of tangent on the low energetic edge of the absorption spectrum with baseline, HOMO and LUMO\(^{\text{elec}}\) are calculated from oxidation and reduction potentials obtained from cyclic voltammetry, \(E_{\text{g}}^{\text{elec}} = \text{LUMO}^{\text{elec}} - \text{HOMO}\), LUMO\(^{\text{opt}}\) calculated using the equation: HOMO + \(E_{\text{g}}^{\text{opt}}\).

is lower compared to 4RTaz/Th (Table 2.1). Therefore, we believe that 1,2,3-triazole attached as a side-chain in P3TzT increases the conjugation and electron density on polymer better than 1,2,4-triazole introduced in the main chain. To understand the effect of triazole versus thiophene as a side chain on the thiophene back bone, we compared P3TzT with the reported polymer, 2D-PT.\(^{17}\) The thin film absorption \(\lambda_{\text{max}}\) of all the polymers - 4RTaz/Th, 2D-PT, and P3TzT- are blue shifted compared to rrP3HT. However, the \(\lambda_{\text{max}}\) for P3TzT is much closer to P3HT than 4RTaz/Th or 2D-PT. The red shift in \(\lambda_{\text{max}}\) of all the polymers from solution to thin film is in the following order: P3HT > P3TzT > 4RTaz/Th > 2D-PT. From the onset absorption values, the band gaps of P3TzT, 4RTaz/Th, and 2D-PT were calculated to be 1.9, 2.61, and 1.98 eV, respectively. It is noteworthy that the absorption \(\lambda_{\text{max}}\) of P3TzT in the solution is blue shifted compared to 2D-PT. Nonetheless, in thin films, the absorption maxima are close. There is a 91 nm
red shift in P3TzT absorption from solution to thin film absorption, whereas 2D-PT shows only a 30 nm red shift. Since the red shifts in thin films are related to polymer packing and interaction between the polymer chains, we speculate that triazole facilitates better packing in thin films in P3TzT than conjugated side chains in 2D-PT. We had anticipated that the interaction between the polymer chains in this films will be poor in P3TzT because it has 1,2,3-triazoles on every repeat unit and the triazole ring is not coplanar with the polymer backbone. We therefore conclude that 1,2,3-triazole as a side chain also provides better π-π interactions between polymer chains in thin films compared to that of thiophene side chains. The solution and thin film emission $\lambda_{\text{max}}$ of P3TzT are found to be 556 nm and 630 nm, respectively. The stoke shift for the solution and thin film are calculated to be 141 nm and 124 nm, respectively. The higher stoke shift in P3TzT indicates a higher degree of structural reorganization in P3TzT, which might be facilitated by the conjugated triazole side chains.

P3TzT thin film was cast from chloroform solution onto the Pt electrode and the cyclic voltammogram (CV) was recorded and the oxidation/reduction potentials were compared with P3HT. The CV of P3TzT thin film was recorded in two ways: (i) by oxidizing the polymer (positive potential sweep); (ii) by first reducing the polymer (negative potential sweep) (Figure 2.9). Since the oxidation and reduction of P3TzT are not completely reversible, the onset oxidation and reduction potentials from Figures 2.9 were used to calculate the HOMO and LUMO$^{\text{elec}}$ energy levels (equation 1).
oxidation and reduction potentials of P3HT and P3TzT are 0.286 V, -2.18 V and 0.266 V, -1.766 V respectively with respect to Ag/Ag⁺. The HOMO, LUMO energy levels and electrical band gaps of P3HT, P3TzT, 4RTaz/Th, and 2D-PT are shown in Table 1 for comparison. The HOMO levels of all the polymers, except P3TzT are lower than P3HT. In 2D-PT, both the HOMO and LUMO opt levels are lower in energy compared to P3TzT, but both the polymers have very close band gap (E_g opt). The electrochemical and UV-Vis spectroscopic data are consistent with the fact that triazole is behaving as an electron donor instead of an electron acceptor. Electrostatic charges calculated on a dimeric unit in P3TzT using RB3LYP method and 6-31G (D) basis set is also consistent with the observation that 1,2,3-triazole behaves as an electron donor (Figure 2.9). P3TzT was treated with trifluoroacetic acid (TFA) to protonate the nitrogen on the triazole moiety and decrease the electron donating nature of triazole. After the addition of TFA, the absorption and emission λ max of P3TzT, as expected, are blue shifted by 20 nm and 21 nm respectively. Cyclic voltammetry after addition of TFA indicates that the energy of the

**Figure 2.9** Cyclic voltammetry traces of P3TzT; b) electrostatic charges on dimer.
HOMO level is lowered and LUMO^{elec} is increased in energy, thus increasing the band gap \((E_g^{elec})\). All the above observations indicate that 1,2,3-triazole when attached as a pendant group to a thiophene backbone acts as an electron donating group, pushing both the HOMO and LUMO levels up in energy and reducing the band gap. The triazole moiety does not hinder the packing of the polymer backbone in thin films.

The hole mobility of \textbf{P3TzHT} was determined using time of flight (ToF) technique (Figure 2.10). We chose ToF to measure the mobility because the charge transport in ToF device configuration occurs across the polymer film, which is similar to organic photovoltaic devices.\textsuperscript{39} The samples were prepared by drop casting the polymer solutions onto ITO coated glass slides followed by the thermal evaporation of aluminum on top of polymer film. The photocurrent transient of \textbf{P3TzHT} at various applied field are shown in and the shape of photocurrent transit is characteristic of dispersive transport. Charge carrier mobility \((\mu)\) was determined using the following equation: \(\mu = L/(E \cdot t_{TR})\), where \(L\) is the film thickness. Hole mobilities of the polymers at various applied fields are shown in Figure 2.10. \textbf{P3TzHT} exhibit high hole mobility of \(10^{-3}\) cm\(^2\)/V.s, comparable to those of P3HT thin films. The dispersive charge transport is explained by a variation of local transport rates due to a high spatial and/or energetic disorder in the material. Each data set is averaged over 128 photocurrent transients.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.10.png}
\caption{Time of flight hole mobility of P3TzT.}
\end{figure}
generated by the light pulses. In order to determine the electron mobility, the polarity of the applied field was changed. However, negligible photocurrent transients were observed in this configuration, indicating that the electron mobility could be orders of magnitude lower than the hole mobility.

Electron donating nature of P3TzHT was further confirmed by fluorescence quenching studies with PCBM. Fluorescence quenching studies of P3TzHT solution in chloroform at different weight ratios of PCBM were carried out and are shown in Figure 2.11. The fluorescence intensity of P3TzT polymer was observed to decrease gradually with the increase in the weight ratio of PCBM, indicating the electron transfer from P3TzT and PCBM and hence fluorescence quenching. Thin films casted onto a glass plate from chloroform solution containing 1:1wt% P3TzT and PCBM did not exhibit any fluorescence, indicating complete fluorescence quenching. Thus, the above observations indicate that P3TzT is a good hole transporting polymer (and electron donating) rather than electron transporting polymer.

Figure 2.11 a) Increase in fluorescence quenching by the addition of more PCBM (in chloroform); b) complete fluorescence quenching in thin film.
2.3 Conclusion

In conclusion, we have shown that the thiophene-based polymers with 1,2,3-triazole moiety attached as a pendant group can be synthesized using Ni(0)-mediated Grignard metathesis polymerization using a modified monomer. When compared with a triazole on the main chain, the pendant triazole moiety acts as an electron donor and lowers the band gap of the polymer. But N-heterocyclic compounds are generally known as electron withdrawing groups because of higher electronegativity of nitrogen (compared to carbon and hydrogen atoms). Electronically, 1,2,3-triazole can interact with thiophene via both inductive and resonance effect, and a combination of these two effects determine the electronic nature of 1,2,3-triazole on thiophene. We think that 1,2,3-
triazole should inductively be electron withdrawing because of the high electronegative nitrogen atoms, whereas resonance effect depends on the position of substitution on 1,2,3-triazole. Resonance structures of thiophene connected at its 3\textsuperscript{rd} position to the 4\textsuperscript{th} and 5\textsuperscript{th} position of 1,2,3-triazole are shown in Figure 2.12. From the delocalization of pi-electrons between thiophene and 1,2,3-triazole it is clear that 1,2,3-triazole acts as electron donating group when it is connected at 4\textsuperscript{th} position to a thiophene. Even though 1,2,3-triazole is twisted by 40 degrees compared to the pi-conjugated backbone in P3TzHT, the resonance effect dominated over the inductive effect making 1,2,3-triazole an electron donor. We have also shown that P3TzHT acts as a good hole transporter, which also indicates that twisting of Triazole moiety does not hinder the packing of conjugated backbone. From the resonance structures, 1,2,3-triazole that has thiophene substituted at 5\textsuperscript{th} position may act as electron withdrawing group.

2.4. General Experimental Methods

GPC analyses were performed on a Polymer Laboratories GPC50 integrated system with DMF (1.0 mL/min, 120 °C) elution, 3 x Mixed C (300 x 7.5 mm) columns, and RI detection. Molecular weights were obtained based on PMMA standards, with toluene as the flow rate marker. UV–vis absorption spectra were recorded stock solutions of polymers (c=1 mg/10 mL) were prepared in spectrophotometric grade chloroform (Fisher, Optima). UV–Vis experiments for thin films were done by spin casting (1400 rpm) 1wt % solution of polymer in chloroform on a glass plate. Similarly, to the 1wt % solution of polymer in chloroform, PCBM (1:1 wt % with respect to polymer) was added and spin casted (600 rpm) onto a glass plate. These films were annealed at 100 °C for 30 minutes. UV-Vis and Fluorescence spectra were recorded before and after annealing.
Stock solutions of polymer (1 wt% polymer in chloroform) were prepared and films were spin casted on to the platinum working electrode and CV was recorded with tetrabutylammonium hexafluorophosphate as a supporting electrolyte (0.1 M) in acetonitrile. The redox potentials were determined against Ag/AgNO₃ reference electrode. In these conditions, the onset oxidation potential of ferrocene was -0.04 V versus Ag/Ag⁺. It is assumed that the redox potential of Fc/Fc⁺ has an absolute energy level of -4.80 eV to vacuum.⁴⁰,⁴¹ HOMO and LUMO values were calculated using Fc/Fc⁺ as a reference. The working and auxiliary electrodes were cleaned after each run.

2.5 Experimental Procedures

2.5.1 Monomer Syntheses

![chemical structure](image)

3-iodothiophene (2)

A Schlenk tube was charged with CuI (0.70 g, 3.68 mmol) and NaI (22.0 g, 147.2 mmol) under a nitrogen atmosphere. Xylene (57.6 mL) and diglyme (14.4 mL) were added followed by the addition of the ligand N, N-dimethylethylenediamine(0.79 g,7.36 mmol). Finally, 3-bromothiophene (12 g, 73.6 mmol) was added under nitrogen atmosphere. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for 22-24 h. The resulting suspension was allowed to reach room temperature. The solvents xylene and diglyme were removed under reduced pressure and the resulting mixture was extracted with hexanes (2x75 mL). The combined organics were washed with water (1x75 mL), saturated NaCl solution (1x75 mL) and were dried.
over Na$_2$SO$_4$, concentrated, and the residue was purified by silica gel chromatography (hexanes) to provide 2 as a yellow liquid. (12.3 g, 80%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 (dd, $J = 4.8, 3.0$, 1H), 7.21-7.19 (m, 1H), 7.11-7.09 (dd, $J = 4.8$, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 134.74, 128.65, 127.34.

2,5-Dibromo-3-iodothiophene (3)

In the absence of external light, N- Bromosuccinimide (NBS) (11.9 g, 66.6 mmol) was added to a round bottom flask equipped with stirrer and covered with an aluminum foil, in one portion, to a solution of (2) (7 g, 33.3 mmol) in DMF (200 mL). After stirring at room temperature for 1 h, the reaction mixture was heated and maintained at 60°C for 5 h and then quenched with water (200 mL). The reaction mixture was extracted with hexane (2x75mL) and layers were separated. The organic layer was washed with water (2x75mL), saturated NaCl solution (1x75 mL) and dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (hexanes) afforded (3) (9.8 g, 80%) as pale yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.92 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.08, 116.31, 113.46, 85.21.
(2, 5-Dibromo-thiopen-3-ylethynyl)-trimethyl-silane (M3)

A Schlenk tube was charged with CuI (0.052 g, 0.27 mmol) and Pd(PPh₃)₂Cl₂ (0.39 g, 0.55 mmol) under argon atmosphere. Triethylamine (TEA) (60 mL) was added to it and degassed. The reaction mixture was brought to 0°C, followed by the addition of (3) (4.0 g, 13.9 mmol) and trimethylsilylacetylene (1.5 g, 15.2 mmol) and stirred for further 6 h maintaining the temperature at 0 °C. The solvent TEA was removed under reduced pressure and the resulting mixture was extracted with hexanes (2x50 mL). The organic layer was washed with water (1x75 mL), saturated NaCl solution (1x50 mL) and was dried over Na₂SO₄, concentrated, and the residue was purified by silica gel chromatography (hexanes) to provide (M3) (2.57 g, 70%) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 6.93 (s, 1H), 0.25 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 132.15, 125.25, 116.84, 110.82, 99.69,97.00.

4-(2, 5-Dibromo-thiophen-3-yl)-1-hexyl-1H-[1, 2, 3] triazole (M4)

To an oven dried round bottom flask, was added CuI (0.472 g, 2.48 mmol) and THF (50 mL). To this stirred solution, N,N-Diisopropylethylamine (3.845 g, 29.81 mmol) and water (10 mL) was added followed by the addition of monomer (2,5-Dibromo-thiopen-3-ylethynyl)-trimethyl-silane (M3) (1.68 g, 4.96 mmol) and 1-azido hexane (0.947 g, 7.45 mmol). The reaction was stirred for 15 h under reflux conditions and quenched.
with water. The layers were separated and the aqueous layer was extracted with ethyl acetate (2x50 mL). The combined organics were washed with Brine (2x50 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (20:80 EtOAc: hexanes) afforded M₄ as white solid in (1.37 g, 70%) isolated yield. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.64 (s, 1H), 4.42 (t, J = 7.0, 2H), 1.98-1.91 (m, 2H), 1.37-1.29 (m, 6H), 0.90 (t, J = 7.0, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.03, 132.61, 131.35, 120.65, 112.52, 107.02, 50.58, 31.14, 29.72, 26.15, 22.43, 13.96. MS (FAB +) m/z 393.9 [M+H]⁺

2-Bromo-3-iodo-thiophene (4)

In the absence of light, NBS (7.8 g, 49.22 mmol) was added in one portion to a stirred solution of 2 (8.1 g, 44.74 mmol) in DMF (200 mL). After stirring at room temperature for 12 h, the reaction was quenched with water (200 mL) and extracted with hexanes (2x75mL). The combined organics were washed with Brine (2x75 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (hexanes) afforded 4 (8.35 g, 75%) as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.24 (d, J = 5.6, 1H), 6.95-6.96 (d, J = 5.6, 1H) ¹³C NMR (75 MHz, CDCl₃) δ 137.08, 116.31, 113.46, 85.21.
(2-Bromo-thiophen-3-ylethynyl)-trimethyl-silane (5)

A Schlenk tube was charged with CuI (0.105 g, 0.55 mmol) and Pd(PPh₃)₂Cl₂ (0.77 g, 1.1 mmol) under argon. Triethylamine (TEA) (110 mL) was added to it and degassed. The reaction mixture was brought to 0°C, followed by the addition of (4) (8.0 g, 27.68 mmol) and trimethylsilylacetylene (2.99 g, 30.45 mmol) and stirred for further 6 h maintaining the temperature at 0°C. The reaction mixture was brought to room temperature and further stirred for 12 h. The solvent TEA was removed under reduced pressure and the resulting mixture was extracted with hexanes (2x50 mL). The combined organics were washed with water (1x75 mL), saturated NaCl solution (1x50 mL) and were dried over Na₂SO₄, concentrated, and the residue was purified by silica gel chromatography (hexanes) to provide (5) (5.02 g, 70%) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.16 (d, J=6.0, 1H), 6.94-6.96 (d, J= 5.6, 1H) ¹³C NMR (100 MHz, CDCl₃) δ 129.93, 125.61, 124.56, 117.83, 98.83, 98.07.

4-(2-Bromo-thiophen-3-yl)-1-hexyl-1H-[1,2,3] triazole (6)
To an oven dried round bottom flask, was added CuSO$_4$$\cdot$5H$_2$O (462.15 mg, 1.85 mmol) and sodium ascorbate (1.83 g, 9.25 mmol) followed by the addition of tetra-$n$-butyl ammonium fluoride (TBAF) (37 mL) and tetrahydrofuran (THF) (150 mL). To this stirred solution, water (50 mL) was added followed by the addition of 1-azido hexane (4.7 g, 37.03 mmol) and (2,5-Dibromo-thiopen-3-ylethynyl)-trimethyl-silane (5) (4.8 g, 18.51 mmol). The reaction was stirred for 16 h. The reaction was quenched with water and extracted with ethyl acetate (2x50 mL). The combined organics were washed with water (2x50 mL), saturated NaCl solution (1x50 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (20:80 EtOAc: hexanes) afforded (6) as colorless oil (4.07 g, 70%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (s, 1H), 7.63-7.65 (d, $J$=5.6, 1H), 7.31-7.32 (d, $J$=5.6, 1H), 4.39-4.42 (t, $J$= 7.0, 2H), 1.98-1.91 (m, 2H), 1.37-1.29 (m, 6H), 0.87-0.90 (t, $J$= 7.0, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.9, 131.8, 127.92, 126.36, 120.60, 108.2, 50.50, 31.15, 30.32, 26.15, 22.44, 13.97.

![Image of 4-(2-Bromo-5-iodo-thiophen-3-yl)-1-hexyl-1H-[1, 2, 3] triazole (M5)]

4-(2-Bromo-5-iodo-thiophen-3-yl)-1-hexyl-1H-[1, 2, 3] triazole (M5)

Compound 6 (1.6 g, 5.091 mmol) was dissolved in dichloromethane. To this solution, trifluoromethanesulphonic acid (3.82 g, 25.45 mmol) was added and the solution cooled to 0 °C using an ice bath. N-iodo succinimide (1.15 g, 5.091 mmol) was added in small portions and the reaction mixture was stirred for 12 h at room temperature.
The reaction mixture was quenched with ice water and extracted with CH$_2$Cl$_2$ (3 X 25 mL). The combined organic extracts were washed with aqueous 10 % sodium bisulfate solution and water and dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by silica gel chromatography (15% ethyl acetate/hexane) to provide M2 as a white powder. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (s, 1H), 7.85 (s, 1H), 4.42 (t, $J$=7.0, 2H), 1.98-1.91 (m, 2H), 1.37-1.29 (m,6H),0.90(t, $J$=7.0,3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.84, 137.63, 133.85, 120.61, 110.84, 72.68, 50.70, 31.27, 30.42, 26.28, 22.56, 14.09.

(2, 5-Dibromo-thiopen-3-ylethynyl)-trimethyl-silane (M1)

A Schlenk tube was charged with CuI (9.5 mg, 0.30 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.21 g, 0.306 mmol) under argon atmosphere. Triethylamine (TEA) (10 mL) was added to it and degassed. To the reaction mixture 3-bromothiophene (1.0 g, 6.1 mmol) and trimethylsilylacetylene (0.78 g, 7.9 mmol) and stirred at 85 °C for 48 h. The solvent TEA was removed under reduced pressure and the resulting mixture was extracted with hexanes (2x50 mL). The organic layer was washed with water (1x75 mL), saturated NaCl solution (1x50 mL) and was dried over Na$_2$SO$_4$, concentrated, and the residue was purified by silica gel chromatography (hexanes) to provide (M1) (0.4 g, 36%) as yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (dd, $J$=3,1.4, 1H), 7.23 (dd, $J$=4.8,3, 1H), 7.12 (dd, $J$=5.1, 1H). 0.23 (s, 9H).
(2, 5-Dibromo-thiopen-3-ylethynyl)-trimethyl-silane (1)

A round bottom flask was charged with M1 (0.28 g, 1.55 mmol) and to it TBAF (3.88 mL, 1M in THF) was added drop by drop. The reaction mixture was stirred for 4 h. To the reaction mixture water was added and extracted with ether (2x50 mL). The organic layer was washed with water (1x75 mL), saturated NaCl solution (1x50 mL) and was dried over Na₂SO₄, concentrated and NMR was recorded. Yield was not recorded. 

$^1$H NMR (400 MHz, CDCl₃) δ 7.52 (dd, J=3,1, 1H), 7.26 (dd, J=4.5,2.8, 1H), 7.15 (dd, J=5,1, 1H). 3.05 (s, 1H).

(2, 5-Dibromo-thiopen-3-ylethynyl)-trimethyl-silane (M2)

A round bottom flask was charged with 1 and to it THF (10 mL) was added. To the reaction mixture CuI (0.14 g, 0.77 mmol) and N,N-diisopropylethylamine (0.6 g) and hexyl azide (0.23 g, 1.8 mmol) was added and the reaction mixture was stirred at reflux for 12 h. To the reaction mixture water was added and extracted with ether (2x50 mL). The organic layer was washed with water (1x75 mL), saturated NaCl solution (1x50 mL)
and was dried over Na₂SO₄, concentrated and NMR was recorded. Yield was not recorded. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.617 (dd, \(J=4.2\), 1H), 7.612 (s, 1H), 7.41 (dd, \(J=5\), 1H), 7.31 (dd, \(J=5.2\), 1H), 4.3 (t, \(J=7.0\), 2H), 1.9 (m, 2H), 1.37-1.29 (m, 6H), 0.85(t, \(J=7.0\), 3H).

\[
\begin{array}{c}
\text{N}^3 \text{N}^2 \text{C}_8 \text{H}_{13} \\
\text{S} \text{S} \text{S} \\
\end{array}
\]

4-([2,2\':5',2\''-terthiophen]-3\'-yl)-1-hexyl-1\(H\)-1,2,3-triazole (7)

To an oven dried Schlenk, compound (6) (100 mg, 0.254 mmol) was added followed by the addition of Pd (PPh₃)₄ (29.35 mg, 0.025 mmol) in glove box. Dry THF (7.5 mL, 0.034 M) was deoxygenated for 2 h and added to the Schlenk. Aqueous K₂CO₃ (1 mL, 0.25 M) was added and the reaction mixture was stirred for 15 minutes. To this, 2-thiophene boric acid (127.6 mg, 0.997 mmol) was added and further stirred for 36 h at 60 °C. After stirring for 36 h, water was added to the mixture and then extracted with ethyl acetate (2x25 mL). The combined organics were washed with water (2x25 mL), saturated NaCl solution (1x25 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (30:70 EtOAc: hexanes) afforded the product (7) (70\%). \(^1\)H NMR (400MHz, CD₃COCD₃) \(\delta\) 7.83 (s, 1H), 7.59 (s, 1H), 7.54- 7.55 (dd, \(J=5.2\), 1H), 7.47- 7.49 (dd, \(J=5.2\), 1H), 7.36 (dd, \(J=5.2\), 1H), 4.3 (t, \(J=7.0\), 2H), 1.9 (m, 2H), 1.37-1.29 (m, 6H), 0.85(t, \(J=7.0\), 3H).
3.6, 1H), 7.35 (dd, J=3.6, 1H), 7.10 (dd, J= 5.2, 2H), 4.39 (t, J= 7.0, 2H), 1.85- 1.91(m, 2H), 1.28-1.30 (m, 6H), 0.88 (t, J= 7.0, 3H). $^{13}$C NMR (100 MHz, CD$_3$COCD$_3$) δ 142.46, 137.21, 137.08, 135.22, 131.28, 130.84, 129.19, 129.09, 128.69, 128.15, 126.41, 125.34, 123.0, 50.71, 31.96, 31.08, 23.23, 14.33.

1-Azido hexane

To a round bottom flask charged with stirrer, DMSO (60 mL), 1-bromohexane (5 g, 3.62 mmol) and sodium azide (3.52g, 5.43 mmol) were added and stirred for overnight. Water was added to quench the reaction and extracted with ethyl acetate (2x50mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate (1x25mL). The combined organics were washed with water (2x50mL), saturated NaCl solution (1x50 mL) and dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to afford the colorless oily liquid as product in (3.15 g, 82%) isolated yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.23 (t, J = 7.0, 2H), 1.60-1.53 (m, 2H), 1.36-1.29 (m, 6H), 0.89 (t, J = 7.0, 2H).

2.5.2 Polymer Syntheses

Polymerization Procedure: (P3TzT)
M5 (150 mg, 0.340 mmol) was dissolved in dry THF in a Schlenk flask covered with aluminum foil under argon atmosphere. The Schlenk was cooled to 0 °C using an ice bath. The reagent t-butylmagnesium chloride (0.22 mL, 0.374 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 2 h. Ni(dppp)Cl$_2$ (1.37 mg, 0.0025 mmol) was added under argon atmosphere. The reaction mixture was taken out from the ice bath and allowed to run for 18 h at room temperature and then quenched using allyl magnesium chloride (0.02 mL, 0.034 mmol). The reaction mixture was precipitated into ice-cold methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, CHCl$_3$. The CHCl$_3$ fraction, after concentration under reduced pressure, afforded 52 mg of the polymer. The material isolated from the hexanes fraction was analyzed by GPC. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (s, 1H), 7.64 (s, 1H), 4.36-4.40 (t, $J =$7.0, 2H), 1.87-1.95 (m, 2H), 1.22-1.34 (m, 6H), 0.81-0.83(t, $J =$7.0, 3H). $M_n = 24.7$k, PDI = 1.48.

**Quenching Studies**

M4 (134 mg, 0.340 mmol) was dissolved in THF and transferred into a Schlenk flask under argon atmosphere. t-Butylmagnesium chloride (0.22 mL, 0.374 mmol) was added via syringe and the reaction mixture was stirred at room temperature for 2 h. It was then quenched with water and extracted with diethylether (3 X 25 mL). The combined organic extracts were washed with brine and dried over sodium sulfate and evaporated under reduced pressure. $^1$H NMR was recorded without further purification (Figure 2.4 and Figure 2.5). The M5 was also subjected to same reaction conditions as M4, except that the Schlenk was cooled to 0 °C throughout the reaction. Work up for M5 was same
as M4, and 1H NMR was recorded without further purification (Figure 2.4 and Figure 2.5).

**Attempted synthesis of M3 from M1**

M1 (200 mg, 1.11 mmol) was dissolved in acetic acid (1.7 mL). To this mixture N-bromosuccinimide (500 mg, 2.78 mmol) dissolved in chloroform (1.7 mL) or dimethyl formamide (1.7 mL) was added and stirred for 3 days. TLC indicated 4 spots. After the column chromatography NMR was recorded and none of them correspond to M3.

**Attempted synthesis of polymer from M1**

M1 (200 mg, 1.11 mmol) was dissolved in chloroform (2.5 mL) in a round bottom flask under argon atmosphere. The reagent FeCl₃ chloride (900 mg, 5.55 mmol) was added to the solution and the mixture was allowed to stir for 6 h. The reaction mixture was added to ice-cold methanol, but no precipitate was observed.

**Attempted synthesis of polymer from M2**

M2 (140 mg, 0.56 mmol) was dissolved in chloroform (1.2 mL) in a round bottom flask under argon atmosphere. The reagent FeCl₃ chloride (482 mg, 2.98 mmol) was added to the solution and the mixture was allowed to stir for 2 days. The reaction mixture was added to ice-cold methanol, but no precipitate was observed.

**Attempted synthesis of polymer from M3**

M3 (800 mg, 2.36 mmol) was dissolved in dry THF (15 mL) in a Schlenk flask under argon atmosphere. The reagent t-butylmagnesium chloride (1.38 mL, 2.36 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 3 h. After 3 h, Ni(dppp)Cl₂ (21.3 mg, 0.0394 mmol) was added under argon atmosphere. The reaction mixture was allowed to run for 24 h at room temperature and
then quenched using allylmagnesium chloride (0.39 mL, 0.67 mmol). The reaction mixture was added to ice-cold methanol, but no precipitate was observed.

**Attempted synthesis of polymer from M4**

M4 (300 mg, 0.763 mmol) was dissolved in dry THF in a Schlenk flask under argon atmosphere. The reagent t-butylmagnesium chloride (0.49 mL, 0.839 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 3 h. After 3 h, Ni(dppp)Cl₂ (4.18 mg, 0.0076 mmol) was added under argon atmosphere. The reaction mixture was allowed to run for 24 h at room temperature and then quenched using allylmagnesium chloride (0.044 mL, 0.076 mmol). The reaction mixture was added to ice-cold methanol, but no precipitate was observed.

**Attempted synthesis of polymer from M4 at elevated temperature**

M4 (300 mg, 0.763 mmol) was dissolved in dry THF into the Schlenk flask under argon atmosphere. The reagent t-butylmagnesium chloride (0.49 mL, 0.839 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 3 h. After 3 h, Ni(dppp)Cl₂ (4.18 mg, 0.0076 mmol) was added under argon atmosphere. The reaction mixture was allowed to run for 24 h at 60 °C. After 24 h, the reaction mixture was brought to room temperature and then quenched using allylmagnesium chloride (0.044 mL, 0.076 mmol). The reaction mixture was added to ice-cold methanol, but no precipitate was observed.

**2.6 References**


Copolymers Containing 4-Alkyl-1,2,4-Triazole or 1,3,4-Thiadiazole Unit as the Partner Unit. *Macromolecules* **2005**, *38*, 1500-1503.


CHAPTER 3

STRAIGHTFORWARD ROUTE TO ELECTRON TRANSPORTING
CONJUGATED POLYMERS

3.1 Introduction

In order to design a wide variety of electron transporters from readily available monomers, we focused our attention on the acceptor monomers that are used in donor-acceptor (D-A) alternating copolymers.\textsuperscript{1-10} A plethora of D-A polymers is synthesized to lower the band gap and broaden the absorption range in solar spectrum. Acceptor comonomers used in D-A polymers have relatively high electron affinity compared to the donor comonomer and pull the electron density away from the donor. Thus, in D-A polymers, the LUMO and HOMO predominantly lie on the acceptor and donor monomers, respectively thereby lowering the band gap. Charge transporting nature of D-A polymers depends on the strength of the donor and acceptor comonomers. Rylene diimides, such as NDI and PDI, have high electron affinity and the small molecules themselves are electron transporting in nature.\textsuperscript{1, 11, 12} Thus, D-A polymers made of NDI or PDI as acceptor comonomer are electron transporting in nature.\textsuperscript{1-3, 13-20} Most of the nitrogen and/or oxygen containing aromatic heterocyclic compounds, except rylene diimide acceptor monomers, have moderate to low electron affinity. Thus, a majority of the D-A polymers of these heterocycles are hole transporting while a few of them are both hole and electron transporting (ambipolar).\textsuperscript{2, 3, 7-10, 21} The homopolymers of these acceptor comonomers could be electron transporting.\textsuperscript{22-25} Homopolymers of few acceptor monomers were synthesized in early 1990’s but their electron transport properties are not reported.\textsuperscript{25, 26} Moreover, these homopolymers suffer from narrow absorption range, high
band gap and are not easily processable. Recently, a conjugated alternating copolymer of two acceptor monomers is reported to be electron transporting with low band gap. But the synthetic protocol reported to synthesize homopolymers of an acceptor monomer and alternating copolymer of two acceptor monomers is specific to few monomers and cannot be readily extended to other acceptor monomers. Herein, we report a straightforward synthetic route via Stille coupling to generate solution processable low band gap conjugated polymers from readily available acceptor monomers. We hypothesized that vinyl spacer, a weak electron donor, will maintain the electron affinity of the polymer, decrease the steric between neighbouring repeating units and reduce the band gap. We demonstrate the efficacy of our approach using widely used electron acceptor, 2,1,3-benzothiadiazole and commercially available trans-1,2-bis(tri-n-butylstannyl)ethylene. The polymer has wide absorption range and the electron mobility is comparable to that of PCBM, the widely used electron transporter in organic solar cells. We believe that our method can be readily extended to a wide array of acceptor monomers to rapidly generate a library of electron transporters.

3.2 Results and Discussion

We chose 2,1,3-benzothiadiazole as our monomer and electron accepting moiety because of the ready availability of the monomer and it is also widely used to synthesize D-A alternating conjugated copolymers. To ensure the solubility of the polymer,
dialkoxy substituted 2,1,3-benzothiadiazole was chosen as the target acceptor monomer.
To study the effect of alkyl chain length on the optical, packing and charge transport properties of the polymer, 2,1,3-benzothiadiazoles substituted with tetracoxyloxy and octyloxy side chains were synthesized. Synthesis of the monomers and polymers is shown in Figures 3.2 and 3.3. Dialkoxy substituted 2,1,3-benzothiadiazole was synthesized using established protocols. M1 was synthesized by brominating compound 4a using established protocol.9 PBTDV1 was synthesized through a Stille coupling27 of M1 and commercially available trans-1,2-bis(tri-n-butylstannyl)ethylene. PBTDV1 was successfully synthesized using Pd(PPh3)4 in toluene at 90 °C. Other attempted polymerization conditions are shown in Table 3.3. Polymerization of PBTDV1 took 6 days. In general, Stille coupling of aryl iodides is much faster than the aryl bromide. To decrease the polymerization time, we synthesized diiodo derivative of dioctyloxy substituted 2,1,3-benzothiadiazole (M2). Iodination of compound 4b was not successful under the similar established iodination conditions used for unsubstituted 2,1,3-benzothiadiazole. This might be because of the degradation of dioctyloxy substituted 2,1,3-benzothiadiazole under harsh acidic conditions. All the attempted iodinating conditions for 4b are shown in Table 3.1. All the reactions after the work up showed multiple spots on TLC and the crude NMR showed no product peak. M2 was successfully synthesized from 4b using highly active but mild iodinating conditions. PBTDV2 was synthesized from M2 using Pd(PPh3)4 and mixture of NMP and ODCB at 90 °C. There was no appreciable difference in the polymerization time for M2 compared to M1, thus metal insertion between aryl halogen bond is not the rate determining step. All other attempted polymerization conditions for PBTDV2 are shown in Table 3.4.
**Table 3.1** Attempted iodinating conditions for compound 4b.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Acid</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIS</td>
<td>H₂SO₄</td>
<td>DCM</td>
<td>RT</td>
<td>24</td>
</tr>
<tr>
<td>NIS</td>
<td>CF₃SO₃H</td>
<td>DCM</td>
<td>RT</td>
<td>12</td>
</tr>
<tr>
<td>I₂</td>
<td>CH₃COOH</td>
<td>CHCl₃</td>
<td>50</td>
<td>48</td>
</tr>
<tr>
<td>I₂</td>
<td>H₂SO₄</td>
<td>CH₃COOH, H₂O</td>
<td>70</td>
<td>24</td>
</tr>
<tr>
<td>I₂</td>
<td>H₂SO₄, NaIO₃</td>
<td>CH₃COOH, H₂O</td>
<td>110</td>
<td>24</td>
</tr>
<tr>
<td>I₂</td>
<td>H₂SO₄, HIO₃</td>
<td>CH₃COOH, H₂O</td>
<td>90</td>
<td>24</td>
</tr>
<tr>
<td>I₂</td>
<td>H₂SO₄, H₅IO₆</td>
<td>CH₃COOH, H₂O</td>
<td>70</td>
<td>12</td>
</tr>
</tbody>
</table>

**Table 3.2** Attempted polymerization conditions for PBTD2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Base</th>
<th>Temperature (°C)</th>
<th>M_w (KDa)³¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(PPh₃)₄</td>
<td>NMP/ODCB</td>
<td>K₂CO₃</td>
<td>90</td>
<td>2.7</td>
</tr>
<tr>
<td>Pd(OAc)₂</td>
<td>NMP/ODCB</td>
<td>K₂CO₃</td>
<td>90</td>
<td>2.8</td>
</tr>
<tr>
<td>Pd('Bu₃P)₂</td>
<td>NMP/ODCB</td>
<td>K₂CO₃</td>
<td>90</td>
<td>3.5</td>
</tr>
<tr>
<td>Pd(PPh₃)₄</td>
<td>Toluene</td>
<td>K₂CO₃</td>
<td>80</td>
<td>2.0</td>
</tr>
<tr>
<td>Pd(PPh₃)₄</td>
<td>Toluene</td>
<td>LiOH.H₂O</td>
<td>80</td>
<td>2.8</td>
</tr>
<tr>
<td>Pd('Bu₃P)₂</td>
<td>THF</td>
<td>LiOH.H₂O</td>
<td>60</td>
<td>3.5</td>
</tr>
<tr>
<td>Pd('Bu₃P)₂</td>
<td>'Bu₂O</td>
<td>LiOH.H₂O</td>
<td>110</td>
<td>15.7, 3.9, 2.5</td>
</tr>
</tbody>
</table>

³¹GPC (THF) with polystyrene standards
Table 3.3 Attempted polymerization conditions for PBTDV1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temperature ( °C)</th>
<th>M_w (KDa)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(PPh₃)₄</td>
<td>ODCB</td>
<td>110</td>
<td>2.0</td>
</tr>
<tr>
<td>Pd₂(dba)₃P(o-tol)₃</td>
<td>CB</td>
<td>110</td>
<td>-</td>
</tr>
</tbody>
</table>

aGPC (CHCl₃) with polystyrene standards.

Table 3.4 Attempted polymerization conditions for PBTDV2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temperature ( °C)</th>
<th>M_w (KDa)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd₂(db₃)₃P(o-tol)₃</td>
<td>NMP/ODCB</td>
<td>140</td>
<td>9.6</td>
</tr>
<tr>
<td>Pd('Bu₃P)₂, CuI</td>
<td>NMP/ODCB</td>
<td>130</td>
<td>3.6</td>
</tr>
<tr>
<td>Pd('Bu₃P)₂, CuI</td>
<td>'Bu₂O</td>
<td>100</td>
<td>3.5b</td>
</tr>
</tbody>
</table>

aGPC (THF) with polystyrene standards

bGPC (CHCl₃) with polystyrene standards
Figure 3.2 Synthesis of monomers.

Figure 3.3 Synthesis of polymers using Suzuki and Stille condensation polymerization.
In order to probe the effect of the vinylene linker, we also synthesized conjugated polymers, **PBTD1** and **PBTD2**, containing 2,1,3-benzothiadiazole alone. Conjugated polymers made of single electron deficient unit are rare and most of them are not solution processable.25, 26 **PBTD1** and **PBTD2** are the first reported solution processable conjugated polymers containing 2,1,3-benzothiadiazole alone. These polymers were synthesized using a palladium-mediated Suzuki coupling of the benzothiadiazole dihalide monomer with the commercially available diborate **BTD** (Figure 3.3). The Suzuki coupling, to yield polymers, required a binary or ternary solvent mixture, highly active Pd(bu$_3$P)$_2$ catalyst, and a strong base such as LiOH.H$_2$O. The solvents for the polymerization were chosen based on the activity of catalyst and the solubility of polymer in that solvent. In general, palladium catalysts are highly active in polar solvents such as di-n-butylether and conjugated polymers are soluble in 1,2-dichlorobenzene. The polymerization was not successful with less active but widely used Pd(PPh$_3$)$_4$ catalyst for Suzuki coupling (see Table 3.2 for other attempted polymerization conditions). Much like in **PBTDV1** and **PBTDV2**, we did not find any significant difference in the reaction time if the monomer was an aryl bromide or an aryl iodide. The synthesis of **PBTDV1** and **PBTDV2**, unlike **PBTD1** and **PBTD2**, involves the condensation of dihalo derivative of 2,1,3-benzothiadiazole with commercially available trans-1,2-bis(tri-n-butylstannyl)ethylene. Since dihalo derivatives of many acceptor monomers are already known, this strategy can be readily extended to a wide range of acceptor monomers. From now on **PBTD1** and **PBTD2** are referred as homopolymers and **PBTDV1** and **PBTDV2** are called as alternating polymers.
Polymers were purified via soxhlet (see the experimental section for solvents used for each polymer) and were characterized. Gel Permeation Chromatograms (GPC) of polymers is shown in Figure 3.4a. GPC was recorded using tetrahydrofuran (THF) as a solvent. Both alternating polymers, PBTDV1 and PBTDV2, have one broad peak. Both the homopolymers, PBTD1 and PBTD2, have two peaks in GPC, one at low molecular weight and the other at high molecular weight. Two peaks for homopolymers might be because of the presence of either both low and high molecular weight polymers or aggregation of polymers in THF. $^1$H NMR spectra of the polymers were recorded in tetrachloroethane-d2 (TCE-d2) at high temperature (100 °C). All the polymers were aggregating in TCE-d2 at high concentration; hence NMR was recorded at high temperature.

Solution and thin film UV-Vis absorption spectra of all the polymers are shown in Figure 3.4b and Figure 3.11. Solution state UV-Vis absorption spectra were recorded by dissolving the polymer in chloroform. The solution and thin films of homopolymers are in yellow color, while those of alternating polymers are in bluish purple color. The absorption range for PBTD1 and PBTD2 thin films is around 400 nm. The large band gap and narrow absorption range of these polymers might be due to the steric nature between the neighboring repeat units, leading to a twist and thereby disrupting the π-π conjugation along the polymer backbone, consistent with our expectation. PBTDV1 and PBTDV2 with the vinylene linkers have the absorption range of 250-735 nm with the absorption maximum around 580 nm and shoulders at 630 nm and 680 nm. The optical band gap of PBTDV1 and PBTDV2 was found to be 1.68 eV, which is 1.0 eV less than for PBTD1 and PBTD2 (Table 3.5). The lowering of the band gap clearly indicates that
the vinylic spacer unit facilitates the reduction in steric between neighbouring benzothiadiazole units, and thus enhancing the π-π conjugation along the polymer backbone. There is also an increase in the absorption range of alternating polymers compared to their non-vinylene counterparts. We found that there was no appreciable difference between the solution and thin film absorption for all the polymers. This might be because the polymers are already aggregated in solution and/or there is absence of π-π aggregation of polymers in thin films. The vinylene polymers, PBTDV1 and PBTDV2, exhibit a vibronic structure in the absorption spectra of both solution and thin film. Since the presence of vibronic structure
Table 3.5 Optical, redox and assembly properties of polymer thin films.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mw (Mw/Mn)</th>
<th>$\lambda_{\text{film max}}$ (nm)</th>
<th>HOMO$^{\text{elec}}$ (eV)$^d$</th>
<th>LUMO$^{\text{elec}}$ (eV)$^d$</th>
<th>LUMO$^{\text{opt}}$ (eV)$^e$</th>
<th>$E_g^{\text{elec}}$ (eV)</th>
<th>$E_g^{\text{opt}}$ (eV)</th>
<th>001 spacing$^f$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTD1$^b$</td>
<td>79.1 (1.2)</td>
<td>411</td>
<td>-</td>
<td>-2.93</td>
<td>-</td>
<td>-</td>
<td>2.69</td>
<td>3.25</td>
</tr>
<tr>
<td>PBTD2$^b$</td>
<td>16.2 (1.1)</td>
<td>396</td>
<td>-5.96</td>
<td>-3.03</td>
<td>-3.27</td>
<td>2.93</td>
<td>2.69</td>
<td>2.25</td>
</tr>
<tr>
<td>PBTDV1</td>
<td>19.2 (1.8)</td>
<td>584 (633,686)$^c$</td>
<td>-5.45</td>
<td>-3.42</td>
<td>-3.77</td>
<td>2.03</td>
<td>1.68</td>
<td>3.45</td>
</tr>
<tr>
<td>PBTDV2</td>
<td>15.0 (1.6)</td>
<td>579 (627,675)$^c$</td>
<td>-5.24</td>
<td>-3.45</td>
<td>-3.59</td>
<td>1.79</td>
<td>1.68</td>
<td>2.28</td>
</tr>
</tbody>
</table>

$^a$GPC (THF) with respect to polystyrene standards. $^b$Shows a small molecular weight peak in GPC. $E_g^{\text{opt}}$ calculated from the onset of thin film UV-Vis absorption spectra. $^c$Shoulders in absorption spectra. $^d$Calculated from cyclic voltammetry. $^e$Calculated from HOMO$^{\text{elec}}$ + $E_g^{\text{opt}}$. $^f$Calculated from the WAXS and the values correspond to side-chain interdigitated distance between polymers.
in the absorption spectrum is an indication of inter-chain π-π interactions,\textsuperscript{28-34} we believe that the vinylene polymer may be aggregating in solution. On the other hand, no vibronic structure was observed in the absorption spectra for PBTD1 and PBTD2 indicating the absence of inter-chain π-π interactions. This might be due to the twist in the polymer backbone caused by the sterics. That is, even though homopolymers aggregate in solution due to lack of π-π interactions there is no characteristic absorption peak in the UV-Vis absorption spectra. Thus, homopolymers may or may not be aggregating in solution. Interestingly, the side chains have negligible effect on the optical properties of all the polymers.

Frontier energy levels of the polymers were determined using cyclic voltammetry. The redox properties of the polymers are shown in Figure 3.4c. All the polymers, except PBTD1, undergo both oxidation and reduction. PBTD1 showed only a reduction peak. The frontier energy levels of polymers are determined using established protocols (see experimental section).\textsuperscript{35, 36} LUMO energy level is calculated from both the reduction onset (electrical) and optical band gap (optical). Both values are tabulated in Table 3.5. LUMO values calculated from reduction onset is lower in energy compared to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.5.png}
\caption{Figure 3.5 Frontier energy levels of PBTDV1 and various low band gap hole transporting polymers. For these hole transporting polymers, charge transfer energy loss is minimum with PBTDV1 compared to PCBM (HOMO-dashed line, LUMO-solid line, \textsuperscript{a}electrochemical LUMO, \textsuperscript{b}optical LUMO).}
\end{figure}
the LUMO calculated from optical band gap. The frontier energy levels and electrical band gap values of the polymers are tabulated in Table 3.5. The vinylene polymers PBTDV1 and PBTDV2 are much easier to oxidize and reduce compared to PBTD1 and PBTD2. This is expected because the charges in the vinylene polymers can be better stabilized because of the increased delocalization along the conjugated polymer back bone. This observation once again is consistent with vinylic spacer unit facilitating the π-π conjugation along the polymer back bone by reducing the steric interactions between the neighbouring repeat units. PBTDV1 and PBTDV2 have optimal frontier energy levels offset with respect to many low band gap hole conductors such as P3HT, PCPDTBT, PBDTTT-CF, and PBnDT-FTAZ, making them promising candidates for use as electron conductors in all polymer solar cells (Figure 3.5). Polymer packing in thin films was determined using wide angle X-ray scattering (WAXS) and the data is shown in Figure 3.4d. PBTD2 and PBTDV2 polymers with octyloxy side chains exhibit peaks at 2.25 nm and 2.28 nm, respectively. This distance correlates well with the expected octyloxy-octyloxy inter-chain distance. On the other hand PBTD1 and PBTDV1, polymers with tetradecyloxy side chains, exhibit peaks at 3.25 nm and 3.45 nm respectively, which are smaller than the expected tetradecyloxy side chain packing distance of 4.3 nm. The simulation of polymer packing on Cerius2 for the corresponding interchain packing indicated partial
interdigitation between side chains (Figure 3.6). Side chain interdigitation is commonly observed in many semiconducting conjugated polymer packing.\textsuperscript{1, 31, 32, 34, 38} Side chain interdigitation decreases the distance between polymer backbones and can enhance the charge transport. Band gap simulations for the polymers and their theoretical band gap are shown in Figure 3.7.

The electron mobilities of \textbf{P}BTDV\textsubscript{1} and \textbf{P}BTDV\textsubscript{2} are determined using time of flight (ToF) technique.\textsuperscript{39} We chose ToF to measure the mobility because the charge transport occurs across the polymer film in a device configuration similar to organic
photovoltaic devices. The samples were prepared by drop casting the polymer solutions onto ITO coated glass slides followed by the thermal evaporation of aluminum on top of polymer film. In ToF, a short laser pulse incident on a sample generates a thin sheet of charge carriers. Transit time (t_{TR}), time to migrate the generated charge carriers across the sample under the influence of an applied electric field (E), is determined. The photocurrent transient of polymers (PBDV1 and PBDV2) at various applied field are shown in Figure 3.12 and the shape of photocurrent transit is characteristic of dispersive transport.\(^{39}\) Charge carrier mobility (\(\mu\)) was determined using the following equation: \(\mu = L/(E \cdot t_{TR})\), where \(L\) is the film thickness. Electron mobilities of the polymers at various applied fields are shown in Figure 3.8. PBDV1 and PBDV2 exhibit high electron mobilities of \(10^{-3}\) cm\(^2\)/V.s, comparable to those of PCBM and F8BT thin films.\(^{21,40,41}\) A slight increase in the electron mobility was observed with a decrease in inter-chain distance from PBDV1 (3.45 nm) to PBDV2 (2.25 nm). The dispersive charge transport is explained by a variation of local transport rates due to a high spatial and/or energetic disorder in the material.\(^{42}\) Each data set is averaged over 128 photocurrent transients generated by the light pulses. In organic photovoltaics there should be a balance in charge transport between hole and electron transporters. The hole mobility of most of the conjugated polymers used in organic photovoltaics.
photovoltaics is on the order of $10^{-2}$-$10^{-5}$ cm$^2$/V.s making PBTDV1 and PBTDV2 as excellent electron transporters for organic photovoltaic devices. We compared the electron transport and absorption properties of alternating polymers with existing electron transporting 2,1,3-benzothiadiazole based alternating copolymers, F8BT$^{21}$ and F8TBT$^{43}$. F8BT has similar electron mobility as alternating polymers but has poor absorption range and high band gap. F8TBT has low band gap and broad absorption range but suffers from low electron mobility ($10^{-5}$ cm$^2$/V.s) (Figure 3.9).

Alternating polymers have high electron mobility as well as low band gap and broad absorption range. Alternating polymers meet both the requirements to be a good electron transporter in all polymer solar cells. In order to determine the hole mobilities, the polarity of the applied field was changed. However, negligible photocurrent transients were observed in this configuration, indicating that the hole mobility could be orders of magnitude lower than the electron mobility.

### 3.3 Conclusions

In conclusion, we have shown that poly(arylene vinylene) derivative of an acceptor unit such as 2,1,3-benzothiadiazole is a good electron transporter ($\mu_e \sim 10^{-3}$ cm$^2$/V.s) with low band gap and broad absorption range (250-735 nm). Electron transporting properties of PBTDV1 and PBTDV2 indicate that vinyl spacer indeed maintains the electron affinity of 2,1,3-benzothiadiazole unlike other donor-acceptor...
polymers of 2,1,3-benzothiadiazole that exhibit hole transporting properties. Moreover, vinyl spacer also reduces the band gap and widens the absorption range of PBTDV1 and PBTDV2 compared to the conjugated homopolymers of 2,1,3-benzothiadiazole (PBTD1 and PBTD2). The synthesis of PBTDV1 and PBTDV2 involves the condensation of dihalo derivative of 2,1,3-benzothiadiazole with commercially available trans-1,2-bis(tri-n-butylstannyl)ethylene. Since dihalo derivatives of many acceptor monomers are already known, this strategy can be readily extended to a wide range of acceptor monomers to generate solution processable electron transporting polymers with low band gap and wide absorption range.

Figure 3.10 Chemical structures of the polymers derived from known electron acceptor monomers.

The proposed acceptor monomers that could be used to generate electron transporting polymers are shown in Figure 3.10. The acceptor monomers are arranged based on the strength of their electron affinity. Polymers of these acceptor monomers could provide: i) electron transporting polymers with different chemical moieties, ii) wide variety of frontier energy levels and absorption ranges that could be complemented with desired hole transporters. Thus, the proposed strategy breaks one of the road blocks for realizing all polymer solar cells by providing access to a wide variety of electron
transporting polymers. To enhance the efficiency of all polymer solar cells, the morphology of the active layer needs to be controlled.

3.4 General Experimental Methods

The $^1$H NMR spectra of polymers were recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C and the solvent peak was set at 6.0 ppm on all spectra. For UV-Vis absorption spectra, stock solutions of polymers ($c = 1\text{mg/10mL}$) were prepared in spectrophotometric grade chloroform (Fisher, Optima). UV-Vis absorption spectra of polymer thin films were recorded by spin casting polymer solutions onto a glass plate. The polymer solutions were drop cast onto a platinum working electrode and the CV was recorded with tetrabutylammonium hexfluorophosphate as a supporting electrolyte (0.1M) in acetonitrile. The redox potentials were determined versus a Ag/Ag$^+$ reference electrode. The working and auxiliary electrodes were cleaned after each run. The HOMO and LUMO values were calculated using Fc/Fc$^+$ as a reference. Time of flight (ToF) measurements was done at room temperature under vacuum ($10^{-2}$ Torr). A frequency doubled YAG laser (532 nm) was utilized as the pulsed excitation source and the

![Figure 3.11 UV-Vis absorption spectra of polymers in chloroform.](image)

Figure 3.11 UV-Vis absorption spectra of polymers in chloroform.
photocurrent was measured across a 50 Ω resistor by a digitizing oscilloscope HP 54510B.

3.5 Experimental Procedures

3.5.1 Monomer Syntheses

![1,2-bis-octyloxy-benzene (1b)](image)

To a solution of catechol (15 g, 0.136 mol) in DMF (75 mL) was added 1-bromooctane (0.34 mol, 59.2 mL) and K₂CO₃ (56.5 g, 0.408 mol). The mixture was stirred at 100 °C under a nitrogen atmosphere for 48 hours. After cooling the mixture to room temperature (RT), 150 mL of water was added. The organic layer was separated and the aqueous layer was extracted with DCM. The organic layers were mixed and washed with sodium thiosulfate and brine solution. The combined organic phase was dried over Na₂SO₄. After filtration, the mixture was concentrated under vacuum. The residual DMF and 1-bromooctane were distilled out at 120 °C under reduced pressure (300 millitorr). The purification of the residue by silica gel chromatography (10:90 dichloromethane:
hexanes) afforded 1b as colorless oil. Yield: 35.5 g (78%), colorless liquid. $^1$H NMR (CDCl$_3$): $\delta = 6.89$ (s, 4H), 3.99 (t, $J = 6.6$ Hz, 4H), 1.85-1.78 (m, 4H), 1.57-1.22 (m, 20H), 0.89 (t, $J = 6.6$ Hz, 6H). $^{13}$C NMR (CDCl$_3$): $\delta = 149.38$, 121.12, 114.23, 69.40, 31.98, 29.55, 29.49, 29.44, 26.20, 22.82, 14.24.

1,2-dinitro-4,5-bis-octyloxy-benzene (2b)

A two neck round-bottom flask containing dichloromethane (420 mL), acetic acid (420mL), and 1b (35 g, 0.104 mol) was cooled to 10 °C and 65% nitric acid (550 mL) was added drop wise. The mixture was allowed to warm to room temperature and stirred for 48 hours. After completion of the reaction, the reaction mixture was poured into ice-water and the dichloromethane layer separated. The water phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated. The crude product was recrystallized from ethanol. Yield: 36 g (81%), yellow solid. $^1$H NMR (CDCl$_3$): $\delta = 7.29$ (s, 2H), 4.09 (t, $J = 6.5$ Hz, 4H), 1.90-1.82 (m, 4H), 1.51-1.28 (m, 20H), 0.88 (t, $J = 6.6$ Hz, 6H). $^{13}$C NMR (CDCl$_3$): $\delta = 151.93$, 136.55, 108.01, 70.31, 31.87, 29.30, 28.81, 25.92, 22.75, 14.18.

4,5-bis(octyloxy)benzene-1,2-diaminium chloride (3b)

A mixture of 2b (10 g, 0.0235 mol), Sn(II)Cl$_2$ (0.188 mol, 42.5 g) in ethanol (350 mL), and conc. HCl (140 mL) were heated to 85 °C for overnight. The reaction mixture was cooled to room temperature and the product was filtered and washed with water and
methanol. The product was finally dried at RT under a stream of argon and used directly (unstable). Yield: 21 g (quantitative yield), off-white solid.

\[
\text{5,6-bis-octyloxy-benzo[1,2,5]thiadiazole (4b)}
\]

To a mixture of \(3b\) (17g, 38.85 mmol) and triethylamine (388.5 mmol, 55 mL) in 500mL dichloromethane, a solution of thionyl chloride (77.72 mmol, 5.67mL) in 80 mL dichloromethane was added slowly. The mixture was refluxed for 6 hours and the solution was cooled. The solution was then concentrated in vacuum followed by trituration in water. The mixture was stirred for 30 min and the product was filtered and reprecipitated from ethanol. The reprecipitated compound was purified by silica gel chromatography (4:96 EtOAc: hexanes) to afford \(4b\) as off-white solid. Yield: 9.0 g (59 %). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.13\) (s, 2H), 4.09 (t, \(J = 6.5\) Hz, 4H), 1.94-1.87 (m, 4H), 1.53-1.29 (m, 20H), 0.90-0.87 (m, 6H). \(^13\)C NMR (CDCl\(_3\)): \(\delta = 154.29, 151.54, 98.55, 69.28, 31.95, 29.47, 29.41, 28.88, 26.16, 22.82, 14.25.\)

\[
\text{4,7-Diiodo-5,6-bis-octyloxy-benzo[1,2,5]thiadiazole (M2)}
\]

In a round bottom flask compound \(4b\) (1g, 2.547 mmol), iodine (0.775g, 3.056 mmol), and PhI(OOCF\(_3\))\(_2\) (1.31g, 3.056 mmol) were added along with 60 mL
dichloromethane. The reaction mixture was refluxed for 5 h. After 5 h, the reaction was brought to room temperature and sodium thiosulphate solution (100mL) was added and stirred further for 1 h. Water (100mL) was added and the reaction mixture was extracted with DCM (4x50mL). The organic layer was washed with NaHCO₃ (100mL) and sat. NaCl (100mL) solution and dried over Na₂SO₄. The crude was purified by silica gel chromatography (40:60 DCM: hexanes) to afford 2 as light yellow solid. Yield: 1.35g (82%).

\[ ^1H \text{ NMR (CDCl}_3\): } \delta = 4.12 (t, J = 6.5 \text{ Hz}, 4\text{H}), 1.94-1.87 (m, 4\text{H}), 1.58-1.30 (m, 20\text{H}), 0.91-0.87 (m, 6\text{H}). \]

\[ ^{13}C \text{ NMR (CDCl}_3\): } \delta = 157.24, 151.96, 82.80, 75.10, 31.99, 30.51, 29.59, 29.43, 26.28, 22.82, 14.26. \]

HRMS (EI+) Calculated for C₂₂H₃₄I₂N₂O₂S M⁺ 644.04; Found 644.043.

Compound M₁ was synthesized using established protocols. (Helgesen et. al. Chemistry of Materials, 2009, 21, 4669-4675)

1,2-bis(tetradecyloxy)benzene (1a)

\[ ^1H \text{ NMR (CDCl}_3\): } \delta = 6.91 (s, 4\text{H}), 3.99-4.03 (t, J = 6.6 \text{ Hz}, 4\text{H}), 1.88-1.81 (m, 4\text{H}), 1.52-1.15 (m, 44\text{H}), 0.94-0.90 (t, J = 6.6 \text{ Hz}, 6\text{H}). \]

\[ ^{13}C \text{ NMR (CDCl}_3\): } \delta = 149.3, 121.0, 114.1, 69.3, 32.0, 29.79, 29.75, 29.72, 29.53, 29.45, 29.43, 26.1, 22.8, 14.2. \]

1,2-dinitro-4,5-bis(tetradecyloxy)benzene (2a)
$^1$H NMR (CDCl$_3$): $\delta = 7.29$ (s, 2H), 4.10 (t, $J = 6.5$ Hz, 4H), 1.90-1.83 (m, 4H), 1.51-1.26 (m, 44H), 0.88 (t, $J = 6.6$ Hz, 6H). $^{13}$C NMR (CDCl$_3$): $\delta = 151.8$, 136.4, 107.9, 70.2, 31.9, 29.73, 29.69, 29.60, 29.55, 29.40, 29.26, 28.72, 25.83, 22.71, 14.11.

5,6-bis(tetradecyloxy)benzo[c][1,2,5]thiadazole (4a)

$^1$H NMR (CDCl$_3$): $\delta = 7.13$ (s, 2H), 4.09 (t, $J = 6.5$ Hz, 4H), 1.94-1.87 (m, 4H), 1.56-1.26 (m, 44H), 0.89-0.85 (m, 6H). $^{13}$C NMR (CDCl$_3$): $\delta = 154.1$, 151.40, 98.4, 69.1, 31.9, 29.72, 29.68, 29.62, 29.4, 28.7, 26.0, 22.7, 14.1.

4,7-dibromo-5,6-bis(tetradecyloxy)benzo[c][1,2,5]thiadazole (M1)

$^1$H NMR (CDCl$_3$): $\delta = 4.16$ (t, $J = 6.6$ Hz, 4H), 1.92-1.85 (m, 4H), 1.62-1.46 (m, 4H), 1.46-1.19 (m, 40H), 0.88 (t, $J = 6.6$ Hz, 6H). $^{13}$C NMR (CDCl$_3$): $\delta = 154.5$, 150.4, 106.3, 75.2, 31.9, 30.3, 29.72, 29.70, 29.69, 29.65, 29.63, 29.45, 29.39, 26.0, 22.7, 14.1.

LRMS (FAB+) Calculated for C$_{34}$H$_{58}$Br$_2$N$_2$O$_2$S (M+H)$^+$ 719.26; Found 719.2.

3.5.2 Polymer Syntheses
Polymer PBTD1

Compound **M1** (250 mg, 0.347 mmol) was added to the Schlenk flask and taken into the glove box. Compound **BTD** and Pd(‘Bu_3P)_2 (17.7 mg, 0.0347 mmol) catalyst were added to the Schlenk flask inside the glove box. The solvents *n*-butyl ether (*n*-Bu_2O) and *ortho*-dichlorobenzene (ODCB) (1:1) were taken into another Schlenk flask and degassed thrice by freeze pump thaw technique. THF was also degassed thrice by freeze pump thaw technique. 4 mL of degassed *n*-Bu_2O and ODCB mixture was added to aliquat 336 (12 drops) under argon atmosphere and the solution was deoxygenated by bubbling argon into it for 30 minutes. This solution and the degassed THF were added to the Schlenk flask containing compound **M1**, compound **BTD**, and catalyst under argon atmosphere. Deoxygenated aq.LiOH (2.6 mL) was also subsequently added to the Schlenk flask containing all other reagents and the Schlenk flask was immered in to an oil bath preheated to 90 °C. The polymerization was carried out for 7 days maintaining the same temperature and the reaction mixture was precipitated in to methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, EtOAc, ether, and CHCl_3. The CHCl_3 fraction, after concentration under reduced pressure, afforded 170 mg of the polymer. The polymer isolated from the chloroform fraction was analyzed by GPC. The ¹H NMR spectrum of the polymer was recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C.
Polymer PBTD2

Compound M2 (404 mg, 0.626 mmol) was added to a Schlenk flask and taken into the glove box. Compound BTD and Pd(But$_3$P)$_2$ (32.02 mg, 0.0626 mmol) catalyst were added to the Schlenk flask inside the glove box. The solvents n-butyl ether (n-Bu$_2$O) and ortho-dichlorobenzene (ODCB) (1:1) were taken into another Schlenk flask and degassed thrice by freeze pump thaw technique. 12 mL of n-Bu$_2$O and ODCB mixture was added to aliquat 336 (20 drops) under argon atmosphere and the solution was deoxygenated by bubbling argon into it for 30 minutes. This solution was added to the Schlenk flask containing compound M2, compound BTD, and catalyst under argon atmosphere. Deoxygenated aq.LiOH (5 mL) was also subsequently added to the Schlenk flask containing all other reagents and the Schlenk flask was immersed in to an oil bath preheated to 110 °C. The polymerization was carried out for 8 days maintaining the same temperature and the reaction mixture was precipitated in to methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, EtOAc, and CHCl$_3$. The CHCl$_3$ fraction, after concentration under reduced pressure, afforded 90 mg of the polymer. The polymer isolated from the chloroform fraction was analyzed by GPC. The $^1$H NMR spectrum of the polymer was recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C.
Polymer PBTDV 1

Compound M1 (210 mg, 0.292 mmol) was added to a Schlenk flask and the flask was taken into the glovebox. Pd(PPh₃)₄ (33.7mg, 0.0292 mmol) catalyst was added to the Schlenk flask inside the glove box. Toluene (10 mL) was taken into another Schlenk flask and degassed thrice by freeze pump thaw technique. Approximately 5 mL of the degassed Toluene was added to a Schlenk flask containing trans-1,2-bis(tri-n-butylstannyl)ethylene (195 mg, 0.3214 mmol) and the solution was deoxygenated by bubbling argon into it for 30 minutes. This solution was added to the Schlenk flask containing compound M1 and Pd(PPh₃)₄ catalyst under argon atmosphere, followed by the addition of 5 mL of deoxygenated Toluene. The Schlenk flask was immersed in to an oil bath preheated to 90 °C. The polymerization was carried out for 5 days maintaining the same temperature and the reaction mixture was precipitated in to methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, acetone, and CHCl₃. The CHCl₃ fraction, after concentration under reduced pressure, afforded 180 mg of the polymer. The polymer isolated from the chloroform fraction was analyzed by GPC. The ¹H NMR spectrum of the polymer was recorded in 1,1,2,2-tetrachloroethane-d2 at 100 °C.
Polymer PBTDV2

Compound **M2** (400mg, 0.620 mmol) was added to a Schlenk flask and the flask was taken into the glovebox. Pd(PPh$_3$)$_4$ (71.7 mg, 0.062 mmol) catalyst was added to the Schlenk flask inside the glove box. N-methyl-2-pyrrolidone and 1,2-dichlorobenzene (20 mL (1:2 v/v)) were taken in another Schlenk flask and degassed by thrice by freeze pump thaw technique. Approximately 3 mL of degassed N-methyl-2-pyrrolidone and 1,2-dichlorobenzene solvent mixture was added to the Schlenk flask containing trans-1,2-bis(tri-n-butylstannyl)ethylene (413mg, 0.6828 mmol) and the solution was deoxygenated by bubbling argon into it for 30 minutes. This solution was added to the Schlenk flask containing compound **M2** and Pd(PPh$_3$)$_4$ catalyst under argon atmosphere, followed by the addition of the remaining 17 mL of degassed polymerization was carried out for 5 days maintaining the same temperature and the reaction mixture was precipitated in to methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, acetone, ethyl acetate, and CHCl$_3$. The CHCl$_3$ fraction, after concentration under reduced pressure, afforded 150 mg of the polymer. The polymer isolated from the chloroform fraction was analyzed by GPC. The $^1$H NMR spectrum of the polymer was recorded in 1,1,2,2-tetrachloroethane-d2 at 100 $^\circ$C.

3.6 References


CHAPTER 4
FABRICATION OF NANOPARTICLES TO GAIN CONTROL OVER THEIR
ASSEMBLY AND POLYMER PACKING WITHIN NANOPARTICLES

4.1 Introduction

The photoactive material of an APSC can be designed to have hole and electron
transporting polymers with complementary absorption range and proper frontier energy
level offset.\textsuperscript{1} Thus the power conversion efficiency (PCE) of APSC is expected to be
higher than the polymer/fullerene and small molecule/small molecule solar cells. But the
highest reported PCE of APSC is 5 times less than that of polymer/fullerene solar cell.\textsuperscript{2,3}
This is mainly due to: i) low charge separation efficiency; i) lack of optimal morphology
to facilitate charge transfer and transport; and iii) lack of control over the exciton and
charge transport in each phase.\textsuperscript{4,5} Chapter 3 dealt with improving the charge separation
efficiency by designing novel electron transporting polymers with required
characteristics. In this chapter, I will discuss about how to obtain the optimal morphology
to facilitate charge transfer and transport and how to control the exciton and charge
transport within each phase of hole and electron transporters.

In APSCs, due to low entropy of mixing, polymers tend to micro-phase segregate
rather than forming more useful nano-phase segregation.\textsuperscript{5} A continuous network of nano-
phases of each carrier is required to facilitate charge transfer and transport. In order to
control the morphology of active layer in APSCs, several optimization techniques that are
followed in polymer/fullerene solar cells are employed. However, optimizing the
morphology of polymer blend to obtain nano-phase segregation is time consuming,
specific to the system under study and not trivial. Thus to avoid micro-phase segregation, nanoparticles of hole and electron transporters are synthesized and blended. Nanoparticles (diameter less than ~30nm) provide the necessary interface for charge transfer. But due to: i) lack of optimal assembly of nanoparticles to facilitate charge transfer and transport processes; and ii) lack of control over the exciton and charge transport properties within the nanoparticles, the PCEs of nanoparticle blends are far less than the polymer/polymer blend.

Polymer packing within the nanoparticle controls the exciton and charge transport properties of the nanoparticle. In this work I have shown that the solvent used to synthesize nanoparticles plays a crucial role in determining the assembly of polymer chains inside the nanoparticle, thereby affecting its exciton and charge transport processes. We have also shown that the surfactant used to synthesize nanoparticles also plays a crucial role in determining the size and optical properties of the nanoparticles. To obtain optimal morphology for better charge transfer and transport, we have also synthesized nanoparticles of different radius with surfactants of opposite charge. We have also synthesized the electron transporting polymer nanoparticles with surfactants of opposite charge to blend with hole transporting polymer nanoparticles. We propose that

Figure 4.1 Illustration of the mineral structure-types obtained depending on the radius of atoms.
depending on the radius and/or Coulombic interactions these nanoparticles can be assembled into mineral structure-types that are useful for photovoltaic devices (see Figure 4.1).

Regioregular poly(3-hexylthiophene) (P3HT) has emerged as an important organic semiconducting material in the area of organic electronics, particularly in the area of organic photovoltaics. P3HT has a high propensity to aggregate into crystalline domains in thin films. The optoelectronic and charge transport properties depend on the degree of crystallinity in thin films. In this regard, rrP3HT is different from poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] MEH-PPV, which is a well-studied conjugated polymer within the nanoparticle field; PPV has been designed to have a low propensity to aggregate. P3HT is the archetypical example of a hole conductor, particularly in organic photovoltaic cells. For this reason, P3HT has been a subject of numerous studies to uncover the correlation between the aggregated structure and its optoelectronic properties. We chose P3HT for our investigation because these studies serve as excellent benchmarks for us to compare and unravel the impacts of confinement on the optoelectronic properties. Later, we have also synthesized nanoparticles of the novel electron transporting polymer, PBTDV2 discussed in Chapter 3 and characterized the charge transport and photovoltaic metrics of the device comprising PBTDV2 nanoparticles.

4.2 Synthesis of P3HT Nanoparticles

Stable P3HT nanoparticles were synthesized through a miniemulsion process; the optimized protocol is provided in the experimental section (Figure 4.2). A typical
The synthesis of P3HT nanoparticles involves injection of a solution of P3HT dissolved in an organic solvent (oil phase) into an aqueous surfactant solution, followed by ultrasonication and evaporation of the organic solvent by heating. Chloroform is widely used as the oil phase to synthesize conjugated polymer nanoparticles via miniemulsion process because chloroform is immiscible with water and most of the conjugated polymers are soluble in it. In this work, we have synthesized P3HT nanoparticles using different composition of organic solvents and studied their optoelectronic properties to understand the effect of solvent on P3HT aggregation inside the nanoparticles. This has enabled us to synthesize nanoparticles of similar size but of different optoelectronic properties. We have also synthesized smaller size P3HT nanoparticles and studied their optoelectronic properties to understand the nature of P3HT aggregation in smaller nanoparticles. Organic solvents chosen for this study are chloroform, toluene, and a
To determine the effect of solvent on the size of nanoparticles, P3HT nanoparticles are synthesized from different solvent compositions using 0.5 wt% P3HT and 1mM SDS concentration. Size and dispersity in size of the nanoparticles were determined using dynamic light scattering (DLS). For each solvent composition, the nanoparticles were synthesized at least six times and the average size along with the average dispersity in size is reported in Table 4.1. We found that the average size of P3HT nanoparticles made from chloroform were consistently larger than the particles obtained from toluene. The size of nanoparticles made from a mixture of toluene and chloroform (1:4 v/v) is in between the particle sizes obtained from chloroform and toluene. In order to see if the size differences arose from inconsistencies in weighing

Table 4.1 Size and optical properties of P3HT nanoparticles synthesized from different wt%.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>P3HT 0.5 wt%</th>
<th>P3HT 0.05 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size (nm)(^a)</td>
<td>A(<em>{0.0}/A</em>{0.1})(^b)</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>116±15</td>
<td>0.71±0.05</td>
</tr>
<tr>
<td>Toluene/CHCl(_3)(^c)</td>
<td>112±14</td>
<td>0.68±0.03</td>
</tr>
<tr>
<td>Toluene</td>
<td>99±13</td>
<td>0.66±0.05</td>
</tr>
</tbody>
</table>

\(^a\)Mean of number-average peak from several experiments and the error is mean of half width of the peak. \(^b\)Mean of several experiments along with standard deviation. \(^c\)Mixture of chloroform and toluene in 1:4 (v/v) ratio.
small amounts of P3HT (~5 mg), a 0.5 wt% P3HT solution in chloroform was prepared and was equally distributed into three pre-weighed vials and then chloroform was evaporated. Vials were kept under reduced pressure over 3 h and were weighed again to determine the amount of P3HT transferred. Within experimental errors, the amount of P3HT transferred into each vial was the same and was consistent with the amount of P3HT dissolved in the volume of chloroform transferred. The solvent was then added to each vial to generate 0.5 wt% P3HT solution in chloroform, toluene, and the chloroform/toluene mixture. The sizes of the nanoparticles were determined using DLS and are 122, 110, and 73 nm respectively (see Table 4.2), reaffirming our observations. Thus, the solvent used to synthesize nanoparticles indeed has an effect on the size of nanoparticles.

How does solvent impact the size of the nanoparticles? We hypothesized that the size differences in nanoparticles synthesized from different solvents might be due to the differences in size of the solvent droplets formed immediately after ultrasonication or P3HT packing density inside the nanoparticles. To determine the size of solvent droplets

### Table 4.2 Size of the P3HT nanoparticles.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Size$^a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl$_3$</td>
<td>121±13</td>
</tr>
<tr>
<td>Toluene\ Chloroform$^b$</td>
<td>110±11</td>
</tr>
<tr>
<td>Toluene</td>
<td>73±10</td>
</tr>
</tbody>
</table>

$^a$Number-average peak and the error is half width of the peak.

$^b$1:4(v/v).

### Table 4.3 Size of the droplets.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Size$^a$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl$_3$</td>
<td>3.5±0.6</td>
</tr>
<tr>
<td>Toluene\ Chloroform$^b$</td>
<td>4.3±0.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>4.0±0.8</td>
</tr>
</tbody>
</table>

$^a$Number-average peak and the error is half width of the peak.

$^b$1:4(v/v).
formed immediately after ultrasonication, DLS measurements were performed on the emulsion of chloroform, toluene and chloroform/toluene mixture without P3HT and the sizes were found to be 3.5, 4.3 and 4.0 µm, respectively (see Table 4.3). Since the sizes of initial droplets formed are similar for various solvents, the size differences in nanoparticles might be due to the differences in P3HT packing density inside the nanoparticles. We surmise that the size differences arise from the differences in the boiling points of toluene and chloroform. At 80 °C, toluene should take a longer time to evaporate from the emulsion compared to chloroform and chloroform/toluene mixture. This is clearly evidenced by the color change of emulsion as they are heated at 80 °C. For 0.05 wt% P3HT and 1 mM SDS, the time taken for chloroform emulsion to change color from initial orange (P3HT color in solution) to clear purple (P3HT color in thin film) is around 15 minutes; whereas for toluene emulsion, the color change happens after 40 minutes. For 0.5 wt% P3HT and 1 mM SDS, even though the color change was observed within 15 minutes, the sample was heated for 40 minutes to ensure complete removal of toluene. The observed color change within 15 minutes might be because of the formation of P3HT aggregates in toluene at such high concentration (0.5 wt%) of P3HT. Thus, in case of toluene emulsion, we speculate that the size of the droplet decreases slowly. Therefore, the concentration of

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Size* (nm)</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>123±17</td>
<td>-65±5</td>
</tr>
<tr>
<td>Toluene\CHCl₃ᵇ</td>
<td>99±14</td>
<td>-63±6</td>
</tr>
<tr>
<td>Toluene</td>
<td>108±15</td>
<td>-67±6</td>
</tr>
</tbody>
</table>

*Number-average peak and the error is half width of the peak.ᵇ1:4(v/v).
P3HT inside the nano-droplet increases slowly, giving enough time for P3HT polymer chains/aggregates to pack densely. In case of chloroform, since the solvent evaporation and thus the decrease in the droplet size is rapid, polymer chains may not have enough time to pack densely and hence yield less densely packed bigger size P3HT nanoparticles. TEM images of P3HT nanoparticles that are synthesized from different organic solvent using 0.5 wt% P3HT solution and 1 mM SDS are shown in Figure 4.3. Zeta potential of the nanoparticle indicates the stability of nanoparticles against aggregation of nanoparticles. Zeta potential of all the nanoparticles synthesized from different solvents has almost same value and is shown in Table 4.4. A zeta potential of around ~ -65 mV indicates all these nanoparticles are stable against agglomeration.

**Figure 4.3** TEM images of the P3HT nanoparticles synthesized from (P3HT: 0.5 wt%, SDS: 1mM) a) chloroform; b) toluene/chloroform (1:4); and c) toluene.
Table 4.5 Zeta potential of P3HT nanoparticles at different surfactant concentration.

<table>
<thead>
<tr>
<th>SDS</th>
<th>Size(^a) (nm)</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mM</td>
<td>120±16</td>
<td>-65±5</td>
</tr>
<tr>
<td>8.2 mM</td>
<td>66±8</td>
<td>-73±12</td>
</tr>
<tr>
<td>16 mM</td>
<td>79±11</td>
<td>-78±7</td>
</tr>
</tbody>
</table>

\(^a\)Number-average peak and the error is half width of the peak.
Table 4.6 Size and optical properties of P3HT nanoparticles synthesized at different SDS concentrations.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>[SDS] = 1 mM</th>
<th>[SDS] = 8.2 mM</th>
<th>[SDS] = 16 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size (nm)(^a)</td>
<td>(A_{0.0}/A_{0.1})^(^b)</td>
<td>W (meV)</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>116±15</td>
<td>0.71±0.05</td>
<td>93</td>
</tr>
<tr>
<td>Toluene/CHCl(_3)^(^c)</td>
<td>112±14</td>
<td>0.68±0.03</td>
<td>105</td>
</tr>
<tr>
<td>Toluene</td>
<td>99±13</td>
<td>0.66±0.05</td>
<td>112</td>
</tr>
</tbody>
</table>

\(^a\)Number-average peak and the error is half width of the peak. \(^b\)Mean of several experiments along with standard deviation. \(^c\)Mixture of chloroform and toluene in 1:4 (v/v) ratio.
ultrasonication, smaller droplets generated have high surface area and require higher SDS concentration to stabilize them. Thus, the smaller nanodroplets and nanoparticles are stable only at higher SDS concentration. Zeta potential of all the nanoparticles synthesized from different surfactant concentration is shown in Table 4.5. A zeta potential higher than $\sim -65$ mV indicates all these nanoparticles are stable against agglomeration.

To understand the limits of decreasing the size of P3HT NP by increasing the SDS concentration, P3HT NPs of different SDS concentration (from 1 mM to 30 mM) were synthesized at 0.05 wt% P3HT concentration in chloroform (see Figure 4.4). As expected, the size of nanoparticles decreases with increase in SDS concentration up to 12 mM; the size of nanoparticles did not change after 12 mM SDS concentration. Similarly, to understand the limits of size variation by changing the P3HT wt%, P3HT NPs of different P3HT wt% (from 0.01 wt% to 0.1 wt%) at 16 mM SDS concentration were synthesized. Unlike surfactant study, there is no saturation in the size of P3HT NPs formed with increasing P3HT wt% (see Figure 4.4). This might be because even though the solvent droplet sizes are around 4 $\mu$m, the amount of P3HT used is insufficient to fill the entire droplet.

**Figure 4.4** Sizes of P3HT nanoparticles synthesized by varying the a) SDS concentration (fixed [P3HT]:0.05 wt%); b) P3HT concentration (fixed [SDS]: 16 mM) in CHCl$_3$. 

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4.3 Optical Properties of P3HT Nanoparticles

Several studies have correlated the features in the UV-Vis absorption spectra of P3HT thin films to P3HT aggregate structure.\textsuperscript{8, 10, 14, 16, 23-27} Thus, to understand the effect of solvent on the aggregation of P3HT chains within the nanoparticle, UV-Vis absorption spectra of nanoparticles dispersed in water were recorded (Figure 4.5). The UV-Vis absorption spectra of nanoparticles dispersed in water shows features similar to those observed in thin films with peaks around 510 nm, 553 nm and 605 nm. These peaks are assumed to arise from a single vibronic progression and are typically designated as $A_{0-2}$, $A_{0-1}$, and $A_{0-0}$ peaks. The $A_{0-0}/A_{0-1}$ peak intensity ratios in the UV-spectra for the nanoparticles synthesized at different solvent compositions are tabulated in Table 1. Using $A_{0-0}/A_{0-1}$ peak ratios, the free exciton band width ($W$) in the P3HT aggregates can be calculated using the equation 1 where $E_p$ is the energy of the intramolecular vibration coupled to the electronic transition;\textsuperscript{28} the calculated $W$ values are shown in Table 4.1. Assuming similar interchain order in P3HT thin films, $W$ value is a measure of degree of conjugation length, intrachain order and crystalline quality.\textsuperscript{28} Thus, in P3HT thin films, higher the $W$ lower the conjugation length, intrachain order and crystalline quality and there is a correlation of $W$ (or $A_{0-0}/A_{0-1}$) to the X-ray diffraction and charge transport properties in
Assuming that the interchain order in nanoparticles is also invariant with respect to size of nanoparticle and organic solvent used to prepare nanoparticle, we have correlated W values to the intrachain order and crystalline quality of P3HT aggregates inside the nanoparticle. A$_{0.0}$/A$_{0.1}$ peak ratio less than one indicate that the P3HT aggregates are of H-type. Within the given solvent, depending on the P3HT wt% and surfactant concentration, different W values are obtained. Also, for a given P3HT wt% and surfactant concentration, different W values are obtained depending on the solvent. So the solvent, P3HT wt% and surfactant concentration each play a role in determining the W value of nanoparticles.

Before going into the details of how P3HT wt% and surfactant concentration affect the W values of P3HT nanoparticles within the solvent series, we compared the W values of nanoparticle and thin films that are prepared from the same organic solvent to determine the effect of nano-confinement on the assembly of P3HT chains. For this comparison we have used the W value of nanoparticles that are prepared using 0.5 wt% P3HT and 1mM SDS. W values for the nanoparticles that are prepared under these conditions using chloroform, mixture and toluene are 93, 105, and 112 meV respectively. W values for thin films cast from chloroform and xylene are 120 and 60 meV, respectively. By comparing the W values of thinfilms and nanoparticles, we could say that the change in W values with solvent is small for nanoparticles compared to thinfilm values. Moreover, in thinfilms, when a high boiling and marginal solvent such as xylene (bp: 130 °C) is used to cast P3HT thinfilms, the W value halved compared to chloroform. In nanoparticles, on the contrary, when toluene (bp: 110 °C) which is similar to xylene in terms of solubilizing P3HTwas used there is a marginal increment in the W value. Higher
W value indicates less intrachain order and low quality P3HT crystallites; the increase in W value of nanoparticles when toluene is used as solvent is very surprising because it is believed that the higher boiling point and marginal solvent such as toluene would enhance the intrachain order and facilitate the ordered assembly of P3HT chains. Thus, the observed high W value and hence less intra chain order and low quality crystals in nanoparticles should be because of the difference in processing conditions between thinfilms and nanoparticles. During the preparation of nanoparticles, the two-layer solution made of toluene (containing P3HT) and water (containing SDS) are emulsified using ultrasonication followed by heating at 80 °C to evaporate toluene. Thus, during the nanoparticle synthesis, the P3HT chains dissolved in toluene are subjected to two more additional processing steps of ultrasound and heating compared to thinfilms.

Thin films casted from high boiling and marginal solvents show low W value because the preformed P3HT aggregates in solution act as nucleating sites during the thin film fabrication, leading to more ordered packing and high quality crystals.\textsuperscript{16, 19, 30} The presence of preformed aggregates in solution is confirmed by the appearance of a new

![Figure 4.6 UV-Vis absorption spectra of P3HT (0.5 wt%) solution. Size of P3HT aggregates in corresponding solutions at 25 °C is shown in inset. Only for toluene aggregates size are measured at 70 °C.](image)
peak at 610 nm in the UV-Vis absorption spectrum of P3HT solution in toluene (Figure 4.6). The presence of aggregates is also confirmed by DLS measurements with aggregate size of 47nm (Figure 4.6 inset). During the nanoparticle synthesis, the toluene and water mixture is ultrasonicated for 2 minutes to create emulsion, thus there is a possibility for the formation of preformed P3HT aggregates. However, the droplets are heated at 80 °C to evaporate the organic solvent to yield nanoparticles. At this high temperature P3HT is expected to be completely dissolved in toluene. This expectation is confirmed by the absence of 610 nm peak in the high temperature UV-Vis absorption spectrum and absence of larger aggregates in DLS measurements (see Figure 4.6). Thus in toluene-nanoparticles, P3HT chains are redissolved in toluene nanodroplet and starts aggregating at 80 °C. Since polymer can have different conformations at such high temperature, the P3HT intrachain order is low and the aggregation of these disordered chains leads to low quality crystallites leading to high W value compared to thinfilms. In case of chloroform, there is a marginal decrease in the W value of nanoparticle compared to thinfilm. That is P3HT chains in the nanoparticles from chloroform have more intrachain order and there are high quality P3HT crystallites in the nanoparticle compared to thinfilms. In case of chloroform also there are preformed P3HT aggregates after the ultrasonication. But during the solvent evaporation step, since the boiling point of chloroform(bp: 60 °C) is low, there is a competition between re-dissolving the P3HT aggregates in chloroform and evaporation of chloroform leading to increase in P3HT concentration within the droplet. Thus, in case of chloroform we believe that due to rapid evaporation of chloroform there are few P3HT aggregates and/or ordered P3HT chains in the nanodroplet that act as nucleating sites for P3HT aggregation, thereby resulting in low W value compared to
thin film. The $W$ value of nanoparticles from mixture solvent is in between those from pure chloroform and toluene, indicating that the quality of crystals and intrachain order in the nanoparticles from solvent mixture are in between those from pure solvents. Thus for all the solvent compositions, P3HT chains aggregate and/or have high intrachain order after ultrasonication. However, depending on the boiling point of the solvent and solubility of P3HT, these aggregates and/or intrachain order are either completely or partially lost during the solvent evaporation step.

Since P3HT wt% and surfactant concentration affect the size of the nanoparticle within the given solvent, the change in $W$ value could be directly correlated to change in size of the nanoparticle. As you can see from Table 4.6, the size of the nanoparticle reduces with increase in the surfactant concentration. Also, the size of the nanoparticle reduces with the decrease in P3HT wt%. However, the decrease in size with decreasing P3HT wt% is much higher than with increasing surfactant concentration. To find out the effect of P3HT nanoparticle size on the $A_{0,0}/A_{0,1}$ peak ratio and $W$, absorption spectra of nanoparticles synthesized at lower P3HT concentration (P3HT:0.05 wt% and SDS: 1 mM) and higher surfactant concentration (SDS: 8.2 mM, 16 mM and P3HT: 0.5 wt%) were recorded. $A_{0,0}/A_{0,1}$ peak ratio and the corresponding $W$ values are reported in Table 4.1 and Table 4.6. $A_{0,0}/A_{0,1}$ peak ratio less than one indicate that the P3HT aggregates are of H-type. Within a solvent series, $W$ value increases with the decrease in the size of nanoparticles. Smaller the size of nanoparticle, higher is the $W$ value. Smaller $W$ value indicates less intrachain order and low quality P3HT crystallites inside the smaller nanoparticles. This might be because of the increase in surface to volume ratio as the size of the nanoparticles decreases. It is known that for polythiophene nanoparticles, polymers
that are on and near the surface cannot assemble into ordered structure.\textsuperscript{31, 32} Similarly, P3HT chains that are on and near the surface might not be planar thus hampering the intrachain order and forming low quality crystallites. Thus, the higher W ratio in smaller nanoparticles might be due to more number of P3HT chains with less intrachain order and low ordered P3HT aggregates than the P3HT chains with high intrachain order and highly ordered crystallite aggregates inside smaller P3HT nanoparticles because of higher surface to volume ratio. Optoelectronic properties of P3HT nanoparticles were also recorded to determine the percent crystallinity of P3HT aggregates within nanoparticles, their fluorescence lifetime distribution, electron-hole radius ($\mu$) and orientation of the crystalline aggregates inside the nanoparticles (see Appendix). Combining this data with the data in Appendix, we are able to describe the structure of the aggregate within the nanoparticle and it is depicted in Figure 4.7.

4.4 Summary

To conclude, organic solvent used to make the nanoparticle and size of the nanoparticle have an effect on the P3HT aggregation thereby affecting optical,
optoelectronic and exciton transport properties. Ultrasonication and evaporation of the organic solvent at 80 °C are the two additional processing steps during the synthesis of nanoparticles compared to thinfilms. Depending on the solubility of P3HT and boiling point of organic solvent, aggregation of P3HT inside the nanoparticle varies. Nanoparticles are composed of polycrystalline $H$ and $J$-type aggregates. Intrachain order and quality of crystallites are good in nanoparticles made from chloroform. But nanoparticles made from mixture solvent have large crystalline aggregates and same intra and interchain order are obtained mostly in all the nanoparticles compared to pure solvents (Figure 4.7). Smaller size nanoparticles compared to larger nanoparticles synthesized from same solvent have negative effect on the intra and interchain order and quality of aggregates inside the nanoparticle.

### 4.5 Ongoing work

#### 4.5.1 Synthesis of P3HT Nanoparticles with Positive Charge Surfactant

<table>
<thead>
<tr>
<th>P3HT (wt%)</th>
<th>Surfactant (mM)</th>
<th>Size (nm)</th>
<th>W (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SDS$^a$</td>
<td>CTAB$^a$</td>
<td>SDS</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>116±15</td>
<td>67±9</td>
</tr>
<tr>
<td>0.5</td>
<td>16</td>
<td>80±11</td>
<td>29±4</td>
</tr>
<tr>
<td>0.05</td>
<td>1</td>
<td>62±8</td>
<td>27±4</td>
</tr>
</tbody>
</table>

*Table 4.7 Size and W value comparison for P3HT nanoparticles made from SDS and CTAB in chloroform.*

$^a$Number-average peak and the error is half width of the peak.
Now we switch our attention to obtaining assemblies of nanoparticles to facilitate charge transfer and transport. This could be achieved by assembling the nanoparticles of different radii to mimic mineral structure-types as shown in Figure 4.1. The work discussed above addresses synthesizing nanoparticles of different radii. Nanoparticles can be assembled into ordered structures by blending nanoparticles of opposite charges. To this end, we have synthesized P3HT nanoparticles using CTAB as surfactant. Unlike SDS, CTAB head group has positive charge and we expect that the Coulombic interaction between surfactants of opposite charge will provide an ordered assembly.

To understand the effect of surfactant on the optical, and charge transport properties, P3HT nanoparticles using 0.5 wt% P3HT and 1mM CTAB in chloroform are synthesized. Optical and charge transport properties of the P3HT nanoparticles synthesized under similar conditions using SDS and CTAB are compared in Table 4.7 (Figure 4.8 and Figure 4.9). From the table it is clear that under similar conditions, CTAB always generates nanoparticles of small size. This could be because of larger stabilization of interfacial tension by CTAB compared to SDS. Thus the overall large surface area generated by smaller nanodroplets is easily stabilized by the low concentration of CTAB compared to SDS, thus generating smaller nanoparticles. Thus the nanoparticles
generated using CTAB as surfactant have small diameter and high W value compared to the nanoparticles made from SDS. As observed earlier, this could be because of the smaller size nanoparticles generated with CTAB. To delineate the effect of surfactant from size on W value, we have compared the W value of similar size nanoparticles made from SDS and CTAB. We have compared 62 nm diameter nanoparticles made from SDS (P3HT: 0.05 wt%, SDS: 1mM in chloroform) with the 67 nm diameter nanoparticles made from CTAB (P3HT: 0.5 wt%, CTAB: 1mM in chloroform). W values for these nanoparticles made from SDS and CTAB are 132 and 162 meV respectively. This clearly indicates that surfactant has an effect on the assembly of P3HT chains; moreover CTAB decreases the intrachain order in P3HT chains and generates low quality crystallites.

4.5.2 Charge Transport Properties of P3HT Nanoparticles

To find out the effect of solvent, size and surfactant on the charge transport properties of P3HT nanoparticles, hole mobilities of the P3HT nanoparticles are measured using time of flight technique as shown in Figure 4.19. Table 4.8 shows the
conditions used to synthesize nanoparticles, their sizes, W values, and hole mobilities. Contrary to the common belief, surfactant did not impede the charge transport properties of P3HT nanoparticle and their hole mobility is comparable to the thin film value ($10^{-3}$ cm$^2$/Vs). Moreover, from the table it could be clearly noted that the hole mobility is almost constant irrespective of the size, solvent, surfactant, and W values. This clearly indicates that intra and interchain order and quality of crystallites do not affect charge transport, Thus charge hopping from one nanoparticle to the other and grain boundaries might be the rate limiting steps for charge transport in these nanoparticles. Interestingly, hole mobility doesn’t depend on the charge of the surfactant. In summary, unlike exciton transport, the charge transport properties of nanoparticles do not depend on the solvent, size, and surfactant used to synthesize nanoparticles.

Table 4.8 Comparison of W and hole mobilities of P3HT nanoparticles made from different solvents and surfactants.

<table>
<thead>
<tr>
<th>P3HT (wt%)</th>
<th>Surfactant (1 mM)</th>
<th>Solvent</th>
<th>W (meV)</th>
<th>$\mu_h$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>SDS</td>
<td>Toluene</td>
<td>112</td>
<td>$~10^{-4}$</td>
</tr>
<tr>
<td>0.5</td>
<td>SDS</td>
<td>CHCl$_3$</td>
<td>93</td>
<td>$~10^{-4}$</td>
</tr>
<tr>
<td>0.5</td>
<td>CTAB</td>
<td>CHCl$_3$</td>
<td>162</td>
<td>$~10^{-4}$</td>
</tr>
</tbody>
</table>

$^a$ $\mu_h$: hole mobility.

Figure 4.10 UV-Vis absorption spectra of PBTDV2 nanoparticles made from different surfactants.
Figure 4.11 a) TEM images and b) phototransients of PBTDV2 nanoparticles made from 0.5 wt% polymer in chloroform and 1mM SDS.

4.5.3 Nanoparticles of Electron Transporting Polymer

We have also synthesized the nanoparticles of electron transporters with positive and negative surfactants for generating ordered assemblies with hole transporters. The nanoparticles of PBTDV2, electron transporter discussed in Chapter 3, are synthesized using both SDS and CTAB with 0.5 wt% of polymer in chloroform. The size of the nanoparticles synthesized with SDS and CTAB are 109 and 68 nm respectively. TEM image and electron transport properties of the PBTDV2 nanoparticles synthesized with SDS are shown in Figure 4.11, respectively. UV-Vis absorption spectra of the nanoparticles made from SDS and CTAB are shown in

\[ J_{sc} = 1.2 \text{ mA/cm}^2 \]
\[ V_{oc} = 0.32 \text{ V} \]
\[ FF = 0.27 \]
\[ Efficiency = 0.1 \% \]

Figure 4.12 Photovoltaic metrics of P3HT nanoparticles and PCBM nanoparticles blend.
Figure 4.10. Unlike P3HT nanoparticles, PBTDV2 nanoparticles absorption spectrum is marginally affected by the surfactant. Similar to the observation made with P3HT nanoparticles, electron mobility of the PBTDV2 nanoparticle ($10^{-4}$ cm$^2$/Vs) is one order of magnitude lower than that of PBTDV2 thinfilm ($10^{-3}$ cm$^2$/Vs) and electron transport is not affected by the negative charge on the surfactant. This clearly indicates that charge transport is not affected by the presence of surfactant as well as the charge on the surfactant (Figure 4.11). We have also synthesized PCBM nanoparticles using 0.5 wt% PCBM and 1mM SDS in chloroform. P3HT nanoparticle (P3HT: 0.5 wt%, 1mM SDS in chloroform) and PCBM nanoparticles active layer was deposited using air-brush technique. Photovoltaic metrics of the device was measured under the device configuration ITO/PEDOT-PSS/P3HT:PCBM/Al gave 0.1% power conversion efficiency (see Figure 4.12).

Blending hole and electron transporters of different radii and opposite surfactants to obtain optimal assembly of charge transporters for efficient photovoltaic device is under study.

4.6 Experimental Section

P3HT (4002-EE, Mw = 52.3 kDa, $\bar{D}$ = 2.15 and regioregularity = 90-93 %) was purchased from Rieke metals. Sodium dodecyl sulfate (SDS) was purchased from Sigma Aldrich. Solvents were purchased from Fisher (optima grade). Distilled water was used for the synthesis of nanoparticles. MISONIX SONICATOR® 3000 ultrasonic liquid processor was used to create a miniemulsion for the synthesis of nanoparticles. A VWR
scientific product, MODEL 50T Aquasonic bath sonicator, was used to sonicate SDS and P3HT solutions. Nanoparticles were passed through MILLEX®GP, Millipore Express® Syringe driven filter unit of PES membrane with 0.22 µm pore size and 33 mm diameter to remove micron size impurities. The size and zeta potential of nanoparticles were estimated using Malvern Nanosizer ZS dynamic light scattering instrument (Contin software). Nanoparticles were imaged using JEOL 100CX Transmission Electron Microscopy (TEM). TEM copper grids with formvar films were purchased from Electron Microscopy Services (FF400-Cu-50)400 square mesh. UV-Vis absorption spectra were measured with a Shimadzu UV 3600PC spectrometer in the Polymer-Based Materials Harvesting Solar Energy EFRC (Energy Frontier Research Center at the University of Massachusetts Amherst) laboratory.

The time resolved photoluminescence data described in this section was acquired using Time-Tagged-Time-Resolved (TTTR) Single Photon Counting to study the PL decay with 16ps resolution over a 50 ns window, and then with 32 ps resolution with a time window of 100ns. In both cases, nanoparticles were illuminated with a PicoQuant PDL with 440 nm wavelength and 50 ps pulse width, which was weakly focused in epi illumination geometry. The input intensity is approximately 1kW/cm² over a 10 µm spot size. The instrument response is approximately Gaussian, with a FWHM of 180 ps.

In a typical synthesis of P3HT nanoparticles, P3HT of a desired concentration was dissolved in a desired organic solvent. Organic solvent was slightly warmed to ensure the complete solubility of P3HT. P3HT of 0.5 mg/mL concentration is bright orange in color for all three organic solvents used in this study. P3HT of 5 mg/mL concentration is bright orange color in chloroform and chloroform/toluene mixtures,
whereas in toluene the solution is dark red. SDS solutions of desired concentration were prepared using distilled water, then warmed and sonicated using VWR Aquasonic to ensure complete solubility. During the preparation of SDS solutions, caution was taken to prevent foaming by not shaking the solution vigorously to solubilize SDS. Also, during the synthesis of nanoparticles, the solution was transferred slowly via syringe. SDS solutions were filtered through syringe filters before use in the synthesis of nanoparticles. 2.5 mL SDS solution was taken in a 20 mL vial and ~0.35 mL P3HT solution was taken in a 7 mL vial. Both the solutions were sonicated for 10 seconds using VWR Aquasonic and 0.25 mL of P3HT solution was immediately injected rapidly into the SDS solution using a 1 mL syringe fitted with a 22G11/2 needle. The resulting solution was immediately ultrasonicated using MISONIX ultrasonicator for 2 minutes at 6 Watts power. During ultrasonication, the probe was submerged halfway into the solution and make sure that the probe was not touching the vial throughout the ultrasonication. After ultrasonication, a magnetic stir bar was added into the emulsion and the vial was immersed into a preheated oil bath to evaporate organic solvent. The temperature of oil bath was maintained at ~85 °C and the vial was immersed into oil bath up to the emulsion level. The vial was heated for 15 minutes in the case of chloroform or toluene/chloroform mixture emulsions, and was heated for ~50 minutes in the case of toluene emulsions. The nanoparticle suspension was allowed to come to room temperature and filtered via syringe before characterization.

4.7 References


CHAPTER 5
ENHANCING SENSING OF NITROAROMATIC VAPOURS BY THIOPHENE-BASED POLYMER FILMS

5.1 Introduction

Polythiophenes have several features such as absorption in the visible range, fluorescence with large stoke shift, and exciton diffusion length of around 10 nm\(^1\) that make them suitable for thin film based optical sensors. However, there are only few reports of thiophene based systems, for example poly[2-(3-thienyl)ethanol \(n\)-butoxy carbonylmethylurethane] (PURET), that exhibit good sensory response towards nitroaromatics.\(^4\) Studies related to thin film fluorescence based sensory materials for explosives detection are mostly dominated by poly(p-phenyleneethynlenes) (PPE), poly(p-phenylenevinylene) and polycarbazoles.\(^5\)-\(^20\) Of all these polymers, Swager’s pentiptycene based PPE polymer is well known for fluorescence based explosive sensing for nitroaromatics\(^19\) and is also commercialized under the name of Fido\(^\text{TM}\) (Nomadics Inc.). Studies on PPE systems have shown that the sensing ability of polymer correlates with permeability and binding strength of the analyte in polymer thin films.\(^12\),\(^18\) Therefore several strategies have been developed to optimize these parameters and enhance the sensing ability in PPE based and other polymers.\(^5\),\(^11\),\(^17\) However, such strategies cannot be easily translated to thiophene based polymers. We had recently reported a synthetic protocol for appending \(\pi\)-conjugated moieties to a polythiophene backbone using 1, 3-Huisgen cycloaddition.\(^21\) Herein, we show that the same chemistry provides a straightforward route to enhance the sensory response of polythiophenes towards nitroaromatics.
5.2 Results and Discussion

The permeability of an analyte depends on its intermolecular interaction with the polymer and diffusivity in polymer thin film. The interaction of nitroaromatics in thin films can be increased by appending dipolar and polarizable side chains on to the polymer backbone. The diffusivity of nitroaromatics in thin films can be enhanced by decreasing chain packing in the film, which in turn can be easily modulated by varying the side chains on the polymer. We reasoned that employing a dipolar 1,2,3-triazole with various side chains as a pendant group on polythiophene can be used as a strategy to enhance the sensory response of polythiophenes towards nitroaromatics. Thus, our molecular design strategy was to append various side chains to a polythiophene backbone through the Huisgen 1,3-dipolar cycloaddition and simultaneously take advantage of the ability of the triazole moiety created by the functionalization chemistry to interact with the nitroaromatics. In this report we demonstrate the efficacy of our approach using 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) as analytes. A control polymer without a triazole ring was also studied to confirm that the enhancement in solubility of analyte was indeed due to the triazole ring. Thus, we synthesized three polymers: poly(3-triazole dihexyl thiophene) (P3TzdHT), poly(3-triazole hexyl thiophene) (P3TzHT), and poly(3-butyne...
triisopropylsilyl thiophene) (P3BSiT), and investigated their sensing ability towards TNT and DNT (structures are shown in Figure 5.1).

The monomers were synthesized according to the reported synthetic protocols (Figure 5.2).\textsuperscript{21, 26} Polymers were synthesized using Stille coupling (Figure 5.3); the molecular weights and polydispersity indices (PDI) are shown in Table 5.1. Alkyl chains bearing a terminal azide were coupled with thiophene bearing an acetylene moiety using conditions established for Huisgen 1,3-dipolar cycloaddition to synthesize thiophene monomers bearing triazole moieties.\textsuperscript{27} This reaction conveniently allowed us to append various alkyl groups for rapid screening and modulation of the analyte – polymer interactions in the polymer thin film. Hexyl azide and dihexyl azide were coupled with
3-ethylthiophene and the corresponding monomers were subsequently polymerized using Stille-type polymerization conditions to obtain P3TzHT and P3TzdHT, respectively. P3BSiT was synthesized by following the protocol reported by us earlier. All the polymers were soluble in common organic solvents such as chloroform and tetrahydrofuran. Cyclic voltammograms of the polymers were recorded by drop casting a chloroform solution of the polymer on to a platinum electrode (Figure 5.4b). Frontier molecular orbital energies (HOMO and LUMO) obtained using established procedures from CV and UV-Visible absorption spectra are tabulated in Table 5.1. All the four polymers have similar LUMO values (-2.8±0.1 eV) and thus have similar exergonicity for electron transfer from polymer to analyte.

The polymer thin films for optical and sensing studies were fabricated by spin coating a chloroform solution of the polymer on to a glass slide. Absorption spectra of the polymers in solution and in thin film are shown in Figure 5.5a and 5.5b. The bathochromic shift in absorption maximum from solution to thin film is considered to be a measure of the strength of the interchain π-π stacking interactions and thus aggregation.
Table 5.1 Optical, fluorescence quenching properties and frontier energy levels of polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (KDa)</th>
<th>Thickness (nm)</th>
<th>UV-Vis λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>P.L λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>Quantum Yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Quenching (%) 5 min</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3BSiT</td>
<td>10.7</td>
<td>45</td>
<td>441</td>
<td>524</td>
<td>83</td>
<td>566 654</td>
<td>0.21</td>
<td>-5.35</td>
</tr>
<tr>
<td>P3TzHT</td>
<td>6.3</td>
<td>40</td>
<td>409</td>
<td>488</td>
<td>79</td>
<td>560 620</td>
<td>0.18</td>
<td>-4.95</td>
</tr>
<tr>
<td>P3TzdHT</td>
<td>10.6</td>
<td>30</td>
<td>405</td>
<td>451</td>
<td>46</td>
<td>554 579</td>
<td>0.20</td>
<td>-5.27</td>
</tr>
<tr>
<td>P3TzdHT2</td>
<td>38.5</td>
<td>30</td>
<td>405</td>
<td>473</td>
<td>68</td>
<td>549 591</td>
<td>0.24</td>
<td>-5.32</td>
</tr>
</tbody>
</table>

<sup>a</sup>Fluorescence quantum yield compared to fluorescein.
polymer chains in thin film.\textsuperscript{5, 18} The trend in the difference of the absorption maxima from solution to thin film is as follows: P3BSiT \(\approx\) P3TzHT \(>\) P3TzdHT. The difference in the absorption maximum of the solution compared to thin film was similar for P3BSiT and P3TzHT. We therefore inferred that these two polymers should have similar aggregation in thin films. We also attributed the small shift in absorption maximum from solution to thin film of P3TzdHT bearing branched side chains to poor chain aggregation caused by the branched side chains.\textsuperscript{25} Therefore, by comparing the sensing abilities of polymer pairs: P3BSiT-P3TzHT and P3TzHT-P3TzdHT, we can elucidate the role of 1,2,3-triazole and side chains on the sensing ability of polythiophenes. The fluorescence spectra of the polymers in solution and in thin films are shown in Figure 5.5. The quantum yields of fluorescence for the polymers in THF solution (compared to a fluorescein standard) are summarized in Table 5.1.

![Figure 5.4](image)

**Figure 5.4** a) GPC chromatographs of polymers (chloroform as eluent); b) cyclic voltammetry traces of polymers.
The sensory response of polymer thin films towards nitroaromatics was measured by the decrease in fluorescence intensity of polymer thin films upon exposure to a saturated vapour pressure of DNT and TNT in a sealed chamber. In Figure 5.5C and Figure 5.5D, we show the percentage of fluorescence quenching over 5 minutes; the values are tabulated in Table 5.1. The percent fluorescence quenching of the three polymers towards DNT are in the following order: P3TzdHT > P3TzHT > P3BSiT. We found that the quenching efficiency of P3TzHT is 13% higher than that of P3BSiT of polymers upon exposure to DNT for 5 minutes. As aforementioned, the shift in
absorption maximum from solution to thin film is same for both the polymers and thus the aggregation of polymer in thin film can be similar. Moreover, it is very well known that the diffusivity of the analyte in polymer thin film depends upon the aggregation of polymer chains.\textsuperscript{5, 18} Thus, we expect both P3BSiT and P3TzHT have similar diffusivity of the analyte in thin film. Therefore any difference in the sensing abilities of P3BSiT-P3TzHT polymers should arise from the differences in interaction of the analyte with the polymer chains in the thin film. It is known that nitroaromatics can engage in intermolecular interactions through dipole–dipole, dipole-induced dipole and hydrogen bonding interactions.\textsuperscript{22–24} 1,2,3-triazole has a large dipole moment (5 Debye)\textsuperscript{28, 29} and therefore has the ability to interact with nitroaromatics via dipole-dipole interactions or through hydrogen bonding or both. A search of the Cambridge Crystal Structure Database shows intermolecular C-H⋯O-N distances of 2.4±0.3 Å between the 1,2,3-triazole C-H proton and aromatic nitro group in 1-(2-nitro-phenyl)-4-phenyl-1H-[1,2,3]triazole and related compounds (Table 5.2). Thus, although the interaction between the nitro group and triazole may be weak,\textsuperscript{30} we believe that it helps to enhance interaction between the analyte and the polymer chain, thus leading to enhanced sensing ability of P3TzHT.

We turn our attention to the effect of side chains in these polymers. The fluorescence quenching of P3TzdHT is enhanced by 19% compared to P3TzHT. Since both polymers have 1,2,3-triazole as a pendant group, we expect that the interactions of

<p>| Table 5.2 C-H⋯O-N distance in [1,2,3]-triazole containing compounds. |
|-------------------------|-----------------------|</p>
<table>
<thead>
<tr>
<th>Ref code</th>
<th>C-H⋯O-N Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOLGAV</td>
<td>2.471</td>
</tr>
<tr>
<td>LOLGID</td>
<td>2.316</td>
</tr>
<tr>
<td>LOLHEA</td>
<td>2.471</td>
</tr>
<tr>
<td>LOLHEA</td>
<td>2.438</td>
</tr>
<tr>
<td>LOLJAY</td>
<td>2.329</td>
</tr>
<tr>
<td>LOLJEC</td>
<td>2.357</td>
</tr>
<tr>
<td>LOLJEC</td>
<td>2.314</td>
</tr>
<tr>
<td>POZFUG</td>
<td>2.345</td>
</tr>
</tbody>
</table>
the analyte with a polymer chain should be similar. P3TzdHT exhibits a smaller red shift in absorption from solution to thin film compared to P3TzHT. This indicates that a higher degree of interchain aggregation in P3TzHT compared to P3TzdHT. We therefore surmised that the effective concentration of the nitroaromatic compounds should be higher in P3TzdHT possibly due to the ease of diffusion of the analyte in thin films with lower degree of polymer aggregation. Thus the enhanced sensing ability of P3TzdHT compared to P3TzHT can be attributed to the increased diffusion of 2, 4-DNT into P3TzdHT thin films. We therefore conclude that the pendant 1,2,3-triazole with bulky dihexyl group as a side chain on polythiophene enhances the sensing ability compared to polythiophenes with linear alkyl side chains towards 2,4-DNT.

We then synthesized P3TzdHT2, a higher molecular weight analogue of P3TzdHT using GRIM polymerization. From GPC, chain length of P3TzdHT2 (\(M_n=38\) kDa) was determined to be 3.8 times that of P3TzdHT (\(M_n=10\) kDa). Its optical properties and sensory response against DNT and TNT are shown in Figure 5.5. The sensory response of P3TzdHT2 is 10% and 24% higher than that of P3TzdHT for DNT and TNT respectively. In thin films, the absorption \(\lambda_{\text{max}}\) of P3TzdHT2 is 20 nm red shifted compared to the P3TzdHT, whereas in solution no such shift is observed. This indicates that the higher molecular weight polymer may have a higher level of aggregation or have an extended conjugation length in the thin film. To explain the increased quenching of P3TzdHT, we considered two possibilities. The first possibility is that the increased quenching may be due to the increased quantum efficiency of the polymer. However, we were unable to find any correlations between quantum efficiency and quenching efficiency in the literature and there is also no compelling reason to expect
one. The second possibility is that the quenching efficiency is related to the length of the polymer. It is very well known for polymers in solution, the fluorescence quenching increases with molecular weight.\textsuperscript{31} The increased quenching is attributed to the increased diffusion length of the exciton. Thus in P3TzdHT2, if the red shift of the $\lambda_{\text{max}}$ in thin films is attributed to the extended $\pi$ conjugation, then it may provide the higher exciton diffusion length leading to enhancement in the sensory response. The quenching efficiencies for P3TzdHT2 of 30 nm thick film and Swager’s pentiptycene derived polymer of 20 nm thick film\textsuperscript{18} (Figure 5.6b) towards DNT and TNT for 5 minutes are 89\%, 95\% and 47\%, 65\% respectively. P3TzdHT2 thin film was also tested for its

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_6}
\caption{a) Absorption (solid line) and photoluminescence (dotted line) of P3TzdHT2; b) photoluminescence quenching and recycled sensitivity of P3TzdHT2 in the presence of c) DNT; d) TNT.}
\end{figure}
recyclability in sensory applications and found that it exhibits consistent sensitivity towards both DNT (Figure 5.6c) and TNT (Figure 5.6d).

5.3 Conclusions

From the above discussion, it is clear that 1,2,3-triazole as a side chain on thiophene based polymers provides a simple tool to modulate the interaction of nitroaromatics in thin films. This strategy is attractive because: (i) 1,2,3-triazole can be readily appended by a simple 1,3-dipolar cycloaddition reaction, also known as click chemistry, (ii) 1,2,3-triazole has a large dipole moment, which aids in enhancing the interaction between the nitroaromatic analytes and the polymer chain, (iii) desired side chains can be easily attached by clicking the corresponding azides, and (iv) side chains can be tuned modularly to obtain the desired properties such as strong analyte-polymer interactions and/or lower chain packing in the thin film.

5.4 General Experimental Methods

DNT and TNT were purchased from Sigma Aldrich and Cerrilliant respectively. UV-Vis absorption spectra were measured with a Lambda 9 spectrometer. Stock solutions of polymers were prepared in spectrophotometric grade chloroform (Fisher, Optima). Fluorescence spectra were measured with a Perkin Elmer LS-55 spectrometer. Cyclic Voltammetry studies were done using BAS CV-50 W instrument. Polymer solutions were drop casted on the platinum working electrode and CV was recorded with tetrabutylammonium hexfluorophosphate as a supporting electrolyte (0.1M) in acetonitrile. The redox potentials were determined versus an Ag/Ag+ reference electrode. The working and auxiliary electrodes were cleaned after each run. In these conditions, the redox potential of Fc/Fc+ (Fc = ferrocene) was +0.09 V versus Ag/Ag+. It is assumed
that the redox potential of Fc/Fc\(^+\) has an absolute energy level of -4.80 eV to vacuum. HOMO and LUMO values were calculated using Fc/Fc\(^+\) as a reference. For sensory studies films were spun cast (1000 rpm) using c = 0.5 mg/mL for P3TzHT and P3BSiT and c = 0.25 mg/mL for P3TzdHTand P3TzdHT2. Thickness was measured using Ellipsometry. For sensory studies, the cuvette was saturated with analyte vapour (about 50 mg and 10 mg mg for DNT and TNT respectively) and thin films were inserted into the cuvette and fluorescence quenching was measured up to 300 seconds. For recyclability experiments the thin film was taken out and flushed with dry air for about a minute. The film was again inserted in the cuvette and fluorescence quenching was measured.

5.5 Experimental Procedures

5.5.1 Monomer Syntheses

The synthesis of compounds (1-4 & 6) was reported in our previous paper Macromolecules, 2010, 43, 8045–8050.

The synthesis of compounds 7, 8, M4 and P3BSiT were reported in our previous paper Macromolecules, 2008, 41, 8312-8315.

4-(2-Bromo-thiophen-3-yl)-1-(1-hexyl-heptyl)-1H-[1,2,3]triazole (5)

To an oven dried round bottom flask, was added CuSO\(_4\).5H\(_2\)O(462.15 mg, 1.85 mmol) and sodium ascorbate (1.83 g, 9.25 mmol) followed by the addition of tetra-\(n\)-butyl ammonium fluoride (TBAF) (37 mL) and tetrahydrofuran (THF) (150 mL). To this
stirred solution, water (50 mL) was added followed by the addition of 7-Azido-tridecane (4.7 g, 37.03 mmol) and ((2-bromothiophen-3-yl)ethynyl)trimethylsilane (3) (4.8 g, 18.51 mmol). The reaction was stirred for 16 h. The reaction was quenched with water and extracted with ethyl acetate (2x50 mL). The combined organics were washed with water (2x50 mL), saturated NaCl solution (1x50 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (20:80 EtOAc: hexanes) afforded 5 as colorless oil (4.07 g, 70%). ¹H NMR (400 MHz; CDCl₃; Me₄Si) δ 8.12 (1H, s, triazole-H), 7.65-7.66 (1H, d, J=5.6, thiophene-H), 7.31-7.32(1H, d, J =5.6, thiophene-H), 4.48-4.55 (1H, m, CH), 1.83-1.98 (4H, m, CH₂), 1.21-1.27 (16H, m, CH₂), 0.82-0.86(6H, t, J=7.0, CH₃). ¹³C NMR (400 MHz; CDCl₃) – 141.72, 131.98, 127.96, 126.29, 118.99, 108.06, 62.48, 35.75, 31.55, 28.81, 25.90, 22.51, 14.01. HRMS(ESI+) Calc for C₁₉H₃₁N₃SBr (M+H)⁺ 412.1422; Found 412.1424.

(2-Bromo-5-iodo-thiophen-3-yl)-1-(1-hexyl-heptyl)-1H-[1,2,3] triazole (M1)

Compound 5 (1.2 g, 3.00 mmol) was dissolved in dichloromethane in a Schlenk flask. To this solution, trifluoromethanesulfonic acid (1.33 mL, 15.02 mmol) was added and the solution is cooled to 0°C using an ice bath. N-iodo succinimide (0.676 g, 3.00 mmol) was added in small portions and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with ice-water and extracted with CH₂Cl₂ (3x25 mL). The combined organic extracts were washed with aqueous 10 %
sodium bisulfate solution and water (2x25 mL), saturated NaCl solution (1x25 mL) and dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by silica gel chromatography (15:85 EtOAc: hexanes) to provide M1 (0.94 g, 60%) as a yellow liquid. \(^1\)H NMR (400 MHz; CDCl\(_3\); Me\(_4\)Si) \(\delta\) 8.07 (1H, s, triazole-H), 7.84 (1H, s, thiophene-H), 4.47-4.54 (1H, m, CH), 1.81-1.96 (4H, m, CH\(_2\)), 1.21-1.27 (16H, m, CH\(_2\)), 0.82-0.86(6H, t, J=7.0, CH\(_3\)). \(^{13}\)C NMR (400 MHz; CDCl\(_3\)) \(\delta\) 140.5, 137.5, 133.9, 118.93, 110.59, 72.49, 62.58, 35.72, 31.54, 28.79, 25.89, 22.51,14.03. HRMS(ESI+) Calc for C\(_{19}\)H\(_{30}\)N\(_3\)SBrI (M+H)\(^+\) 538.0389; Found 538.0388.

\[
\text{4-(2-Bromo-5-tributylstannanyl-thiophen-3-yl)-1-hexyl-1H-[1,2,3]triazole (M2)}
\]

4-(2-bromo-5-iodothiophen-3-yl)-1-hexyl-1H-1,2,3-triazole (6) (0.9 g, 2.044 mmol) was dissolved in THF in a Schlenk flask under argon atmosphere and kept in ice bath. To this solution, t-Butylmagnesium chloride (1.32 mL, 2.249 mmol) was added and the solution is stirred for 2 h maintaining the temperature at 0 °C using an ice bath. After 2 h, tributyltin chloride (2.20 mL, 8.176 mmol) was added and reaction mixture was stirred for further 2 h maintaining the temperature of the ice bath and monitored by TLC. The reaction mixture was quenched with ice-water and extracted with CHCl\(_3\) (3x25 mL). The combined organic extracts were washed with aqueous 10 % sodium bisulfate solution and water (2x25 mL), saturated NaCl solution (1x25 mL) and dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by
silica gel chromatography (10:90 EtOAc: hexanes) to provide **M2** as a yellow liquid. $^1$H NMR (400 MHz; CDCl$_3$; Me$_4$Si) $\delta$ 8.19 (1H, s, triazole-H), 7.68 (1H, s, thiophene-H), 4.39-4.42 (2H, m, CH$_2$), 1.91-1.98 (2H, m, CH$_2$), 1.55-1.70 (6H, m, CH$_2$), 1.25-1.40 (12H, m, CH$_2$), 1.05-1.15 (6H, m, CH$_2$), 0.87-0.91(12H, m, CH$_3$). $^{13}$C NMR (400 MHz; CDCl$_3$) $\delta$ 150.34, 142.01, 130.79, 123.39, 120.74, 107.07, 70.00, 62.43, 50.59, 36.30, 31.14, 30.26, 28.73, 26.14, 22.43, 13.97. HRMS (ESI+) Calc for C$_{24}$H$_{43}$N$_3$SBrSn (M+H)$^+$ 604.1383; Found 604.1392.

![Molecule structure](image)

**4-(2-Bromo-5-tributylstannanyl-thiophen-3-yl)-1-(1-hexyl-heptyl)-1H-[1,2,3]triazole (M3)**

Compound **M1** (0.4 g, 0.74 mmol) was dissolved in THF in a Schlenk flask under argon atmosphere and kept in ice bath. To this solution, t-Butylmagnesium chloride (0.48 mL, 0.81 mmol) was added and the solution stirred for 2 h maintaining the temperature at 0 °C using an ice bath. After 2 h, tributyltin chloride (0.80 mL, 2.96 mmol) was added and the reaction mixture was stirred for further 2 h maintaining the temperature of the ice bath and monitored by TLC. The reaction mixture was quenched with ice-water and extracted with CHCl$_3$ (3x25 mL). The combined organic extracts were washed with aqueous 10 % sodium bisulfate solution and water (2x25 mL), saturated NaCl solution (1x25 mL) and dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by silica gel chromatography (10:90 EtOAc: hexanes) to
provide M3 as a yellow liquid. $^1$H NMR (400 MHz; CDCl$_3$, Me$_4$Si) $\delta$ 8.14 (1H, s, triazole-H), 7.71 (1H, s, thiophene-H), 4.49-4.56 (1H, m, CH), 1.87-1.95 (4H, m, CH$_2$), 1.57-1.61 (6H, m, CH$_2$), 1.24-1.37 (28H, m, CH$_2$), 0.88-0.92 (15H, m, CH$_3$). $^{13}$C NMR (400 MHz; CDCl$_3$) – 141.99, 139.02, 135.78, 132.81, 118.84, 112.49, 62.40, 35.77, 31.56, 28.82, 27.25, 25.89, 22.52, 17.53, 14.02, 13.65, 10.92. HRMS (ESI+) Calc for C$_{31}$H$_{57}$N$_3$SBrSn (M+H)$^+$ 702.2479; Found 702.2473.

Azide Syntheses

1-Azido hexane

In a round bottom flask charged with stirrer, DMSO (60 mL), 1-bromohexane (5 g, 3.62 mmol) and sodium azide (3.52g, 5.43 mmol) were added and stirred overnight. Water was added to quench the reaction and extracted with ethyl acetate (2x50mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate (1x25mL). The combined organics were washed with water (2x50mL), saturated NaCl solution (1x50 mL) and dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to afford the colorless oily liquid as product in (3.15 g, 82%) isolated yield. $\delta$H (400 MHz; CDCl$_3$, Me$_4$Si) $\delta$ 3.23 (2H, t, CH$_2$), 1.60-1.53 (2H, m, CH$_2$), 1.36-1.29 (6H,m, CH$_2$), 0.89 (3H,t, CH$_3$).

7-Azido-tridecane syntheses

Tridecan-7-ol (a)

Tridecan-7-one (4.0g, 20.17mmol) was added to an isopropanol/water mixture. Sodium borohydride was added slowly and the reaction was stirred for 12h. After 12 h,
ice water (50mL) was added to the reaction mixture and stirred for another 30 min. The layers were separated and the aqueous layer was extracted with hexane (2x25mL). The combined organics were washed with water (2x50mL), saturated NaCl solution (1x50 mL) and dried over Na₂SO₄, filtered, and concentrated under reduced pressure to afford the product (a) as white solid (3.5g, 88%) in isolated yield. ¹H NMR (400 MHz; CDCl₃, Me₄Si) δ 3.58 (1H, m, CH), 1.42-1.28 (20H, m, CH₂), 0.90-0.87 (6H, t, CH₃).

Methanesulfonic acid 1-hexyl-heptyl ester (b)

Tridecan-7-ol (3.0g, 14.97mmol) was dissolved in THF (100mL) and triethylamine (2.29mL, 16.46 mmol) was added to it. To this solution, methanesulfonyl chloride (3.31mL, 42.82mmol) was added dropwise and stirred for 30 min at room temperature. After 30 min, the resulting suspension was filtered and the filtrate was washed with water (1x100mL) and saturated NaCl (1x100mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure to afford the product (b) as yellow oil (3.3g, 80%). It was used in the next step without further purification.

7-Azido-tridecane (c)

Methanesulfonic acid 1-hexyl-heptyl ester (9.0g, 32.32mmol) was dissolved in DMF (225mL) in a round bottom flask. Sodium azide (10.29g, 158.37mmol) was added slowly to it and the reaction mixture was stirred for 14h in a preheated oil bath at 80 °C. Water was added to quench the reaction and extracted with ethyl acetate (2x50mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate (1x25mL). The combined organics were washed with water (2x50mL), saturated NaCl solution (1x50 mL) and dried over Na₂SO₄, filtered, and concentrated under reduced
pressure to afford the product (c) as yellow oily liquid (6.54 g, 90%) isolated yield. $^1$H NMR (400 MHz; CDCl$_3$, Me$_4$Si) $\delta$ 3.25-3.19 (1H, m, CH), 1.51-1.47 (6H, m, CH$_2$), 1.30-1.26 (14H, m, CH$_2$), 0.90-0.87 (6H, t, CH$_3$).

5.5.2 Polymer Syntheses

Polymerization Procedure: (P3TzdHT2)

Monomer M1 (175 mg, 0.325 mmol) was dissolved in dry THF in a Schlenk flask (Schlenk-1) covered with aluminum foil under argon atmosphere. The Schlenk was cooled to 0 °C using an ice bath. The reagent t-butylmagnesium chloride (0.21 mL, 0.357 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 2 h. In another Schlenk flask (Schlenk-2), Ni(dppp)Cl$_2$ (0.8 mg, 0.0014 mmol) was added in a glove box. The schlenk was taken out of the glove box and 1mL of dry THF was added under argon atmosphere, the solution was stirred for 5 min. The resulting solution was transferred to Schlenk-1. The reaction mixture was taken out from the ice bath and allowed to run for 40 h at 50°C and then quenched using allyl magnesium chloride (0.6 mL, 1.02 mmol). The reaction mixture was precipitated in methanol/water mixture. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, CHCl$_3$. The CHCl$_3$ fraction, after
concentration under reduced pressure, afforded 80 mg of the polymer. The polymer was washed thrice with hexanes. The polymer isolated was analyzed by GPC. $^1$H NMR (400 MHz; CDCl$_3$, Me$_4$Si) $\delta$: 7.68 (1H, s, triazole-H), 7.56 (1H, s, thiophene-H), 4.46 (1H, m, CH), 1.83-1.85 (4H, m, CH$_2$), 1.15 (16H, m, CH$_2$), 0.75-0.79 (6H, t, CH$_3$). $M_n$= 38.5k, PDI= 1.33.

Polymerization Procedure: (P3TzHT)

Monomer M2 (100 mg, 0.165 mmol) and Pd(PPh$_3$)$_4$ (50 mg, 0.0432 mmol) catalyst were taken in a Schlenk flask inside the glove box. In another Schlenk flask, DMF (2 mL) was degassed for 2 h followed by freeze pump thaw. It was then added to the Schlenk flask containing the monomer and the catalyst. The reaction mixture was degassed again for 3 times by applying vacuum and argon alternately and then transferred to a preheated oil bath (95 $^\circ$C). The reaction was carried out for 6 days and the polymer was precipitated into methanol/water mixture. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, CHCl$_3$. The CHCl$_3$ fraction, after concentration under reduced pressure, afforded 25 mg of the P3TzHT polymer. The polymer was washed thrice with hexanes. The polymer isolated was analyzed by GPC. $^1$H NMR (400 MHz; CDCl$_3$, Me$_4$Si) $\delta$: 7.65 (1H, s, triazole-H), 7.64 (1H, s, thiophene-H), 4.36-4.40 (2H, t, CH$_2$), 1.89-1.95 (2H, m, CH$_2$), 1.22-1.34 (6H, m, CH$_2$), 0.80-0.83 (3H, m, CH$_3$). $M_n$= 6.3k, PDI= 1.39.
Polymerization Procedure:(P3TzdHT)

Monomer M3 (153 mg, 0.218 mmol) and Pd(PPh₃)₄ (63 mg, 0.0545 mmol) catalyst were taken in a Schlenk flask inside the glove box. In another Schlenk flask, Toluene (2 mL) was degassed for 2 h followed by freeze pump thaw. It was then added to the Schlenk flask containing the monomer and the catalyst. The reaction mixture was degassed again for 3 times by applying vacuum and argon alternately and then transferred to a preheated oil bath (90 °C). The reaction was carried out for 4 days and the polymer was precipitated into methanol/water mixture. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, CHCl₃. The CHCl₃ fraction, after concentration under reduced pressure, afforded 30 mg of the P3TzdHT polymer. The polymer was washed thrice with hexanes. The polymer isolated was analyzed by GPC. ¹H NMR (400 MHz; CDCl₃, Me₄Si) δ: 7.67 (1H, s, triazole-H), 7.56(1H, s, thiophene-H), 4.46 (1H, m, CH), 1.84-1.86 (4H, m, CH₂), 1.15 (16H, m, CH₂), 0.75-0.79 (6H, t, CH₃). Mₙ= 10.6k, PDI= 1.69.
Polymerization Procedure: (P3BSiT)

(4-(2,5-dibromothiophen-3-yl)but-1-yn-1-yl)triisopropylsilane (M4) (1.722 g, 3.82 mmol) was dissolved in dry THF in a Schlenk flask covered with aluminum foil under argon atmosphere. The reagent t-butylmagnesium chloride (2.4 mL, 4.08 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 18 h. After 18 h, Ni(dppp)Cl₂ (24.4 mg, 0.0045 mmol) was added under argon atmosphere and the reaction mixture was stirred for further 2 h. After 2 h, the reaction mixture was quenched using allyl magnesium bromide (0.6 mL, 1.02 mmol). The reaction mixture was precipitated in ice-cold methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, CHCl₃. The CHCl₃ fraction, after concentration under reduced pressure, afforded 233 mg of the P3SiBT polymer. The polymer isolated from the CHCl₃ fraction was analyzed by GPC. 

1H NMR (400 MHz; CDCl₃; Me₄Si) δ: 7.25 (1H, s, thiophene-H), 3.05-3.08 (2H, t, CH₂), 2.63-2.66 (2H, t, CH₂), 1.04-1.06 (21H, m, TIPS), Mₙ= 10.7 k, PDI= 1.12.

5.6 References


CHAPTER 6
REVISITING MELTING POINT ALTERNATION IN HYDROCARBONS USING PIXEL

6.1 Introduction

In recent years, Semi-Classical Density Sums (SCDS)-PIXEL is emerging as a powerful tool to calculate intermolecular and lattice energies and to predict crystal structures.\textsuperscript{1-5} PIXEL has been used to calculate interaction energies of dimers of organic molecules. It has also been used to calculate the lattice energies of organic crystals; the obtained values are comparable or better than those obtained by other programs. PIXEL is available at no-cost to the academic community, is relatively easy to use and it is not computationally time intensive. Despite these advantages, PIXEL has not found widespread use in understanding intermolecular interactions, particularly in understanding and explaining the trends in a series of closely related molecules. Herein, we explore the utility of PIXEL to understand the trends in a well-studied system - the melting point alternation in aliphatic hydrocarbons.

Linear alkanes with even number of carbons have higher melting points than linear alkanes with odd number of carbons; the difference disappears with the increase in chain length. The dominant explanation for this trend focuses on the differences in the packing of odd- and even-numbered alkanes in the solid state. Boese and co-workers crystallized the alkanes and showed that the even numbered hydrocarbons pack more densely than odd numbered ones, leading to the higher melting points in the former compared to the later.\textsuperscript{6} They extended this argument to explain the observed alternation
in melting points in \(\alpha,\omega\)-alkanedithiols, \(\alpha,\omega\)-alkanediols, \(\alpha,\omega\)-alkanediamines and \(\alpha,\omega\)-alkanedicarboxylic acids.\(^{7,9}\) Monson and co-workers, using Monte Carlo simulations, showed that the odd-even effects can be understood in terms of the close packing densities of the solids.\(^{10,11}\) Alternate explanations for the melting point trend have focused on molecular symmetry and shape.\(^{12-14}\) Although Boese and co-workers have reported the lattice energies for the alkanes,\(^6\) which were obtained from Cerius\(^2\) program, to the best of our knowledge there are no detail analyses of the lattice energies for alkanes. Such calculations will help understand the roles of packing and molecular symmetry in the physical constants of organic solids.

### 6.2 Results and Discussion

For an overview of PIXEL,\(^1\) we refer the readers to the review article by Dunitz and Gavezzotti.\(^2\) As a first step, the parameters in PIXEL should be optimized such that the calculated lattice energy of a crystal corresponds to its experimental enthalpy of sublimation (\(\Delta_{\text{sub}}H\)). In order to do so, the crystal box radius, which dictates how many molecules are included in the calculation, was varied to find the optimal value and the calculated lattice energies were compared with the \(\Delta_{\text{sub}}H\). Using atomic coordinates of linear alkanes (ethane to nonane) from the Cambridge Crystal Structure Database (see Table 6.1 for REFCODES), we calculated the lattice energy for each of the alkane by varying the box radius from 7 Å to 18 Å. We found that with the exception of nonane, the lattice energies converge at the box radii of 13 Å; for nonane, the lattice energy converges at the box radius of 16 Å (Figure 6.1). In Figure 6.2, we plot the calculated lattice energies at box radius of 13 Å and the observed enthalpy of sublimation (\((-)\Delta_{\text{sub}}H\)).
For this box radius, the calculated lattice energies are in agreement with the observed (-)Δ<sub>sub</sub>H for C2-C7; deviations are observed for octane and nonane. These deviations are smaller at higher box radius for octane and nonane (Table 6.2). In contrast to the lattice energy obtained through PIXEL, the lattice energy values reported by Boese and co-workers<sup>6</sup> do not match with the enthalpy of sublimation (Figure 6.7).

Thus far, the explanation for the alternation in melting points has largely focused on packing of the alkanes.<sup>6, 15</sup> Therefore, if packing is the dominant reason, then one would expect to see alternation in the total energy. Surprisingly, the calculated lattice energy or the experimental enthalpy of sublimation does not show the expected alternation (Figure 6.2).

**Figure 6.1** Variation of the calculated lattice energy as a function of the box radius.
In PIXEL, the total energy can be partitioned into coulombic (\(E_c\)), polarization (\(E_p\)), dispersion (\(E_d\)) and repulsion energies (\(E_r\)). Since the total lattice energy does not show any alternating trend, we wanted to see if the components of the total energy, especially the dispersion energy, showed patterns concomitant with the melting point alternation. For this study, we used the lattice energy values for each alkane that closely matched with the enthalpy of sublimation. As expected for the non-polar alkanes, the dispersion energy is dominant and contributes to over 90% of the total attractive energy. Nonetheless, the dispersion energy does not show the expected alternation trend (Figure 6.3 and Table 6.4). More interestingly, the gain in the dispersion energy going from the odd-numbered alkane to an even-numbered alkane is unexpected. For example, the dispersion energy in propane is 8.6 kJ/mol more that of ethane. However, the dispersion energy in butane is only 3.0 kJ/mol more than that of propane. The gain in dispersion energy is more when going from an even numbered hydrocarbon to the odd numbered hydrocarbon and not vice versa. The gain in repulsion energy is also more when going

![Figure 6.2](image.png)
from an even numbered hydrocarbon to an odd numbered hydrocarbon (Figure 6.4, Figure 6.5 and Table 6.3). Thus, the trend in total energy (i.e. lattice energy) is dictated by differences in the gain in the dispersion energy over the repulsion energy; the total energy, as aforementioned, does not show the alternating trend in the melting points. The calculated lattice energy of propane is higher than ethane but the melting point of propane is lower than ethane. However, for alkanes with carbon number 4 and above, the gain in total energy going from an odd numbered hydrocarbon to an even numbered hydrocarbon is slightly more than the gain in the total energy in going from an even numbered hydrocarbon to an odd numbered hydrocarbon. Thus, alternation in the melting point of linear alkanes cannot be solely attributed to commonly held view that even alkanes pack better and have higher dispersion energies. PIXEL calculations indicate that the trend for

![Figure 6.3](image)  
**Figure 6.3** Variation of the various components of the attractive parts of the total energy in linear alkanes.  

higher alkanes is the result of the interplay between repulsion and dispersion energies. The calculated lattice energy values using PIXEL indicate that (a) the repulsive energy plays a crucial role in determining the total lattice energy and (b) the trend in the melting
points of linear alkanes cannot be explained by exclusively looking at the solid state packing and lattice energy.

**Figure 6.4** Comparison of the variation in repulsion energy, dispersion energy and total energy in linear alkanes.

**Figure 6.5** Changes in dispersion energy, repulsion energy and total energy in linear alkanes.
In general, the melting points of solids can be correlated to lattice energies. Solids with higher lattice energies tend to have higher melting points. At the melting point, the change in the Gibbs free energy is zero and the change in the interactions energy between molecules in going from solid to liquid phase is the enthalpy of fusion; the change in the degrees of freedom is the entropy of fusion. The ratio between changes in the enthalpy of fusion and the entropy of fusion is the melting point temperature. Thus far, all the discussions on melting points of alkanes have focused on the packing and thus the enthalpy term. The calculated lattice energies from PIXEL and the experimental heats of sublimation or fusion indicate that packing is insufficient in explaining the melting point trends in alkanes. Therefore the entropy changes that occur during the phase transition should be taken into account to explain the trends.

![Figure 6.6 Enthalpy of fusion and entropy of fusion of linear alkanes.](image)

The $\Delta_{\text{fus}}S$ can be calculated from the experimental $\Delta_{\text{fus}}H$ values for alkanes. A plot of the $\Delta_{\text{fus}}S$ with respect to the carbon number shows that $\Delta_{\text{fus}}S$ steadily increases until propane. After a slight decrease for butane, the $\Delta_{\text{fus}}S$ shows a non-linear increase.
Entropy changes in phase transition play a crucial role in the melting point alternation of linear alkanes. Until octane (Figure 6.6 and Table 6.5). On the other hand, the $\Delta_{\text{fus}}H$ increases non-linearly from C1-C8 alkanes. For C1-C4 alkanes, the $\Delta_{\text{fus}}S$ is highest for propane but the $\Delta_{\text{fus}}H$ for propane is lower than that of butane. Propane is the first non-spherical and non-linear molecule of the linear alkane series and therefore suffers a greater loss of entropy during the liquid-solid phase transition when compared to ethane and butane. Thus, propane has the lowest melting point among linear alkanes. The correlation between the entropy change and the melting points for alkanes has been explored in the chemical engineering literature\textsuperscript{10-12, 14, 16} but has been largely ignored in the chemistry literature.\textsuperscript{17} PIXEL calculations show that the entropy changes that occur during the liquid-solid phase transition should be taken into account to explain the melting point trends in linear alkanes.

6.3 Conclusions

We revisit the explanations for the alternation in melting points of linear alkanes by calculating the lattice energies using PIXEL. The lattice energies obtained from PIXEL at optimal box radium are in excellent agreement with the enthalpy of sublimation. Partitioning of the lattice energy indicate that arguments based on the gain in dispersion energy is insufficient to explain the alternation in melting points in linear alkanes. Entropy of fusion plays a major role in the explanation for the observed melting point alternation in alkanes.

In summary, we have shown the PIXEL can be reliably used to understand the trends in
intermolecular packing. We have used PIXEL calculations to understand the melting point trends in linear alkanes. At optimal box radius, the lattice energies obtained through PIXEL matches with the experimental enthalpy of sublimation values. PIXEL calculations show that solid state packing alone is insufficient and the entropy of fusion should be taken into account to explain the trends in melting points of linear alkanes.

6.4 Computational Details

All the calculations are done using PIXEL. The input files were generated from the crystallographic coordinates obtained from the Cambridge Structural Database. The REFCODES are provided in Table S1. For alkanes with multiple structures, the structure with the lowest R value was used. Total lattice energies were computed using Pixel, version 2. The standard recommended parameters were used for lattice energy calculations.

Table 6.1 CSD REFCODES for the crystal structures used in PIXEL lattice energy calculations.

<table>
<thead>
<tr>
<th>Alkane</th>
<th>REFCODE</th>
</tr>
</thead>
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Table 6.2 Optimization of box radius for lattice energy calculations for linear alkanes.

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<th>Box Radius (Å)</th>
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<th>Nonane</th>
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<td>LE#</td>
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<td>LE</td>
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* NMI = Number of molecules included in calculation, # LE – Lattice energy in kJ/mole
Table 6.3 Gain in Dispersion, repulsion and total energies for linear alkane homologation.

<table>
<thead>
<tr>
<th>Change in Alkanes</th>
<th>Lattice Energy Calculations</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Gain in Dispersion Energy (kJ/mole)*</td>
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<tr>
<td>Ethane to Propane</td>
<td>8.6</td>
</tr>
<tr>
<td>Propane to Butane</td>
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</tr>
<tr>
<td>Butane to Pentane</td>
<td>14.9</td>
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<tr>
<td>Pentane to hexane</td>
<td>10.3</td>
</tr>
<tr>
<td>Hexane to heptane</td>
<td>10.6</td>
</tr>
<tr>
<td>Heptane to octane</td>
<td>4.9</td>
</tr>
<tr>
<td>Octane to nonane</td>
<td>18.1</td>
</tr>
</tbody>
</table>

* Gain in Dispersion Energy = (Dispersion Energy of C<sub>n</sub> alkane) – (Dispersion Energy of C<sub>n-1</sub> alkane)
Table 6.4 Comparison of the total energy with enthalpy of sublimation and partitioning of total energies into coulombic, polarization, dispersion, and repulsion energies.

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Coulombic energy (kJ/mol)</th>
<th>Polarization (kJ/mol)</th>
<th>Dispersion (kJ/mol)</th>
<th>Repulsion Energy (kJ/mol)</th>
<th>Total Lattice Energy (kJ/mol)</th>
<th>$\Delta_{\text{subH}}^*$ (kJ/mol)</th>
</tr>
</thead>
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<tr>
<td>2</td>
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<td>-31.6</td>
<td>17.5</td>
<td>-18.7</td>
<td>20.5</td>
</tr>
<tr>
<td>3</td>
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<td>-40.2</td>
<td>14.9</td>
<td>-29.0</td>
<td>28.5</td>
</tr>
<tr>
<td>4</td>
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<td>-0.8</td>
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<td>13.6</td>
<td>-33.2</td>
<td>35.9</td>
</tr>
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<td>5</td>
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<td>-1.4</td>
<td>-58.1</td>
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<tr>
<td>7</td>
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<td>-1.6</td>
<td>-79.0</td>
<td>27.9</td>
<td>-57.8</td>
<td>57.9</td>
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<tr>
<td>8</td>
<td>-4.6</td>
<td>-1.4</td>
<td>-83.9</td>
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<tr>
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<td>-102.0</td>
<td>38.7</td>
<td>-72.9</td>
<td>74.6</td>
</tr>
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</table>

* values obtained from NIST
Table 6.5 Comparison of Enthalpy of fusion and entropy of fusion for linear alkanes.

<table>
<thead>
<tr>
<th>Alkane</th>
<th>$\Delta_{\text{fus}}H/\text{kJ/mol}$</th>
<th>$\Delta_{\text{fus}}S/\text{J/mol}^*$</th>
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</thead>
<tbody>
<tr>
<td>Methane</td>
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<td>10.36</td>
</tr>
<tr>
<td>Ethane</td>
<td>-2.72</td>
<td>30.10</td>
</tr>
<tr>
<td>Propane</td>
<td>-3.50</td>
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<td>Butane</td>
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<td>Pentane</td>
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<td>Hexane</td>
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<td>Nonane</td>
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<td>70.41</td>
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</table>

* Values obtained from NIST

# Calculated from the melting point and enthalpy of fusion. These values are identical to the values reported in *TRC Thermodynamic Tables, Hydrocarbons*, Thermodynamics Research Center, Texas Engineering Experiment Station, Texas A&M University System, 1985.
Figure 6.7 Comparison of lattice energy values obtained through PIXEL, reported by Boese and co-workers\textsuperscript{6} and the enthalpy of sublimation.
Sample input files for lattice energy calculations

Input file for ethane with box radius 7Å

```plaintext
#Eth 'P 21/n' original Hs
0 -1 8 0
 0.000 0.000
1 3 -0.2962 1.0500
2 3 -0.2962 1.0500
3 1 0.0988 0.0000
4 1 0.0986 0.0000
5 1 0.0988 0.0000
6 1 0.0988 0.0000
7 1 0.0986 0.0000
8 1 0.0988 0.0000
 0.0000 7.0000 35.0000
4.2260 5.6230 5.8450 90.0000 90.4100 90.0000
1.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000 1.000
0.000 0.000 0.000
0.352972 0.913548 -0.202091 0.694608 -0.111150 0.710750 0.626842 -0.391249 -
0.673791
 0.000000 0.000000 0.000000
2
1.00 0.00 0.00 0.00 1.00 0.00 0.00 0.00 1.00
0.000000 0.000000 0.000000
-1.00 0.00 0.00 0.00 1.00 0.00 0.00 0.00 -1.00
0.500000 0.500000 0.500000
99
```

6.5 References


7.1 Summary

N-heterocyclic compounds are generally known as electron withdrawing groups because of the high electronegativity of nitrogen (compared to carbon and hydrogen atoms) and indeed 1,2,4-triazole acts as an electron withdrawing group in an alternating donor-acceptor copolymer of 1,2,4-triazole and thiophene. Thus, our first strategy to generate electron transporting polymer was to attach an N-heterocyclic compound directly onto polythiophene, expecting an increase in the electron affinity of the resulting

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**Figure 7.1** Resonance structures of 1,4-disubstituted triazole (left) and 1,5-disubstituted triazole(right) attached to thiophene where 1,2,3-triazole as (top) electron donating and (bottom) electron withdrawing.
polythiophene polymer, P3TzHT. But contrarily, 1,2,3-triazole appended to the polythiophene backbone acted as an electron donating group and the charge transport characteristics of P3TzHT showed that the polymer was a hole transporter and its mobility is as good as that of P3HT. We believe that the observed change in the electronic behavior of 1,2,3-triazole is mainly due to the dominance of resonance effect over inductive effect. The electronic effect of 1,2,3-triazole might also depend on the position at which it is attached to thiophene backbone (Figure 7.1). For instance, from the resonance structures, it is clear that 1,5-disubstituted triazole compared to the 1,4-disubstituted triazole (to the 3rd position of thiophene) may act as an electron withdrawing group.

Due to dipolar, hydrogen bond donor and electron donating nature of 1,2,3-triazole group, P3TzHT showed good sensory response towards electron deficient and hydrogen bond acceptor nitroaromatics such as DNT and TNT. Sensory response of P3TzHT towards DNT and TNT is further enhanced by modulating the bulkiness of side chains on 1,2,3-triazole. 1,2,3-triazole serves as a handle to easily vary the side chains on polythiophene backbone. Thus, this strategy could be used to easily: i) change the polarity and bulkiness of side chains; ii) change the strength of analyte-polymer interactions; and iii) tune the assembly of polymer chains in thin films. These properties are very useful in fluorescence based sensory applications of conjugated polymers.

To generate new classes of electron transporting polymers from readily available monomers, we have polymerized known electron deficient molecules instead of converting electron rich polymers into electron deficient polymers. To show that conjugated polymers of a single electron deficient monomer will be electron transporting
we have polymerized an electron deficient molecule, 2,1,3-benzothiadiazole. Indeed homopolymers of 2,1,3-benzothiadiazole, PBTD, exhibited optimal frontier energy levels and redox properties to be a good electron transporter. But PBTD suffers from high band gap and narrow absorption range. Moreover this synthetic methodology is applicable to very few electron deficient molecules. To broaden the absorption and lower the band gap of PTBD homopolymers, we introduced a vinylene spacer between 2,1,3-benzothiadiazole units and synthesized poly(arylene vinylene) derivative of 2,1,3-benzothiadiazole, PBTDV. We have shown that PBTDV is a good electron transporter ($\mu_e \sim 10^{-3}$ cm$^2$/V.s) with low band gap and broad absorption range (250-735 nm). Electron transporting properties of PBTDV indicate that vinyl spacer indeed maintains the electron affinity of 2,1,3-benzothiadiazole unlike other donor-acceptor polymers of 2,1,3 benzothiadiazole that exhibit hole transporting properties. Moreover, vinyl spacer also reduces the band gap and widens the absorption range of PBTDV compared to the conjugated homopolymers of 2,1,3-benzothiadiazole (PBTD). The synthesis of PBTDV involves condensation of dihalo derivative of 2,1,3-benzothiadiazole with commercially available trans-1,2-bis(tri-n-butylstannyl)ethylene. Since dihalo derivatives of many acceptor monomers are already known, this synthetic strategy can be readily extended to a wide range of acceptor monomers to generate solution processable electron transporting polymers with low band gap and wide absorption range.

Conjugated polymer nanoparticles can be used to generate nano-domains of hole and electron transporting polymers. Control over the diameter of conjugated polymer nanoparticles by varying the surfactant and polymer concentration is very well established. We have shown the impact of solvent on: i) density of polymer chain
aggregation; ii) percentage of crystalline and amorphous aggregates; and iii) polymer chain order within those crystalline domains inside the nanoparticle. We showed that, organic solvent, surfactant used to make the nanoparticle and size of the nanoparticle have an effect on the P3HT aggregation thereby affecting optical, optoelectronic and exciton transport properties. Ultrasonication and evaporation of the organic solvent at 80 ºC are the two additional processing steps during the synthesis of nanoparticles compared to thinfilms. Depending on the solubility of P3HT and boiling point of organic solvent, aggregation of P3HT inside the nanoparticle varies. Nanoparticles are composed of polycrystalline $H$ and $J$-type aggregates. Intrachain order and quality of crystallites are good in nanoparticles made from chloroform. But nanoparticles made from mixture solvent have large crystalline aggregates and same intra and interchain order are obtained mostly in all the nanoparticles compared to pure solvents. Smaller size nanoparticles compared to larger nanoparticles synthesized from same solvent have negative effect on the intra and interchain order and quality of aggregates inside the nanoparticle.

7.2 Future Directions

7.2.1 Synthesis of Electron Transporting Polymers

To enhance the efficiency of all-polymer solar cells (APSCs) and to understand the structure-property relations of electron transporting polymers, new classes of electron transporting conjugated polymers with broad absorption, high electron mobility and high dielectric constant need to be synthesized. So far, only three classes of polymers, CN substituted PPV, 2,1,3 benzothiadiazole derived polymers, and rylene diimide (NDI and PDI) derived polymers, are synthesized and tested as electron transporting polymers. The
synthetic strategy developed for 2,1,3-benzothiadiazole based PBTDV polymer (discussed in Chapter 3) is widely applicable for several electron acceptor molecules. This synthetic strategy paves the way to design new classes of electron transporting polymers from readily available electron deficient monomers and generate conjugated electron transporting polymers with different chemical and electronic structure. Few examples of electron deficient conjugated polymers that can be synthesized based on the proposed strategy are shown in Figure 7.2. Studying the charge transfer, separation and transport properties of different classes of polymers will be helpful to understand the impact of molecular structure on these properties. This would also help to generate efficient and ideal electron transporting polymers for APSC.

7.2.2 Morphology of Polymer/Polymer Blend

To achieve high power conversion efficiency APSCs, it is essential to have continuous nano-size domains of hole and electron transporting polymers in addition to the complementary absorption, optimal frontier energy level offset and balance in charge transport. But due to low entropy of mixing of polymers, polymer/polymer blend tend to micro-phase segregate rather than forming the useful nano-phase segregation. Thus to assemble hole and electron transporting polymers into continuous nanodomains for efficient charge separation and transport, diblock conjugated polymers containing hole
transferring and electron transporting blocks with different block sizes should be synthesized and assembled. Diblock polymers are known to phase segregate into various morphologies depending on the size of hole and electron transporting blocks as shown in Figure 7.3. Each of the morphologies shown in Figure has different domain size, interfacial area between each phase, and the charge percolation network within each phase. Thus, assembly of diblock conjugated polymers of hole and electron transporting polymers may provide the necessary morphology to obtain high PCE. And also, the optoelectronic and charge transport measurements on these different morphologies will help us understand the impact of interfacial area, domain size and morphology on the optoelectronic and charge transport properties of the photovoltaic device.

### 7.2.3 Synthesis of Conjugated Polymer Nanoparticles

Control over the diameter of conjugated polymer nanoparticles by varying the surfactant and polymer concentration is very well established. We have shown the impact of solvent on: i) density of polymer chain aggregation; ii) percentage of crystalline and amorphous aggregates; and iii) polymer chain order within those crystalline domains.
inside the nanoparticle. However to completely realize the potential of conjugated polymer nanoparticles in organic electronics, the following issues should be addressed: i) synthesize nanoparticles with less dispersity in size; ii) synthesize nanoparticles with uniform geometry; and iii) gain control over the crystallite domain size inside nanoparticle. Since the interfacial area between hole and electron transporter phases and polymer conformation at the interface also play crucial role in charge separation, nanoparticles with different geometry with control over the polymer conformation at the interface need to be synthesized and tested for photophysics, charge transport and photovoltaic metrics. Since we have shown that the solvent and surfactant used to synthesize nanoparticle have an effect on polymer aggregation inside nanoparticles, the above parameters can be studied by varying solvent and surfactant.

**Figure 7.4** Illustration of the mineral structure-types obtained from the assembly of nanoparticles with different radius.
7.2.4 Assembly of Conjugated Polymer Nanoparticles

We have measured the power conversion efficiency (PCE) of P3HT and PCBM nanoparticle blend and it is found to be 0.12%. The low PCE might be because of two reasons: i) larger diameter of nanoparticles (>100 nm) compared to the excitons dissociation length (<20 nm) leading to poor charge separation; and ii) lack of control over the morphology of nanoparticle/nanoparticle assembly. Nanoparticles of diameter ~40 nm (radius ~20 nm) can be easily synthesized because of the control over size of nanoparticles. However, the more challenging task is to assemble them into an optimum morphology for efficient PCE. In inorganic nanoparticles it is shown that the spherical nanoparticles with small size dispersity can be assembled into morphologies that mimic mineral structure-type packing. Similarly, hole and electron transporting polymer nanoparticles of different radii can be assembled into the morphologies shown in Figure 7.4. Four out of the five nanoparticle assemblies shown in Figure can provide the necessary hole and electron transporter interface for charge separation and percolation pathway for charge carriers to reach electrodes. These assemblies can be obtained by

Figure 7.5 Assembly of nanocubes into various morphologies with the increase in interfacial area (from left to right) between hole (purple) and electron (yellow) transporter phases.
blending the nanoparticles of different radius. Assembly of nanoparticles can be further assisted by blending the hole and electron transporting nanoparticles with surfactants of opposite charges to increases the coulombic interaction. Since the interfacial area between hole and electron phases and polymer conformation at the interface also play crucial role in charge separation, nanoparticles of different geometry should be assembled and their photovoltaic metrics should be measured. Compared to the nanospheres, nanocubes have high surface area and can provide high interfacial area between hole and electron transporting phases. Further, nanocubes of hole and electron transporters can be assembled into various morphologies with the increase in interfacial area between hole and electron transporter phases as shown in Figure 7.5. Moreover, the configuration of the polymers/molecules on the nanocube surface may be different compared to the

![Figure 7.6 Nanoparticles may provide a general strategy to assemble hole and electron transporting polymers/small molecules into desired assemblies for photovoltaics.](image)
nanospheres. Nanoparticles of any organic material (polymer and small molecules) that is: i) insoluble in water; ii) soluble in an organic solvent that is immiscible with water; and iii) turns into solid state when the solvent is evaporated can be prepared. These nanoparticles can be assembled into desired morphologies for optimal photovoltaic metrics. Thus nanoparticles assembly will provide a general strategy to generate efficient photovoltaic devices of polymer/polymer, polymer/small molecule and small molecule/small molecule blends as shown in Figure 7.6.
APPENDIX

OPTOELECTRONIC PROPERTIES OF P3HT NANOPARTICLES

(This section of the document (data and discussion) is taken from a manuscript under preparation and was prepared by Joelle Labastide and Mina Baghgar from Prof. Michael D. Barnes group, Department of Chemistry, University of Massachusetts Amherst)

A.1 Percent Crystalline P3HT Aggregates Within Nanoparticles

In order to determine the percentage of crystalline material inside the nanoparticle, we modeled the aggregate absorption spectrum of the nanoparticles made from 0.5 wt% P3HT and 1mM SDS with all three different solvents and 0.05 wt% P3HT and 1mM SDS with mixture solvent. Figure A.1 shows the modeled absorption spectra of P3HT nanoparticles along with the normalized experimental absorption spectra of P3HT nanoparticles and P3HT solution in corresponding organic solvent. Absorption spectrum is modeled as a progression of (up to) five Gaussian functions (indexed by vibronic quantum number, n) characterized by the following adjustable parameters: full-width half-maximum ($\sigma_n$), peak position ($\omega_n$), and absorption strength ($\varepsilon_n$) (see Table A.1). By determining the ratio of the integrated areas for the aggregated and unaggregated spectra (without correction for differences in absorption cross-sections), we obtained an estimate of $\approx 50\%$ crystalline material for each of the NP samples, apparently independent of size and solvent mixture.
Table A.1 Fit parameters of the Gaussian components assigned to the different vibronic components of the P3HT nanoparticles absorption spectra.

<table>
<thead>
<tr>
<th>Solvent(^a)</th>
<th>P3HT wt%</th>
<th>Size (nm)</th>
<th>(A_{0.0}/A_{0.2})</th>
<th>(\sigma_0)(^b) (meV)</th>
<th>(A_{0.1}/A_{0.2})</th>
<th>(\sigma_1)(^b) (meV)</th>
<th>(\Delta_{01})(^c) (meV)</th>
<th>(\lambda)(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl(_3)</td>
<td>0.5</td>
<td>136</td>
<td>0.62</td>
<td>0.91(\omega_0)</td>
<td>0.84</td>
<td>1.2 (\omega_0)</td>
<td>178</td>
<td>1.35</td>
</tr>
<tr>
<td>Toluene</td>
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<td>97</td>
<td>0.46</td>
<td>0.8(\omega_0)</td>
<td>0.75</td>
<td>1.2 (\omega_0)</td>
<td>174</td>
<td>1.63</td>
</tr>
<tr>
<td>Tol/CHCl(_3)</td>
<td>0.5</td>
<td>100</td>
<td>0.55</td>
<td>0.8(\omega_0)</td>
<td>0.84</td>
<td>1.2 (\omega_0)</td>
<td>173</td>
<td>1.52</td>
</tr>
<tr>
<td>Tol/CHCl(_3)</td>
<td>0.05</td>
<td>60</td>
<td>0.45</td>
<td>0.76(\omega_0)</td>
<td>0.75</td>
<td>1.2 (\omega_0)</td>
<td>182</td>
<td>1.66</td>
</tr>
</tbody>
</table>

\(^a\)1mM SDS. \(^b\)\(\sigma_n\) is the full width half maximum of the 0-n vibronic transition. \(^c\)\(\Delta_{01}\) is the energy spacing between the first two (0-0, and 0-1) vibronic transitions. Note that these values are typically larger than the “accepted” value of \(\omega_0\) (168 meV). Note also the increase in line-width for the higher sidebands. \(^d\)\(\lambda\) is the Huang-Rhys factor that dictates the relative peak intensity of 0-1 and 0-0 transitions.
A.2 Optoelectronic Properties of P3HT Nanoparticles

Since photoluminescence spectrum is very sensitive to the order in the polymer aggregation and the defects, time resolved photoluminescence studies were done on the nanoparticles. To find out the effect of solvent on the aggregation of P3HT inside the nanoparticle, fluorescence lifetimes of individual P3HT nanoparticles synthesized using 0.5 wt% P3HT and 1 mM SDS from chloroform, toluene and chloroform/toluene mixture were recorded. Decay dynamics from all P3HT nanoparticles studied here are approximately double exponential at early times (less than 5 ns), and the PL seems to be dominated by the prompt decay component, which accounts for more than 90 percent of the total decay dynamics. Figure A.2 shows the contribution of the prompt decay component as a

Figure A.1 Experimental absorption spectra (black line with circle) normalized to 0-2 absorption strength for nanoparticles made from 0.5 wt% P3HT and 1 mM SDS in a) CHCl₃; b) toluene/CHCl₃; c) toluene; d) 0.05 wt% P3HT and 1 mM SDS in toluene/CHCl₃ (1:4). In each panel, the scaled absorption spectrum of unaggregate P3HT in CHCl₃ is shown with blue open circles. The aggregate spectrum (closed red circles) was modeled as a progression of five Gaussian functions with FWHM, peak position, and peak extinction coefficient as adjustable parameters.
function of the time constant for single nanoparticles in each polymer solvent. Total photoluminescence intensity is color-encoded, to illustrate the intensity dependence of both the amplitude and value of the fluorescence lifetime component. AFM correlated photoluminescence measurements similar to the one described in Figure A.5 revealed that, under constant laser power, nanoparticles with similar PL intensities were of similar size, and we can therefore attribute the presence of a PL intensity value distribution to a size distribution within each sample. The dispersion in the lifetime distributions for each family of particles may mirror the heterogeneity of nanoparticle internal environments within a family. The photophysics are very tightly clustered in general, with contributions ranging from 95 to 99 percent and a lifetime ranging from 0.13 to 0.19 ns, but there is a notable convergence in the lifetime distribution in both dimensions in sample c. The distribution of life times is in the order of mixture < toluene < chloroform. High convergence in life times indicates that all the P3HT aggregates that are emitting have similar inter and intrachain

**Figure A.2** Prompt component of the fluorescence lifetimes and the percent contribution of the prompt component to the total PL decay of nanoparticles made from 0.5 wt% P3HT and 1 mM SDS in a) CHCl₃; b) toluene; and c) toluene/CHCl₃(1:4). The color bars show the PL intensity of each nanoparticle within a particular family.
order in nanoparticle irrespective of quality of the order. That is, mixture of chloroform and toluene compared to the pure solvent provides the proper environment to generate the P3HT aggregates of same intra and interchain order. We believe that this is mainly because of the difference in boiling point and solubility of P3HT in those solvents. As the emulsion is heated to evaporate the solvent, chloroform evaporates much faster compared to the solvent mixture and toluene, thereby trapping the aggregates of different intra and interchain order in the nanoparticles. On the other hand, due to high boiling point of toluene, all the P3HT aggregates are re-dissolved in the nanodroplet and P3HT chains start aggregating at 80 °C. But since toluene is a marginal solvent for P3HT solubility, P3HT chains may not have enough conformational freedom to generate aggregates that are more uniform in intra and interchain order. However, since the mixture solvent contains both good and high boiling solvent, P3HT chains can assemble into more uniform aggregates of same intra and interchain order.

To find out the effect of nanoparticle size on the aggregation of P3HT inside the nanoparticle, fluorescence

![Figure A.3](image)

**Figure A.3** Fluorescence lifetimes and the percent contribution of each time constant to the total PL decay of P3HT nanoparticles made from 0.5 wt% (magenta squares) and 0.05 wt% (blue circles) solutions of P3HT and 1mM SDS in toluene/CHCl₃(1:4). As in Figure A.2, the color bars show the PL intensity of each nanoparticle within a particular family.
lifetimes of individual P3HT nanoparticles synthesized in solvent mixture using 0.5 wt% and 0.05 wt% P3HT and 1 mM SDS are recorded. The ten-fold reduction in polymer concentration yielded a particle diameter decrease from 116 nm to nominally 60 nm. Figure A.3 shows the contribution of both lifetime components to the total PL decay vs the decay constant values, and is coded for intensity information in the same manner as Figure A.3. The dispersions in the lifetime and amplitude distributions are far larger in the 0.05 wt% nanoparticles than in any other sample. We speculate that this might be because of restricted conformational freedom and low effective conjugation length of P3HT chains in a smaller droplet compared to larger droplets. For low concentration of P3HT such as 0.05 wt% P3HT, the solvent mixture saturation limit for P3HT solubility won’t reach until most of the solvent evaporates and the droplets size decreases substantially. Thus, most of the P3HT aggregation is happening in a smaller droplet where the effective conjugation length and conformation freedom of P3HT chains is very less, leading to large variations in the intra and interchain order among different P3HT aggregates (Table A.2). From the Figure A.3, it is also notable that the photophysics of
nanoparticles that fall in the range where the size distributions of 0.5 wt% and 0.05 wt% P3HT nanoparticle samples overlap are the same, alluding to the fact that size of the nanoparticle plays a crucial role in formation of P3HT aggregates and exciton recombination dynamics.

This is further confirmed by the long time PL decay dynamics. Figure A.4 shows the long time PL decay and power law fit for nanoparticles made from different solvents using 0.5 wt% P3HT and mixture solvent using 0.05 wt% P3HT at 1mM SDS. The regime in which the PL decay follows a power law consists of recombination of charge-separated species that probably do not exist in highly disordered polymer phases, and are therefore associated with crystalline domains. Under the assumption that the tunneling parameter is a property of the material and thus β is the same for all phases of P3HT, the comparison of the parameter μ=ε/β is taken to be a comparison of mean electron- hole distances given by 1/ε.\(^1,2\) Within the confines of this model, the average e\(^-\)/h\(^+\) distances for the 0.5 wt% P3HT nanoparticles are in the order of chloroform ~ toluene < mixture, (Table A.2 ) indicating that there are larger crystalline domains in the mixture solvent compared to pure solvents. The smallest value of μ for nanoparticles from mixture indicates that largest average e\(^-\)/h\(^+\) distances is observed for 0.05 wt% P3HT

<table>
<thead>
<tr>
<th>Solvent [P3HT]</th>
<th>Lifetime distribution (ns)</th>
<th>μ(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl(_3) 0.5 wt%</td>
<td>0.14-0.19</td>
<td>1.14</td>
</tr>
<tr>
<td>Toluene 0.5 wt%</td>
<td>0.14-0.18</td>
<td>1.19</td>
</tr>
<tr>
<td>Tol/CHCl(_3)(^a) 0.5 wt%</td>
<td>0.13-0.15</td>
<td>0.76</td>
</tr>
<tr>
<td>Tol/CHCl(_3)(^a) 0.5 wt%</td>
<td>0.15-0.25</td>
<td>0.57</td>
</tr>
</tbody>
</table>

\(^a\)1:4(v/v). \(^b\)P3HT thinfilm μ value is 0.54.
nanoparticles made from mixture. We believe that the observed largest average $e^-/h^+$ distance in 0.05 wt% P3HT samples compared to 0.5 wt% is physically not possible. Thus the observed larger average $e^-/h^+$ distances might be because of presence of more traps in the amorphous and crystalline domains of P3HT that trap and release the charges thereby artificially increasing the time to recombine the charges. Figure 4.7 shows the schematic picture of P3HT aggregates inside the nanoparticles.

In an effort to understand the effect of nanoparticle size and three-dimensional confinement on the orientation of crystalline aggregates with respect to each other inside the nanoparticle, size correlated polarization anisotropy measurements were conducted by rotation of the linearly polarized excitation. Atomic Force Microscopy was done in situ, and then the fluorescence and AFM surface height images were correlated. The AFM image in Figure A.5 shows three dominant sizes of NPs: 20 nm, 60 nm, and 130 nm.

**Figure A.5** Size correlated fluorescence polarization anisotropy of P3HT nanoparticles with 440 nm laser excitation. (a) PL image (2 seconds exposure), and (b) corresponding surface height image of the same region, indicating significant heterogeneity in particle size. (c) Excitation polarization anisotropy trace for selected particles, I, II, and III highlighted in (a) and (b). (d) Shows a scatter plot correlating linear excitation anisotropy parameter, M, with particle size.
Both non-crystalline and crystalline parts of the NPs absorb 440 nm light, so the fluorescence trajectory is composed of emission from both non-crystalline and crystalline phases. Steady-state polarization anisotropy is very small for all sizes of NPs, indicating that the aggregates inside the nanoparticles have high degree of polycrystallinity coupled with the disorganized emission from the non-crystalline polymer phase.

Figure A.6 shows the fluorescence emission spectra of P3HT nanoparticles under 440 nm laser excitation. Graphs a, b, and c are the spectra of nanoparticles made using 0.5 wt% P3HT in chloroform, toluene and mixture. The spectra in d are from NPs made from 0.05 wt% P3HT in mixture solvent. Inspection of the emission spectra reveals that the main central peak of the emission line shape of all the NPs with different sizes and from different solvents has the same small Stokes shift from the absorption origin (~70 meV or 600 cm⁻¹), and that the 0-0/0-1 oscillator strength ratio is larger than 1; clearly indicating the presence of J-type aggregates in these NPs. This is
very surprising because from the absorption spectra, $A_{0.0}/A_{0.1}$ ratio is less than one indicating $H$-type aggregates for all the studied nanoparticles. This means the nanoparticles contain both $H$-type and $J$-type aggregates and the emission is mainly happening from $J$-type aggregates. This could be because of energy transfer and/or charge transfer happening from high energy amorphous and $H$-type aggregates to relatively low energy $J$-type aggregates. The excitons and/or charges are radiatively recombining in $J$-type aggregates leading to more than 1 oscillator strength ratio.

**A.4 Experimental Section**

The time resolved photoluminescence data described in this section was acquired using Time-Tagged-Time-Resolved (TTTR) Single Photon Counting to study the PL decay with 16ps resolution over a 50 ns window, and then with 32 ps resolution with a time window of 100ns. In both cases, nanoparticles were illuminated with a PicoQuant PDL with 440 nm wavelength and 50 ps pulse width, which was weakly focused in epi illumination geometry. The input intensity is approximately 1kW/cm$^2$ over a 10 μm spot size. The instrument response is approximately Gaussian, with a FWHM of 180 ps.

**A.5 References**


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