Conjugated Materials for Organic Electronics

by

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Department of Chemistry
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Abstract

This thesis describes the design and synthesis of novel conjugated materials for applications in organic electronics. The first half of the thesis focuses on conjugated polymers to be used as p-type (hole-transporting) donor materials in organic solar cells. I was first interested in studying how the open-circuit voltage of an organic solar cell could be increased by lowering the HOMO level of the donor polymer via functional group substitution. I chose to study the benchmark poly(3-hexylthiophene) structure and substituted the 3-hexyl chain with a less-electron donating 3-thiohexyl group. In Chapter 2, I synthesized an equally proportioned diblock copolymer containing 3-hexylthiophene and 3-thiohexylthiophene blocks, and found that the open-circuit voltage of the block copolymer device was as high as that of the device containing only the lower HOMO polymer. This inspired me to investigate the minimum amount of the lower HOMO unit required to reach this maximum voltage and thus I synthesized a series of statistical copolymers, presented in Chapter 3. For this new system I was also interested in investigating the effect of polymer sequence on device performance and thus switched from a block to statistical architecture.

In the second half of the thesis, I focus on novel n-type (electron-transporting) materials based on arylene diimides. In chapter 4, I synthesized a one donor-two acceptor random terpolymer
containing naphthalene diimide (NDI) and perylene diimide (PDI) as the two electron-deficient units and 2,7-carbazole as the electron-rich unit. I varied the ratio of the two acceptor units and found that while the optical and electrochemical properties varied with acceptor composition, the composition dependence was not evident in device performance. Rather, any amount of the NDI monomer reduced the device efficiency to the value of the one donor-one acceptor NDI parent copolymer due to a pinning of the short-circuit current at the lowest value. In chapter 5, I studied the effect of the single atom substitution of oxygen with sulfur on the optoelectronic and self-assembly properties of a series of small molecule naphthalene diimides. The low LUMO levels and strong intermolecular interactions of these thionated molecules make them ideal candidates for use in n-channel organic thin film or micro/nanowire transistors.
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# Table of Contents

Abstract ........................................................................................................................................... ii
Acknowledgments ............................................................................................................................ iv
Table of Contents ............................................................................................................................ v
List of Tables ................................................................................................................................... ix
List of Figures .................................................................................................................................... x
List of Schemes ............................................................................................................................... xviii
List of Abbreviations ....................................................................................................................... xix

**Chapter 1: Introduction** ................................................................................................................ 1

1 Organic solar cells ......................................................................................................................... 1

2 Device architecture ....................................................................................................................... 1

3 Mechanism .................................................................................................................................... 2

4 Device parameters ........................................................................................................................ 3

4.1 Power conversion efficiency (PCE) .......................................................................................... 4

4.1.1 Short-circuit current density ($J_{sc}$) .................................................................................. 4

4.1.2 Open-circuit voltage ($V_{oc}$) ............................................................................................ 5

4.1.3 Fill factor ($FF$) ............................................................................................................... 5

4.2 Quantum efficiency .................................................................................................................. 6

4.2.1 Internal quantum efficiency (IQE) .................................................................................... 6

4.2.2 External quantum efficiency (EQE) ................................................................................... 6

5 Donor materials ............................................................................................................................ 6

5.1 Poly(phenylenevinylene)s (PPVs) ............................................................................................ 6

5.2 Poly(3-alkylthiophene)s (P3ATs) ............................................................................................. 7

5.2.1 Early regioregular P3AT synthesis ...................................................................................... 8

5.2.2 Kumada catalyst transfer polymerization ......................................................................... 9

5.2.3 P3HT in OSCs ................................................................................................................... 11

5.3 Donor-acceptor (D-A) copolymers ......................................................................................... 12

5.4 Small molecules ....................................................................................................................... 17
Chapter 2: Donor-Donor Block Copolymers .......................................................... 35

1 Statement of contributions.............................................................................. 35
2 Introduction ........................................................................................................ 35
3 Results and discussion.................................................................................... 38
   3.1 Design and calculations............................................................................. 38
   3.2 Synthesis ..................................................................................................... 40
   3.3 Solution-based characterization ............................................................... 42
   3.4 Solid-state characterization .................................................................... 45
   3.5 Device characterization .......................................................................... 50
4 Conclusions ...................................................................................................... 53
5 Experimental ..................................................................................................... 54
   5.1 General considerations .......................................................................... 54
   5.2 Instrumentation and methods ................................................................ 54
   5.3 Density functional theory calculations ................................................ 55
   5.4 Photovoltaic device fabrication and characterization .......................... 56
   5.5 Synthesis ................................................................................................... 56
6 References ........................................................................................................ 58

Chapter 3: Poly(3-hexylthiophene)-stat-(3-thiohexylthiophene) Statistical Copolymers..... 63

1 Statement of contributions.............................................................................. 63
2 Introduction ...................................................................................................... 63
3 Results and discussion.................................................................................... 64
   3.1 Synthesis ................................................................................................... 64
   3.2 Regioregularity and randomness .............................................................. 67
   3.3 Mechanism ................................................................................................ 72
   3.4 Absorbance spectroscopy ...................................................................... 75
Chapter 4: One Donor-Two Acceptor Random Terpolymers

1 Statement of contributions

2 Introduction

3 Results and discussion

3.1 Polymer design and synthesis

3.2 Variable temperature $^1$H NMR

3.3 Optical properties

3.4 Electrochemical properties

3.5 Photovoltaic properties

4 Conclusions

5 Experimental

5.1 General considerations

5.2 Instrumentation and methods

5.3 Photovoltaic device fabrication and characterization

5.4 Synthesis

6 References

Chapter 5: Thionated Naphthalene Diimides

1 Statement of contributions

2 Introduction

3 Results and discussion

vii
Chapter 6: Summary and Outlook

1 Conclusions and future work ................................................................. 140
2 References ............................................................................................... 144
Appendices .................................................................................................. 146
List of Tables

Table 2.1 HOMO and LUMO Energy Levels and Electrochemical and Optical Bandgaps of P3HT, P3THT and P3THT-b-P3HT (in eV relative to vacuum) .................................................................................................................. 48

Table 2.2 Photovoltaic Properties of Binary and Ternary Blend BHJ Solar Cells with Different Donor Components.\textsuperscript{\text{a,b}} .................................................................................................................................................. 53

Table 3.1 Properties of P3HT-s-P3THT Statistical Copolymers .......................................................................................................................... 65

Table 3.2 Photovoltaic Properties of P3HT-s-P3THT:PC\textsubscript{71}BM Solar Cells at Different A:B Ratios.\textsuperscript{\text{a}} ........................................................................................................................................ 79

Table 4.1 Properties of PC-PDI-NDI Copolymers ........................................................................................................................................... 93

Table 4.2 Solid-State Absorption and Electrochemical Properties of PC-PDI-NDI Copolymers. .................................................................................................................................................. 97

Table 4.3 Solution Fluorescence Properties of PC-PDI-NDI Copolymers ........................................................................................................... 100

Table 4.4 Photovoltaic Properties of PBDTTT-C:PC-PDI-NDI Solar Cells ........................................................................................................ 103

Table 5.1 Optical Properties of P-S4 .............................................................................................................................................................. 119

Table 5.2 Electrochemical Properties of P-S3 .............................................................................................................................................. 121

Table 5.3 Crystallographic Data for P, cis-S2, trans-S2, and S3 ..................................................................................................................... 124

Table 5.4 Intermolecular Distances in P, cis-S2, trans-S2, and S3 ..................................................................................................................... 126
List of Figures

**Figure 1.1** Schematic of bilayer (left) and bulk heterojunction (right) device architectures (layers not to scale). ................................................................................................................................. 2

**Figure 1.2** Photoexcitation and charge transfer mechanism in a donor acceptor blend .............. 3

**Figure 1.3** Representative $J-V$ curve (left) and EQE spectrum (right) for an organic solar cell... 4

**Figure 1.4** Chemical structures of MEH-PPV and MDMO-PPV. ...................................................... 7

**Figure 1.5** Diad linkages of 3-substituted thiophenes ........................................................................ 7

**Figure 1.6** Molecular orbital interactions of donor and acceptor units ............................................. 14

**Figure 1.7** Common donor units for D-A copolymers ................................................................. 15

**Figure 1.8** Common acceptor units for D-A copolymers .............................................................. 16

**Figure 1.9** Common small molecule donor materials ................................................................. 18

**Figure 1.10** Common fullerene-based acceptors ............................................................................. 20

**Figure 1.11** Non-fullerene acceptors with device performances >5% ........................................ 22

**Figure 2.1** Selected all-conjugated P3AT-containing block copolymers .......................................... 36

**Figure 2.2** Flat energy band diagram of a binary (left) and donor-donor-acceptor ternary (right) device. $D_1$ and $D_2$ represent the two donor materials and $A$ represents the acceptor. ............... 37

**Figure 2.3** HOMO-4 to LUMO+4 energy levels for eight unit P3HT and P3THT, and sixteen unit P3THT-b-P3HT model compounds (left), and HOMO-2 to LUMO+2 energy density diagrams for a sixteen unit P3THT-b-P3HT model (right). The energy scale only corresponds to the left figure. The dotted lines are a guide for the eye. ......................................................... 40

**Figure 2.4** GPC traces of P3THT and P3THT-b-P3HT measured in 1,2,4-trichlorobenzene at 140 °C using a UV detector, relative to polystyrene standards ......................................................... 43
Figure 2.5 (a) Solution absorbance, (b) normalized emission, and (c) relative emission spectra (all measured in chloroform). The key shows the polymer structures and their corresponding line colors in the spectra. .......................................................... 44

Figure 2.6 (a) Solid-state absorbance and (b) emission spectra. Films were spin-coated from 6 mg/mL chloroform solutions at 1000 rpm onto glass substrates and annealed at 140 °C for 30 minutes under nitrogen. .......................................................... 46

Figure 2.7 Cyclic voltammogram (a, c) oxidation and (b, d) reduction curves of (a, b) P3THT and (c, d) P3THT-b-P3HT thin films in acetonitrile/TBAPF₆ electrolyte. A ferrocene redox couple (Fc/Fc⁺) was used as an internal standard. .......................................................... 47

Figure 2.8 X-ray diffraction pattern of P3HT, P3THT, and P3THT-b-P3HT annealed thin films. Films were prepared by drop-casting 7 mg/mL polymer solutions in chloroform onto silicon wafers and annealed at 200 °C for 30 minutes under nitrogen. .......................................................... 49

Figure 2.9 AFM (a-e) height and (f-j) phase images of (a, f) P3THT-b-P3HT, (b, g) P3THT-b-P3HT:PC₇₁BM, (c, h) P3HT-b-P3HT, and (d, i) P3HT-P3THT, and (e, j) P3HT-P3THT:PC₇₁BM annealed thin films spin-coated from 6 mg/mL chloroform solutions at 1000 rpm on glass substrates and annealed 140 °C for 30 minutes under nitrogen.......................................................... 50

Figure 2.10 Flat energy band diagrams for (a) P3HT:PC₇₁BM, (b) P3THT:PC₇₁BM, and (c) P3HT-P3THT:PC₇₁BM BHJ devices. ΔΦ denotes the offset energy between the HOMO of the electron donor (P3HT or P3THT) and the LUMO of the electron acceptor (PC₇₁BM). .............. 51

Figure 2.11 (a) J-V curves and (b) EQE spectra for polymer:PC₇₁CM devices where the donor polymer is denoted by the line color........................................................................................................... 52

Figure 3.1 GPC traces of P3HT-s-P3THT copolymers measured in 1,2,4-trichlorobenzene at 140 °C using a UV detector, relative to polystyrene standards. A:B = 3-hexylthiophene:3-thiohexylthiophene monomer incorporated into the chain.......................................................... 66

Figure 3.2 ¹H NMR aromatic resonances of poly(3-thiohexylthiophene), poly(3-hexylthiophene)-block-(3-thiohexylthiophene), poly(3-hexylthiophene)-stat-(3-thiohexylthiophene), and poly(3-hexylthiophene) (from top to bottom) (400 MHz, CDCl₃)........ 68
Figure 3.3  Structures of the HT-HT conformational triads for P3HT-s-P3HT copolymers with experimental and (predicted) $^1$H NMR resonances for the H labeled proton (ppm). A = 3-hexylthiophene and B = 3-thiohexylthiophene. ................................................................. 69

Figure 3.4  $^1$H NMR spectra of P3HT-s-P3THT copolymers with distinct aromatic shifts for each HT-HT conformation (left) and each $\alpha$-methylene proton (right). A = 3-hexylthiophene, B = 3-thiohexylthiophene and H is the proton of interest (400 MHz, CDCl$_3$). ................................................. 71

Figure 3.5  Predicted and experimental fractions of each HT-HT conformation for each P3HT-s-P3THT composition; A = 3-hexylthiophene and B = 3-thiohexylthiophene. Full structures for each conformation are depicted in Figure 3.3. Experimental values were obtained by $^1$H NMR integration. ................................................................. 71

Figure 3.6  $^1$H NMR spectrum of the species present after quenching the metathesis reaction with HCl (400 MHz, CDCl$_3$). ........................................................................................................... 74

Figure 3.7  Solid-state absorbance of 50:50 P3HT:P3THT block (dotted line) and statistical (solid line) copolymers. Thin films were spin-coated from 6 mg/mL chloroform solution at 2500 rpm onto glass substrates. .................................................................................................................. 76

Figure 3.8  Optical absorption spectra of P3HT-s-P3THT copolymers in chloroform solution (left) and solid-state (right). Thin films were spin-coated from 6 mg/mL chloroform solution at 2500 rpm onto glass substrates. The polymer is denoted by the line color. A:B = 3-hexylthiophene:3-thiohexylthiophene monomer incorporated into the chain. ................................................. 77

Figure 3.9  J-V curves (left) and EQE spectra (right) for polymer:PC$_{71}$BM devices under AM 1.5G illumination (100 mW/cm$^2$) at the optimal conditions for solar cell performance, where the polymer is denoted by the line color. A:B = 3-hexylthiophene:3-thiohexylthiophene monomer incorporated into the chain............................................................... 78

Figure 3.10  HOMO energy levels of P3HT-s-P3THT copolymers in the solid state determined by cyclic voltammetry (blue squares) and $V_{oc}$ of the optimized devices (red circles) as a function of the amount of 3-hexylthiophene monomer in the polymer backbone. The dashed lines are a guide for the eye and the arrows indicate the appropriate axis........................................................................... 80
Figure 3.11 Cyclic voltammogram oxidation curves of the copolymer thin films in acetonitrile/TBAPF₆ electrolyte. A ferrocene redox couple (Fc/Fc⁺) was used as an internal standard. .................................................................................................................................................. 81

Figure 3.12 Photovoltaic parameters as a function of 3-hexylthiophene content for OSCs fabricated using P3HT-s-P3THT:PC₇₁BM and tested under AM 1.5G illumination (100 mW/cm²). .............................................................................................................................................. 83

Figure 4.1 (a) Synthesis of PC-PDI-NDI random copolymers, (b) structure of PBDTTT-C donor polymer, and (c) energy level diagrams for the PC-PDI-NDI random copolymers. HOMO and LUMO energies are shown in electron volts and have errors of ±0.1 eV. ........................................................................ 92

Figure 4.2 GPC traces of PC-PDI100 (black), PC-PDI75-NDI25 (orange), PC-PDI50-NDI50 (blue), PC-PDI25-NDI75 (green) and PC-NDI100 (red) measured in 1,2,4-trichlorobenzene at 140 °C using a UV detector, relative to polystyrene standards. ....................................................................................... 93

Figure 4.3 Variable temperature ¹H NMR (600 MHz, 1,1,2,2-tetrachloroethane-d₂) of the aromatic region of PC-PDI-NDI copolymers. ........................................................................................................................................ 95

Figure 4.4 ¹H NMR spectra (600 MHz, 1,1,2,2-tetrachloroethane-d₂) of the aromatic region of PC-PDI-NDI copolymers at 120 °C. In the expansion, H and A refer to height and area, respectively. ...................................................................................................................................... 96

Figure 4.5 (a) Solution absorbance spectra, (b) film absorbance spectra, (c) solution emission spectra, and (d) solution fluorescence decays and fits of PC-PDI100 (black), PC-PDI75-NDI25 (orange), PC-PDI50-NDI50 (blue), PC-PDI25-NDI75 (green) and PC-NDI100 (red). ............... 98

Figure 4.6 Relationship between fluorescence quantum yield and percent of PDI acceptor unit. The quantum yields were measured in CHCl₃ relative to 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) (Φ = 0.44 in CH₃CN) at an excitation wavelength of 500 nm. .................................................................................................................................................. 99

Figure 4.7 Cyclic voltammogram reduction curves of (a) PC-PDI100, (b) PC-PDI75-NDI25, (c) PC-PDI50-NDI50, (d) PC-PDI25-NDI75, and (e) PC-NDI100 in acetonitrile/TBAPF₆ electrolyte. A ferrocene redox couple (Fc/Fc⁺) was used as an internal standard. ..................... 102
Figure 4.8 (a) $J-V$ curves and (b) EQE spectra of OPV devices based on PBDTTT-C as the donor component and PC-PDI100 (black), PC-PDI75-NDI25 (orange), PC-PDI50-NDI50 (blue), PC-PDI25-NDI75 (green) and PC-NDI100 (red) as the acceptor component.

Figure 5.1 Structures of common n-type building blocks containing carbonyl groups.

Figure 5.2 Chemical structures of the six $N,N'$-di(dodecyl)-4,5,8,9-naphthalene diimide derivatives.

Figure 5.3 Optical absorption spectra of P-S4 in $10^{-5}$ M chloroform solution (left) and solid-state (right). Thin films were spin-coated from 5 mg/mL chloroform solution at 2000 rpm onto glass substrates. The compound is denoted by the line color.

Figure 5.4 Cyclic voltammogram reduction curves of P-S3 in anhydrous dichloromethane solution in the presence of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) electrolyte. A ferrocene redox couple (Fc/Fc$^+$) was used as an internal standard.

Figure 5.5 Differential scanning calorimetry (DSC) traces of P-S4 obtained under nitrogen at a heating/cooling rate of 10 $^\circ$C/min. The first heating and cooling cycles are shown in blue and the second shown in black.

Figure 5.6 Thermogravimetric analysis plot of P-S4 obtained under nitrogen at a heating rate of 10 $^\circ$C/min.

Figure 5.7 Long-range crystal packing motif of (a) P, (b) cis-S2, (c) trans-S2, and (d) S3. Hydrogens have been omitted for clarity.

Figure 5.8 Crystal structures of (a) P, (b) cis-S2, (c) trans-S2, and (d) S3 viewed from the top of the molecular plane (top) and along the long molecular axis (bottom). N-dodecyl chains and hydrogens have been omitted for clarity. Sulfur and oxygen sites are disordered 50:50 in cis-S2 and S3 so both atoms are shown.

Figure 5.9 AFM images of P-S3 thin films as-cast (top) and after annealing at 200 $^\circ$C for 30 min (bottom). P, S1, and cis-S2 were spin-cast onto glass substrates from 8 mg/mL and trans-S2 and S3 from 5 mg/mL CHCl$_3$ solutions, all at 50 $^\circ$C.
Figure 5.10 Optical absorption spectra of P-S3 thin films (spin-coated from 5 mg/mL chloroform solution at 2000 rpm onto glass substrates), as-cast (black line) and after annealing for 20 minutes under nitrogen (red, black and green lines).

Figure 5.11 Optical micrographs of self-assembled P-S4 structures at 5x magnification.

Figure 5.12 AFM images of self-assembled S1-S4 structures.

Figure 5.13 SEM images of self-assembled P-S4 structures.

Figure 5.14 PXRD of self-assembled P-S4 structures on a SiO2 wafer.

Figure 6.1 Synthesis of S-PBTTPD and S-PBFTPDP.

Figure A.1 1H NMR spectrum (400 MHz, CDCl3) of poly(3-thiohexylthiophene).

Figure A.2 1H NMR spectrum (400 MHz, CDCl3) of poly(3-thiohexylthiophene)-b-(3-hexylthiophene).

Figure A.3 1H NMR spectrum (400 MHz, CDCl3) of 99:1 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).

Figure A.4 1H NMR spectrum (400 MHz, CDCl3) of 97:3 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).

Figure A.5 1H NMR spectrum (400 MHz, CDCl3) of 85:15 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).

Figure A.6 1H NMR spectrum (400 MHz, CDCl3) of 80:20 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).

Figure A.7 1H NMR spectrum (400 MHz, CDCl3) of 67:33 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).

Figure A.8 1H NMR spectrum (400 MHz, CDCl3) of 50:50 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).
Figure A.9 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of $N,N'$-di(2-ethylhexyl)-1,6/7-dibromo-3,4,9,10-perylene diimide. .......................................................... 154

Figure A.10 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of $N,N'$-di(2-ethylhexyl)-2,6-dibromo-1,4,5,8-naphthalene diimide. .................................................................................................................. 155

Figure A.11 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-PDI100. ........................................................................................................................................................................ 156

Figure A.12 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-PDI75-NDI25. ........................................................................................................................................................................ 157

Figure A.13 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-PDI50-NDI50. ........................................................................................................................................................................ 158

Figure A.14 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-PDI25-NDI75. ........................................................................................................................................................................ 159

Figure A.15 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-NDI100. ........................................................................................................................................................................ 160

Figure A.16 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of P .................................................................................................................. 161

Figure A.17 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of P .................................................................................................................. 162

Figure A.18 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of S1. .................................................................................................................. 163

Figure A.19 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of S1. .................................................................................................................. 164

Figure A.20 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of cis-S2. .................................................................................................................. 165

Figure A.21 gCOSY spectrum (400 MHz, CDCl$_3$) of cis-S2. .................................................................................................................. 166

Figure A.22 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of cis-S2. .................................................................................................................. 167

Figure A.23 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of trans-S2. .................................................................................................................. 168

Figure A.24 gCOSY spectrum (400 MHz, CDCl$_3$) of trans-S2. .................................................................................................................. 169
Figure A.25 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of S3. ................................................................. 170

Figure A.26 $^1$H NMR spectrum (500 MHz, CDCl$_3$, 40 $^\circ$C) of S4. ................................................. 171
List of Schemes

**Scheme 1.1** (a) Iraqi (Stille), (b) Guillerez (Suzuki), (c) McCullough, (d) Rieke, and (e) GRIM (KCTP) methods for the synthesis of regioregular P3ATs................................................................. 9

**Scheme 1.2** Mechanism of the nickel-catalyzed cross-coupling polymerization of P3ATs. .......... 11

**Scheme 1.3** General synthetic route to D-A copolymers via the Suzuki (a) and Stille (b) coupling reactions. ................................................................................................................................................. 12

**Scheme 1.4** Catalytic cycle of palladium-catalyzed cross coupling reactions......................... 13

**Scheme 2.1** Synthesis of poly(3-thiohexylthiophene)-*block-* (3-hexylthiophene)...................... 41

**Scheme 3.1** Synthesis of poly(3-hexylthiophene)-*stat-* (3-thiohexylthiophene)......................... 65

**Scheme 3.2** Regioselectivity of the metathesis step and subsequent polymerization for P3ATs (top), P3TATs (middle), and P3AT-s-P3TATs (bottom) under GRIM conditions. Monomer abundances were obtained by a Grignard quenching experiment. Doubly-activated species are excluded for clarity. ................................................................................................................................................. 73

**Scheme 3.3** Probable couplings for P3AT-s-P3TATs when the active chain end is (a) alkylthiophene or (b) thioalkylthiophene................................................................. 73
List of Abbreviations

-b- block
-co- copolymer
-s- statistical
-stat- statistical
Å angstrom
a. u. arbitrary units
AFM atomic force microscopy
Al aluminum
B3LYP Becke Three Parameter Hybrid Functionals Lee-Yang-Parr
BHJ bulk heterojunction
BODIPY boron dipyrromethene
bp boiling point
br broad
Br2 bromine
Bu3SnCl tributyl tin chloride
C6H13SSC6H13 hexyl disulfide
CDCl3 deuterated chloroform
CH3CN acetonitrile
cm centimeter
CN chloronaphthalene
CV cyclic voltammetry
d doublet
D dispersity
D-A donor-acceptor
DArp direct arylation polymerization
DART direct analysis in real time
DBFI-T 2,5-bis(8-(17-phenyl)-7,9,16,18-tetraazabenzo[8]flouranthene-3,4,12,13-tetracarboxylic acid diimide)thiophene
DBI dibromoisoocyanuric acid
DFT  density functional theory
DI  deionized
DIO  diiodooctane
DMF  dimethylformamide
DPP  diketopyrrolopyrrole
DSC  differential scanning calorimetry
E  energy
$E_g$  bandgap
EQE  external quantum efficiency
eV  electron volt
Fc  ferrocene
FF  fill factor
FMO  frontier molecular orbital
FWHM  full width at half maximum
g  gram
GPC  gel permeation chromatography
GRIM  Grignard metathesis
h  hour
H$_2$O  water
H$_2$SO$_4$  sulfuric acid
HBr  hydrobromic acid
HCl  hydrochloric acid
HH  head-to-head
HOMO  highest occupied molecular orbital
HRMS  high resolution mass spectrometry
HT  head-to-tail
$i$-PrMgCl  isopropylmagnesium chloride
$i$-PrMgCl*LiCl  isopropylmagnesium chloride lithium chloride complex
I$_2$  iodine
ICBA  indene-$C_{60}$ bisadduct
IQE  internal quantum efficiency
ITO  indium tin oxide
$J$ current density
$J_{sc}$ short-circuit current density
$\text{K}_2\text{CO}_3$ potassium carbonate
$\text{KCTP}$ Kumada catalyst transfer polymerization
$k\text{Da}$ kilodalton
$L$ liter
$L\text{DA}$ lithium diisopropylamide
$\text{LiCl}$ lithium chloride
$\text{LiF}$ lithium fluoride
$\text{LR}$ Lawesson’s reagent
$L\text{UMO}$ lowest unoccupied molecular orbital
$M$ molarity
$m$ multiplet
$m\text{A}$ milliampere
$\text{MDMO-PPV}$ poly(2-methoxy-5-(3’,7’-dimethyloxy)-1,4-phenylenevinylene)
$\text{MEH-PPV}$ poly(2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene)
$mg$ milligram
$\text{MgBr}_2$ magnesium bromide
$\text{MgBr}_2^*\text{Et}_2\text{O}$ magnesium bromide diethyl ether complex
$\text{MgSO}_4$ magnesium sulfate
$\text{MHz}$ megahertz
$\text{min}$ minute
$\text{mL}$ milliliter
$\text{mM}$ millimolar
$\text{mmol}$ millimole
$M_n$ number average molecular weight
$\text{mol}$ $6.02 \times 10^{23}$
$\text{mol}\%$ mole percent
$M_w$ weight average molecular weight
$m/z$ mass to charge ratio
$n$-$\text{BuLi}$ $n$-butyllithium
$n$-$\text{BuOH}$ $n$-butanol
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>nitrogen</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>sodium carbonate</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>sodium sulfate</td>
</tr>
<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>NDI</td>
<td>naphthalene diimide</td>
</tr>
<tr>
<td>Ni(dppe)Cl₂</td>
<td>[1,3-bis(diphenylphosphino)ethane]nickel (II) chloride</td>
</tr>
<tr>
<td>Ni(dppp)Cl₂</td>
<td>[1,3-bis(diphenylphosphino)propane]nickel (II) chloride</td>
</tr>
<tr>
<td>NIR</td>
<td>near-infrared</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>OFET</td>
<td>organic field effect transistor</td>
</tr>
<tr>
<td>OSC</td>
<td>organic solar cell</td>
</tr>
<tr>
<td>P3AT</td>
<td>poly(3-alkylthiophene)</td>
</tr>
<tr>
<td>P3EHT</td>
<td>poly(3-ethylhexylthiophene)</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>P3TAT</td>
<td>poly(3-thioalkylthiophene)</td>
</tr>
<tr>
<td>P3THT</td>
<td>poly(3-thiohexylthiophene)</td>
</tr>
<tr>
<td>PBDTTT-C</td>
<td>poly[{(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b;4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl}]</td>
</tr>
<tr>
<td>PC₆₁BM</td>
<td>(6,6)-phenyl-C₆₁-butyric acid methyl ester</td>
</tr>
<tr>
<td>PC₇₁BM</td>
<td>(6,6)-phenyl-C₇₁-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>Pd(OAc)₂</td>
<td>palladium (II) acetate</td>
</tr>
<tr>
<td>Pd(PPh₃)₄</td>
<td>tetrakis(triphenylphosphine)palladium(0)</td>
</tr>
<tr>
<td>PDI</td>
<td>perylene diimide</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)</td>
</tr>
<tr>
<td>Ph-B(OH)₂</td>
<td>phenylboronic acid</td>
</tr>
<tr>
<td>Ph-Br</td>
<td>bromobenzene</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>PNDI2OD-T2</td>
<td>poly[(N,N')-bis(2-octyldecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PPV</td>
<td>poly(phenylenevinylene)</td>
</tr>
<tr>
<td>PXRD</td>
<td>powder x-ray diffraction</td>
</tr>
<tr>
<td>q</td>
<td>quintet</td>
</tr>
<tr>
<td>RMgX</td>
<td>alkylmagnesium halide</td>
</tr>
<tr>
<td>RMS</td>
<td>root mean squared roughness</td>
</tr>
<tr>
<td>rpm</td>
<td>rotations per minute</td>
</tr>
<tr>
<td>rr</td>
<td>regioregularity</td>
</tr>
<tr>
<td>s</td>
<td>seconds</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>silicon oxide</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>sulfur trioxide</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>TBAPF(_6)</td>
<td>tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>TCSPC</td>
<td>time-correlated single photon counting</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TPD</td>
<td>thieno[3,4-c]pyrrole-4,6-dione</td>
</tr>
<tr>
<td>TT</td>
<td>tail-to-tail</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>volt</td>
</tr>
<tr>
<td>(V_{oc})</td>
<td>open-circuit voltage</td>
</tr>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>molar absorption coefficient</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>wavelength</td>
</tr>
<tr>
<td>(\mu)A</td>
<td>microampere</td>
</tr>
<tr>
<td>(\mu)m</td>
<td>micrometer</td>
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</tbody>
</table>
Chapter 1
Introduction

1 Organic solar cells

Increasing global energy demands coupled with growing evidence for climate change related to carbon dioxide emissions have accelerated the development of renewable energy technologies including hydro, wind, and solar, as alternatives to traditional carbon-based sources. Solar energy is an abundant, carbon-neutral source but new technologies are required to capture and store energy from the sun. Current commercial solar cells are based on inorganic materials and require bulky, expensive modules containing high purity silicon and therefore are not sustainable or financially viable for widespread use. Organic solar cells (OSCs) offer several potential advantages over their inorganic counterparts including low cost, lightweight, little to no toxicity and the ability to be processed from solution (eg. roll-to-roll printing). Since the first reported solution-processed bulk heterojunction solar cell in 1995 with an efficiency of less than 1%,\(^1\) there has been a tremendous increase in OSC research with efficiencies now reaching 9-10%.\(^2\text{-}^6\)

This chapter aims to introduce the basic operation of an organic solar cell and give a brief history of the progress made in the field over the last 20 years. Specifically, it will highlight how the optoelectronic and solid-state properties of conjugated materials can be rationally designed and controlled via synthesis to optimize individual device parameters leading to an overall higher efficiency.

2 Device architecture

Organic solar cells are multilayer devices, the most basic of which is composed of an organic conducting layer (active layer) sandwiched between a transparent anode (typically tin-doped indium oxide, ITO) and a metal cathode. Typically, a hole-conducting layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is deposited between the active layer and ITO to improve contact between layers and better align the energy levels. A thin layer of LiF is often deposited between the active layer and the cathode, also to improve the interfacial contact and optimize the electrode work function. The active layer is made up of a p-type electron donor (eg. conjugated polymer or small molecule) and an n-type electron acceptor (eg. fullerene derivative). The use of a single semiconducting polymer produces very little photocurrent because absorbed light results in short lived excitons that rapidly recombine or lose...
energy through other pathways and therefore the active layer is typically composed of a donor acceptor pair. The two most common active layer architectures are the bilayer and the bulk heterojunction (BHJ) (Figure 1.1). A bilayer device is typically fabricated via vacuum deposition of the donor and acceptor layers and contact between the two materials is limited to the bilayer interface. In a BHJ device, the two materials are first mixed in solution and deposited via a solution processing technique such as spin-coating, doctor blading or spray coating. This results in an interpenetrating network of the two materials which has a far greater donor acceptor interfacial area than a bilayer device. For this reason, the BHJ architecture has become the current state-of-the-art device structure and has yielded some of the highest device efficiencies to date. Furthermore, the BHJ offers the ability to be processed from solution rather than using high temperature vacuum deposition which is much more viable from an industrial standpoint, both financially and in terms of scalability.

Figure 1.1 Schematic of bilayer (left) and bulk heterojunction (right) device architectures (layers not to scale).

3 Mechanism

The charge photogeneration process begins when an incoming photon is absorbed by the active layer, promoting an electron from the HOMO to the LUMO of the donor material and leaving behind a hole in the HOMO (Figure 1.2). This electron-hole pair, known as an exciton, is still Coulombically bound and must diffuse to a donor acceptor interface to overcome this Coulombic attraction and separate into free charge carriers. The exciton is neutral and will therefore diffuse randomly. An exciton can typically diffuse about 10-20 nm before it recombines or relaxes back to its ground state and this is why it is so important to maximize the donor acceptor area so that each domain is smaller than the exciton diffusion length. Furthermore, in order for charge transfer to occur there must be a suitable energetic driving force at the donor acceptor interface, typically thought to be a minimum of 0.3 eV offset between LUMO energies. If this criterion is
met, then the electron will transfer from the LUMO of the donor to the LUMO of the acceptor. If the dielectric constant of the materials is high enough, then the charge carriers in this so-called charge transfer state can now diffuse away from each other forming free charge carriers, with the electron travelling through the acceptor material towards the cathode and the hole travelling through the donor material towards the anode, generating a current throughout the device.

Figure 1.2 Photoexcitation and charge transfer mechanism in a donor acceptor blend.

Though the ultimate goal of an efficient device is for every absorbed photon to result in free charge carriers collected at the electrodes, there are many loss pathways throughout the charge photogeneration process. As previously mentioned, excitons may relax back to the ground state if they fail to diffuse to a donor acceptor interface. Geminate recombination of the charge transfer state may occur at the donor acceptor interface if the geminate pair (ie. charge carriers created from the same photon) fails to fully dissociate. Non-geminate, or bimolecular, recombination may occur between free charge carriers (ie. those generated from a different photon) if they encounter each other before reaching their respective electrodes.

4 Device parameters

In a typical research laboratory, devices are tested using a solar simulator under simulated AM 1.5 G conditions with a power intensity of 100 mW/cm². Testing yields a current density-voltage (J-V) curve from which the device parameters can be extracted (Figure 1.3).
4.1 Power conversion efficiency (PCE)

The overall performance of the device is known as the power conversion efficiency (PCE or $\eta$) and can be calculated using equation (1) where $J_{\text{sc}}$ is the short circuit current density, $V_{\text{oc}}$ is the open-circuit voltage, $FF$ is the fill factor and $P_{\text{in}}$ is the incident power intensity.

$$PCE = \frac{J_{\text{sc}} V_{\text{oc}} FF}{P_{\text{in}}} \quad (1)$$

4.1.1 Short-circuit current density ($J_{\text{sc}}$)

The short-circuit current density (current density at zero voltage) is related to the optical properties of the active layer, specifically the absorption range and absorption coefficient. In general, a high $J_{\text{sc}}$ will be obtained for a device that strongly absorbs in the range of the solar spectrum. The $J_{\text{sc}}$ is often related to the optical bandgap of the donor material ($E_{\text{g}}^{\text{opt}}$) which is typically reported as the onset of absorption in the solid-state (usually at 10% of the peak absorption). The OSC community typically uses this term interchangeably with the HOMO-LUMO energy gap of the donor material, which will be referred to simply as the “bandgap” for the remainder of this thesis. One of the most common strategies for improving device performance is the design of low bandgap polymers that absorb into the near IR. This has recently been achieved through the use of donor-acceptor (D-A) copolymers that are comprised of alternating electron-rich and electron-poor units, and $J_{\text{sc}}$ values of over 17 mA/cm$^2$ have been
reported using this polymer architecture. D-A copolymers and their potential for use as both donor and acceptor materials will be discussed in greater detail in Section 5.2.

4.1.2 Open-circuit voltage ($V_{oc}$)

The open-circuit voltage (voltage at zero current density) is related to the offset between the HOMO of the donor and the LUMO of the acceptor. A study comprising a series of 26 polymer donors with different HOMO levels and the same acceptor showed that the $V_{oc}$ could be described empirically according to the equation: $V_{oc} = (1/q)(|E_{\text{HOMO, D}}| - |E_{\text{LUMO, A}}| - 0.3 \ \text{V})$. From Figure 1.2, it is clear that the HOMO energy of the donor material will have a significant but conflicting effect on both the $J_{sc}$ and $V_{oc}$, as lowering the HOMO should increase the $V_{oc}$ but also widen the bandgap thereby decreasing the $J_{sc}$, and vice versa. The relationship between the HOMO of the donor and the $V_{oc}$ is a vital component in the rational design of donor materials and is the focus of the studies described in Chapters 2 and 3 of this thesis. It is important to note that the origin of the $V_{oc}$ is still under intense debate and is influenced by a number of other factors in addition to the HOMO-D-LUMO offset including side-chain bulkiness, interchain distances, active layer morphology, and dielectric constant.

4.1.3 Fill factor ($FF$)

The fill factor is a ratio of the product of the current density and voltage at the maximum power point on the $J$-$V$ curve, and the product of the current density and voltage at short-circuit and open-circuit conditions, respectively, as shown in equation 2.

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (2)$$

The fill factor is depicted visually as the area formed on the $J$-$V$ curve between the maximum power point, $V_m$, $J_m$ and zero (see grey box in Figure 1.3). The shape of the $J$-$V$ curve, and hence the $FF$, are related to the resistance in the device. A high $FF$ is achieved when the device series resistance ($R_s$) is small and the shunt resistance ($R_{sh}$) is large. These values are largely affected by the morphology of the active layer and thus the $FF$ can be maximized by optimizing the morphology to maximize charge separation and transport.
4.2 Quantum efficiency

The quantum efficiency is a measure of the number of photons of a given wavelength that contribute to the overall photocurrent (Figure 1.3, right). It is related to absorption events in both the donor and acceptor materials and therefore should span the absorbance range of both materials.

4.2.1 Internal quantum efficiency (IQE)

The internal quantum efficiency is the ratio of the number of charge carriers collected at the electrodes to the number of photons that are absorbed by the active layer. A low IQE is representative of the failure of excitons to separate, either due to relaxation before reaching an appropriate donor acceptor interface, lack of sufficient driving force to overcome the exciton binding energy, or recombination of charge carriers, either through geminate or non-geminate recombination pathways (vide supra).

4.2.2 External quantum efficiency (EQE)

The external quantum efficiency is the ratio of the number of charge carriers collected at the electrodes to the number of incident photons, regardless of if they are absorbed by the active layer. The EQE is thus representative of how well and how strongly the active layer materials absorb solar energy.

5 Donor materials

5.1 Poly(phenylenevinylene)s (PPVs)

The majority of research in the field of organic photovoltaics has focused on the design of novel donor materials. The earliest OSCs were based on poly(phenylenevinylene)s (PPVs) such as poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) (Figure 1.4). A maximum PCE of 3.3% was achieved for a PPV-based BHJ device using (6,6)-phenyl-C61-butyric acid methyl ester (PC61BM) as the acceptor, however, the relatively large bandgap of PPV-based polymers limits the $J_{sc}$ to 5-6 mA/cm² and therefore efforts shifted to developing alternative donor polymers with narrower bandgaps.
5.2 Poly(3-alkylthiophene)s (P3ATs)

Until recently, the state-of-the-art in BHJ solar cells was considered the poly(3-hexylthiophene):fullerene system which dominated OSC research into the late 2000s. One of the major advantages of polythiophenes, in addition to their narrower bandgap relative to PPV, is their controlled polymerization and the ability to synthesize polymers with high regioregularity and narrow dispersity. Early work on unsubstituted polythiophene demonstrated that it was a highly conductive material but had very poor solubility, limiting its use in solution-processed devices. The introduction of an alkyl chain at the 3-position improved solubility but also introduced a new factor, regioregularity, due to the nature of the asymmetrical monomer. Coupling of two asymmetric thiophene units yields three possible dimers: head-to-tail (HT), tail-to-tail (TT), or head-to-head (HH) (Figure 1.5).

![Figure 1.5 Diad linkages of 3-substituted thiophenes.](image)

It has been shown that a high degree of regioregularity (ie. HT linkages) is needed to maximize device efficiency since regiorandom (ie. TT or HH) linkages result in twisting of the polymer backbone, reducing the conjugation length of the polymer and decreasing both absorption and mobility. Another consideration in the synthesis of poly(3-alkylthiophene)s (P3ATs), like any polymer, is the ability to control the molecular weight and dispersity, which both have an effect on photovoltaic performance.
5.2.1 Early regioregular P3AT synthesis

The earliest P3ATs were synthesized by oxidative or electrochemical polymerization, however these methods have no regiochemical control and thus produce regiorandom polymers.\textsuperscript{16,17} The regiorandom couplings cause a twisting of the polymer backbone due to increased steric repulsion between alkyl chains, which causes a decrease in $\pi$-conjugation, resulting in an increased bandgap and decreased conductivity. One approach to the synthesis of regioregular P3ATs is the use of palladium-catalyzed cross-coupling reactions. Iraqi reported the polymerization of regioregular P3AT employing the Stille reaction, using the asymmetric 3-hexyl-2-iodo-5-(tri-$n$-butylstanny)thiophene monomer (Scheme 1.1a).\textsuperscript{18} Similarly, Guillarez employed the Suzuki reaction using 3-octyl-2-iodo-5-boronatothiophene (Scheme 1.1b).\textsuperscript{19} A major disadvantage of these methods is the need to install the organometallic functional group prior to polymerization, as well the need for cryogenic conditions, and poor atom economy with the loss of the tin or boron containing group.

In 1992, McCullough and Lowe reported the first synthesis of regioregular P3ATs.\textsuperscript{20} The key step in this reaction is the selective lithiation of 2-bromo-3-alkylthiophene at the 5-position under cryogenic conditions followed by the addition of MgBr$_2$*Et$_2$O to yield 2-bromo-5-bromomagnesio-3-alkylthiophene in 98-99% yield (Scheme 1.1c). This reactive intermediate then undergoes Kumada-type coupling polymerization using a Ni(dppp)Cl$_2$ catalyst to give the P3AT with 98-100\% HT regioregularity.\textsuperscript{21} Soon afterwards, Chen and Rieke developed a similar method involving the treatment of 2,5-dibromo-3-alkylthiophene with highly reactive zinc (Zn*) to yield the two regioisomers in a ratio of 90:10 (Scheme 1.1d).\textsuperscript{22} This mixture is then treated with Ni(dppe)Cl$_2$ catalyst to yield regioregular P3AT.
Scheme 1.1 (a) Iraqi (Stille), (b) Guillerez (Suzuki), (c) McCullough, (d) Rieke, and (e) GRIM (KCTP) methods for the synthesis of regioregular P3ATs.

5.2.2 Kumada catalyst transfer polymerization

In 1999, the Grignard metathesis (GRIM) polymerization method, later generalized as Kumada catalyst transfer polymerization (KCTP), was developed by McCullough, which eliminated the use of cryogenic temperatures and highly reactive metals. This new method yielded P3AT not only having high regioregularity but also narrow dispersity, and allowed for molecular weight control based on monomer:catalyst ratio. In this method, 2,5-dibromo-3-alkylthiophene is first activated using one equivalent of an alkyl Grignard reagent (RMgX) yielding two regioisomers in a ratio of 85:15 to 75:25 (Scheme 1.1e). The activated monomer mixture is then treated in situ with a nickel (II) catalyst (typically Ni(dppp)Cl2) which selectively polymerizes 2-bromo-5-halomagnesio-3-alkylthiophene due to steric effects to yield a regioregular polymer. The high regioregularity can be attributed to high selectively for the reactive monomer in the metathesis step, as well as the selectivity of the Ni catalyst for this monomer.
Another important advantage of the GRIM method is that it occurs via a quasi-living chain growth polymerization. Numerous studies have confirmed that after the first monomer-monomer coupling step, the nickel catalyst remains associated with the growing polymer chain and continues to oxidatively add new monomers to end of the chain via a “ring-walking” mechanism (Scheme 1.2).\textsuperscript{24-28} In a typical chain growth polymerization, molecular weight increases linearly with monomer conversion and the dispersity remains low and relatively constant throughout the polymerization. Furthermore, molecular weight increases with monomer:catalyst ratio, since ideally one Ni catalyst will initiate one polymer chain and stay associated with the same chain until the reaction is terminated (usually through quenching with dilute acid). KCTP has also been applied to other systems including polypyrrole,\textsuperscript{29,30} polyfluorene,\textsuperscript{30-33} polyphenylene,\textsuperscript{29,34} poly(3-alkylselenophene),\textsuperscript{35} poly(3-alkyltellurophene),\textsuperscript{36} and polybenzotriazole.\textsuperscript{37} KCTP can also be used to synthesize random copolymers if the reactivity ratios of the two monomer species are similar, as will be discussed in further detail in Chapter 3.

Another important advantage of the living nature of this system is the possibility for chain extension by the addition of another compatible monomer. Once all of the initial monomer has been consumed, the catalyst remains associated with the chain end and upon addition of additional monomer, additional reactions may occur. This allows for the synthesis of all-conjugated block copolymers or for end-capping with functional groups that can be useful for characterization or post-polymerization reactions. Many all-thiophene block copolymers have been synthesized with different alkyl chain lengths or functional groups,\textsuperscript{38-41} including the donor-donor diblock copolymer that was the subject of study in Chapter 2. Furthermore, this allows for the possibility of blocks containing different heterocycles altogether, such as the poly(3-alkylthiophene)-\textit{b}-poly(3-alkylselenophene) system studied extensively by our group.\textsuperscript{42-44}
Scheme 1.2 Mechanism of the nickel-catalyzed cross-coupling polymerization of P3ATs.

5.2.3 P3HT in OSCs

Compared to the first generation PPV-based solar cells, regioregular P3HT-based devices demonstrated noticeably higher \( J_{sc} > 10 \text{ mA/cm}^2 \) due to a lower \( E_g \) (~1.9 eV), as well as increased hole mobility and crystallinity due to strong \( \pi-\pi \) stacking interactions. Device efficiencies were found to be highly dependent upon polymer molecular weight, dispersity and regioregularity, as well as active layer processing such as thermal or solvent annealing, or the use of additives. In spite of these significant improvements, the \( V_{oc} \) of P3HT:fullerene devices is limited (~0.6 V for PC\(_{61}\)BM acceptors) due to the high HOMO level of P3HT (~5.1
eV), and the majority of P3HT-based devices have efficiencies between 4 and 5%,\textsuperscript{7,53} which has led to the development of new donor materials with lower lying HOMOs and even narrower bandgaps.

5.3 Donor-acceptor (D-A) copolymers

There are three main approaches to narrowing the bandgap of donor polymers: (1) expansion of the $\pi$-system,\textsuperscript{54-56} (2) transition from aromatic to quinoid structure, and (3) synthesis of donor-acceptor (D-A) or push-pull copolymers. D-A copolymers are comprised of alternating electron-rich “donor” units and electron-poor “acceptor” units. D-A copolymers are typically synthesized using palladium-catalyzed Stille\textsuperscript{57} or Suzuki\textsuperscript{58} cross-coupling reactions, which involve organic tin or boron nucleophiles reacting with electrophilic aryl halides, respectively (Scheme 1.3).

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Scheme 1.3 General synthetic route to D-A copolymers via the Suzuki (a) and Stille (b) coupling reactions.}
\end{figure}
\end{center}

The general mechanism of these two transition metal-catalyzed couplings involves oxidative addition, transmetallation, and reductive elimination (Scheme 1.4). In the first step, the aryl halide ($R_1X$) oxidatively adds to the Pd(0) catalyst to yield a Pd(II) complex, which then undergoes transmetallation with the organoboron (Suzuki) or organotin (Stille) monomer ($R_2M$), followed by reductive elimination of the organic partners ($R_1-R_2$), resulting in carbon-carbon bond formation and regeneration of Pd(0).
Suzuki coupling is typically used for polymerizing donor monomers containing benzene units, whereas Stille coupling is chosen for polymerizing monomers containing thiophene rings. In contrast to KCTP, Suzuki and Stille couplings proceed via a step-growth mechanism and dispersities are typically >2.0 (prior to purification). Furthermore, it is essential to have stoichiometric amounts of each monomer in order to achieve high percent conversions and high molecular weights. Recently, many groups have reported using microwave reactors to achieve high molecular weights while also decreasing reaction time.\textsuperscript{59} Another approach to the synthesis of D-A copolymers is direct arylation polymerization (DArP) which eliminates the use of boron or tin functionalities but may not be as regiospecific.\textsuperscript{60-66} Currently, extensive optimization of reaction conditions is required for each set of monomers and therefore more research is necessary to develop a set of universal conditions before this method is widely applied.

Narrow bandgaps are achieved in D-A copolymers due to orbital mixing of the donor and acceptor units. As per molecular orbital theory, orbital mixing of the HOMO and LUMO orbitals from each monomer unit will result in a higher HOMO, lower LUMO, and an overall narrower bandgap (Figure 1.6). Furthermore, the push-pull effect of alternating electron rich and electron poor units increases the double bond character between the two units, which increases the planarity of the polymer backbone. Increased backbone planarity further increases the $\pi$-conjugation and narrows the bandgaps.
It is important to note that the model shown in Figure 1.6 only works if the reacting fragments (i.e., monomer units) are of proper symmetry and energy to mix effectively, thus leading to new electronic structures whose frontier orbitals can be viewed as true hybrids with appropriately weighted contributions from the molecular orbitals of the starting fragments.

The HOMO of the D-A copolymer typically has a large contribution from the donor, or electron-rich, unit. The two most basic donor units are thiophene and benzene, which are also the main building blocks for constructing new donor units. Many common donor units are comprised of bithiophene or dibenzene units bridged by a heteroatom such as carbon, nitrogen, silicon, or germanium. The bridging atom has considerable effects on the copolymer optoelectronic properties and crystallinity.\textsuperscript{67,68} In general, the bithiophene-based units are stronger donors and tend to produce copolymers with higher planarity than dibenzene-based monomers. Common dibenzene units include fluorene, carbazole, dibenzosilole, and dibenzogermole (Figure 1.7, top row). Common dithiophene units include cyclopentadithiophene, dithienopyrrole, dithienosilole, and dithienogermole (Figure 1.7, middle row). Stronger donor units tend to produce narrower bandgaps (corresponding to a higher $J_{sc}$) and higher HOMO levels (corresponding to a lower $V_{oc}$), while weaker units produce wider bandgaps (corresponding to a lower $J_{sc}$) and lower HOMO levels (corresponding to a higher $V_{oc}$). Monomers containing both benzene and thiophene units result in ideal electronics, producing copolymers with narrow bandgaps but relatively low HOMO levels to maintain high $J_{sc}$ and $V_{oc}$. Some of the most common donor units employ this structure including benzodithiophene and highly planar ladder-type donors,
indacenodithiophene, pyrroloindacenodithiophene, and silaindacenodithiophene (Figure 1.7, bottom row).

Figure 1.7 Common donor units for D-A copolymers.

The LUMO of the D-A copolymer typically has a large contribution from the acceptor, or electron-deficient, unit. Many common acceptor units contain benzene or thiophene fused ring systems to ensure planarity of the copolymer backbone and almost all contain the electron-withdrawing imine nitrogen (-C=N-) or carbonyl (-C=O) groups. The strength of the acceptor unit is based on its LUMO level such that the lower the LUMO level, the stronger the electron-accepting ability. In general, for D-A copolymers with common donor units, the acceptor strength can be evaluated by the optical bandgap, such that the narrower the bandgap, the stronger the acceptor. Common weak acceptors include phthalimide, bithiazole, and benzobisthiazole (Figure 1.8, top row). Common medium acceptors include benzotriazole, thiazolo[5,4-d]thiazole, and thieno[3,4-c]pyrrole-4,6-dione (Figure 1.8, middle row). Common strong acceptors include benzothiadiazole, isoindigo, and diketopyrrolo[3,4-c]-pyrrole-1,4-dione (Figure 1.8, bottom row).
Although almost all donor-acceptor combinations are possible to synthesize, it has been found that the weak donor-weak acceptor, medium donor-weak acceptor, and weak donor-medium acceptor combinations generally result in large bandgaps due to poor D-A orbital mixing and thus perform poorly in solar cells. Relatively higher device performances are generally achieved using strong donor-strong acceptor, strong donor-medium acceptor, and medium donor-strong acceptor combinations. The weak donor-strong acceptor combination leads to polymers with low lying HOMO levels via the weak donor while maintaining a narrow bandgap, two ideal characteristics for optimal device performance. Another important consideration in the design of D-A copolymers is the backbone planarity. Increased planarity extends the π-system, which narrows the optical bandgap, and increases π-π stacking, both of which contribute to improved device performance. Strategies to control backbone planarity include selection of monomer units, type (linear or branched) and position (and regioregularity) of alkyl side-chains, and use of spacers (typically thiophene) between donor and acceptor units to reduce any steric hindrance.

**Figure 1.8** Common acceptor units for D-A copolymers.
5.4 Small molecules

Though conjugated polymers have proven to be low cost, lightweight, solution-processable alternatives to inorganics in photovoltaic research, they suffer from batch to batch variations and their performance is highly dependent on molecular weight and dispersity. Throughout the rise of the polymer solar cell there has also been a significant amount of work on small molecule organic photovoltaics. Common classes of small molecule donors include discotic molecules such as phthalocyanine, porphyrin and hexabenzocoronene derivatives, thiophene oligomers and dendrimers, acenes and fused polycycles, organic dyes, and push-pull chromophores (Figure 1.9). Some of the first small molecule donors, reported shortly after the first reports of the BHJ polymer solar cell, were based on blends of phthalocyanine or hexabenzocoronene donors with perylene small molecule acceptors, however these devices performed very poorly due to extremely low current densities of less than 1 mA/cm$^2$. In 2006, reports of branched oligothiophene donors emerged and were followed by a number of different 1-, 2- and 3-dimensional structures including linear, branched, and star-shaped. In general, it was found that the oligomers with highest molecular weight and longest conjugation length showed the best device performance. Modification of the oligothiophene end-capping groups with various electron-withdrawing functionalities increased device efficiencies up to 6%, making them on par with P3HT polymeric devices. Another interesting class of small molecule donors that emerged around the same time as 3D oligothiophenes was soluble acenes based on acenes and polycyclic acenes such as pentacene and rubrene, which are known to have high charge mobilities and broad absorption spectra. It was found that the soluble acenes have a strong tendency to crystallize into well-defined structures, which results in efficient charge carrier transport. When blended with acceptor materials, however, the acenes tend to phase separate into large domains which minimize the donor acceptor interfacial area and result in inefficient exciton dissociation. For this reason the efficiency of acene based devices has remained around 2%, much lower than the performance of typical polymer-based devices. A number of other small molecule donors have been reported in the literature including several well-known classes of organic dyes including BODIPY, squarine, isoindigo, merocyanine, and diketopyrrolopyrrole. These compounds have extremely high absorption coefficients and broad absorption ranges, however, device performance of dye-based small molecule donors currently remains below 5%.
Figure 1.9 Common small molecule donor materials.
Currently, the most successful class of small molecule solar cells uses the D-A, push-pull chromophore approach. Like their polymeric counterparts, the alternation of electron-rich and electron-deficient units results in a narrowing of the bandgap, while judicious choice of the donor and acceptor units allows for fine-tuning of the energy levels. The best performances to date have been reported using the D1-A-D2-A-D1 motif,\textsuperscript{111-115} with a highest efficiency of 8.9% for $p$-DTS(FBTTh$_2$)$_2$ when used with a PC$_{71}$BM acceptor at the time of writing.\textsuperscript{112}

A general trend for small molecule BHJ solar cells is that the $V_{oc}$ tends to be higher than in polymer devices, while the $J_{sc}$ and $FF$ remain lower.\textsuperscript{120} This is likely a result of differences in active layer morphology, where small molecules tend to phase separate on a larger scale resulting in a larger number of trapped charges, while polymers are able to form interpenetrating networks with the acceptor material resulting in improved charge separation and transport. Current studies are exploring the use of solvent additives and different processing conditions to improve the active layer morphology and early results suggest that these small molecule devices will soon perform on par with their polymeric counterparts.\textsuperscript{121-124}

6 Acceptor materials

Although very early OSCs were comprised of a single layer of semi-conducting polymer, these devices lacked sufficient driving force to separate excitons and thus suffered from extremely low efficiencies of less than 0.1%.\textsuperscript{125,126} It was discovered that a second n-type material was necessary to aid in charge separation and the transport of negative charge. With the introduction of this second material, additional considerations came into effect, such as the miscibility and co-crystallinity of the two materials, and the ability of this material to also absorb incoming photons and contribute to the overall photocurrent. Furthermore, the acceptor LUMO level must be appropriately matched with the donor LUMO to provide sufficient driving force for charge transfer but cannot be too low as to compromise the $V_{oc}$. It has been shown that the electron mobility of the acceptor should be relatively well-balanced with the hole mobility of the donor to facilitate efficient charge transport.

6.1 Fullerene acceptors

The very first OSCs used fullerene-based materials as the acceptor component and they remain the most popular acceptors to date, and are currently being used in the record efficiency D-A
copolymer devices discussed previously. C$_{60}$ is a strongly electron accepting molecule, however its solubility is severely limited. In 1995, Wudl and co-workers synthesized a soluble derivative, [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) which has been used extensively in OSCs due to its high electron-accepting and transporting abilities (Figure 1.10, left). A major disadvantage of PC$_{61}$BM is that it has a very low absorption coefficient for visible light due to the lowest-energy transitions being dipole forbidden. This implies that PC$_{61}$BM, which typically makes up approximately 50% of the active layer material, cannot harvest excitons or contribute to the overall photocurrent of the device, which limits the theoretical efficiency of PC$_{61}$BM-based devices. The larger, less symmetrical fullerene, PC$_{71}$BM, has therefore been developed, in which these previously forbidden transitions are now allowed, greatly increasing its absorption (Figure 1.10, middle). The PC$_{71}$BM acceptor typically yields better device efficiencies however is much more expensive due to difficult purification, and thus is unlikely to be used on a commercial scale. Indene-C$_{60}$ bisadduct (ICBA) has also been developed which has a higher lying LUMO level and thus results in higher voltages than when using a PCBM derivative (Figure 1.10, right). Furthermore, ICBA is easily synthesized from C$_{60}$ and indene, has high solubility in organic solvents, and has stronger visible light absorption compared to PCBM. Regardless, since the first report of ICBA in 2010, it remains a less popular acceptor material than PC$_{61}$BM and PC$_{71}$BM, likely due to non-ideal miscibility and co-crystallinity with the majority of donor materials.

![Figure 1.10](image) Common fullerene-based acceptors.

### 6.2 Non-fullerene acceptors

Although fullerene-based acceptors have led to high efficiency devices with countless donor polymers and small molecules they still suffer from low LUMO levels and poor absorption of the solar spectrum, ultimately limiting the theoretical $V_{oc}$ and $J_{sc}$, respectively. Furthermore, they are

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127 A major disadvantage of PC$_{61}$BM is that it has a very low absorption coefficient for visible light due to the lowest-energy transitions being dipole forbidden. (128) This implies that PC$_{61}$BM, which typically makes up approximately 50% of the active layer material, cannot harvest excitons or contribute to the overall photocurrent of the device, which limits the theoretical efficiency of PC$_{61}$BM-based devices. The larger, less symmetrical fullerene, PC$_{71}$BM, has therefore been developed, in which these previously forbidden transitions are now allowed, greatly increasing its absorption (Figure 1.10, middle). (129) The PC$_{71}$BM acceptor typically yields better device efficiencies however is much more expensive due to difficult purification, and thus is unlikely to be used on a commercial scale. Indene-C$_{60}$ bisadduct (ICBA) has also been developed which has a higher lying LUMO level and thus results in higher voltages than when using a PCBM derivative (Figure 1.10, right). (130,131) Furthermore, ICBA is easily synthesized from C$_{60}$ and indene, has high solubility in organic solvents, and has stronger visible light absorption compared to PCBM. Regardless, since the first report of ICBA in 2010, it remains a less popular acceptor material than PC$_{61}$BM and PC$_{71}$BM, likely due to non-ideal miscibility and co-crystallinity with the majority of donor materials. (132)
costly and difficult to synthesize and therefore there is increasing interest in developing new non-fullerene acceptor materials that are capable of harvesting photons and increasing the overall efficiency of the device. A surge in research in recent years has resulted in the discovery of highly efficient solution-processable non-fullerene acceptors which have been shown to have comparable OSC performances to conventional fullerene-based acceptors.\textsuperscript{124,133-157}

Early examples of non-fullerene acceptors include thiophene-S, S-dioxide,\textsuperscript{158,159} cyano-PPV and other cyano-based materials,\textsuperscript{160-162} metallophthalocyanines and subphthalocyanines,\textsuperscript{163-165} fused acenes,\textsuperscript{166,167} and pigments and dyes,\textsuperscript{168-170} however most of these materials resulted in poor device performances under 1\%. Recent efforts have seen a significant increase in performance through the use of both small molecule and polymer acceptor materials often containing imide, amide, and benzothiadiazole units with efficiencies now exceeding 5\% (Figure 1.11).\textsuperscript{133-138,157}

Many of these new materials are based on the donor-acceptor architecture also employed in the design of narrow bandgap donor copolymers and small molecules. In general, perylene diimide containing small molecules (eg. \textit{bis-PDI-T-EG}, \textit{di-PDI}, helical PDI in Figure 1.11) and naphthalene diimide copolymers (eg. PNDI2OD-T2 and PSe-PDI-NDI in Figure 1.11) have received the most attention and their performance can be greatly enhanced with device processing conditions.

In general, the limiting factor in achieving high performance in non-fullerene devices is optimization of the morphology, due to difficulties in forming the desired donor acceptor interpenetrating network. This is typically due to the two materials being too miscible in one another or to the tendency for one or both components to crystallize and undergo phase separation. Furthermore, the good performance of fullerene acceptors is largely associated with their spherical shape and ability to transport charge in 3-dimensions which is difficult to achieve in the typically planar non-fullerene alternatives. Finally, the performance of these new materials is very dependent on device fabrication and processing conditions and therefore significant challenges remain to find a universal new material to replace PCBM.
The main goal of this thesis was to rationally design novel conjugated materials for organic electronic applications and to determine the relationship between structure and device performance. It is important to note that the primary goal was not to reach record device performance.

Figure 1.11 Non-fullerene acceptors with device performances >5%.

7 Scope of thesis

The main goal of this thesis was to rationally design novel conjugated materials for organic electronic applications and to determine the relationship between structure and device performance. It is important to note that the primary goal was not to reach record device performance.
efficiencies, but rather to understand the fundamental relationships. In particular, I wanted to emphasize the complicated nature of these relationships, how they are not universal to every device system, and how rational design is not always translated to materials performance. My role in the research was the synthesis and characterization of the materials, while Dong Gao, another graduate student in the group, was responsible for all device fabrication and testing.

I was first interested in studying how the open-circuit voltage of an organic solar cell could be increased by lowering the HOMO level of the donor polymer via functional group substitution. I chose to study the benchmark poly(3-hexylthiophene) structure and substituted the 3-hexyl chain with a less-electron donating 3-thiohexyl group. In Chapter 2, I synthesized an equally proportioned diblock copolymer containing 3-hexylthiophene and 3-thiohexylthiophene blocks, and found that the open-circuit voltage of the block copolymer device was as high as that of the device containing only the lower HOMO polymer. This inspired me to investigate the minimum amount of the lower HOMO unit required to reach this maximum voltage and thus I synthesized a series of statistical copolymers, presented in Chapter 3. For this new system I was also interested in investigating the effect of polymer sequence on device performance and thus switched from a block to statistical architecture.

In the second half of the thesis I focus on novel n-type materials based on arylene diimides. In chapter 4, I synthesized a one donor-two acceptor random terpolymer containing naphthalene diimide and perylene diimide as the two electron-deficient units and 2,7-carbazole as the electron-rich unit. I varied the ratio of the two acceptor units and found that while the optical properties varied with acceptor composition, the composition dependence was not evident in device performance. Rather, any amount of the NDI monomer reduced the device efficiency to the value of the one donor-one acceptor NDI parent copolymer due to a pinning of the short-circuit current at the lowest value. In chapter 5, I studied the effect of the single atom substitution of oxygen with sulfur on the optoelectronic and self-assembly properties of a series of small molecule naphthalene diimides. The low LUMO levels and strong intermolecular interactions of these thionated molecules make them ideal candidates for use in n-channel organic thin film or micro/nanowire transistors.

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Chapter 2
Donor-Donor Block Copolymers

1 Statement of contributions

AFM images were collected by Jon Hollinger. PXRD was performed by Srebri Petrov. Solar cell fabrication and testing were performed by Dong Gao. I carried out all other synthesis, characterization, computations, and experiments presented in this chapter. I drafted the manuscript for publication, which was edited by Dwight Seferos. Portions of this work have appeared in print.\(^1\)

2 Introduction

Block copolymers are desirable in organic solar cells because they have been shown to phase separate in the solid state into domains on the order of the exciton diffusion length of approximately 10-20 nm. Poly(3-alkylthiophenes) (P3ATs) are an exceptionally well-studied class of conjugated polymers due their good conductivity, semi-crystallinity, and ability to be synthesized under quasi-living conditions, with good control of molecular weight and polydispersity.\(^2\)\(^-\)\(^8\) Recently, several block copolymers have been synthesized using P3ATs, including rod-coil block copolymers containing one conjugated and one non-conjugated block,\(^9\)\(^-\)\(^12\) and all-conjugated rod-rod block copolymers (Figure 2.1).\(^13\)\(^-\)\(^17\) Although rod-coil block copolymers are typically more processable than P3AT homopolymers due to the increased solubility of the non-conjugated block, the insulating nature of this block leads to a decrease in conductivity, which is detrimental to device performance. In contrast, all-conjugated block copolymers maintain high conductivity along the conjugated backbone, and the block copolymer architecture can still lead to phase separation and morphology control. Hashimoto and coworkers used Kumada catalyst transfer polymerization to synthesize an all-thiophene diblock copolymer containing poly(3-hexylthiophene) (P3HT) and poly(3-(2-ethylhexyl)thiophene) (P3EHT) blocks.\(^18\)\(^,\)\(^19\) Phase separation occurred due to differences in the crystallinity of the crystalline P3HT phase and amorphous P3EHT phase, and it was found that the sizes of the two domains could be controlled by the composition of the blocks. Jenekhe and coworkers used a similar to method to synthesize a totally crystalline all-thiophene diblock copolymer containing poly(3-butylthiophene) (P3BT) and poly(3-octylthiophene) (P3OT) blocks.\(^15\) Phase separation was observed through the presence of two diffraction peaks measured by wide angle x-ray
diffraction corresponding to the two crystalline domains of the phase separated block copolymers, as well as by the presence of two distinct melting transitions measured by differential scanning calorimetry. Although the optoelectronic properties of these all-thiophene block copolymers are distinct from their constituent homopolymers, the differences are relatively minor and arise solely from the slight differences in intermolecular interactions due to the side-chain modification. An alternative approach to directly control the optoelectronic properties is the use of optoelectronically distinct monomers, either through the block copolymerization of a thiophene block with a conjugated non-thiophene block, or the copolymerization of two thiophene monomers with chemically distinct functional groups (ie. not just two different alkyl chains). My group for example, has described the synthesis of selenophene-thiophene block copolymers that undergo a significant amount of phase separation in the solid-state, and that exhibit optoelectronically distinct properties from either of the parent homopolymers.20-23 Other examples of all-conjugated thiophene-containing block copolymers with optoelectronically distinct blocks include poly(9,9-diocylfluorene)-block-(3-hexylthiophene) (PF8-b-P3HT),24 poly(p-phenylene)-block-(3-hexylthiophene) (PPP-b-P3HT),25 poly(3-hexylthiophene)-block-(3-thiophene hexylacetate) (P3HT-b-P3THA),26 poly(3-hexylthiophene)-block-(3-(2-(2-methoxyethoxy)ethoxy)methylthiophene) (P3HT-b-P3MEEMT),25 and poly(3-hexylthiophene)-block-(3-(3,7-dimethyloctyloxy)thiophene) (P3HT-b-P3OOT).27 Because both blocks are energetically positioned to be donors in a typical device configuration, these systems are expected to function in a similar manner to a three component or ternary solar cell.

Figure 2.1 Selected all-conjugated P3AT-containing block copolymers.
The main advantage of a ternary system is that both the short circuit current ($J_{sc}$) and open circuit voltage ($V_{oc}$) can be tuned simultaneously by judicious choice of the three components. In the hypothetical system shown in Figure 2.2, the ternary device should theoretically have a higher efficiency than the binary device due to the larger HOMO$_D$-LUMO$_A$ offset imposed by the low HOMO level of D$_2$. The $J_{sc}$ should remain constant, since the narrow bandgap donor (D$_1$) is still present in the ternary device. A binary device containing only D$_2$ and acceptor would be expected to perform worse than the ternary device even though it will have the same $V_{oc}$ because it will have a lower $J_{sc}$ due the wide bandgap donor.

![Figure 2.2](image)

**Figure 2.2** Flat energy band diagram of a binary (left) and donor-donor-acceptor ternary (right) device. D$_1$ and D$_2$ represent the two donor materials and A represents the acceptor.

In systems with two polymer donors and one fullerene acceptor, the $V_{oc}$ of the ternary device was initially shown to be limited to the lowest $V_{oc}$ of the corresponding polymer:fullerene binary device. Recently, the Thompson group reported a ternary system with a P3HT donor and two fullerene acceptors (PC$_{61}$CM and ICBA). By changing the ratio of the two fullerenes, the $V_{oc}$ could be varied between the $V_{oc}$ values of the corresponding binary systems, and was not limited to the lowest $V_{oc}$ of the binary device. The theoretical upper limit $V_{oc}$, which is that of the binary P3HT:ICBA device, however, could not be obtained when any amount of the third component (PC$_{61}$BM) was present. The You group investigated two ternary systems, each with two polymer donors and a PCBM acceptor, and similarly found that the $V_{oc}$ could be varied between the voltages of the two component systems. Again, the upper limit voltages could not be obtained when any amount of the lower voltage polymer was present. It is also worth noting
that the device fabrication conditions, especially annealing temperatures, and the morphology of the active layer play important roles in determining the performance of ternary systems.32-34

Herein, I describe the molecular modeling, synthesis, characterization, and preliminary device testing of donor-donor block copolymers for organic solar cells. I have designed a system to understand how a ternary solar cell functions when two donor materials are covalently bound in a block copolymer arrangement. The polymer is poly(3-thiohexylthiophene)-block-(3-hexylthiophene) (P3HT-b-P3HT), and is one of only a few examples of a conjugated block copolymer with two optoelectronically distinct blocks. These polymers have been developed to (1) have a deep HOMO level in one block; and (2) span a wider breadth of the incident solar spectrum by covalently coupling two distinct chromophore units.

3 Results and discussion

3.1 Design and calculations

Poly(3-thioalkylthiophenes) (P3TATs) have lower energy absorption and lower lying electronic levels relative to their P3AT analogues, due to the less effective electron-donating ability of the thioalkyl substituent, relative to an alkyl group.35-38 Furthermore, the bulky sulfur atom in the 3-position causes the polymer backbone to twist, resulting in an increase in the ionization potential and decrease in the HOMO energy.39 A similar observation was recently made with poly(3-hexylthiophene-co-3-(2-ethylhexyl)thiophene) copolymers, in which the bulky ethylhexyl side chain caused a decrease in interchain π-π stacking interactions which decreases electron delocalization, raising the oxidation potential (and lowering the HOMO energy).40 In the context of a donor material for a photovoltaic device, a deep HOMO is desirable because it can lead to a high $V_{oc}$ when paired with an appropriate acceptor. Although P3TAT block copolymers have been synthesized with conjugated and non-conjugated groups,41,42 there have been no reports of copolymerization with alkylthiophenes (block, alternating or random).

Prior to synthesis, density functional theory (DFT) calculations were performed to predict the energy levels of the frontier molecular orbitals (FMOs) of the proposed block copolymer. To reduce the processing time, each block consists of eight repeat units and a 3-methyl substituent is used to approximate the electronic contribution from the hexyl side chains. These DFT calculations predict that the energy density of the HOMO will lie largely on the 3-
hexylthiophene block, while that of the LUMO will be concentrated on the 3-thiohexylthiophene block (Figure 2.3, right). This suggests the possibility of an intramolecular charge transfer, with P3HT acting as the donor, and P3THT acting as the acceptor. This hypothesis is further explored in fluorescence experiments (vide infra).

The calculated energy levels for the eight unit homopolymers are compared to those of the sixteen unit P3THT-b-P3HT (Figure 2.3, left). The average spacing between the energy levels of P3THT-b-P3HT (0.21 eV; not including the HOMO-LUMO gap) is approximately half that of the homopolymers (0.42 eV for P3HT, and 0.36 eV for P3THT) due to the increased conjugation length. This suggests that the interface between the two blocks does not break conjugation, as it would if the blocks behave as two isolated eight unit homopolymers. The values for the HOMO (-4.99 eV) and LUMO (-2.63 eV) of the model diblock are almost identical to the HOMO of the eight unit P3HT model (-4.98 eV), and LUMO of the eight unit P3THT model (-2.61 eV), respectively. It is important to note here, and in all theoretical discussions in this thesis, that DFT calculations are modeled in the gas phase, and that experimental energies will be perturbed from calculated values including through solvent and concentration/aggregation effects in solution, and via intermolecular interactions in the solid-state/thin films.

This prompted me to ask whether P3THT-b-P3HT acts as one energetically hybridized system, with unique molecular orbitals that delocalize over the entire chain, as in a typical donor-acceptor alternating copolymer,43-45 or as two isolated electronic units, with two “sets” of molecular orbitals corresponding to the two homopolymers. In the case of the latter, the “HOMO” of the sixteen unit P3THT-b-P3HT model would simply refer to the highest overall occupied molecular orbital, which is the HOMO of the 3-hexylthiophene block. Similarly, the “LUMO” of P3THT-b-P3HT model would refer to the lowest overall unoccupied molecular orbital, which is the LUMO of the 3-thiohexylthiophene block. When considering the energy density diagrams of additional FMOs (Figure 2.3, right), it was found that, like the HOMO and LUMO, these orbitals are not symmetrically localized over both blocks. When the FMO energies of the model oligomers are compared, the energy density of the P3THT-b-P3HT model tends to lie on the block whose corresponding homopolymer has an orbital with the most similar energy level. The energy density does not alternate from block to block for each successive orbital. For example, the energy density of the P3THT-b-P3HT model LUMO (-2.63 eV), LUMO + 1 (-2.34 eV) and HOMO – 1 (-5.16 eV) is concentrated on the P3THT block because the P3THT
homopolymer has similar energy FMOs (-2.61 eV, -2.23 eV, -5.20 eV). Similarly, the energy
density of the P3THT-b-P3HT model HOMO (-4.99 eV) and LUMO + 2 (-2.13 eV) is
concentrated on the P3HT block because the P3HT homopolymer has similar energy FMOs (-
4.98 eV, -2.07 eV). Moving further away from the FMOs, the P3THT-b-P3HT model orbitals
become more delocalized, likely because the homopolymers have more overlapping energies.
This suggests that there is some delocalization within the system, and potential communication
between the blocks.

Figure 2.3 HOMO-4 to LUMO+4 energy levels for eight unit P3HT and P3THT, and sixteen
unit P3THT-b-P3HT model compounds (left), and HOMO-2 to LUMO+2 energy density
diagrams for a sixteen unit P3THT-b-P3HT model (right). The energy scale only corresponds
to the left figure. The dotted lines are a guide for the eye.

3.2 Synthesis

To synthesize the polymers for this study, a 2,5-dibromo-3-thiohexylthiophene monomer was
synthesized according to previously reported procedure,\textsuperscript{37} and a 2,5-dibromo-3-hexylthiophene
monomer was used as received. Homopolymers were prepared by Grignard metathesis
polymerization using \( i \)-propylmagnesium chloride and \([1,3\text{-bis(diphenylphosphino)propane} ]\)nickel (II) chloride \([\text{Ni(dppp)}\text{Cl}_2]\). After 60 minutes, the reaction was quenched with 2 M HCl and precipitated into methanol. The precipitate was then subject to Soxhlet extraction with methanol, hexanes, and chloroform (the chloroform fraction was further purified by silica gel column chromatography to remove any trace metal or catalyst). Poly(3-thiohexylthiophene) was isolated from the chloroform fraction in 72% yield \((M_n = 10.4 \text{ kDa}, M_w = 19.9 \text{ kDa}, D = 1.9)\).

The 50:50 block copolymer (Scheme 2.1) was prepared by first activating the thioalkylated monomer with an \( i \)-propylmagnesium chloride-lithium chloride complex (Turbo Grignard) and treating the activated monomer with \([\text{Ni(dppp)}\text{Cl}_2]\) to initiate polymerization. In a second vessel, an equimolar amount 3-hexylthiophene was activated and added to the polymerization reaction after 60 min. After an additional 60 minutes, the reaction was quenched with 2 M HCl and precipitated into methanol. The precipitate was then subject to Soxhlet extraction with methanol, hexanes, and chloroform. Poly(3-thiohexylthiophene-\textit{block}-3-hexylthiophene) was isolated from the chloroform fraction and subjected to silica gel column chromatography (to remove any trace metal or catalyst) in 43% yield \((M_n = 7.8 \text{ kDa}, M_w = 13.4 \text{ kDa}, D = 1.7\), regioregularity of P3HT block = 80%).

\[\text{Scheme 2.1 Synthesis of poly(3-thiohexylthiophene)-\textit{block}-3-hexylthiophene).}\]

It should be noted that the GRIM method produces regiorandom P3TATs.\textsuperscript{38} Regiorandom P3TATs have a shorter conjugation length in solution than regioregular P3TATs, but in the solid-state, both regioisomers planarize and stack, and have an equal conjugation length.\textsuperscript{38} Although regioregularity is known to affect the device performance of P3ATs, it is not expected...
to have as great an effect on P3TATs, since their regioregularity does not seem to change their solid-state properties. The regioregularity of the P3HT block (80%) can be calculated from $^1$H NMR by integrating the $\alpha$-methylen protons signals at 2.81 ppm (HT) and 2.58 ppm (HH), which are absent in the P3THT homopolymer spectrum.

### 3.3 Solution-based characterization

The polystyrene equivalent molecular weights were lower than expected for a quasi-living polymerization with 1 mol% catalyst loading which should give 100 repeat units per chain ($M_n = 20.0$ kDa for P3THT and $M_n = 18.2$ kDa for P3THT-$b$-P3HT). Due to the nature of the fractionation procedure, it can be concluded that both monomers were completely consumed, as no monomer (brominated or hydrogenated) was detected in the methanol fraction by $^1$H NMR. Low molecular weight oligomers were collected in the hexanes fraction, and account for approximately 10% (P3THT) and 6% (P3THT-$b$-P3HT) of the total “polymer” yield. The low molecular weights may be due to the lower solubility of the 3-thiohexyl containing polymers relative to P3HT, which could cause the polymers to precipitate out of solution before a high molecular weight can be achieved.

All GPC traces are Gaussian in nature, and there is no evidence of a higher $M_n$ shoulder in either the homo- or block copolymers (Figure 2.4). This observation confirms that triblock copolymers have not been formed via the chain coupling of two active chains (ie. the disproportionation of the two Ni(dppp)Br active chain ends), which would result in a P3HT-P3THT-P3HT triblock copolymer with an $M_n$ up to double that of the desired diblock copolymer. There is still the possibility, however, that triblock copolymers may have been formed via “chain-walking” of the nickel catalyst.$^{46,47}$ This is unlikely since the initial P3THT block is sufficiently long and the polymerization rate of P3HT is fast.
The uniquely substituted thiophene repeat units each have distinct $^1$H NMR resonances, a sharp singlet at 6.99 ppm for 3-hexylthiophene, and a broad multiplet from 7.42-7.01 for 3-thiohexylthiophene, as previously reported.\textsuperscript{37} Integration of these signals indicates that the P3HT:P3THT ratio is approximately 50:50 (the monomer feed ratio), within integration error. Furthermore, the integration of the $\alpha$-methylene protons on the side-chains (2.81 ppm for P3HT; 2.94 ppm for P3THT) can be roughly integrated to give a P3HT:P3THT ratio of 48:52, which is similar to the integration of the aromatic signals.

To further determine structure, optical absorption spectroscopy was carried out in chloroform. To provide context, the absorbance spectra of the homopolymers were measured and compared to those of the block copolymer (Figure 2.5a). The onset of absorption of P3THT-$b$-P3HT (587 nm) is closer to P3THT (597 nm) than P3HT (545 nm) and the spectrum is much broader than either homopolymer. Specifically, the full width at half maximum (FWHM) of P3THT-$b$-P3HT is 0.90 eV, in comparison to 0.70 eV, and 0.77 eV for P3THT and P3HT, respectively (Figure 2.5a). These observations indicate that both P3HT and P3THT chromophores are present in P3THT-$b$-P3HT. The bathochromic shift of P3THT relative to P3HT has been attributed to the less electron-donating nature of the thiohexyl side chain,\textsuperscript{37} and it can be inferred that this effect is also responsible for the bathochromic shift in the block copolymer. This observation is consistent with time-dependent DFT calculations, which predict that the state with the highest oscillator strength has significant contributions from P3THT-centered transitions.
Figure 2.5 (a) Solution absorbance, (b) normalized emission, and (c) relative emission spectra (all measured in chloroform). The key shows the polymer structures and their corresponding line colors in the spectra.

Solution fluorescence measurements were taken to probe relaxation pathways and electronic communication between the blocks in the excited state (Figure 2.5b and c). All three polymers (P3HT, P3THT, P3THT-b-P3HT) as well as a 1:1 mol/mol P3HT:P3THT mixture were compared where each solution had an identical absorbance (0.01 a.u) at 470 nm (the excitation wavelength). For reference, P3HT emits at 573 nm and P3THT at 597 nm. If the copolymer behaved as two distinct but isolated chromophores, the block copolymer spectrum should be dominated by emission from the P3HT block, due to its greater fluorescence intensity (vide infra). In contrast, P3THT-b-P3HT emits strongly at 594 nm, and has a very similar profile to P3THT emission, suggesting that the emission is due to a different relaxation pathway than that which occurs in P3HT. A 1:1 mixture of the two homopolymers, however, emits at 590 nm, a frequency more closely positioned between the P3HT and P3THT emissions (585 nm is the average of the two homopolymers). The difference in emission of the block copolymer is likely due to some degree of energy transfer from the P3HT block to the P3THT block or a relaxation from the LUMO (centered on P3THT) to the HOMO (centered on P3HT), near the interface. This is not observed in the binary mixture because of the short distance requirements for these processes.

The difference in emission properties between P3THT-b-P3HT and the mixture is also observed in fluorescence quantum yield measurements ($\Phi_F$). Specifically, the $\Phi_F$ are 15.9, 7.6, 13.9, and 5.2% for P3HT, P3THT, P3THT-b-P3HT, and the 1:1 mol/mol P3HT:P3THT mixture,
respectively (Rhodamine 6G standard). Notably, the $\Phi_F$ of P3THT-b-P3HT is more than double that of the mixture. This implies that the block copolymer emission is not simply due to an averaging of the emission of the two homopolymers, since the $\Phi_F$ of P3THT-b-P3HT is much closer to P3HT than P3THT. Taken together with the emission profiles, these observations suggest that, in solution, electronic communication is occurring between blocks.

The fact that charge transfer can occur at the diblock interface is important generally, because it suggests that exciton dissociation will occur within the polymer, in addition to at the donor-acceptor interface. This is unlikely in our system since the LUMO$_{P3HT}$-LUMO$_{P3THT}$ offset is only 0.1 eV, and 0.3 eV is considered the minimum offset required for exciton dissociation. This observation does suggest however that in a block copolymer with suitably offset energy levels, electronic communication between blocks could help promote exciton dissociation and prevent geminate recombination, which is another potential advantage of using block copolymers in devices.

Overall, the absorbance and emission characteristics of P3THT-b-P3HT in solution are consistent with the DFT calculations, which both suggest that the block copolymer behaves as two covalently bound but energetically isolated chromophores, which are capable of electronic communication near the diblock interface in dilute solution, but not necessarily in the solid-state.

### 3.4 Solid-state characterization

I next conducted absorption spectroscopy in the solid-state on films that were spin-coated from chloroform and annealed at 140 °C for 30 minutes. The P3THT-b-P3HT absorption (Figure 2.6a) is broader than either homopolymer, and the onset occurs at 674 nm, which is much closer to P3THT (676 nm) than P3HT (649 nm). The P3THT-b-P3HT curve has a weaker shoulder at 620 nm than P3THT, suggesting that the block copolymer packs differently and undergoes less $\pi-\pi$ stacking interactions.
Figure 2.6 (a) Solid-state absorbance and (b) emission spectra. Films were spin-coated from 6 mg/mL chloroform solutions at 1000 rpm onto glass substrates and annealed at 140 °C for 30 minutes under nitrogen.

Fluorescence measurements were carried out on the same thin films to understand how energy flows in the solid state. Here, P3THT-b-P3HT is compared with the two homopolymers as well as a 1:1 (mol/mol) physical blend (P3HT:P3THT). The profile of the P3THT, P3THT-b-P3HT and P3HT:P3THT emission curves are quite similar, with shoulders at 790 and 720 nm (Figure 2.6b) suggesting that relaxation pathways are similar in all three films. The small shoulder at 720 nm is only present in the P3THT-containing films. Overall the differences between the optical properties of the block copolymer and its constituent blend of homopolymers are much less pronounced in the solid-state than in solution, which is likely due to the close distances between P3HT and P3THT in the blend. The unique intramolecular relaxation pathways observed for P3THT-b-P3HT in solution cannot be distinguished in the solid-state since the same type of transitions can occur in a physical mixture P3HT and P3THT homopolymers in the solid-state. No evidence of solid-state photoluminescence (PL) quenching was observed in either the block copolymer or blend since all films are sufficiently fluorescent. This suggests that the energies of P3HT and P3THT are not offset enough such that photoinduced charge transfer takes place from P3HT to P3THT, as it would in a true donor-acceptor block copolymer system.49

To better understand the position of the FMOs in the block copolymer, cyclic voltammetry was performed (Figure 2.7). The HOMO energy is calculated from the onset of oxidation, the LUMO from the onset of reduction, and the electrochemical HOMO-LUMO gap from the difference in these two values (Table 2.1). The HOMO energy of P3THT-b-P3HT (-5.3 eV) has an
intermediate value between P3HT (-5.1 eV) and P3THT (-5.5 eV). The LUMO energy of the block copolymer (-2.9 eV) is less negative than the electrochemical values for either P3HT (-3.2 eV) or P3THT (-3.3 eV) homopolymer resulting in a greater electrochemical HOMO-LUMO gap (2.4 eV) than either homopolymer (1.9 eV for P3HT, 2.2 eV for P3THT). Nonetheless, introduction of the thioalkylated block was successful in lowering the HOMO relative to P3HT, which should effectively increase the $V_{oc}$ of the corresponding device.

Figure 2.7 Cyclic voltammogram (a, c) oxidation and (b, d) reduction curves of (a, b) P3THT and (c, d) P3THT-b-P3HT thin films in acetonitrile/TBAPF$_6$ electrolyte. A ferrocene redox couple (Fc/Fc$^+$) was used as an internal standard.
Table 2.1 HOMO and LUMO Energy Levels and Electrochemical and Optical Bandgaps of P3HT, P3THT and P3THT-b-P3HT (in eV relative to vacuum).

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{HOMO}}$</th>
<th>$E_{\text{LUMO}}$</th>
<th>$E_g^{\text{echm},c}$</th>
<th>$E_g^{\text{opt},d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>-5.1</td>
<td>-3.2</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>P3THT</td>
<td>-5.5</td>
<td>-3.3</td>
<td>2.2</td>
<td>1.8</td>
</tr>
<tr>
<td>P3THT-b-P3HT</td>
<td>-5.3</td>
<td>-2.9</td>
<td>2.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*a*Calculated from onset of oxidation by cyclic voltammetry; *b*Calculated from onset of reduction by cyclic voltammetry; *c*Calculated from $E_{\text{HOMO}} - E_{\text{LUMO}}$ as determined in *a* and *b*; *d*Calculated from onset of absorption (wavelength at 10% of the baseline signal).

The crystallinity of the films was studied next. Powder x-ray diffraction (PXRD) profiles of thin films have distinct interlayer spacings (d-spacing) of 16.3, 18.1, and 17.4 Å for P3HT, P3THT, and P3THT-b-P3HT, respectively (Figure 2.8). Although the P3THT-b-P3HT peak lies between the P3HT and P3THT peaks, it is much broader than either homopolymer, with a FWHM of 0.54° compared to 0.26° and 0.24° for P3HT and P3THT, respectively. It is likely that the P3THT-b-P3HT peak is a superposition of the two homopolymer peaks, which would indicate that the blocks crystallize separately and there is no intermixing of the hexyl and thiohexyl chains. Overall, the sharpness and intensity of the 2θ peak of P3THT and P3THT-b-P3HT confirm that the thioalkylated polymers are semi-crystalline, even though computational modeling suggests that the sulfur atom causes a twist in the polymer backbone. This is likely due to the π-π interactions overcoming the steric strain of the thioalkyl side chains in the solid-state.
Figure 2.8 X-ray diffraction pattern of P3HT, P3THT, and P3THT-b-P3HT annealed thin films. Films were prepared by drop-casting 7 mg/mL polymer solutions in chloroform onto silicon wafers and annealed at 200 °C for 30 minutes under nitrogen.

The morphology of P3THT-b-P3HT thin films was studied next. Atomic force microscopy (AFM) height and phase images were obtained on P3THT-b-P3HT films, as well as on films of P3THT-b-P3HT blended with [6,6]-phenyl-C_{71}-butyric acid methyl ester (PC_{71}BM; e.g. the typical device configuration) (Figure 2.9). The images reveal a structured morphology, with distinct domains, suggesting that some phase separation occurs both with and without fullerene. In both cases the domain size is relatively fine, and structured at the nanoscale (~20 nm). In contrast, the P3HT:P3THT (1:1) and P3HT:P3THT:PC_{71}BM (0.5:0.5:1) blend films have a different morphology than the P3THT-b-P3HT films.
Figure 2.9 AFM (a-e) height and (f-j) phase images of (a, f) P3THT-\textit{b}-P3HT, (b, g) P3THT-\textit{b}-P3HT:PC\textsubscript{71}BM, (c, h) P3THT, (d, i) P3HT:P3THT, and (e, j) P3HT:P3THT:PC\textsubscript{71}BM annealed thin films spin-coated from 6 mg/mL chloroform solutions at 1000 rpm on glass substrates and annealed 140 °C for 30 minutes under nitrogen.

3.5 Device characterization

Based on the above theoretical and experimental observations, I hypothesized that when P3THT-\textit{b}-P3HT is mixed with PC\textsubscript{71}BM, both blocks will absorb light, and excitons will be generated in both block domains. Photoinduced charge transfer is energetically allowed between P3HT and PC\textsubscript{71}BM, and P3THT and PC\textsubscript{71}BM.\textsuperscript{32} In turn, holes will be generated in both P3HT and P3THT, and can be transported to the anode from either block. In the context of a photovoltaic device, it is expected that the energy levels of P3THT-\textit{b}-P3HT will behave independently of each other, electronically resembling a P3HT:P3THT:PC\textsubscript{71}BM blend, as was observed in the solid-state optical experiments. The $V_{oc}$ in bulk heterojunction (BHJ) solar cells is proportional to the difference between the HOMO energy of the donor (HOMO\textsubscript{D}) and the LUMO energy of the acceptor (LUMO\textsubscript{A}). For a conjugated polymer-PCBM solar cell, the $V_{oc}$ can be estimated by $V_{oc} = (1/e)(\mid \text{HOMO}_D \mid - \mid \text{LUMO}_A \mid) - 0.3$ V.\textsuperscript{50} The potential at the anode will differ depending on which block the holes are harvested from, and therefore the $V_{oc}$ for this 50:50 block copolymer is expected to lie between the values of the corresponding binary devices. The offset energy between the HOMO\textsubscript{D} and LUMO\textsubscript{A} of our system (calculated from cyclic voltammetry) lies between 0.8 and 1.2 eV (Figure 2.10) and the low energy HOMO of P3THT can be expected to increase the potential of the ternary device by up to 0.4 V, relative to a P3HT:PC\textsubscript{71}BM device.
Employing Brabec’s equation, the $V_{oc}$ of our device should then lie between 0.5 and 0.9 V. When considering the “HOMO” of P3THT-$b$-P3HT found by cyclic voltammetry (5.3 eV), the $V_{oc}$ of the ternary device is expected to be 0.7 V.

**Figure 2.10** Flat energy band diagrams for (a) P3HT:PC$_{71}$BM, (b) P3THT:PC$_{71}$BM, and (c) P3HT:P3THT:PC$_{71}$BM BHJ devices. $\Delta \Phi$ denotes the offset energy between the HOMO of the electron donor (P3HT or P3THT) and the LUMO of the electron acceptor (PC$_{71}$BM).

To test this hypothesis, BHJ solar cells were fabricated with a structure of ITO/PEDOT:PSS/polymer:PC$_{71}$BM/LiF/Al and characterized (Figure 2.11). Fabrication conditions (polymer concentration, spin speed, annealing time and temperature) were optimized for each polymer, however, the polymer:PC$_{71}$BM ratio was kept constant at 1:1. The optimized conditions for each polymer likely correspond to the conditions that give the most optimal morphology, which increase charge-separation and mobility within the bulk material. Since the bulky sulfur atom in the thioalkyl side chain causes a twist in the polymer backbone, less $\pi-\pi$ interactions can occur in P3THT (and hence P3THT-$b$-P3HT to a lesser degree), and therefore different processing conditions are required to optimize this system. Interestingly, the $V_{oc}$ of both the P3THT-$b$-P3HT and P3THT device is 0.66 V, compared to 0.58 V for a P3HT:PC$_{71}$BM device fabricated under the same conditions (Table 2.2). This potential is equivalent to the *upper limit* of a binary blend P3THT:PC$_{71}$BM device even though both P3HT and P3THT are present in a roughly 1:1 ratio. This observation is consistent with the previous report that the $V_{oc}$ of ternary devices is not limited to the smallest value of the corresponding binary devices, and in fact confirms that the $V_{oc}$ can actually reach the upper limit of the binary system.
Figure 2.11 (a) $J$-$V$ curves and (b) EQE spectra for polymer:PC$_{71}$CM devices where the donor polymer is denoted by the line color.

The covalent linkage between the two blocks is very important for controlling active layer morphology. In control experiments using a true ternary blend of 0.5:0.5:1 P3HT:P3THT:PC$_{71}$BM, devices have a lower fill factor ($FF$) (0.32) than the P3THT-$b$-P3HT:PC$_{71}$BM device (0.42). The P3HT:P3THT:PC$_{71}$BM device also exhibits an “s-shaped” $J$-$V$ curve which suggests poorer contact at the electrodes, compared to the block copolymer device. Furthermore, the standard deviation of the average PCE for the P3THT-$b$-P3HT:PC$_{71}$BM device is only ±0.01, but increases to ±0.15 for P3HT:P3THT:PC$_{71}$BM, suggesting greater batch-to-batch variability for the blend system. Given that reproducible devices are a critical figure of merit, when considering the average efficiencies only, the P3THT-$b$-P3HT:PC$_{71}$BM device (1.04%) outperforms P3HT:P3THT:PC$_{71}$BM (0.87%).
Table 2.2 Photovoltaic Properties of Binary and Ternary Blend BHJ Solar Cells with Different Donor Components.

<table>
<thead>
<tr>
<th>Conc. (mg/mL)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCEmax (%)</th>
<th>PCEavg c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PC₇₁BMd</td>
<td>10:10</td>
<td>8.09</td>
<td>0.58</td>
<td>65.8</td>
<td>3.09</td>
</tr>
<tr>
<td>P3THT:PC₇₁BMd</td>
<td>10:10</td>
<td>3.48</td>
<td>0.66</td>
<td>28.9</td>
<td>0.66</td>
</tr>
<tr>
<td>P3THT-b-P3HT:PC₇₁BMe</td>
<td>7.5:7.5</td>
<td>3.83</td>
<td>0.66</td>
<td>41.6</td>
<td>1.05</td>
</tr>
</tbody>
</table>

aDevices were spin-coated from 1,2-dichlorobenzene at 800 rpm; bActive layer thickness is approximately 100 nm; cAverage PCE of five devices fabricated under identical conditions ± standard deviation; dAnnealed at 120 °C for 30 min; eAnnealed at 100 °C for 30 min.

Although the focus of this study was the effect of the thioalkyl chain and the block copolymer structure on the Voc, a significant decrease in both the Jsc and FF for the P3THT containing devices is observed relative to P3HT. The Jsc and FF of the P3THT-b-P3HT device lie in between those of the P3HT and P3THT binary devices. This is again likely due to the effect of the bulky thioalkyl side chain causing a twist in the polymer backbone, which decreases π-π stacking.

The Voc of the block copolymer device can be increased to a maximum of 0.72 V using a diiodooctane (DIO) additive in the active layer. Solvent additives have been reported to increase device efficiency by modifying the morphological length scales of the donor and acceptor domains. The champion P3THT-b-P3HT:PC₇₁BM device with a DIO additive thus far has a short circuit current density (Jsc) of 4.12 mA cm², Voc of 0.72 V, FF of 0.38 and PCE of 1.14% which is the highest value of any previously reported P3TAT containing device.

4 Conclusions

Poly(3-thiohexylthiophene)-block-(3-hexylthiophene) has been synthesized by Grignard metathesis polymerization, characterized, and used as the “double donor” material in a bulk heterojunction solar cell. The fundamental behavior of P3THT-b-P3HT was studied and it was found that there is electronic communication between the blocks resulting in unique absorption and emission properties in solution. In the solid-state, P3THT-b-P3HT acts similarly to a blend of the two constituent homopolymers. DFT calculations and cyclic voltammetry experiments confirm that the introduction of the thioalkyl group lowers the HOMO energy level of P3THT-b-
P3HT. When testing P3THT-\textit{b}-P3HT:PC71BM solar cell devices, the measured \( V_{oc} \) is as high as the \( V_{oc} \) of the control device composed of the single donor material with the deepest HOMO level (P3THT). The block copolymer structure is essential to maintain a good \( FF \) relative to the control device composed of a blend of the two homopolymers. This demonstrates that even in an equally proportioned ternary BHJ organic solar cell, the measured \( V_{oc} \) can reach the upper limit of the corresponding binary devices. All-conjugated block copolymers are a promising optoelectronic “double donor” material for solar cells, and a high \( V_{oc} \) can be obtained even if one of the donor blocks is composed of a material with a high-lying HOMO level such as P3HT. The relatively straightforward synthesis should motivate the preparation, characterization, and testing of other donor-donor block copolymers.

5 Experimental

5.1 General considerations

All reagents were used as received unless otherwise noted. 3-Bromo thiophene, \textit{n}-butyllithium (1.6 M in hexanes), \textit{N}-bromosuccinimide, \textit{i}-propylmagnesium chloride (2.0 M in THF), \textit{i}-propylmagnesium chloride-lithium chloride complex (1.3 M in THF), and [1,3-bis(diphenylphosphino)propane]nickel (II) chloride (Ni(dppp)Cl2) were purchased from Sigma-Aldrich. \textit{N}-bromosuccinimide was purchased from Acros Organics and recrystallized in water prior to use.

5.2 Instrumentation and methods

NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 400 MHz for \(^1\text{H}\) and 100 MHz for \(^{13}\text{C}\). Chemical shifts are reported in ppm at ambient temperature. \(^1\text{H}\) chemical shifts are referenced to the residual protonated chloroform peak at 7.26 ppm. Polymer molecular weights were determined with a Viscotek HT-GPC (1,2,4-trichlorobenzene, 140 °C, 1 mL/min flow rate) using Tosoh Bioscience LLC TSK-GEL GMH\textsubscript{HR}-HT mixed-bed columns and narrow molecular weight distribution polystyrene standards. A refractive index detector was used to detect the eluted polymer with respect to elution volume. Absorption spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer. Emission spectra were recorded on a Photon Technology International QuantaMaster 40-F NA spectrofluorometer with a photomultiplier detector and a xenon arc lamp source. Electrochemistry was performed with a BASi Epsilon
potentiostat. AFM images were obtained with a Vecco Dimension 3000 microscope. Powder X-ray diffraction spectra were recorded on a Bruker AXS D8 Discovery with a GADDS area detector.

For the solid-state absorbance and emission experiments, solutions of polymer (6 mg/mL) in chloroform were spin-coated at 1000 rpm onto glass substrates that had been washed with methanol. The films were annealed at 140 °C for 30 minutes in a nitrogen atmosphere. The annealed films were also used for AFM imaging. For XRD, the samples were prepared by drop-casting polymer solutions (7 mg/mL) in chloroform onto silicon wafers. The samples were annealed at 200 °C for 30 minutes in a nitrogen atmosphere.

For photoluminescence measurements, polymer solutions were prepared in chloroform such that they all absorbed at 0.01 a.u. at 470 nm. The solutions were excited at 470 nm and emission was measured over the 500-800 nm range. Integration time was 1 second with a 1 nm step size. The area under the average trace (5 repeats) was integrated and $\Phi_{PL}$ was calculated relative to a Rhodamine 6G standard in chloroform. Solid-state emission was measured on the same thin films as were used for the absorbance measurements. The films were excited at 480 nm and emission was collected over the 560-900 nm range. The film was positioned in the sample holder at 280° and the excitation and emission monochromator slits were opened to 4 and 3.5 nm, and 2 and 2 nm, respectively.

For cyclic voltammetry measurements, the electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in acetonitrile. A solution of polymer in chloroform (7 mg/mL) was drop-cast onto the working electrode, and the solvent evaporated in air. The working electrode was a 2 mm Pt-disc, the counter electrode was a platinum wire, and the pseudoreference electrode was a silver wire, with a ferrocene internal reference, and a scan rate of 25 mV/s.

### 5.3 Density functional theory calculations

Geometry optimizations were performed for the eight unit homopolymers and sixteen unit block copolymer using the *Gaussian 09* program,$^{55}$ employing the Becke Three Parameter Hybrid Functionals Lee-Yang-Parr (B3LYP) level of theory.$^{56,57}$ The standard 6-31G(d) basis set was used. The structures were generated using Gausview 5.0 and optimized to a minimum. From the
optimized geometry the first ten singlet and triplet transitions were calculated using time-dependent DFT.\textsuperscript{58}

5.4 Photovoltaic device fabrication and characterization

Polymer and PC\textsubscript{71}BM (American Dye Source) were mixed in 1,2-dichlorobenzene at 1:1 wt ratio (7.5:7.5 or 10:10 mg/mL). The concentrations were optimized individually for each polymer to optimize device performance. Solutions were stirred at 50 °C overnight to ensure complete dissolution. Devices were fabricated on commercial indium tin oxide (ITO) substrates (Colorado Concept Coatings) that had a sheet resistance of \( \sim 10 \ \Omega/\square \). These substrates were cleaned in aqueous detergent, deionized (DI) water, acetone and methanol, and subsequently treated in an oxygen-plasma cleaner for 5 min. Next, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P VP AI 4083) was coated onto the substrates at 3000 rpm and annealed in air at 130 °C for 15 min. After annealing, the substrates were transferred into a nitrogen-filled glove box, where polymer:PC\textsubscript{71}BM blends were coated at 800 rpm and dried at room temperature in closed petri-dishes. The polymer layer was annealed on a hot plate before transferring the samples into an evaporator. Finally, a 0.8 nm LiF layer and 100 nm Al anode was thermally deposited through a shadow mask at \( \sim 10^6 \) torr. Device area is 0.07 cm\textsuperscript{2} as defined by the area of circular Al anode. I-V characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5 G conditions with a power intensity of 100 mW/cm\textsuperscript{2}. The mismatch of simulator spectrum was calibrated using a Si diode with a KG-5 filter. EQE spectra were recorded and compared with a Si reference cell that is traceable to the National Institute of Stands and Technology. Five identical devices were measured for each set of conditions and both the average and maximum PCE are reported in Table 2.2.

5.5 Synthesis

![Reaction](image)

**3-Thiohexylthiophene.** 3-Bromothiophene, (10 g, 0.061 mol) in a mixture of hexanes (100 mL) and dry THF (12 mL) under N\textsubscript{2}, was cooled to \(-40 \) °C and \( n\)-BuLi (0.061 mol, 44 mL of freshly
titrated 1.4 M hexanes solution) was added drop-wise. Hexanes (40 mL) was added and the dark brown-yellow suspension was warmed to room temperature. A solution of hexyl disulfide (0.061 mol, 14.3 g) in hexanes (75 mL) was added and the resulting white suspension was stirred under N\textsubscript{2} for 2 hours, and then quenched with a solution of saturated ammonium chloride (80 mL). The solution was extracted with ether, washed with brine, and dried over MgSO\textsubscript{4}. The solvent was evaporated and the product was purified by column chromatography (hexanes) (5.8 g, 47% yield). \textsuperscript{1}H NMR (399 MHz, CDCl\textsubscript{3}) \(\delta\): 7.31 (q, 1H), 7.12 (d of d, 1H), 7.02 (d of d, 1H), 2.84 (t, 2H), 1.66-1.26 (m, 8H), 0.89 (t, 3H). Spectroscopy was identical to that of the previous report of this compound.\textsuperscript{37}

\[ \text{SC}_6\text{H}_{13} \quad \text{NBS} \quad \rightarrow \quad \text{SC}_6\text{H}_{13} \]

2,5-Dibromo-3-thiohexylthiophene. A solution of \textit{N}-bromosuccinimide (0.074 mol, 13.2 g) in dry DMF (200 mL) was added drop-wise to a degassed solution of 3-thiohexylthiophene (0.025 mol, 4.95 g) in dry DMF (250 mL) at 0 °C under N\textsubscript{2} in the dark. The mixture was allowed to slowly warm to room temperature and was stirred under N\textsubscript{2} for 17 hours. The solution was then diluted with ether (20 mL), washed two times each with 10% Na\textsubscript{2}SO\textsubscript{4} and brine, and dried over MgSO\textsubscript{4}. The solvent was evaporated and the product was purified by column chromatography (hexanes) (1.3 g, 15% yield). \textsuperscript{1}H NMR (399 MHz, CDCl\textsubscript{3}) \(\delta\): 6.90 (s, 1H), 2.82 (t, 2H), 1.62-1.26 (m, 8H), 0.89 (t, 3H). Spectroscopy was identical to that of the previous report of this compound.\textsuperscript{37}

\[ \text{Br} \quad \text{SC}_6\text{H}_{13} \quad \text{Br} \quad \text{SC}_6\text{H}_{13} \quad \xrightarrow{\text{NBS}} \quad \text{SC}_6\text{H}_{13} \quad \text{Br} \quad \text{SC}_6\text{H}_{13} \]

\textbf{Poly(3-thiohexylthiophene) (P3THT).} \textit{i}-Propylmagnesium chloride (0.58 mL, 2.0 M in THF) was added drop-wise to a solution of 2,5-dibromo-3-thiohexylthiophene (414 mg, 1.15 mmol) in dry THF (8 mL) under N\textsubscript{2}. The mixture was stirred at 40 °C for 90 minutes and then transferred to a flask containing Ni(dppp)Cl\textsubscript{2} (12.5 mg, 0.023 mmol) and stirred at 60 °C for 2 hours. The deep red solution was cooled to room temperature, quenched with 2 M HCl, and precipitated into
methanol. The product was purified by Soxhlet extraction using methanol, hexanes, and chloroform. The chloroform fraction (165 mg, 72% yield) was further purified by silica gel chromatography, and the resulting solution was concentrated to yield the polymer as a purple solid (126 mg, 55% yield). $^1$H NMR (399 MHz, CDCl$_3$) δ: 7.42-7.12 (m, 1H), 2.94 (br, 2H), 1.69-1.30 (m, 8H), 0.89 (br, 3H). GPC: $M_n = 10.4$ kDa, $M_w = 19.9$ kDa, $Đ = 1.9$. Spectroscopy was identical to that of the previous report of this compound.$^{37}$

**Poly(3-thiohexylthiophene)-block-(3-hexylthiophene).** $i$-Propylmagnesium chloride lithium chloride complex solution (0.54 mL, 1.3 M in THF) was added drop-wise to a solution of 2,5-dibromo-3-thiohexylthiophene (253 mg, 0.706 mmol) in dry THF (5 mL) and stirred under N$_2$ at 40 °C for 1 hour. The solution was then transferred to a nitrogen filled flask containing Ni(dppp)Cl$_2$ (7.65 mg 0.014 mmol) (Solution A) and stirred at 50 °C. Concurrently, $i$-propylmagnesium chloride-lithium chloride complex solution (0.54 mL, 1.3 M in THF) was added drop-wise to a solution of 2,5-dibromo-3-hexylthiophene in dry methyl-THF (5 mL) and stirred under N$_2$ at 40 °C (Solution B). After 1 hour, solution B was added to solution A and the combined mixture was stirred at 50 °C for an additional hour. The deep red solution was then cooled to room temperature, quenched with 2 M HCl, and precipitated into methanol. The product was purified by Soxhlet extraction using methanol, hexanes, and chloroform. The chloroform fraction (110 mg, 43% yield) was further purified by silica gel chromatography, and the resulting solution was concentrated to yield the polymer as a purple solid (75 mg, 29% yield). $^1$H NMR (399 MHz, CDCl$_3$) δ 7.38 (m, 1H), 6.99 (s, 1H), 2.95 (br, 2H), 2.81 (br, 2H), 1.72-1.26 (m, 16H), 0.93-0.91 (br, 6H). GPC: $M_n = 7.8$ kDa, $M_w = 13.4$ kDa, $Đ = 1.7$, regioregularity of P3HT block = 80%.

6 References


2310.


(43) Ono, R. J.; Kang, S.; Bielawski, C. W. Macromolecules 2012, 45, 2321–2326.


Chapter 3
Poly(3-hexylthiophene)-stat-(3-thiohexylthiophene) Statistical Copolymers

1 Statement of contributions

Solar cell fabrication and testing were performed by Dong Gao. I carried out all other synthesis, characterization, computations, and experiments presented in this chapter. I drafted the manuscript for publication, which was edited by Dwight Seferos. Portions of this work have appeared in print.¹

2 Introduction

Following the results of chapter 2, I was next interested in learning if the amount of the 3-thiohexylthiophene unit could be decreased to improve the $J_{sc}$ and $FF$ of copolymer devices while maintaining a high $V_{oc}$. For this study, I chose to synthesize a series of statistical (or random) copolymers of various monomer ratios. Whereas block copolymers can be thought of as two distinct, covalently bound homopolymers, statistical copolymers are a single unique polymer, with properties differing from the block copolymer, the individual homopolymers, or blends of the two. Because the comonomers are randomly incorporated into the chain, statistical copolymers do not undergo phase separation on the 10-20 nm scale, and therefore the solid-state morphology likely differs from the corresponding block copolymer with the same monomer incorporation ratio and chain length. My group recently studied an equally proportioned poly(3-heptylseleophene)-stat-(3-hexylthiophene) system and found that the optical properties are an average of the two constituent homopolymers, whereas the crystallization and melting behavior are distinct from either homopolymer.² Jenekhe and coworkers studied a statistical poly(3-alkylthiophene) (P3AT) with two different linear alkyl chains, and found that the crystalline structure and optoelectronic properties were readily tunable by varying the composition.³ More recently, Thompson and coworkers reported a P3AT copolymer containing linear hexyl and branched ethylhexyl side chains, and studied the effect of the composition on device properties in a BHJ solar cell.⁴ They found that even small amounts of the ethylhexyl side chain led to a decrease in the HOMO level, resulting in an increase in $V_{oc}$ due to the greater HOMO$_D$ – LUMO$_A$ offset. The HOMO level and $V_{oc}$ of the poly(3-hexylthiophene)-co-(3-(2-ethylhexyl)thiophene) (P3HT-co-P3EHT) devices was composition-dependent, and device
performance was optimal for the 75:25 copolymer. This suggests that the incorporation of small amounts of monomer with low-lying HOMO levels is a potential strategy for raising the $V_{oc}$ of a device without lowering the $J_{sc}$ or $FF$. These observations provide motivation to examine the P3HT:P3THT copolymer system as a statistical copolymer.

Herein, I describe the synthesis, characterization, and device performance of the statistical copolymer variant of the P3HT:P3THT system. By statistically incorporating 3-thiohexylthiophene into the chain, a high $V_{oc}$ was achieved. By statistically incorporating 3-hexylthiophene into the chain, the regioregularity of the polymer was improved, relative to what can be achieved with a compositionally equivalent diblock copolymer. The goals of this study were to determine: (1) the effect of the statistical structure on the mechanism of controlling polymer regioregularity, (2) the minimum amount of 3-thiohexylthiophene incorporation required to increase the $V_{oc}$ of the device to a level that is equivalent to pure P3THT, and (3) how the properties and mechanism of the devices change as a function of statistical incorporation.

### 3 Results and discussion

#### 3.1 Synthesis

The statistical copolymers used in this study were synthesized via Grignard metathesis (GRIM) polymerization using a monomer mixture containing the desired ratio of 2,5-dibromo-3-hexylthiophene and 2,5-dibromo-3-thiohexylthiophene (Scheme 3.1). A metathesis step was conducted on the mixture using $i$-propylmagnesium chloride-lithium chloride complex (Turbo Grignard) at 40 °C for 90 minutes, followed by treatment with [1,3-bis(diphenylphosphino)propane]nickel(II) chloride [Ni(dpdp)Cl$_2$] at 50 °C to initiate and carry out copolymerization. The reactions were terminated after 3 hours by treatment with 1 M HCl and precipitated into methanol. The precipitate was then subjected to Soxhlet extraction with methanol, hexanes, and chloroform. The chloroform fraction was further purified by silica gel column chromatography in chloroform.
Scheme 3.1 Synthesis of poly(3-hexylthiophene)-stat-(3-thiohexylthiophene).

Polystyrene equivalent molecular weights and dispersities were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 140 °C (Table 3.1). Incorporated ratios of 3-hexylthiophene:3-thiohexylthiophene, hereafter known as A:B, were determined by $^1$H NMR by integration of the α-methylene protons on the alkyl side-chains (2.81 ppm for A; 2.94 ppm for B). Regioregularity of the AAA linkages was calculated by integrating the α-methylene proton signals at 2.81 ppm (regioregular) and 2.58 ppm (regiorandom). Regioregularity of the other linkages is described in the next section.

Table 3.1 Properties of P3HT-s-P3THT Statistical Copolymers.

<table>
<thead>
<tr>
<th>Monomer ratio</th>
<th>Incorporated ratio</th>
<th>$M_n$ (kDa)</th>
<th>$D^c$</th>
<th>P3HT rr (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:B$^a$</td>
<td>A:B$^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95:5</td>
<td>99:1</td>
<td>17</td>
<td>1.8</td>
<td>93</td>
<td>79</td>
</tr>
<tr>
<td>90:10</td>
<td>97:3</td>
<td>19</td>
<td>1.7</td>
<td>92</td>
<td>63</td>
</tr>
<tr>
<td>75:25</td>
<td>85:15</td>
<td>10</td>
<td>1.5</td>
<td>91</td>
<td>12$^f$</td>
</tr>
<tr>
<td>70:30</td>
<td>80:20</td>
<td>13</td>
<td>1.7</td>
<td>84</td>
<td>49</td>
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<tr>
<td>50:50</td>
<td>67:33</td>
<td>9</td>
<td>1.8</td>
<td>84</td>
<td>29</td>
</tr>
<tr>
<td>40:60</td>
<td>50:50</td>
<td>9</td>
<td>1.5</td>
<td>83</td>
<td>29</td>
</tr>
</tbody>
</table>

$^a$3-hexylthiophene:3-thiohexylthiophene monomer feed ratio; $^b$3-hexylthiophene:3-thiohexylthiophene ratio in polymer backbone determined by integration of α-methylene peaks at 2.94 and 2.81 ppm; $^c$Determined by GPC with polystyrene standards in 1,2,4-trichlorobenzene at 140 °C; $^d$Determined by the relative intensity of the α-methylene peaks at 2.58 and 2.81 ppm; $^e$Yield of polymer after Soxhlet extraction; $^f$Low yield due to experimental error.
Figure 3.1 GPC traces of P3HT-s-P3THT copolymers measured in 1,2,4-trichlorobenzene at 140 °C using a UV detector, relative to polystyrene standards. A:B = 3-hexylthiophene:3-thiohexylthiophene monomer incorporated into the chain.

A typical quasi-living polymerization with 1 mol% of catalyst should yield polymers with 100 repeat units, which is equivalent to $M_n = 16.6$ kDa for a 100:0 A:B ratio, and $M_n = 18.2$ kDa for a 50:50 A:B ratio for the P3HT-s-P3THT system. For polymers with <90% A, however, the GPC determined $M_n$ is about half the expected value. Additionally, B is incorporated at a 10% lower amount than expected based on the pre-polymerization ratio for all copolymers. The yield, as determined by the mass of product from the chloroform fraction before column purification, also decreases with increasing amounts of B. Results are presented for the optimized polymerization conditions (Table 3.1). The lower than expected B incorporation may be explained by the enhanced coupling rate of regioregular A-B relative to regiorandom A-B, which prohibits the consumption of all of the B monomer, as well as the presence of some doubly-activated 2,5-dichloromagnesio-3-thiohexylthiophene after the metathesis reaction (vide infra). It should be noted that the low yield reported for the 75:25 copolymer is due to experimental error, and is considered an outlier when considering the aforementioned trend.
3.2 Regioregularity and randomness

Significant information about the copolymer sequence and regioregularity is learned by analyzing the aromatic proton resonance signals. For the purpose of this discussion, regioregularity refers to the position of adjacent side chains relative to each other, regardless of the identity of the repeat unit; randomness refers to the sequence of repeat units within the polymer backbone. In the equally proportioned P3THT-\(b\)-P3HT block copolymer described in Chapter 2, it was observed that the aromatic \(^1\)H NMR signals for the 3-hexylthiophene block are a sharp singlet (6.99 ppm), while the aromatic \(^1\)H NMR signals for the 3-thiohexylthiophene block are a broad multiplet (7.43 to 7.12 ppm). The differences in peak shape/splitting pattern are attributed to the regioregularity of each block; the P3HT block is regioregular (80%), whereas the P3THT block is regiorandom. Regiorandomness leads to three coupling possibilities: head-to-head (HH), head-to-tail (HT), or tail-to-tail (TT). There are two distinct methodologies for preparing HT regioregular 3-substituted polythiophenes: (1) preparing only one of the two possible activated monomer regioisomers (McCullough method\(^\text{6}\)), or (2) preparing both activated monomer regioisomers and employing a polymerization methodology where only one of the two is consumed (Rieke method, \(^\text{7}\) GRIM method\(^\text{8}\)). When applied to the polymerization of P3ATs, the GRIM methodology uses approach (2). This is due to steric hindrance leading to the selectivity of the Ni catalyst for HT coupling.\(^{9-11}\) In contrast, when the same conditions are used to polymerize 3-alkoxythiophenes\(^{12}\) and 3-thioalkylthiophenes,\(^{13}\) the result is a regiorandom polymer. In these cases, the Ni catalyst is not sterically selective due to the reduced van der Waals radius of O (1.5 Å) or S (1.8 Å) relative to CH\(_2\) (2.0 Å).\(^{13}\)

In the statistical copolymer system under study, linkages between 3-alkylthiophene and 3-thioalkylthiophene units are expected, however, it is unclear whether this would lead to regioregular or regiorandom couplings. It is also important to verify that the structure of the copolymer is indeed random, and that unequal reactivity ratios do not result in the formation of a diblock copolymer or two homopolymers. When comparing the \(^1\)H NMR spectra of the 50:50 P3THT-\(b\)-P3HT to the 50:50 (incorporated ratio) P3HT-\(s\)-P3THT (Figure 3.2), significant differences are observed, which suggest that the statistical copolymer synthesis has resulted in a random sequence. In contrast to the block copolymer spectrum, which contains a sharp singlet and two broad multiplets, the statistical copolymer contains eight major peaks, which appear to be separated into two groups of four. In most P3AT systems, the central proton of each
conformational triad (HT-HT, HT-HH, TT-HT, TT-HH) is a distinct proton resonance.\textsuperscript{14} In a binary system where each monomer has a distinct resonance, there are eight possible triads (AAA, AAB, BAA, BAB, ABA, ABB, BBA, BBB) and four regioisomers of each triad, resulting in thirty-two possible resonance signals. From the \textsuperscript{1}H NMR spectrum of the 50:50 statistical copolymer it is clear that there are not thirty-two equal aromatic peaks. The spectrum appears to be simpler than that. This led to the hypothesis that the eight major peaks correspond to the eight HT-HT conformations, and that the system is regioregular (Figure 3.3). This result was unexpected, as other HT regioregular AB statistical copolymer systems typically exhibit four aromatic peaks corresponding to AA, AB, BA, and BB (where the signal is from the proton in the 4-position on the second repeat unit).\textsuperscript{15,16} In this system, the aromatic resonances seem to be more sensitive to their environment, and the proton shift is dependent on the side-chain that is seven bonds away. This sensitivity is consistent with the aromatic spectrum of regiorandom P3THT which spans a 0.41 ppm range, compared to regiorandom P3HT, with its aromatic signals spanning just 0.07 ppm and showing four distinct signals for each of the four conformational triads.\textsuperscript{17} The increased sensitivity in P3THT must be due changes in shielding based on the presence of the sulfur atom, as well as increased rotational freedom around the C-S bond.

\textbf{Figure 3.2} \textsuperscript{1}H NMR aromatic resonances of poly(3-thiohexylthiophene), poly(3-hexylthiophene)-\textit{block}- (3-thiohexylthiophene), poly(3-hexylthiophene)-\textit{stat}- (3-thiohexylthiophene), and poly(3-hexylthiophene) (from top to bottom) (400 MHz, CDCl\textsubscript{3}).
To lend further support to these findings I used density functional theory (DFT) calculations to predict the $^1$H NMR spectra of the eight geometry-optimized triads. When the $^1$H NMR spectra of the trimers were predicted using 1-dimensional software, the predicted shifts were identical for each conformation. DFT methods are more accurate for predicting these types of resonances than a 1-dimensional program since they take into account through-space interactions as well as the geometry and 3-dimensional environment of the system. Although the predicted values do not exactly correspond to the experimental ones, and despite the fact that the calculated values are all very close, the trends in experimental values assigned to each HT-HT triad based on
shielding arguments and the probability of each conformation (*vide infra*) are consistent with the DFT predictions (Figure 3.3). There are other minor aromatic peaks in the spectrum, most notably at 7.16 and 7.42 ppm, which are also present in the P3THT spectrum and likely correspond to regiorandom BBB couplings.

Assuming equal reactivity ratios of the A and B monomers, the probability of each of the eight triads is expected to be identical for the 50:50 statistical copolymer, and therefore the area under each of the eight peaks should be equal. Upon integration of the peaks, this is found to be true, within error. This technique can be used to predict the intensities of the peaks for all A:B ratios, and compare the probabilities with the experimental values to further confirm that the eight peaks correspond to the eight HT-HT conformations. When increasing the amount of A, a gradual disappearance of the downfield B shifts and enhancement of the upfield A shifts is observed (Figure 3.4, left). At 97:3 and 99:1 A:B incorporation ratios, only the two most probable peaks are observed, corresponding to ABA and AAA conformations. The same trend occurs with the α-methylene peaks of the side-chains (Figure 3.4, right). The 3-thiohexyl peak at 2.94 ppm decreases with increasing A content. When comparing the predicted and experimental percentage of each HT-HT conformation, the values are in good agreement, however, the B-B linkages are consistently experimentally lower than predicted (Figure 3.5). This agrees with the lower B incorporations that were calculated from the α-methylene peaks, and provides further insight into the mechanism.
Figure 3.4 $^1$H NMR spectra of P3HT-s-P3THT copolymers with distinct aromatic shifts for each HT-HT conformation (left) and each $\alpha$-methylene proton (right). $A = 3$-hexylthiophene, $B = 3$-thiohexylthiophene and $H$ is the proton of interest (400 MHz, CDCl$_3$).

Figure 3.5 Predicted and experimental fractions of each HT-HT conformation for each P3HT-s-P3THT composition; $A = 3$-hexylthiophene and $B = 3$-thiohexylthiophene. Full structures for each conformation are depicted in Figure 3.3. Experimental values were obtained by $^1$H NMR integration.
3.3 Mechanism

It is well established that the GRIM polymerization method yields regioregular P3ATs and regiorandom poly(3-thioalkylthiophenes) (P3TATs) (Scheme 3.2). As previously mentioned, the regioselectivity in P3ATs is due to the catalyst selectivity for 1, which is also the more abundant regioisomer. In P3TATs, the catalyst is not selective, and both regioisomers are consumed, although there is some selectivity due to the metathesis step. From the above analysis, it is found that the GRIM method leads to regioregular HT-HT couplings between 3-alkylthiophene and 3-thioalkylthiophene monomers, yielding semi-regioregular statistical copolymers when there is less than 50% of the 3-thioalkylthiophene monomer in the polymer chain. This is likely due to a steric effect, where the larger size of the methylene group is significant enough to prevent a HH coupling with 4. When there is an alkyl group at the 3-position on the active chain end, only HT couplings are permitted and reaction can only occur with 1 or 3 (Scheme 3.3a). When the active chain end contains a thioalkyl substituent at the 3-position, HT couplings can occur with 1 and 3, as well as a HH coupling with 4, due to decreased steric hindrance (Scheme 3.3b). This HH coupling results in a third scenario, where there is a thioalkyl group at the 4-position on the active chain end. In this case, couplings are most likely with 1 and 3 due to steric effects, as well as the higher abundance of these two monomers. These couplings return the system to one of the first two scenarios, where the substituent is at the 3-position on the active chain end. The HH coupling is the least likely out of the five “probable” couplings outlined in Scheme 3.3 for copolymers with less than 50% B, since it involves reaction with 4, the least abundant of the four monomers. These HH-TT trimers likely show up as minor peaks in the \(^1\)H NMR spectrum and their low intensities further suggest that this coupling occurs in minor amounts. As the feed of B further decreases, the probability of the B-B couplings also decreases, and hence the overall polymer regioregularity will increase with increasing amounts of A. P3TATs do not have a unique \(\alpha\)-methylene proton shift for regiorandom couplings, and therefore the regioregularity cannot be quantified.
Scheme 3.2 Regioselectivity of the metathesis step and subsequent polymerization for P3ATs (top), P3TATs (middle), and P3AT-s-P3TATs (bottom) under GRIM conditions. Monomer abundances were obtained by a Grignard quenching experiment. Doubly-activated species are excluded for clarity.

Scheme 3.3 Probable couplings for P3AT-s-P3TATs when the active chain end is (a) alkylthiophene or (b) thioalkylthiophene.

The fact that HH A-B couplings do not occur helps to explain why the yield, $M_n$ and B incorporation decrease with increasing amounts of B in the monomer mixture. As mentioned above, one of the reasons that the GRIM method prepares regioregular P3ATs is that the metathesis reaction is regioselective. It produces 3-alkyl-2-bromo-5-halomagnesiothiophene (1)
and 4-alkyl-2-bromo-5-halomagnesiothiophene (2) in an 80:20 ratio. Since the Ni catalyst is regioselective for P3ATs, it is likely that 80% of the monomer mixture (1) will react to form HT couplings, resulting in a yield and \( M_n \) of at least 80% of the theoretical values. The other 20% of monomer (2) can theoretically still react, although the reaction is much less likely, and any HH or TT couplings will increase the yield but decrease the regioregularity. In contrast, the metathesis reaction for 3-thiohexylthiophenes is less controlled, and a 65:35 ratio is calculated for 3-thiohexyl-2-bromo-5-chloromagnesiothiophene (3) to 4-thiohexyl-2-bromo-5-chloromagnesiothiophene (4) after the reaction is quenched with HCl after the metathesis step (Figure 3.6). Using the same logic as applied to the P3AT system, this implies that only 65% of the B monomer should react in a statistical polymerization with A. If the polymerization gets to a point where there are A groups on all the active chain ends and only B monomers left which will result in HH couplings, then no further reaction will occur and the yield, \( M_n \) and B incorporation will be lower than expected, as observed in the system of study.

**Figure 3.6** \(^1\)H NMR spectrum of the species present after quenching the metathesis reaction with HCl (400 MHz, CDCl\(_3\)).
It is also significant to note that when considering the species present after the activated monomer is quenched with HCl (Figure 3.6), there is about 10% 3-thiohexylthiophene present in the mixture. This is likely formed due to the presence of excess Grignard reagent which reacts with both bromines of the 2,5-dibromo-3-thiohexylthiophene starting material. Interestingly, only B undergoes this double-activation, and 3-hexylthiophene was not observed in the mixture. Since B appears to be more reactive towards Grignard reagents than A, this provides a second explanation as to why the incorporation of B is consistently lower than expected.

### 3.4 Absorbance spectroscopy

Another method used to evaluate the regioregularity of the copolymers is solid-state absorption spectroscopy. When comparing the 50:50 P3HT:P3THT block copolymer to the statistical copolymer, a red-shift in absorbance is observed, as well as an increase in intensity of the shoulder peaks (Figure 3.7). A polymer with higher regioregularity is more planar, which extends conjugation along the polymer backbone and leads to the red-shifted absorbance. Furthermore, a more planar backbone allows for a greater degree of π-π stacking, and increased intermolecular vibronic transitions, leading to the more intense shoulder peak at ~610 nm. Therefore, enhanced regioregularity in the statistical copolymer explains these trends in the optical absorption data.
Figure 3.7 Solid-state absorbance of 50:50 P3HT:P3THT block (dotted line) and statistical (solid line) copolymers. Thin films were spin-coated from 6 mg/mL chloroform solution at 2500 rpm onto glass substrates.

I was also interested in learning how the A:B ratio affects the optoelectronic properties of the copolymer, and determining the minimum amount of B required to have an effect on these properties. A red-shifted solution absorbance spectrum was observed in statistical copolymers that have $\geq 15\%$ B incorporation (Figure 3.8, left). Increasing B leads to a further red-shift relative to P3HT. The absorbance of the 97:3 and 99:1 copolymers are identical to P3HT, and therefore these small amounts of B are not significant enough to affect the solution absorbance properties of the copolymer.
Figure 3.8 Optical absorption spectra of P3HT-s-P3THT copolymers in chloroform solution (left) and solid-state (right). Thin films were spin-coated from 6 mg/mL chloroform solution at 2500 rpm onto glass substrates. The polymer is denoted by the line color. $A:B = 3$-hexylthiophene:3-thiohexylthiophene monomer incorporated into the chain.

The changes in the solid-state absorbance spectra are not as pronounced as in solution, and only the 50:50 copolymer is visibly red-shifted relative to P3HT (Figure 3.8, right). The 50:50 and 67:33 copolymers both exhibit a strong shoulder at ~610 nm, and a weaker one at ~525 nm, suggesting that larger amounts of $B$ change the polymer stacking properties in a way that increases intermolecular interactions.

3.5 Device characterization

In chapter 2, it was found that when using an equally proportioned P3THT-b-P3HT block copolymer as a donor material in a photovoltaic device with a [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) acceptor, the $V_{oc}$ is as high as the $V_{oc}$ of the P3THT:PC$_{71}$BM binary device (0.66 V). This was the first example of an equally proportioned double donor ternary device with a $V_{oc}$ that is as high as the $V_{oc}$ of the corresponding highest voltage binary device and was a promising result as it showed that a high $V_{oc}$ is obtained even if one of the donor materials has a high-lying HOMO level, such as P3HT. Although the $V_{oc}$ of the 50:50 diblock device is high, the $J_{sc}$ and $FF$ are lower than the binary P3HT:PC$_{71}$BM device, resulting in a lower overall PCE. I hypothesized that by decreasing the amount of the P3THT component relative to P3HT, the high $V_{oc}$ could be maintained while increasing the $J_{sc}$ and $FF$ to values more similar to those
obtained for pure P3HT. A second reason for the poor device performance of P3THT-b-P3HT is the regiorandomness of the P3THT block. I further hypothesized that by changing the copolymer from a block to a random sequence, the regioregularity could be improved, leading to a more favorable solid-state morphology, similar to that of P3HT. As shown in the previous section, the 50:50 statistical copolymer is more regioregular than the 50:50 diblock, and the regioregularity improves further with more A incorporation.

To test these hypotheses, BHJ solar cells (ITO/PEDOT:PSS/P3HT-s-P3THT:PC_{71}BM/LiF/Al) were fabricated and characterized (Figure 3.9). The results show that as the amount of the A component increases, the $J_{sc}$ and $FF$ increase (non-linearly), and begin to approach the values measured for pure P3HT (Table 3.2).

![Figure 3.9 J-V curves (left) and EQE spectra (right) for polymer:PC_{71}BM devices under AM 1.5G illumination (100 mW/cm²) at the optimal conditions for solar cell performance, where the polymer is denoted by the line color. A:B = 3-hexylthiophene:3-thiohexylthiophene monomer incorporated into the chain.](image-url)
Table 3.2 Photovoltaic Properties of P3HT-s-P3THT:PC_{71}BM Solar Cells at Different A:B Ratios.

<table>
<thead>
<tr>
<th>Incorporated ratio</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$ (%)</th>
<th>PCE$_{max}$ (%)</th>
<th>PCE$_{avg}$ $^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0$^b$</td>
<td>10.36</td>
<td>0.56</td>
<td>67.10</td>
<td>3.89</td>
<td>3.67±0.16</td>
</tr>
<tr>
<td>99:1$^b$</td>
<td>9.49</td>
<td>0.62</td>
<td>63.15</td>
<td>3.72</td>
<td>3.54±0.15</td>
</tr>
<tr>
<td>97:3$^c$</td>
<td>8.04</td>
<td>0.62</td>
<td>63.34</td>
<td>3.16</td>
<td>3.04±0.11</td>
</tr>
<tr>
<td>85:15$^c$</td>
<td>5.88</td>
<td>0.66</td>
<td>56.80</td>
<td>2.21</td>
<td>1.87±0.23</td>
</tr>
<tr>
<td>80:20$^c$</td>
<td>5.45</td>
<td>0.66</td>
<td>51.53</td>
<td>1.86</td>
<td>1.80±0.04</td>
</tr>
<tr>
<td>67:33$^c$</td>
<td>2.97</td>
<td>0.66</td>
<td>43.48</td>
<td>0.85</td>
<td>0.82±0.03</td>
</tr>
<tr>
<td>50:50$^b$</td>
<td>3.50</td>
<td>0.66</td>
<td>41.97</td>
<td>0.97</td>
<td>0.79±0.08</td>
</tr>
</tbody>
</table>

$^a$Devices were spin-cast from 20:20 mg/mL polymer:PC$_{71}$BM solutions in 1,2-dichlorobenzene at 500 rpm; $^b$Active layer was annealed at 100 °C for 5 minutes; $^c$Active layer was vapor annealed at room temperature; $^d$Average PCE of eight devices fabricated under identical conditions ± standard deviation.

Interestingly, the $V_{oc}$ remains higher than the $V_{oc}$ of the pure P3HT device (0.56 V), even for the 99:1 copolymer (0.62 V). The M$_n$ of this polymer is 17 kDa, equivalent to a polymer with about 100 A units and just 1 B unit per chain. For polymers with 15% or more of the B component, the $V_{oc}$ is equivalent to the $V_{oc}$ of the pure P3THT device (0.66 V). Several examples of composition-dependent open-circuit voltages have been reported for statistical copolymers$^{3,4,18}$ and ternary systems,$^{19-22}$ however, this is the first example of a system where the $V_{oc}$ remains constant and as high as the upper limit voltage of the corresponding binary devices over a very large range of compositions (15 – 100%). Furthermore, no system has ever shown an increase in $V_{oc}$ relative to that of the binary device of the major component, with as low as only 1% of the high $V_{oc}$ component present.
Figure 3.10 HOMO energy levels of P3HT-s-P3THT copolymers in the solid state determined by cyclic voltammetry (blue squares) and $V_{oc}$ of the optimized devices (red circles) as a function of the amount of 3-hexylthiophene monomer in the polymer backbone. The dashed lines are a guide for the eye and the arrows indicate the appropriate axis.

The constant $V_{oc}$ over the 50:50 to 85:15 composition range is consistent with the relatively constant HOMO levels that were measured using cyclic voltammetry (Figure 3.10). The calculated solid-state HOMO levels are between -5.43 and -5.59 eV for A:B compositions ranging from 50:50 to 97:3. For reference, the calculated solid-state HOMO levels of P3HT and P3THT are -5.08 and -5.46 eV, respectively. This suggests that even 3% incorporation of the thiohexyl unit is sufficient to lower the HOMO to the same value as the pure P3THT homopolymer. Even though the 99:1 copolymer has a similar HOMO level to pure P3HT, it still results in a device with a higher $V_{oc}$ (0.62 V), indicating that device $V_{oc}$ may be even more sensitive to composition than electrochemistry. Although the LUMO levels were not calculated, it can be concluded that they must also be lower in the more B-rich copolymers, due to their red-shifted absorbance spectra (Figure 3.8).
Figure 3.11 Cyclic voltammogram oxidation curves of the copolymer thin films in acetonitrile/TBAPF$_6$ electrolyte. A ferrocene redox couple (Fc/Fc$^+$) was used as an internal standard.
The other three device parameters ($J_{sc}$, $FF$, and PCE) are composition-dependent over the entire composition range, and increase with increasing $A$ content. This increase, however, is non-linear and at higher $A$ contents, the increase in all three device parameters is much more pronounced. The difference between the 50:50 and 67:33 devices is almost negligible, and in fact the $J_{sc}$ and PCE slightly decrease with the 17% increase in $A$, suggesting that device parameters are more sensitive to smaller “defects” in the mainly P3HT backbone, rather than compositional changes in a largely random copolymer. The best PCE for the poly(3-butylthiophene)-co-(3-octylthiophene) system was observed in the 50:50 system, however that polymer did not display a compositional dependence on device parameters. The enhanced performance of the equally proportioned copolymer was attributed to optimal phase separation between the polymer and fullerene phases. In contrast, the P3HT-co-P3EHT polymer displayed a quasi-linear increase in $V_{oc}$ with increasing 3-ethylhexylthiophene (3EHT) content, and a drastic decrease in $J_{sc}$, $FF$ and PCE going from a 75:25 to 50:50 3-hexylthiophene:3-ethylhexylthiophene content. The $J_{sc}$, $FF$ and PCE for the 90:10 device were lower than those for 100:0 and 75:25. Overall, the effect of statistical copolymer composition on device parameters is still not fully understood, and seems to differ largely amongst the various systems.

In this study, the device performance of the 50:50 statistical copolymer ($PCE_{max} = 0.97\%$) is comparable to that of the 50:50 diblock ($PCE_{max} = 1.05\%$), with a slight improvement in the PCE of the diblock due to a higher $J_{sc}$ (statistical: 3.50 mA/cm$^2$; block: 3.83 mA/cm$^2$). This suggests that the improved regioregularity and random copolymer sequence do not lead to an improved device performance in the equally proportioned system, and therefore it can be concluded that it is the composition of the thiohexyl-containing copolymers that has the greatest effect on the device performance.
Figure 3.12 Photovoltaic parameters as a function of 3-hexylthiophene content for OSCs fabricated using P3HT-s-P3THT:PC$_{71}$BM and tested under AM 1.5G illumination (100 mW/cm$^2$).

4 Conclusions

Poly(3-hexylthiophene)-stat-(3-thiohexylthiophene) has been synthesized by Grignard metathesis polymerization, characterized, and used as a donor material with PC$_{71}$BM in a bulk heterojunction solar cell. The statistical copolymer is more regioregular than the corresponding block copolymer due to an increased selectivity for HT couplings between 3-alkylthiophene and 3-thioalkylthiophene units. The percentage of each conformational triad, as well as the incorporated ratio of each monomer, was calculated by $^1$H NMR integration. The yield, molecular weight, and 3-thiohexylthiophene incorporation yield decreases with increasing 3-thiohexylthiophene monomer ratio, likely due to the larger amount of the 4-thiohexyl-2-bromo-
5-chloromagnesiothiophene, which is unable to react with 3-hexylthiophene active chain ends, as well as the presence of the doubly-activated monomer after the metathesis step.

When testing P3HT-x-P3THT:PC$_{71}$BM solar cell devices, it was found that the $J_{sc}$ and $FF$ increase non-linearly with increasing 3-hexylthiophene content, and become more sensitive to compositional changes as the copolymers become more P3HT-heavy. The $V_{oc}$ remains constant, and as high as the $V_{oc}$ of a P3THT:PC$_{71}$BM binary device, over all compositions up to and including 85:15. This differs from all other statistical copolymer and ternary blend systems, which display a relatively constant increase or decrease over the composition range. The $V_{oc}$ of the 97:3 and 99:1 devices has an intermediate value, in between that of the P3HT:PC$_{71}$BM and P3THT:PC$_{71}$BM devices, indicating that only a single 3-thiohexyl chain in a polymer with 100 repeat units is required to affect the voltage of the device. The increased $V_{oc}$ can be partially attributed to the lower HOMO level (relative to P3HT), calculated by cyclic voltammetry, however the $V_{oc}$ appears to be even more sensitive to minor amounts of comonomer than electrochemistry.

Statistical copolymers have the potential to be a powerful tool for fine-tuning composition-dependent device parameters. Furthermore, the one-pot synthesis of statistical copolymers is more straightforward than block copolymer synthesis, and thus these results should continue to inspire the design of new statistical copolymers which incorporate narrow bandgap gap or highly absorbing monomers into well-studied, high efficiency polymer backbones, such as P3HT.

5 Experimental

5.1 General considerations

All reagents were used as received unless otherwise noted. 3-bromothiophene, 2,5-dibromo-3-hexylthiophene, n-butyllithium (1.6 M in hexanes), i-propylmagnesium chloride-lithium chloride complex (1.3 M in THF), and [1,3-bis(diphenylphosphino)propane]nickel (II) chloride (Ni(dppp)Cl$_2$) were purchased from Sigma-Aldrich. N-bromosuccinimide was purchased from Acros Organics and recrystallized in water prior to use.
5.2 Instrumentation and methods

$^1$H NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 400 MHz. Chemical shifts are reported in ppm at ambient temperature. $^1$H chemical shifts are referenced to the residual protonated chloroform peak at 7.26 ppm. Polymer molecular weights were determined with a Viscotek HT-GPC (1,2,4-trichlorobenzene, 140 °C, 1 mL/min flow rate) using Tosoh Bioscience LLC TSK-GEL GMH$_{14}$R-HT mixed-bed columns and narrow molecular weight distribution polystyrene standards. A UV detector was used to detect the eluted polymer with respect to elution volume. Absorption spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer. The thin-films used for absorbance spectroscopy were spin-coated from solutions in chloroform (6 mg/mL) at 2500 rpm for 30 seconds onto glass substrates that had been washed with methanol. Electrochemistry was performed with a BASi Epsilon potentiostat. A standard three-electrode cell with a 2 mm Pt button working electrode, a silver wire pseudoreference electrode, and a Pt wire counter electrode was used, with a ferrocene internal standard and a 100 mV/s scan rate. The electrolyte was a 0.1 M solution of tetrabutylammonium hexfluorophosphate (TBAPF$_6$) in acetonitrile. Polymer films were prepared by drop-casting a 7 mg/mL solution of polymer in chloroform onto the working electrode, and the solvent was evaporated in air. HOMO levels were calculated and converted to the vacuum scale using the equation: $E_{\text{HOMO}} = -(E_{\text{onset ox vs. Fc}} + 4.8) \text{ (eV)}$.  

5.3 Density functional theory calculations

Geometry optimizations were performed using the Gaussian 09 program, employing the Becke Three Parameter Hybrid Functionals Lee-Yang-Parr (B3LYP) level of theory and the 6-311G(d) basis set. The hexyl chains were replaced with methyl groups to reduce processing time. Chemical shifts were calculated as the difference of isotropic shielding constants ($\sigma$) with respect to TMS (HF/6-31G(d) GIAO).

5.4 Photovoltaic device fabrication and characterization

Polymers and PC$_{71}$BM (American Dye Source) were mixed in 1,2-dichlorobenzene at 1:1 wt ratio (20:20 mg/mL). Solutions were stirred at 50 °C overnight to ensure complete dissolution. Devices were fabricated on commercial indium tin oxide (ITO) substrates (Colorado Concept Coatings) that had a sheet resistance of $\sim$10 $\Omega/\square$. These substrates were cleaned in aqueous
detergent, deionized (DI) water, acetone and methanol, and subsequently treated in an oxygen-plasma cleaner for 5 min. Next, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P VP AI 4083) was coated onto the substrates at 3000 rpm and annealed in air at 130 °C for 15 min. After annealing, the substrates were transferred into a nitrogen-filled glove box, where polymer:PC_{71}BM blends were coated at 500 rpm and dried at room temperature in closed petri-dishes. Some polymer:PC_{71}BM blends were further annealed. The annealing conditions were optimized individually for each polymer to optimize device performance. The polymers with 100:0, 99:1, and 50:50 A:B ratios were annealed at 100 °C for 5 minutes in the glovebox. The polymers with 99:1, 97:3, 85:15, 80:20, and 67:33 A:B ratios were vapor annealed at room temperature. A 0.8 nm LiF layer and 100 nm Al anode was thermally deposited through a shadow mask at ~10^{-6} torr using an Angstrom Engineering Covap II (Kitchener, Ontario, Canada). Device area is 0.07 cm^2 as defined by the area of circular Al anode. I-V characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5 G conditions with a power intensity of 100 mW/cm^2. The mismatch of simulator spectrum was calibrated using a Si diode with a KG-5 filter. EQE spectra were recorded and compared with a Si reference cell that is traceable to the National Institute of Standards and Technology. Eight identical devices were measured for each set of conditions and both the average and maximum PCE are reported in Table 3.2.

5.5 Synthesis

\[
\begin{align*}
\text{Br} & \quad \xrightarrow{n-\text{BuLi}} \quad \text{SC}_6\text{H}_{13} \\
\text{S} & \quad \text{C}_6\text{H}_{13}\text{SSC}_6\text{H}_{13}
\end{align*}
\]

**3-Thiohexylthiophene.** 3-Bromothiophene, (10 g, 0.061 mol) in a mixture of hexanes (100 mL) and dry THF (12 mL) under N\textsubscript{2}, was cooled to -40 °C and n-BuLi (0.061 mol, 44 mL of freshly titrated 1.4 M hexanes solution) was added drop-wise. Hexanes (40 mL) was added and the dark brown-yellow suspension was warmed to room temperature. A solution of hexyl disulfide (0.061 mol, 14.3 g) in hexanes (75 mL) was added and the resulting white suspension was stirred under N\textsubscript{2} for 2 hours, and then quenched with a solution of saturated ammonium chloride (80 mL). The solution was extracted with ether, washed with brine, and dried over MgSO\textsubscript{4}. The solvent was evaporated and the product was purified by column chromatography (hexanes) (5.8 g, 47%
yield). $^1$H NMR (399 MHz, CDCl$_3$) $\delta$: 7.31 (q, 1H), 7.12 (d of d, 1H), 7.02 (d of d, 1H), 2.84 (t, 2H), 1.66-1.26 (m, 8H), 0.89 (t, 3H). Spectroscopy was identical to that of the previous report of this compound.$^{27}$

2,5-Dibromo-3-thiohexylthiophene. A solution of $N$-bromosuccinimide (0.074 mol, 13.2 g) in dry DMF (200 mL) was added drop-wise to a degassed solution of 3-thiohexylthiophene (0.025 mol, 4.95 g) in dry DMF (250 mL) at 0 ºC under N$_2$ in the dark. The mixture was allowed to slowly warm to room temperature and was stirred under N$_2$ for 17 hours. The solution was then diluted with ether (20 mL), washed two times each with 10% Na$_2$SO$_4$ and brine, and dried over MgSO$_4$. The solvent was evaporated and the product was purified by column chromatography (hexanes) (1.3 g, 15% yield). $^1$H NMR (399 MHz, CDCl$_3$) $\delta$: 6.90 (s, 1H), 2.82 (t, 2H), 1.62-1.26 (m, 8H), 0.89 (t, 3H). Spectroscopy was identical to that of the previous report of this compound.$^{27}$

Poly(3-hexylthiophene)-stat-(3-thiohexylthiophene) (representative procedure for 50:50 copolymer). $i$-Propylmagnesium chloride - lithium chloride complex (1.3 mL, 1.3 M in THF) was added to a solution of 2,5-dibromo-3-hexylthiophene (212 mg, 0.65 mmol) and 2,5-dibromo-3-thiohexylthiophene (367 mg, 1.02 mmol) in 12 mL dry THF, and heated to 40 ºC. After 90 minutes, the solution was transferred to a flask containing Ni(dppp)Cl$_2$ (9.05 mg, 0.0167 mmol) and heated to 50 ºC. After 3 hours, the reaction mixture was treated with 1 M HCl and precipitated into methanol. The dark purple precipitate was then subjected to Soxhlet extraction with methanol, hexanes, and chloroform. The chloroform fraction was concentrated to afford the crude polymer (91.2 mg, 29% yield), which was further purified by silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.38 (s, 0.25H), 7.34 (s, 0.25H), 7.28 (s, 0.25H), 7.24 (s, 0.25H), 7.10, (s, 0.25H), 7.07 (s, 0.25H), 7.03 (s, 0.25H), 6.99 (s, 0.25H), 2.93 (br. 2H), 2.80 (br, 2H), 1.68-1.30 (m, 16H), 0.89 (br, 6H). GPC: $M_n = 9$ 500 g mol$^{-1}$, $M_w = 13$ 400 g mol$^{-1}$, PDI = 1.5. All statistical copolymers were prepared similarly, varying the ratio of each monomer. For clarity, I refer to the A:B incorporation ratio as determined by $^1$H NMR integration when discussing these polymers.
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Chapter 4
One Donor-Two Acceptor Random Terpolymers

1 Statement of contributions

Andrew Tilley assisted in performing and interpreting TCSPC experiments. Solar cell fabrication and testing was performed by Dong Gao. I carried out all other synthesis, characterization, and experiments presented in this chapter. I drafted the manuscript for publication, which was edited by Dwight Seferos. Portions of this work have appeared in print.¹

2 Introduction

The donor-acceptor (D-A) approach to alternating copolymers has led to significant improvements in the efficiency of bulk heterojunction (BHJ) solar cells over the last few years.²⁻⁵ In fact, almost of all the highest performing devices have been achieved using a D-A copolymer donor material in conjunction with a fullerene based acceptor. The D-A approach has now expanded to include terpolymers containing one donor and two acceptors (D₁-A₁)(D₂-A₂) or two donors and one acceptor (D₁-A₁)(D₂-A₂).⁶⁻¹¹ This approach allows for greater coverage of the spectral range as well as meticulous tuning of the energy levels by varying the amount of each monomer. Due to its high cost, low molar absorptivity, and mismatch with the solar spectrum, there is an increasing need to find alternatives to PC₇₁BM.¹²⁻¹⁵ An ideal material would be a strong light absorber and contribute to the overall photocurrent of the device, and thus the D-A approach would be an ideal method to design acceptor materials with strategically aligned energy levels and narrow bandgaps.

Arylene diimides are a promising class of acceptor materials that have high absorption coefficients, high electron mobilities, and can be used as an alternative to fullerene based acceptors.¹⁶⁻²¹ The most common materials in this class are naphthalene diimide (NDI) and perylene diimide (PDI); however, blends of these materials with polymers tend to have high degrees of phase separation due to strong aggregation of the arylene diimides.²²,²³ This aggregation can be minimized by incorporating bulky units into the arylene diimide architecture to disrupt the stacking of the arylene cores. If these additional units have electron-donating character, they can interact with the arylene diimide units in a D-A nature and change the optoelectronic properties of the material, in addition to the morphology. This is a key advance in
the field of acceptor material research, as these new D-A compounds are strong light absorbers, show good mixing with other donor polymers, and their energy levels can be easily tuned by changing the identity of the acceptor. This combination of traits has led to a growing interest in arylene diimide-based D-A copolymers\textsuperscript{24-29} and small molecules\textsuperscript{30-34} as acceptors in BHJ devices with power conversion efficiencies up to 6% reported. Although D-A copolymers containing PDI or NDI as the acceptor have attracted significant attention, prior to this study, there had been no reports of materials that contain both PDI and NDI in the copolymer structure. I hypothesize that when both of these promising materials are incorporated into a (D-A\textsubscript{1})-(D-A\textsubscript{2}) terpolymer, the optoelectronic and materials properties can be controlled by varying the composition of the two acceptors. Herein, I describe the synthesis and characterization of (D-A\textsubscript{1})-(D-A\textsubscript{2}) terpolymers and show how they can potentially be used as acceptor materials. Specifically, I describe how the (D-A\textsubscript{1})-(D-A\textsubscript{2}) composition influences both the photophysics of the polymers as well as various device parameters such as the $J_{sc}$, $V_{oc}$, and spectral coverage.

3 Results and discussion

3.1 Polymer design and synthesis

To prepare terpolymers, 2,7-carbazole (PC) was chosen as the electron-donating monomer unit because PC-PDI was previously shown to have the best device performance in a series of six different PDI-based polymers with different donor units.\textsuperscript{28} PC-NDI has also been previously studied, however it showed poor device performance due to poor energy level alignment with the chosen donor polymer.\textsuperscript{35} Monomers $N,N'$-di(2-ethylhexyl)-1,7-dibromo-3,4,9,10-perylenediimide (1) and $N,N'$-di(2-ethylhexyl)-2,6-dibromo-1,4,5,8-napthalene diimide (2) were synthesized according to literature procedures,\textsuperscript{29,36,37} while 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-N-(1-octynonyl)carbazole (3) was obtained from Sigma-Aldrich and used as received. The copolymers were synthesized using a palladium-catalyzed Suzuki coupling reaction under the same conditions as previously reported for the parent copolymers (Figure 4.1a).\textsuperscript{28,35} Appropriate ratios of monomers were dissolved in a mixture of THF and 2M aqueous Na\textsubscript{2}CO\textsubscript{3} and degassed with argon for 30 min. Pd(PPh\textsubscript{3})\textsubscript{4} was then added and the solution was heated to reflux for 48 hours. The polymers were then end-capped through the sequential addition of phenylboronic acid and bromobenzene, each followed by an additional 2 hours of heating to reflux. The solution was cooled to room temperature and precipitated into methanol.
The precipitate was filtered and purified by Soxhlet extraction with methanol and hexanes, and finally extracted into chloroform. The copolymers all had comparable yields, molecular weights and dispersities (Table 4.1).

Figure 4.1 (a) Synthesis of PC-PDI-NDI random copolymers, (b) structure of PBDTTT-C donor polymer, and (c) energy level diagrams for the PC-PDI-NDI random copolymers. HOMO and LUMO energies are shown in electron volts and have errors of ±0.1 eV.
Table 4.1 Properties of PC-PDI-NDI Copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kDa)$^a$</th>
<th>$M_w$ (kDa)$^a$</th>
<th>$D^a$</th>
<th>Yield (%)$^b$</th>
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</thead>
<tbody>
<tr>
<td>PC-PDI100</td>
<td>7.1</td>
<td>21.3</td>
<td>3.0</td>
<td>96</td>
</tr>
<tr>
<td>PC-PDI75-NDI25</td>
<td>6.9</td>
<td>17.4</td>
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<td>93</td>
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<tr>
<td>PC-PDI50-NDI50</td>
<td>6.4</td>
<td>13.0</td>
<td>2.0</td>
<td>76</td>
</tr>
<tr>
<td>PC-PDI25-NDI75</td>
<td>6.5</td>
<td>13.6</td>
<td>2.1</td>
<td>85</td>
</tr>
<tr>
<td>PC-NDI100</td>
<td>6.5</td>
<td>11.8</td>
<td>1.8</td>
<td>87</td>
</tr>
</tbody>
</table>

$^a$Measured by GPC with polystyrene standards in 1,2,4-trichlorobenzene at 140 °C; $^b$Yield of chloroform fraction after Soxhlet extraction.

Figure 4.2 GPC traces of PC-PDI100 (black), PC-PDI75-NDI25 (orange), PC-PDI50-NDI50 (blue), PC-PDI25-NDI75 (green) and PC-NDI100 (red) measured in 1,2,4-trichlorobenzene at 140 °C using a UV detector, relative to polystyrene standards.

The synthesis of the copolymers has several advantages over other D-A copolymers and acceptor materials. While most of the high-performance polymers in the recent literature require several steps to make the monomers, the dibromo arylene diimides can be synthesized in two steps from the commercially available dianhydride, while the carbazole diboronic ester is itself now commercially available. The use of Suzuki conditions versus Stille coupling is also advantageous
in that it avoids the use of stoichiometric tin reagents, which are potentially toxic. Although Stille conditions are sometimes found to result in higher degrees of polymerization for certain monomers, I did not attempt the Stille coupling on my system because the Suzuki conditions have already been shown to yield the parent copolymers in our desired range of molecular weights.\textsuperscript{28,35} Finally, all three monomers are powders making them easy to purify and deliver accurate amounts to the reaction vessels.

3.2 Variable temperature $^1$H NMR

High-resolution 600 MHz $^1$H NMR spectroscopy was used to help quantify the amount of each acceptor monomer incorporated into the final polymer chains. Due to low solubility in chloroform at the concentrations required to obtain well-resolved peaks, the samples were subjected to variable temperature $^1$H NMR in 1,1,2,2-tetrachloroethane-d$_2$ (bp = 145 °C). As the spectra were obtained at 25, 70 and 120 °C, the peaks became increasingly well-resolved for all copolymer compositions (Figure 4.3). Interestingly, for PC-NDI100 and PC-PDI25-NDI75 (and PC-PDI50-NDI50 to a lesser extent), the peaks at 7.70 and 7.54 ppm at room temperature begin to coalesce into one broad peak at 70 °C and eventually resolve into a sharp peak at 7.68 ppm at 120 °C. This results in the number of aromatic protons decreasing from five to four upon heating from 25 to 120 °C. This is consistent with previous findings of temperature dependence in the $^1$H NMR spectrum of the well-known polymer PNDI2OD-T2, containing both NDI and thiophene units,\textsuperscript{38} and is attributed to changes in the degree of aggregation with temperature. The temperature-dependent peaks in the PC-PDI-NDI copolymers are assigned to protons attached to the carbazole unit and are similarly attributed to changes in aggregation, or additionally, to an averaging of the rotation of the carbazole side-chain or rotation of the NDI-carbazole carbon-carbon bond.
Figure 4.3 Variable temperature $^1$H NMR (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$) of the aromatic region of PC-PDI-NDI copolymers.
Comparison of the spectra of the different copolymers at 120 °C (Figure 4.4) allows the assignment of the aromatic peaks for the protons attached to NDI, PDI, and carbazole units, and in some cases to determine whether the carbazole peaks are on carbazole units attached to PDI or NDI units. Even at elevated temperatures, however, the broadness of peaks in the 7.30-8.40 ppm range, as well as the presence of minor peaks attributed to protons on the phenyl end-groups, make it difficult to reliably quantify the number of each monomer based on these spectra. It should also be noted that the better resolution of the more NDI-heavy polymers is likely due to the difference in isomeric purity of the dibromo arylene diimide monomers. The 2,6- and 2,7-dibromo-NDI isomers are easily purified by column chromatography; however, the 1,6- and 1,7-dibromo-PDI isomers can only be separated by repetitive crystallization over several weeks.\textsuperscript{37}

**Figure 4.4** $^1$H NMR spectra (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$) of the aromatic region of PC-PDI-NDI copolymers at 120 °C. In the expansion, H and A refer to height and area, respectively.

<table>
<thead>
<tr>
<th>Monomer Feed</th>
<th>Peak Height</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>75:25</td>
<td>79:21</td>
<td>81:19</td>
</tr>
<tr>
<td>50:50</td>
<td>52:48</td>
<td>49:51</td>
</tr>
<tr>
<td>25:75</td>
<td>30:70</td>
<td>38:62</td>
</tr>
</tbody>
</table>

$H_{\text{PDI}} = 8.89$ ppm  
$H_{\text{NDI}} = 8.92$ ppm
and therefore the isomeric mixture is often used directly. My sample contained a 4:1 mixture of the 1,7:1,6 isomers and therefore there is likely some regioirregularity in the PDI-carbazole linkages leading to a greater number of conformations and hence more complex NMR spectra. The polymer solubility also increases with increasing NDI content due to its smaller arylene diimide core, which may also explain the better resolution in the NMR spectra.

The signals corresponding to the protons attached to the arylene diimide ring that is directly attached to the carbazole unit are relatively sharp and appear at 8.87-8.89 ppm and 8.90-8.92 ppm for the PDI and NDI units, respectively (H_{PDI} and H_{NDI} in Figure 4.4), depending slightly on the concentration of the sample. The two peaks were fit with a Gaussian function using MestReNova v8.0.1 to obtain their relative areas, as well as relative heights (see expansion in Figure 4.4). These values can be used to estimate the monomer incorporation ratio and both methods give values within ~10% of the value that was expected from the monomer feed ratio (see table in Figure 4.4).

### 3.3 Optical properties

The solution and film absorbance spectra of the PC-PDI100 and PC-NDI100 parent copolymers are consistent with previous reports,\textsuperscript{28,35} whereas the spectra of the terpolymers are weighted averages of the parent copolymers (Figure 4.5a and b). The onset of absorption red-shifts with increasing PDI content, resulting in a 0.10 eV difference in HOMO-LUMO gap between the parent polymers in the solid-state (Table 4.2).

*Table 4.2* Solid-State Absorption and Electrochemical Properties of PC-PDI-NDI Copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_g^{\text{opt}}$ (eV)</th>
<th>$E_{\text{HOMO}}$ ($\pm 0.1$ eV)\textsuperscript{a}</th>
<th>$E_{\text{LUMO}}$ ($\pm 0.1$ eV)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-PDI100</td>
<td>561</td>
<td>702</td>
<td>1.77</td>
<td>-5.65</td>
<td>-3.88</td>
</tr>
<tr>
<td>PC-PDI75-NDI25</td>
<td>537</td>
<td>690</td>
<td>1.80</td>
<td>-5.67</td>
<td>-3.87</td>
</tr>
<tr>
<td>PC-PDI50-NDI50</td>
<td>535</td>
<td>688</td>
<td>1.80</td>
<td>-5.65</td>
<td>-3.85</td>
</tr>
<tr>
<td>PC-PDI25-NDI75</td>
<td>533</td>
<td>680</td>
<td>1.82</td>
<td>-5.68</td>
<td>-3.86</td>
</tr>
<tr>
<td>PC-NDI100</td>
<td>537</td>
<td>662</td>
<td>1.87</td>
<td>-5.72</td>
<td>-3.85</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$E_{\text{HOMO}} = E_{\text{LUMO}} + E_g^{\text{opt}}$; \textsuperscript{b}$E_{\text{LUMO}} = -e(E_{\text{red, onset}} + 4.8)$ where $E_{\text{red, onset}}$ is the onset of reduction versus ferrocene obtained from cyclic voltammetry.
Another interesting property of the terpolymers is observed in their solution emission spectra (Figure 4.5c). While the PC-PDI100 parent copolymer exhibits broad fluorescence from 600-850 nm ($\lambda_{ex} = 500$ nm), the analogous PC-NDI100 copolymer does not fluoresce in this range. Since the peak positions and shape of the terpolymers remain identical to those of PC-PDI100, with only the intensities changing over the composition range, it can be concluded that the emission must be due to a radiative transition associated with the PDI-carbazole unit, which does not occur in the NDI-carbazole unit. There is also a very weak emission at 525 nm from all five copolymers which is possibly due to monomeric arylene diimide emission. The fluorescence quantum yields ($\Phi_f$) were calculated relative to the laser dye 4-(dicyanomethylene)-2-methyl-6-($p$-dimethylaminostyryl)-4H-pyran (DCM) ($\Phi = 0.44$ in CH$_3$CN)\(^39\) using an excitation wavelength of 500 nm. The quantum yields increase with increasing PDI content, however, since both parent copolymers absorb at the excitation wavelength of 500 nm, the quantum yield of the
PDI-carbazole unit cannot be deconvoluted from the experimentally measured quantum yield, which includes contributions from both PDI-carbazole and NDI-carbazole units (Table 4.3 and Figure 4.6).

**Figure 4.6** Relationship between fluorescence quantum yield and percent of PDI acceptor unit. The quantum yields were measured in CHCl₃ relative to 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) (Φ = 0.44 in CH₃CN) at an excitation wavelength of 500 nm.

Time-correlated single photon counting (TCSPC) was used to record fluorescence decay profiles of the polymers in room temperature chloroform solutions. The decay profiles were well modeled by a two component sum-of-exponentials function at the maximum of the polymer emission (680 nm) (Figure 4.5d). The decay profile of PC-NDI100 was not measured since it has negligible emission at 680 nm. While it is difficult to assign individual lifetime components to specific relaxation processes, a general decrease in the weighted average fluorescence lifetime (τ_{avg}) is observed with increasing NDI content (Table 4.3). This decrease in average fluorescence lifetime for the emission at 680 nm is likely due to the presence of an additional non-radiative decay pathway associated with the NDI unit that is not present in PC-PDI100. If the observed decrease in the measured Φ_{fl} with increasing NDI content is solely due to a dilution of the emitting PDI-carbazole chromophore, and not the introduction of an additional quenching
pathway, then the $\tau_{\text{avg}}$ would be expected to remain constant since $\tau_{\text{avg}}$ is independent of chromophore concentration, as shown in equation (2). It is important to note that equations (1) and (2) cannot be related by $\Phi_{\text{fl}} = k_r \tau_{\text{fl}}$ for the values reported in Table 4.3 since the measured $\Phi_{\text{fl}}$ is for the entire PDI-NDI-carbazole system, while the measured $\tau_{\text{fl}}$ is for the emission of the PDI-carbazole chromophore at 680 nm, exclusively. The rate constant for non-radiative decay includes contributions from internal conversion, intersystem crossing, and electron transfer, all of which would be expected to decrease the $\tau_{\text{fl}}$ for the NDI-containing copolymers. Depending on the rates of the processes involved, the additional non-radiative decay pathway(s) in the NDI-containing polymers may act as a competing pathway to charge separation for excitons formed on the acceptor copolymer, leading to a lower acceptor current compared to devices containing the PC-PDI100 homopolymer. Since the relationship between the $\Phi_{\text{fl}}$ and percent of PDI does not appear to be linear (Figure 4.6), it is possible that energy is being funneled towards the NDI unit, and thus fluorescence will be quenched even at very low NDI incorporation. A model could theoretically be developed based on the decay curves to determine the relationship between the amount of quencher (ie. NDI content) and the $\tau_{\text{fl}}$, however this is beyond the scope of the present investigation.

$$\Phi_{\text{fl}} = \frac{k_r}{k_r + k_{nr}}$$  \hspace{1cm} (1)  

$$\tau_{\text{fl}} = \frac{1}{k_r + k_{nr}}$$  \hspace{1cm} (2)

**Table 4.3 Solution Fluorescence Properties of PC-PDI-NDI Copolymers.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\Phi_{\text{fl}}$ (%)$^a$</th>
<th>$\tau_{\text{fl}}$ (ns)$^b$</th>
<th>$\tau_{\text{avg}}$ (ns)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-PDI100</td>
<td>5.39</td>
<td>2.63 (40%)</td>
<td>3.97</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.87 (60%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC-PDI75-NDI25</td>
<td>3.32</td>
<td>1.57 (40%)</td>
<td>2.51</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.14 (60%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC-PDI50-NDI50</td>
<td>1.94</td>
<td>1.45 (72%)</td>
<td>2.38</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.77 (28%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC-PDI25-NDI75</td>
<td>0.92</td>
<td>0.66 (40%)</td>
<td>1.20</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.56 (60%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Fluorescence quantum yield relative to 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM); $^b$Fluorescence lifetimes with contributions in brackets.
3.4 Electrochemical properties

The energy levels of the polymers were measured using cyclic voltammetry (Figure 4.7) relative to a ferrocene/ferrocenium redox couple. At negative potentials a stable, reversible reduction is observed while at positive potentials irreversible oxidation of the film occurs. The LUMO energies were thus calculated from the reduction onset, while the HOMO energies were calculated by adding the optical bandgaps to the LUMO energies. With increasing NDI-content the LUMO energies of the polymers increase slightly, while the HOMO energies decrease, although PC-PDI50-NDI50 behaves as a slight outlier (Figure 4.1c). It is surprising that the change in energy levels is so small given the pronounced differences in optical properties. The photophysics likely involve optical transitions not only from the $S_0$ to $S_1$ states (HOMO to LUMO) but also from other transitions, which differ for the different copolymers. Regardless, the relatively low LUMO energy levels of the copolymers suggest that they are good candidates to be used as acceptor materials in all-polymer solar cells. Although the measured energies suggest a relatively small LUMO offset between PBDTTT-C and the acceptor copolymers which may be insufficient for electron transfer, it is important to note the inherent error of about ±0.1 eV associated with measuring energy levels using onsets of reduction (or oxidation) from cyclic voltammetry experiments. When this error is taken into account, the maximum possible LUMO offsets lie around 0.3 eV which is more favorable for electron transfer from the donor to acceptor. Furthermore, the energy requirement for charge separation and transfer is still an area of debate$^{40-42}$ and a recent report demonstrates that electron transfer between P3HT and a non-fullerene acceptor occurs with a LUMO offset of just 0.12 eV.$^{43}$
Figure 4.7 Cyclic voltammogram reduction curves of (a) PC-PDI100, (b) PC-PDI75-NDI25, (c) PC-PDI50-NDI50, (d) PC-PDI25-NDI75, and (e) PC-NDI100 in acetonitrile/TBAPF$_6$ electrolyte. A ferrocene redox couple (Fc/Fc$^+$) was used as an internal standard.

3.5 Photovoltaic properties

To test the potential of the copolymers in solar cells, devices were fabricated using PBDTTT-C (Figure 4.1b) as the donor material and the various copolymers as the acceptor material with the device structure ITO/PEDOT:PSS/PBDTTT-C:copolymer/LiF/Al. Interestingly, the device
power conversion efficiency remains relatively constant around 0.20-0.25% for all of the NDI-containing polymers and then more than doubles in efficiency to 0.57% for the PC-PDI100 parent copolymer (Table 4.4 and Figure 4.8).

### Table 4.4 Photovoltaic Properties of PBDTTT-C:PC-PDI-NDI Solar Cells.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$ (%)</th>
<th>$PCE_{max}$ (%)</th>
<th>$PCE_{avg}^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-PDI100</td>
<td>2.19</td>
<td>0.84</td>
<td>30.74</td>
<td>0.57</td>
<td>0.52±0.04</td>
</tr>
<tr>
<td>PC-PDI75-NDI25</td>
<td>1.12</td>
<td>0.78</td>
<td>28.53</td>
<td>0.25</td>
<td>0.24±0.01</td>
</tr>
<tr>
<td>PC-PDI50-NDI50</td>
<td>1.11</td>
<td>0.82</td>
<td>26.45</td>
<td>0.24</td>
<td>0.21±0.01</td>
</tr>
<tr>
<td>PC-PDI25-NDI75</td>
<td>0.88</td>
<td>0.82</td>
<td>27.97</td>
<td>0.20</td>
<td>0.19±0.01</td>
</tr>
<tr>
<td>PC-NDI100</td>
<td>0.98</td>
<td>0.88</td>
<td>27.41</td>
<td>0.24</td>
<td>0.22±0.01</td>
</tr>
</tbody>
</table>

$^a$Average PCE of seven devices fabricated under identical conditions ± standard deviation.

The reduced performance of the NDI-containing polymers is mainly due to a decrease in the short-circuit current density ($J_{sc}$), where devices of NDI-containing polymers exhibit $J_{sc}$ only half that of the $J_{sc}$ of PC-PDI100. This is coincident with the faster fluorescence decay in the NDI-containing polymers, which may be acting as a competing pathway to charge separation for excitons created in the acceptor material. The open-circuit voltage ($V_{oc}$) varies by 0.1 V throughout the series; however, the variation does not seem to correlate with polymer composition. Furthermore, there is no obvious correlation between the measured $V_{oc}$ and the LUMO of the polymers, as the polymers with the highest LUMO energies are expected to have the highest $V_{oc}$ values ($V_{oc} \propto$ HOMO$_{donor} -$ LUMO$_{acceptor}$). This suggests that the device performance in this case is not largely dependent on the copolymer composition, rather, it is dependent on the presence (or absence) of the NDI unit. This is not the same trend that has been previously demonstrated in copolymers that are used as donors in solar cells.$^7,44-48$ This difference may arise from the differences in delocalization for the filled orbitals that are involved in donor processes as opposed to the unfilled orbitals that are involved in acceptor processes. There have been previous reports of $V_{oc}$ pinning in ternary blend solar cells where the $V_{oc}$ of ternary devices remains as low as the lowest $V_{oc}$ of the corresponding binary devices.$^{49,50}$ With this series of acceptor copolymers, the $V_{oc}$ is lower for the terpolymers than the $V_{oc}$ of either parent copolymer, while the $J_{sc}$ appears to be pinned at that of the lowest parent copolymer value.
Figure 4.8 (a) J-V curves and (b) EQE spectra of OPV devices based on PBDTTT-C as the donor component and PC-PDI100 (black), PC-PDI75-NDI25 (orange), PC-PDI50-NDI50 (blue), PC-PDI25-NDI75 (green) and PC-NDI100 (red) as the acceptor component.

4 Conclusions

Three new one donor – two acceptor (D-A$_1$)-(D-A$_2$) random terpolymers, as well as the (D-A$_1$) and (D-A$_2$) parent copolymers, containing a carbazole donor and perylene diimide (PDI) and naphthalene diimide (NDI) acceptor units, were synthesized and used as acceptor materials in all-polymer solar cells using PBDTTT-C as the donor polymer. This was the first example of an n-type (D-A$_1$)-(D-A$_2$) random terpolymer containing both PDI and NDI units. The polymers were synthesized through Suzuki coupling polymerization of the dibrominated arylene diimides (each synthesized in two steps) and the carbazole diboronic ester (commercially available) in high yields (on scales of several hundred milligrams) with similar molecular weights and dispersities over the entire composition range. Incorporation of the two acceptor monomers was verified using the arylene diimide $^1$H NMR peaks at 120 °C in 1,1,2,2-tetrachloroethane-d$_2$. The optical and electrochemical properties were shown to vary with acceptor composition, however the composition dependence was not evident in device performance. Rather, any amount of the NDI monomer reduced the device efficiency to the value of the PC-NDI100 parent copolymer due to a pinning of the short-circuit current at the lowest value. The tunability of the optoelectronic properties and two-step monomer synthesis make this (D-A$_1$)-(D-A$_2$) system an interesting model for future work, where changing the donor unit or acceptor side-chains may allow for tuning of the polymer crystallinity and solid-state morphology, in addition to the optoelectronic properties shown here. While device performance was ultimately not improved by
terpolymerization, these results further highlight the significant challenge that the rational design of acceptor materials poses to the polymer community.

5 Experimental

5.1 General considerations

All reagents were used as received unless otherwise noted. Perylene-3,4,9,10-tetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 2-ethyl-1-hexylamine, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-N-(1- octynonyl)carbazole, and tetrakis(triphenylphosphine)palladium(0) were purchased from Sigma-Aldrich. Dibromoisocyanuric acid was purchased from TCI America.

5.2 Instrumentation and methods

$^1$H NMR spectra of the monomers were recorded on a Varian Mercury 400 spectrometer operating at 400 MHz. Chemical shifts are reported in ppm at ambient temperature. $^1$H NMR chemical shifts are referenced to the residual protonated chloroform peak at 7.26 ppm. $^1$H NMR spectra of the polymers were recorded on an Agilent 600 spectrometer operating at 600 MHz. Chemical shifts are reported in ppm at 25, 70 and 120 °C. $^1$H NMR chemical shifts are referenced to the residual protonated 1,1,2,2-tetrachloroethane peak at 6.0 ppm. Polymer molecular weights were determined with a Viscotek HT-GPC (1,2,4-trichlorobenzene, 140 °C, 1 mL/min flow rate) using Tosoh Bioscience LLC TSK-GEL GMH$_{HR}$-HT mixed-bed columns and narrow molecular weight distribution polystyrene standards. A UV detector was used to detect the eluted polymer with respect to elution volume. Absorption spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer. The thin-films used for absorbance spectroscopy were spin-coated from solutions in chloroform (7 mg/mL) at 2500 rpm for 30 seconds onto glass substrates that had been washed with methanol. Emission spectra were recorded on a Photon Technology International (PTI) QuantaMaster 40-F NA spectrofluorometer with a photomultiplier detector and xenon arc lamp source. The optical densities of the solutions were kept below 0.1 at the excitation wavelength to minimize reabsorption effects. Fluorescence decay curves were measured by the time-correlated single photon counting (TCSPC) technique, using an IBH system equipped with a 494-nm NanoLED pulsed diode source. The excitation monochromator was set to 494 nm and the emission monochromator set to 680 nm. Data were
collected with the instrument's built-in multichannel analyzer set at a resolution of 0.1135 ns/channel. Fluorescence decay measurements were run until 5000 counts were recorded in the maximum channel. The instrumental response function was measured with a scattering solution of silica in water (Ludox); these were collected immediately before and after each measurement. The measurements were made in quartz cuvettes on dilute chloroform solutions (optical densities less than 0.1). Fluorescence decays were analyzed within the Edinburgh Instruments FAST software package using iterative reconvolution procedures. The goodness of fits were determined by the reduced chi-squared fitting parameter and inspection of weighted residuals. Electrochemistry was performed with a BASi Epsilon potentiostat. A standard three-electrode cell with a 2.0 mm diameter Pt button working electrode, a Ag/Ag⁺ reference electrode, and a Pt wire counter electrode was used, with a ferrocene internal standard and a 100 mV/s scan rate. The electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile. Polymer films were prepared by drop-casting a 7 mg/mL solution of polymer in chloroform onto the working electrode, and the solvent was evaporated in air. LUMO levels were estimated from cyclic voltammetry reduction onset potentials and converted to the vacuum scale using the equation \( E_{\text{LUMO}} = -e(E_{\text{red}} + 4.8) \), referenced to the ferrocene/ferrocenium redox couple. HOMO levels were estimated by adding the \( E_{\text{LUMO}} \) to the solid-state optical bandgap.

5.3 Photovoltaic device fabrication and characterization

Poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b;4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl] (PBDTTT-C) and PC-PDI-NDI copolymers were mixed in chlorobenzene at 1:1 wt ratio (10:10 mg/mL) with 1 vol% chloronaphthalene (CN). CN was used as a solvent additive as it has been shown to improve device performance by improving the active layer morphology. Solutions were stirred at 50 °C overnight to ensure complete dissolution. Devices were fabricated on commercial indium tin oxide (ITO) substrates (Thin Film Devices) that had a sheet resistance of ~10 Ω/□. These substrates were cleaned in aqueous detergent, deionized (DI) water, acetone and methanol, and subsequently treated in an air-plasma cleaner for 5 min. Next, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P VP AI 4083) was coated onto the substrates at 3000 rpm and annealed in air at 130 °C for 15 min. After annealing, the substrates were transferred into a nitrogen-filled glove box, where PBDTTT-C:copolymer blends were coated at 1500 rpm. A 0.8 nm LiF layer and 100 nm Al anode were thermally
deposited through a shadow mask at $\sim 10^{-6}$ torr using an Angstrom Engineering Covap II (Kitchener, Ontario, Canada). Device area is 0.07 cm$^2$ as defined by the area of circular Al anode. $I-V$ characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5 G conditions with a power intensity of 100 mW/cm$^2$. The mismatch of simulator spectrum was calibrated using a Si diode with a KG-5 filter. EQE spectra were recorded and compared with a Si reference cell that is traceable to the National Institute of Standards and Technology.

5.4 Synthesis

1,6/7-dibromo-3,4,9,10-perylene diimide. A mixture of perylene dianhydride (10 g, 0.025 mol) and H$_2$SO$_4$ (150 mL) was stirred in a 3-neck round bottom flask under air for 4 h after which I$_2$ (244 mg, 0.1 mmol) was added and the mixture heated to 85 °C. Br$_2$ (2.8 mL, 0.055 mol) was then added dropwise via addition funnel over 1 h. An adapter connected to a hose attached to a funnel was attached to one of necks and the funnel placed in a beaker of water to vent the excess HBr into. The mixture was stirred at 85 °C for 17 h under air, after which it was cooled to room temperature and excess Br$_2$ was removed by a stream of N$_2$ gas. Water (50 mL) was slowly added and the resulting precipitate was filtered through a glass frit and washed with H$_2$SO$_4$ (100 mL) and water (500 mL) until the pH of the washes was neutral. The bright red solid was dried under vacuum overnight to yield 13.4 g of product (98% crude yield). The crude product was used directly in the next step without further purification due its lack of solubility in organic solvents.
**N,N'-di(2-ethylhexyl)-1,6/7-dibromo-3,4,9,10-perylene diimide.** A 1:1 v/v mixture of n-BuOH:H₂O (950 mL) was added to the crude bromination product in a 3-neck flask filled with N₂. 2-Ethyl-1-hexylamine was added via syringe, a condenser was attached, and the mixture was heated to 80 °C for 24 h. The mixture was then cooled to 0 °C and concentrated HCl (80 mL) was carefully added and the mixture allowed to warm to room temperature over 1 h. The product was then extracted with chloroform (600 mL) and washed with water until the aqueous washes were neutral (2 L). The organic fraction was then dried over MgSO₄, filtered and concentrated to yield 17.4 g of product (92% crude yield). The product was purified by column chromatography with chloroform. ¹H NMR (CDCl₃, 400 MHz): δ(ppm) 9.27 (d, 2H), 8.72 (s, 2H), 8.50 (d, 2H), 4.09 (m, 4H), 1.91 (m, 2H), 1.38-1.30 (m, 16H), 0.93-0.89 (m, 12H).

**2,6/2,7-dibromo-1,4,5,8-naphthalene dianhydride.** Naphthalene dianhydride (2.62 g) was dissolved in 20% SO₃ fuming H₂SO₄ (oleum) (100 mL) in a round bottom flask under air. Dibromoisocyanuric acid (DBI) (2.85 g) was slowly dissolved in an additional 50 mL of oleum and added dropwise to the reaction flask via addition funnel over 3 h. The mixture was stirred for an additional 2 h after which it was very carefully added to a flask containing 500 g of ice. An additional 1.5 L of water was added to the flask and the mixture was stirred for 3 h. The bright yellow precipitate was then filtered through a glass fritted funnel, washed with water and dried.
under vacuum overnight to yield 3.03 g of product (73% crude yield). The crude product was used directly in the next step without further purification due its lack of solubility in organic solvents.

\[ \text{N,N}'-\text{di(2-ethylhexyl)-2,6-dibromo-1,4,5,8-napthalene diimide}. \]

The brominated product (3 g) was dissolved in glacial acetic acid (80 mL) in a 3-neck round bottom flask with an attached condenser under argon. 2-Ethyl-1-hexylamine (4.6 mL) was added and the mixture was heated to 120 °C for 20 h. The dark red solution was then cooled to room and added to 200 mL of methanol to precipitate a red solid. The precipitate was filtered through a Buchner funnel, washed with methanol and dried under vacuum to yield 2.84 g of red solid. The crude product contained a 1:1 mixture of the \textit{cis} and \textit{trans} dibromo isomers by \textsuperscript{1}H NMR analysis which were separated via column chromatography in dichloromethane. The red-orange \textit{trans} isomer was then recrystallized in hexanes several times until the recrystallized product was a pale yellow-orange powder. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ(ppm) 9.00 (s, 2H) 4.15 (m, 4H), 1.94 (m, 2H), 1.37–1.35 (m, 16H), 0.93–0.88 (m, 12H).

\textbf{PC-PD175-NDI25.} \textit{N,N'-Di(2-ethylhexyl)-1,7-dibromo-3,4,9,10-perylene diimide (monomer 1)} (176.1 mg, 0.228 mmol), \textit{N,N'-di(2-ethylhexyl)-2,6-dibromo-1,4,5,8-napthalene diimide (monomer 2)} (49.5 mg, 0.076 mmol), 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-N-(1-octynonyl)carbazole (monomer 3) (200.1 mg, 0.304 mmol), and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh\textsubscript{3})\textsubscript{4}) (3%, 10.8 mg) were added to a Schlenk flask and the atmosphere was reduced under vacuum for 1 h and then purged with argon. A mixture of THF (17.4 mL) and 2M aqueous Na\textsubscript{2}CO\textsubscript{3} (10.4 mL) was degassed with argon for 30 min and then added to the reaction flask. A condenser was attached and the mixture was heated.
to reflux for 48 h. After 48 h, phenylboronic acid (48 mg) dissolved in 0.5 mL THF was added and the mixture was heated to reflux for an additional 2 h, after which bromobenzene (0.44 mL) was added and reflux continued for a final 2 h. The mixture was then cooled to room temperature, precipitated into 150 mL of methanol and filtered through a Soxhlet thimble. The precipitated polymer was subjected to Soxhlet extraction with methanol, hexanes and chloroform. The final chloroform fraction was then passed through a silica column with chloroform, concentrated by rotary evaporation, and the polymer dried under vacuum overnight. Yield: 280 mg (93%). 1H NMR (1,1,2,2-tetrachloroethane-d$_2$, 120 °C, 600 MHz): δ(ppm) 8.92-8.88 (m, 2H), 8.35-7.35 (m, 9H), 4.68 (br, 1H), 4.22 (br, 4H), 2.35 (br, 1H), 2.09-2.02 (br, 4H), 1.46-0.83 (m, 58H). $M_n = 6.9$ kDa, $M_w = 1.4$ kDa, $D = 2.5$.

**PC-PDI50-NDI50.** Prepared as above starting with monomer 1 (117.5 mg, 0.152 mmol), monomer 2 (99 mg, 0.152 mmol), monomer 3 (200.3 mg, 0.304 mmol), THF (17.4 mL), 2M aqueous Na$_2$CO$_3$ (10.4 mL), and Pd(PPh$_3$)$_4$ (3%, 10.5 mg). Yield: 221 mg (76%). 1H NMR (1,1,2,2-tetrachloroethane-d$_2$, 120 °C, 600 MHz): δ(ppm) 8.92-8.89 (m, 2H), 8.46-7.35 (m, 8H), 4.70 (br, 1H), 4.19 (br, 4H), 2.38 (br, 2H), 2.08 (br, 4H), 1.49-0.86 (m, 58H). $M_n = 6.4$ kDa, $M_w = 13.0$ kDa, $D = 2.0$.

**PC-PDI25-NDI75.** Prepared as above starting with monomer 1 (58.9 mg, 0.0762 mmol), monomer 2 (147 mg, 0.228 mmol), monomer 3 (200 mg, 0.304 mmol), THF (17.4 mL), 2M aqueous Na$_2$CO$_3$ (10.4 mL), and Pd(PPh$_3$)$_4$ (3%, 10.8 mg). Yield: 238.9 mg (85%). 1H NMR (1,1,2,2-tetrachloroethane-d$_2$, 120 °C, 600 MHz): δ(ppm) 8.92-8.88 (m, 2H), 8.46-7.41 (m, 7H), 4.68 (br, 1H), 4.17 (br, 4H), 2.39 (br, 2H), 2.07 (br, 4H), 1.49-0.89 (m, 58H). $M_n = 6.5$ kDa, $M_w = 13.6$ kDa, $D = 2.1$.

**PC-PDI100.** Prepared as above starting with monomer 1 (270 mg, 0.35 mmol), monomer 3 (230 mg, 0.35 mmol), THF (20 mL), 2M aqueous Na$_2$CO$_3$ (12 mL), and Pd(PPh$_3$)$_4$ (3%, 13 mg). Yield: 340 mg (96 %). 1H NMR (1,1,2,2-tetrachloroethane-d$_2$, 120 °C, 600 MHz): δ(ppm) 8.89 (br, 2H), 8.36-7.35 (m, 10H), 4.68 (br, 1H), 4.23 (br, 4H), 2.34 (br, 2H), 2.11-2.01 (br, 4H) 1.51-0.83 (m, 58H). $M_n = 7.1$ kDa, $M_w = 21.3$ kDa, $D = 3.0$.

**PC-NDI100.** Prepared as above starting with monomer 2 (200 mg, 0.31 mmol), monomer 3 (204 mg, 0.31 mmol), THF (17.6 mL), 2M aqueous Na$_2$CO$_3$ (10.6 mL), and Pd(PPh$_3$)$_4$ (3%, 10 mg). Yield: 242 mg (87%). 1H NMR (1,1,2,2-tetrachloroethane-d$_2$, 120 °C, 600 MHz): δ(ppm) 8.92
(br, 2H), 8.34 (br, 2H), 7.69 (br, 2H), 7.40 (br, 2H), 4.69 (br, 1H), 4.17 (br, 4H), 2.40 (br, 2H), 2.06 (br, 4H), 1.44-1.27 (m, 40H), 1.01-0.89 (m, 18H). $M_n = 6.5 \text{ kDa}$, $M_w = 11.8 \text{ kDa}$, $D = 1.8$. 

**PBDTTT-C.** Prepared from a modified literature procedure. Briefly, 1-(4,6-dibromothieno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one (212.1 mg, 0.50 mmol), 2,6-bis(trimethyltin)-4-didodecyloxy-benzo[1,2-b; 3,4-b]dithiophene (386.1 mg, 0.50 mmol), and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$) (4%, 25 mg) were added to a Schlenk flask, purged with vacuum three times and then filled with a nitrogen atmosphere. A mixture of dry DMF (2 mL) and dry toluene (8 mL) were added and the reaction was heated to 120 °C. After 12 h, the mixture was cooled to room temperature, precipitated into methanol and filtered through a Soxhlet thimble. The precipitated polymer was subjected to Soxhlet extraction with methanol, hexanes and chloroform. The final chloroform fraction was concentrated by rotary evaporation and the polymer was obtained as a dark green solid (350 mg; 98% yield). $M_n = 60.0 \text{ kDa}$, $M_w = 150.0 \ D = 2.5$.

6 References


5832.


Chapter 5
Thionated Naphthalene Diimides

1 Statement of contributions

Electrochemistry was performed with assistance from Tyler Schon. AFM images were collected by Joe Manion. Crystal structures were obtained by Alan Lough. SEM images were collected with assistance from Ilya Gourevich. PXRD was performed by Abdolkarim Danaei. I carried out all other synthesis, characterization, computations, and experiments presented in this chapter. Portions of this chapter are being prepared for publication.\(^1\)

2 Introduction

As discussed in chapter 4, while there have been significant advances in the design of \(\pi\)-conjugated p-type materials for organic electronics over the last 20 years, research on complementary n-type materials has gained interest only recently.\(^2\)-\(^6\) In addition to being used as acceptor materials for organic photovoltaics, high-mobility \(\pi\)-conjugated n-type materials are also useful for n-channel organic field-effect transistors (OFETs). As with OPVs, there are many more examples of p-type (ie. hole transporting) OFETs than n-type (ie. electron transporting). Design criteria for new \(\pi\)-conjugated n-type materials for transistor applications include (1) lowering of the LUMO level for efficient electron injection and (2) invoking strong intermolecular interactions for efficient electron transport in the solid-state.\(^6\)-\(^8\) Furthermore, in order for the device to be air-stable, the LUMO level should be lower than -4.0 eV to prevent charge trapping by water or oxygen.\(^9,\)\(^10\)

Many of the best-performing n-type materials for both OPVs and OFETs contain an electron withdrawing carbonyl group in the form of an amide or imide functionality, such as diketopyrrolopyrrole (DPP), thieno[3,4-c]pyrrole-4,6-dione (TPD), perylene diimide (PDI), and naphthalene diimide (NDI). A far less studied electron deficient functional group is the thioimide, that is an imide group where the carbonyl oxygen is replaced with sulfur. This so-called thionation typically results in a lowering of the LUMO energy and increase in electron affinity, satisfying the first design criterion for an ideal n-type OFET material.\(^11\)-\(^14\) Furthermore, thionation gives rise to the possibility of S-S nonbonding interactions, which can decrease \(\pi\)\(-\pi\) stacking distances in conjugated molecules and thus increase intermolecular interactions,
satisfying the second design criterion outlined above. The introduction of S-S interactions has been shown to be an effective strategy for controlling packing in n-type materials and has resulted in improved electron transport in n-channel OFETs.\textsuperscript{11,15,16}

![Chemical structures of common n-type building blocks containing carbonyl groups.](image)

\[R = \text{alkyl}\]

**Figure 5.1** Structures of common n-type building blocks containing carbonyl groups.

In this chapter, I describe the synthesis, characterization and self-assembly of thionated naphthalene diimides, which have a smaller conjugated core and higher energy absorption than the analogous perylene diimides. In contrast to the previous study by Andrew Tilley on thionated PDIs which employed branched 3-hexylundecyl side-chains for solubility,\textsuperscript{13,15} I chose to employ linear dodecyl side-chains in order to increase crystallinity and solid-state packing. In particular, I was interested in studying the self-assembly of the compounds, as arylene diimides functionalized with linear N-alkyl groups have been shown to self-assemble into nanoribbons or nanobelts with high aspect ratios.\textsuperscript{17-19} Recently, organic nanowires self-assembled from small-molecule semiconductors and conducting polymers have attracted significant attention in the field of OFETs and have resulted in high mobility devices.\textsuperscript{17,20,21} One-dimensional (1D) \(\pi\)-conjugated organic micro or nanostructures maintain all the advantages of organic single crystals such as high crystallinity but are typically easier to grow, more robust, and can be processed from solution.\textsuperscript{22} Furthermore, they typically possess fewer structural defects and grain boundaries than their thin film counterparts. I hypothesize that the increased intermolecular interactions in the thionated NDIs, in addition to the linear side-chains, will facilitate growth of highly stable one-dimensional nanostructures with good electron transport properties that may have potential applications in such nanostructured devices.
Figure 5.2 Chemical structures of the six $N,N'$-di(dodecyl)-4,5,8,9-naphthalene diimide derivatives.

3 Results and discussion

3.1 Synthesis

The non-thionated parent NDI (P) was synthesized from naphthalene-4,5,8,9-tetracarboxylic dianhydride and $n$-dodecylamine according to literature procedure.\(^{23}\) The crude product was obtained in high yield and was used in the next step without further purification. Thionation was achieved by treating \(P\) with recrystallized Lawesson’s reagent (LR) in refluxing toluene. The degree of thionation can be controlled by varying the reaction time and stoichiometry. When less than one equivalent of LR is used and the reaction time is 17 h, the major product is \(S1\) (each equivalent of LR is capable of delivering two sulfur atoms per reaction). When two equivalents of LR are used and the reaction time is 17 h, the major products are \(cis-S2\) and \(trans-S2\). When five equivalents of LR are used and the reaction time is 48 h, the major products are \(S3\) and \(S4\). Due to a decrease in solubility with increasing degree of thionation, the compounds must be separated by a series of chloroform columns on both silica gel and aluminum oxide. Similarly to the analogous thionated PDIs, both \(cis\) and \(trans\) isomers of the doubly thionated compound were obtained, as confirmed by gCOSY NMR. The geminate isomer is also present in very minor amounts but could not be isolated.

3.2 Optoelectronic properties

The absorption spectra in both solution and solid-state red-shift with increasing degree of thionation, similarly to the thionated PDIs (Table 5.1, Figure 5.3). This red-shift is attributed to
an increase in the HOMO energy and decrease in LUMO energy, as confirmed by cyclic voltammetry and density functional theory calculations (Table 5.2, Figure 5.4). In contrast to the thionated PDIs, however, a drastic change in the shape of the absorption spectra is observed upon thionation, as well as loss of the characteristic NDI vibronic structure. The spectra are consistent with the 3-hexylundecyl analogues also synthesized during the course of this project, as well as the 2-ethylhexyl analogues disclosed in a 2011 patent by Polyera.\textsuperscript{24} The spectra of the 3-hexylundecyl analogues do not change significantly with temperature or solvent and therefore it can be concluded that the change in shape from the parent compound is not due to solubility or aggregation effects. Since the spectral shape is affected by thionation in NDIs but not PDIs, this suggests that it may be the size of the aromatic core that leads to the change. The smaller core in naphthalene diimides means that the carbonyl groups have a larger overall contribution to the total molecular orbital density than in perylene diimides. Substitution of a carbonyl group with a thionyl group should therefore impart a greater change to the molecular orbital structure in NDIs since the effect of the substitution is effectively diluted down by the larger PDI core. Further work is required to fully understand these spectral changes, which is beyond the scope of this investigation. Regardless, I was fascinated by this significant difference in behavior compared to the thionated PDIs which inspired me to carry out further studies to determine how else the two systems differed.

In the solid-state, the spectra become much broader and the onset of absorption is red-shifted for P-S3 signifying a narrowing of the optical bandgap going from solution to solid-state. Thin films of S4 could not be formed due its low solubility in organic solvents. In contrast to solution, the solid-state spectra of the two S2 isomers have quite distinct shapes and energies, with the spectrum of the \textit{trans} isomer being red-shifted about 0.15 eV relative to the \textit{cis} isomer. This is consistent with the stark difference in color of the two isomers in powder form, where \textit{cis}-S2 is a dark yellow-brown, while \textit{trans}-S2 is bright red. Furthermore, the \textit{trans}-S2 spectrum possesses more vibronic structure than that of \textit{cis}-S2, suggesting it may be more ordered in the solid-state.
Figure 5.3 Optical absorption spectra of P-S4 in 10^{-5} M chloroform solution (left) and solid-state (right). Thin films were spin-coated from 5 mg/mL chloroform solution at 2000 rpm onto glass substrates. The compound is denoted by the line color.

Table 5.1 Optical Properties of P-S4.

<table>
<thead>
<tr>
<th></th>
<th>Solution (CHCl₃)</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ_{max} (nm)</td>
<td>λ_{onset} / E_{g opt} (nm / eV)</td>
</tr>
<tr>
<td>P</td>
<td>381</td>
<td>390 / 3.18</td>
</tr>
<tr>
<td>S1</td>
<td>394</td>
<td>490 / 2.43</td>
</tr>
<tr>
<td>cis-S2</td>
<td>475</td>
<td>527 / 2.35</td>
</tr>
<tr>
<td>trans-S2</td>
<td>476</td>
<td>528 / 2.35</td>
</tr>
<tr>
<td>S3</td>
<td>505</td>
<td>571 / 2.17</td>
</tr>
<tr>
<td>S4</td>
<td>533</td>
<td>639 / 1.94</td>
</tr>
</tbody>
</table>

*Measured using S4 3-hexylundecyl NDI; \(^{a}\)S4 films could not be formed due to poor solubility.

Cyclic voltammetry was performed in solution to determine the reduction properties of the compounds (Figure 5.4). The curves shown are from the second cycles or later (as are all cyclic voltammogram curves in this thesis) for all compounds except S3, in which case the first cycle is shown due the appearance of additional peaks at later scans likely due to decomposition and/or film formation at the electrode. P, S1, and cis-S2 exhibit typical reversible two-electron reductions, while only one reduction peak is observed for trans-S2 and S3, likely due to the low
solubility of these compounds and film formation at the electrodes. The LUMO levels were estimated from the onset of the first reduction peak and reveal a decrease in LUMO level with increasing thionation (Table 5.2). Oxidation peaks were not observed due to the oxidation of the electrolyte and/or solvent in the same potential region. HOMO energies were therefore calculated by subtracting the LUMO energy from the optical bandgap also measured in solution. It was found that the LUMO energies decrease with increasing degree of thionation, while the HOMO energies increase relative to the non-thionated parent derivative but remain relatively constant across the five thionated derivatives, consistent with density functional theory calculations (see bracketed values in Table 5.2) and analogous to the thionated PDIs. Furthermore, the energy levels of the two S2 isomers are identical within error and therefore any differences in their OFET performance will have to be attributed to differences in solid-state packing alone. Electrochemistry was not performed on S4 due to poor solubility.

**Figure 5.4** Cyclic voltammogram reduction curves of P-S3 in anhydrous dichloromethane solution in the presence of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) electrolyte. A ferrocene redox couple (Fc/Fc⁺) was used as an internal standard.
### Table 5.2 Electrochemical Properties of P-S3.

<table>
<thead>
<tr>
<th></th>
<th>$E_{1/2}^{1}$ (V)</th>
<th>$E_{1/2}^{2}$ (V)</th>
<th>$E_{\text{HOMO}}^{a,b}$ (eV)</th>
<th>$E_{\text{LUMO}}^{a,c}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>-1.11</td>
<td>-1.53</td>
<td>-6.97 (-7.42)</td>
<td>-3.79 (-3.87)</td>
</tr>
<tr>
<td>S1</td>
<td>-0.92</td>
<td>-1.30</td>
<td>-6.38 (-6.71)</td>
<td>-3.95 (-4.09)</td>
</tr>
<tr>
<td>cis-S2</td>
<td>-0.79</td>
<td>-1.11</td>
<td>-6.46 (-6.71)</td>
<td>-4.11 (-4.27)</td>
</tr>
<tr>
<td>trans-S2</td>
<td>-0.80</td>
<td>$^d$</td>
<td>-6.50 (-6.69)</td>
<td>-4.15 (-4.25)</td>
</tr>
<tr>
<td>S3</td>
<td>-0.65</td>
<td>$^d$</td>
<td>-6.47 (-6.62)</td>
<td>-4.30 (-4.44)</td>
</tr>
</tbody>
</table>

$^a$Calculated energies are shown in brackets next to the experimentally obtained values. Calculations were performed using DFT applying the B3LYP functional and 6-311G basis set; $^b$E_{\text{HOMO}} = E_{\text{LUMO}} + E_{g}^{\text{opt,soln}}, $^c$E_{\text{LUMO}} = -e(E_{\text{red,onset}} + 4.8) where $E_{\text{red,onset}}$ is the onset of reduction versus ferrocene obtained from cyclic voltammetry; $^{230}$ $^d$A second reduction peak was not observed.

### 3.3 Thermal properties

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on the compounds to determine their thermal transitions and thermal stability (Figures 5.5 and 5.6, respectively). For DSC, the compounds were sealed in aluminum hermetic pans and subject to two heating and cooling cycles between 20 and 200 °C at a heating/cooling rate of 10 °C/min. The DSC curves of P-S3 are characteristic of a typical liquid crystalline material, with the two main heating transitions corresponding to the crystalline to liquid-crystalline and liquid-crystalline to isotropic liquid transitions for each compound. The transitions observed for the parent compound are consistent with previous reports in the literature, $^{26}$ while the deviation from these transitions for the thionated compounds is likely due to their different strengths of intermolecular interactions and solid-state packing. A second heating transition is not observed for S4 below 200 °C, but likely does occur at higher temperatures (DSC was not performed above 200 °C to avoid thermal decomposition). It is also interesting that the only transitions observed for S3 and S4 are during the first heating cycles, after which no further transitions are observed. The experiment was repeated for S3 and S4 with a total of four heating and cooling cycles, and no significant transitions were observed during the additional two cycles. From TGA it is known that less <1% of each compound degrades below 200 °C and therefore the absence of transitions after the first heating cycle is not due to decomposition in this case.
Figure 5.5 Differential scanning calorimetry (DSC) traces of P-S4 obtained under nitrogen at a heating/cooling rate of 10 °C/min. The first heating and cooling cycles are shown in blue and the second shown in black.

The thermal stability of the compounds is relatively good, with 5% weight loss occurring between 260 and 360 °C. The lower thermal stability of the thionated compounds relative to the non-thionated parent is consistent with the analogous thionated PDIs, and is likely due to the weaker C-S thionyl bond relative to the carbonyl C-O. Although thermal stability is somewhat decreased with thionation, it is found that the photostability of the compounds is quite good, in contrast to what was reported for thionated DPP and TPD small molecules. In this work, Leclerc and co-workers found that several of the thionated compounds decomposed over a few hours even when kept in the dark, while I have no evidence of decomposition after storing my compounds in ambient conditions over several months.
3.4 Solid-state properties

3.4.1 Crystal structures

Single crystals of $P$ and $\textit{cis-S2}$ were obtained by layering concentrated chloroform solutions with an excess of methanol. Single crystals of $S3$ were obtained by slow cooling of a saturated 1,2,4-trichlorobenzene solution from 140 °C to room temperature. $\textit{Trans-S2}$ was crystallized similarly, by slow cooling of a saturated o-dichlorobenzene solution. Attempts at growing single crystals of $S1$ and $S4$ suitable for x-ray analysis were unsuccessful. All four compounds lie across crystallographic inversion centers and therefore there is only half of the molecule in the asymmetric unit and the other half is related by symmetry. Since $\textit{cis-S2}$ and $S3$ do not have molecular inversion symmetry, the absolute positions of the sulfur and oxygen sites in the crystal lattice cannot be determined and the sites for O1,O2/S1,S2 are refined without any distance restraints. For the sake of crystallographic analysis it is assumed that the sulfur and oxygen sites are disordered 50:50. Although this assumption makes the C-O and C-S bond distances somewhat unreliable, important information can still be determined regarding the packing of the molecules.

**Figure 5.6** Thermogravimetric analysis plot of $P$-$S4$ obtained under nitrogen at a heating rate of 10 °C/min.
### Table 5.3 Crystallographic Data for P, cis-S2, trans-S2, and S3.

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>cis-S2</th>
<th>trans-S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₃₈H₅₄N₂O₄</td>
<td>C₃₈H₅₄N₂O₂S₂</td>
<td>C₃₈H₅₄N₂O₂S₂</td>
<td>C₃₈H₅₄N₂O₄S₃</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Molecular weight</td>
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<td>634.95</td>
<td>634.95</td>
<td>651.01</td>
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<tr>
<td>Space group</td>
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<td>P-1</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>a (Å)</td>
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<td>4.6420</td>
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<tr>
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<td>c (Å)</td>
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<td>87.1960</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>94.603</td>
<td>85.342</td>
<td>96.678</td>
<td>93.174</td>
</tr>
<tr>
<td>γ (°)</td>
<td>104.495</td>
<td>74.748</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>823.12</td>
<td>854.02</td>
<td>1662.28</td>
<td>1732.32</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>D (g cm⁻³)</td>
<td>1.216</td>
<td>1.235</td>
<td>1.269</td>
<td>1.248</td>
</tr>
<tr>
<td>R₁ (%)</td>
<td>4.61</td>
<td>4.43</td>
<td>4.64</td>
<td>6.94</td>
</tr>
</tbody>
</table>

**P** and **cis-S2** belong to the triclinic crystal system and P-1 space group, while **trans-S2** and **S3** belong to the monoclinic crystal system and P2₁/n space group (Table 5.3). Although the n-dodecyl side-chains adopt an all-trans conformation in all four crystal structures, the side-chains are almost completely interdigitated in the **trans-S2** and **S3** structures but show no overlap at all in either **P** or **cis-S2** (Figure 5.7). The side-chains in the **trans-S2** derivative show the greatest degree of overlap and most compact structure, which is consistent with it having the shortest d-spacing of the series observed by PXRD (*vide infra*), as well as the highest density (Table 5.3). Large channels between side-chains in other arylene diimide derivatives are thought to act as traps for oxygen and water and thus decrease the ambient stability of OFETs composed of these materials. The lack of these channels in the **trans-S2** and **S3** crystals suggest that they may have improved air-stability in single crystal OFETs relative to the **P** and **cis-S2** derivatives.
Figure 5.7 Long-range crystal packing motif of (a) P, (b) cis-S2, (c) trans-S2, and (d) S3. Hydrogens have been omitted for clarity.

All four derivatives crystallize in parallel planes, however, the NDI cores are not cofacial but are displaced along both the short ($D_y$) and long ($D_x$) axes of the molecule (Figure 5.8). This type of slip-stacked structure is common for NDIs with both linear and cyclic alkyl chains. 27,28 Furthermore, the slip-stacked motif has been used as an alternative strategy for developing high efficiency PDI-based acceptors for organic photovoltaics. It was shown that substitution at the PDI 2,5,8,11-positions (“headland positions”) leads to a slip-stacked packing structure which is known to prevent excimer formation that is prevalent in cofacial dimers. 29

Figure 5.8 Crystal structures of (a) P, (b) cis-S2, (c) trans-S2, and (d) S3 viewed from the top of the molecular plane (top) and along the long molecular axis (bottom). N-dodecyl chains and hydrogens have been omitted for clarity. Sulfur and oxygen sites are disordered 50:50 in cis-S2 and S3 so both atoms are shown.
Both the slip-stacking and π-π stacking distances were extracted from the crystallographic data and show an increase in long axis slip and decrease in short axis slip of 1.18 Å and 0.61 Å, respectively, going from P to cis-S2 to S3 (Table 5.4). The trans-S2 isomer seems to deviate from this trend, as it has the largest long axis slip and a very small short axis slip of just 1.18 Å. The π-π stacking distance for P, cis-S2 and trans-S2 is very similar, but decreases by about 0.3 Å for the S3 derivative. This result is somewhat surprising, as a more pronounced decrease in π-π stacking distance was expected with increasing degree of thionation. The major effect, however, seems to be on the slip-stacking distances, which suggests that thionation does have a significant effect on intermolecular packing. It is also significant that substitution of oxygen with a larger sulfur atom does not seem to perturb the NDI core planarity, which is important for retaining strong π-π interactions.

<table>
<thead>
<tr>
<th></th>
<th>$D_x$ (Å)</th>
<th>$D_y$ (Å)</th>
<th>π-π distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1.59</td>
<td>2.81</td>
<td>3.32</td>
</tr>
<tr>
<td>cis-S2</td>
<td>1.65</td>
<td>2.77</td>
<td>3.36</td>
</tr>
<tr>
<td>trans-S2</td>
<td>2.99</td>
<td>1.18</td>
<td>3.36</td>
</tr>
<tr>
<td>S3</td>
<td>2.77</td>
<td>2.20</td>
<td>2.99</td>
</tr>
</tbody>
</table>

Perhaps the most interesting result of the single crystal analysis is the significant difference between the long range crystal packing of the two S2 derivatives. While the cis-S2 derivative crystallizes similarly to the non-thionated P compound, the trans-S2 isomer is more similar to triply thionated S3. This helps explain the observed differences in the solubility of the compounds, where P and cis-S2 have similar and significantly higher solubilities than trans-S2 and S3. When considering the intermolecular short contacts of the four derivatives, only trans-S2 and S3 have short contacts between atoms other than carbon and hydrogen that are less than the sum of the van der Waals radii. In the trans-S2 crystal packing structure, there are four sulfur-oxygen contacts per molecule each with a distance of 3.32 Å, while in the S3 packing motif there are four contacts per molecule with distances of 3.42 Å, which are unspecified sulfur-sulfur, sulfur-oxygen or oxygen-oxygen interactions. There are no sulfur-sulfur, sulfur-oxygen or oxygen-oxygen short contacts (i.e. intermolecular distances less than the sum of the van der Waals radii) in the P or cis-S2 long range packing structures. These contacts may be responsible
for causing the large differences in crystal packing structure between \( \text{P} \) and \( \text{cis-S2} \), and \( \text{trans-S2} \) and \( \text{S3} \), and well as the differences in solubility. Finally, since the \( \text{S2} \) isomers have nearly identical energy levels and solution absorbance properties, any differences in device performance will likely be due to these differences in packing structure, which will be the subject of future study.

3.4.2 Thin film properties

Thin films were prepared by spin-casting from chloroform onto glass substrates, and the surface morphology of the films before and after annealing was studied using atomic force microscopy (AFM) (Figure 5.9). During sample preparation, it was found that the most uniform films were obtained for \( \text{P} \), \( \text{S1} \), and \( \text{cis-S2} \) using an 8 mg/mL solution, and for \( \text{trans-S2} \) and \( \text{S3} \) using a 5 mg/mL solution, all heated to 50 °C. Casting from chlorobenzene resulted in poor adhesion to the substrate, even when coated with \( n \)-dodecyltrichlorosilane. \( \text{S4} \) did not form films when spin-cast from hot chloroform, chlorobenzene, 1,2-dichlorobenzene or 1,2,4-trichlorobenzene due to its low solubility. The surface morphology of the as-cast \( \text{P} \) film is consistent with previous literature reports and reveals a rough surface composed of needle-like grains (RMS = 35.9 nm). The \( \text{S1} \) film has a similar morphology with needle-like grains and a similarly rough surface (RMS = 30.1 nm). The needle-like grains are absent in the \( \text{cis-S2} \) film, which is smoother and composed of cluster-like domains (RMS = 15.1 nm). The \( \text{trans-S2} \) film has a similar morphology with a slightly smoother surface (RMS = 8.3 nm). The \( \text{S3} \) film is the smoothest of the series and composed of crystalline plates with typical dimensions of 45 × 135 nm (RMS = 5.1 nm). Upon annealing at 200 °C for 30 minutes under nitrogen, the morphologies change significantly and the features of the as-cast films are replaced by larger plate-like domains. The \( \text{P} \) film becomes much smoother (RMS = 0.8 nm) and has the smallest domains relative to the other annealed films. The annealed \( \text{S1} \), \( \text{cis-S2} \), and \( \text{trans-S2} \) films are similar and have the largest domains of the series with a surface roughness of 16.9, 15.2 and 22.4 nm, respectively. The \( \text{S3} \) film loses all of the small crystalline domains upon annealing and forms large isolated aggregates.
I was also interested in studying how annealing affects the absorption properties of the films, particularly in relation to the thermal transitions observed by DSC. All films were prepared using the same conditions, spin-casting from 5 mg/mL chloroform solutions at 2000 rpm for 60 seconds. The absorbance spectra were measured on the as-cast films and after annealing at three different temperatures: (1) below the first transition (80 °C for all), (2) between the first and second transitions (130 °C for S3; 140 °C for S1 and cis-S2; 150 °C for trans-S2), and (3) after the second transition (180 °C for all) (Figure 5.10). Interestingly, while the spectrum of the parent film remains unchanged at all annealing temperatures, the spectra of the thionated compounds change significantly. The S1 film absorbance is least affected by annealing and shows only a small fluctuation in the intensity of the lower energy peak after (an increase after 80 °C and 140 °C and a decrease after of 180 °C, relative to the intensity of the as-cast film). The cis-S2, trans-S2, and S3 peaks all shift to lower wavelength with annealing, after 140 °C, 80 °C and 180 °C, respectively. It is interesting that the absorbance is not affected by the same annealing temperature (or thermal transition) for all thionated compounds, and that there is no trend between degree of thionation and temperature of absorbance change. Since the spectral changes do not correspond to the same thermal transition across the series, they are likely not related to changes in the morphology or crystallinity of the films. The blue-shift in absorbance is likely due to decomposition of the main chromophore and thus the trend observed may be related to the thermal stability of the compounds. This is somewhat is surprising since the TGA results
suggest that all of the thionated compounds are stable up to 180 °C, and that thermal stability decreases with degree of thionation. In contrast, the absorbance spectra of the annealed films suggest that trans-S2 is the least thermally stable as its spectrum changes irreversibly after 80 °C, and that the thermal stability of S3 is higher than that of cis-S2 since the spectrum of S3 remains unchanged until 180 °C, while that of cis-S2 blue-shifts significantly after 140 °C.

Figure 5.10 Optical absorption spectra of P-S3 thin films (spin-coated from 5 mg/mL chloroform solution at 2000 rpm onto glass substrates), as-cast (black line) and after annealing for 20 minutes under nitrogen (red, black and green lines).

3.5 Self-assembly

I was also interested in studying the self-assembly properties of the thionated compounds, as perylene diimides with linear side-chains have been shown to assemble into nanobelts or nanoribbons using solution-based techniques. Examples of micro/nanowires using bulkier groups such as perfluorophenyl or spirobifluorene have also been reported, however branched alkyl chains can only assemble into zero-dimensional nanospheres. These types of one-dimensional structure form as a result of strong π-π interactions between the planar aromatic cores, which facilitate face-to-face packing and anisotropic growth. Nanowires of oligothiophene-functionalized naphthalene diimides have been used as acceptor materials in all-
nanowire BHJ solar cells using P3HT nanowires as the donor.$^{33}$ However, to the best of my knowledge, this is the first report of small molecule core-unfunctionalized NDI micro/nanowires.

The 1D solution based self-assembly of P-S4 was performed using the so-called phase transfer method.$^{18}$ Briefly, a larger amount (10:1 v/v) of methanol (poor solvent) was slowly transferred atop a chloroform (good solvent) solution (0.3 mM) of NDI in a test tube and left undisturbed overnight. Self-assembly occurs at the interface due to the slow mixing of the solvents and decreased solubility of the materials in the mixed solvent phase. Crystals of trans-S2, S3 and S4 begin to form instantaneously, while those of cis-S2 form within minutes, and those of P and S1 over several hours. This is likely due to the solubility of the various compounds, such that a decreased solubility results in an increased rate of crystallization. The crystals were then removed via pipette and drop-cast onto glass substrates and the solvent was evaporated in air.

Optical micrographs reveal the formation of long fiber-like structures, which upon magnification appear to be one-dimensional microbelts (Figure 5.11). Although all six compounds do self-assemble into these 1D structures, their dimensions and uniformity do seem to change with degree of thionation. There appear to be three main types of structures which can be classified as (1) microbelts, (2) crystalline microbelts and (3) dendrites. The crystalline microbelts are the widest structures and are the exclusive structure formed by the non-thionated P compound (widths 20-80 µm). Crystalline microbelts with slightly narrower, more monodisperse widths are formed by cis-S2 (15-55 µm), and even narrower ones are formed by S3 and S4 (~20 µm). A small number of the crystalline microbelts are formed by S1 with widths of 50-80 nm. Interestingly, these wider structures are completely absent in trans-S2, which forms thinner microbelts exclusively (~1.5 µm). The width of these microbelts is similar to those formed by cis-S2 and S4, and slightly thinner than those formed by S3 (~7.5 µm). The width of both types of S3 and S4 structure can be increased by decreasing the concentration of the chloroform solution, however no significant change with concentration is observed for the other compounds. This suggests that the dimensions can be controlled by the rate of self-assembly, since decreasing the concentration of the initial solution effectively decreases the rate of crystallization. The dendritic structures are formed exclusively by S1 and appear as several microbelt “arms” growing from a single microbelt structure, all with similar widths. Although it is very difficult to visualize the entire length of an isolated structure, the average length appears to be several
hundred micrometers for all three classes of structure, leading to aspect ratios (length/width) between 10:1 and 100:1.

Figure 5.11 Optical micrographs of self-assembled P-S4 structures at 5x magnification.

The self-assembled structures were investigated under higher magnification using AFM and SEM to confirm their belt-like structure (Figures 5.12 and 5.13, respectively). Both methods confirm the average widths of the cis-S2 and trans-S2 microbelt structures to be around 1.4 µm while AFM reveals their thickness to be around 0.4 µm, leading to an aspect ratio of the belt cross-section (width/thickness) of 3.5. The S3 belts are wider (average width 7.3 µm) and thicker (average height 1.3 µm) with an aspect ratio of 5.6. The S4 structures have the smallest widths (1.2 µm) and heights (0.4 µm). In some areas, the structures appear twisted with the edge lifted up, allowing further confirmation of the belt-like morphology. The larger crystalline structures were too large to be imaged by AFM, however SEM of the P compound reveals large microbelt structures.
Figure 5.12 AFM images of self-assembled S1-S4 structures.

Figure 5.13 SEM images of self-assembled P-S4 structures.

To investigate the crystallinity of these structures, powder X-ray diffraction (PXRD) was conducted on the self-assembled materials. Samples were prepared by gently scraping material...
off the glass substrates used for optical microscopy and onto a SiO\textsubscript{2} wafer for PXRD analysis. A strong peak was observed around 3-4° corresponding to a side-chain interdigitation distance of 23 to 35 Å for the various compounds (Figure 5.14). Additional unidentified peaks are present in the \textit{cis-S2}, \textit{trans-S2}, S3, and S4 patterns, suggesting they may be more highly crystalline than the singly thionated and non-thionated compounds. Unfortunately no \(\pi-\pi\) stacking peak was observed for any of the compounds, however the distances are expected to be similar to those measured for the single crystals.

![PXRD plots](image)

**Figure 5.14** PXRD of self-assembled P-S4 structures on a SiO\textsubscript{2} wafer.

## 4 Conclusions

A series of five thionated naphthalene diimide derivatives were synthesized in a single-step reaction from the parent NDI derivative and their optoelectronic and self-assembly properties were studied. The absorption spectra in both solution and solid-state were found to red-shift with increasing degree of thionation due to a lowering of the LUMO and raising of the HOMO energies, as measured by cyclic voltammetry. Interestingly, the shape of the absorption spectra of the thionated compounds differ significantly from the non-thionated parent compound, in contrast to the analogous series of thionated perylene diimides which retain the same spectral shape. Differential scanning calorimetry reveals that the compounds are liquid crystalline, but that their thermal transitions are distinct, suggesting unique intermolecular interactions in each
compound. Thermogravimetric analysis reveals that all compounds are thermally stable up to 250 °C, and although thermal stability does decrease slightly with thionation, the compounds are stable to both air and light and can be stored under ambient conditions for several months. Single crystal x-ray diffraction reveals strong similarities in the packing motifs of the non-thionated parent compound and the doubly thionated cis isomer, and of the doubly thionated trans isomer and the triply thionated derivative. The stark difference in the packing of the two doubly thionated isomers which otherwise have identical energetics makes this system ideal for directly studying the effect of solid-state packing on charge transport and organic field effect transistor performance, without the complication of additional variables such as differences in structure or electronics.

Solubility of the compounds decreases with thionation, which results in poor film formation for the higher thionated derivatives. This decreased solubility is likely due to strong S-S intermolecular interactions which suggests that these compounds may demonstrate improved charge transport. Fortunately, the decreased solubility in addition to the linear side-chain, facilitates the solution based self-assembly of the compounds into microstructures. Three main types of structures (microbelt, crystalline microbelt and dendrite) are observed, and vary in dimension and abundance throughout the series. These materials are therefore potential candidates as n-type materials for microwire transistors. Furthermore, the low LUMO levels of the higher thionated derivatives, as well as their more compact solid-state packing, may result in ambient stable devices, which is an essential requirement for the scalability of these systems.

5 Experimental

5.1 General considerations

All reagents were used as received unless otherwise noted. 1,4,5,8-Naphthalenetetracarboxylic dianhydride, n-dodecylamine, and Lawesson’s reagent were purchased from Sigma-Aldrich. Lawesson’s reagent was recrystallized from boiling toluene (10 g per 100 mL) prior to use.

5.2 Instrumentation and methods

$^1$H NMR spectra of the monomers were recorded on a Varian Mercury 400 spectrometer operating at 400 MHz. Chemical shifts are reported in ppm at ambient temperature. $^1$H NMR chemical shifts are referenced to the residual protonated chloroform peak at 7.26 ppm.
Absorption spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer. The thin-films used for absorbance spectroscopy were spin-coated from solutions in chloroform (7 mg/mL) at 2500 rpm for 30 seconds onto glass substrates that had been washed with methanol. Electrochemistry was performed with a BASi Epsilon potentiostat. A standard three-electrode cell with a 2.0 mm diameter Pt button working electrode, a Ag/Ag⁺ reference electrode, and a Pt wire counter electrode was used, with a ferrocene internal standard and a 100 mV/s scan rate. Measurements were conducted in a nitrogen-filled glovebox in dry dichloromethane solution against ferrocene/ferrocenium (Fc/Fc⁺) in the presence of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) electrolyte. LUMO levels were estimated from cyclic voltammetry reduction onset potentials and converted to the vacuum scale using the equation

$$E_{LUMO} = -e(E_{red} + 4.8),$$

referenced to the ferrocene/ferrocenium redox couple.²⁵ HOMO levels were estimated by adding the E_LUMO to the solution state optical bandgap. TGA was performed using an SDT Q600 instrument at heating rate of 10 °C/min under nitrogen in an aluminum pan. DSC was performed on a DSC Q100 TA instrument at heating rate of 10 °C/min under nitrogen in an aluminum hermetic pan.

Microstructures were assembled through slow crystallization at the interface between chloroform (good solvent) and methanol (poor solvent). Briefly, methanol was slowly transferred atop a 0.3 mM chloroform solution of Sₓ-DD-NDI (10:1 v/v methanol:chloroform) in a test tube. The mixture was left undisturbed until crystal formation was complete (solution became colorless). The crystals were transferred via pipette onto a glass slide for further analysis.

5.3 Density functional theory calculations

Geometry optimizations were performed for the eight unit homopolymers and sixteen unit block copolymer using the Gaussian 09 program,³⁴ employing the Becke Three Parameter Hybrid Functionals Lee-Yang-Parr (B3LYP) level of theory.³⁵,³⁶ The standard 6-31G(d) basis set was used.

5.4 Synthesis

\(N,N'-\text{di}(n\text{-dodecyl})\text{naphthalene-4,5,8,9-tetracarboxylic acid diimide (P).}\) Naphthalene-4,5,8,9-tetracarboxylic dianhydride (4.21 g, 15.7 mmol) and \(n\text{-dodecylamine (11.6 g, 62.6 mmol)}\) were added to anhydrous DMF (200 mL) in a round bottom flask with attached condenser under
argon. The mixture was stirred at 140 °C for 23 h. After reaction, the solution was cooled to room temperature and then in the fridge for 30 min. The crude product was filtered and washed with cold methanol to yield a pale brown solid (7.8 g, 83%). The product was used without further purification. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.76 (s, 4H), 4.22-4.17 (m, 4H), 1.79-1.69 (m, 4H) 1.38, 1.47-1.25 (m, 36H), 0.90-0.85 (t, 6H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.8, 130.9, 126.7, 126.6, 41.0, 31.9, 29.6, 29.6, 29.5, 29.3, 28.1, 27.1, 22.7, 14.09. HRMS (DART) \(^+\) \(m/z\) 603.41343 (C\(_{38}\)H\(_{54}\)N\(_2\)O\(_4\)) [M+1] \(^+\) requires 603.41618).

**S1.** N,N'-bis(n-dodecyl)naphthalene-4,5,8,9-tetracarboxylic acid diimide (1.01 g, 1.68 mmol) and Lawesson’s reagent (0.51 g, 1.26 mmol) were added to anhydrous toluene (166 mL) in a 3-neck round bottom flask with an attached condenser under argon. The mixture was stirred at 140 °C for 17 h. The resulting solution was cooled to room temperature and concentrated under reduced pressure to give a dark brown solid. The solid was purified by column chromatography (chloroform) to yield the product as a dark yellow powder (430 mg, 41%). Trace amounts of cis-S\(_2\), trans-S\(_2\), and S\(_3\) were also formed but not isolated. \(^1\)H NMR (399 MHz, CDCl\(_3\)) \(\delta\) 9.07 (d, 1H), 8.74 (q, 2H), 8.64 (d, 1H), 4.73-4.69 (m, 2H), 4.20-4.16 (m, 2H), 1.85-1.70 (m, 4H), 1.48-1.25 (m, 36H), 0.90-0.86 (m, 6H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 192.8, 163.0, 160.1, 135.7, 131.3, 130.8, 130.4, 130.1, 126.7, 126.3, 125.3, 125.0, 47.7, 41.0, 31.9, 29.6, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 28.1, 27.1, 27.0, 26.6, 22.7, 14.1. HRMS (DART) \(^+\) \(m/z\) 619.39304 (C\(_{38}\)H\(_{54}\)N\(_2\)O\(_3\)S\(_1\)) [M+1] \(^+\) requires 619.39334).

cis-S\(_2\), trans-S\(_2\), S\(_3\), and S\(_4\) . N,N'-bis(n-dodecyl)naphthalene-4,5,8,9-tetracarboxylic acid diimide (3.0 g, 4.98 mmol) and Lawesson’s reagent (6.05 g, 15.0 mmol) were added to anhydrous toluene (500 mL) in a 3-neck round bottom flask with an attached condenser under argon. The mixture was stirred at 140 °C for 48 h. The resulting solution was cooled to room temperature and concentrated under reduced pressure to give a dark red-brown sticky solid. The solid was then precipitated into methanol (300 mL) and filtered to remove excess Lawesson’s reagent and Lawesson’s reagent byproducts. The resultant dark purple powder was washed with methanol and purified by column chromatography (chloroform) to yield the products.

cis-S\(_2\). \(^1\)H NMR (399 MHz, CDCl\(_3\)) \(\delta\) 8.94 (s, 2H), 8.72 (s, 2H), 4.71-4.67 (m, 2H), 1.84-1.76 (m, 4H), 1.48-1.26 (m, 36H), 0.90-0.86 (t, 6H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 192.8, 160.7,
trans-S2. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.07 (d, 2H), 8.64 (d, 2H), 4.73-4.67 (m, 4H), 1.86-1.75 (m, 4H), 1.47-1.26 (m, 36H), 0.90-0.86 (t, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) Failed due to limited solubility. HRMS (DART)$^+ m/z$ 635.37049 (C$_{38}$H$_{54}$N$_2$O$_2$S$_2$ [M+1]$^+$ requires 635.37049).

S3. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.94 (dd, 2H), 8.83 (d, 1H), 8.60 (d, 1H), 5.28-5.23 (m, 4H), 4.71-4.66 (m, 2H), 1.92-1.75 (m, 4H), 1.44-1.26 (m, 36H), 0.90-0.86 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) Failed due to limited solubility. HRMS (DART)$^+ m/z$ 651.34618 (C$_{38}$H$_{54}$N$_2$O$_1$S$_3$ [M+1]$^+$ requires 651.34765).

S4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.81 (s, 4H), 5.28-5.25 (m, 4H), 1.93-1.87 (m, 4H), 1.46-1.29 (m, 36H), 0.91-0.88 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) Failed due to limited solubility. HRMS (DART)$^+ m/z$ 667.32640 (C$_{38}$H$_{54}$N$_2$S$_4$ [M+1]$^+$ requires 667.324810.

6 References


Chapter 6  
Summary and Outlook

1  Conclusions and future work

The work outlined in this thesis highlights how materials design and synthesis can be used to tailor optoelectronic properties and affect device properties in a (somewhat) predictable way. Starting with the well-known P3HT donor polymer, I investigated how the introduction of a structurally similar monomer possessing a lower HOMO level into a copolymer structure would affect the $V_{oc}$ of polymer:fullerene solar cells. It was demonstrated that both block and statistical copolymers containing 3-thiohexylthiophene (3THT) and 3-hexylthiophene (3HT) units could be synthesized via Kumada catalyst coupling to give polymers with narrow dispersities and desired molecular weights. The equally proportioned block copolymer synthesized in chapter 2 was head-to-tail regioregular in the P3HT block and regiorandom in the P3THT, due to a lack of catalyst selectivity for the less sterically bulky 3THT monomer. The analogous statistical copolymer synthesized in chapter 3 had a higher degree of regioregularity due to catalyst selectivity for head-to-tail couplings between 3-thiohexylthiophene and 3-hexylthiophene units, which are not present in the block structure. When used as a donor material, the block copolymer device had a $V_{oc}$ that was as high as the $V_{oc}$ of the control device composed of the 3-thiohexylthiophene homopolymer with the deepest HOMO level. This was the first example of an equally proportioned ternary device where the measured $V_{oc}$ was as high as the upper limit $V_{oc}$ of the corresponding binary device. When testing the analogous statistical copolymers as donor materials with the same PC$_{71}$BM acceptor, it was found that the upper limit $V_{oc}$ could be maintained for devices containing as low as 15% of the 3-thiohexylthiophene unit. Furthermore, the $V_{oc}$ of devices containing as low as 1% 3-thiohexylthiophene remained higher than that of the binary P3HT:PC$_{71}$BM device, suggesting that only a single 3-thiohexylthiophene unit in a 100 unit copolymer is required to affect the voltage of the device. This result highlights the significant impact that side-chain engineering can have on polymer solar cell device properties and how the $V_{oc}$ can be optimized through minimal incorporation of a low HOMO unit without compromising the $J_{sc}$ of the device.

There is a great deal of interest in the Seferos group in the synthesis of polymers of other group 16 heterocyles including furan, selenophene, and tellurophene; however thus far, the majority of
these heterocycles have been limited to those having alkyl chains at the 3-position. It would be interesting to study the effect of thioalkyl substitution on these alternative heterocycles to determine if it has the same effect on the optoelectronic and device properties as in the thiophene system. Over the course of my PhD, I attempted to synthesize both furan and selenophene versions of the 3-thioalkylthiophene monomer, and found that the syntheses were significantly more challenging with these more exotic heterocycles. An alternative approach, which would be more aligned with the goal of using simple chemical modifications to enhance the eventual commercial feasibility of these organic electronic materials, would be to incorporate the easily synthesized 3-thioalkylthiophene monomer into copolymers (block or statistical) of the various 3-alkyl heterocycles, and determine if the incorporation of the low HOMO monomer has the same effect on these copolymers as in the thiophene systems presented in Chapter 2 and 3.

Following the publication of my P3HT-P3THT copolymer work, a number of groups investigated the effect of thioalkyl side chains in donor-acceptor copolymers, and observed a similar effect of a lowering of the HOMO level and increase in $V_{oc}$. In many of these systems, the increase in $V_{oc}$ resulted in an increase in the overall efficiency, which was not observed in the P3HT-P3THT system, with PCE values of the thioalkyl containing polymers reaching over 9%. The major disadvantage of this type of modification in D-A copolymers is that in order to test its applicability in a wide range of polymers, a wide range of new monomers would need to be synthesized, the synthesis of many of which would not be trivial. An alternative approach would be to incorporate the 3-thioalkylthiophene unit into semi-random D-A acceptor polymers, which should result in same effect of lowering the HOMO and raising the $V_{oc}$, but would be a much easier approach than synthesizing a new monomer for every new donor and acceptor combination.

In the third chapter of the thesis, I studied the effect of monomer composition on the device properties of an n-type one donor-two acceptor random terpolymer. I was able to synthesize a series of five copolymers containing naphthalene diimide (NDI), perylene diimide (PDI) and carbazole units via Suzuki coupling from monomers that were either commercially available or easily synthesized in high yields in two steps, which is a significantly more facile route than many of the popular D-A copolymers in the literature. Although I initially hypothesized that the properties of the copolymers would be dependent on monomer composition, it was found that that while the optical properties varied with acceptor composition, the composition dependence
was not evident in device performance. Surprisingly, the device properties solely depended on the presence (or absence) of the NDI unit. I hypothesized that this may be due to the presence of a competing pathway to charge separation associated with NDI-carbazole dimer unit. Perhaps inspired by this study, Jenekhe and coworkers recently reported the second example of a one donor-two acceptor random terpolymer containing NDI and PDI acceptor units, substituting a selenophene for the carbazole donor unit. They measured a record device efficiency of 6.3% for the 30:70 PDI:NDI copolymer using an extended π-conjugated PBDTTT-CT donor, which was the highest efficiency for an all-polymer solar cell at the time of writing. They found that the polymer crystallinity was composition dependent and that the bulk crystallinity had a significant effect on donor acceptor compatibility and on the overall performance of the device. This result demonstrates that my method of incorporating two acceptor units into the polymer backbone can, in fact, result in composition dependent device properties and suggests that the (D-A₁)-(D-A₂) random terpolymer architecture is extremely promising for the design of new, high-efficiency n-type (or p-type) materials. Further work in this area includes the screening of other donor units in the PDI:NDI two acceptor system, which should be relatively facile due to the straightforward synthetic route described previously.

In the final study of the thesis, I described the effect of the single-atom substitution of oxygen with sulfur in small molecule naphthalene diimides. It was found that thionation results in a decrease in LUMO level and increase in intermolecular interactions, likely due to strong S-S contacts. Due to their linear alkyl chains, the compounds showed liquid crystalline behavior and could be self-assembled into crystalline microbelt structures via a solution-based phase transfer method. Future work on the thionated NDIs includes mobility measurements and fabrication of both thin film and microwire transistors in collaboration with Prof. Yuning Li at the University of Waterloo. Recent work in the Seferos group has shown that the electron mobility and transistor performance of thionated PDIs increase with increasing degree of thionation and I expect to see a similar trend with the NDIs.

The effect of thionation on the optoelectronic and solid-state properties of the NDIs described in chapter 5, as well as on thionated PDIs studied by Andrew Tilley in my group, is remarkable, however there remain few other examples of this type of chemistry in the organic electronic literature. I believe that this single-atom substitution can be used on many current carbonyl-containing materials of interest to organic electronic applications to improve their absorbance
properties, as well as charge carrier mobilities. Thionation chemistry is attractive because it can be done in a single step on both polymers and small molecules, which eliminates much of the tedious synthesis currently required in the design of new materials. Furthermore, the degree of thionation can be controlled through reaction time and stoichiometry, allowing for the synthesis of materials with a range of different sulfur compositions, which may give rise to different properties and device performances. I recently designed a project for an undergraduate student in my group, Ellen Yan, to study the effect of thionation on the popular p-type copolymer, PBTTPD (Figure 6.1). The polymer was synthesized through post-polymerization thionation using Davy’s reagent to yield the fully thionated polymer as confirmed by $^1$H NMR, IR, and MALDI. Surprisingly, she found that the bandgap of the thionated polymer was actually wider than that of the parent polymer, in both solution and solid-state. DFT calculations revealed that the increased bandgap was due to a decrease in $\pi$-conjugation resulting from a twisting of the polymer backbone due to the loss of S-O contacts between the sulfur of the thiophene ring and oxygen of the TPD unit. I hypothesize that the backbone planarity can be recovered through the substitution of the bithiophene unit with a bifuran to give the previously unpublished polymer, PBFTPD, which upon thionation will re-establish S-O contacts, now between the oxygen of the furan ring and sulfur of the TPD unit. DFT calculations suggest that this copolymer does have a more planar backbone and narrower bandgap than the non-thionated parent polymer, and thus is expected to have a red-shifted absorbance. It would also be interesting to study the effect of the partial thionation of PBTTPD to determine at what the percent thionation the backbone twisting could be overcome, while still maintaining a red-shifted absorbance spectrum.

![Figure 6.1 Synthesis of S-PBTTPD and S-PBFTPD.](image)

Thionation is also a promising method for narrowing the bandgap of existing arylene diimide based polymers and small molecules currently being used as non-fullerene acceptor materials. Through Ellen’s project described above, it was found that the thionyl group likely poisons the
Pd catalyst and thus thionation must be performed after any Pd-catalyzed coupling step. Post-coupling thionation of arylene diimide containing materials could theoretically be achieved using Lawesson’s or Davy’s reagent, and sulfur incorporation could be controlled through reaction time and stoichiometry.

In conclusion, I must emphasize that regardless of the system of study, there is always a significant relationship between material structure, properties, and device performance. In such an interdisciplinary field as organic electronics, this means there must be constant communication and understanding between the synthetic chemists and device engineers in order to design the right material and use the right processing conditions to maximize device performance. It is very likely that the ideal organic solar cell material has already been designed, and is waiting to be tested under the right conditions. A key consideration, however, is that in order for the ideal material to be commercialized and have widespread usage, it needs to be easily and inexpensively synthesized. Throughout this thesis I have emphasized that large changes in material properties can be achieved using small chemical modifications, such as changing copolymer sequence from diblock to statistical, varying monomer composition in the block, statistical or donor-acceptor copolymer backbone, or by simple single-atom substitution in polymer side-chain (eg. alkyl to thioalkyl) or functional group (eg. carbonyl to thionyl). I hope that these findings have led to further understanding of the effect of these modifications on materials properties and device performance, and that they inspire future work in the design of new materials for all types of applications.

2 References
(7) Tilley, A. J.; Guo, C.; Miltenburg, M. B.; Schon, T. B.; Yan, H.; Li, Y.; Seferos, D. S.
Appendices
NMR Spectra

Figure A.1 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of poly(3-thiohexylthiophene).
Figure A.2 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of poly(3-thiohexylthiophene)-b-(3-hexylthiophene).
Figure A.3 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 99:1 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).
Figure A.4 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 97:3 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).
Figure A.5 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 85:15 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).
Figure A.6 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 80:20 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).
Figure A.7 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 67:33 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).
Figure A.8 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 50:50 poly(3-hexylthiophene)-s-(3-thiohexylthiophene).
Figure A.9 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of $N,N'$-di(2-ethylhexyl)-1,6/7-dibromo-3,4,9,10-perylene diimide.
Figure A.10 \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\)) of \(N,N'\)-di(2-ethylhexyl)-2,6-dibromo-1,4,5,8-naphthalene diimide.
Figure A.11 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-PDI100.
Figure A.12 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-PDI75-NDI25.
Figure A.13 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-PDI50-NDI50.
Figure A.14 \textsuperscript{1}H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-\textit{d\textsubscript{2}}, 120 °C) of PC-PDI25-NDI75.
Figure A.15 $^1$H NMR spectrum (600 MHz, 1,1,2,2-tetrachloroethane-d$_2$, 120 °C) of PC-NDI100.
Figure A.16 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of P.
Figure A.17 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of P.
Figure A.18 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of S1.
Figure A.19 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of S1.
Figure A.20 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of cis-S2.
Figure A.21 gCOSY spectrum (400 MHz, CDCl₃) of cis-S₂.
Figure A.22 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of cis-S2.
Figure A.23 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of *trans*-S2.
Figure A.24 gCOSY spectrum (400 MHz, CDCl₃) of trans-S².
Figure A.25 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of S3.
Figure A.26 $^1$H NMR spectrum (500 MHz, CDCl$_3$, 40 °C) of S4.