SYNTHESIS OF CONJUGATED POLYMERS

A Dissertation

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Conjugated polymers (CPs) are a unique class of materials because they possess the electronic properties of semi-conductors and processability of polymers. Their electronic and optical properties can be controlled by their chemical structures and conjugation length.

To enhance the electron affinity of CPs, a series of boron-containing CPs were synthesized with arylene-borylene units. One of the boron-containing polymer had indeed shown the ability of quenching the photoluminescence of poly(3-hexylthiophene) (P3HT), indicating possible exciton separation and charge transfer.

Next, a ketone group was introduced to polythiophene to lower its LUMO level and increase the electron affinity. Regioregular poly(3-heptanoylthiophene) (PHOT) was synthesized. The polymerization was realized by Ni-catalyzed Kumada coupling with a chain-growth mechanism. Schlenk equilibrium played a key role in the generation of the monomer for the polymerization. PHOT was fully characterized by various techniques. However, only $p$-channel activity was observed in field-effect transistors (FETs) for PHOT. The hole mobility was one order lower than that of P3HT. Photovoltaic devices with an active layer of 1:1 blend of PHOT and PC$_{71}$BM had a low power conversion efficiency of $\sim 0.5\%$. 
Finally, the synthesis of graphene nanoribbons (GNRs) was attempted which could be potentially used as a good charge carrier. To prevent intramolecular and intermolecular side reactions during Scholl reaction, the precursors, oligo-naphthalenes with alkoxy groups capping the 2, 3, 6, and 7-positions had been synthesized. Intramolecular ring fusion via the Scholl reactions was tested, but no expected GNRs were formed.
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I dedicate this dissertation to my parents for their endless love, support and encouragement.
# TABLE OF CONTENTS

| LIST OF TABLES | ix |
| LIST OF FIGURES | x |
| LIST OF SCHEMES | xiii |

## CHAPTER

### I. CONJUGATED POLYMERS AND THEIR APPLICATIONS

1.1 History of Conjugated Polymers .................................................. 1

1.2 Synthesis of Conjugated Polymers ................................................ 3

   1.2.1 Conjugated Polymers via Electropolymerization .......................... 3

   1.2.2 Boron Containing Conjugated Polymers from Non-Catalyzed Step-Growth Polymerization Synthesis ........................................... 6

   1.2.3 Transition Metal-Catalyzed Coupling Reactions ......................... 11

   1.2.4 Application of Transition Metal-Catalyzed Coupling Reactions in Step-Growth Polymerization .............................................. 13

   1.2.5 Chain-Growth and Livingness of Polycondensation of Aryls .......... 15

   1.2.6 Head-to-Tail Regioregular Poly(3-Alkylthiophene) (\textit{rr}-P3ATs) via Transition Metal-Catalyzed Chain-Growth Polymerization ...... 16

   1.2.7 Functionalization of Regioregular Polythiophenes ...................... 25

   1.2.8 Other types of Conjugated Polymers via Transition Metal-Catalyzed Chain-Growth Polymerization ........................................... 26
1.2.9 Attempted Transition Metal-Catalyzed Polymerization of Electron-Acceptor Materials ........................................ 33

1.3 Application of Conjugated Polymers in Organic Solar Cells .......................................................... 35

1.3.1 Working Principles of Organic Solar Cells ................................................................. 35

1.3.2 Device Structure Improvement of Organic Solar Cells .............................................. 37

1.3.3 Materials Challenges for OPV .......................................................... 40

1.4 Summary and Outlook ........................................................................................................ 42

II. SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF BORON-CONTAINING CONJUGATED POLYMERS .................................................................................. 43

2.1 Introduction .......................................................................................................................... 43

2.2.1 Synthesis .................................................................................................................... 46

2.2.2 Solution and Solid State Optical Properties .............................................................. 51

2.2.3 Cyclic Voltammetric Study ....................................................................................... 54

2.2.4 Detection of Charge Transfer by Photoluminescence Quenching ......................... 55

2.3 Conclusion .......................................................................................................................... 58

2.4.1 Materials .................................................................................................................... 59

2.4.2 Measurements ............................................................................................................. 60

2.4.3 Synthesis .................................................................................................................... 61

III. SYNTHESIS AND CHARACTERIZATION OF REGIOREGULAR POLYTHIOPHENE WITH ELECTRON-WITHDRAWING GROUPS .................................................. 65

3.1 Introduction .......................................................................................................................... 65

3.2.1 Synthesis of Monomer Precursors ........................................................................ 67

3.2.2 Generation of Monomers ......................................................................................... 68

3.2.3 Polymer Synthesis ....................................................................................................... 69

3.2.4 Cyclic Voltammetry ................................................................................................... 74
3.2.5 Optical Absorption and Photoluminescence Spectra ........................................ 75
3.2.6 Thermal and Morphological Properties .................................................................. 77
3.2.7 Charge Transport and Photovoltaic Properties ...................................................... 79
3.2.8 Attempted Synthesis of \textit{rr}-Poly(3-(1,1-difluoroalkyl)thiophene) .................. 84

3.3 Conclusions .................................................................................................................. 85

3.4.1 Materials .................................................................................................................. 86
3.4.2 Measurements .......................................................................................................... 87
3.4.3 Synthesis ................................................................................................................. 91

IV. ATTEMPT OF SYNTHESIS OF GRAPHENE NANORIBBONS .................................... 99

4.1.1 Physical Properties of Graphene and Graphene Nanoribbons ....................... 99
4.1.2 Successes in Fabrication and Synthesis of GNRs ............................................ 101
4.1.3 Development of Solution Synthesis of PAHs and Attempted Synthesis of GNRs ................................................................................................................................. 104

4.2.1 Attempted Synthesis of PPN via Intermolecular Scholl Reaction ................ 109
4.2.2 Attempted Synthesis of PPN via Intramolecular Scholl Reaction .................. 110
4.2.3 Attempted Synthesis of PPA Model Compounds ........................................... 115

4.3 Conclusions .................................................................................................................. 118

4.4.1 Materials .................................................................................................................. 119
4.4.2 Measurements .......................................................................................................... 120
4.4.3 Synthesis ................................................................................................................. 121

V. SUMMARY ..................................................................................................................... 136

REFERENCES .................................................................................................................... 138

APPENDIX .......................................................................................................................... 159

viii
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Summary of side chains and terminal groups on <em>rr</em>-P3ATs</td>
<td>26</td>
</tr>
<tr>
<td>2.1 Comparison of reduction potentials of boranes  </td>
<td>45</td>
</tr>
<tr>
<td>2.2 UV-Visible absorption data</td>
<td>53</td>
</tr>
<tr>
<td>3.1 The solubility of PHOT in different solvents</td>
<td>73</td>
</tr>
<tr>
<td>3.2 Electrical parameters of the thin film transistors of PHOT</td>
<td>81</td>
</tr>
<tr>
<td>3.3 <em>J-V</em> characteristics and PCE of BHJ cells under different conditions</td>
<td>83</td>
</tr>
<tr>
<td>4.1 Failed polymerization. (Isomers of monomers are omitted for clarity.)</td>
<td>112</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.1</td>
<td>Coupling region-isomers of 3-alkylthiophene dimers</td>
</tr>
<tr>
<td>1.2</td>
<td>Regioirregular P3AT in non-planar and <em>rr</em>-P3AT in planar structure</td>
</tr>
<tr>
<td>1.3</td>
<td>Orbital overlapping in vinylboranes</td>
</tr>
<tr>
<td>1.4</td>
<td>$^1$H NMR spectra of (a) regiorandom (1:1:1:1, HT-HT:HH:TT-HT:TT-HH) P3HT and (b) regioregular (98.5%) P3HT</td>
</tr>
<tr>
<td>1.5</td>
<td>$^{13}$C NMR spectra of (a) regiorandom (1:1:1:1, HT-HT:HH:TT-HT:TT-HH) P3HT and (b) regioregular (98.5%) P3HT</td>
</tr>
<tr>
<td>1.6</td>
<td>MALDI-TOF mass spectrum of <em>rr</em>-P3HT</td>
</tr>
<tr>
<td>1.7</td>
<td>$M_n$ and $M_w/M_n$ values of <em>rr</em>-P3HT as a function of the molar ratio of converted monomer to catalyst</td>
</tr>
<tr>
<td>1.8</td>
<td>Bilayer OPV cell</td>
</tr>
<tr>
<td>1.9</td>
<td>BHJ OPV cell</td>
</tr>
<tr>
<td>1.10</td>
<td>Ideal structure of a BHJ solar cell</td>
</tr>
<tr>
<td>1.11</td>
<td>Self-assembly of block polymers into the ideal structure of a BHJ solar cell</td>
</tr>
<tr>
<td>2.1</td>
<td>Aryborylene units structure</td>
</tr>
<tr>
<td>2.2</td>
<td>A $^1$H NMR of polymer 2 in CDCl$_3$. B $^1$H NMR of compound 2-M in CDCl$_3$</td>
</tr>
<tr>
<td>2.3</td>
<td>$^1$H NMR spectrum of polymer 3 in DMF-$d_7$. Peaks with star are due to deuterated solvents and end groups. B $^1$H NMR spectrum of compound 3-M in CDCl$_3$.</td>
</tr>
<tr>
<td>2.4</td>
<td>A $^1$H NMR spectrum of 4 in 1:2 CD$_3$CN:$d$-THF. B $^1$H NMR spectrum of compound 4-M in CDCl$_3$.</td>
</tr>
</tbody>
</table>
2.5 GPC trace of polymer 4

2.6 UV-Vis spectra of model compounds and polymers in the presence of a coordinated Lewis base and in the absence of a coordinated Lewis base

2.7 Cyclic voltammograms of model compounds and polymers

2.8 Comparison of LUMO energies

2.9 Photoluminescence spectra of pure rr-P3HT, a blend of 3 and rr-P3HT, and a blend of 4 and rr-P3HT. These samples were excited at 530 nm

3.1 Isomers after quenching

3.2 1H NMR of PHOT with assignments. The HT/HH ratio was estimated to be ~96:4 using the α-methylene protons at shown in the inset to the right

3.3 A. Total conversion of monomers as a function of time and temperature. B. Plot of $M_n$ vs total conversion of 9a and 9b. The number over each point was the PDI of the particular sample

3.4 A. Cyclic voltammograms of PHOT (solid) and rr-P3HT. B. Comparison of HOMO and LUMO levels of PHOT and rr-P3HT

3.5 Chemical structure of Polymer A

3.6 A. UV-Vis absorption spectra of PHOT (solid) and rr-P3HT in chloroform. B. UV-Vis absorption spectra of PHOT (solid) and rr-P3HT as spin-cast film

3.7 A. Solution photoluminescence spectra of PHOT (solid) and rr-P3HT in chloroform solution. The spectra are normalized. B. Thin film photoluminescence spectra of PHOT (solid), rr-P3HT, and their 1:1 blend (dot). The spectra were not normalized for comparison of the emission intensity

3.8 A. TGA thermogram of PHOT. B. DSC thermogram of PHOT

3.9 A. WAXD powder pattern of PHOT annealed at various temperatures. B. Change of $d$-spacing after annealing

3.10 Inter-chain distance and possible π-stacking of PHOT

3.11 The device structure of field effect transistor

3.12 Output and transfer characteristics of the thin film transistor of PHOT after thermal annealing at 150 °C
3.13 UV-Vis absorption spectrum and TEM image of a BHJ cell with an active layer of PHOT:PC$_{71}$BM blend in 1:1 weight ratio..................................................82

3.14 Current density-voltage curves of a BHJ cell with an active layer of PHOT:PC$_{71}$BM blend in 1:1 weight ratio..................................................83

3.15 Current density-voltage curves of a BHJ cell with an active layer of PHOT:P3HT blend in 1:1 weight ratio..................................................84

4.1 Charge carrier mobility of different materials........................................101

4.2 A. Overview STM image after cyclodehydrogenation, showing straight N=7 GNRs. B. Raman spectrum (532 nm) of straight N=7 ribbons.....................103

4.3 b) HRTEM of GNRs. c) STM image of GNRs........................................106

4.4 $^1$H NMR of 18.............................................................................114

4.5 MALDI-TOF spectrum and GPC trace of 18........................................114

4.6 $^1$H NMR of boron-doped nanographene............................................118
LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Mechanism of electropolymerization of heterocycles</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Hydroboration polymerization of ArBH₂</td>
<td>7</td>
</tr>
<tr>
<td>1.3</td>
<td>Haloboration polymerization of diyne monomers</td>
<td>8</td>
</tr>
<tr>
<td>1.4</td>
<td>Polycondensation of aryldimethoxyborane using Grignard and organolithium reagents</td>
<td>8</td>
</tr>
<tr>
<td>1.5</td>
<td>Tin-boron exchange polymerization of bis(trimethylstannyl) monomers</td>
<td>9</td>
</tr>
<tr>
<td>1.6</td>
<td>Synthesis of conjugated organoborane oligomers</td>
<td>10</td>
</tr>
<tr>
<td>1.7</td>
<td>Hydroboration polymerization of 5,10-dihydroboranthrene</td>
<td>10</td>
</tr>
<tr>
<td>1.8</td>
<td>Equation of coupling reaction</td>
<td>12</td>
</tr>
<tr>
<td>1.9</td>
<td>General mechanism of coupling reactions</td>
<td>12</td>
</tr>
<tr>
<td>1.10</td>
<td>Preparing polyacetylenes from prepolymer</td>
<td>13</td>
</tr>
<tr>
<td>1.11</td>
<td>Soluble polyacetylene from monosubstituted cyclooctatetraene</td>
<td>14</td>
</tr>
<tr>
<td>1.12</td>
<td>Polythiophene from Stille coupling reaction</td>
<td>15</td>
</tr>
<tr>
<td>1.13</td>
<td>Regio-irregular Poly(thienylenevinylene)s via Stille coupling reaction</td>
<td>15</td>
</tr>
<tr>
<td>1.14</td>
<td>Synthetic routes of rr-P3ATs</td>
<td>17</td>
</tr>
<tr>
<td>1.15</td>
<td>Mechanism of chain-growth condensation polymerization of rr-P3ATs</td>
<td>21</td>
</tr>
<tr>
<td>1.16</td>
<td>Synthesis of 100% HT regioregular P3HT</td>
<td>23</td>
</tr>
<tr>
<td>1.17</td>
<td>Synthesis of monodisperse HT oligothiophene</td>
<td>25</td>
</tr>
<tr>
<td>1.18</td>
<td>Synthesis of poly(p-phenylene) via chain-growth polycondensation</td>
<td>27</td>
</tr>
</tbody>
</table>
1.19 Strategies of synthesis of poly(p-phenylene)-b-poly(3-alkylthiophene)..........................28
1.20 Synthesis of poly(p-phenylene) via Suzuki polycondensation........................................28
1.21 Synthesis of poly(N-alkylpyrrole) via chain-growth polycondensation..........................29
1.22 Synthesis of poly(p-phenylene)-b-poly(N-hexylpyrrole)..............................................29
1.23 Synthesis of polyfluorenes via Suzuki polycondensation.............................................30
1.24 Synthesis of polyfluorenes via lithiated fluorene monomer..........................................30
1.25 Synthesis of polyfluorene via GRIM.............................................................................31
1.26 Synthesis of polycarbazole via GRIM...........................................................................31
1.27 Synthesis of poly(meta-pyridine) via GRIM.................................................................32
1.28 Synthesis of poly(para-pyridine) via GRIM.................................................................33
1.29 Synthesis of n-type conjugated polymer from acceptor monomers..............................34
1.30 Working principles of OPV cells. A. Light absorption and excitons generation.  
B. Excitons diffusion.  C. Charge separation.  D. Charge transportation.............36
2.1 Synthesis of compound 1, 2-M and polymer 2............................................................46
2.2 Synthesis of compound 3-M and polymer 3...............................................................47
2.3 Synthesis of compound 4-M and polymer 4...............................................................49
2.4 Illustration of photoluminescence quenching of excited states...................................56
3.1 Synthesis of monomer precursor...............................................................................67
3.2 Schlenk equilibrium of monomer generation............................................................68
3.3 Polymer synthesis.....................................................................................................70
3.4 Polymerization mechanism.......................................................................................73
3.5 Synthetic route of rr-poly(3-(1,1-difluoroalkyl)thiophene).........................................85
4.1 Arm-chair GNRs (PPN and PPA) and zig-zag GNR.....................................................100
4.2 Bottom-up synthesis of GNRs...................................................................................102
4.3 Proposed mechanism of surface-assisted GNR synthesis..............................................103
4.4 Two synthetic routes toward the HBC core molecule. (Functional groups around the HBC core are omitted for clarity.).................................................................104
4.5 GNR from polyaromatic precursor..............................................................................105
4.6 Synthesis of linear GNRs from hexaphenylbenzene type prepolymer.....................106
4.7 Intermolecular side reactions of Scholl reaction of o-terphenyl................................107
4.8 100% conversion via Scholl reaction of substituted o-terphenyl.............................107
4.9 Attempted synthesis of PPN derivative.................................................................108
4.10 Intramolecular side reaction under Scholl reaction and the formation of a five-member ring..........................................................108
4.11 Synthesis of monomer 14......................................................................................119
4.12 Unfavorable intermolecular reaction.................................................................110
4.13 Synthesis of monomer precursors 15.....................................................................110
4.14 Synthesis of model compounds 16 and 17.........................................................111
4.15 Synthesis of polymer precursor 18. X and Y are functional groups.........................112
4.16 Synthesis of polymer precursor using PhPd(t-Bu)3Br as initiator..............................113
4.17 Synthesis of different model precursors..............................................................116
4.18 Carbocation rearrangement of anthracenes.........................................................117
4.19 Synthesis of boron-doped nanographene.............................................................118
CHAPTER I
CONJUGATED POLYMERS AND THEIR APPLICATIONS

1.1 History of Conjugated Polymers

The first reported conjugated polymer can be traced back to the mid-19th century. Letheby reported the formation of polyaniline as an electrochemical oxidation product of aniline in acidic media.\(^1\) In 1965, Australian scientists Weiss, Willis and co-workers reported iodine-doped oxidized polypyrrole blacks with resistivity as low as \(\sim 1 \, \Omega/cm\).\(^2,3\) These findings invalidate the previous concept that organic molecules are insulators or at most weakly conducting materials and opened the door of conductive polymer research.

The discovery of well-defined polyacetylene in the 1974 by Shirakawa and Ikeda accelerated interest of conjugated polymers in the fields of microelectronics.\(^4\) Although the first polymerization of acetylene was reported by Natta and co-workers in 1958,\(^5\) the work did not attract much attention. In addition to the many side reactions such as the formation of benzene — a cyclic trimer of acetylene, the heterogeneous Ziegler-Natta catalysts could only form an intractable solid. With the discovery of a new catalyst system, \(\text{Ti(OC}_4\text{H}_9)_4\)-\(\text{Al(C}_2\text{H}_3)_3\) (\(\text{Al/Ti}=3-4\)), the homogeneous polymerization of acetylene became feasible. According to Shirakawa, a polyacetylene thin film was initially obtained by a fortuitous error.\(^6\) One student made a wrong calculation and used a
concentration of the Ziegler-Natta catalyst nearly 1000 times greater than that usually used. As a result, a silvery polyacetylene film was formed on the surface of the reaction solution. After thermal annealing at various temperatures, the cis- and trans- contents could be changed. Shortly after this discovery, Shirakawa, Heeger and Macdiarmid published two seminal papers in 1977 and 1978 on the oxidation of polyacetylene with halogens, resulting in a $10^8$ fold increase in conductivity.\textsuperscript{7,8} The conductivity of this doped material could approach the conductivity of silver. Based on these discoveries, the three are awarded the Nobel Prize in Chemistry in 2000.

In general, conjugated polymers are defined as polymer chains with carbon or other main group atoms in the sp$^3$p$\!\!\!\!_z$ hybridized configuration. They are semiconductors that can be doped to become conducting or even metallic materials.\textsuperscript{9} After several decades of study since their discovery, conjugated polymers have been demonstrated to combine the electronic properties of metals and semiconductors with the ease of processing and mechanical advantages of polymers.

A wide range of electrical and optical devices have been demonstrated using conjugated polymers. Light-emitting devices have been fabricated which are as bright as fluorescent lamps at very low applied voltages.\textsuperscript{10-12} Organic photovoltaic cells using conjugated polymers have shown high solar energy conversion and are on the verge of industrial production.\textsuperscript{13-15} The advances in ink-jet printing technology will change the way in which electronic devices are manufactured.\textsuperscript{16-18} The development of Polymer organic field effect transistors (OFET) has surged in the last two decades to produce flexible displays with low-cost.\textsuperscript{10,19} In addition, conjugated polymers can be used in applications which require special mechanical properties such as flexibility and
stability. The field of conjugated polymers has become one of the most interesting areas of interdisciplinary science and technology.

1.2 Synthesis of Conjugated Polymers

Conjugated polymers can be synthesized from electropolymerization, non-catalyzed polymerization, transition metal-catalyzed coupling reactions and etc.

1.2.1 Conjugated Polymers via Electropolymerization

Until 1980s, although chemical syntheses are the adequate methods of preparation of oligomers with conjugated structures, most conjugated polymers have been prepared by electrochemical polymerization. For example, poly(phenylene)s, polypyrroles and polythiophenes have been prepared by cathodic route involving electro-reduction and oxidative anodic electropolymerization of the corresponding monomers. Compared to other chemical syntheses of conjugated polymers, electropolymerization of the monomer presents several distinct advantages such as the absence of catalysts, control of film thickness, direct grafting onto electrode surface etc. Scheme 1.1 represents the mechanism of electropolymerization of five-membered heterocycles.

\[
\begin{align*}
\text{Scheme 1.1 Mechanism of electropolymerization of heterocycles.}
\end{align*}
\]
Monomer is oxidized into its radical cation form at the beginning. Because the electron-transfer reaction is faster than the diffusion of the monomer, more cation radicals are continuously formed near the electrode surface. After coupling of two radicals to produce a dihydro dimerized dication, a dimer is formed after further loss of two protons and rearomatization. Due to the applied potential, the dimer is more easily oxidized than the monomer into its radical cation form and further couples with another monomeric radical. Electropolymerization proceeds in such a fashion until the polymers become insoluble in the electrolytic medium and precipitate onto the electrode surface.

Since the first synthesis of poly(3-alkylthiophene) in 1986, this method has attracted extensive interest owing to the improvement in solubility compared to the unsubstituted polythiophenes.\textsuperscript{30-33} However, contradictory results have been reported concerning the effects of the alkyl chain length on the solubility\textsuperscript{34,35} which might be attributed to the regioregularity and cross-linking of the polymers.\textsuperscript{36,37} The properties of polymers depend on the electro-synthesis conditions\textsuperscript{36-39} and the regio-selectivity is missing.\textsuperscript{23}

Due to the asymmetric structure of the 3-substituted thiophene molecule, three relative orientations are available when two of these thiophene rings are coupled between 2- and 5- positions (Figure 1.1). The first orientation is 2,2’ or head-to-head (HH) coupling, the second is 2,5’ or head-to-tail (HT) coupling and the last is 5,5’ or tail-to-tail (TT) coupling. And the orientation becomes much more complicated for substituted oligo-thiophenes and polythiophenes.
The contamination of the HH couplings will not only cause the loss of the regioregularity, but also introduce a sterically twisted geometry in the polymer backbone which results the loss of π-conjugation of the whole system. This is due to the increased steric hindrance between the alkyl substituents on the 3-postions of the thiophene rings and the lone electron pairs of the sp² sulfur atoms (Figure 1.2). These repulsive interactions lead to increased bandgaps and decreased intermolecular packing. In comparison, regioregular HT coupled P3ATs (rr-P3ATs) which consist of near-perfect structures, thus can easily access planar polymer backbones and form well-organized packing geometry. These structures provide efficient interchain charge carrier pathways which lead to high charge mobility and other desirable physical properties for electronic applications. The contradictory observations of conjugation length and conductivity of electopolymerized poly(3-alkylthiophene) can be explained by this fact. As the result, it is important to synthesize polymers with structure control.
1.2.2 Boron Containing Conjugated Polymers from Non-Catalyzed Step-Growth Polymerization Synthesis

Conjugated polymers that contain boron are synthesized from step-growth polymerization and was first reported by Chujo and co-workers in 1998. Developments over the past decade prove that stable boron-containing conjugated polymers of high molecular weight can be achieved readily. The incorporation of boron, which is an element with high Lewis acidity resulting from the vacant $p$-orbital of boron atom, into $\pi$-conjugated systems leads to extension of the $\pi$-conjugation via the empty orbitals of boron atoms. This concept has been explored theoretically much earlier by Good and Ritter. Their study predicts that the $\pi$-orbitals of the vinyl group in low molecular weight vinylborane derivatives overlap conjugatively with the vacant $p$-orbital of the boron atom (Figure 1.3). Thus, the fully aromatic boron-containing polymers are expected to possess unusual electronic states with positive holes built in. Poirier predicts that poly-boroles will show fairly low bandgaps because of their quinoidal structures in
the ground state.\textsuperscript{44} Yamabe also predicts that poly(bora-acetylene)s would show metallic conductivity without doping.\textsuperscript{45} Due to these intriguing theoretic predictions of the organo-boron $\pi$-conjugated system, increasing efforts have been devoted to the preparation of boron-containing conjugated polymers.

Figure 1.3 Orbital overlapping in vinylboranes.

As mentioned above, synthesis of boron-containing conjugated polymers was first achieved by Chujo group via hydroboration polymerization of bifunctional alkynes with sterically hindered strong electron acceptor arylboranes ArBH$_2$ (Scheme 1.2).\textsuperscript{41,46} The bulky aryl groups on boron prevent nucleophilic attack, resulting in good stability in air. The polymers are highly fluorescent, and the polymer derived from diethynylpyridine exhibits white emission.

Scheme 1.2 Hydroboration polymerization of ArBH$_2$.

Haloboration polymerization of aromatic diyne monomers with bromo-diphenylborane has been achieved by Chujo and co-workers (Scheme 1.3).\textsuperscript{47} The
resulting polymers are soluble in common organic solvents and stable enough for GPC analysis which are around several thousands. Efficient red-shifts of the maximum absorption peaks of polymers relative to the respective monomers indicate the $\pi$-conjugation through the $p$-orbital of the boron atoms.

Scheme 1.3 Haloboration polymerization of diyne monomers.

Poly($p$-phenylene-borane)s are prepared by polymerization of aryldimethoxyboranes lithiated diacetylenes or bifunctional Grignard reagents generated $in$ $situ$ as shown in Scheme 1.4.48,49 These polymers are expected to be stable to air and heat due to the bulky aromatic groups.

Scheme 1.4 Polycondensation of aryldimethoxyborane using Grignard and organolithium reagents.
Synthesis of boron-containing conjugated polymers via tin-boron exchange polymerization under mild conditions of bis(trimethylstannyl) monomers has been reported by Jäkle and co-workers (Scheme 1.5). Using this route, polymerization could be conducted in non-coordinating solvents to eliminate possible side reactions of ether cleavage or Lewis acid/base complex formation.

Scheme 1.5 Tin-boron exchange polymerization of bis(trimethylstannyl) monomers.

This route is different from the above methodologies for that various aromatic structures could be easily introduced into the conjugated system simply by changing the bis(trimethylstannyl) monomers. As the result, the whole polymers are color tunable from blue to dark-red luminescence, indicating the relative HOMO and LUMO energy levels are tunable, too. From this method, it would be also possible to synthesize monodisperse oligomer with a specific conjugation length as shown in Scheme 1.6 by repeating a number of reactions. A gradual decrease in the bandgap is evident in the absorption and emission spectra with the increasing molecular weight. Higher molecular weight organoborane oligomers are highly fluorescent with quantum yield up to 95% and with emission maxima in the blue region.
Scheme 1.6 Synthesis of conjugated organoborane oligomers.

The \( \pi \)-conjugated diorganoboron polymers poly(\( p \)-phenylenevinlylene-diboraanthracene), which are structurally related to poly(\( p \)-phenylene-anthracene), have been reported by Jäkle group and Jia group independently (see Chapter II).\(^{52,53}\) These polymers are prepared from hydroboration polymerization of bifunctional alkynes with ladder-like polymeric dibora-anthracene (Scheme 1.7).

Scheme 1.7 Hydroboration polymerization of 5,10-dihydroboranthrene.
The interesting two-electron-three-center B-H-B bonds structure of diboraanthracene precursor is confirmed according to single crystal X-ray diffraction studies. Although 1,4-diethynylbenzene furnished polymer is air sensitive and only sparingly soluble in non-coordinating solvents, the hexyloxy substituted dialkynylbenzene derivative has good solubility in common organic solvents and is stable enough for the matrix-assisted laser desorption ionization- time-of-flight (MALDI-TOF) mass spectrometric analysis. The thin film of this boron-containing polymer emits strong green light at 518 nm.

1.2.3 Transition Metal-Catalyzed Coupling Reactions

Coupling reactions between two hydrocarbon species are important organic transformations in organic chemistry. Coupling reactions between two aryls, aryls and vinyls, two vinyls, etc. are often catalyzed by transition metals. In these reactions, usually one of the specie is an organic halide (RX), and the other one is a main group organometallic compound (RM). After losing the MX as a salt, the newly formed species RR' with a new carbon-carbon bond is regarded as a coupled product (equation 1.1). Common coupling reaction types includes: Ullmann reaction\textsuperscript{54}, Kumada coupling\textsuperscript{55,56}, Heck reaction\textsuperscript{57-59}, Sonogashira coupling\textsuperscript{60,61}, Negishi reaction\textsuperscript{62,63}, Stille coupling\textsuperscript{64-66}, Suzuki coupling\textsuperscript{67-70}, Hiyama coupling\textsuperscript{71,72}, Buchwald-Hartwig reaction\textsuperscript{73-75} and etc. Because of the development of these reactions, Richard F. Heck, Ei-ichi Negishi and Akira Suzuki received the 2010 Nobel Prize in Chemistry.\textsuperscript{76} Highly selective catalysts and mild reaction conditions are being developed. These reactions have been applied to polymer synthesis.
Scheme 1.8 Equation of coupling reaction.

The detailed mechanisms of the individual types of reactions can be complicated and different from one another. However, a simplified general mechanism can be described as shown in Scheme 1.9.

Scheme 1.9 General mechanism of coupling reactions.

The metal catalyst is inserted into one organic halide (RX) bond to form its oxidative state first. The other molecule (R' B) then will undergo trans-metallation and add onto the same metal center. Eventually, after reductive elimination of the two species to regenerate the metal catalyst, the coupled product RR' is formed. The unsaturated organic compounds have higher reactivity since they couple more easily with the metal catalyst center, for example: vinyl-vinyl > phenyl-phenyl > vinyl-alkyl > alkyl-alkyl. Nickel and
palladium are mostly used as the catalyst. Other factors such as complex ligands, leaving groups and operating conditions are also crucial for the coupling reactions.\textsuperscript{19,78-80}

1.2.4 Application of Transition Metal-Catalyzed Coupling Reactions in Step-Growth Polymerization

Since transition metal-catalyzed coupling reactions have advantages in coupling between two aryls, aryls and vinyls, two vinyls, etc. Schrock and co-workers have developed a number of well-defined ring opening metathesis step-growth polymerization (ROMP) initiators of the type $M(\text{CH}-\tau-\text{Bu})(\text{NAr})(\text{O}-\tau-\text{Bu})_2$, which allows better control over the polyacetylene synthesis (Scheme 1.10).\textsuperscript{81,82} Using these systems, polyacetylene prepolymer are obtained through step-growth ring opening metathesis. The prepolymer decomposes spontaneously into polyacetylene film at room temperature (half-life: 20 h). Furthermore, the use of these catalytic systems allows the introduction of functionalized end-groups to the polymer chain (R in Scheme 1.10).\textsuperscript{82}

Scheme 1.10 Preparing polyacetylenes from prepolymer.
However, irrespective of the method adopted for the synthesis of polyacetylene, it is an insoluble, infusible and generally intractable material.\textsuperscript{83} In order to obtain soluble polyacetylene analogues, substituted acetylenes have been polymerized to polymers with side groups attached.\textsuperscript{84-87} The electrical conductivity of all substituted polyacetylene analogues is significantly lower than that of polyacetylene itself.\textsuperscript{88} This is attributed to steric repulsion between adjacent side groups that causes the polymer chains to twist and loses planarity.\textsuperscript{89} Grubbs and co-workers demonstrated that the ROMP of monosubstituted cyclooctatetraene derivatives leads to partially substituted polyacetylenes that are soluble and highly conjugated (Scheme 1.11).\textsuperscript{85,87} The molecular weight can be up to 345,000 and polydispersity index (PDI, depending on the ratio of $M_w/M_n$) between 1.7 and 7.6.

Scheme 1.11 Soluble polyacetylene from monosubstituted cyclooctatetraene.

Besides polycondensation of vinyls, transition metal-catalyzed step-growth polymerization of aryls has also been developed. For example, Stille coupling reaction has been used extensively in conjugated polymer synthesis due to its advantages of good tolerance of different functional groups and mild reaction conditions.\textsuperscript{19} Yang and co-workers employed Stille coupling polymerization to prepare a polythiophene with fewer alkyl side chains than typical poly(alkylthiophene)s in order to reduce the electron-donating effect of the alkyl side chains (Scheme 1.12).\textsuperscript{90} Coupling conditions using the Pd(PPh\textsubscript{3})\textsubscript{4} catalyst in toluene give polythiophene with acceptable molecular weight and a broad PDI near 2.
McCullough and co-workers have prepared a series of regional irregular poly(thienylene-vinylene)s via Stille coupling (Scheme 1.13), while the regioregular polymer is obtained via Heck reaction conditions. Polymers are prepared in relatively high molecular weights up to 15,000 and PDIs between 1.80 and 2.46.

In general, conjugated polymers prepared from Stille and Heck coupling reactions are from polycondensation of two A—A and B—B type monomers (A represents functional tin group or proton and B represents halogen atom). It follows a step-growth mechanism, leading to broad PDI and low regioselectivity.

1.2.5 Chain-Growth and Livingness of Polycondensation of Aryls

As described above, conjugated polymers can be synthesized via polycondensation methods, such as electrochemical approaches and transition metal-catalyzed polycondensation reactions. The molecular weight, the distribution and the regioregularity of these polymers are difficult to control. Under classical Flory’s
assumption for step-growth polymerization, all the end groups of monomers, oligomers
and polymers in the reaction mixture react equally, resulting in an uncontrolled molecular
weight and broad distribution. However, this is not essentially true for all condensation
polymerization which has already been demonstrated by nature for the synthesis of
perfectly mono-dispersed biopolymers such as proteins and DNA. It is because their
mechanisms of condensation polymerization could be converted from step-growth to
chain-growth. In recent years, it is found that chain-growth condensation polymerization
could be realized by Kumada-Tamao coupling polymerization with a Ni catalyst and
Suzuki-Miyaura coupling polymerization with a Pd catalyst. If polycondensation could
proceed by a chain-growth mechanism, the ability of a growing polymer chain to
terminate could be removed and living polymerization will be possible.

1.2.6 Head-to-Tail Regioregular Poly(3-Alkylthiophene) (rr-P3ATs) via Transition Metal-
Catalyzed Chain-Growth Polymerization

The control synthesis of different regioregular polythiophenes has been tested in the
past decades and is the most well-established. Well-defined rr-P3ATs can be prepared by
one of the following methods as shown in Scheme 1.14: McCullough, Rieke, Grignard metathesis (GRIM), Yokozawa, Iraqi, Guillerez and Ozawa. Among
these strategies, GRIM and Yokozawa’s methods are most popular.
Scheme 1.14 Synthetic routes of \textit{rr}-P3ATs.

The key synthetic strategy feature is the regioselective metallation of the regiospecific monomers, which generates the corresponding intermediates 2-bromo-5-metalo-3-alkylthiophenes (Scheme 1.14). Although a small portion of the undesirable 5-bromo-2-metalo-3-alkylthiophenes is generated in the case of the three Ni catalyzed methods, the desired intermediate reacts preferentially to produce fully HT arranged \textit{rr}-
P3ATs. All these synthetic methods for the production of \( rr \)-P3ATs yield similar materials that are not chemically and physically different. In all these methods, GRIM, Yokozawa and Ozawa’s routes have the advantage over the two palladium catalyzed methods in terms of easy accessibility to the \( rr \)-P3ATs. They do not require extra purification of the monomers or precursors and the whole polymerization can be handled in one pot and an economical way.

The first synthesis of \( rr \)-P3ATs is reported by McCullough and co-workers in 1992 (Scheme 1.14).\(^{95}\) Through their route, a regio-specific 2-bromo-5-bromomagnesio-3-alkythiophene is generated with an overall 98% yield. The polymerization is then engaged \textit{in situ} by Kumada coupling reactions using catalytic amount of Ni(DPPP)Cl\(_2\) (DPPP= 1,3-diphenylphosphinopropane). Purified \( rr \)-P3ATs has around 70% yield and afford HT-HT regioregularity of above 98% which was identified by \(^1\)H NMR spectrum. The number average molecular weight \((M_n)\) is typically around 20,000 to 40,000 which could be controlled by the feed ratio between monomers and nickel catalyst, and the PDI is around 1.4 to 1.5.\(^{40,95,102}\) In the same year, Rieke and co-workers reported an approach to \( rr \)-P3ATs through Negishi coupling reactions (Scheme 1.14).\(^{96,103}\) In this strategy, 2,5-dibromo-3-alkythiophene is treated with highly reactive zinc to yield a mixture of isomeric intermediates in a ratio of 9:1. The polymerization is then realized \textit{in situ} using catalytic amount of Ni(DPPE)Cl\(_2\) (DPPE=1,3-diphenylphosphinoethane) and gives \( rr \)-P3ATs with around 75% yield. The resulting polymers have the \( M_n\) about 24,000 to 40,000 and PDI around 1.4. Only one sharp band for the vinyl group in \(^1\)H NMR spectrum and four triad structures in \(^{13}\)C NMR spectrum clearly demonstrate the high regioregularity of the polymer (Figure 1.4 and Figure 1.5).
Figure 1.4 $^1$H NMR spectra of (a) regiorandom (1:1:1:1, HT-HT:HT-HH:TT-HT:TT-HH) P3HT and (b) regioregular (98.5%) P3HT. Reproduced with permission from Ref. 96. Copyright 1992, American Chemical Society.

Figure 1.5 $^{13}$C NMR spectra of (a) regiorandom (1:1:1:1, HT-HT:HT-HH:TT-HT:TT-HH) P3HT and (b) regioregular (98.5%) P3HT. Reproduced with permission from Ref. 96. Copyright 1992, American Chemical Society.

UV-Vis data shows that $rr$-P3HT has longer wavelength of maximum absorption either in solution (chloroform, 456 nm) or in the solid state (film, 560 and 610 nm) when compared with the values of other regiorandom P3HT (427 nm in chloroform and 438 nm as film).$^{95,96,104,105}$ This indicates the increased effective conjugation through the polymer
chain, apparently due to complete HT regularity. The physical properties between
regioregular and regiorandom polymers are quite different.106

In 1999, a facile and economical synthetic route for \textit{rr}-P3ATs was reported by
McCullough group which is now known as Grignard Metathesis (GRIM).107 This method
does not require expensive chemicals used in previous strategies but a cheap Grignard
reagent (R`MgBr) to treat 2,5-dibromo-3-alkylthiophenes to form a mixture of
intermediates in a ratio of 85:15 (Scheme 1.14). Although the ratio of desirable to
undesirable isomers is relatively higher compared to either the McCullough or the Rieke
method, polymerization \textit{in situ} by Kumada coupling reactions using catalytic amount of
Ni(DPPP)Cl\textsubscript{2} still generate \textit{rr}-P3ATs with over 99\% high HT regioregularity. Another
advantage of this method is that the reaction can be realized at room temperature in one
pot without any further purification, which eliminates the precaution of handling at low
temperatures. The resulting polymers typically have the $M_n$ about 24,000 to 35,000 and
PDIs between 1.2 and 1.4.

However, recent research by Luscombe and co-workers demonstrates that the high
degree of regio-control from GRIM polymerization should not simply be explained by
stERIC hindrance largely preventing formation of HH bithiophene coupling. The actual
reason is the inability of 5-bromo-2-metalo-3-alkylthiophenes to polymerize. It is
believed to be due to the lack of \textit{ortho}-stabilization group in the propagating nickel
complex, preventing oxidative addition of the nickel into the Ar-Br bond.108 Additionally,
regioregular polyselenophenes could be also prepared through GRIM method.109 The
resulting polymer has a broader optical absorption range and 80 nm red-shift compared to
that of \textit{rr}-P3HT.
The GRIM method is later advanced by Yokozawa and co-workers (Scheme 1.14) by treating 2-bromo-5-iodo-3-alkylthiophenes with stoichiometric Grignard reagent which generate the desirable isomer as the only starting material quantitatively. A chain-growth condensation polymerization mechanism has been proposed as shown in Scheme 1.15. They have pointed out that the existence of excess Grignard reagents is harmful for the polymerization. It is because that the remaining Grignard reagents would terminate the on-going chain ends and broaden the PDI of the product, which is commonly seen in GRIM method.

Scheme 1.15 Mechanism of chain-growth condensation polymerization of \( rr \)-P3ATs.

At the beginning, two monomers undergo coupling reaction with the generation of a zero-valent Ni complex after reductive elimination step. Once the TT dimer has been formed, the Ni(0) complex does not diffuse freely to the reaction mixture but is inserted intramolecular into the Ar-Br bond at the chain end. Another monomer reacts with the Ni
catalytic center, followed by the reductive elimination and intramolecular oxidative insertion to the next Ar-Br bond. Growth continues in such a fashion and a regioregular HT polymer is formed, with the only regio-mistake happens at the beginning dimmer position.

After quenching with HCl, the resulting polymer has one end group as bromine atom and the other is a hydrogen atom, which is consistent with the MALDI-TOF spectrum containing only one series of peaks (Figure 1.6). As a result, polymers from this method typically have the $M_n$ up to 28,700 and can be controlled by the feed ratio (Figure 1.7). The PDI can be as low as 1.10. These evidences support the living chain-growth polycondensation mechanism.

![Figure 1.6 MALDI-TOF mass spectrum of $\text{rr}$-P3HT. Reproduced with permission from Ref. 110. Copyright 2005, American Chemical Society.](image)
Figure 1.7 $M_n$ and $M_w/M_n$ values of $rr$-P3HT as a function of the molar ratio of converted monomer to catalyst. Reproduced with permission from Ref. 110. Copyright 2005, American Chemical Society.

It should be pointed out again that polymerization from 5-bromo-2-iodo-3-alkylthiophenes did not produce any polymeric material. There is no problem for the near-complete conversion with Grignard reagent, but the bithiophene in the first step was not formed in any detectable amount after addition of catalyst. Therefore 2-bromo-5-magnesio-3-alkylthiophenes is the only polymerizable monomer.

Recently, 100% regioregular polythiophene have been achieved by initiation of 2-bromo-5-magnesiobromo-3-alkylthiophenes with an externally added initiator by Luscombe and co-workers as shown in Scheme 1.16. This route eliminates the TT regio-mistake formed in Yokozawa’s method and all the polymer chains are initiated at the same time.

Scheme 1.16 Synthesis of 100% HT regioregular P3HT.

R=H or CH₃
Stille and Suzuki palladium catalyzed coupling polycondensation are alternative strategies to afford \( rr \)-P3ATs (Scheme 1.14). These methods require purification of the corresponding organometallic monomers before polymerization. Iraqi and co-workers explored the synthesis of \( rr \)-P3ATs through Stille coupling reactions, using 3-alkyl-2-iodo-5-(tri-\( n \)butylstannyl)thiophene as monomers.\(^9\) \( rr \)-P3ATs with regioregularity above 96% are readily achieved, and the \( M_n \) around 10,000 to 16,000 with PDI around 1.2 to 1.4.

Suzuki reaction using 3-alkyl-2-iodo-5-boronothiophene has been reported by Guillerez and co-workers (Scheme 1.14) to give \( rr \)-P3ATs with 96-97% regioregularity and \( M_n \) up to 27,000.\(^1\)

Recently, Ozawa group successfully employed polymerization of 2-bromo-3-hexylthiophene as monomer using Herrmann’s catalyst and special ligands (Scheme 1.14) at elevated temperature.\(^1\) This dehydrohalogenative polycondensation affords \( rr \)-P3ATs with regio-regularity about 96-98% and \( M_n \) around 24,000 to 30,600. Compared to other methods, their products have much broader PDI, but the yield is readily above 98% to nearly quantitative.

Although all the above methods give \( rr \)-P3ATs with controlled molecular weights and their PDI can be as low as 1.10, the final product is still not a monodisperse macromolecule. Mori and co-workers recently developed a strategy that 100% HT oligothiophene can be realized by single-step extension from regioselective metalated 3-substituted thiophene using the Knochel-Hauser base (TMPMgCl•LiCl).\(^1\) Treatment of 3-substituted thiophene with TMPMgCl•LiCl generates a 5-metalo-3-substituted thiophene selectively due to the steric hindrance as shown in Scheme 1.17. Subsequent addition of the 2-bromo-3-substituted thiophene and the nickel catalyst leads to the formation of the
corresponding HT dimer. Longer regioregular oligothiophene is obtained by repeating via the similar protocol. This facile method provides a tool toward the synthesis of monodisperse regioregular oligothiophene with different functional groups or alternating block copolymers.

![Scheme 1.17 Synthesis of monodisperse HT oligothiophene.](image)

1.2.7 Functionalization of Regioregular Polythiophenes

The development of synthesis of \( rr \)-P3ATs has led to the success in producing a wide range of functional regioregular polythiophenes not only at the 3-position of the thiophene rings,\(^{113-122}\) but also at the end position of polymer chains as summarized in Table 1.1.\(^{123,124}\) Due to the nature of chain-growth polymerization mechanism, well-defined block polymers are easily accessible.\(^{125,126}\)
Table 1.1 Summary of side chains and terminal groups on \textit{rr}-P3ATs.

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<tr>
<th>Side chains</th>
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<td><img src="image15.png" alt="Side chain 8" /></td>
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1.2.8 Other types of Conjugated Polymers via Transition Metal-Catalyzed Chain-Growth Polymerization

The methodologies for the synthesis of \textit{rr}-P3ATs have been demonstrated to be applicable to other aromatic π-conjugated. Yokozawa and co-workers first apply the GRIM polycondensation synthesis of poly(\(p\)-phenylene) which contain no heteroatoms in the aromatic rings. However, under similar conditions, polymers obtained in this method
all give low molecular weights and broad PDI.\textsuperscript{79} To solve the problem, they find that the existence of LiCl is essential to optimize the chain growth polycondensation (Scheme 1.18). The resulting polymers have the $M_n$ in range of 9,200 to 35,000 which is controlled by the feed ratio of monomer to Ni catalyst.

\begin{center}
\begin{align*}
\text{ClMgH}_3\text{OC}_6\text{H}_{13} & \xrightarrow{\text{Ni(DPPE)Cl}_2, \text{LiCl}} \text{OC}_6\text{H}_{13} \text{OC}_6\text{H}_{13} \\
\text{C}_6\text{H}_{13} \text{O} & \text{C}_6\text{H}_{13} \text{O}
\end{align*}
\end{center}

Scheme 1.18 Synthesis of poly($p$-phenylene) via chain-growth polycondensation.

Additionally, block copolymers of poly($p$-phenylene) and polythiophene are affordable through this method. This first example of the successive chain-growth polycondensation for the synthesis of block copolymers consisting of these two different $\pi$-conjugated systems is reported by Yokozawa group.\textsuperscript{127} The sequence of addition of monomers is important to yield copolymers with PDI control. A well-defined copolymer is obtained by first synthesizing the poly($p$-phenylene) block and subsequent polythiophene block, and a broad PDI copolymer is generated with the reverse order (Scheme 1.19). The broad up of the PDI is believed due to the difficulty of cross-coupling from poly($p$-phenylene) pre-polymer to thiophene monomers and the intramolecular oxidative insertion into the terminal Ar-Br bond.
Scheme 1.19 Strategies of synthesis of poly(p-phenylene)-b-poly(3-alkylthiophene).

Chain-growth polycondensation through Suzuki coupling of \( p \)-phenylene monomers has also been investigated. The polymerization is initiated with a special initiator PhPd(P-\( \tau \)-Bu\(_3\))Br as shown in Scheme 1.20. Polymers with \( M_n \) up to 21,000 and PDI below 1.5 are obtained.\(^{128}\)

Scheme 1.20 Synthesis of poly(p-phenylene) via Suzuki polycondensation.

The GRIM polymerization of \( N \)-alkylpyrrole has been investigated by Yokozawa group.\(^{129}\) Under similar conditions for the synthesis of \( rr \)-P3ATs using Ni(DPPP)Cl\(_2\) catalyst, a polymer with PDI \( \sim 1.26 \) is obtained together with low molecular weight oligomers. However, polymerization with Ni(DPPE)Cl\(_2\) and excess DPPE ligand afford high molecular weight polymer with much narrower PDI (\( \sim 1.11 \)), without the formation
of any by-products as shown in Scheme 1.21. The $M_n$ could be controlled by the feed ratio of monomers to catalyst which is in the range of 2,800 to 12,400.

Scheme 1.21 Synthesis of poly(N-alkylpyrrole) via chain-growth polycondensation.

The block copolymers are also available by first polymerizing $p$-phenylene monomers with Ni(DPPE)Cl$_2$ in the presence of LiCl and subsequent addition of $N$-hexylpyrrole monomers to afford desired block copolymer with a narrow PDI ~1.16 (Scheme 1.22). The copolymerization in the reverse order offers a broader PDI ~1.38 which could be explained using similar analogs as for the synthesis of poly($p$-phenylene)-$b$-poly(3-alkylthiophene).

Scheme 1.22 Synthesis of poly($p$-phenylene)-$b$-poly($N$-hexylpyrrole).

The synthesis of well-defined polyfluorene was first reported via Suzuki-Miyaura coupling polymerization. Yokozawa and co-workers found that the desired polymer can be obtained from chain-growth mechanism (Scheme 1.23), instead of the commonly seen step-growth mechanism in Suzuki-Miyaura coupling polymerization due to the large fluorene units. The use of the special initiator PhPdP(i-Bu)$_3$Br is the key to achieve...
high $M_n$ (7,700-17,700) and low PDI (1.33-1.39). The MALDI-TOF analysis of the mass spectrum indicates that all the polymers bore the phenyl group at one end. These evidences clearly demonstrate that the polymerization is initiated by PhPdP(t-Bu)$_3$Br. Since this special initiator is not easily accessible, an economical way to generate it in situ from Pd$_2$(dba)$_3$/ P(t-Bu)$_3$/PhI without separation or purification is applied for the Suzuki chain-growth polycondensation. Comparable results are obtained for different fluorene monomers.$^{131}$

Scheme 1.23 Synthesis of polyfluorenes via Suzuki polycondensation.

After this report, Carter and co-workers investigated the polymerization of lithiated fluorene monomer which is generated by the reaction of the dibromofluorene with t-BuLi in situ as shown in Scheme 1.24.$^{132}$

Scheme 1.24 Synthesis of polyfluorenes via lithiated fluorene monomer.

Similar to the GRIM polycondensation of polythiophene, the excess t-BuLi is harmful to the polymerization which would decrease the molecular weight of the final product due to chain termination. The polyfluorenes made using this method have the $M_n$ in the range of 16,800 to 32,700 and the PDI from 1.92 to 2.91. Therefore, a step-growth polymerization mechanism is proposed for this route.
Geng and co-workers reported the GRIM polymerization of fluorene monomers with Ni(DPPP)Cl$_2$.\textsuperscript{133} The bromo-iodo-fluorene is treated with $i$-PrMgCl•LiCl to generate the monomer. The polymerization goes rapidly at 0 °C and finishes within 10 min as shown in Scheme 1.25. Polyfluorenes with high molecular weight ($M_n \sim 18,800$ to 86,000) and PDI between 1.49 and 1.77 are obtained. The MALDI-TOF spectrum of the product shows an evident amount of Br/Br ended polymers, which is deduced to be formed by intermolecular chain transfer after reductive elimination and is attribute to be the reason for the broad PDI.

![Scheme 1.25 Synthesis of polyfluorene via GRIM.](image)

The GRIM has also been applied to the synthesis of polycarbazole.\textsuperscript{134} Unlike the cases for polythiophenes and polyfluorenes, the magnesium halogen exchange of dibromo-$N$-alkylcarbazole with $i$-PrMgCl•LiCl is considerably slowly and $n$-Bu$_3$MgLi is needed for effective magnesium halogen exchange as shown in Scheme 1.26. The polymerization carried out in this method results in a polycarbazole with $M_n$ up to 26,000 and PDI around 1.23.

![Scheme 1.26 Synthesis of polycarbazole via GRIM.](image)
Recently, the synthesis of polypyridine via GRIM was examined by Yokozawa and co-workers as shown in Scheme 1.27.\textsuperscript{135} \textit{meta}-substituted pyridine monomer is generated quantitatively by treatment of the corresponding bromo-iodo-pyridine molecule with stoichiometry $i$-PrMgCl$\cdot$LiCl at 0 $^\circ$C. The so-formed polypyridines have a $M_n$ in range of 5,000 to 10,000 and PDI around 1.22 to 1.34. The $M_n$ is controlled by the feed ratio of monomers to catalyst. MALDI-TOF analysis of mass spectrum shows that the polypyridines uniformly have a Br at one end and an H at the other end. All these results confirm that the polymerization follows a chain-growth mechanism.

Scheme 1.27 Synthesis of poly(\textit{meta}-pyridine) via GRIM.

However, if \textit{para}-substituted pyridine monomer is used, polymer with broad PDI (>4) is obtained.\textsuperscript{136} Although the product has a broad distribution, MALDI-TOF is still able to clarify that major products have Br at both ends. This result is different from the above case and in polythiophene synthesis which one end of the polymer is Br and the other is H. Therefore, it was proposed that disproportionation happens continually through the whole polymerization process (Scheme 1.28). The tendency of disproportionation in the polymerization of \textit{para}-substituted pyridine monomer is ascribed to the coordination of the Ni catalyst center in the Ar-Br bond to the nitrogen atom of pyridine ring on the other chain end. Suzuki-Miyaura polycondensation of the same \textit{para}-substituted pyridine unit has the similar disproportionation problem.\textsuperscript{137}
1.2.9 Attempted Transition Metal-Catalyzed Polymerization of Electron-Acceptor Materials

Up till now, the main challenge of transition metal-catalyzed polymerization is the synthesis of *n*-type (electron accepting) conjugated polymers partially due to the use of the Grignard reagents or active Zinc to the functional groups. Thus, most *n*-type conjugated polymers are synthesized via Stille coupling reactions containing base-sensitive heterocycles or electron-withdrawing groups. Due to the weak \( \pi \)-donation of the *n*-type polymer backbone to the metal catalyst center, polymerization of acceptor monomers may not facilitate intramolecular transfer insertion to the Ar-Br bond. Although successive chain-growth polymerizations of monomers with high \( \pi \)-donating
ability have been achieved as above sections, monomers with low \(\pi\)-donating ability are retarded to be polymerized.\textsuperscript{127-129,140}

Recently, Kirity and co-workers have demonstrated that Ni catalyst not only can undergo intramolecular transfer on pyridine, but also on a good acceptor material—naphthalenediimide.\textsuperscript{141} The polymers so-formed have \(M_n\) in the range of 10,400 to 25,000 and PDI around 1.3 to 1.7. Meanwhile, Huch and co-workers have confirmed that Pd catalyst can experience intramolecular transfer on benzothiaziazole with polymers having PDI < 1.27 and \(M_n\) about 3,300 to 7,400 (Scheme 1.29).\textsuperscript{136} MALDI-TOF shows that the polymer has one end as the aromatic group from the initiator and the other end is Br/H, indicating the polymerization follows the chain-growth polymerization mechanism.

![Scheme 1.29 Synthesis of \(n\)-type conjugated polymer from acceptor monomers.](image_url)

Their strategies are to combine two, three or more aromatic monomers together which consist strong acceptor and weak \(\pi\)-donating aromatic rings, though the weak \(\pi\)-donating arenes will slightly increase the HOMO levels of the whole conjugated polymer. Even the conjugation length of the repeating units is increased, the intramolecular
catalyst transfer will still take place.\textsuperscript{142} These efforts open the door of the synthesis of \textit{n}-type conjugated polymers from acceptor monomers.

1.3 Application of Conjugated Polymers in Organic Solar Cells

Conjugated polymers are unique semiconductors and can be used in organic solar cells.

1.3.1 Working Principles of Organic Solar Cells

Solar energy is an abundant energy source.\textsuperscript{143} Organic photovoltaic (OPV) potentially have the advantage of low cost of manufacture and easy processability.\textsuperscript{144} They are generally considered to be one of the viable methods for solar energy conversion.

A typical organic solar cell contains an electron-donor material (or \textit{p}-type material) and an electron-acceptor material (or \textit{n}-type material). The simplest and original device reported by Tang\textsuperscript{143} has a bilayer structure as shown in Figure 1.8. The process of converting solar energy by OPV can be conceptually divided into four main events as shown in Scheme 1.30.

![Figure 1.8 Bilayer OPV cell.](image-url)
First, photons are absorbed by both donor \((p\text{-type})\) and acceptor \((n\text{-type})\) materials, leading to the formation of an excited state. This excited state is generally accepted as an exciton, which is the bound state of an electron and hole that are associated with each other by electrostatic Coulombic force. It exists in semi-conductors as an electrically neutral quasi-particle. The so-formed excitons could transport energy without carrying charges in both donor and acceptor domains. Due to the short lifetime of exciton which is only around 100 ps, the exciton diffusion lengths in conjugated polymers and in organic semiconductors are usually estimated to be around 10-20 nm.

To prevent the decay of excitons via radiative or non-radiative pathways, strong local electric fields as well as interfaces are necessary for efficient charge dissociation. For example, the lowest unoccupied orbital (LUMO) of the acceptor material must be lower than that of the donor material so that the energy offset between the LUMOs ($\Delta E_{\text{LUMO}}$) is larger than the electrostatic Coulombic force of the photo-generated excitons in the $p$-type material. Similarly, it is required that the energy offset between the highest occupied orbitals (HOMOs) is larger than the Coulombic binding energy of excitons generated in the acceptor material for efficient charge separation. It has been proved that the photo-induced charge separation at interfaces happens on a time scale around 100 fs, which is much faster than other competing decay processes.

After separation, the generated charges need to be transported to the appropriate electrodes within their lifetime which require donor and acceptor materials to have high charge mobilities. This step is driven by the gradient in the chemical potentials of electrons and holes created by the difference between the HOMO level of the donor and the LUMO level of the acceptor. This internal electrical field also impacts on the maximum open circuit voltage ($V_{\text{oc}}$). Eventually, the charge carriers are collected from the device through elective contacts and electricity is generated in the outside circuit.

1.3.2 Device Structure Improvement of Organic Solar Cells

The efficiencies of the four events determine the overall power conversion efficiency (PCE). The problem of bilayer structure is mainly due to the conflicting requirements for light absorption and for excitons to reach the interfaces. Even for materials like
conjugated polymers which have very high absorption coefficient exceeding $10^5 \text{ cm}^{-1}$, it still needs around 100 nm thickness to fully absorb the solar light. However, only excitons generated within the distance of 10-20 nm from the interface can reach the heterojunction boundary, resulting in the loss of absorbed photons far away from the interface. Expectedly, the device fabricated using bilayer structure usually has a PCE lower than 1%.\(^{143}\)

Solar cell device design advanced from bilayer construction to bulk heterojunction (BHJ) as shown in Figure 1.9.\(^{13}\)

![Figure 1.9 BHJ OPV cell.](image)

The BHJ structure is composed of a blend of donor and acceptor materials in bulk volume. The main goal of utilizing this morphology is to increase the interfacial area between donor and acceptor phases. In such penetrating networks, each interface is within a distance less than the exciton diffusion length (10-20 nm) to ensure efficient charge dissociation.\(^{144}\) Furthermore, tandem (multi-junction) solar cells structure can be adopted which consisting of several $p$-$n$ junctions and each junction is tuned to absorb a different wavelength range of solar light to achieve a higher efficiency.\(^{13}\) An increased PCE is observed that polymer/fullerene derivatives BHJs have by far been the most successful material combination with reported power conversion efficiency over 9%.\(^{148}\)
Theoretically, an maximum PCE of 11.7% for single BHJ cell has been calculated and an ultimate efficiency of about 20% is possible through the optimum configuration of tandem cell structures.\textsuperscript{149}

The conceptually ideal structure of a BHJ solar cell is shown in Figure 1.10. The donor and acceptor materials are interdigitated with a length scale around 10 nm which is below the exciton diffusion length. The interspaced phases will ensure high mobility charge transportation with reduced charge recombination as in common BHJ structure. The pure thin layers of donor and acceptor at the collecting electrodes will minimize the losses by recombination as diffusion barriers. However, such well-organized nanostructure is hard to achieve technically. Attempts by nanostructure templates such as nano-imprint lithography have been tried,\textsuperscript{150,151} but the final structure is still far away from the ideal configuration and the resulting PCE is usually lower than 1%.

Besides the cell structures, solvent effects, thermal annealing, additives and morphologies are all important factors in cell fabrication.\textsuperscript{152}
1.3.3 Materials Challenges for OPV

All polymer solar cells (PSCs) have unique advantages over polymer/bucky balls BHJs which have the best performance so far for the following reasons. First, semi-conducting conjugated polymers have broad overlap with solar spectrum and high absorption coefficients of UV-Vis light in the spectral region, while fullerene derivatives only absorb lights with a very limited range (typically < 400 nm). Although C70 derivatives provide enhanced absorption in the blue region compared to C60 derivatives due to the breakdown of symmetry,153 it is difficult to increase the absorption of bucky balls into red and near-infrared (NIR) region. Second, bucky balls and their derivatives such as phenyl-C61-butyric acid methyl ester (PCBM) have intrinsic high exciton binding energy and morphology fabrication problems which lower the overall PCE.154 Third, n-type acceptor conjugated polymers have a large potential for fine adjustment of energy levels which is crucial for the development of high performance PSCs, simply by varying their repeating structures. Theoretically, it is required that the acceptor should have a low-lying LUMO to overcome the Coulombic binding energy for more efficient photo-induced charge separation at the donor/acceptor interfaces. However, an excessively low LUMO in fullerene derivatives will result in a decreased $V_{oc}$ and PCE of polymer solar cells.147,155 A significant number of fullerene derivatives have been synthesized to improve the HOMO/LUMO levels.155-158 Despite all these valuable efforts, only small shifts (< 200 mV) of the LUMO level of derivatized C60 have been achieved by attaching electron-donating groups to the bucky ball.156,159 Fullerene derivatives have shown limited change of relative energy levels due to the absence of various chemical
structures, resulting in a low $V_{oc}$ in OPV.\textsuperscript{159} As the result, careful control of the energy levels is necessary to maximize the overall conversion efficiency. Fourth, polymer/polymer blends offer increased stability and superior flexibility which can be processed via large scale solution film coating.\textsuperscript{160} Additionally, all polymer solar cells can be made using the strategy of block polymers methods to solve the problems of undesirable morphological properties such as large phase separation,\textsuperscript{161,162} inhomogeneous internal phase composition\textsuperscript{163-165} and poor crystallinity in polymer/bucky balls BHJs.\textsuperscript{166,167} By careful control of the molecular weight and distribution of each block, the co-polymer will be self-assembled into a desirable lamella structure to form the ideal interspaced nanostructure as shown in Figure 1.11. Due to this morphological control for excitons diffusion and charge separation,\textsuperscript{114,134} increased conversion efficiency would be expected. Although much less researches have been devoted to all-polymer solar cells, promising improvements in efficiency around 2.7% have been reported recently by Mori and co-workers.\textsuperscript{168}

Figure 1.11 Self-assembly of block polymers into the ideal structure of a BHJ solar cell.
1.4 Summary and Outlook

Conjugated polymers are one of the most attractive conducting materials due to their unique set of chemical and physical properties. Significant efforts have been devoted for exploring their potential applications in optical and electronic fields.

Although remarkable progress has been made in the research of developing new conjugated polymers, many challenges remain unmet. For example, conjugated polymers with relative low HOMO and LUMO levels are rare, and their charge mobilities are in general inferior to inorganic semiconductors or even organic small molecular semiconductors (see Chapter IV). The present thesis work seeks to use rational concepts and methodologies for tuning relative energy levels and increasing charge mobilities of conjugated polymers to develop novel $n$-type acceptor materials.
2.1 Introduction

Design and synthesis of $\pi$-conjugated organic molecules and polymers with high electron affinity continue to be a research challenge because of the demand of $n$-type semiconducting materials for photovoltaic, optical and electronic applications.\textsuperscript{169} As discussed in Chapter I, for organic solar cells, the lowest unoccupied orbital (LUMO) of the $n$-type material must be lower than that of the $p$-type material by a minimal margin so that the energy offset between the LUMOs ($\Delta E_{\text{LUMO}}$) is larger than the Coulombic binding energy of the photo-generated electron-hole pairs in the $p$-type material,\textsuperscript{145} i.e., $\Delta E_{\text{LUMO}} > E_{\text{c-p}}$. This proves not an easy task when regioregular poly(3-hexylthiophene) ($rr$-P3HT), which has the desirable optical absorption range and high charge carrier mobility for photovoltaic application, are used as the $p$-type material in a heterojunction cell.\textsuperscript{144} For example, the LUMO of the cyano-substituted poly(phenylene vinylene) (CN-PPV), which is normally used as the $n$-type material, is actually higher in energy than that of $rr$-P3HT.\textsuperscript{170,171} Not surprisingly, CN-PPV does not quench the photoluminescence of
In fact, only fullerenes and their derivatives, of which the exceptionally high electron affinities arise from the topological characteristics of their π-orbitals and their surface curvatures,\textsuperscript{173,174} have been shown to be able to quench the photoluminescence of \textit{rr}-P3HT.\textsuperscript{175-177} As the result, the all conjugated polymer photovoltaic cells commonly use a \textit{p}-type polymer other than \textit{rr}-P3HT. A polymeric material with adequate electron affinity to separate the electron–hole pair in \textit{rr}-P3HT would be therefore very desirable from the point of photovoltaic application as well as in the general context of organic optical and electronic devices.

The concept of using the empty \textit{p}-orbital of boron to gain electron affinity has been applied to both small molecular or macromolecular conjugated systems in the past.\textsuperscript{41,48,52,178-190} In all of the boron-containing systems that have been investigated for this purpose, arylborylene units (A) are inserted into the π-conjugated carbon backbone.

![Figure 2.1 Aryborylene units structure.](image)

In comparison to A, the diborylene molecules of the type B (X = \textit{o,o}-phenylene, vinylene, S, or NH.)\textsuperscript{191-198} are an interesting series of π-conjugated boranes with dissimilar π-bond connectivity compared to A. These electron-deficient diboranes have been investigated previously as ligands for electron-rich transition metals,\textsuperscript{184,193,199-207} but electrochemical data concerning their single electron-accepting ability are rare. Only two 9,10-diboroanthracene derivatives are studied electrochemically.\textsuperscript{208} Even if the reduction potential of 9,10-diido-9,10- diboroanthracene (-0.45 V vs SCE) is discounted, which
might conceivably involve iodide, 9,10-dimethyl-9,10-diboroanthracene is reduced at a more positive potential than a number of highly electron-accepting representative boranes as shown in Table 2.1. These evidences indicate that the diborylenes B may possess exceptionally high electron affinity.

Table 2.1 Comparison of reduction potentials of boranes.

<table>
<thead>
<tr>
<th>Structure</th>
<th>LUMO (eV)</th>
<th>Structure</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(\text{B} \text{B-Me})</td>
<td>-3.26</td>
<td>(\text{B}_2\text{B-B}_2)</td>
<td>-3.01</td>
</tr>
<tr>
<td>(\text{B} \text{F}_2\text{F}_2)</td>
<td>-3.20</td>
<td>(\text{B}_2\text{B}\text{B} )</td>
<td>-2.60</td>
</tr>
</tbody>
</table>

*a* All values are referenced against the saturated calomel electrode (SCE).212

Here, several 9,10-diboroanthracene-derived polymers as well as small molecules that served as models for better characterization and understanding of the corresponding polymers were synthesized. The reversible coordination of Lewis base solvents with the boron-containing rigid polymers proves a property that the \(\pi\)-conjugated polymers could be dissolved and processed into thin films. The electron affinities of the polymers and small molecules were evaluated using cyclic voltammetry. One of them had a LUMO appreciably lower in energy than that of \(rr\)-P3HT and effectively quenched the photoluminescence of \(rr\)-P3HT in the solid thin film state.
2.2.1 Synthesis

Scheme 2.1 Synthesis of compound 1, 2-M and polymer 2.

9,10-Dihydro-9,10-diboroanthracene (1) was prepared in nearly quantitative yield by reaction of 9,10-dibromo-9,10-diboroanthracene and Et₃SiH in toluene at room temperature (equation 1). Compound 1 was then used as the hydroboration reagent for the synthesis of polymer 2 and its small molecular analog 2-M. Reaction of 1 with phenylacetylene proceeds cleanly at room temperature to give exclusively the anti-Markovnikov cis-addition product 2-M (equation 2). The structure of 2-M was fully characterized by ¹H, ¹³C and ¹¹B NMR spectroscopies and elemental analysis. Polymer 2 was prepared under identical conditions as 2-M and was isolated as a yellow powder (equation 3).
Figure 2.2  

A $^1$H NMR spectrum of polymer 2 in CDCl$_3$.  
B $^1$H NMR spectrum of compound 2-M in CDCl$_3$.

Assignments of the $^1$H NMR signals of 2 could be made by comparing the $^1$H NMR spectra of 2-M and 2 (Figure 2.2). Both 2 and 2-M were very sensitive to moisture. This precluded the possibility of determining the molecular weight of 2 by GPC.

\[
\begin{align*}
\text{BrB} \quad \text{BBr} & \quad + \quad 2 \quad \text{Bu}_3\text{Sn} \quad \text{toluene} \quad \text{reflux} \quad \rightarrow \quad \text{BrB} \quad \text{BBr} \quad + \quad 2 \quad \text{Bu}_3\text{SnBr} \\
3-M & \\
\text{BrB} \quad \text{BBr} & \quad + \quad \text{Bu}_3\text{Sn} \quad \text{Sn' Bu}_3 \quad \text{toluene} \quad \text{reflux} \quad \rightarrow \quad (\text{BrB} \quad \text{BBr})_n \quad + \quad 2 \quad \text{Bu}_3\text{SnBr} \\
3 & 
\end{align*}
\]

Scheme 2.2 Synthesis of compound 3-M and polymer 3.

Polymers 3 and its small molecule analog 3-M were synthesized by the reaction of 9,10-dibromo-9,10-dihydro-9,10-diboroanthracene with the corresponding stannyl reagent (equations 4 and 5). The $^{11}$B NMR resonance of 3-M appears at 65 ppm in CDCl$_3$.  

47
but shifted upfield to 30 ppm in THF-d₈, indicating THF-coordination to boron in the THF solution. The coordinated THF was labile. ¹H NMR spectroscopy (Figure 2.3) showed that the base-free 3-M was recovered after the solid sample of THF/3-M adduct was evacuated overnight under vacuum at room temperature or left open to the nitrogen atmosphere in the glove box overnight.

![Figure 2.3](image)

Figure 2.3 A ¹H NMR spectrum of polymer 3 in DMF-d₇. Peaks with star are due to deuterated solvents and end groups. B ¹H NMR spectrum of compound 3-M in CDCl₃.

The structure of polymer 3 was supported by its ¹H NMR spectrum in DMF-d₇ and by comparison of the spectrum with that of 3-M in Figure 2.3. The ¹¹B NMR spectrum of 3 in DMF-d₇ showed a broad peak at 0 ppm, indicating the boron atoms were tetra-coordinate in DMF. Polymer 3 was also moderately soluble in THF but only sparsely soluble in toluene. The tendency for the coordinated THF to dissociate could be easily assessed by ¹H NMR spectrum in DMF-d₇. Like 3-M, 3 easily lose THF when allowed to dry at the ambient temperature under one atmosphere pressure of nitrogen in the glove box. The lability of the coordinated Lewis base solvent was an important attribute to the boron-containing polymers because it allowed the polymers to be processed by solution processes without losing their electron accepting ability. Although much less sensitive to
air than 2, polymer 3 still must be manipulated under the protection of an inert atmosphere. GPC analysis was not attempted due to its sensitivity to air. The number average degree of polymerization for 3 prepared under the conditions specified in the experimental section could be estimated to be ~24 (i.e., the average number of repeat units is ~12) by comparing the $^1$H NMR spectrum integrations of the –Sn$^{n}$Bu$_3$ end group and the aromatic protons assuming that each chain was terminated on statistical average by one –Sn$^{n}$Bu$_3$ end group and one -Br end group.

Scheme 2.3 Synthesis of compound 4-M and polymer 4.

Polymer 4 and the small molecule model 4-M were synthesized in a similar manner as 3 and 3-M (equations 6 and 7), but the reactions were carried out at higher temperatures. The more reactive trimethylstannyl reagents instead of tri-$n$-butylstannyl reagents were used to achieve higher conversion. Compound 4-M was formed essentially quantitatively under these conditions and was fully characterized by $^1$H (Figure 2.4 B), $^{13}$C, $^{19}$F, and $^{11}$B NMR spectroscopy and elemental analysis. Again, polymer 4 was prepared using the same procedure as its small-molecule analog 4-M was.
Figure 2.4 A $^1$H NMR spectrum of 4 in 1:2 CD$_3$CN:d-THF. Peaks with star are due to deuterated solvents and grease. B $^1$H NMR spectrum of compound 4-M in CDCl$_3$.

The solubility of 4 was poor in normal single organic solvents, but dissolved well in the acetonitrile/THF mixture in 1:2 volume ratio. The $^1$H (Figure 2.4 A), $^{19}$F and $^{11}$B NMR spectra were consistent with the proposed polymeric structure especially when compared with the NMR spectra of 4-M. The number average molecular weight was estimated to be 4,500 according to $^1$H NMR end group analysis using the –SnMe$_3$ end group (δ 0.45 ppm) and the aromatic resonances in the chain (δ 7.37 and 7.71 ppm).

Although not indefinitely stable, polymer 4 was stable enough to stand moisture and oxygen for GPC analysis. The GPC sample was first dissolved in the 2:1 mixture of THF and CH$_3$CN and then diluted with CHCl$_3$. The $M_n$ value determined by GPC (Figure 2.5) was 5,050 relative to polystyrene standards with PDI=1.14. The narrow polydispersity was unexpected for a polymer synthesized by step-growth polymerization but may be attributable to the low solubility of 4 in refluxing toluene, i.e., the molecular weight was controlled by the solubility, which likely progressively decreased as the molecular weight increased.
Coordination and departure of the Lewis base to 4-M and 4 was studied. After removal of the solvents from the CH$_3$CN/THF solution of 4-M, CH$_3$CN was the only observable coordinated Lewis base according to $^1$H NMR spectrum in CDCl$_3$. Each boron Lewis acid center coordinated with approximately one CH$_3$CN. The coordinated CH$_3$CN was rather labile. After the solid 4-M/CH$_3$CN adduct was left to dry in the atmosphere of the glove box for 1-2 days, CH$_3$CN was completely lost. Because 4 could only be dissolved in the CH$_3$CN/THF mixture, the departure of CH$_3$CN from 4 was confirmed by elemental analysis in addition to the evidence provided by the above experiments using 4-M as a model compound. The 4/CH$_3$CN adduct was left in the glove box for two days, and then shipped for elemental analysis. The elemental analysis results indicated that only 4.2% of the boron Lewis acid centers retained CH$_3$CN. The above results confirmed that coordinative solvents could be used for processing the polymers and these solvents could be easily removed afterwards.

2.2.2 Solution and Solid State Optical Properties

The optical absorption spectra of the model compounds 2-M – 4-M and polymers 2 – 4 were shown in Figure 2.6.
Figure 2.6 UV-Vis spectra of model compounds and polymers in the presence of a coordinated Lewis base and in the absence of a coordinated Lewis base.

The solid films were semi-crystalline and scatter light, rendering the apparent non-zero absorption value below the absorption bands. The highest wavelength absorption maxima were summarized in Table 2.2. The first absorption maxima were at 352 nm and 384 nm for 2-M and 2, respectively, in CH₂Cl₂. The red shift was likely the result of an
increase in the effective length of \(\pi\)-conjugation through the polymer backbone in comparison to the small molecule. The UV-visible spectrum of 2 in the solid state was obtained with a thin film drop-casted on the inside of the quartz cuvette from the CH\(_2\)Cl\(_2\) solution of 2. The solid state and solution spectra were very similar.

Table 2.2 UV-Visible absorption data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{max}}) (nm) in CH(_2)Cl(_2)</th>
<th>(\lambda_{\text{max}}) (nm) in THF</th>
<th>(\lambda_{\text{max}}) (nm) in solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-M</td>
<td>352</td>
<td>290</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>384</td>
<td>N/A</td>
<td>387</td>
</tr>
<tr>
<td>3-M</td>
<td>350</td>
<td>291</td>
<td>361</td>
</tr>
<tr>
<td>3</td>
<td>N/A</td>
<td>293</td>
<td>362</td>
</tr>
<tr>
<td>4-M</td>
<td>369</td>
<td>303</td>
<td>383</td>
</tr>
<tr>
<td>4</td>
<td>N/A</td>
<td>303</td>
<td>372</td>
</tr>
</tbody>
</table>

Due to the poor solubility of polymer 3 and 4 in non-coordinating solvents, their solution UV-visible spectra could only be obtained in coordinating solvents. The UV-visible spectra of 3 and 4 free of coordinated Lewis base were obtained using their thin solid films by taking advantage of the fact that 3 and 4 readily lose the coordinated solvents in the solid state as discussed above. The thin film samples were first left in the glove box for at least two days to allow the complete departure of the coordinated Lewis base at 40 °C. The absorption maximum of 3 was observed at 362 nm in the solid state. In comparison, the first absorption maximum of 3 in THF solution was observed at 295 nm. The absorption maximum of 4 also shifted from 372 nm in the thin film state to 303 nm in the CH\(_3\)CN/THF solution. The absorption shifts was attributed primarily to the coordination of the Lewis base solvents because shifts of the same magnitude could be observed when comparing the THF and chloroform solutions of 3-M and the CH\(_3\)CN/THF and chloroform solutions of 4-M. Furthermore, the UV-visible spectra of the thin films of 3 and 4 did not change after being annealed at 90 °C for 2 hours.
2.2.3 Cyclic Voltammetric Study

Cyclic voltammetry is a type of potentiodynamic electrochemical measurement based on the onset potentials of reduction and oxidation. The reduction potentials were measured using cyclic voltammetry to evaluate the electron affinity of the electron-deficient polymers and the small molecules. The cyclic voltammograms were shown in Figure 2.7.

Figure 2.7 Cyclic voltammograms of model compounds and polymers.

The Lewis-base free films of 3 and 4 were prepared by drop-casting on the flat head formed by the platinum electrode and its plastic cladding. The reductions of 3 and 4 occurred at much more negative potentials in a coordinating solvent than in the Lewis base-free state as expected due to solvent coordination.211
The LUMO energies of 2, 3, and 4 could be estimated from the onset potential of their reduction waves in their Lewis base-free forms according to an empirical scale factor that relates the SCE potential to vacuum (typically 4.4 eV).\textsuperscript{170,171,213} The LUMO levels of 2, 3, and 4 were compared with those of C\textsubscript{60} and rr-P3HT\textsuperscript{170,171} in Figure 2.8. Apparently, 2, 3, and 4 were less electron accepting than C\textsubscript{60}. However, the LUMO level of 4 was lower than that of rr-P3HT by an appreciable margin, and the LUMO of 3 also appeared somewhat lower than that of rr-P3HT.

![Figure 2.8 Comparison of LUMO energies.](image)

2.2.4 Detection of Charge Transfer by Photoluminescence Quenching

Quenching of the photoluminescence (PL) of \textit{p}-type conjugated polymers such as \textit{rr}-P3HT in the presence of C\textsubscript{60} or its derivatives had been attributed to the electron transfer from the excited state of the \textit{p}-type materials to fullerenes.\textsuperscript{214} This charge transfer process was the milestone of the organic bulk heterojunction photovoltaic cells. Interestingly, beside C\textsubscript{60} and some of its derivatives, no other \textit{n}-type materials had been reported that could quench the photoluminescence of \textit{rr}-P3HT before this work.\textsuperscript{53} As one of the motivations of this research was to find a polymeric material to replace the fullerene
derivatives in photovoltaic applications, the photoluminescence studies were carried out to prove the possible electron transfer from the excited \( rr \)-P3HT to 3 or 4 since both have a relative low-lying LUMO.

After photo-induced generation of exciton in \( rr \)-P3HT, it would either undergo charge separation or decay via radiative or non-radiative pathways to give out energy as the form of fluorescence and heat as shown in Scheme 2.4. If the energy offset was large enough to overcome the exciton binding energy, possible electron transfer from LUMO level of donor to LUMO level of acceptor would dominate over the decay process, resulting in decreased photoluminescence intensity.

![Diagram of photoluminescence quenching of excited states](image)

Scheme 2.4 Illustration of photoluminescence quenching of excited states.

Before carrying out the photoluminescence experiments, whether there was any Lewis acid/Lewis base interaction between the boron-containing species 3 and 4 with \( rr \)-P3HT was first probed. No changes of \(^1\text{H}\) NMR chemical shifts were observed for the mixtures of 3-M and \( rr \)-P3HT or 4-M and \( rr \)-P3HT compared to the spectra of the pure individual compounds, indicating the absence of the Lewis acid-base interaction.
Thin films of $rr$-P3HT, the 4/$rr$-P3HT blend, and the 3/$rr$-P3HT blend were coated on 2x2 cm$^2$ ITO substrates. The UV-visible spectra of the blends on ITO were simple additions of the individual spectra of the blend components. These indicated no significant mixing of the electronic wave functions in the ground state. The photoluminescence experiments were carried out using the films coated on 2x2 cm$^2$ silicon wafers. The polymer film thicknesses on the silicon wafers were approximately 1 μm, well above the thickness required for the maximum absorption and thus the highest photoluminescence of $rr$-P3HT (that thickness was ~160 nm in our hands).

The photoluminescence intensity of $rr$-P3HT in its blend with 3 was only marginally lower than that of pure $rr$-P3HT as shown in Figure 2.9. Although the lack of quenching may be attributed to a number of reasons, the insufficient energy difference between the LUMOs of 3 and $rr$-P3HT to effectively separate the Coulombically bounded electron–hole pairs (excitons) in $rr$-P3HT appeared an easy explanation to cite. In comparison, the photoluminescence of $rr$-P3HT in its blend with 4 was quenched to <1% of the level of the pure $rr$-P3HT sample. This indicated a strong interaction between the two components in the excited states and rapid electron transfer from the excited $rr$-P3HT to 4. Also worth noting was that the ~0.18 eV energy offset between $rr$-P3HT and 4 was apparently enough to overcome the Coulombic binding energy of the $rr$-P3HT exciton, consistent with the notion that the exciton binding energies of well conjugated macromolecules were often rather low and the exciton binding energy was reported to be around 0.2 eV for $rr$-P3HT.$^{154,215}$ Although the detailed mechanisms$^{216-221}$ involved in the non-radiative decay of the excitons was unknown at the present stage, to the best of our knowledge, 4 was the first reported polymer that had been demonstrated to completely
quench the photoluminescence of \textit{rr}-P3HT when this work was published.\textsuperscript{53,222} Recently, some other \textit{n}-type polymers had been synthesized to quench the photoluminescence of \textit{rr}-P3HT. Mixture of these \textit{n}-type conjugated polymers and \textit{rr}-P3HT was used as polymer/polymer blend solar cells.\textsuperscript{151,160,166,168,223-226}

Figure 2.9 Photoluminescence spectra of pure \textit{rr}-P3HT, a blend of 3 and \textit{rr}-P3HT, and a blend of 4 and \textit{rr}-P3HT. These samples were excited at 530 nm.

2.3 Conclusion

Several electron-deficient polymers containing the 9,10-diboroanthracene unit had been synthesized and characterized. Electrochemical study showed that they had relatively high electron affinity. Only when the approach of utilizing the empty \textit{p}-orbital of boron was combined with the approach of utilizing the electron withdrawing substituent, a polymer had with a LUMO appreciably lower than that of \textit{rr}-P3HT. Quenching of the photoluminescence of \textit{rr}-P3HT by 4 demonstrated the electron transfer from the excited state of \textit{rr}-P3HT to 4 indeed occurs in the solid state.
However, all these boron-containing conjugated polymers all absorbed less than 400 nm, resulting in limited overlap of the solar spectrum. To be a suitable organic solar cell material, it was desirable to introduce other functional groups into the polymer backbone to increase its absorption range, especially in the 400-800 nm range. Due to the instability of the 9,10-diboroanthracene unit, polymer 2 and 3 could only be handled in glove box, and underwent rapid decomposition in atmosphere. Although polymer 4 had the lowest LUMO and seems to be the most stable, it was still sensitive to moisture and oxygen to some degree. As the result, even other functional groups could be introduced into the polymer backbone, the instability issue made these boron-containing polymers not suitable for further device fabrication.

To sum up, it was urgent to find some robust materials with low energy levels and high charge mobilities to be the suitable candidates of n-type materials. This leads me to the next project which is the synthesis of regioregular polythiophene with electron-withdrawing groups.

2.4.1 Materials

All experiments were conducted under nitrogen using Schlenk techniques or in a glove box. Anhydrous THF, hexanes, diethyl ether and toluene, rr-P3HT were purchased from Aldrich and used without further purification. Chloroform was refluxed over CaH2, distilled, and stored over molecular sieves. Deuterated tetrahydrofuran was stirred over a Na/K alloy, vacuum-transferred, and stored in the glove box. All other deuterated solvents were refluxed over CaH2, distilled, and stored over molecular sieves in the glove
Compounds 1,4-C\textsubscript{6}H\textsubscript{4}(SnMe\textsubscript{3})\textsubscript{2}\textsuperscript{227}, 1,4-C\textsubscript{6}F\textsubscript{4}(SnMe\textsubscript{3})\textsubscript{2}\textsuperscript{228}, 1,4-C\textsubscript{6}H\textsubscript{4}(SnBu\textsubscript{3})\textsubscript{2}\textsuperscript{229}, 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene\textsuperscript{230}, C\textsubscript{6}H\textsubscript{5}SnBu\textsubscript{3}\textsuperscript{230} and C\textsubscript{6}F\textsubscript{5}SnMe\textsubscript{3}\textsuperscript{231} were prepared according to literature methods.

2.4.2 Measurements

NMR spectra were obtained on either a Varian Mercury 300 MHz or a Varian Inova 400 MHz instruments. All \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were referenced with respect to residual proton in the deuterated solvent. \textsuperscript{19}F NMR spectra were referenced with respect to tetrafluoro-p-xylene (-146.21 ppm). \textsuperscript{11}B NMR spectra were recorded on a Varian Inova 400 MHz instrument and referenced with respect to boron-trifluoride diethyl ether. Elemental analysis was carried out by Galbraith Laboratories, Inc.

Ultraviolet-visible (UV) spectra were acquired on a Hewlett-Packard 8453 diode-array spectrophotometer. Photoluminescent spectra were obtained on a HORIBA Jobin Yvon NanoLog spectrofluorometer. The solid film of 2 was prepared by drop-casting its THF solution on the inside of the quartz cuvette. The solid films of 3 and 4 were prepared by spin-coating on quartz or ITO glass wafers for the UV-visible spectroscopic measurements and on silicon wafers for the photoluminescence measurements. The spectra were recorded after the sample were left open to the atmosphere in the glove box (~ 35 °C) overnight to allow the coordinated Lewis base to escape from the film.

Cyclic voltammetric \textsuperscript{232} measurements were performed under a nitrogen atmosphere in a gas-tight three-electrode electrochemical cell. n-Bu\textsubscript{4}N\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-} (0.1 M) was used as the supporting electrolyte. A platinum wire was used as the counter electrode. A silver wire
was used as a quasi-reference electrode and is calibrated with the ferrocene/ferrocenium redox couple. The working electrode was a platinum rod with a plastic cladding, which render a flat area large enough for drop-casting thin films. The polymer films were prepared by first dissolving the polymer in the appropriate solvent and then drop-casting onto the electrode. The film was allowed to dry for 24 hours. All the preparation steps were carried out in the glove box under nitrogen. The electrochemical cell was then assembled and taken out the glove box to be connected with the potentiostat for the cyclic voltametric measurement.

Gel permeation chromatography was performed using a Waters 150C system equipped with a refractive index detector. The relative molecular weight was determined at 35 °C using monodisperse polystyrene standards as the references and chloroform as eluent phase.

2.4.3 Synthesis

Preparation of 1

At −78 °C, Et₃SiH (1.8 g, 15.6 mmol) in toluene (10mL) was added into a suspension of 9,10-dibromo-9,10-dihydro-9,10-dibora-anthracene (2.0 g, 6.0 mmol) in toluene (30 mL) under nitrogen. The mixture was allowed to warm to room temperature and stirred for 24 hours. The colorless precipitate was isolated by filtration and washed with hexane (2× 10 mL). Dried under vacuum gave as white solid (0.98 g, 93%). $^1$H NMR (300 MHz, THF-d₈): δ 4.67 (br, B–H, 2 H), 7.16 (t, $J = 3.9$ Hz, 4 H), 7.60 (t, $J = 4.1$ Hz, 8 H). $^{13}$C {$^1$H} NMR (75 MHz, THF-d₈): δ 127.8, 136.6, 152.6 (br, B–C). $^{11}$B {$^1$H} NMR (400
MHz, THF-d$_8$): $\delta$ 26. Anal. Calc. for C$_{12}$H$_{10}$B$_2$ (175.62): C 82.00, H 5.71; found: C 81.51, H 5.53.

Preparation of 2

A suspension of 1 (1.00 g, 5.70 mmol) and 1,4-diethynylbenzene (0.700 g, 5.70 mmol) in toluene (60 mL) was stirred under nitrogen for 24 hours at room temperature. The yellow precipitate was collected by filtration and washed with hexane. Dried under vacuum gave as yellow powder (1.45 g, 85%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.30–8.04 (several broad signals, B-C$_6$H$_4$, B-CH=CHC$_6$H$_4$CH=CH–, 12 H), 8.16 (br, B-C$_6$H$_4$, 4 H). $^{11}$B $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 30.

Preparation of 2-M

A suspension of 1 (0.50 g, 2.80 mmol) and phenylacetylene (0.64 g, 6.30 mmol) in toluene (30 mL) was stirred under nitrogen for 14 hours at room temperature. All volatile components were removed under vacuum. The solid residue was dissolved in hexane at room temperature. Recrystallization at $-32$ °C gave as white solid (0.66 g, 63%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.32–7.45 (m, 6H), 7.48 (d, $J$ = 18.2 Hz, 2 H), 7.60 (dd, $J$ = 5.3, 3.4 Hz, 4 H), 7.7 (d, $J$ = 6.8 Hz, 4 H), 7.80 (d, $J$ = 18.2 Hz, B-CH, 2 H), 8.18 (dd, $J$ = 5.3, 3.4 Hz, 4 H). $^{13}$C $^1$H NMR (75 MHz, CDCl$_3$) : $\delta$ 118.4, 127.8, 128.9, 129.4, 131.5 (br), 131.8, 136.3, 138.4, 146.6 (br), 151.6. $^{11}$B $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 63. Anal. Calc. for C$_{28}$H$_{22}$B$_2$ (379.62): C 88.51, H 5.80; found: C 88.32, H 5.45.

Preparation of 3

A solution of 9,10-dibromo-9,10-dihydro-9,10-diboroanthracene (1.0 g, 3.0 mmol) and 1,4-C$_6$H$_4$(SnBu$_3$)$_2$ (1.96 g, 3.0 mmol) in toluene (40 mL) was refluxed under nitrogen
for 12 hours. The precipitate was collected by filtration and washed with hexane. Dried under vacuum gave as yellow powder (0.68 g, 91%). $^1$H NMR (300 MHz, DMF-d$_7$): δ 7.0 (C$_6$H$_4$, 4 H), 7.24 (BC$_6$H$_4$B, 4 H), 7.41 (C$_6$H$_4$, 4 H). $^{11}$B $^1$H NMR (400 MHz, DMF-d$_7$): δ13.

Preparation of 3-M

A solution of 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene (0.67 g, 2.0 mmol) and C$_6$H$_5$SnBu$_3$ (1.47 g, 4 mmol) in toluene (30 mL) was refluxed under nitrogen for 12 hours. After the mixture was cooled to room temperature, all volatile components were removed under vacuum. The residue was dissolved in toluene (10 mL). Hexane (15mL) was then layered on top of the toluene solution. Recrystallization at $−32 \degree$C gave as pale yellow solid (0.43 g, 65%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.51 (m, 10 H), 7.62 (dd, $J =$ 5.9, 3.0 Hz, 4 H), 7.83 (dd, $J =$ 5.3, 3.0 Hz, 4 H). $^{13}$C $^1$H NMR (75 MHz, CDCl$_3$) : δ 127.2, 128.2, 132.1, 132.9, 140.2, 143.5 (br, B–C), 146.2 (br, B–C). $^{11}$B $^1$H NMR (400 MHz, CDCl$_3$): δ 65. Anal. Calc. for C$_{24}$H$_{18}$B$_2$ (327.62): C 87.91, H 5.49; found: C 87.62, H 5.42.

Preparation of 4

A solution of 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene (1.0 g, 3.0 mmol) and 1,4-C$_6$F$_4$(SnMe$_3$)$_2$ (1.43 g, 3.0 mmol) in toluene (40 mL) was sealed in a thick-walled glass tube with a teflon screw cap and was heated at 120 °C under nitrogen for 12 hours. The precipitate was collected by filtration and washed with toluene. Dried under vacuum gave as pale yellow powder (0.87 g, 90%). $^1$H NMR (300 MHz, CH$_3$CN-d$_3$/THF-d$_8$ in 1:2 volume ratio): δ 7.37 (C$_6$H$_4$, 4 H), 7.71 (C$_6$H$_4$, 4 H). $^{19}$F NMR (CH$_3$CN-d$_3$/THF-d$_8$ in 1:2 volume ratio): δ $−133.58$. $^{11}$B $^1$H NMR (CH$_3$CN-d$_3$/THF-d$_8$ in 1:2 volume ratio): δ $−4$. 63
Preparation of 4-M

A solution of 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene (0.67 g, 2 mmol) and C₆F₅SnMe₃ (1.33 g, 4 mmol) in toluene (30 mL) was sealed in a thick-walled glass tube with a teflon screw cap and was heated at 120 °C under nitrogen for 12 hours. After the mixture was cooled to room temperature, all volatile components were removed under vacuum. The residue was dissolved in toluene (10 mL) at 80 °C. The solution was left at room temperature overnight to allow the initial crystallization. Further recrystallization at −32 °C gave as pale yellow solid (0.72 g, 71%). ¹H NMR (300 MHz, CDCl₃): δ 7.60–7.75 (m, 8 H). ¹⁹F NMR (CDCl₃): δ −129.8 (dd, J = 24.4, 9.8 Hz, o-C₆F₅, 4F), −153.0 (t, J = 20.1 Hz, p-C₆F₅, 2F), −161.3 (ddd, J = 23.8, 24.0, 9.8 Hz, m-C₆F₅, 4F). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 137.7 (d, J_C–F = 251), 141.6 (d, J_C–F = 254 Hz), 145.5 (d, J_C–F = 245 Hz), 135.4, 140.7, 113.9 (br), 144.0 (br). ¹¹B {¹H} NMR (400 MHz, CDCl₃): δ 65. Anal. Calc. for C₂₄H₈B₂F₁₀ (507.93): C 56.74, H 1.58; found: C 56.42, H 1.53.
CHAPTER III
SYNTHESIS AND CHARACTERIZATION OF REGIOREGULAR POLYTHIOPHENE
WITH ELECTRON-WITHDRAWING GROUPS

3.1 Introduction

The seminal works of McCullough\textsuperscript{95} and Rieke\textsuperscript{96} on the Ni-catalyzed synthesis of poly(3-alkylthiophene)s with high HT regioregularity \textit{rr}-P3ATs have led to the widespread use of these polymers as \textit{p}-type materials in organic photovoltaics (OPVs) and field-effect transistors (FETs) as described in Chapter I. Since the Ni-catalyzed polymerization is living,\textsuperscript{92,98,125,233,234} \textit{p}/\textit{n}-block co-polythiophenes are attractive synthetic targets for the purpose of achieving morphological control in ambipolar devices such as bulk heterojunction (BHJ) solar cells.

However, only a relatively small number of polythiophenes with electron-withdrawing substituents have been synthesized, and an even smaller number of them have the HT regioregularity. Collard and coworkers\textsuperscript{235,236} and Rikukawa and coworkers\textsuperscript{237} reported poly(3-fluoroalkylthiophene)s with high HT regioregularity (\textit{rr}-P3FATs) and very high electron affinities. The helical conformation of the fluoroalkyl side chains slightly twists the adjacent thiophene rings away from coplanar conformation. This

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feature renders \( rr \)-P3FATs highly emissive, but the extent of \( \pi \)-conjugation in the ground state is reduced compared to \( rr \)-P3ATs. Pomerantz and coworkers reported the synthesis of polythiophenes with ester side chains via the Ni-catalyzed polycondensation but only obtained low molecular weight polymers in low yields.\(^{238}\) They also reported ester-substituted polythiophenes with HH regioregularity via Ullman-type coupling.\(^{239,240}\) Several examples of polythiophenes with electron-withdrawing cyano and ester substituents on alternating thiophene repeat units have been reported.\(^{241-247}\)

The use of the less reactive stannyl reagents or zinc reagents for transmetallation apparently avoided the potential side reaction between the metallated thiophene with the ester and cyano substituents. Functionalization of \( rr \)-P3ATs at the 4-position of the thiophene rings after polymerization have also been reported,\(^{248}\) but the UV-visible absorption of the 3,4-disubstituted polymers is significantly blue-shifted compared to the parent \( rr \)-P3ATs, indicating a highly sterically encumbered backbone.

In view of the need for \( n \)-type conjugated polymers and the general usefulness of controlling the electronic structure of \( \pi \)-conjugated polymers for optical and electronic applications,\(^{169,249-253}\) it appears worthwhile to further examine polythiophenes with electron-withdrawing substituents.

Here, the synthesis and studies of a representative member of the regioregular poly(3-alkanoylthiophene)s (PHOT) were developed. The target polymer had been synthesized via the Ni-catalyzed Kumada polycondensation, taking advantage of protection-deprotection chemistry of the ketone and ketal functional groups.

Cyclic voltammetry was used to evaluate the energy levels of the HOMO and LUMO. Optical absorption and emission spectroscopies of the new polymer were studied. The
new polymer as an active component in field-effect transistors (FETs) and BHJ solar cells were also evaluated.

3.2.1 Synthesis of Monomer Precursor

Organic carbonyl functionalities reacted with Grignard reagents at room temperature or below. The inherent incompatible reactivity required protection of the electron-withdrawing acyl substituent in the monomer in order to carry out the Ni-catalyzed polycondensation. The synthetic route to monomer precursor 7 was outlined in Scheme 3.1.

Scheme 3.1 Synthesis of monomer precursor.

Most synthetic steps were straightforward. An extended reaction time was necessary to ensure the complete conversion of 6 to 7. Otherwise, the mono-brominated intermediate 8b (Figure 3.1), which could be isolated if one equivalent of NBS was used (see Experimental Section), was difficult to remove. All these molecules, 5, 6 and 7 were purified by distillation to ensure the high purity.
3.2.2 Generation of Monomers

Reaction of 7 with one equivalent of \( \text{t}-\text{PrMgCl} \) was first attempted in THF at various temperatures from \(-40^\circ\text{C}\) to room temperature. The reaction mixture was quenched with water and analyzed by \(^1\text{H} \text{NMR} \) spectrum. The persistence of 7 in the quenched mixture even after a prolonged reaction time indicated that the products and reactants were in equilibrium. About 70\% of 7 was converted to the two regio-isomeric Grignard reagents (equation 3.1) as shown in Scheme 3.2.

Scheme 3.2 Schlenk equilibrium of monomer generation.

The reaction temperature or the use of \( \text{t}-\text{BuMgCl} \) did not significantly shift the equilibrium. When the equilibrium mixture was directly subjected to Ni (DPPP)Cl\(_2\) for polymerization, catalyst poisoning was evident as no polymeric product was obtained at all. The detrimental effect of excess alkyl Grignard reagent was reported by Yokozawa and coworkers.\(^{110}\) The equilibrium observed here apparently was not a serious problem in the previously reported syntheses of other polythiophene derivatives due to the higher reactivity of those monomers.
The equilibrium involving an alkyl Grignard and an aryl halide had recently been studied by Straub and Knochel. They reported that addition of LiCl and 1,4-dioxane, which coordinates to the Mg$^{2+}$ ion, shifts the Schlenk equilibrium to $i$-Pr$_2$Mg•LiCl and allows the exchange reaction to go to completion. The methodology fortunately proved applicable to overcome the problem in our case. In the presence of LiCl and 1,4-dioxane, 7 was completely converted to the thiophene magnesium species 9a and 9b by one equivalent of $i$-PrMgBr (equation 3.2). The ratio of 9a and 9b was estimated to be ~1:4 according to the ratio of 8a and 8b in their hydrolysis product determined by $^1$H NMR spectrum integration.

![Figure 3.1 Isomers after quenching.](image)

3.2.3 Polymer Synthesis

Synthesis of the target polymer 11 (PHOT) was outlined in Scheme 3.3. The polymerization was catalyzed by Ni(DPPP)Cl$_2$ in THF using the mixture of 9a and 9b as the monomers in-situ generated following the method detailed above. The reaction was run first at 0 ºC for 1 h and then heated at 40 ºC overnight. Polythiophene 10 was obtained essentially in near quantitative yield. Deprotection of 10 following the common protocol for small molecule ketals did not occur readily in chloroform/water mixtures likely because of the very unfavorable partition coefficients of organic polymers in the
aqueous phase. Addition of 1,4-dioxane proved necessary for deprotection to proceed to any substantial extent. Still, the deprotection procedure must be repeated or preferably performed three times to cleanly convert 10 to PHOT 11.

The aromatic region in the $^1$H NMR spectrum of PHOT was diagnostic of the completeness of deprotection (Figure 3.2). The spectrum also demonstrated the relatively high regioregularity of PHOT. A maximum of four peaks were possible in the aromatic region corresponding to the HT-HT, TT-HT, HT-HH, and TT-HH triads in the $^1$H NMR spectrum of PHOT. Only one major peak was observed, indicating that one triad, presumably HT-HT, was dominant. The four triads were not completely resolved as only two minor peaks are observable. We therefore used the $\alpha$-methylene protons to estimate the HT/HH dyad ratio, which was typically > 95:5.

Scheme 3.3 Polymer synthesis.

The high HT regioregularity despite the ~1:4 regioisomeric ratio in the monomer mixture was previously explained by McCullough and coworkers$^{97}$ on the basis of the difference in reactivity of the regioisomeric monomers in their study of $rr$-P3HT synthesis. A similar explanation was likely applied here. To confirm it, the progress of the polymerization by periodically sampling the reaction mixture was monitored by quenching the samples with methanol, and analyzing them by $^1$H NMR spectrum.
After the polymerization was started at 0 °C, the minor isomer 9a was depleted within 1 h, while the major isomer 9b was intact after 1 day (Figure 2 A). When the polymerization temperature was raised to 40 °C, the consumption of 9b started and reached completion in ~10 h. Therefore, the product of the polymerization was essentially composed of two stereo-regular blocks arising from 9a and 9b, respectively. The HH region-chemical mistakes were more likely to be located at the block junction (Scheme 3.4) than the rest of the polymer chain with the exception of perhaps the terminus of the chain.

The number average degree of polymerization ($M_n$) increased linearly with the total conversion of 9a and 9b (Figure 2.3 B). $M_n$ of 20,000 could be easily achieved. The
polydispersity index (PDI) was narrow before 9b polymerizes but broadened afterward. It was tentatively suggested that the polymerization was quasi-living and attribute the broad molecular weight distribution to the slow initiation of the second stereo-regular block. In other words, the first enchainment of 9b at the block junction after the complete consumption of 9a, where the region-chemical mistake was made as discussed above (Scheme 3.4), was particularly slow compared to the subsequent 9b enchainment. The slow rate of this step could be understood by the high steric hindrance of both reactants involved in this step.

Figure 3.3 A. Total conversion of monomers as a function of time and temperature. B. Plot of $M_n$ vs total conversion of 9a and 9b. The number over each point was the PDI of the particular sample.
PHOT polymer had good solubility in chlorinated solvents and THF. It also had certain solubility in other solvents (Table 3.1).

Table 3.1 The solubility of PHOT in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling point</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloroform</td>
<td>61 °C</td>
<td>above 10 mg/mL at RT</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>180 °C</td>
<td>9.0 mg/mL at 100 °C</td>
</tr>
<tr>
<td>Methanesulfonic acid</td>
<td>167 °C (10 mm Hg)</td>
<td>Less than 0.05 mg/mL at b.p.</td>
</tr>
<tr>
<td>DMF</td>
<td>153 °C</td>
<td>Less than 0.1 mg/mL at b.p.</td>
</tr>
<tr>
<td>NMP</td>
<td>203 °C</td>
<td>Around 0.90 mg/mL at b.p.</td>
</tr>
<tr>
<td>Phenol</td>
<td>181 °C</td>
<td>Above 2.1 mg/mL at b.p.</td>
</tr>
<tr>
<td>2-chloroethanol</td>
<td>130 °C</td>
<td>Less than 0.1 mg/mL at b.p.</td>
</tr>
<tr>
<td>1,2,4-trichloro benzene</td>
<td>215 °C</td>
<td>Above 6.8 mg/mL at b.p.</td>
</tr>
<tr>
<td>pyridine</td>
<td>115 °C</td>
<td>Around 2.1 mg/mL at b.p.</td>
</tr>
<tr>
<td>trifluoroethanol</td>
<td>78 °C</td>
<td>Less than 0.1 mg/mL at b.p.</td>
</tr>
</tbody>
</table>
3.2.4 Cyclic Voltammetry

Cyclic voltammetry was used to evaluate the HOMO and LUMO levels of PHOT. The voltammogram of thin film of PHOT was shown in Figure 3.4 A along with that of \textit{rr}-P3HT for comparison. The LUMO and HOMO energy levels were estimated from the onset potential of the reduction and oxidation waves, respectively, taking the SCE potential as 4.4 eV below vacuum (see experimental section).

![Cyclic voltammograms of PHOT (solid) and rr-P3HT. Comparison of HOMO and LUMO levels of PHOT and rr-P3HT.](image)

The LUMO and HOMO levels of PHOT were lower than those of \textit{rr}-P3HT by ~0.5 eV in the solid thin film (Figure 3.4 B). Interestingly, the LUMO levels of the polythiophenes with carboxyl side chains on every other thiophene ring, for example polymer A, were also ~0.5 eV lower than \textit{rr}-P3HT (Figure 3.5). Therefore, the electron affinity of the polythiophene did not increase after doubling the density of electron-withdrawing groups despite the fact that the electron-withdrawing abilities of acyl and
carboxyl functionalities were very similar according to Hammet substituent constants.\textsuperscript{257,258} The HOMO level of PHOT did seem somewhat lower than polymer \textbf{A} by \textasciitilde0.1-0.2 eV.

![Chemical structure of Polymer A]

Figure 3.5 Chemical structure of Polymer \textbf{A}.

3.2.5 Optical Absorption and Photoluminescence Spectra

The visible absorption maximum of PHOT in chloroform solution was at 442 nm and shifted to 543 nm in a spin-casted film (Figure 3.6). The absorption spectra of PHOT and \textit{rr}-P3HT were almost identical in both the solid state and in solution. The introduction of the acyl group in the side chain hence did not obviously alter the bandgap or hinder the effective conjugation of the polythiophene backbone.

![Absorption spectra](A: UV-Vis absorption spectra of PHOT (solid) and \textit{rr}-P3HT\textsuperscript{256} in chloroform. B: UV-Vis absorption spectra of PHOT (solid) and \textit{rr}-P3HT\textsuperscript{256} as spin-cast film)

Figure 3.6 \textbf{A}. UV-Vis absorption spectra of PHOT (solid) and \textit{rr}-P3HT\textsuperscript{256} in chloroform. \textbf{B}. UV-Vis absorption spectra of PHOT (solid) and \textit{rr}-P3HT\textsuperscript{256} as spin-cast film.
The PL emission maximum of PHOT was slightly red-shifted compared to \( rr-P3HT \) in chloroform solution (Figure 3.7 A). The difference was more pronounced for the spin-cast thin films (Figure 3.7 B). A possible rationale was that the 3-acyl substituent was included in the \( \pi \)-system in the excited state more than in the ground state. The difference may also had been exaggerated by the nonlinear response of the photo-detector above 750 nm wavelength. The inherent difficulty of quantifying luminescence in the near-infrared region was manifested by the inconsistency of the PL spectra of \( rr-P3HT \) films that had appeared in the literature.\(^{259-262}\)

![Figure 3.7 A. Solution photoluminescence spectra of PHOT (solid) and \( rr-P3HT \) in chloroform solution. The spectra are normalized. B. Thin film photoluminescence spectra of PHOT (solid), \( rr-P3HT \), and their 1:1 blend (dot). The spectra were not normalized for comparison of the emission intensity.](image)

To test whether any photo-induced electron-transfer would happen between PHOT and \( rr-P3HT \), the PL spectrum of the thin film of PHOT/\( rr-P3HT \) blend in 1:1 weight ratio was recorded. As mentioned above, in order to make a valid comparison of the photoluminescence intensity, we paid special attention to running the experiments under identical conditions using the same instrument. As shown in Figure 3.7 B, some PL
quenching occurred but the quenching efficiency was low. Since cyclic voltammetry revealed a convincing 0.5 eV offset at both the HOMO and LUMO levels between the two polymers. The low quenching efficiency was attributed to the morphology of the blend or other factors that might contribute to the kinetics of the electron-transfer process at the heterojunction interface.

3.2.6 Thermal and Morphological Properties

Thermal decomposition of PHOT was noticeable as the temperature approaches ~300 ºC under a nitrogen environment according to thermogravimetric analysis (TGA) (Figure 3.8 A). Decomposition was accompanied by severe volume expansion or foaming, causing the ups and downs in the thermogram beyond 300 ºC. No thermal transitions could be observed on the heating scan in differential scanning calorimetry (DSC) experiments (Figure 3.8 B). However, a glass transition-like feature could be observed at ~269 ºC on the cooling scan after the sample was heated to 290 ºC.

Figure 3.8 A. TGA thermogram of PHOT.  B. DSC thermogram of PHOT.
The WAXD experiment on a drop-cast film of PHOT showed that the as-casted film had very low crystallinity. Only one broad Bragg diffraction could be observed, corresponding to a $d$-spacing of 1.96 nm at room temperature (Figure 3.9 A). The intensity and number of diffraction did not change after the sample was annealed at 150 and 200 °C for 1 h. The samples annealed at 240, 260, and 280 °C, however, displayed additional and progressively more intense diffraction peaks. The $d$-spacings of these diffractions for the sample annealed at 280 °C were 2.11, 1.03, and 0.69 nm at room temperature.

Figure 3.9 A. WAXD powder pattern of PHOT annealed at various temperatures. B. Change of $d$-spacing after annealing.

The 1:2:3 $d$-spacing relationship indicated that the observed diffractions were the progressively higher order diffractions due to the same set of periodic structures similar to what is observed in the $rr$-P3AT series.\textsuperscript{40,103,126,263-265} The $d$-spacings increased after annealing according to the primary diffraction (Figure 3.9 B). If we apply the diffraction assignments of the $rr$-P3AT series to PHOT, the observed $d$-spacings correspond to the inter-chain periodicity of the lamellar structure. This result was consistent with the $d$-spacing of $rr$-P3HT which was around 1.57 nm,\textsuperscript{266} considering there was one more
carbonyl group on the side chains on PHOT. The diffraction in the π-stacking direction (010) was never observed in PHOT (Figure 3.10). \textit{rr}-P3HT had sharp peak corresponded to the periodicity of π-stacking distance around 0.39 nm.\textsuperscript{267} A comparable WAXD peak was not found or negligible for PHOT.

Figure 3.10 Inter-chain distance and possible π-stacking of PHOT.

3.2.7 Charge Transport and Photovoltaic Properties

Thin film transistors were fabricated as in Figure 3.11 to evaluate the charge transport properties of PHOT. After charge injection at source, current would change by tuning the gate voltage. The carrier mobility was calculated from the transfer characteristics ($I_{ds}^{1/2}$ vs $V_{gs}$) in the saturation region. No $n$-channel activity was observed, but the transistors showed fair current modulation and saturation when they were operated in the $p$-channel mode. Figure 3.12 showed the typical output and transfer characteristics.
Figure 3.11 The device structure of field effect transistor.268

Figure 3.12 Output and transfer characteristics of the thin film transistor of PHOT after thermal annealing at 150 °C.

The average hole mobility increased from $7.3 \times 10^{-6}$ cm$^2$/Vs without annealing to $2.7 \times 10^{-4}$ cm$^2$/Vs after thermal annealing at 150 °C, then decreased to $7.9 \times 10^{-5}$ cm$^2$/Vs after annealing at 250 °C (Table 3.2). Films deposited from dichlorobenzene showed slightly lower mobility (Table 3.2). The on/off ratio was on the order of $10^3$. 
Table 3.2 Electrical parameters of the thin film transistors of PHOT.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T_a (°C)</th>
<th>Average Mobility (cm²/Vs)</th>
<th>V_t (V)</th>
<th>On/off ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>N/A</td>
<td>7.3×10⁻⁶</td>
<td>3.1</td>
<td>&gt;10²</td>
</tr>
<tr>
<td>Chloroform</td>
<td>100</td>
<td>2.8×10⁻⁵</td>
<td>-17</td>
<td>&gt;10²</td>
</tr>
<tr>
<td>Chloroform</td>
<td>150</td>
<td>2.7×10⁻⁴</td>
<td>3.9</td>
<td>&gt;10³</td>
</tr>
<tr>
<td>Chloroform</td>
<td>200</td>
<td>1.6×10⁻⁴</td>
<td>-1.8</td>
<td>&gt;10³</td>
</tr>
<tr>
<td>Chloroform</td>
<td>250</td>
<td>7.9×10⁻⁵</td>
<td>-9.2</td>
<td>&gt;10³</td>
</tr>
<tr>
<td>Hot ODCB</td>
<td>150</td>
<td>1.8×10⁻⁴</td>
<td>-7.1</td>
<td>&gt;10³</td>
</tr>
</tbody>
</table>

T_a: Annealing temperature.

Unlike rr-P3HT, the super-linear increase of currents in output characteristics (I_{ds} vs V_{ds}) suggested that there was a contact resistance between gold electrode and the polymer semiconductor. The contact resistance was likely from the energy barrier due to the low-lying HOMO level of PHOT (5.64 eV in Figure 3.4 B) compared to rr-P3HT (5.15 eV in Figure 3.4 B). The work function of gold was believed to be around 5.1~5.47 eV, which was consistent with the cyclic voltammetry results. The hole mobility (~3×10⁻⁴ cm²/Vs) that obtained for PHOT (M_n ~ 13.6 kDa, PDI~1.8) was similar to the hole mobility (~4-5×10⁻⁴ cm²/Vs) of rr-P3HT with comparable molecular weight (M_n ~ 13.4 kDa, PDI~ 1.8). A sudden drop was observed for the device annealed at 280 °C, possibly signaling the onset of thermal decomposition (T_d ~ 300 °C).

The lack of mobility improvement with device annealing temperature did not necessarily contradicted the WAXD study because effective π-stacking had been indicated to be of principal importance in achieving high mobility, and the diffraction
peak due to π-stacking was not observed in the films of PHOT after annealing at various temperatures from 150-280 °C.

The photovoltaic properties of PHOT were evaluated by using it as a p-type material in BHJ solar cells and using PC_{71}BM as the electron acceptor. The standard BHJ device structure (ITO/PEDOT:PSS/Active layer/LiF/Al) was used.

Absorption spectrum and morphology of the active layer 90 nm thick composed of PHOT and PC_{71}BM in 1:1 weight ratio were similar to those of the \textit{rr}-P3HT:PC_{71}BM blend (Figure 3.13). TEM images of the active layers from actual devices showed that donor and acceptor materials were uniformly mixed. However, commonly observed \textit{rr}-P3HT fibrilar nanostructures in \textit{rr}-P3HT:PC_{71}BM blend thin films were missing. This may be attributed to the retarded ability to form self-assembled nanostructures of PHOT.

![Image](image_url)

Figure 3.13 UV-Vis absorption spectrum and TEM image of a BHJ cell with an active layer of PHOT:PC_{71}BM blend in 1:1 weight ratio.

The typical $J$-$V$ characteristics were shown in Figure 3.14. PCE results of BHJ cells under different conditions were summarized in Table 3.3.
Table 3.3 $J$-$V$ characteristics and PCE of BHJ cells under different conditions.

<table>
<thead>
<tr>
<th>Fabrication condition</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>PCEave (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200 rpm</td>
<td>2.18</td>
<td>0.65</td>
<td>0.38</td>
<td>0.53</td>
<td>0.44</td>
</tr>
<tr>
<td>1400 rpm</td>
<td>0.86</td>
<td>0.63</td>
<td>0.32</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>1200 rpm, SA</td>
<td>0.99</td>
<td>0.64</td>
<td>0.32</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>1400 rpm, SA</td>
<td>1.15</td>
<td>0.65</td>
<td>0.32</td>
<td>0.24</td>
<td>0.15</td>
</tr>
<tr>
<td>ODCB, Vacuum</td>
<td>2.05</td>
<td>0.41</td>
<td>0.31</td>
<td>0.26</td>
<td>0.22</td>
</tr>
<tr>
<td>ODCB, TA</td>
<td>1.7</td>
<td>0.60</td>
<td>0.34</td>
<td>0.34</td>
<td>0.30</td>
</tr>
<tr>
<td>ODCB/DIO, Vacuum</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ODCB/DIO, TA</td>
<td>0.52</td>
<td>0.46</td>
<td>0.32</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>OCDB/CHCl$_3$, Vacuum</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OCDB/CHCl$_3$, TA</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*SA stands for the solvent annealing. Active layers were coated from chloroform solution. Devices were thermal annealed at 100 °C for 5 min. TA stands for thermal annealing at 110 °C. DIO stands for 1,8-diiodooctane.

Figure 3.14 Current density-voltage curves of a BHJ cell with an active layer of PHOT:PC$_{71}$BM blend in 1:1 weight ratio.
The best device had a power conversion efficiency (PCE) of 0.53%. However, the fill factor ($FF = 0.38$) and short circuit current ($J_{sc} = 2.18 \text{ mA/cm}^2$) were low. The open-circuit voltage ($V_{oc} = 0.65 \text{ V}$) was comparable to the highest ($V_{oc} = 0.66 \text{ V}$) achieved in devices with $rr$-P3AT:PC$_{71}$BM active layers in our hands and was consistent with the low HOMO energy level of PHOT as depicted (Figure 3.14). This was because $V_{oc}$ relied on the difference between the HOMO of the $p$-type donor material and the LUMO of the $n$-type acceptor material. The poor photovoltaic performance of $rr$-P3HT:PC$_{71}$BM was likely due to the poor hole charge mobility in PHOT, and insufficient percolation between donor and acceptor phases due to poor self-assembly of PHOT. Attempts were also made using PHOT as an $n$-type material with $rr$-P3HT as the $p$-type material, but the polymer/polymer BHJ devices showed negligible PCEs (Figure 3.15).

![Figure 3.15 Current density-voltage curves of a BHJ cell with an active layer of PHOT:P3HT blend in 1:1 weight ratio.](image)

3.2.8 Attempted Synthesis of $rr$-Poly(3-(1,1-difluoroalkyl)thiophene)

The synthesis of $rr$-poly(3-(1,1-difluoroalkyl)thiophene) had also been attempted as outlined in Scheme 3.5. After retro-analysis, 3-(1,1-difluoroalkyl)thiophene was chosen
as the starting synthetic target. It was easy to make a 3-(1,1-difluoroalkyl)benzene from phenyl alkyl ketone. However, it was impossible to generate the precursor via similar chemistry from 1-(thiophen-3-yl)heptan-1-one. Many reactions had been attempted, and no expected product was formed according to $^{19}$F NMR spectrum.

Scheme 3.5 Synthetic route of $rr$-poly(3-(1,1-difluoroalkyl)thiophene).

1-(thiophen-3-yl)heptan-1-one was then protected into dithiol form (Scheme 3.5). After treating with reactive fluorinating reagents such as Deoxo-Fluor®, the expected molecule could be detected as the only fluorinated product. As the result, it would be possible to synthesize the $rr$-poly(3-(1,1-difluoroalkyl)thiophene) using a similar method as the polymerization of $rr$-P3HT or $rr$-PHOT. However, compared to regioregular poly(3-fluoro-alkylthiophene)s ($rr$-P3FAT), this polymer might still have a similar helical conformation and limited interchain $\pi$-stacking due to the –CF₂– adjacent. As the result, $rr$-poly(3-(1,1-difluoroalkyl)thiophene) should have low charge carrier mobility.

3.3 Conclusions

In summary, $rr$-PHOT polymer had been synthesized and investigated as a representative member of regioregular head-to-tail poly(3-alkanoylthiophene)s. The HOMO and LUMO levels of PHOT were lower than those of $rr$-P3HT by ~0.5 eV. Red-
shift of the UV-visible absorption maximum of PHOT in the solid state compared to the solution confirmed effective backbone conjugation along the polymer chain. WAXD indicated that PHOT had low crystallinity and particularly lacked order in the $\pi$-stacking direction in the solid state. The higher electron affinity of PHOT than $rr$-P3HT suggested that it could be potentially used as an $n$-type material. However, PHOT did not display any electron-transport activity in FET devices. The average field-effect hole mobility of PHOT was $\sim3\times10^{-4}$ cm$^2$/Vs. The lack of electron mobility and the relative low hole mobility in PHOT could be likely, not in small part, attributable to the lack of $\pi$-stacking order. Improvement of the crystallinity of PHOT was prevented by its very high glass transition temperature in proximity to its decomposition temperature. Photovoltaic devices with an active layer of 1:1 blend of PHOT and PC$_{71}$BM had a power conversion efficiency of $\sim0.5\%$. The PCE was partially attributed to the low hole mobility of the PHOT polymer. As the result, a conjugated polymer with robust structure which has good packing ability for high charge mobilities is crucial in OPV. This leads me to the next project which is the attempt to synthesis of graphene nanoribbons.

3.4.1 Materials

The anhydrous solvents, [1,3-bis(diphenylphosphino)propane]d nickel(II) chloride (Ni(DPPP)Cl$_2$), $p$-toluenesulfonic acid monohydrate, magnesium turnings, triethylamine (TEA), $N$-bromosuccinimide (NBS), 2,2-dimethyl-1,3-propanediol, isopropylmagnesium chloride (2.0 M in THF), 3-cyanothiophene, Deoxo-Fluor$^\text{®}$ and trifluoroacetic acid (TFA) were purchased from Alfa Aesar, Aldrich or Acros. They were used without purification.
Lithium chloride (LiCl) from Acros Organics was flame-dried under vacuum. [6,6]-phenyl-C71 butyric acid methyl ester (PC71BM, >99.0%) was purchased from American Dye Source (Quebec, Canada) and used as received. Poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT; Baytron P VP AI 4083) was purchased from H. C. Stark (Newton, MA). Deuterated chloroform (CDCl₃) and deuterated benzene (C₆D₆) were purchased from Cambridge Isotope Laboratories. CDCl₃ was kept over molecular sieves, and C₆D₆ was stirred over a Na/K alloy, vacuum-transferred, and stored in a glove box. \( rr \)-P3HT (HT content = \( \sim \)96%, \( M_n = 12,000, M_w = 14,400 \)) was synthesized following the GRIM procedure reported by McCullough et al.\(^{233} \)

3.4.2 Measurements

\(^1\)H and \(^{13}\)C NMR spectra were obtained on a Varian Mercury 300 MHz instrument. Chemical shifts were referenced internally using solvent peaks.

Cyclic voltammetric\(^{232} \) measurements were performed under a nitrogen atmosphere in a gas-tight three-electrode electrochemical cell at 20 °C and recorded on a BAS-100-W electrochemical apparatus from Bioanalytical systems, Inc. \( \text{nBu}_4\text{N}^+\text{PF}_6^- \) (0.1 mol/L in acetonitrile) was used as the supporting electrolyte. A platinum wire was used as the counter electrode. A silver wire was used as a quasi-reference electrode and is calibrated with ferrocene dissolved in the electrolyte solution. The electrodes were polished and washed with deionized water and acetone before each test. The working electrode was a glassy carbon rod with a plastic cladding, which render a flat area large enough for drop-casting thin films. Polymer films were prepared by casting one drop of a dilute polymer
solution (~0.1 mg/mL) onto the working electrode and allowing it to dry. Each polymer sample was measured at least three times, and the average data were reported. The LUMO and HOMO energy levels were estimated from the onset potentials of the reduction or oxidation waves, respectively. The SCE potential was taken to be 4.4 eV below the vacuum energy level.

Ultraviolet-visible (UV-Vis) spectra were acquired on a Hewlett-Packard 8453 diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained on a HORIBA Jobin Yvon NanoLog spectrofluorometer. Polymer films were prepared by spin-coating chloroform solutions on quartz wafers for the UV-Vis measurements and on silicon wafers for the PL measurements. A quartz cuvette was used for solution samples.

Size exclusion chromatography (SEC) was performed using a TOSOH EcoSEC HLC-8320 GPC instrument equipped with a differential refractometer. Two Varian Resipore columns (300 x 7.5 mm) were used in tandem as the stationary phase, and chloroform was used as the mobile phase at a flow rate of 0.5 mL/min at 45.0 ºC. Calibrations were conducted with polystyrene standards from Varian.

The fabrication and characterization of thin film transistors were done as follows. Thin film transistors with standard bottom-contact/bottom-gate device architecture was fabricated and tested under inert atmospheres. Silicon substrates with 200–300 nm thermal oxide and patterned gold source/drain electrodes were used. Channel widths and lengths were 800–1000 μm and 20–100 μm, respectively. Surface of silicon dioxide was treated with octyltrichlorosilane to minimize possible charge-trapping sites. The film of PHOT was deposited by spin-coating of its chloroform or dichlorobenzene solutions onto the substrates. Devices were then dried and annealed under inert conditions.
Thermogravimetric analysis (TGA) was carried out on a TGA Q500 V20.7 instrument (TA Instruments). The sample was heated at the rate of 5 °C/min under nitrogen protection. During the decomposition of PHOT, the sample expended dramatically and likely foamed. The escaped substance from the sample holder touched the interior housing of the sample holder. This always happened even when a minimal amount of 7 (5 mg) was used.

Wide angle X-ray diffraction (WAXD) was measured as follows. The samples were prepared by drop-casting the chloroform solution of PHOT (5 mg/mL) onto silver-plated aluminum foil. After evaporation under ambient conditions, the samples were annealed under nitrogen at the designated temperatures for 24 h. WAXD powder pattern was taken at room temperature with a Rigaku MultiFlex 2 kW tube-anode X-ray (Cu Kα radiation) generator coupled to a diffractometer. The samples were scanned at a 1°/min scanning rate. The peak positions were calibrated using silicon powder in the high-angle region (>15°) and silver behenate in the low-angle region (<15°). Background scattering was subtracted from the sample pattern.

Output ($I_{ds}$ vs. $V_{ds}$) and transfer ($I_{ds}$ vs. $V_{g}$) characteristics of the devices were measured using a HP4145B semiconductor parameter analyzer (Yokogawa Hewlett-Packard). Field-effect mobility was calculated from the standard equation for saturation region in metal-oxide-semiconductor field-effect transistors: 

$$I_{ds} = \mu(W/2L)C_i(V_g - V_t)^2,$$

where $I_{ds}$ is drain-source current, $\mu$ is field-effect mobility, $W$ and $L$ are the channel width and length, $C_i$ is the capacitance per unit area of the gate insulator, $V_g$ is the gate voltage, and $V_t$ is the threshold voltage.
Differential scanning calorimetry (DSC) was performed with a DSC Q2000 instrument (TA Instruments). The samples were sealed in a Hermetic Aluminum pan. The process was carried out in a quadruple cycle under nitrogen: first heating up, subsequent cooling down, second heating up and final cooling down, in the temperature range from 25 to 290 °C. The rate of heating and cooling was controlled as 10 °C/min. The glass transition temperature was determined from the middle point of the transition in the curve of the second cooling cycle.

Fabrication and Characterization of PV Cells were done as follows. ITO-coated glass substrates (10 Ω/square, Shanghai B. Tree Tech, P. R. China) were cleaned sequentially with acetone, deionized water and isopropyl alcohol in an ultrasonic bath, and completely dried in a vacuum oven at 120 °C. A 50 nm PEDOT:PSS layer was spin-coated on top of ITO and dried at 150 °C for 10 min under vacuum. The chloroform solutions of poly(3-alkanoylthiophene)s (PHOT) and PC_{71}BM (15 mg/mL and 30 mg/mL, respectively) were prepared and mixed to make a solution with PHOT/PC_{71}BM weight ratio of 1:1. The blend solution was filtered with a 0.45 μm PTFE filter and then spin-coated on top of the PEDOT:PSS layer in a glove box to make the active layer with a thickness of around 80 nm. The devices were annealed at (110 ± 10) °C on a hot plate for 5 min. The devices were loaded in a thermal evaporator (BOC Edwards, 306), where a cathode consisting of 1.0 nm lithium floride and 80 nm aluminum was deposited through a shadow mask under high vacuum (8×10^{-7} Torr). Five bulk heterojunction photovoltaic cells were produced per substrate, with an active area of 4.0 mm² each. The current density-voltage (J-V) curves were measured using a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard) under laboratory ambient air condition. AM1.5 illumination at 100
mW/cm² was provided by a filtered Xe lamp and calibrated by using an NREL-calibrated Si diode.

3.4.3 Synthesis

Synthesis of 1-(thiophen-3-yl)heptan-1-one (5).

Magnesium turnings (13.5 g, 563 mmol) and anhydrous diethyl ether (50 mL) were charged into a pre-dried 500 mL three-neck flask under nitrogen. The flask was placed in a water bath at room temperature. Iodine (0.54 g, 2 mmol) was added into the above mixture. 1-Bromohexane (74 mL, 527 mmol) dissolved in anhydrous diethyl ether (120 mL) was added dropwise into the flask while the reaction was vigorously stirred. After the addition was finished, the reaction was allowed to continue for another 2 h. The solution was then filtered into another pre-dried three-neck flask under nitrogen. The three-neck flask was placed in an ice bath. 3-Cyanothiophene (50 g, 458 mmol) dissolved in anhydrous diethyl ether (60 mL) was added dropwise into the above solution while it was stirred. The reaction was allowed to continue for 24 h at room temperature. Then, the solution was poured to a 1000-mL beaker charged with ice (75 g), ammonium chloride (30 g), and sodium chloride (30 g). The organic layer was decanted out, and the aqueous phase was extracted by diethyl ether (100 mL x 2). The combined organic phase was washed with a saturated sodium bicarbonate solution (150 mL) and a saturated saline solution (150 mL) and dried over anhydrous sodium sulfate. Distillation (85 °C/85 milliTorr) gave 5 as a colorless liquid, which slowly crystallized over a long time at room temperature (59.4 g, 66% yield). ¹H NMR (300 MHz, CDCl₃): δ 8.04 (dd, J = 3.0 and 1.2
Hz, 1 H), 7.56 (dd, \( J = 5.1 \) and 1.2 Hz, 1 H), 7.32 (dd, \( J = 5.1 \) and 3.0 Hz, 1 H), 2.874 (t, \( J = 2.5 \) Hz, 2 H), 1.73 (m, 2 H), 1.34 (m, 6 H), 0.90 (t, \( J = 6.6 \) Hz, 3 H). \(^{13}\text{C} \{^{1}\text{H}\} \text{NMR (75 MHz, CDCl}_3\): \( \delta 195.2, 142.7, 131.8, 127.3, 126.4, 40.2, 31.9, 29.2, 24.6, 22.7, 14.3.\}

Synthesis of 2-hexyl-2-(thiophen-3-yl)-5,5-dimethyl-1,3-dioxane (6).

Compound 5 (59.0 g, 301 mmol), 2,2-dimethylpropane-1,3-diol (45 g, 431 mmol), benzene (150 mL) and \( p \)-toluenesulfonic acid monohydrate (2.2 g, 13 mmol) were added into a 500 mL three-neck flask with a Dean-Stark apparatus. The mixture was refluxed for 24 h, during which time water was collected in the Dean-Stark apparatus and removed. Then, benzene was removed under vacuum, and the resulting oil was dissolved in diethyl ether (100 mL) and transferred into a separatory funnel. The ether solution was washed successively with a saturated sodium bicarbonate solution (150 mL) and a saturated saline solution (150 mL) and dried over anhydrous sodium sulfate. Distillation (68 °C/50 milliTorr) gave 6 as a colorless oil (59.4 g, 70% yield). \(^1\text{H} \text{NMR (300 MHz, CDCl}_3\): \( \delta 7.30 (dd, \( J = 5.1 \) and 3.0 Hz, 1 H), 7.19 (dd, \( J = 3.0 \) and 1.2 Hz, 1 H), 6.99 (dd, \( J = 5.1 \) and 1.2 Hz, 1 H), 3.47 (AB-spin system, 4 H), 1.74 (m, \( J = 2.5 \) Hz, 2 H), 1.36 (m, 2 H), 1.24 (m, 9H), 0.85 (t, \( J = 6.6 \) Hz, 3 H), 0.61 (s, 3 H). \(^{13}\text{C} \{^{1}\text{H}\} \text{NMR (75 MHz, CDCl}_3\): \( \delta 142.6, 127.4, 125.7, 123.3, 100.9, 72.0, 44.3, 32.0, 30.2, 29.6, 23.2, 22.8, 22.1, \) and 14.3.\}

Synthesis of 2-(2,5-dibromothiophen-3-yl)-2-hexyl-5,5-dimethyl-1,3-dioxane (7).

Compound 6 (29.3 g, 104 mmol), NBS (22.2 g, 125 mmol), and DMF (150 mL) were added into a 500-mL three-neck flask under nitrogen in a water bath. After the mixture was stirred for 72 h at room temperature, diethyl ether (200 mL) was added into the mixture. The organic phase was washed successively with a saturated sodium bicarbonate
solution (150 mL) and a saturated saline solution (150 mL) and dried over anhydrous sodium sulfate. Distillation (175 °C/50 milliTorr) gave 7 as a light yellow oil (40.6 g, 88.9%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 6.84 (s, 1 H), 3.44 (AB-spin system, 4 H), 1.74 (m, 2 H), 1.40 (m, 2 H), 1.24 (m, 9 H), 0.87 (t, \(J = 6.9\) Hz, 3 H), 0.67 (s, 3 H). \(^{13}\)C \(^1\)H NMR (75 MHz, CDCl\(_3\)): δ 140.8, 131.9, 111.3, 109.1, 100.7, 72.2, 42.5, 32.0, 30.0, 29.5, 23.0, 22.8, 22.1, 14.3.

Synthesis of 2-(5-bromothiophen-3-yl)-2-hexyl-5,5-dimethyl-1,3-dioxane (8b).

Compound 5 (2.13 g, 7.5 mmol) and NBS (1.61 g, 9.0 mmol) were successively added into a pre-dried 100 mL three-neck flask under nitrogen. The flask was placed in a water/ice bath. The mixture was dissolved in DMF (30 mL) and stirred for 8 h at 0 °C. A saturated sodium dicarbonate aqueous solution (50 mL) was added into the mixture. The aqueous solution was extracted with diethyl ether (20 mL x 3). The organic phase was combined and washed with saturated saline solutions (50 mL x 2) and dried over anhydrous sodium sulfate. After ether was removed by distillation, the resulting crude product was distilled under dynamic vacuum to give 8b as a colorless oil (2.32 g, 85% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.08 (d, \(J = 1.5\) Hz, 1 H), 6.94 (d, \(J = 1.8\) Hz, 1 H), 3.44 (AB spins, 4 H), 1.70 (m, 2 H), 1.33 (m, 2 H), 1.22 (m, 9 H), 0.85 (t, \(J = 6.6\) Hz, 3 H), 0.63 (s, 3 H).

Reaction of 7 and i-PrMgCl.

Compound 7 (0.540 g, 1.23 mmol) was loaded into a 25-mL Schlenk flask in a glove box and was dissolved in THF (10 mL). The flask was removed from the glove box and placed into a bath at a certain temperature from -40 °C to room temperature. i-PrMgCl (2.0 M solution in THF, 0.612 mL, 1.22 mmol) was injected into the flask with an air-
tight syringe under a stream of nitrogen. The reaction was kept at the desired temperature for several hours. Aliquots of the reaction mixture were withdrawn and quenched with methanol. After the volatile components were evaporated under reduced vacuum, the nonvolatile residual was analyzed by $^1$H NMR spectrum. The ratio of $8b$ and its regioisomer 2-(2-bromothiophen-3-yl)-2-hexyl-5,5-dimethyl-1,3-dioxane ($8a$) was determined by the areas of the peaks at $\delta$ 7.08 and 6.93 ppm for $8b$ and 7.24 and 6.87 ppm for $8a$. The assignment of the isomers was made based on the magnitude of the coupling constants (1.5 Hz and 5.7 Hz, respectively). The same method for product analysis was used when the reaction was performed in the presence of LiCl and 1,4-dioxane.

**General procedure of polymerization and isolation of polymer 10.**

All glass apparatus were dried in an oven prior to use. Air-tight syringes were used for addition of reagents and sampling the reaction mixture. All operations were carried out under nitrogen protection. Flamed dried LiCl (0.094 g, 2.22 mmol), anhydrous 1,4-dioxane (2 mL), and anhydrous THF (4 mL) were loaded into a 25 mL Schlenk flask in the glove box. $\text{t-PrMgCl}$ (2.0 M solution in THF, 2.1 mL, 4.15 mmol) was then added via a syringe. After the flask was stirred for 3 h in an ice/water bath, a solution of 7 (1.830 g, 4.16 mmol) in 6 mL THF was added. The reaction was stirred for another 7 h in ice/water bath. Next, the solvent was removed under vacuum. The solid residual was dissolved in 20 mL THF at 0 ºC. Then Ni(DPPP)Cl$_2$ (0.032 g) and THF (5 mL) was added successively into the above flask. The mixture was stirred at 0 ºC for 2 h and at 40 ºC for 1 day. Methanol was then added to quench the reaction. The solvent was removed the solid residual was extracted with a Soxhlet extractor with methanol and chloroform. The
product 10 (0.95 g, 81.7%) was collected from the chloroform extraction after removal of the solvent. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.18 (1 H), 3.40 (4 H), 1.94 (2 H), 1.44 (2 H), 1.25 (9 H), 0.87 (3 H), 0.65 (3 H). $^{13}$C $^1$H NMR (75 MHz, CDCl$_3$): $\delta$ 137.8, 133.4, 131.8, 101.2, 72.1, 43.5, 32.1, 30.1, 29.8, 23.2, 22.9, 22.3, 14.3. SEC against polystyrene standards: $M_n = 9,090, M_w/M_n = 1.70.$

In the experiments where the progress of the polymerization was monitored, an excess of 7 (1.1 eq vs $i$-PrMgCl) was added in order to use it as an internal reference for quantification. Small aliquots of the reaction mixture was withdrawn via a syringe periodically and quenched with methanol. After evaporation of methanol, the solid residual was extracted by CDCl$_3$, and the conversions were determined according to the $^1$H NMR spectrum integrations of the aromatic resonances belonging to 10, 8a, and 7. The same samples after dilution were used for SEC analysis.

Synthesis of polymer 11 (PHOT).

Polymer 10 (950 mg) was dissolved in chloroform (15 mL) and 1,4-dioxane (4 mL). TFA (3 mL) and water (6 mL) was added into the solution. The mixture was vigorously stirred at 40 ºC for 24 h. The volatile components were completely removed with a rotary evaporator. The solid residual was subjected to the above process again. If the reaction scale was larger, a third repetition might be necessary. The final solid residual was extracted with a Soxhlet extractor with methanol, hexanes and chloroform. The product (530 mg, 80%) was collected from the chloroform extracted after removal of the solvent. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.91 (s, 1 H), 2.96 (t, 2 H), 1.76 (m, 2 H), 1.34 (m, 6 H), 0.90 (t, 3 H). $^{13}$C NMR (300 MHz, CDCl$_3$): $\delta$ 197.2, 142.1, 136.1, 133.2, 131.5, 42.4, 31.9, 29.1, 24.5, 22.7, 14.2. SEC against polystyrene standards: $M_n = 7,939, M_w/M_n =$
1.74. Calcd for C₄₅₂H₅₇₁BrO₄₁S₄₁ (M = 8060.96): C, 67.25; H, 7.21%. Found: C, 66.87; H, 7.37%.

Synthesis of 2-hexyl-2-(thiophen-3-yl)-1,3-dithiolane (12).

5 (9.4 g, 48.0 mmol), benzene (150 mL), ethane-1,2-dithiol (5.1 g, 54.1 mmol), boron trifluoride diethyl etherate (1.5 g, 10.6 mmol) and p-toluenesulfonic acid monohydrate (1.1 g, 6.5 mmol) were added into a 300 mL three-neck flask with a Dean-Stark apparatus. The mixture was refluxed for 24 h, during which time water was collected in the Dean-Stark apparatus and removed. Then, benzene was removed under vacuum, and the resulting oil was dissolved in diethyl ether (100 mL) and transferred into a separatory funnel. The ether solution was washed successively with a saturated sodium bicarbonate solution (120 mL) and a saturated saline solution (120 mL) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO₂, 7:1 hexanes: dichloromethane) gave 12 as a colorless oil (11.9 g, 91% yield). ¹H NMR (300 MHz, CDCl₃): δ 7.38 (dd, J = 5.1 and 3.0 Hz, 1 H), 7.28 (dd, J = 3.0 and 1.2 Hz, 1 H), 6.14 (dd, J = 5.1 and 1.2 Hz, 1 H), 3.44 (m, 4 H), 2.32 (t, J = 6.0 Hz, 2 H), 1.29 (m, 8 H), 0.86 (t, J = 6.0 Hz, 3 H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 147.3, 127.0, 126.0, 122.2, 70.2, 44.9, 39.2 31.6, 29.3, 27.8, 22.5 and 14.0.

Synthesis of 1-(2,5-dibromo thiophen-3-yl)heptan-1-one (13).

7 (2.2 g, 5.0 mmol), DI water (3 mL), TFA (0.5 mL) and chloroform (6 mL) were added into a 100-mL single-neck flask under nitrogen in a water bath. After the mixture was stirred for 24 h at 50 °C, diethyl ether (60 mL) was added into the mixture. The organic phase was washed successively with a saturated sodium bicarbonate solution (50 mL) and a saturated saline solution (60 mL) and dried over anhydrous sodium sulfate.
Flash column chromatography (SiO$_2$, 7:1 hexanes: dichloromethane) gave 13 as a colorless oil (1.3 g, 74%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.31 (s, 1 H), 2.88 (t, $J = 4.8$ Hz, 2 H), 1.69 (m, 2 H), 1.33 (m, 4 H), 0.90 (t, $J = 6.0$ Hz, 3 H).

Synthesis of 2-(2,5-dibromothiophen-3-yl)-2-hexyl-1,3-dithiolane (14).

13 (7.0 g, 19.8 mmol), benzene (150 mL), ethane-1,2-dithiol (5.6 g, 59.4 mmol), boron trifluoride diethyl etherate (1.5 g, 10.6 mmol) and $p$-toluenesulfonic acid monohydrate (1.1 g, 6.5 mmol) were added into a 300 mL three-neck flask with a Dean-Stark apparatus. The mixture was refluxed for 24 h, during which time water was collected in the Dean-Stark apparatus and removed. Then, benzene was removed under vacuum, and the resulting oil was dissolved in diethyl ether (100 mL) and transferred into a separatory funnel. The ether solution was washed successively with a saturated sodium bicarbonate solution (120 mL) and a saturated saline solution (120 mL) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO$_2$, 6:1 hexanes: dichloromethane) gave 14 as a colorless oil (5.1 g, 60% yield). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.07 (s, 1 H), 3.35 (m, 4 H), 2.24 (t, $J = 6.0$ Hz, 2 H), 1.24 (m, 8 H), 0.85 (t, $J = 6.0$ Hz, 3 H).

Synthesis of 3-(1,1-difluoroheptyl)thiophene (15).

12 (0.46 g, 1.7 mmol), Deoxo-Fluor® (0.65 g, 2.9 mmol), dichloromethane (4 mL) and anhydrous ethanol (40 $\mu$L) were added into a 100 mL BOLA flask. The mixture was stirred at room temperature for 8 hours and then was warmed to 85 °C for 3 hours. The reaction was quenched with saturated aqueous sodium bicarbonate (10 mL). The mixture was extracted with diethyl ether (15 mL), washed with a saturated saline solution (20 mL) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO$_2$, 8:1 hexanes: dichloromethane) gave 15 as a colorless oil (0.32 g, 79%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.06 (s, 1 H), 3.07 (m, 4 H), 2.22 (t, $J = 6.0$ Hz, 2 H), 1.24 (m, 8 H), 0.85 (t, $J = 6.0$ Hz, 3 H).
hexanes: dichloromethane) gave 15 as a colorless oil (0.08 g, 22% yield). A good $^1$H NMR spectrum was not got, but its $^{19}$F NMR spectrum was clean. $^{19}$F NMR (CDCl$_3$) : $\delta$ $-90.0$ (t, $J = 16.3$ Hz, 2F). This result is consistent with the literature value of (1,1-difluoroalkyl)-thiophenes.$^{276}$
CHAPTER IV
ATTEMPT OF SYNTHESIS OF GRAPHENE NANORIBBONS

4.1.1 Physical Properties of Graphene and Graphene Nanoribbons

Since the discovery by Novoselov and Geim,\textsuperscript{277} graphene has attracted significant attention as a novel two-dimensional (2-D) carbon allotrope. Its unique intrinsic properties are different from the conventional three-dimensional (3-D) materials. The widespread fascination about this 2-D atomic thin sheet arises from its extraordinary charge carrier mobility, mechanical strength and elasticity.\textsuperscript{278-280} However, due to the lack of a bandgap, graphene has limited applications to optical and electronic areas.\textsuperscript{281}

Graphene nanoribbon (GNR), defined as narrow strips of graphene with widths below 10 nm, has finite bandgaps and is a semiconductor.\textsuperscript{282,283} The extraordinary charge mobility and the small size in comparison to the scaling limit of the complementary metal–oxide–semiconductor (CMOS) devices\textsuperscript{284,285} make the semiconducting GNRs the suitable materials for microelectronic and optoelectronic applications.\textsuperscript{249,286}

However, to use GNRs for building functional devices, the bandgap must be precisely controlled. The bandgap of GNR is a keen topic of theoretical investigations in the past decade. A number of studies have demonstrated that the bandgap of GNRs is depending on not only the ribbon width but also the topography and edge structure.
GNRs can be either in zig-zag or arm-chair configuration (Scheme 4.1). GNRs can be divided into three subclasses in arm-chair configuration based on the topological connection of the conjugated \( \pi \)-electron system.\textsuperscript{287,288} The bandgap gradually decreases with the increase of ribbon width within each subclass,\textsuperscript{174,175} and the change in bandgap is abrupt and substantial across the topological subclasses. For example, poly(peri-naphthalene) (PPN) belongs to the subclass with the lowest bandgap, and poly(peri-anthracene) (PPA) belongs to the subclass with the highest bandgap (Scheme 4.1).

![Scheme 4.1 Arm-chair GNRs (PPN and PPA) and zig-zag GNR.](image)

Depending on the specific theoretical method used, the bandgaps of PPN and PPA are calculated to be 0.3–1.7 and 1.5–3.7 eV,\textsuperscript{289-293} respectively. Regardless of the method used, all theoretical studies predicted a difference of more than 1 eV in the bandgaps, with the narrower PPN having a lower bandgap than PPA. For various edge structures in between the arm-chair and zigzag edge (Scheme 4.1), they have been expected to generate different bandgap characteristics.\textsuperscript{291} In short, these theoretical studies demonstrate that atomic precision of the structure of GNRs must be achieved to control the bandgap. Recently, Mullen and co-workers have synthesized atomic precisely PPA\textsuperscript{292} ribbon and use angle-resolved photoelectron spectroscopy measurement to reveal its bandgap of 2.3 eV.\textsuperscript{294}
4.1.2 Successes in Fabrication and Synthesis of GNRs

A number of ways to make GNRs have been reported in the literature by using chemical, sono-chemical, lithographic methods and through the unzipping of carbon nanotubes (CNTs). These methods can all be categorized as top-down approaches. The GNRs synthesized from these methods have been proved to exhibit much higher charge carrier mobility than conjugated polymers or small molecules, which is around 40 to 1,500 cm$^2$/Vs (Figure 4.1). The on/off ratio of FET devices from these ribbons could exceed $10^4$. 

Recently, researchers at IBM and the University of California-Riverside have succeeded in making the narrowest ever GNR from top-down method in 2012. Each nanoribbon has a width of just 10 nm, which is theoretically predicted to have a bandgap of about 0.2 eV. However, up till now, the reliable production of GNRs smaller than 10 nm with chemical precision control remains a considerable challenge. More importantly, none of the above top-down methods have any control over the topography and edge structure. In addition to the poor structural control, GNRs made through these ways are
difficult or costly to scale up. As a result, chemical synthesis through bottom-up strategy is of the most interest (Scheme 4.2).

Scheme 4.2 Bottom-up synthesis of GNRs.

The accurate bottom-up synthesis of GNRs has recently been achieved by Mullen and co-workers in 2010.$^{312,313}$ They reported a simple way for the production of atomic precise GNRs with different topologies and widths, using surface-assisted coupling approaches. Polymer precursors are synthesized into linear or kinked polyphenylenes and undergo subsequent cyclodehydrogenation to afford the corresponding ribbon.$^{314,315}$ The width and topology are defined by the structure of the starting molecules with specific design. Take the synthesis of PPA for example (Scheme 4.3). 10,10$'$- dibromo-9,9$'$-bianthryl molecules are first sublimed and deposited onto a gold surface to remove the halogen atoms, yielding a biradical species. After thermal activation, the biradical species diffuse across the gold surface and undergo radical addition reactions to form linear polymer chains. These polyaromatic precursors are conformationally restricted on the gold surface. As a result, the intramolecular cyclodehydrogenation reaction becomes much more selective in further thermal activation step. A surface-assisted fully coupled PPA is established with evidences from scanning tunneling microscope (STM) and Raman spectrum shown in Figure 4.2.
Figure 4.2 A. Overview STM image after cyclodehydrogenation, showing straight N=7 GNRs. B. Raman spectrum of straight N=7 ribbons. Reproduced with permission from Ref. 292. Copyright 2010, Nature publishing group.

However, because the key steps in the synthesis are surface-assisted, the quantity of so-formed GNRs is limited that only one layer of GNRs on gold surface can be made. Further physical characterizations and device fabrication are not possible. Therefore, solution synthesis appears to be the only way to meet the strict requirement of atomic precision and is potentially scalable for practical applications.

In fact, successful bottom-up synthesis of graphene sheets or giant polycyclic aromatic hydrocarbons (PAHs) has paved ways for the synthesis of GNRs. Remarkable discotic PAHs have been synthesized using standard reactions in solution.$^{316-318}$
solution-phase synthesis that allows access of atomically defined GNRs in substantial quantity is urgent.

4.1.3 Development of Solution Synthesis of PAHs and Attempted Synthesis of GNRs

Early synthetic attempts of small graphene molecules date back to the pioneering works by Clar and Scholl at the beginning of last century. Subsequently, more efficient and milder reaction conditions as well as characterization techniques have been developed, leading to the expansion of graphene molecules. The most investigated molecules of this type are Hexa-\textit{peri}-hexabenzocoronene (HBC) and its derivatives, a discotic PAH consisting of 42 carbon atoms (Scheme 4.4). A number of experimental protocols have been developed for the oxidative dehydrogenation synthesis of HBCs. Of the many oxidizing system, Scholl reaction (Lewis acids and oxidants) using FeCl$_3$ and DDQ/H$^+$ or Sc(OTf)$_3$ (DDQ= 2,3-dichloro-5,6-dicyanobenzoquinone) appear to have met the most success. Functionalized HBC derivatives could be synthesized in solution with high yields (>90%) as shown in Scheme 4.4 and have been employed as advanced materials in varies applications from batteries and transistors to chemical sensors and solar cells.

Scheme 4.4 Two synthetic routes toward the HBC core molecule. (Functional groups around the HBC core are omitted for clarity.)
The protocol for the synthesis of HBC or graphene molecules has been applied to build GNRs from linear polyphenylene precursors. Mullen and co-workers develop a route which involves first synthesis of polyaromatic precursors and then stepwise dehydrogenative cyclization of these polyaromatic precursors via the Scholl reaction (Scheme 4.5). The aromatic groups bear side groups R (alkyl, alkoxy and etc.), which should engender solubility in common solvents and subsequently solution processability. Although other routes can be conceived, Mullen’s route appears the most feasible. One of the critical issue is to achieve high molecular weight precursor polymers, which could eventually deliver GNRs with a large aspect ratio.\(^\text{342}\)

![Scheme 4.5 GNR from polyaromatic precursor.](image)

A type of linear GNRs is achieved by oxidative cyclo-dehydrogenation of polymer containing hexaphenylbenzene subunits via Scholl reaction as shown in Scheme 4.6.\(^\text{297}\) The formation of the GNRs is confirmed by transmission electron microscopy (TEM) and STM (Figure 4.3). However, the \(^1\text{H\ NMR}\) spectrum of the ribbon have aromatic peaks in a broad envelop of chemical shifts (δ 7.0~7.9 ppm), indicating the incompletely fusion of phenyl rings. Estimation of cyclodehydrogenation efficiency from MALDI-TOF reveals an average number of 94%.
Despite the progress achieved in the bottom-up synthesis of graphene macro-molecules and GNRs by solution chemical methods, several drawbacks still need to be resolved. Intramolecular oxidative cyclo-dehydrogenations under Scholl reaction conditions suffer from intrinsic problems of reactivity and regioselectivity, and the mechanism is still not clear yet. For instance, the Scholl reaction of \( o \)-terphenyl gives a mixture of PAHs of various sizes as shown in Scheme 4.7 due to unfavorable intermolecular reactions.
Unlike atomic precise synthesis of PPA, the polyaromatic precursors are conformationally restricted on the gold surface and the intramolecular cyclo-dehydrogenation is much more selective (Scheme 4.3). To ensure 100% conversion of the intramolecular ring fusion product in solution, it is necessary to introduce some alkyl or alkoxy groups to block the active sites to suppress the intermolecular couplings (Scheme 4.8).\textsuperscript{343} The presence of alkoxy groups at the \textit{o,p}-positions also accelerates intramolecular ring fusion because of their electron-donating effect.\textsuperscript{343,346}

Furthermore, intramolecular side reactions should be taken into consideration as well. Polyphenylene precursor may not be graphenized due to incomplete reactions, unexpected migrations/rearrangements of precursors, or lack of regioselectivity.\textsuperscript{347-349} Different substitution and steric hindrance of the precursors also make the intramolecular Scholl reaction less predictable.\textsuperscript{342} Mullen group did try to synthesize the PPN derivative through a polyperylene polymer via Scholl reaction in 2002 (Scheme 4.9).\textsuperscript{350} By the careful design of the repeating units, the intermolecular side reactions are mostly suppressed by introduction of the bulky phenoloxy groups. However, only partial ring
fusions are observed with the formation of quarterylene units, which is deduced simply by UV-Vis absorption change.

Scheme 4.9 Attempted synthesis of PPN derivative.

It is not realized until their work toward the synthesis of terylene in 2006 that reveals the existence of another intramolecular side reaction (Scheme 4.10). Starting from naphthyl-perylene, a five-member ring is formed preferentially under the exact same Scholl condition as in Scheme 4.9. In short, both intramolecular and intermolecular side reactions should be taken into account.

Scheme 4.10 Intramolecular side reaction under Scholl reaction and the formation of a five-member ring.

To sum up, in view of the need for atomic precise GNRs of scalable quantities, it is highly desirable to further develop a solution synthesis of GNRs. This led to my attempt to make well-defined GNRs, especially the PPN derivative. The strategy is divided into two parts. First, the synthesis of PPN is attempted via intermolecular Scholl reaction directly with equivalent reactive site strategy but failed due to intermolecular side reactions. Afterwards, oligo-naphthalenes precursor with alkoxy groups capping the 2, 3,
6 and 7- positions have been synthesized via Suzuki polycondensation with the help of a highly reactive catalyst. The purpose of capping the 2, 3, 6 and 7-positions is mainly to prevent both intra-molecular and intermolecular side reactions and promote ring fusion. Different Scholl reactions have been tested on these oligomers for the intramolecular ring fusion to form the final GNRs. Model precursors with anthracene units have also been prepared and tested under various Scholl reactions.

4.2.1 Attempted Synthesis of PPN via Intermolecular Scholl Reaction

Compound 14 was chosen as the monomer (Scheme 4.11). 12 was synthesized using a modified route according to literature. The synthesis of PPN was first tried using 14 as monomer through Scholl reactions directly. By blocking the unwanted reactive sites using alkoxy substituents, the remaining reactive sites in the D2h symmetric 2, 3, 6, and 7-tetrasubstituted naphthalenes are all equivalent.

![Scheme 4.11 Synthesis of monomer 14.](image)

i. C6H13Br, K2CO3, KI, Methyl Ethyl Ketone, Reflux, 24 h
ii. C6H13ONa, DMF, CuBr, Reflux, 24 h

After treating with Scholl reagents like DDQ/H⁺ or Sc(OTf)₃ in dichloromethane at room temperature or 0 °C, the crude product contained much less aromatic resonances compared to alkyl hydrogen on side chains according to ¹H NMR spectrum. This indicated the consumption of monomers and the formation of highly conjugated macromolecules. However, MALDI-TOF spectra did not support the formation of the
expected GNRs, but usually with a very complicated spectrum. It should be pointed out that the use of 14 to form the all capped precursors did not absolutely exclude the undesirable intermolecular Scholl reaction in Scheme 4.12. This intermolecular reaction can be expected to be much sensitive to the steric congestion imposed by the 2, 3, 6 and 7-substituents and the adjacent naphthyl group. Structural errors caused by such intermolecular Scholl reactions can be expected to be rare, if exist at all, due to the steric and entropic factors. Practically, highly diluted condition might help to suppress this intermolecular side reaction, but experimental results with 100 times dilution did not show obvious improvement.

Scheme 4.12 Unfavorable intermolecular reaction.

4.2.2 Attempted Synthesis of PPN via Intramolecular Scholl Reaction

The precursors 15 could be prepared from 14 in about 78% yield (Scheme 4.13).

Scheme 4.13 Synthesis of monomer precursors 15.

i. NBS, CHCl₃, AcOH, 60 °C, 24 h

R=⁻C₆H₁₃
According to Mullen’s route, model compounds of polyaromatic precursors are prepared. Formation of graphene molecules are demonstrated with high efficiency and selectivity via Scholl reaction. Therefore, model compounds 16 and 17 had been prepared from 15 (Scheme 4.14) from Suzuki coupling reactions. As discussed in the previous sections, it was important to block all the possible reactive 2, 3, 6, 7- positions of naphthalene units to suppress both intramolecular and intermolecular side reactions. Therefore, model compounds 16 and 17 could not form the respective graphene molecules via various Scholl reactions.

Scheme 4.14 Synthesis of model compounds 16 and 17.

As the result, in order to further prevent all known side reactions as discussed above, the synthesis of PPN derivative have to be divided into two stages. A polymer precursor 18 should be first synthesized as shown in Scheme 4.15 in order to suppress both intramolecular and intermolecular side reactions. Additionally, all these alkoxy sites would promote the final ring fusion reaction for that they are regarded as activating groups of o,p- positions in Scholl reactions, even the resulting PAHs are steric hindered.
Scheme 4.15 Synthesis of polymer precursor 18. X and Y are functional groups.

Table 4.1 Failed polymerizations. (Isomers of monomers are omitted for clarity.)

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Catalysts</th>
<th>Solvents</th>
<th>Temp. and Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(dppp)Cl₂</td>
<td>THF</td>
<td>0 °C to reflux</td>
<td></td>
</tr>
<tr>
<td>Ni(dppe)Cl₂</td>
<td>THF/Dioxane</td>
<td>2 days</td>
<td></td>
</tr>
<tr>
<td>Ni(dppp)Cl₂</td>
<td>THF</td>
<td>0 °C to reflux</td>
<td></td>
</tr>
<tr>
<td>PdCl₂</td>
<td>Dioxane</td>
<td>2 days</td>
<td></td>
</tr>
<tr>
<td>NiBr₂</td>
<td>DME</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(COD)₂</td>
<td>THF</td>
<td>r.t. to reflux</td>
<td></td>
</tr>
<tr>
<td>Ni(COD)₂</td>
<td>DMF</td>
<td>3 days</td>
<td></td>
</tr>
<tr>
<td>Pd(PPh₃)₄</td>
<td>THF</td>
<td>60 °C to reflux</td>
<td></td>
</tr>
<tr>
<td>Pd(OAc)₂</td>
<td>DME</td>
<td>3 days</td>
<td></td>
</tr>
<tr>
<td>Pd₂(DBA)₃</td>
<td>Toluene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
However, the synthesis of polymer 18 was not easy, even the oligomers were hard to make. A number of polymerizations with various monomers, catalysts, solvents, temperature and reaction time were tested as summarized in Table 4.1. For all these reactions, $^1$H NMR spectrum showed negligible formation of oligomers. MALDI-TOF analysis confirmed that only very limited amount of dimer and trimer were formed.

Recently, Yokozawa group has reported the synthesis of polyphenylenes via Suzuki coupling chain-growth polycondensation using a highly reactive initiator PhPdP($t$-Bu)$_3$Br as described in Chapter I. Different from other commonly used catalysts such as Pd(PPh$_3$)$_4$, only one bulky phosphine ligand is bonding to the metal center due to steric hindrance. The Pd center of this special catalyst has 14 electrons, 2 electrons fewer than using other ligands. It renders this special initiator less stable and much more reactive.

19 were synthesized from 15 after lithiation, substitution with B(OMe)$_3$ and hydrolysis steps and purified by recrystallization. Upon treating 19 with PhPdP($t$-Bu)$_3$Br and additives (Scheme 4.16), formation of oligomer precursors 18 was observed. $^1$H NMR spectrum (Figure 4.4), GPC and MALDI-TOF spectrum (Figure 4.5) all support the formation of oligomers.

![Scheme 4.16 Synthesis of polymer precursor using PhPdP($t$-Bu)$_3$Br as initiator.](image)

113
Although oligomers 18 were successfully formed, the 30% overall conversion was still low. One of the main reasons was that monomers 19 were unreactive and not stable under the reaction condition. It was found that about 50% monomers would be decomposed under the same condition except the addition of initiator. The change of boronic acid groups of 19 into boronic ester groups had been tested to increase the
stability of the monomers. However, these molecules were still not stable and apparently less reactive, resulting in a similar or lower overall yield. After column separation, molecules smaller than trimer were removed. The highest molecular weight of the oligomers could be up to 9,000 from MALDI-TOF analysis. As discussed above, the intramolecular and intermolecular side reactions would be essentially suppressed for these oligomers.

Further ring fusion reactions were tested based on these oligomers. However, no expected ribbons were identified after various Scholl reactions or other special conditions (see experimental section). Usually the residue was too complicated to interpret or the starting oligo-naphthalenes were still intact after the reaction. Mullen group has proved that the energy bandgap of rylene decreases with increasing naphthalene units, and it obeyed the one-particle-in-the-box behavior (i.e., $E \propto L^{-2}$, where $E$ is the energy gap and $L$ is the length of the molecule in the longest dimension).\textsuperscript{355} Hexarylene with six repeating naphthalene units already showed a UV-Vis maximum absorption peak around 900 nm. However, no absorption peaks corresponding to the formation of rylene units were observed in the NIR region. \textsuperscript{1}H NMR and MALDI-TOF spectra did not support any expected GNR.

4.2.3 Attempted Synthesis of PPA Model Compounds

Although very few researches had been devoted to the synthesis of GNRs with anthracene units to form PPA ribbons, reactions towards bisanthene and teranthene using solution chemistry were reported.\textsuperscript{356,357} However, the synthetic routes involved are quite
complicated which could be more than twenty steps. Hence, it will be interesting to develop the synthesis of these ribbons via simple chemistry like Scholl reactions.

Several model compounds 20-23 with anthracene units and its boron/nitrogen derivatives were synthesized as shown in Scheme 4.17. It should be noticed that the 9, 10- positions of anthracene unit were quite sensitive to Scholl condition. For example, directly treating 9,10'-bianthracene with Scholl reagents led to no ring fusion to PAH of bisanthene, but 10,10'-dichloro-9,9'-bianthracene as a clean product (See experimental section). As the result, these active sites should be blocked in advance.

![Scheme 4.17 Synthesis of different model precursors.](image)

The above model precursors were synthesized via nucleophilic substitution or metal-catalyzed coupling reactions. Subsequently, these molecules were subjected to various
Scholl conditions like DDQ/H⁺, DDQ/Sc(OTf)₃, FeCl₃/MeNO₂/CH₂Cl₂, AlCl₃/CuCl₂ or special conditions like I₂/toluene, K/THF and NaO(t-Bu)/DBN/ethanolamine. However, no expected fully coupled products were found after all these reactions. This might be attributed to the low reactivity of the molecules themselves and side reactions caused by the uncapped 2, 3, 6, 7- positions of the anthracene subunits. As pointed out by King and co-workers in Scheme 4.18, a rearrangement reaction could also complicate the outcome of the Scholl reactions. Additionally, although the PPA GNR made by Mullen and co-workers with anthracene units as building blocks is stable in atmosphere, small graphene molecules like teranthene is proved to be unstable and have a half-life only about one day.

Scheme 4.18 Carbocation rearrangement of anthracenes.

Recently, Yamaguchi and co-workers reported the synthesis of a boron-doped nanographene (Scheme 4.19). The precursor has a similar backbone structure with 20. The 9 positions of anthracene units are protected by the bulky mesityl groups at 1,8- positions to suppress the chlorination from FeCl₃. 4,5- positions are activated by electron-donating groups at para- positions. The α-H of diborapentacene also has higher reactivity compared to that of diboraanthracene in 20. These two improvements lead to the yield of the air-stable boron-doped nanographene as a deep purple solid, which has good solubility in chlorinated solvents. Its structure has been characterized by NMR spectroscopy (Figure 4.6), mass spectrometry and X-ray crystallography.

An = anthryl; E = alkyl and alkoxy.

Scheme 4.18 Carbocation rearrangement of anthracenes.
4.3 Conclusions

Several precursors to GNRs with naphthalene and anthracene units were synthesized. However, the solution ring fusion chemistry was not selective. Without capping all the 2, 3, 6, and 7-positions, intermolecular couplings would inevitably happen, together with the other possible intramolecular side reactions like carbocation rearrangements and etc. Eventually, the all sites blocked oligo-naphthalenes were prepared to exclude both
intramolecular and intermolecular side reactions. These oligomers could only be made via Suzuki polycondensation with a highly reactive initiator. The low overall yield was because of the instability of the monomers under basic condition. However, upon treating with different Scholl reagents, no expected ribbons were formed from these oligonaphthalenes. This might be explained from the similar phenomenon that alkoxy-functionalized HBCs from the corresponding hexaphenylbenzene were not obtainable. Oxidative cyclization using Scholl reactions often led to variable results with byproducts due to quinine formation,360 alkoxy migration361 and indenofluorene formation.362,363

4.4.1 Materials

The anhydrous solvents, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(DPPP)Cl2), PdCl2, Pd(OAc)2, Ni(COD)2, hexanol, sodium, N-bromosuccinimide (NBS), tri-t-butyl phosphine, 1-bromohexane, tetrabutylammonium bromide, methyl ethyl ketone, potassium iodide, potassium carbonate, naphthalene-2,3-diol, naphthalene-2,7-diol, acetic acid, tin powder, isopropyl magnesium chloride (2.0 M in THF), t-BuLi in hexane (1.6 M in hexane), n-BuLi in hexane (1.6 M in hexane), 9,10-dibromoanthracene, bromine, and sodium bicarbonate, sodium chloride, concentrated hydrochloric acid, TFA, methane sulfonic acid, DDQ, 1,2-dichlorobenzene were purchased from Alfa Aesar, Aldrich or Acros. They were used without purification. Lithium chloride (LiCl) from Acros Organics was flame-dried under vacuum. Deuterated chloroform (CDCl3) and deuterated benzene (C6D6) were purchased from Cambridge Isotope Laboratories. CDCl3 was kept over molecular sieves, and C6D6 was stirred over a Na/K alloy, vacuum-
transferred, and stored in a glove box. FeCl₃ was purified by refluxing in thionyl chloride overnight and followed by removal of all the volatile. Nitromethane, nitrobenzene were stirred over CaH₂, distilled and stored in a storage flask. 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene²³⁰, 9,10'-bianthracene⁵³ and PhPdP(–Bu)₃Br⁸⁰ were synthesized according to the literatures.

4.4.2 Measurements

¹H and ¹³C NMR spectra were obtained on a Varian Mercury 300 MHz instrument. Chemical shifts were referenced internally using solvent peaks. Ultraviolet-visible (UV-Vis) spectra were acquired on a Hewlett-Packard 8453 diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained on a HORIBA Jobin Yvon NanoLog spectrofluorometer. Polymer films were prepared by spin-coating chloroform solutions on quartz wafers for the UV-Vis measurements and on silicon wafers for the PL measurements. A quartz cuvette was used for solution samples.

Size exclusion chromatography (SEC) was performed using a TOSOH EcoSEC HLC-8320 GPC instrument equipped with a differential refractometer. Two Varian Resipore columns (300 x 7.5 mm) were used in tandem as the stationary phase, and chloroform was used as the mobile phase at a flow rate of 0.5 mL/min at 45.0 ºC. Calibrations were conducted with polystyrene standards from Varian.

MALDI-TOF mass spectra were acquired with Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Dlatonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). All spectra were measured in positive reflection mode. The instrument was
calibrated using external polystyrene or PMMA standards at the molecular weight under consideration. A solution of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2- propenylidene]-malononitrile (DCTB, Santa Cruz Biotechnology, Inc., >99%) which was used as matrix was prepared in chloroform at a concentration of 20 mg/mL. Solutions of sodium trifluoroacetate or silver trifluoroacetate, which were used as cationizing salt, were prepared in methanol/chloroform (v/v= 1/3) at a concentration of 10 mg/mL. All the samples were dissolved in chloroform. Matrix and cationizing salt were mixed in a ratio of 10/1 (v/v). The sample preparation involved depositing 0.5 micro liter of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the samples to air-dry, depositing 0.5 micro liter of sample on the matrix spot, and adding another 0.5 micro liter of matrix and salt mixture on the dry sample spot. After evaporation of solvent, the target plate was inserted into the MALDI source. The laser was adjusted and attenuated to minimize undesired polymer fragmentation and to optimize the peak intensity.

4.4.3 Synthesis

Synthesis of 1,3,6-tribromonaphthalene-2,7-diol

Naphthalene-2,7-diol (10 g, 62 mmol) and acetic acid (250 mL) were added into a 500-mL three-neck flask under nitrogen. Bromine (10.5 mL, 205 mmol) was added dropwise through an equal-pressure addition funnel. The mixture was allowed to reflux for 60 hours. After cooled to room temperature, DI water (100 mL) was added and the solid was collected by filtering through a Büchner funnel. Drying under vacuum gave 1,3,6-tribromonaphthalene-2,7-diol as a white solid (21 g, 85%). $^1$H NMR (300 MHz,
Synthesis of 3,6-dibromonaphthalene-2,7-diol (12)

1,3,6-Tribromonaphthalene-2,7-diol (20 g, 50.4 mmol), acetic acid (200 mL) and tin turnings (9.6 g, 75.6 mmol) were added into a 500-mL three-neck flask under nitrogen. The mixture was allowed to reflux for 96 hours. After cooled to room temperature, DI water (200 mL) was added into the flask. The mixture was then filtered through a Büchner funnel. Drying under vacuum gave 12 as a white solid (13.8 g, 86%). 1H NMR (300 MHz, CDCl3): δ 7.89 (s, 1H), 7.87 (s, 2 H), 7.24 (s, 2 H), 5.67 (s, 2 H).

Synthesis of 2,7-dibromo-3,6-bis(hexyloxy)naphthalene (13)

3,6-Dibromonaphthalene-2,7-diol (12 g, 37.7 mmol), potassium carbonate (20.4 g, 150 mmol), tetrabutylammonium bromide (1.1 g, 3.4 mmol), 1-bromohexane (13.7 g, 83.0 mmol) and methylethylketone (120 mL) were added into a 300-mL three-neck flask under nitrogen. The mixture was allowed to warm to reflux overnight. After cooled to room temperature, the mixture was filtered through a Büchner funnel. The liquid phased was rotavapored to remove methylethylketone. The solid was extracted with ethyl acetate (120 mL). Then the organic phase was washed successively with a saturated sodium bicarbonate solution (100 mL) and a saturated saline solution (100 mL) and dried over anhydrous sodium sulfate. Recrystallization from hexanes/chloroform gave 13 as a yellow crystal (16.7 g, 91%). 1H NMR (300 MHz, CDCl3): 87.87 (s, 2 H), 7.01 (s, 2 H), 4.10 (t, J = 4.8 Hz, 4 H), 1.91 (m, J = 4.5 Hz, 4 H), 1.55 (m, 4 H), 1.39 (m, 8H), 0.93 (t, J = 4.5 Hz, 6 H).
Synthesis of 2, 3, 6, 7-tetrakis(hexyloxy)naphthalene (14)

Dry hexanol (70 mL) and sodium (2.3 g, 100 mmol) were successively added into a 250-mL Schlenk flask with vigorous stirring until bubbling ceased. 2,7-dibromo-3,6-bis(hexyloxy)naphthalene (15.0 g, 30.9 mmol), copper bromide (14.0 g, 73.3 mmol) and anhydrous DMF (15 mL) were added into the flask. The mixture was allowed to reflux overnight. After cooled to room temperature, DI water (100 mL) was added into the flask to quench the reaction. The mixture was extracted with chloroform (150 mL). Then the organic phase was washed successively with a saturated sodium bicarbonate solution (100 mL) and a saturated saline solution (100 mL) and dried over anhydrous sodium sulfate. Recrystallization from hexanes/chloroform gave 14 as a white or colorless crystal (12.4 g, 76%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.02 (s, 4H), 4.07 (t, \(J = 4.5\) Hz, 8 H), 1.88 (m, \(J = 4.2\) Hz, 8 H), 1.52 (m, 8 H), 1.37 (m, 16H), 0.93 (t, \(J = 4.2\) Hz, 12 H). \(^{13}\)C \{\(^1\)H\} NMR (75 MHz, CDCl\(_3\)): \(\delta\) 148.13, 124.5, 108.0, 69.1, 31.6, 29.2, 25.8, 22.6 and 14.0. \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)): \(\delta\) 7.13 (s, 4 H), 3.96 (t, \(J = 4.2\) Hz, 8 H), 1.81 (m, \(J = 5.1\) Hz, 8 H), 1.50 (m, 8 H), 1.30 (m, 16 H), 0.91 (t, \(J = 4.2\) Hz, 12 H). \(^{13}\)C \{\(^1\)H\} NMR (75 MHz, C\(_6\)D\(_6\)): \(\delta\) 148.9, 125.2, 108.3, 68.8, 31.8, 29.6, 26.1, 22.8 and 14.0.

Synthesis of 1,4-dibromo-2,3,6,7-tetrakis(hexyloxy)naphthalene and 1,5-dibromo-2,3,6,7-tetrakis(hexyloxy)naphthalene (15)

2,3,6,7-Tetrakis(hexyloxy)naphthalene (11.0 g, 20.8 mmol), NBS (8.2 g, 46.0 mmol), chloroform (40 mL) and acetic acid (15 mL) was added into a 100-mL flask. The solution was allowed to warm to 60 °C overnight. Then the mixture was extracted with diethyl ether (100 mL). The organic phase was washed successively with a saturated
sodium bicarbonate solution (100 mL), a saturated saline solution (100 mL) and dried over anhydrous sodium sulfate. Recrystallization from hexanes/dichloromethane gave 15 as a white crystal (13.3 g, 93%). These two isomers had identical $^1$H and $^{13}$C spectra in CDCl$_3$, but could be differentiated by solution NMR spectroscopy in C$_6$D$_6$. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.51 (s, 2 H), 4.13 (t, $J = 6.0$ Hz, 4 H), 4.08 (t, $J = 6.0$ Hz, 4 H), 1.89 (m, 8 H), 1.55 (m, 8 H), 1.39 (m, 16 H), 0.93 (t, $J = 4.5$ Hz, 12 H). $^{13}$C {$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ 151.2, 146.5, 125.2, 115.2, 107.7, 73.6, 68.8, 31.72, 31.57, 30.2, 29.2, 25.8, 22.66, 22.63, 14.09 and 14.02. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 7.81 (s, 1 H), 7.75 (s, 1 H), 4.21 (t, $J = 6.0$ Hz, 4 H), 4.11 (t, $J = 6.0$ Hz, 4 H), 3.91 (t, $J = 6.0$ Hz, 4 H), 3.81 (t, $J = 6.0$ Hz, 4 H), 1.89 (m, 8 H), 1.69 (m, 8 H), 1.35 (m, 48 H), 0.92 (m, $J = 6.0$ Hz, 24 H). $^{13}$C {$^1$H} NMR (75 MHz, C$_6$D$_6$): $\delta$ 150.5, 149.9, 147.8, 146.1, 124.8, 124.6, 114.5, 114.1, 106.7, 73.1, 72.3, 67.5, 67.4, 30.7, 30.5, 29.3, 28.1, 24.8, 24.7, 21.7, 21.6, 12.9 and 12.8.

Synthesis of 1-bromo-2, 3, 6, 7-tetrakis(hexyloxy)naphthalene

2,3,6,7-Tetrakis(hexyloxy)naphthalene (3.2 g, 6.1 mmol), NBS (1.2 g, 6.7 mmol), chloroform (40 mL) and acetic acid (15 mL) was added into a 100-mL flask. The mixture was allowed to warm to 45 °C overnight. Then the mixture was extracted with diethyl ether (100 mL). Then the organic phase was washed successively with a saturated sodium bicarbonate solution (100 mL) and a saturated saline solution (100 mL) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO$_2$, 7:1 hexanes: dichloromethane) gave 1-bromo-2,3,6,7-tetrakis(hexyloxy)naphthalene as a white solid (2.3 g, 63%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.46 (s, 1 H), 7.02 (s, 2 H), 4.15 (t, $J = 3.6$ Hz, 2 H), 4.08 (m, 6 H), 1.90 (m, $J = 4.5$ Hz, 8 H), 1.55 (m, 8 H), 1.39 (m, 16 H), 0.94 (t,
$J = 4.5 \text{ Hz, 12 H)}$. $^{13}\text{C} \quad \{^1\text{H}\}$ NMR (75 MHz, CDCl$_3$): $\delta$ 150.6, 149.3, 148.9, 145.1, 126.6, 123.2, 115.1, 107.9, 107.5, 107.2, 73.5, 69.02, 68.98, 68.8, 31.7, 31.59, 31.57, 31.56, 30.3, 29.3, 29.1, 25.8, 25.78, 25.74, 25.71, 22.64, 22.59, 14.05 and 13.98.

Synthesis of 2',3',6',7'-tetrakis(hexyloxy)-1,1':4',1''-ternaphthalene and 2',3',6',7'-tetrakis(hexyloxy)-1,1':5',1''-terbenzobenzene (16)

15 (1.35 g, 1.97 mmol), naphthalen-1-ylboronic acid (1.05 g, 6.1 mmol), Pd(PPh$_3$)$_4$ (30 mg), potassium carbonate (510 mg, 3.75 mmol) and anhydrous THF (15 mL) were loaded into a 25 mL Schlenk flask in the glove box. Under nitrogen, degassed water (1 mL) was added via a syringe. The mixture was refluxed for 3 days. The solvent was removed under vacuum. The solid residual was dissolved in 30 mL ethyl acetate and washed successively with water (20 mL), a saturated sodium bicarbonate solution (20 mL) and a saturated saline solution (20 mL) and dried over anhydrous sodium sulfate. The solvent was removed by rotavapor. Flash column chromatography (SiO$_2$, 7:1 hexanes: dichloromethane) gave 16 as a yellowish viscous liquid (1.09 g, 71%). The $^1$H NMR spectrum was hard to interpret due to the existence of regio- and configurational-isomers. MALDI-TOF confirmed the structure by m/z 780.54 [M]$^+$ (calcd. m/z = 780.51).

Synthesis of 2,7-bis(hexyloxy)naphthalene

Naphthalene-2,3-diol (5 g, 31 mmol), potassium carbonate (20.4 g, 150 mmol), tetrabutylammonium bromide (1.1 g, 3.4 mmol), 1-bromohexane (11.3 g, 68 mmol) and methyl ethyl ketone (120 mL) were added into a 300-mL three-neck flask under nitrogen. The mixture was allowed to reflux overnight. After cooled to room temperature, the
mixture was filtered through a Büchner funnel. The liquid phased was rotavapored to remove methyl ethyl ketone. The solid was extracted with ethyl acetate (120 mL). The organic phase was washed successively with a saturated sodium bicarbonate solution (100 mL) and a saturated saline solution (100 mL) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO₂, 7:1 hexanes: dichloromethane) gave 2,7-bis(hexyloxy)naphthalene as a yellow oil (9.1 g, 89%). ¹H NMR (300 MHz, CDCl₃): δ 8.26 (m, 4 H), 7.57 (m, 4 H), 4.13 (t, J = 6.6 Hz, 4 H), 1.92 (m, 4 H), 1.58 (m, 4 H), 1.39 (m, 8 H), 0.94 (t, J = 6.9 Hz, 6 H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 150.1, 130.2, 127.2, 126.9, 116.4, 74.5, 31.7, 30.2, 25.7, 22.6 and 14.0.

Synthesis of 1-bromo-2,7-bis(hexyloxy)naphthalene

2,3-Bis(hexyloxy)naphthalene (6.2 g, 18.9 mmol), NBS (7.40 g, 41.6 mmol), acetic acid (15 mL) and chloroform (50 mL) were added into a 100 mL flask. The mixture was warmed to 50 °C and stirred for overnight. Diethyl ether (60 mL) was added into the mixture. The organic phase was washed successively with a saturated sodium bicarbonate solution (150 mL) and a saturated saline solution (50 mL) and dried over anhydrous sodium sulfate. Recrystallization from hexanes/chloroform gave 1-bromo-2,7-bis(hexyloxy)naphthalene as a white solid (7.7 g, 84%). ¹H NMR (300 MHz, CDCl₃): δ 7.65 (m, 2 H), 7.30 (m, 2 H), 7.10 (s, 1 H), 4.09 (t, J = 6.6 Hz, 4 H), 1.93 (m, 4 H), 1.55 (m, 4 H), 1.36 (m, 8 H), 0.91 (t, J = 6.9 Hz, 6 H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 149.5, 129.3, 126.2, 123.9, 107.9, 68.8, 31.6, 29.1, 25.7, 22.6 and 14.0.
Synthesis of (2,7-bis(hexyloxy)naphthalen-1-yl)boronic acid

1-Bromo-2,7-bis(hexyloxy)naphthalene (2.1 g, 5.16 mmol) was dissolved in THF (25 mL) in a 100 mL Schlenk flask. The mixture was cooled to -78 °C. 1.6 M n-BuLi (3.23 mL, 5.17 mmol) was added dropwise via syringe over 30 min. The homogeneous solution was allowed to gradually warmed up to room temperature and stirred for another 2 hours. After cooling to 0 °C, 1.0 M HCl (10 mL, 10 mmol) was added dropwise. The mixture was stirred vigorously overnight. The organic phase combined with ethyl acetate (75 mL) was washed successively with water (50 mL X2), a saturated sodium bicarbonate solution (100 mL) and a saturated saline solution (100 mL) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO$_2$, 3:1 hexanes: dichloromethane) gave (2,7-bis(hexyloxy)-naphthalen-1-yl)boronic acid as a waxy yellowish solid (0.69 g, 36%). This compound was not stable in air. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$8.35 (s, 1 H), 7.84 (d, $J$ = 9.0 Hz, 1 H), 7.67 (d, $J$ = 9.0 Hz, 1 H), 7.10 (d, $J$ = 9.0 Hz, 1 H), 7.07 (d, $J$ = 9.0 Hz, 1 H), 4.22 (t, $J$ = 6.0 Hz, 2 H), 4.12 (t, $J$ = 6.0 Hz, 2 H), 1.87 (m, 4 H), 1.55 (m, 4 H), 1.37 (m, 8 H), 0.92 (t, $J$ = 6.9 Hz, 6 H).

Synthesis of 2,2',2'',3',6',7',7'',7''-octakis(hexyloxy)-1,1':4',1''-ternaphthalene and 2,2',2'',3',6',7',7'',7''-octakis(hexyloxy)-1,1':5',1''-terbenzobenzene (17)

15 (1.75 g, 2.55 mmol), (2,7-bis(hexyloxy)naphthalen-1-yl)boronic acid (2.23 g, 6.0 mmol), Pd(PPh$_3$)$_4$ (34 mg), potassium carbonate (580 mg, 4.26 mmol) and anhydrous THF (15 mL) were loaded into a 25 mL Schlenk flask in the glove box. Under nitrogen, degassed water (1 mL) was added via a syringe. The mixture was refluxed for 3 days. The solvent was removed under vacuum. The solid residual was dissolved in 30 mL ethyl
acetate and washed successively with water (20 mL), a saturated sodium bicarbonate solution (20 mL) and a saturated saline solution (20 mL) and dried over anhydrous sodium sulfate. The solvent was removed by distillation. Flash column chromatography (SiO₂, 7:1 hexanes: dichloromethane) gave 17 as a yellowish viscous liquid (1.87 g, 62%). The ¹H NMR spectrum was hard to interpret due to the existence of regio- and configurational-isomers. MALDI-TOF confirmed the structure by m/z 1180.88 [M]⁺ (calcd. m/z = 1180.87).

Synthesis of (4-bromo-2,3,6,7-tetrakis(hexyloxy)naphthalen-1-yl)boronic acid and (5-bromo-2,3,6,7-tetrakis(hexyloxy)naphthalen-1-yl)boronic acid (19)

15 (2.302 g, 3.35 mmol) was dissolved in THF (25 mL) in a 100 mL Schlenk flask. The mixture was cooled to -78 °C. 1.6 M n-BuLi (2.10 mL, 3.36 mmol) was added dropwise via syringe over 30 min. The homogeneous solution was then allowed to gradually warmed up to room temperature and stirred for another 2 hours. After cooling to 0 °C, 1.0 M HCl (10 mL, 10 mmol) was added dropwise. The mixture was stirred vigorously overnight. Then the organic phase combined with ethyl acetate (75 mL) was washed successively with water (50 mL ×2), a saturated sodium bicarbonate solution (100 mL) and a saturated saline solution (100 mL) and dried over anhydrous sodium sulfate. Recrystallization from hexanes/ether gave 19 as a white solid (0.94 g, 43%). ¹H NMR (300 MHz, CDCl₃): δ 8.25 (s, 1 H), 7.64 (s, 1 H), 6.57 (s, 2 H), 4.11 (m, 8 H), 1.88 (m, 8 H), 1.55 (m, 8 H), 1.38 (m, 16 H), 0.93 (m, 12 H).

General Procedure of Polymerization and Isolation of Oligomer 18

19 (230 mg, 0.353 mmol), Cs₂CO₃ (400 mg, 1.22 mmol), PhPdP(⁻Bu)₃Br (8 mg, 0.017 mmol) and anhydrous THF (5 mL) were loaded into a 25 mL Schlenk flask in the
glove box. Under nitrogen, degassed water (1 mL) was added via a syringe. The mixture was stirred at 60 °C for 2 days. The solvent was removed under vacuum. The solid residual was dissolved in 30 mL ethyl acetate and washed successively with water (20 mL), a saturated sodium bicarbonate solution (20 mL), a saturated saline solution (20 mL X2) and dried over anhydrous sodium sulfate. The solvent was removed by distillation. The solid was loaded on a silica gel. 10:1 hexanes: dichloromethane was first used to wash off small molecules, and the oligomers were collected by rinsing with 2:1 hexanes: dichloromethane. The 1H NMR spectrum was hard to interpret due to the existence of regio- and configurational-isomers. Both GPC and MALDI support the formation of oligomers with highest molecular weight up to 9,000.

General Procedures of Ring-fusion and Isolation of 18

Method A. 18 (1 equiv) was dissolved in dichloromethane (10 mL) in a 25 mL Schlenk flask. A constant stream of nitrogen was bubbled into the solution via a syringe. A solution of FeCl₃ or MoCl₅ (4 equiv) in anhydrous nitromethane was added dropwise. Throughout the whole reaction, nitrogen stream was bubbled through the mixture to remove the HCl generated in situ. The reaction was stirred overnight and quenched by adding methanol (20 mL). The mixture was extracted with dichloromethane and concentrated. After removal of the solvent, a black solid was formed. If needed, the residue was further purified by column chromatography (chloroform:hexanes= 3:1).

Method B. 18 (1 equiv), Sc(OTf)₃ (1.5 equiv) and DDQ (1.5 equiv) were dissolved in 10 mL anhydrous toluene, nitromethane or nitrobenzene. The mixture was stirred at 110 °C for 24 h under nitrogen. After cooling to room temperature, the mixture was poured
into water and the product was extracted with THF. The organic layer was separated. The solvent was removed under reduced pressure to give a black residue. If needed, the residue was further purified by column chromatography (chloroform:hexanes= 3:1).

Method C. \textbf{18} (1 equiv), AlCl$_3$ (2 equiv) and CuCl$_2$ (2 equiv) were dissolved in chloroform (10 mL) in a 25 mL Schlenk flask. The reaction was stirred overnight and quenched by addition of methanol (20 mL). The mixture was extracted with dichloromethane and concentrated. The solvent was removed under reduced pressure to give a black residue.

Method D. \textbf{18} (1 equiv), AlCl$_3$ (2 equiv) and chlorobenzene (50 equiv) were flushed with nitrogen and stirred in a 25 mL Schlenk flask at 80 °C for 12 h. The mixture was cooled to room temperature and quenched with diluted HCl (10%, 15 mL). The resulting two-phase system was cooled and filtered under suction. The precipitate from the filter and the reaction flask were rinsed with dichloromethane. The solid product was collected from the filter paper and dried under vacuum.

Method E. \textbf{18} (1 equiv), methane sulfonic acid (MSA, 5 equiv) or trifluoro- acetic acid (TFA, 5 equiv) and 2,3-dichloro-5,6- dicyanobenzoquinone (DDQ, 1.5 equiv) were dissolved in 10 mL anhydrous dichloromethane, nitrobenzene or dichlorobenzene (DCB). The mixture was stirred at room temperature or at 110 °C for 24 h under nitrogen. After cooling to room temperature, the mixture was poured into water and the product was extracted with ethyl acetate. The organic layer was separated. The solvent was removed.
under reduced pressure to give a black residue. If needed, the residue was further purified by column chromatography (chloroform:hexanes = 3:1).

Method F. 18 (1 equiv), potassium tert-butoxide (3 equiv), DBU (3 equiv) and ethanolamine (4 mL) were added in a 25 mL Schlenk flask. The mixture was heated to 140 °C for 12 h. Then the same amount of potassium tert-butoxide, DBU and ethanolamine were added and the mixture was kept at 140 °C for another 12 h. After cooled to room temperature, the mixture was poured into 1M HCl (50 mL), filtered and washed with DI water. The dark solid was collected.

Method G. 18 (1 equiv) and freshly cut potassium (10 equiv) were dissolved in THF (15 mL) in a 25 mL storage flask. The mixture was stirred vigorously at 90 °C for 24 h. The reaction was quenched by addition of an excess of iodine solution in THF. The mixture was poured into water (75 mL) and extracted with ethyl acetate (15 mL X2). The organic phase was separated and dried under vacuum and the residue was collected. If needed, the residue was further purified by column chromatography (chloroform:hexanes = 3:1).

Synthesis of 9-bromo-10-hexylanthracene

9,10-Dibromoanthracene (4.66 g, 13.9 mmol) and anhydrous diethyl ether (30 mL) were mixed in a 100 mL Schlenk flask. The mixture was cooled to -78 °C. t-BuLi in hexane (1.6 M, 8.67 mL, 13.9 mmol) was added via a gas-tight syringe. 3 hours later, 1-bromohexane (2.52 g, 15.3 mmol) was added. The mixture was allowed to warm to room
temperature and stirred overnight. A saturated sodium bicarbonate aqueous solution (50 mL) was added into the mixture. The aqueous solution was extracted with diethyl ether (30 mL x 3). The organic phase was combined and washed with saturated saline solutions (50 mL x 2) and dried over anhydrous sodium sulfate. After ether was removed by distillation, the resulting crude product was recrystallized from chloroform/hexanes to give 9-bromo-10-hexylanthracene as a yellow solid (2.55 g, 54% yield). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.64 (d, $J = 9.0$ Hz, 2 H), 8.31 (d, $J = 9.0$ Hz, 2 H), 7.58 (m, 5 H), 3.61 (t, $J = 6.0$ Hz, 2 H), 1.86 (m, 2 H), 1.62 (m, 2 H), 1.43 (m, 4 H), 0.97 (t, $J = 6.0$ Hz, 3 H).

Synthesis of 5,10-bis(10-hexylanthracen-9-yl)-5,10-dihydroboranthrene (20)

9-Bromo-10-hexylanthracene (1.2 g, 3.52 mmol) and anhydrous THF (30 mL) were added into a 100 mL Schlenk flask. The mixture was cooled to -78°C. t-BuLi in hexane (1.6 M, 2.20 mL, 3.52 mmol) was added via a gas-tight syringe. The mixture was allowed to warm to room temperature and stirred overnight. 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene (0.58 g, 1.74 mmol) was added into the flask. The mixture immediately formed a bright red color solution together with lots of precipitates. After the mixture was stirred for another 8 hours, all volatile components were removed under vacuum. Recrystallization from ether/hexanes gave 20 as a red solid (0.25 g, 21%). 20 is not stable in air. $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 8.32 (d, $J = 8.0$ Hz, 4 H), 7.63 (d, $J = 8.0$ Hz, 4 H), 7.43 (m, 4 H), 7.33 (m, 4 H), 7.23 (m, 4 H), 7.15 (m, 4 H), 3.64 (t, $J = 6.0$ Hz, 4 H), 1.89 (m, 4 H), 1.62 (m, 4 H), 1.39 (m, 8 H), 0.88 (t, $J = 6.0$ Hz, 6 H).
Synthesis of 10,10'-dichloro-9,9'-bianthracene

9,10'-Bianthracene (100 mg, 0.28 mmol) and anhydrous chloroform (15 mL) were added into a 100 mL Schlenk flask. FeCl₃ (366 mg, 2.26 mmol) in anhydrous nitromethane (5 mL) was added dropwise over a period of 30 minutes. Then a stream of nitrogen was bubbled through the solution and the mixture was kept stirring vigorously for 8 hours. After quenching with methanol (10 mL), a saturated sodium bicarbonate aqueous solution (30 mL) was added into the mixture. The aqueous solution was extracted with diethyl ether (30 mL x 3). The organic phase was combined and washed with saturated saline solutions (50 mL x 2) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO₂, 8:1 hexanes: dichloromethane) gave 10,10'-dichloro-9,9'-bianthracene as a yellow solid (98 mg, 82% yield). The above procedure was under a typical Scholl reaction condition, but only chlorinated products were obtained. ¹H NMR (300 MHz, CDCl₃): δ 8.71 (d, J = 9.0 Hz, 4 H), 7.60 (t, J = 6.0 Hz, 4 H), 7.20 (t, J = 6.0 Hz, 4 H), 7.11 (d, J = 9.0 Hz, 4 H).

Synthesis of 10,10'-dibromo-9,9'-bianthracene

9,10'-Bianthracene (1.0 g, 2.8 mmol) and chloroform (40 mL) were added into a 100 mL flask. Bromine (1.0 g, 6.25 mmol) was added into the flask dropwise at 0 °C. Then the mixture was allowed to warm to room temperature and stirred overnight. A saturated sodium bicarbonate aqueous solution (30 mL) was added into the mixture. The aqueous solution was extracted with diethyl ether (30 mL x 3). The organic phase was combined and washed with saturated saline solutions (50 mL x 2) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO₂, 8:1 hexanes: dichloromethane) gave 10,10'-
dibromo-9,9'-bianthracene as a yellow solid (1.23 g, 85% yield). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.71 (d, $J = 9.0$ Hz, 4 H), 7.60 (t, $J = 6.0$ Hz, 4 H), 7.20 (t, $J = 6.0$ Hz, 4 H), 7.11 (d, $J = 9.0$ Hz, 4 H).

Synthesis of 9',10-dihexyl-9,10'-bianthracene (21)

9',10-Dibromo-9,10'-bianthracene (1.5 g, 2.9 mmol), Ni(DPPP)Cl$_2$ (0.10 g, 0.18 mmol) and anhydrous diethyl ether (40 mL) were added into a 250 mL Schlenk flask. Hexyl magnesium bromide$^{364}$ in diethyl ether (0.11 M, 40 mL, 4.4 mmol) was added into the flask via a cannula. The mixture was stirred overnight at room temperature. A saturated sodium bicarbonate aqueous solution (30 mL) was added into the mixture. The aqueous solution was extracted with diethyl ether (30 mL x 3). The organic phase was combined and washed with saturated saline solutions (50 mL x 2) and dried over anhydrous sodium sulfate. Flash column chromatography (SiO$_2$, 8:1 hexanes: dichloromethane) gave 21 as a yellow solid (0.66 g, 44% yield). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.49 (d, $J = 9.0$ Hz, 4 H), 8.19 (d, $J = 9.0$ Hz, 4 H), 7.49 (m, 4 H), 7.03 (m, 4 H), 3.64 (t, $J = 9.0$ Hz, 4 H), 2.05 (m, 4 H), 1.76 (m, 4 H), 1.38 (m, 8 H), 0.92 (t, $J = 6.0$ Hz, 6 H). $^{13}$C {$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ 136.1, 131.6, 129.4, 127.9, 125.2, 125.1, 124.7, 31.9, 31.7, 30.2, 28.5, 22.8 and 14.2.

Synthesis of 10,10''-dihexyl-9',10'-dihydro-9,9':10',9''-teranthracene (22)

9-Bromo-10-hexylanthracene (458 mg, 1.34 mmol), 9,10-dihydroanthracene (122 mg, 0.67 mmol), Sodium $t$-butoxide (200 mg), Palladium acetate (3 mg), tri-$t$-butyl phosphine (0.07 mL) and anhydrous THF (10 mL) were added into a 25 mL Schlenk flask. The mixture was microwave to 60 °C for 5 hours. After cooled to room temperature, the
solution was filtered by a short alumina column. Solvent was removed by distillation. The product 22 was hard to separate by flash column chromatography and was identified by NMR spectroscopy with a conversion around 50%. MALDI-TOF confirmed the structure by m/z 679.17 [M]+ (calcd. m/z = 679.19).

Synthesis of 5,10-di(acridin-10(9H)-yl)-5,10-dihydroboranthrene (23)

5,10-Dibromo-5,10-dihydroboranthrene (69 mg, 0.21 mmol), triethylamine (0.2 mL), 9,10-dihydroacridine (76 mg, 0.419 mmol) and toluene (10 mL) were added into a 25 mL Schlenk flask. The mixture was refluxed overnight. After cooled to room temperature, solvent was removed. The crude was a mixture and hard to separate. The product 23 was identified by the two new doublets around 4.0 ppm.
A series of Boron-containing conjugated polymers have been successfully synthesized and well characterized by means of $^1$H, $^{13}$C NMR spectroscopy, cyclic voltammetry, UV-Vis absorption, and photoluminescence quenching experiments. One of the polymers has been proved to be able to quench the photoluminescence of $rr$-P3HT, suggesting the possible charge separation and electron transfer from Boron-containing polymer to $rr$-P3HT.

Considering the stability and charge mobility are important features for conjugated polymers in photo-electron applications, a regioregular polythiophene (PHOT) with strong electron-withdrawing groups has been successfully synthesized. $^1$H, $^{13}$C NMR spectroscopies demonstrate the polymer has a regioregularity over 95%. Cyclic voltammetry results show PHOT has LUMO and HOMO levels both lowered by around 0.5 ev than $rr$-P3HT, indicating that it could be potentially used as an $n$-type material. However, WAXD indicates that PHOT lacks order in the $\pi$-stacking direction in the solid state. PHOT does not exhibit any electron-transport activity in FET devices, but a low average field-effect hole mobility. The lack of electron mobility and the relative low hole mobility in PHOT could be likely attributable to the lack of $\pi$-stacking order. Photovoltaic devices of PHOT and PC$_{71}$BM have a low power conversion efficiency.
To further increase the charge mobility of a conjugated polymer, a number of soluble GNRs are chosen as the synthetic targets. However, the successful ring-fusion reactions are not well-established and only Scholl reaction has been proved by Mullen’s group to be the most feasible. To prevent the possible intermolecular and intramolecular side reactions in Scholl reactions, oligo-naphthalenes capping the 2, 3, 6, and 7-positions are synthesized. The oligomers can be achieved through Suzuki polycondensation with a highly reactive initiator. Although various Scholl reactions have been tested, no expected ribbon has been achieved.
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300M $^1$H NMR spectrum of compound 5.
300M $^{13}$C NMR spectrum of compound 5 in CDCl$_3$. 
300M $^1$H NMR spectrum of compound 6.
300M $^{13}\text{C}$ NMR spectrum of compound 6.
300M $^1$H NMR spectrum of 8a in CDCl$_3$. 
300M $^1$H NMR spectrum of 7 in CDCl$_3$. 
300M $^{13}$C NMR spectrum of 7 in CDCl$_3$. 
$300\text{M}^1\text{H} \text{ NMR spectrum of compound 10 in CDCl}_3$. 
300M $^1$H NMR spectrum of compound 11 in CDCl$_3$. 
300M $^1$H NMR spectrum of 2-(2-bromo-5-iodothiophen-3-yl)-2-hexyl-5,5-dimethyl-1,3-dioxane in CDCl$_3$. 

168
300M $^1$H NMR spectrum of 2-hexyl-2-(thiophen-3-yl)-1,3-dithiolane in CDCl$_3$. 
300M $^{13}$C NMR spectrum of 2-hexyl-2-(thiophen-3-yl)-1,3-dithiolane in CDCl$_3$. 
300M $^1$H NMR spectrum of 3-(1,1-difluoroheptyl)thiophene in CDCl$_3$. 
300M $^{19}$F NMR spectrum of 3-(1,1-difluoroheptyl)thiophene in CDCl$_3$. 
300M $^1$H NMR spectrum of compound 13 in CDCl$_3$. 
$500\text{M }^1\text{H NMR spectrum of compound 14 in CDCl}_3$. 
300M $^{13}$C NMR spectrum of compound 14 in CDCl$_3$. 
$\text{300M} \, ^1\text{H NMR spectrum of 15 in CDCl}_3$. 
300M $^1$H NMR spectrum of 15 in C$_6$D$_6$. 

177
500M $^{13}$C NMR spectrum of 15 in CDCl$_3$. 
$500\text{M}^{13}\text{C NMR spectrum of 15 in C}_6\text{D}_6$. 
$300\text{M}^1\text{H NMR spectrum of 16 in CDCl}_3.$
300M $^1$H NMR spectrum of (2,7-bis(hexyloxy)naphthalen-1-yl)boronic acid in CDCl$_3$. 
300M $^1$H NMR spectrum of 17 in CDCl$_3$. 

$R = O_{C_6H_{13}}$
300M $^1$H NMR spectrum of 19 in CDCl$_3$. 
300M $^1$H NMR spectrum of 9,9'-bianthracene in CDCl$_3$. 
300M $^1$H NMR spectrum of 10,10'-dibromo-9,9'-bianthracene in CDCl$_3$. 
300M $^1$H NMR spectrum of 21 in CDCl$_3$. 
300M $^{13}$C NMR spectrum of 21 in CDCl$_3$. 
300M $^1$H NMR spectrum of 9-bromo-10-hexylanthracene in CDCl$_3$. 
400M $^1$H NMR spectrum of compound 20 in CDCl$_3$. 

189
300M $^1$H NMR spectrum of compound 22 in CDCl$_3$. 
300M $^1$H NMR spectrum of compound 23 in CDCl$_3$. 

191