LOW BAND-GAP DONOR POLYMERS FOR ORGANIC SOLAR CELLS

A dissertation submitted for the degree of Doctor of Philosophy
by
Kok Haw Ong

Department of Chemistry, Imperial College London
and
Institute of Materials Research and Engineering, Singapore

October 2010
Acknowledgements

Doing a PhD is no easy endeavour, and I would like to take this opportunity to thank all the people who have helped me along this journey.

First and foremost, I would like to thank my supervisors, Dr. John de Mello and Dr. Chen Zhikuan for their invaluable help. Without their guidance, encouragement, and insights, it would not have been possible to complete this thesis.

I would also like to thank all those with whom I have worked in IMRE. To all the members and alumni of Lab 9 (#04-31), thank you for your friendship, technical assistance, and useful discussions. Special thanks go out to Dr. Jun Li and Dr. Zhun Ma, from whom I have learnt a lot about polymer synthesis, and those who have made devices using the materials that I have synthesised (Ging Meng, Siew Lay, Ivy, Phoebe and Lionel).

Thanks also to those at Imperial who have helped me during my attachment periods – especially Siva, Andrea, Rick and Mikael – and to everyone at the basement office.

Funding is an essential part of every PhD, and I am blessed to have received funding support from A*Star. I would also like to thank all at A*Star Graduate Academy, especially the scholarship officers in charge of the AIP programme, and their counterparts at Imperial, Jen Martin, Christine Doran and Helen Challis.

Much appreciation goes out to my family for their support during the past 4 years, especially for my mum, who always made sure that my food was warm even when I returned home late from the laboratory.

Last but not least, I would like to thank my fiancée Yang Choo, who has been beside me for much of this journey. Thank you for your constant encouragement and companionship. I love you!
Except where specific reference is made, the material contained in this thesis is the result of my own work. This dissertation has not been submitted in whole or in part for the reward of a degree at this or any other university.

Kok Haw Ong, October 2010
Abstract

One of the key challenges of organic solar cells is their relatively low power conversion efficiency. One way to improve the efficiency of these cells is to develop donor materials with improved photon harvesting capabilities, well-located highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy levels, good hole transport characteristics and good processability.

In this thesis, the design, synthesis and characterization of fifteen low band gap donor-acceptor type polymers are described. Two different acceptor moieties, 3,6-bis(thien-2-yl)-2,5-di-N-alkylpyrrolo[3,4-c]pyrrole-1,4-dione (DPP) and 2,1,3-benzothiadiazole (BT) were used in our polymer designs and the polymers were synthesised using the palladium-catalysed Stille cross-coupling method.

The first series of polymers were random co-polymers of DPP and dithienothiophene. By tuning the solubility and absorption characteristics of the polymers, we achieved a polymer that gave power conversion efficiencies of up to 4.85 % when applied in solar cells. Low open-circuit voltages were obtained for these cells, hence the next series of polymers was designed with the aim of improving the open-circuit voltages. Although the lower HOMO levels of these polymers resulted in higher open-circuit voltages when applied in solar cells, the low hole mobility of the polymers and poor morphology of the polymer:fullerene films resulted in low solar cell power conversion efficiencies.

Finally, a series of benzothiadiazole-oligothiophene polymers were synthesised. These polymers had high hole mobilities and wide absorption spectra. When these polymers were applied in organic thin-film transistors, good hole mobilities of up to 0.20 cm²/Vs were achieved, and when applied in solar cells, power conversion efficiencies of up to 6.2 % were achieved. These results show that benzothiadiazole-oligothiophene systems are promising candidates for both transistor and solar cell applications.
# Table of Contents

ACKNOWLEDGEMENTS ................................................................................................................. 1
ABSTRACT ........................................................................................................................................ 3
TABLE OF CONTENTS ................................................................................................................... 4
LIST OF FIGURES .......................................................................................................................... 7
LIST OF TABLES ............................................................................................................................. 13
LIST OF REACTION SCHEMES ...................................................................................................... 14
PUBLICATIONS .............................................................................................................................. 15

## CHAPTER 1: INTRODUCTION ........................................................................................................ 16

1.1 Motivation .................................................................................................................................. 16
1.2 Objectives and Outline ............................................................................................................... 17

## CHAPTER 2: LITERATURE REVIEW .............................................................................................. 19

2.1 Organic Semiconductors and Solar Cells .................................................................................... 19
   2.1.1 An Introduction to Organic Semiconductors ....................................................................... 19
   2.1.2 Device Structures For Polymer Solar Cells ........................................................................ 20
   2.1.3 Processes And Loss Mechanisms In Organic Solar Cells..................................................... 22
2.2 Design Considerations For Polymeric Donor Materials ............................................................... 25
   2.2.1 Absorption Properties ....................................................................................................... 26
   2.2.2 Charge Transport ............................................................................................................... 27
   2.2.3 Energy Level Control ........................................................................................................ 27
   2.2.4 Solubility and Processability ............................................................................................. 27
   2.2.5 Thermal and Photo Stability ............................................................................................. 28
2.3 Principles Of Band-gap Tuning ................................................................................................... 28
   2.3.1 Bond Length Alternation (BLA) ....................................................................................... 28
   2.3.2 Planarity ............................................................................................................................ 30
   2.3.3 Inter-molecular interactions ............................................................................................... 31
2.4 Low Band-gap Polymers in Organic Solar Cells ......................................................................... 32
   2.4.1 Copolymers based on 2,1,3-benzothiadiazole ..................................................................... 32
   2.4.2 Copolymers based on Dithienyldiketopyrrolopyrole ......................................................... 36
   2.4.3 Polymers based on oligothiophene and its derivatives ...................................................... 38
   2.4.4 Polymers based on bridged thiophene units ....................................................................... 41
2.5 Experimental Methods ............................................................................................................... 43
   2.5.1 Synthesis ............................................................................................................................ 43
   2.5.2 Characterisation of precursors .......................................................................................... 44
   2.5.3 Polymer Characterisation .................................................................................................. 45
   2.5.4 Device Fabrication and Characterisation ........................................................................... 48
CHAPTER 3: LOW BAND-GAP DITHIENOTHIOPHENE-DIKETOPYRROLOPYRROLE POLYMERS: ABSORPTION AND SOLUBILITY TUNING........................................52

3.1 INTRODUCTION..................................................................................52

3.2 POLYMER DESIGN AND SYNTHESIS..................................................53
   3.2.1 Polymer Design.............................................................................53
   3.2.2 Monomer Synthesis.................................................................54
   3.2.3 Polymer Synthesis.......................................................................56

3.3 POLYMER CHARACTERISATION............................................................57
   3.3.1 Absorption properties...............................................................57
   3.3.2 Thermal Characterisation..........................................................59
   3.3.3 Electrochemical characterisation..............................................60

3.4 OPV CHARACTERISATION..................................................................61
   3.4.1 Comparing the performances of copolymers with different m:n ratios ...........................................61
   3.4.2 Comparing the performances of copolymers with different alkyl substituents .......................64

3.5 TFT CHARACTERISATION.................................................................67

3.6 CONCLUSION......................................................................................67

3.7 EXPERIMENTAL SECTION..................................................................68

CHAPTER 4: ENERGY LEVEL TUNING FOR DPP-BASED POLYMERS ..........79

4.1 INTRODUCTION..................................................................................79

4.2 POLYMER DESIGN AND SYNTHESIS..................................................79

4.3 POLYMER CHARACTERISATION............................................................81
   4.3.1 Optical Characterisation..........................................................81
   4.3.2 Thermal Characterisation.........................................................82
   4.3.3 Electrochemical Characterisation............................................82

4.4 OPV CHARACTERISATION..................................................................83

4.5 TFT CHARACTERISATION.................................................................87

4.6 CONCLUSION......................................................................................89

4.7 EXPERIMENTAL SECTION..................................................................89

CHAPTER 5: HIGH MOBILITY, LOW BAND-GAP POLYTHIOPHENE POLYMERS ....94

5.1 INTRODUCTION..................................................................................94

5.2 POLYMER DESIGN AND SYNTHESIS..................................................95
   5.2.1 Polymer Design.............................................................................95
   5.2.2 Monomer Synthesis.................................................................98
   5.2.3 Polymer Synthesis.......................................................................100

5.3 POLYMER CHARACTERISATION............................................................101
   5.3.1 Optical Characterisation..........................................................101
   5.3.2 Electrochemical characterisation............................................102
   5.3.3 Thermal Characterisation.........................................................104

5.4 TFT CHARACTERISATION..................................................................106
5.5 OPV CHARACTERISATION............................................................................................................. 110
  5.5.1 General device characterisation................................................................................................. 110
  5.5.2 Solvent Annealing and Solvent Vapour Annealing for POD2T-DTBT:PC71BM Cells ...... 115
  5.5.3 Effect of cathode material on POD2T-DTBT:PC71BM cells .................................................. 118
5.6 CONCLUSIONS.............................................................................................................................. 119
5.7 EXPERIMENTAL SECTION............................................................................................................ 120

CHAPTER 6: CONCLUSIONS AND FUTURE WORK.................................................................................. 130
6.1 CONCLUSIONS................................................................................................................................. 130
6.2 FUTURE WORK................................................................................................................................. 131
REFERENCES........................................................................................................................................ 133
APPENDIX............................................................................................................................................. 141
MONOMERS FROM CHAPTER 3 ............................................................................................................. 141
MONOMERS FROM CHAPTER 5 ............................................................................................................. 143
List of Figures

Figure 2-1 ...........................................................................................................................................19
A π-bond formed by the overlap of 2 p_z orbitals in ethylene. The solid line between the 2 carbons represents the σ-bond.

Figure 2-2 ...........................................................................................................................................20
Development of the band structure of polythiophene from the monomer to the tetramer.

Figure 2-3 ...........................................................................................................................................21
Schematic 3-dimensional representation of a bulk heterojunction with top and back electrodes.

Figure 2-4 ...........................................................................................................................................22
Energy diagram of an organic solar cell with a donor-acceptor interface. The photocurrent generation processes are explained below.

Figure 2-5 ...........................................................................................................................................23
Energy level diagram showing the losses due to (1) the inability to absorb photons with energies smaller than the band-gap and (2) hot carrier thermalisation. E_c and E_v represent the conduction and valence band, respectively, E_g represents the band-gap, and V_h and V_e are the potential of the photogenerated holes and electrons, respectively.

Figure 2-6 ...........................................................................................................................................26
Absorbance spectra of P3HT:PC_{71}BM and low band-gap (LBG) polymer POD2T-DTBT:PC_{71}BM films with the AM 1.5G spectrum as a reference.

Figure 2-7 ...........................................................................................................................................29
a) The aromatic and quinoidal forms of polythiophene, b) potential energy diagram of polymers containing aromatic units, showing the non-equivalency of the aromatic (A) and quinoid (Q) forms, c) evolution of the band-gap with increasing quinoidal character.

Figure 2-8 ...........................................................................................................................................30
Band-gap reduction through the hybridisation of donor and acceptor energy levels. D and A represent the donor and acceptor, respectively.

Figure 2-9 ...........................................................................................................................................31
Rigidification of the bithiophene structure (a) with carbon and sulphur leading to cyclopentadithiophene (b) and dithienothiophene (c), respectively. The “rigidification points” are highlighted in red.

Figure 2-10 .......................................................................................................................................31
Absorbance of a polymer PDTT-ODDTBT (further described in Chapter 5) showing the red-shift of the film spectra compared to the solution, indicating a reduction in the band-gap in the solid-state.

Figure 2-11 .......................................................................................................................................32
The structures of (a) 2,1,3-benzothiadiazole (BT) and (b) 4,7-di(thien-2-yl)-2,1,3-benzothiadiazole (DTBT)
Structures of benzothiadiazole-based copolymers P1 – P10

The 3,6-bis(thien2-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (dithienyl DPP) moiety. The 2,5 positions are functionalised with alkyl groups (R) to increase the solubility of the polymers.

Structures of some DPP polymers in the literature.

Structures of some polythiophene derivatives with high hole mobilities

Structures of benzothiadiazole-oligothiophene polymers P21 to P31.

Structures of cyclopentadithiophene and dithienothiophene polymers P32 to P40.

UV-Vis spectra for Copolymers 1-3. a) solution spectra in chlorobenzene, b) thin film spectra.

TGA scans of Copolymers 1 to 6. The samples were heated at 10 °C/min from room temperature to 800 °C and the weight losses were recorded. The 5 % weight loss temperature was taken to be the sample’s decomposition temperature.

DSC scans of a) Copolymer 5 and b) Copolymer 6 showing their melting and recrystallisation peaks. The samples were heated from room temperature to 300 °C and back to room temperature at a ramp rate of 10 °C/min.

Cyclic voltammograms of thin films of Copolymers 1 to 6. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocenium couple was used as an internal reference and the oxidation onsets were used to calculate the HOMO values of the polymers.

Current-voltage characteristics of PDPP-T-DTT:PC61BM solar cells. Polymer:PCBM ratios of 1:1, 1:2, 1:4 and 1:5 were tested. The device structure was ITO/PEDOT:PSS/Polymer:PCBM blend/Ca/Ag and the device active area was 0.09 cm².

Current-Voltage characteristics of solar cells made from 1:2 blends of Copolymers 2 (R = dodecyl), 4 (R = 2-ethylhexyl), 5 (R = 2-butyloctyl) and 6 (R = 2-octyldodecyl) and PC71BM.
a) Height and phase AFM images of Copolymer 5:PC$_{71}$BM film b) Height and phase AFM images of Copolymer 6:PC$_{71}$BM film.

Output (a) and transfer characteristics (b) of a top contact TFT made from Copolymer 5. This device had a width of 4 mm and a length of 120 µm.

$^1$H NMR spectrum of Copolymer 1 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.

$^1$H NMR Spectrum of Copolymer 2 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.

$^1$H NMR Spectrum of Copolymer 3 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.

$^1$H NMR Spectrum of Copolymer 4 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.

$^1$H NMR Spectrum of Copolymer 5 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.

$^1$H NMR Spectrum of Copolymer 6 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.

(a) Solution and (b) Film absorption spectra for the PF-mT-DPP polymers. The spectra were normalised to the absorption peak around 680 nm.

TGA scans of PF-mT-DPP polymers. The samples were heated at 10 °C/min from room temperature to 800 °C and the weight losses were recorded. The 5 % weight loss temperature was taken to be the sample’s decomposition temperature.

Cyclic voltammetry measurements for thin-films of PF-mT-DPP polymers. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocnium couple was used as an internal reference and the oxidation onsets were used to calculate the HOMO values of the polymers.

Current-Voltage characteristics of solar cells made from 1:1 blends of PF-mT-DPP polymers and PC$_{71}$BM. The device structure was ITO/PEDOT:PSS/PF-mT-DPP:PCBM/Ca/Ag.
Figure 4-5 .......................................................................................................................... 85
Structures of fluorene-DPP polymers PDPP-F, PF-DTDPP and PFDP2T.

Figure 4-6 .......................................................................................................................... 86
AFM height and phase images of a) PF-T-DPP:PC71BM film, b) PF-2T-DPP:PC71BM film and c) PF-3T-DPP:PC71BM film.

Figure 4-7 .......................................................................................................................... 88
Transfer curves at saturation regime for a) PF-T-DPP, b) PF-2T-DPP and c) PF-3T-DPP TFT devices

Figure 4-8 .......................................................................................................................... 91
1H NMR spectrum of PF-T-DPP in 1,1,2,2-tetrachloroethane-d2.

Figure 4-9 .......................................................................................................................... 92
1H NMR spectrum of PF-2T-DPP in 1,1,2,2-tetrachloroethane-d2.

Figure 4-10 ......................................................................................................................... 93
1H NMR spectrum of PF-3T-DPP in 1,1,2,2-tetrachloroethane-d2.

Figure 5-1 .......................................................................................................................... 101
Solution and film UV-Vis spectra (solid lines) of the polymers, and photoluminescence spectra (dashed lines) of the pristine polymer films and 1:1 polymer-PCBM blends. The photoluminescence spectra were normalised for the absorbance of the films.

Figure 5-2 .......................................................................................................................... 103
Cyclic voltammograms of thin-films of the polymers. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocenium couple was used as an internal reference and the oxidation onsets were used to calculate the HOMO values of the polymers.

Figure 5-3 .......................................................................................................................... 104
Weight loss data obtained from thermogravimetric analysis. The samples were heated to 900 °C at 10 °C/min and the decomposition temperature determined from the temperature at which the weight loss reached 5 %.

Figure 5-4 .......................................................................................................................... 104
DSC curves showing the second heating/cooling cycle for each polymer.

Figure 5-5 .......................................................................................................................... 106
a) Output curves and b) transfer curves of a POD2T-DTBT TFT. The hole carrier mobility was 0.13 cm²/Vs, the on/off ratio was 7x10⁴ and the threshold voltage was -3.91 V.

Figure 5-6 .......................................................................................................................... 106
a) Output curves and b) transfer curves of a P2T-ODDTBT TFT. The hole carrier mobility was 0.01 cm²/Vs, the on/off ratio was 1x10⁴ and the threshold voltage was -1.73 V.

Figure 5-7 .......................................................................................................................... 107
a) Output curves and b) transfer curves of a PDTD-ODDTBT TFT. The hole carrier mobility was 0.184 cm²/Vs, the on/off ratio was 2x10⁶ and the threshold voltage was -2.83 V.
Figure 5-8 ................................................................................................................................. 107
   a) Output curves and b) transfer curves of a POD4T-DTBT TFT. The hole carrier
   mobility was 0.022 cm²/Vs, the on/off ratio was $8 \times 10^5$ and the threshold voltage was 3.70 V.

Figure 5-9 ................................................................................................................................. 108
   XRD spectra of non-annealed and annealed POD2T-DTBT films.

Figure 5-10 ................................................................................................................................. 109
   Transfer curves for an POD2T-DTBT TFT comparing the as-prepared device and aged
device (43 days, 58 days and 150 days aged). No significant deterioration in the mobility
and on/off ratios were observed even after 150 days.

Figure 5-11 ................................................................................................................................ 109
   Current-voltage characteristics of POD2T-DTBT transistors under cyclic stressing. Top:
   Drain-source current of devices. Bottom: Applied gate voltage. a) overview of 100 cycles,
b) magnified view.

Figure 5-12 ................................................................................................................................ 111
   Current-voltage characteristics of POD2T-DTBT:PC$_{71}$BM cells.

Figure 5-13 ................................................................................................................................ 112
   Current-voltage characteristics of P2T-ODDTBT:PC$_{71}$BM cells.

Figure 5-14 ................................................................................................................................ 113
   Current-voltage characteristics of PDTT-ODDTBT:PC$_{71}$BM cells.

Figure 5-15 ................................................................................................................................ 114
   Current-voltage characteristics of POD4T-DTBT:PC$_{71}$BM cells.

Figure 5-16 ................................................................................................................................ 116
   Current-voltage characteristics of solvent-annealed and solvent-vapour annealed POD2T-
   DTBT:PC$_{71}$BM cells.

Figure 5-17 ................................................................................................................................ 118
   AFM height and phase images of a) the control sample and b) the solvent annealed
   sample.

Figure 5-18 ................................................................................................................................ 119
   a) Current-voltage characteristics of POD2T-DTBT:PC$_{71}$BM (1:1) cells illustrating the
   effect of different cathode materials. The device with an Al cathode had a larger $V_{oc}$ than
   the device with the Ca/Ag electrode as a result of a decrease in the dark current. b) The
   IPCE spectra of the two devices, shown together with the absorbance of the blend film.

Figure 5-19 ................................................................................................................................ 126
   $^1$H NMR spectrum with peak assignments for POD2T-DTBT in 1,1,2,2-tetrachloroethane-
d$_2$ at 70 °C. The asterisk represents the solvent peak.

Figure 5-20 ................................................................................................................................ 127
   $^1$H NMR Spectrum with peak assignments for P2T-ODDTBT in 1,1,2,2-tetrachloroethane-
d$_2$ at 70 °C. The asterisk represents the solvent peak.
Figure 5-21 ........................................................................................................................................128

$^1$H NMR spectrum with peak assignments for PDTT-ODDTBT in 1,1,2,2-tetrachloroethane-d2 at 70 °C. The asterisk represents the solvent peak.

Figure 5-22 ........................................................................................................................................129

$^1$H NMR Spectrum with peak assignments for POD4T-DTBT in 1,1,2,2-tetrachloroethane-d2 at 120 °C. The asterisk represents the solvent peak.
List of Tables

Table 3-1 ........................................................................................................................................57
Summary of monomer feed ratios and N-alkyl substituents for Copolymers 1 to 6 and the corresponding calculated and experimental carbon and nitrogen contents. The results show that the compositions of the polymers correspond with the monomer feed ratio.

Table 3-2 ........................................................................................................................................62
Device parameters of Copolymer 1:PC₅₇BM solar cells.

Table 3-3 ........................................................................................................................................63
Device parameters of Copolymer 2:PC₅₇BM solar cells.

Table 3-4 ........................................................................................................................................63
Device parameters of Copolymer 3:PC₅₇BM solar cells.

Table 3-5 ........................................................................................................................................65
Device parameters of 1:2 blends of Copolymers 4 and 5 with PC₅₇BM and PC₇₁BM.

Table 4-1 ........................................................................................................................................84
Device parameters for solar cells made from 1:1 blends of PF-mT-DPP and PC₇₁BM.

Table 4-2 ........................................................................................................................................85
Device characteristics of fluorene-DPP polymers in the literature.

Table 4-3 ........................................................................................................................................88
Summary of TFT device characteristics for PF-mT-DPP polymers

Table 5-1 ........................................................................................................................................102
Summary of the number-averaged molecular weights, absorbance maxima for solution and film and optical band-gaps of the polymers.

Table 5-2 ........................................................................................................................................105
Summary of the HOMO and LUMO energy levels, decomposition temperatures and melting points of the four polymers in this series. The HOMO levels were determined by cyclic voltammetry and the LUMO levels were obtained using the HOMO levels and the optical band-gap.

Table 5-3 ........................................................................................................................................111
Summary of the device parameters for POD2T-DTBT:PC₇₁BM cells.

Table 5-4 ........................................................................................................................................112
Summary of the device parameters for P2T-ODD-TBT:PC₇₁BM cells.

Table 5-5 ........................................................................................................................................113
Summary of the device parameters for PDTT-ODD-TBT:PC₇₁BM cells.

Table 5-6 ........................................................................................................................................114
Summary of the device parameters for POD4T-DTBT:PC₇₁BM cells.

Table 5-7: ........................................................................................................................................116
Summary of the device characteristics of solvent annealed and solvent vapour annealed cells, showing a marginal improvement in device performance for solvent annealed and solvent vapour annealed cells.
List of Reaction Schemes

Scheme 3-1 ........................................................................................................................................52
  Structure and synthetic route of PBTDTT-15. PBTDTT-15 was synthesised using palladium-catalysed Stille cross-coupling in chlorobenzene.

Scheme 3-2 ........................................................................................................................................53
  Structure and synthetic route of PDPP-T-DTT polymers. The polymerisation was carried out via Stille coupling between the bis-stannylated monomer M3 and two dibrominated monomers M1 and M2. The composition of the polymers were controlled by changing the monomer feed ratios.

Scheme 3-3 ........................................................................................................................................55
  Synthetic route of 3,6-bis(5-bromothien-2-yl)-2,5-di-N-alkylpyrrolo[3,4-c]pyrrole-1,4-dione (M1).

Scheme 3-4 ........................................................................................................................................55
  Synthetic route of 2,6-dibromo-3,5-dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene (M8) in 6 steps from 3-bromo-6-pentadecyl-thieno[3,2-b]thiophene, with an overall yield of 29%.

Scheme 4-1 ........................................................................................................................................80
  Synthetic route of PF-mT-DPP polymers.

Scheme 5-1 ........................................................................................................................................95
  Possible synthetic routes for P2T-DDTBT. (i) Zn, NiCl₂, COD, DMF. (ii) Pd(PPh₃)₄, aliquat 336, toluene. (iii) Pd₂(dba)₃, P(o-tol)₃, chlorobenzene.

Scheme 5-2 ........................................................................................................................................96
  Polymer design and synthetic route. (i) – Pd₂(dba)₃, P(o-tol)₃, chlorobenzene, 120°C

Scheme 5-3 ........................................................................................................................................97
  Synthetic route of P22. This polymer was synthesised via Stille co-polymerisation between 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole and 5,5'-bis(trimethylstannyl)-4,4'-di((3,7,11-trimethyl)dodecyl)-2,2'-bithiophene.

Scheme 5-4 .......................................................................................................................................99
  Synthesis of 4,7-bis(thien-2-yl)benzothiazole monomers M1 and M3

Scheme 5-5 .....................................................................................................................................100
  Synthesis of bithiophene and quaterthiophene monomers. R₁ = 2-octyldodecyl
Publications

“Diketopyrrolopyrrole-based Low Bandgap Polymers”,
Z.K. Chen, J. Li, B.S. Ong, P. Sonar, K.H. Ong, G.M. Ng, S.L. Lim, S.P. Singh and Y.N. Li,
PCT Patent Application PCT/SG2010/000175

“Polymeric Semiconductors, Devices and Related Methods”,
Z.K. Chen, J. Li, B.S. Ong, S.P. Singh, K.H. Ong and H.K. Wong,
PCT Patent Application PCT/SG2010/000172

“A Versatile Low Band-gap Polymer For Air-Stable, High Mobility Field Effect Transistors and Efficient Polymer Solar Cells”
K.H. Ong, S.L. Lim, H.S. Tan, J. Li, Z. Ma, L.C.H. Moh, S.H. Lim, J.C. de Mello and Z.K. Chen,
Advanced Materials, in press, DOI: 10.1002/adma.201003903
Chapter 1: Introduction

1.1 Motivation

Statistics from the U.S. Department of Energy show that the average worldwide power consumption was over 15 terawatts (TW) in 2006.\textsuperscript{1} 85\% of that power came from burning fossil fuels, which releases large amounts of carbon dioxide into the atmosphere.\textsuperscript{2} There has been worldwide recognition of the need to reduce carbon emissions to slow down the build-up of carbon dioxide in the atmosphere and the global warming that it causes.\textsuperscript{3} Efforts to reduce the emissions of carbon dioxide are made more difficult by the ever-increasing demand for energy due to the growing world population and economic development in developing nations. Unless renewable sources of energy are used to meet this demand, it will be impossible to reduce carbon emissions.

The harnessing of solar energy through the use of photovoltaic technology has the potential to become an important component of future energy production. Over 100,000 TW of solar energy is incident on the earth’s surface, which is far more than is needed. However, the efficient, low cost harvesting of solar energy is a considerable challenge.\textsuperscript{4}

One of the biggest issues for conventional photovoltaic technology is that it is not cost-competitive against fossil fuel or other types of renewable energy. Solar panels based on silicon have a retail price of around $4 per peak watt (W\textsubscript{p}),\textsuperscript{5} which translates to between $0.25 to $0.50 per kilowatt hour (kWh). In contrast, power generated using natural gas only costs $0.025 to $0.05 (although these low costs are due in part to an established system of subsidies).\textsuperscript{2} Even with reductions in cost due to economies of scale, silicon cells are unlikely to be able to meet the cost target of $0.33 per W\textsubscript{p}. Therefore, cost reductions need to be delivered by breakthroughs in solar cell technology.

One potential way to reduce the cost of solar power is by greatly improving the power conversion efficiencies of solar cells. By using multiple junctions, solar cells with
efficiencies above the theoretical limit of 31% (Shockley-Queisser Limit\(^6\)) for single junction silicon cells can be fabricated.\(^7\) Researchers from Spectrolab have reported multijunction GaInP/GaInAs/Ge cells which achieved a record efficiency of 40.7\%.\(^8\) The high costs of manufacturing such cells, however, means that the cost of harnessing solar power in this way is larger than for conventional single junction technology.

Another more promising approach to reducing the costs of solar energy would be to develop solar cells with reasonable efficiencies, but at a much lower cost. Solar cells based on organic materials have the potential to achieve these goals. Due to the high absorption coefficients of these materials, very thin films of the order of 100 nm are sufficient to absorb incident light effectively. In particular, solution processible polymers could allow solar cells to be fabricated on flexible substrates using low-temperature, solution-based and high throughput processes such as spray and contact printing.\(^9\) The use of such techniques would result in significant cost savings compared with the high temperature fabrication techniques requiring vacuum chambers that are typical for inorganic solar cells. Despite recent breakthroughs in the power conversion efficiencies of organic solar cells, further improvements are still needed to make them commercially viable.

### 1.2 Objectives and Outline

This thesis explores one of the key components of polymeric solar cells – the polymer donor. The key design considerations for these polymers are reviewed, and they are then applied to the design and synthesis of three series of polymers with the aim of achieving improved power conversion efficiencies. In each series of polymers, structure-property relationships are investigated and correlated with the solar cell performance.

The remainder of this thesis is structured as follows:

**Chapter 2** presents a review of the literature. A brief overview of the basic principles of organic solar cells is given. On the basis of these principles, we then look at the criteria required for donor materials and review some of the building blocks used for
donor polymers. Finally, we describe some of the characterisation tools and experimental techniques that have been used in the course of this thesis.

**Chapter 3** describes the design, synthesis and characterisation of a series of low band-gap polymers based on diketopyrrolopyrole and dithienothiophene, and our efforts to tailor the polymer structure to achieve better absorption characteristics and improved solubility. The application of these materials to solar cells is also described.

**Chapter 4** describes the modification of our best performing polymer from Chapter 3 with the aim of improving the open circuit voltage. The dithienothiophene units in the polymers were replaced with fluorene units with a view to lower the energy levels of the highest occupied molecular orbitals of the polymers, and the resulting changes in the polymer properties and device performances are discussed.

**Chapter 5** describes the design, synthesis and characterisation of a series of low band-gap polymers with high charge carrier mobilities. The effects of modifying the polymer structure on the absorption properties of the solid-state films and solar cell performance are investigated. The optimisation of cells based on the best performing polymer are also described.

**Chapter 6** concludes the thesis. The key findings of this thesis are summarised, and possible directions for future work are explored.
Chapter 2: Literature Review

2.1 Organic Semiconductors and Solar Cells

2.1.1 An Introduction to Organic Semiconductors

Recent interest in organic materials as semiconducting materials started in the 1970s with the discovery of electrical conductivity in oxidatively-doped polyacetylene. Since then, organic semiconductors based on aromatic moieties such as fluorene, thiophene, benzene, carbazole and pyrrole have been developed. Organic semiconductors are now used in devices such as light-emitting diodes, field-effect transistors, and solar cells.

The semiconducting properties of organic materials originate from their extensively \(\pi\)-conjugated electronic structures. The molecule/polymer backbones are composed of \(sp^2\) hybridised carbon atoms which have 3 \(sp^2\) hybridised orbitals in a trigonal planar arrangement, and a \(p_z\) orbital which is perpendicular to the \(sp^2\) orbitals. The \(sp^2\) orbitals overlap with \(sp^2\) orbitals on adjacent carbon atoms to form strong \(\sigma\)-bonds. The unhybridised \(p_z\) orbital overlaps “edgewise” with those on adjacent carbon atoms to form \(\pi\)-bonds. These \(\pi\)-bonds are not localized between 2 atoms as the \(\sigma\)-bonds are, but are delocalized over the entire conjugated system. The degree of overlap of these orbitals (and thus the extent of conjugation) is affected by the angle between the \(p_z\) orbitals.

Figure 2-1 A \(\pi\)-bond formed by the overlap of 2 \(p_z\) orbitals in ethylene. The solid line between the 2 carbons represents the \(\sigma\)-bond. From ref. 17.
As the number of units in the conjugated system increases, the number of molecular orbitals increases correspondingly. When the number of atoms is large enough, the orbitals form continuous ‘bands’ - the valence band, formed by the bonding $\pi$-orbitals and the conduction band, formed by the anti-bonding $\pi^*$-orbitals - rather than discrete energy levels. The energy gap between the top of the valence band, known as the Highest Occupied Molecular Orbital (HOMO) and the bottom of the conduction band, known as the Lowest Unoccupied Molecular Orbital (LUMO) is the band-gap of the system. Conjugated polymers have much lower band-gaps than non-conjugated ones, and this makes them semiconductors instead of insulators.

2.1.2 Device Structures For Polymer Solar Cells

The absorption of a photon by an organic semiconductor promotes an electron from the HOMO to the LUMO. Due to the low dielectric constants of these materials, a tightly bound electron-hole pair called an exciton is formed rather than free electron-hole pairs. Estimates of the exciton binding energy in various organic semiconductors range from 0.1 to 1.4 eV\cite{19}. The thermal energy ($kT$) is thus insufficient to dissociate these excitons, and a strong electric field is required for this purpose. This can be achieved at the interface between two materials that have a sufficient energy level mismatch (see Figure 2-4 on page 22), resulting in the transfer of an electron from one material (the donor material) to the other (the acceptor material). Tang first
introduced this heterojunction concept in bilayer solar cells in 1986. These cells, which utilised thin layers of copper phthalocyanine and a perylene derivative, resulted in a much improved efficiency of about 1 % compared with typical efficiencies of less than 0.1 % for single layer cells.\textsuperscript{20}

As the exciton diffusion length of organic materials is typically on the order of 5 to 10 nm,\textsuperscript{21-23} only excitons that are generated within about 10 nm of the interface in a bilayer device can contribute to the photocurrent without recombining. The bulk heterojunction, which is effectively an interpenetrating network of a donor and acceptor, greatly increases the interfacial area of the two semiconductors and increases the chances that excitons are generated close to an interface. These cells can harvest a significantly larger number of photons, provided there are continuous pathways for charge transport to the electrodes in both materials.\textsuperscript{24,25}

![Figure 2-3: Schematic 3-dimensional representation of a bulk heterojunction with top and back electrodes. Reprinted with permission from reference 26. Copyright 2007 American Chemical Society](image)

Most polymer-based solar cells are of the bulk heterojunction (BHJ) variety. The active layer of these cells typically consists of a polymeric donor material blended together with an electron-accepting small molecule, which is usually a solution-processible $C_{60}$ or $C_{70}$ derivative like [6,6]-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC$_{71}$BM). The active layer is deposited using solution-based methods such as spin-coating onto a transparent
anode such as glass coated with indium tin oxide (ITO) and a layer of (poly[3,4-(ethylenedioxy)-thiophene]:poly(styrene sulfonate) (PEDOT:PSS) which smoothen the ITO surface\textsuperscript{27} and increases the work function of the electrode.\textsuperscript{28} A low work function metal such as aluminium, silver or calcium is then deposited upon the active layer to form the cathode.

### 2.1.3 Processes And Loss Mechanisms In Organic Solar Cells

There are four main processes involved in obtaining photogenerated current in organic bulk heterojunction solar cells\textsuperscript{15, 29}. We now take a closer look at these processes, as well as the loss mechanisms associated with them.

![Energy diagram of an organic solar cell with a donor-acceptor interface](image.png)

**Figure 2-4**: Energy diagram of an organic solar cell with a donor-acceptor interface. The photocurrent generation processes are explained below. Adapted with permission from reference 30. Copyright 2009 American Chemical Society

1. **Exciton generation**

The absorption of photons in the active materials leads to the generation of excitons as previously described. The fraction of absorbed photons ($\eta_A$) is dependent largely on the absorption characteristics and thickness of the active layer.

Optical losses occur due to reflection at the interfaces between the air and the substrate, and between the different layers in the device. For the air-glass interface, Fresnel reflection losses of about 4 % occur. The total losses due to reflection at the other interfaces are around 30 % of the incident radiation over the absorption band of
a typical 100nm thick P3HT:PCBM solar cell.\textsuperscript{31} Losses also occur due to absorption by the ITO layer, the PEDOT:PSS layer and the metal electrode.

Optical losses also occur due to the mismatch between the absorption spectra of the active layer and the solar spectrum.\textsuperscript{29} The polymer does not absorb photons which have energies smaller than its band-gap. For a donor polymer like P3HT, the band-gap of 1.9 eV means that the solar cell does not absorb photons with wavelengths above 650 nm. This means that the maximum percentage of solar flux that can be absorbed (assuming absorption of all available photons with energies above the band-gap) is only 30 %.\textsuperscript{32}

The absorption of photons with energies above the band-gap also lead to losses due to thermalisation of the hot carriers, which occurs when the difference between the photon energy and the band-gap is emitted as heat.

![Energy level diagram](image)

**Figure 2-5:** Energy level diagram showing the losses due to (1) the inability to absorb photons with energies smaller than the band-gap and (2) hot carrier thermalisation. $E_c$ and $E_v$ represent the conduction and valence band, respectively, $E_g$ represents the band-gap, and $V_h$ and $V_e$ are the potential of the photogenerated holes and electrons, respectively. Reproduced with permission from reference \textsuperscript{33}, Copyright 2009 Royal Society of Chemistry

Finally, losses also occur if the active layer is not sufficiently thick to absorb all the incident photons. Organic materials typically have high absorption coefficients, and typical 100 nm films can absorb about 90 % of the incident light.
2. Exciton diffusion

After excitons have been generated, they diffuse to the donor-acceptor interface. The efficiency of this process ($\eta_D$) reflects the proportion of generated excitons that reach the donor-acceptor interface.

The exciton diffusion length, which is usually 5-10 nm,\textsuperscript{21-23} is an indicator of the effective distance away from the interface within which photogenerated excitons can reach the interface before recombination.

Here, we note the importance of achieving good morphological control over the nanostructure of the donor/acceptor blend film in order to maximise $\eta_D$. The mixture must be intimately mixed, such that the interfaces are within an exciton diffusion length away of a donor/acceptor interface. At the same time, the individual phases must remain continuous to facilitate charge transport to the electrodes (step 4, Figure 2-4).

3. Charge transfer

When an exciton reaches a donor-acceptor interface, it dissociates into a geminate pair, which is a coulombically bound electron and hole pair. The binding energy for this electron and hole pair can be up to 0.5 eV, and this needs to be overcome in order to generate free charge carriers. The efficiency of this process can be denoted as $\eta_{CT}$.

Empirically, it has been observed that the LUMO of the acceptor must be at least 0.3 eV lower than that of the donor for efficient dissociation.\textsuperscript{34} When this condition is fulfilled, the $\eta_{CT}$ is close to unity as dissociation occurs within a few hundred femtoseconds, which is faster than any other competing process.\textsuperscript{29}
The limiting value of the open-circuit voltage that can be obtained for any donor-acceptor pair can be given by the difference between the HOMO of the donor and the LUMO of the acceptor, minus the binding energy of the geminate pair at the donor-acceptor interface.\(^{35}\)

\[
V_{oc} = \frac{1}{e}(|E_{\text{HOMO}}(\text{donor})| - |E_{\text{LUMO}}(\text{acceptor})| - 0.3)
\]

4. Charge transport and collection

After the free holes and electrons have been generated, they migrate towards the electrodes and are collected at the electrodes. The efficiency of this process (\(\eta_{\text{CC}}\)) depends on the charge carrier mobilities in the active materials.

The holes and electrons are transported separately through the donor and acceptor materials, respectively, but due to the abundance of nearby interfaces, bimolecular recombination is possible. The rates of both charge extraction and bimolecular recombination both depend on the charge carrier mobility. It has been suggested that the slowest carrier (which are the holes in both P3HT\(^{36}\) and PPV\(^{37}\) devices) governs the recombination process in a blend. A modelling study by Mandoc et. al suggests that there exists an optimum range of 10\(^{-2}\) to 1 cm\(^2\)/Vs for the charge carrier density in a BHJ device.\(^{38}\) A lower charge carrier mobility leads to slower extraction of charges and a build-up of charges within the device, hence increasing losses due to recombination. For example, for a P3HT:PCBM device, the bimolecular recombination was calculated to increase from 0.38 % to 45 % under short circuit conditions when the hole mobility was decreased from 1 x 10\(^{-2}\) cm\(^2\)/Vs to 1 x 10\(^{-7}\) cm\(^2\)/Vs. Good charge transport properties are thus crucial for efficient solar cells.

2.2 Design Considerations For Polymeric Donor Materials

To improve the performance of organic solar cells, it is necessary to minimise the energy lost through the various routes mentioned in the previous section. In this section, we take a look at the principles for designing polymer donors for efficient solar cells.
2.2.1 Absorption Properties

To minimise the losses due to unabsorbed photons, it is necessary for the band-gap of the polymer to be reduced. In Figure 2-6, the absorbances of blend films of two polymers (P3HT and a low band-gap (LBG) polymer POD2T-DTBT (described in Chapter 5)) with PC$_{71}$BM are shown together with the AM 1.5 reference spectrum.\(^{39}\) The lower band-gap of POD2T-DTBT allowed it to harvest photons from longer wavelengths where there is additional photon flux.

In a recent review of polymeric donor materials, Chen et al. used statistical analysis to show that a low band-gap of below 1.9 eV was a necessary condition for achieving a high PCE (arbitrarily defined as a PCE above 3%).\(^{40}\) However, as the band-gap of the system is decreased beyond a certain point (a constraint due to the LUMO level requirements for efficient charge separation – see Section 2.2.3), the HOMO level of the polymer also increases, which adversely affects the solar cell $V_{oc}$. A model by Scharber et al. has suggested that the band-gap of polymer donors should be between 1.3 to 1.74 eV in order to maximise the efficiency of organic solar cells.\(^{41}\)

![Figure 2-6: Absorbance spectra of P3HT:PC$_{71}$BM and low band-gap (LBG) polymer POD2T-DTBT:PC$_{71}$BM films with the AM 1.5G spectrum\(^{39}\) as a reference.](image)
In addition to having a low band-gap, which allows the polymer to absorb light of longer wavelengths, it also needs to have high absorption across a broad range of wavelengths, in order to maximise photon absorption.

### 2.2.2 Charge Transport

In section 2.1.3, we discussed that poor charge mobility leads to increased losses due to recombination. It is therefore imperative that the donor polymer has a good hole mobility. Using the same statistical analysis approach as that used for the polymer band-gap on the previous page, it was established that a hole mobility of at least $6 \times 10^{-4} \text{ cm}^2/\text{Vs}$ is necessary for high efficiency cells.40 Most reviews agree that a hole mobility on the order of $10^{-2}$ to $10^{-3} \text{ cm}^2/\text{Vs}$ is necessary to prevent it from being the limiting factor in charge transport and fill factor.30, 41.

### 2.2.3 Energy Level Control

In addition to having a low band-gap, well-located HOMO and LUMO levels are also important. The LUMO level of the polymer should be around 0.3 eV higher than the LUMO of the acceptor, so as to provide a sufficient driving force for charge separation.34 Taking the LUMO of PC$_{61}$BM to be -4.3 eV as is commonly reported (although literature values have ranged from -3.7 eV to -4.3 eV due to the ambiguities involved in the experimental process), the LUMO of the donor polymer cannot be below -4.0 eV. It is also not desirable for the LUMO of the polymer to be too far above this figure, as it would lead to energy losses and a lowered $V_{oc}$ assuming the band-gap remained constant.

### 2.2.4 Solubility and Processability

In order to enable the polymer to be solution processed, it must have good solubility in common organic solvents such as chloroform and chlorobenzene. Poor solubility
affects the quality of the films deposited, and this in turn affects charge transport in
the cell and ultimately the efficiency of the cell.

2.2.5 Thermal and Photo Stability

Solar cells are exposed to heat and light during the course of usage. Thus, the
materials which are used in these cells need to have good stability against these
elements, in order to minimise degradation and ensure an acceptable lifetime.

2.3 Principles Of Band-gap Tuning

The factors affecting the band-gap of a conjugated polymer include bond length
alternation, resonance, substituent effects, planarity and inter-molecular interactions. Below, we take a closer look at these factors, and how they can be applied in
designing low band-gap polymers.

2.3.1 Bond Length Alternation (BLA)

In a conjugated system like polyacetylene, the complete delocalization of $\pi$-electrons
would lead to a structure where all the bonds are equivalent. However, this structure
is unstable, and the actual structure is composed of alternating single and double
bonds. This leads to a finite band-gap.

The band-gap can be reduced by using methods which reduce BLA, such as donor-
acceptor structures and stabilising quinoidal structures as discussed below.

a) Resonance effects

Aromatic polymers such as those containing thiophene and phenylene rings in the
main chain have non-degenerate ground states. The two mesomeric forms, the
aromatic form and the quinoid form, are not equivalent, with the quinoid form having
a higher energy and a lower band-gap. The band-gap decreases as quinoidal character increases.43

\[ \text{aromatic} \quad \text{quinoid} \]

b)

\[ \Delta r \]

\[ \Psi_A \quad \Psi_Q \]

\[ E \]

\[ \Delta r (\text{Å}) \]

\[ \text{INCREASING QUINOID CHARACTER} \]

\[ E_g (\text{eV}) \]

\[ -0.03 \quad 0.02 \quad 0.07 \]

\[ 0.0 \quad 0.1 \quad 0.2 \]

\[ 0.13 \quad 0.06 \quad 0.03 \]

\[ \text{Aromatic-type structure} \quad \text{Quinoid-type structure} \]

Figure 2-7: a) The aromatic and quinoidal forms of polythiophene, b) potential energy diagram of polymers containing aromatic units, showing the non-equivalency of the aromatic (A) and quinoid (Q) forms, c) evolution of the band-gap with increasing quinoidal character. \( \Delta r \) represents the bond-length alternation. Figures 2-7b and 2-7c are reproduced with permission from references 44 and 45, Copyright 2001, 1987 Elsevier Science.

The quinoidal character is determined by the resonance stabilisation energy of the aromatic units. The higher this energy is, the more confined the electrons are to the aromatic rings, thus leading to a smaller degree of electron delocalization and a higher band-gap.
b) Substituent effects

The introduction of electron-donating (such as alkoxy and amine) and electron-withdrawing substituents (such as cyano and thiadiazole groups) can alter the band-gap of the system by affecting the HOMO and LUMO levels. The alternation of strong donors and strong acceptors on a polymer chain can result in a low band-gap if the HOMO level of the donor and the LUMO level of the acceptor are close.\textsuperscript{46,47}

Figure 2-8: Band-gap reduction through the hybridisation of donor and acceptor energy levels. D and A represent the donor and acceptor, respectively. Reproduced from reference \textsuperscript{48} with permission. Copyright 2007, Elsevier Science.

Another way of explaining the effects of alternating donors and acceptor groups is that it allows for increased electron delocalization along the polymer chain as these units can accommodate the charges associated with such a resonance structure. Hence the BLA and band-gap are lowered.\textsuperscript{18}

\[
D - A \leftrightarrow D^+ = A^-
\]

2.3.2 Planarity

The dihedral angle between adjacent aromatic units along the conjugated backbone of the polymer affects the polymer band-gap. A large dihedral angle will reduce the delocalization of $\pi$-electrons along the polymer backbone, thus leading to an increase in band-gap. ‘Rigidification’ of the polymer backbone is one method that has been applied to the design of low band-gap systems. In the context of organic solar cell materials, the concept of rigidification has been demonstrated in low band-gap polymers based on bridged thiophene units such as those of cyclopentadithiophene and dithienothiophene (Figure 2-9).
2.3.3 **Inter-molecular interactions**

The band-gaps of some polymers are lower in the solid phase than in solution due to ordering. This can most easily be seen from the differences in the absorbance of the polymers in solution and in the solid state. Therefore, the degree of ordering of the polymer in the solid phase has an influence on the band-gap. As such, features that facilitate ordering in the solid phase, such as regioregularity in the case of P3HT, can help to lower the polymer band-gap.\(^{49}\)

![Absorbance of a polymer PDTT-ODD-19TBT (further described in Chapter 5) showing the red-shift of the film spectra compared to the solution, indicating a reduction in the band-gap in the solid-state.](image)

**Figure 2-10**: Absorbance of a polymer PDTT-ODD-19TBT (further described in Chapter 5) showing the red-shift of the film spectra compared to the solution, indicating a reduction in the band-gap in the solid-state.
2.4 Low Band-gap Polymers in Organic Solar Cells

In the past few years, there has been significant progress on low band-gap polymers for organic solar cells. The development of these materials has helped to increase the reported PCE from around 5 % for P3HT:PCBM cells to more than 7 %. The vast majority of the low band-gap polymers used for organic solar cells have utilised the donor-acceptor approach. The large number of donor and acceptor moieties, as well as the numerous ways in which these moieties can be put together, make this approach a highly versatile and effective way to synthesise new materials. In the past few years, there have been a number of comprehensive reviews of low band-gap polymer donors for organic solar cells.\textsuperscript{40, 48, 50} In this section, we look briefly at some of the building blocks for low band-gap polymers that we have used in this thesis.

2.4.1 Copolymers based on 2,1,3-benzothiadiazole

![Figure 2-11: The structures of (a) 2,1,3-benzothiadiazole (BT) and (b) 4,7-di(thien-2-yl)-2,1,3-benzothiadiazole (DTBT)](image_url)

In this section, we look briefly at some of the building blocks for low band-gap polymers that we have used in this thesis.
The 2,1,3-benzothiadiazole (BT) moiety is one of the most commonly used electron-accepting moieties in donor-acceptor type polymers, partly due to its ease of synthesis. The benzothiadiazole is usually incorporated on its own, or together with a thiophene ring on either side of the benzothiadiazole moiety (commonly abbreviated as DTBT). These benzothiadiazole-containing monomers have been co-polymerised together with a large number of electron-rich (donor) moieties and many of these polymers have proven to be promising in OPV applications due to their low band-gaps.

**Copolymer of BT with Dithienylpyrrole**

One of the first low band-gap donor-acceptor polymers was a copolymer of benzothiadiazole with 2,5-bis(thien-2-yl)pyrrole. This polymer, P1, was synthesised via Stille coupling. It had a low optical band-gap of 1.6 eV, and cells utilising this polymer had photosensitivity extending to 750 nm. A solar cell made from a 1:1 blend
of P1:PCBM was reported to have a PCE of 0.34 %,\textsuperscript{51} which later increased to 1% when the ratio of polymer to fullerene was changed to 1:3.\textsuperscript{52}

**Copolymers of Fluorene and DTBT**

Both random and alternating copolymers of fluorene and DTBT have been reported in the literature. Zhou et al. reported on a series of solar cells made from random copolymers of dioctylfluorene and DTBT (P2) which contained 5 % to 35 % of the DTBT unit. The highest PCE of 1.95 % under 78.2 mW/cm\textsuperscript{2} AM 1.5 illumination was achieved for the polymer with 35 % DTBT content, which can be attributed to improvements in the polymer’s absorption at around 540 nm with increasing DTBT content. This cell had a high $V_{oc}$ of 0.95 V, which can be attributed to the polymer’s low lying HOMO level of -5.4 eV.\textsuperscript{53}

Alternating fluorene-DTBT polymers with a large variety of solubilising alkyl chains have been reported. The initial polymers (P3) had a hexyl and 2-ethylhexyl chain on each fluorene as solubilising groups, and these gave good PCEs of 2.2 % for solar cells with an active area of 1.0 cm\textsuperscript{2}.\textsuperscript{54} Dihexyl, dioctyl (P4) and didecyl derivatives were also investigated.\textsuperscript{55} The molecular weight of the chloroform-soluble fraction was found to increase with alkyl chain length, due to the improved solubility imparted by longer alkyl chains. The copolymer with octyl chains was found to have the best solar cell performance, with a PCE of 2.1 % and a high $V_{oc}$ of 1.01 V despite its low $M_n$ of 4.9 kg/mol. The didecyl derivative of these polymers (P5) were later synthesised with an improved $M_n$ of around 17 kg/mol. Cells with a much improved PCE of 4.2 % were reported with this polymer, thus demonstrating the importance of molecular weight control for donor polymers in solar cells.\textsuperscript{56} Further investigations on the effect of alkyl chain substitution on PFDTBT polymers were carried out by Chen et al.\textsuperscript{57} These polymers, P6 and P7, had 2-ethylhexyl and 3,7-dimethyloctyl alkyl substituents respectively. P6 gave a PCE of 3.5 %, and P7 gave a PCE of 4.5 %. The better performance of P7 vis-à-vis P6 was attributed to the less bulky alkyl chains which allowed better $\pi-\pi$ stacking and hence better charge transport.

**Copolymers of Carbazole and DTBT**

Relatively low hole mobilities have been reported for low band-gap polyfluorenes. By substituting fluorene with 2,7-carbazole, which has been used in polymers for high
mobility OTFTs, the hole transport properties of the polymer can be improved. Blouin et al. investigated a series of poly(2,7-carbazole) derivatives with different N-alkyl substituents and found that the best results were obtained using a secondary N-alkyl chain which made the structure similar to that of 9,9-dialkylfluorene. This polymer, P8, was reported to have PCE of 3.6%. The PCE improved to 6.1%, which was a record for OPVs at the time, when a titanium sub oxide (TiO_x) electron-blocking/optical spacer layer was incorporated into the device structure. The TiO_x layer served to redistribute the light intensity within the cell, such that the maximum intensity was within the active layer where photogeneration takes place; as well as improve the electron collection at the cathode. P8 was also found to have a high TFT hole mobility of up to 0.02-0.03 cm^2/Vs.

Other BT polymers
Silicon-containing heterocycles such as dibenzosilole and dithieno[3,2-b:2',3'-d]silole have emerged recently as promising co-monomers for the synthesis of donor polymers. Two different groups independently reported a copolymer of 2,7-dibenzosilole with DTBT (P9) which was synthesised via Suzuki coupling. This polymer had a band-gap of around 1.82-1.85 eV, which was around 0.1 eV lower than that of its fluorene-based analogue. A very high M_n of 79 kg/mol was reported by Wang et al, which helped to contribute to an excellent PCE of 5.4% for solar cells utilising blends of P9 with PCBM. A relatively high TFT hole mobility of 1x10^{-3} cm^2/Vs was also reported for this polymer.

An even higher TFT hole mobility of 3x10^{-3} cm^2/Vs was reported for a copolymer of dithieno[3,2-b:2',3-d]silole and BT (P10). This polymer was synthesised via Stille coupling with a M_n of 18 kg/mol, and it had a low optical band-gap of 1.45 eV. A PCE of up to 5.1% was reported for blends of P10 with PC_{71}BM.
2.4.2 Copolymers based on Dithienyldiketopyrrolopyrole

Figure 2-13: The 3,6-bis(thien2-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (dithienyl DPP) moiety. The 2,5 positions are functionalised with alkyl groups (R) to increase the solubility of the polymers.

Derivatives of diketopyrrolopyrrole (DPP) have been used in pigments for a number of years. Such DPP derivatives possess superior chemical, light and heat resistances. However, they are also highly insoluble in common organic solvents due to the presence of strong intermolecular interactions. The attachment of solubilizing alkyl chains to the 2,5-positions of the DPP moieties greatly increased their solubility, and made it possible to investigate the use of DPP derivatives in organic electronics. Small molecules and polymers incorporating the dithienyl DPP moiety have attracted much interest because of their small band-gap, high hole mobility, and good performance when applied in solar cells.

The first dithienyl-DPP polymers were synthesised through the nickel-catalysed Yamamoto coupling reaction. One such polymer (P11) was reported to exhibit ambipolar charge transport properties, with field effect transistors (TFTs) made from this material exhibiting good hole and electron mobilities of 0.1 cm$^2$/Vs and 0.09 cm$^2$/Vs respectively. A similar polymer with different $N$-alkyl substituents (P12) was reported to have an absorption onset of 860 nm in o-dichlorobenzene and a band-gap of 1.4 eV. Solar cells made from blends of P12 with PC$_{61}$BM and PC$_{71}$BM exhibited PCEs of 3.2 % and 4.0 % respectively.

A similar polymer with one less thiophene unit (P13) in the structure was also synthesised via Suzuki coupling with a high molecular weight of over 50 kg/mol. This polymer had no solubilising groups on the bridging thiophene unit, hence longer 2-hexyldecyl chains were used on the DPP moiety to ensure solubility of the polymer. TFTs fabricated from this polymer showed ambipolar charge transport, with hole and
electron mobilities of 0.04 cm²/Vs and 0.01 cm²/Vs respectively. In combination with PC⁷₁BM, solar cells with PCEs of 4.7 % were achieved.⁶⁸

![Chemical structures](image)

**Figure 2-14: Structures of some DPP polymers in the literature**

When the bridging thiophene unit in P13 was substituted by a phenyl ring (polymer P14), the HOMO level was reduced by close to 0.2 eV.⁶⁹ A higher $V_{oc}$ of up to 0.8 V could therefore be obtained when P13 was applied in solar cells (compared with up to 0.68 V for P13⁶⁸). This contributed towards an improved PCE of 5.5 %.

Polymers P15⁷⁰,⁷¹ and P16⁷² which incorporate dithienyl-DPP and carbazole have also been reported. Preliminary device data showed that P15:PC₆₁BM solar cells could achieve a PCE of 1.6 %. TFT devices from the same polymer showed a hole mobility of 0.02 cm²/Vs with an on/off ratio in the order of $10^6$. Subsequent
optimisation of the devices resulted in a doubling of the PCE to 3.2 %.\textsuperscript{73} P14, which had a similar structure but different alkyl groups on both the carbazole and DPP moieties, achieved a PCE of 2.26 % in combination with PC\textsubscript{61}BM.

Another series of dithienyl-DPP polymers which was synthesised by Stille cross-coupling was reported by Yang et. al. These polymers incorporated dithienosilole (P17), fluorene (P18), benzo[1,2-b;3,4-b]dithiophene (P19) and benzo[2,1-b:3,4-b’]dithiophene (P20). The highest PCE of 4.45 % was obtained for P20:PC\textsubscript{71}BM cells which were annealed for 30 min.\textsuperscript{74}

Clearly, DPP polymers have much potential both for TFT and solar cell applications. In Chapter 3, we describe the design and synthesis of DTT-DPP polymers which resulted in solution processible polymers with good solar cell PCEs.

### 2.4.3 Polymers based on oligothiophene and its derivatives

Polythiophenes have been extensively studied in the field of organic thin-film transistors and organic solar cells. Polythiophene derivatives have been reported to have high field effect mobilities of up to 0.6 cm\textsuperscript{2}/Vs,\textsuperscript{75,76} which is a desirable property for solar cell materials. Until recently, cells made from poly(3-hexylthiophene) (P3HT) and PCBM have held the record for power conversion efficiencies which was around 5 %.\textsuperscript{77-79} However, as previously mentioned, its band-gap of 1.9 eV means that it is unable to absorb photons with wavelengths above 650 nm (see Figure 2-6). The band-gap of polythiophene systems can be reduced through introducing acceptor moieties into the polymer backbone. To a lesser extent, the use of bridged thiophenes such as cyclopentadithiophene and
Dithienothiophene can also contribute to a lower polymer band-gap by increasing the planarity of the polymer chain and increasing the effective $\pi$-conjugation length.\textsuperscript{80}

**Donor-acceptor polymers based on polythiophene**

Thiophene and bridged thiophenes have been copolymerised with acceptor moieties such as 2,1,3-benzothiadiazole, thienopyrazine, thiadiazoloquinoxaline and diketopyrrolopyrole (DPP).

**Copolymers of thiophene and benzothiadiazole**

Thiophene-benzothiadiazole polymers with the number of thiophene rings in the repeat unit ranging from two to eight have been reported in the literature. Xia et al. reported on a terthiophene-benzothiadiazole polymer (P21) that was synthesised via Stille cross coupling. This polymer had a number averaged molecular weight ($M_n$) of 7.4 kg/mol and a band-gap of 1.38 eV. Solar cells based on a 1:3 blend of this polymer and PCBM achieved a PCE of 0.13 %.\textsuperscript{81}

Polymers containing quaterthiophene together with benzothiadiazole (P22) and benzobis(thiadiazole) (P23) have also been reported.\textsuperscript{82} P23 had a very low band-gap of 0.67 eV, but gave a very poor solar cell performance which was ascribed to the mismatch of its LUMO with that of PCBM.\textsuperscript{83} P22, which had a band-gap of 1.65 eV, fared much better and gave a PCE of 0.62 % with large-area cells (3 cm$^2$), and 1 % with small-area cells (0.1 cm$^2$).\textsuperscript{84}

Yue et al. synthesised a series of thiophene-benzothiadiazole polymers, with the number of thiophenes in the repeat unit ranging from two to six (polymers P24 to P28). P26 to P28 contained the same number of solubilising groups but different numbers of thiophene rings in the repeat unit. The $M_n$ of these polymers dropped as the number of thiophene rings increased, which reflected the reduced solubility of the polymers with a high number of unsubstituted thiophenes. The band-gaps of polymers P24 to P28 were between 1.97 and 1.52 eV, which made them good candidates for OPV applications. Indeed, P28 gave a solar cell PCE of 2.23 % when blended with PCBM in a 1:3 ratio. TFT devices made from P27 and P28 showed hole mobilities of 0.025 cm$^2$/Vs and 0.014 cm$^2$/Vs respectively.\textsuperscript{85}
Figure 2-16: Structures of benzothiadiazole-oligothiophene polymers P21 to P31.

At around the same time, another group reported polymer P29, which differed from P28 only by the lengths of the alkyl substituents.\(^6\) This polymer gave a PCE of 1.39 %. Polymers P30 and P31 were also reported in the same publication. P30 incorporated 8 thiophene rings with benzothiadiazole and had an optical band-gap of 1.82 eV, which was slightly higher than that of P29. The PCE of cells utilising this material was 1.73 %. Both of these polymers demonstrated photocurrent generation in the near infrared (NIR) region.\(^6\)

The introduction of benzothiadiazole into the polythiophene backbone has indeed been successful in improving the absorption properties of the polymers. By increasing
the number of alkyl chains in the polymers’ repeat units, polymers with good solubility and high molecular weight have also been synthesised. However, further improvements in the charge carrier mobility and solar cell PCE are still desired. In Chapter 5 of this thesis, we will discuss the design, synthesis and characterisation of a new series of thiophene-benzothiadiazole copolymers which have good hole mobilities as well as PCEs.

2.4.4 Polymers based on bridged thiophene units

As mentioned in section 2.3, using bridged thiophene units in place of unbridged ones can be an effective method for reducing the band-gap by increasing planarity and hence conjugation length. Systems such as cyclopentadithiophene and dithienothiophene have been successfully used in low band-gap polymers for solar cell applications, and these are reviewed in this section.

Cyclopenta[2,1-b:3,4-b’]dithiophene based polymers

Cyclopenta[2,1-b:3,4-b’]dithiophene (CPDT) is a derivative of thiophene in which two thiophene units are covalently bound by a bridging carbon atom. The CPDT structure is fully coplanar,\(^87\) and this allows for an increase in electron delocalisation and a corresponding reduction in polymer band-gap. Indeed, the homopolymer of CPDT (P32) has an optical band-gap of around 1.7-1.8 eV depending on the molecular weight of the polymer, which is 0.1-0.2 eV lower than that of P3HT.\(^88\)

Further reductions in the polymer band-gap have been achieved by incorporating CPDT into a donor-acceptor type polymer PCPDTBT (P33) with 2,1,3-benzothiadiazole (BT) as the acceptor.\(^89, 90\) The optical band-gap for this polymer was determined to be 1.4 eV, and its absorption maximum was at 775 nm. A bathochromic shift of ca. 70 nm was observed between the solution and film spectra, indicating that there is strong interchain interaction in the polymer film. Initial solar cell device data for P33:PC\(_{71}\)BM cells showed a promising PCE of 3.2 % and the onset of the photocurrent exceeded 900 nm. Modification of the device processing conditions led to further improvements in the solar cell performance. By adding a small percentage of alkane dithiols to the polymer:PCBM blend, a stronger interchain
interaction was achieved as evidenced by a red-shift of the absorption spectrum. The PCE also increased to 5.5 %, and this was attributed to improved photocurrent generation brought about by an improved morphology in the active layer.\textsuperscript{91}

P33 has a transmission window in its absorption spectrum at around 500 nm. In order to tailor the absorption properties of the polymer, a series of random copolymers (P34) was also synthesised by substituting some BT units with bithiophene. By altering the ratios of the monomer feeds, the absorption properties of the polymers could be tuned to achieve good absorption across the visible spectrum. These polymers gave PCEs of up to 3 % in initial studies.\textsuperscript{90}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures of cyclopentadithiophene and dithienothiophene polymers P32 to P40.}
\end{figure}

\textbf{Polymers based on dithienothiophene}
Molecules and polymers incorporating the dithieno[3,2-\textit{b};2',3'-\textit{d}]thiophene (DTT) unit have been attracting interest in the field of organic electronics. Like CPDT, DTT is also a coplanar molecule. DTT-based molecules and polymers have demonstrated promise in organic field-effect transistor (OTFT) applications, showing field effect mobilities of up to 0.42 cm\textsuperscript{2}/Vs.\textsuperscript{92, 93} A star-shaped molecule based on DTT has been tested in solar cells and has achieved a PCE of 1.4 %.\textsuperscript{94}
A copolymer of DTT and 4,4’-didodecylthiophene (P35) was reported to have hole mobilities of up to 0.3 cm\(^2\)/Vs and on/off ratios of \(10^7\) in OTFT applications.\(^{95}\) A similar polymer (P36) was also reported in OPV applications. This polymer, which differed in alkyl chain positioning from the previous polymer, had a low HOMO value of -5.84 eV. Solar cells made from blends of this polymer and PCBM showed a high \(V_{oc}\) of 0.8 V and a PCE of up to 0.8 %.\(^{96}\)

The alkylation of DTT is much more complex than that of CPDT, nevertheless the successful synthesis of dialkylated DTT has opened up new possibilities in polymer design.\(^{97}\) One publication reported on the synthesis of dialkylated DTT polymers with single (P37), double (P38) and triple bond linkages (P39) between the DTT units, and their OPV characteristics were evaluated. The polymer with double bond linkages was found to have the best absorption and solubility characteristics. Solar cells utilising this polymer with PCBM achieved a PCE of 0.45 % after annealing.\(^{98}\) A didecyl DTT-thiophene polymer (P40) was also reported by the same group and this polymer achieved a PCE of 0.71 % and a \(V_{oc}\) of 0.7 V.\(^{99}\)

To the best of our knowledge, these have been the only reports of dialkylated DTT polymers for organic solar cell applications. In view of the high hole mobilities achieved by DTT polymers, the dialkylated DTT moiety merits further investigation as a building block for donor-acceptor type polymers. In Chapter 3, the synthesis and OPV characterisation of a series of polymers containing the dialkyl DTT unit is described.

\section*{2.5 Experimental Methods}

\subsection*{2.5.1 Synthesis}
Chemicals were purchased from Aldrich, Pacific Chemical Source, Acros Organics and Alfa Aesar, and were used as received. Anhydrous tetrahydrofuran was obtained by distilling over sodium/benzophenone under nitrogen. Anhydrous chlorobenzene was obtained from Acros Organics. All other solvents used were reagent grade and used as received from JT Baker.
Microwave-assisted Suzuki and Stille cross-coupling has been utilised in place of conventional methods for the synthesis of some intermediate compounds. The microwave-assisted syntheses described in this thesis were carried out in sealed glass vials equipped with septa using a Biotage Initiator system.

All the polymers described in this thesis were synthesised using palladium-catalysed Stille co-polymerisation in chlorobenzene, and purified via soxhlet extraction with appropriate solvents to remove low molecular weight material.

2.5.2 Characterisation of precursors

The purity and structure of the synthesised compounds were verified using a combination of nuclear magnetic resonance (NMR) spectroscopy, mass spectra (MALDI-TOF-MS) and elemental analysis.

NMR Spectroscopy

When NMR-active nuclei such as $^1$H and $^{13}$C are placed in a magnetic field, they absorb electromagnetic energy at a frequency which is characteristic of the isotope. This frequency is affected slightly by the chemical environment of the nuclei. This frequency is then divided by the frequency of the magnetic field to obtain a value known as the chemical shift which is expressed in parts per million (ppm). The chemical shifts are referenced to tetramethylsilane and the peak intensities are plotted against the chemical shifts to give the spectrum of the compound. Analysis of the spectra can give insights into the chemical structure and purity of a compound.$^{100}$

The NMR spectra were obtained using a Bruker 400 MHz spectrometer. The samples were dissolved in deuterated solvents such as dichloromethane-$d_2$ and chloroform-$d$ prior to testing. $^1$H NMR spectra were obtained using a frequency of 400 MHz and $^{13}$C NMR spectra were obtained using a frequency of 100 MHz. Due to the poor solubility many of the synthesised polymers at room temperature, their NMR spectra were obtained in 1,1,2,2-tetrachloroethane-$d_2$ which has a high boiling point of 146°C and thus enabled the samples to be heated to above 100°C.
Matrix-Assisted Laser Desorption/Ionisation Time Of Flight Mass Spectrometry (MALDI-TOF-MS)

MALDI-TOF-MS is a form of mass spectrometry that was originally developed for biomolecules\textsuperscript{101} and can be used as a tool to characterise organic compounds. The sample is mixed with a matrix, which is a crystalline compound that absorbs strongly either in the ultraviolet or infra-red regions (depending on the laser used), and deposited onto a target plate. The target is then irradiated with a laser beam. This causes structural decomposition of the matrix and generates a plume of ions (usually singly charged ions), which are extracted by an electric field and accelerated towards a time-of-flight detector. From the time taken for the ion to travel to the detector, its mass to charge ($m/z$) ratio, and hence its mass, can be calculated.

MALDI-TOF-MS measurements were carried out on an autoflex TOF/TOF system from Bruker Daltonics. Peptide standards were used to calibrate the mass measurements and dithranol was used as the matrix whenever necessary.

Elemental Analysis

In the context of organic chemistry, elemental analysis is a method for confirming the elemental composition and purity of a compound. The sample is burnt in excess oxygen in a furnace and the combustion products are separated using gas chromatography and analysed quantitatively. The weight percentages of carbon, hydrogen, nitrogen and sulphur content are determined and these can be compared against calculated values to verify the purity of the compound.

Elemental analysis was carried out using a Flash EA 1112 series elemental analyser from Thermo Electron Corporation.

2.5.3 Polymer Characterisation

Ultraviolet-Visible Spectroscopy

The absorption properties of the polymers were characterized by UV-Vis spectroscopy. In this experiment, the sample, which is either a film on a quartz slide or a solution in a quartz cuvette, is placed in the path of a light beam. The transmitted
light is then detected by a photodiode equipped with a monochromator. The intensity of the transmitted light at various wavelengths \( I \) is compared against a reference light beam \( I_0 \) which is passed through a blank quartz slide or cuvette filled with the solvent with which the sample solution was prepared. The absorbance of the sample is then given by the formula \( A = -\log_{10} \left( \frac{I}{I_0} \right) \). ^{102}

The spectra were recorded on a Shimadzu model 3101-PC UV-VIS spectrometer. Solution spectra were obtained in chlorobenzene solution and thin-film spectra were obtained from polymer films which were drop-cast from chlorobenzene solution onto quartz slides. The onset in optical absorption was used to calculate the optical band-gap of the polymer.

**Photoluminescence Spectroscopy**

Photoluminescence (PL) is a process in which photons are absorbed by a material (excitation to a higher energy level) and subsequently re-emitted (to return to the ground state). In the field of organic photovoltaics, the quenching of photoluminescence peaks in polymer-PCBM blends can indicate the presence of charge-transfer from the excited-state of the polymer to the fullerene. ^{103} PL measurements were carried out on a Perkin-Elmer LS 50B luminescence spectrometer with a xenon lamp as a light source.

**Gel Permeation Chromatography (GPC)**

The molecular weight of a polymer is an important parameter which affects its charge transport properties, and hence its performance as a photovoltaic material. ^{104, 105} Gel Permeation Chromatography is commonly used to determine the molecular weight and polydispersity of polymer samples. Samples are typically dissolved in a solvent and passed through columns of porous beads. The smaller molecules can enter these pores more easily than the larger molecules, and have longer retention times in the columns. The retention times are compared against those of standard samples (e.g. monodisperse polystyrene with known molecular weight) to obtain the molecular weight and polydispersity of the unknown sample. ^{102}
Due to the poor solubilities of most of the polymers, the GPC analyses were carried out at elevated temperatures, and chlorinated solvents such as chlorobenzene and 1,2,4-trichlorobenzene were used as eluents.

GPC measurements using chlorobenzene were carried out at 60 °C using a Waters 2695 GPC system equipped with a Waters 2420 Evaporative Light Scattering (ELS) detector. GPC measurements using 1,2,4-trichlorobenzene were carried out at 160 °C on a Polymer Labs PL-220 system using a refractive index detector. Polystyrene standards were used to calibrate both systems.

**Thermal Analysis**

**Thermogravimetric analysis (TGA)** was carried out on the samples to determine the stability of the polymers. The TGA analyses were carried out using a TGA Q500 system from TA Instruments. Samples were typically heated from room temperature to 800 °C at 10 °C/min in air. As the temperature increased, chemical reactions occurred which cause the weight of the sample to change. The changes in the weight of the sample were measured and the decomposition temperature ($T_d$) was determined from the 5 % weight loss temperature. The $T_d$ represents the upper limit to which the polymers can be heated during device fabrication.

**Differential Scanning Calorimetry (DSC)** was carried out to obtain the phase transitions of the polymers. For our experiments, the samples were loaded into an aluminium pan, and a blank aluminium pan was used as the reference. The samples were then heated (and then cooled) at a constant ramp rate. The samples were kept at almost the same temperature by varying the heat flow to these samples. The difference between the heat flows to the sample and reference were then recorded as a function of temperature. When phase transitions occur in the sample, more heat is needed to raise the temperature of the sample if the transition is endothermic, with the reverse being true if the transition is exothermic. The recorded changes in heatflow thus indicate the presence of these transitions, such as glass transition, melting and recrystallisation.
The system used was a Photo differential scanning calorimeter, PDSC Q100 from TA Instruments. The ramp rate was 10 °C/min and the experiments were done in a nitrogen atmosphere.

**Cyclic Voltammetry**

Cyclic voltammetry was used to determine the energy levels of the polymers.

Cyclic voltammetry measurements were performed using an Autolab potentiostat (model PGSTAT30, Echorchime) at room temperature in a glovebox with a conventional three electrode configuration consisting of a glass carbon working electrode, a platinum counter electrode, and a silver wire as a quasi-reference electrode. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The polymer sample was drop-cast onto the working electrode from chlorobenzene. Ferrocene was used as an internal standard for calculating the redox potentials of the samples following each batch of samples, and the ferrocene/ferrocenium redox couple was assumed to have a value of -4.8 eV relative to the vacuum. The onset of the first oxidation peak was used to calculate the value of the HOMO. The LUMO was then calculated using this HOMO value and the optical bandgap.

**2.5.4 Device Fabrication and Characterisation**

**General OPV Device Fabrication and Characterisation**

The polymer and PCBM (C_{61} or C_{71}) were dissolved separately in anhydrous 1,2-dichlorobenzene (DCB). The polymer solution was heated on a magnetic hotplate stirrer at 70 °C for 2 hours; while the PCBM solution was stirred at 40 °C for 2 hours. The 2 solutions were then mixed together and the solution blend was stirred overnight at 40 °C. The polymer concentration in the blend ranged from 8 to 10 mg/mL, and the ratios (polymer:PCBM) typically ranged from 1:1 to 1:5.

Devices were prepared on indium tin oxide (ITO) patterned glass substrates which were first sonicated in a detergent (Hellmanex) bath for 30 min, followed by 2 rounds
of sonication in de-ionized water for 10 min. This was followed by successive sonication in acetone and isopropanol for 15 min and 20 min, respectively. The cleaning step was concluded by blow-drying the substrates using a nitrogen-gun. The substrates were then placed in an oven at 80 °C for at least one hour.

The substrates were subjected to an UV ozone treatment for 10 min before a PEDOT:PSS (CLEVIOS™ P VP Al 4083) layer of 40-45 nm thickness was spin-coated onto the ITO surface. The PEDOT:PSS-coated substrates were then annealed at 120 °C for 10 min. Next, the active layer was spin-coated with spin rates of between 500 and 1000 rpm for 120 s in an inert glove-box (N₂ atmosphere) and the films were allowed to dry slowly for 2 h. Finally, 10 nm calcium and 100 nm silver were deposited by thermal annealing as the cathode. One set of devices in Chapter 5 utilised 100 nm of aluminium as the electrode instead of Ca/Ag. The active area of each device was 9 mm².

The thickness of the films were measured using a surface profiler (KLA-Tencor P10 surface profiler). Current density-voltage (J-V) measurements were carried out in an inert environment (MBraun glovebox, N₂ atmosphere) under 1 Sun (AM1.5G) conditions using a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA) with an intensity of 100 mW/cm². The lamp was calibrated using a silicon diode fitted with a KG5 colour filter. The J-V results reported for each sample are those of the best cell among the four cells on each substrate. The power conversion efficiency was calculated using the formula below:

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}$$

where $V_{oc}$ is the open circuit voltage, $J_{sc}$ is the short circuit current, FF is the fill factor and $P_{in}$ is the incident illumination per unit area.

The incident photon to current conversion efficiency (IPCE) as a function of wavelength was measured with a home-built setup consisting of an Oriel 300 W Xe lamp in combination with an Oriel Cornerstone 130 monochromator and a SRS 810 lock-in amplifier (Stanford Research Systems). The incident photon flux on the device was calculated for each wavelength by using a calibrated Si diode as the reference.
Charge Carrier Mobility Determination

Charge transport is an important characteristic of organic semiconductors. The charge carrier mobilities of some of the polymers described in this thesis were determined from the transfer characteristics of field effect transistors made using these polymers.

TFT Device fabrication and characterization

Top-contact, bottom-gate TFT test devices were prepared on a silicon wafer in ambient conditions without taking any special precautions to exclude air, moisture and ambient light. A heavily n-doped silicon wafer <100> with a 210 nm surface layer of silicon dioxide (SiO₂) was used as the substrate/gate electrode, with the top SiO₂ layer serving as the gate dielectric (capacitance 15.6 nF/cm²). The SiO₂ surface of the Si wafer substrate was cleaned by sonication in acetone, and then immersed in piranha solution (volume ratio of H₂SO₄ to H₂O₂ was 2:1) for 8 minutes at room temperature. The cleaned wafer was then immersed in a 0.1 M solution of octyltrichlorosilane (OTS-8) in toluene at 60 °C for 30 min, followed by rinsing with toluene and then drying with N₂. The semiconductor layer was deposited on top of the OTS-8-modified SiO₂ surface by spin coating a hot solution of the polymer in 1,2-dichlorobenzene (8mg/ml) at 1000 rpm for 60 seconds and vacuum annealed at 200 °C for 30 min. Subsequently, a series of gold source/drain electrode pairs were deposited by vacuum deposition through a shadow mask to create a series of TFTs with various channel length (L) and width (W) dimensions. Silicon oxide at the backside of the silicon wafer of the TFT device was removed with sandpaper to provide a conductive gate contact. The TFT devices were then characterized using a Keithley SCS-4200 probe station under an ambient environment with relative humidity level of 65 %. The TFT mobility was extracted using the following equation in the saturation regime from the gate sweep:

\[ I_D = \mu C_i (V_G - V_T)^2 \frac{W}{2L} \]

where \( I_D \) is the drain current, \( \mu \) is the field-effect mobility, \( C_i \) is the capacitance per unit area of the gate dielectric layer (SiO₂, 220 nm, \( C_i = 15.6 \) nFcm⁻²), and \( V_G \) and \( V_T \) are respectively gate voltage and threshold voltage. \( V_T \) was derived from the relationship between the square root of \( I_D \) at the saturated regime and \( V_G \) by extrapolating the measured data to \( I_D = 0 \). W and L refer to the channel width and length, respectively.
**Atomic Force Microscopy (AFM)**

Atomic Force Microscopy (AFM) is a high resolution form of microscopy, capable of resolutions of less than a nanometer. A sharp, micromachined cantilever tip (usually silicon or silicon nitride) is used to scan the sample surface. When the tip is brought into close proximity to the surface, it interacts with the surface and is deflected. The deflections are measured using a laser spot which reflects off the tip of the cantilever onto an array of photodiodes, and the data are processed using software to generate an image of the sample.

AFM images were obtained using a Digital Instruments Nanoscope IV multimode AFM in tapping mode. In this mode, the probe cantilever is oscillated near its resonant frequency. When the tip comes close to the sample surface, it experiences repulsive forces that cause the amplitude of the oscillation to decrease. The feedback mechanism adjusts the height of the cantilever tip above the sample in order to maintain a fixed distance between the tip and the sample. These adjustments in height are recorded as the “height” image, which contains topographical information. In addition, the phase lag between the drive signal and the actual oscillation of the cantilever can be recorded. Changes in the phase lag reflect differences in the surface properties of the sample. In the field of organic photovoltaics, “phase” images can thus be used to determine the phase separation behaviour of the polymer and PCBM blend.
Chapter 3: Low Band-gap Dithienothiophene-Diketopyrrolopyrrole Polymers: Absorption and solubility Tuning

3.1 Introduction

In recent years, small molecules and polymers based on the dithienothiophene (DTT) unit (reviewed in section 2.4.4 on page 41) have shown promise in organic thin-film transistor applications, with hole mobilities of up to 0.42 cm²/Vs being obtained for small molecules⁹³ and up to 0.30 cm²/Vs for polymers⁹⁵ based on this moiety.

In our group, Dr. Jun Li and co-workers have recently synthesised a copolymer based on 3,5-dipentadecyldithieno[3,2-b:2',3'-d]thiophene, PBTDTT-15, which has achieved OTFT mobilities of 0.05-0.06 cm²/Vs. In addition, blends of PBTDTT-15 and PC₇₁BM have achieved promising solar cell PCEs of up to 3.2 %.¹⁰⁷ Considering the relatively narrow absorption spectrum of PBTDTT-15, which has an absorption onset of around 640 nm,¹⁰⁷ the results suggest that the dialkyl-substituted DTT is a promising building block for donor polymers. By combining the electron-donating DTT moiety with an electron accepting moiety, a donor-acceptor type polymer with a lower band-gap and better photon-absorption characteristics could be achieved, which could lead to more efficient photon-harvesting and improved solar cell performances.

Scheme 3-1: Structure and synthetic route of PBTDTT-15. PBTDTT-15 was synthesised using palladium-catalysed Stille cross-coupling in chlorobenzene.¹⁰⁷
3.2 Polymer Design and Synthesis

3.2.1 Polymer Design

The design and synthesis of the polymers in this chapter were carried out jointly with Dr. Jun Li.

For this study, we selected the 3,6-bis(thien2-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) unit (reviewed in Section 2.4.2 on page 36) as the acceptor moiety, and the dithieno[3,2-b;2′,3′-d]thiophene (DTT) unit as the donor moiety. To prevent solubility issues due to having too many unsubstituted aromatic rings, we used dipentadecyl-substituted DTT units, which were the same as those used in PBTDTT-15. Bis(trimethylstannyl)thiophene (M3) was used as the bridging unit between the dibrominated monomers 3,6-bis(5-bromothen-2-yl)-2,5-di-N-alkylpyrrolo[3,4-c]pyrrole-1,4-dione (M1) and 2,6-dibromo-3,5-dipentadecyl-dithieno[3,2-b;2′,3′-d]thiophene (M2). One of the advantages of using such a design is that composition of the polymer can be easily tailored by changing the feed ratios of the monomers. By using this strategy, we were able to synthesise random polymers with different ratios of DPP to DTT moieties in order to tune the absorption properties of the polymers. The first polymer (Copolymer 1, m:n = 1:1) had a relatively low absorption in the short wavelength region (see Figure 3-1 on page 57), thus the DTT content was increased in Copolymers 2 and 3 to 1:2 and 1:3 respectively.

\[
\text{Copolymer 1: } \frac{\text{Copolymer 1}}{\text{Copolymer 2}} = \frac{1}{1}, \quad \frac{\text{Copolymer 1}}{\text{Copolymer 3}} = \frac{1}{2}, \quad \frac{\text{Copolymer 2}}{\text{Copolymer 3}} = \frac{1}{3}
\]

Scheme 3-2: Structure and synthetic route of PDPP-T-DTT polymers. The polymerisation was carried out via Stille coupling between the bis-stannylated monomer M3 and two dibrominated monomers M1 and M2. The composition of the polymers were controlled by changing the monomer feed ratios.
The first polymers in this series utilised dodecyl substituents on the DPP moiety and were found to have relatively poor solubility, being soluble only in very hot chlorobenzene or dichlorobenzene. In spite of this, promising solar cell PCEs of above 3% were obtained for these polymers as discussed in Section 3.4. The best performance was given by Copolymer 2, therefore, we endeavoured to improve the solubility and processability of this polymer by substituting the dodecyl chains with long, branched alkyl chains – 2-ethylhexyl, 2-butyloctyl and 2-octyldodecyl. The alkyl chains on the DTT moieties were not changed due to the relative difficulty of the process, which entails a 10-step synthetic procedure (see Scheme 3-4 on page 55).

The m:n ratios of the copolymers and the alkyl chains used are summarised in Table 3-1 on page 57.

### 3.2.2 Monomer Synthesis

3,6-Bis(5-bromothien-2-yl)-2,5-di-N-alkylpyrrolo[3,4-c]pyrrole-1,4-dione\textsuperscript{108} (M\textsubscript{1}) and 2,5-bis(trimethylstannyl)thiophene\textsuperscript{109} (M\textsubscript{3}) were synthesised according to literature procedures. The dodecyl- and 2-ethylhexyl-substituted DPP monomers were synthesised by Dr. Prashant Sonar. The synthetic route for M\textsubscript{1} is illustrated in Scheme 3-2 below. Firstly, diisopropyl succinate was condensed with 2-thiophenecarbonitrile in the presence of a strong base. The resulting dithienyl-DPP compound was then alkylated with the desired alkyl bromide in the presence of potassium carbonate and dimethylformamide. The alkylated DPP was then brominated with bromine in chloroform to afford M\textsubscript{1}. 

---

54
Scheme 3-3: Synthetic route of 3,6-bis(5-bromothien-2-yl)-2,5-di-N-alkylpyrrolo[3,4-c]pyrrole-1,4-dione (M1).

2,6-Dibromo-3,5-dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene (M2) was synthesised from 3-bromo-6-pentadecyl-thieno[3,2-b]thiophene\(^1\) in 6 steps (Scheme 3-3) with an overall yield of 29%. First, 3-bromo-6-pentadecyl-thieno[3,2-b]thiophene (1) was lithiated with lithium diisopropylamide (LDA) and quenched with hexadecanal. The resulting alcohol (2) was oxidised to the corresponding ketone (3) using chromic acid. Compound 3 was then reacted with ethyl thioglycolate to form the ester 4, followed by hydrolysis with sodium hydroxide in ethanol. Decarboxylation of the dithienothiophene carboxylic acid (5) by copper/quinoline and subsequent bromination of the dithienothiophene (6) by N-bromosuccinimide (NBS) afforded the desired compound M2.

Scheme 3-4: Synthetic route of 2,6-dibromo-3,5-dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene (M8) in 6 steps from 3-bromo-6-pentadecyl-thieno[3,2-b]thiophene, with an overall yield of 29%.
3.2.3 Polymer Synthesis

The polymerisation reactions were carried out under Stille coupling conditions. **Copolymers 1 to 4** (see Table 3-1 on following page), which were relatively insoluble, were subjected to soxhlet extraction with ethanol and hexanes, following which the remaining polymers were removed from the extraction thimble, dissolved in hot chlorobenzene, and precipitated into methanol to obtain the final polymers in yields of 75 % to 96 %. **Copolymer 5** was more soluble, hence soxhlet extraction was continued with chloroform and chlorobenzene. **Copolymer 5** was then obtained by concentrating and precipitating the chlorobenzene fraction into methanol. **Copolymer 6**, being soluble in hot chloroform, was obtained by soxhlet extraction with chloroform. GPC analysis using chlorobenzene as the eluent showed that the polymers had moderate to high number-averaged molecular weights of between 15 to 78 kg/mol.

The composition and alkyl substituents of all the polymers are summarised in Table 3-1 below. NMR and elemental analyses were carried out on the polymers to verify that the composition of the polymers corresponded with the monomer feed ratios. The NMR spectra of the copolymers are shown in Section 2.7 at the end of this chapter. The peak at ca 7.2 ppm, which was attributed to the protons on the bridging thiophene ring, increased accordingly as the m/n ratio changed from 1:1 to 1:2 to 1:3. The elemental analyses on the polymers (Table 3-1) also show a decrease in the nitrogen content of the polymers and an increase in the carbon content as the proportion of the DPP units decrease, which is consistent with the calculated values.
Table 3-1: Summary of monomer feed ratios and N-alkyl substituents for Copolymers 1 to 6 and the corresponding calculated and experimental carbon and nitrogen contents. The results show that the compositions of the polymers correspond with the monomer feed ratio.

<table>
<thead>
<tr>
<th>Polymer #</th>
<th>m/n</th>
<th>R</th>
<th>C, N content (calculated) (%)</th>
<th>C, N content (experimental) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer 1</td>
<td>1:1</td>
<td>C_{12}H_{25}</td>
<td>71.23, 1.98</td>
<td>71.20, 1.90</td>
</tr>
<tr>
<td>Copolymer 2</td>
<td>1:2</td>
<td>C_{12}H_{25}</td>
<td>71.60, 1.33</td>
<td>71.83, 1.37</td>
</tr>
<tr>
<td>Copolymer 3</td>
<td>1:3</td>
<td>C_{12}H_{25}</td>
<td>71.79, 1.00</td>
<td>71.41, 1.02</td>
</tr>
<tr>
<td>Copolymer 4</td>
<td>1:2</td>
<td>2-ethylhexyl</td>
<td>70.82, 1.40</td>
<td>70.32, 1.38</td>
</tr>
<tr>
<td>Copolymer 5</td>
<td>1:2</td>
<td>2-butyloctyl</td>
<td>71.60, 1.33</td>
<td>71.95, 1.37</td>
</tr>
<tr>
<td>Copolymer 6</td>
<td>1:2</td>
<td>2-octyldodecyl</td>
<td>72.95, 1.20</td>
<td>72.65, 1.20</td>
</tr>
</tbody>
</table>

3.3 Polymer Characterisation

3.3.1 Absorption properties

The absorption spectra for Copolymers 1-3 are shown in Figure 3-1. Two distinct absorption peaks were observed, which can be attributed to the $\pi-\pi^*$ transition of the dithienothiophene segment (short wavelength region) and the $\pi-\pi^*$ transition segment of the diketopyrrolopyrrole segment (long wavelength region). The solution and film spectra were similar, although the absorbance of all the polymers at short wavelengths was enhanced in the film. When the ratio of the dithienothiophene units in the
polymer was increased, absorbance at the short wavelength region increased relative to that of the long wavelength region. In the 1:2 polymer, the absorption in the short wavelength region and the long wavelength region were almost equal; further increases in the DTT content caused the absorption in the short wavelength region to exceed that in the long wavelength region.

Changes in the polymer absorption spectrum due to changes in composition have previously been observed in donor-acceptor fluorene-based copolymers. In these polymers, increasing the acceptor content resulted in an increase in the absorption at long wavelengths.\textsuperscript{53}

The optical band-gaps of \textbf{Copolymers 1-3} were determined from their absorption onsets. \textbf{Copolymer 1} had an absorption onset in the near infra-red region of around 910 nm, which corresponded to a band-gap of 1.37 eV. \textbf{Copolymers 2} and \textbf{3} had slightly larger band-gaps of 1.40 eV and 1.45 eV respectively. It can be seen that the band-gap of the polymer increased as the DPP content in the polymer decreased. This can be attributed to the reduced ratio of the electron-accepting (DPP) units to the electron donating (DTT and thiophene) units, which weakened the band-gap lowering from the donor-acceptor effect.

We note that PBTDTT-15 has a band-gap of ca. 1.93 eV, and an absorption onset of ca. 640 nm.\textsuperscript{107} Thus, compared with PBTDTT-15, the band-gaps of \textbf{Copolymers 1-3} are 0.48 to 0.56 eV lower. The absorption onsets of \textbf{Copolymers 1-3} are also red-shifted by around 215 to 270 nm compared to PBTDTT-15, indicating that these polymers have greater potential for photon-harvesting.

Photoluminescence spectroscopy was performed on the polymers. No photoluminescence peak was observed, which may be due to the limitations of the spectrometer used.
3.3.2 Thermal Characterisation

Figure 3-2: TGA scans of Copolymers 1 to 6. The samples were heated at 10 °C/min from room temperature to 800 °C and the weight losses were recorded. The 5 % weight loss temperature was taken to be the sample's decomposition temperature.

a) Copolymer 5

b) Copolymer 6

Figure 3-3: DSC scans of a) Copolymer 5 and b) Copolymer 6 showing their melting and recrystallisation peaks. The samples were heated from room temperature to 300 °C and back to room temperature at a ramp rate of 10 °C/min.

All of the copolymers exhibited excellent thermal stability with 5 % weight loss temperatures between 370 and 420 °C. By comparing the 5 % weight loss temperatures of Copolymers 2, 4, 5 and 6 (Figure 3-2), it can be observed that the thermal stability of the polymers decreased slightly as the bulk of the alkyl chains
increased. DSC scans on the **Copolymers 1** to **4** revealed no clear thermal transitions from room temperature to 350 °C. **Copolymers 5** and **6**, however, had sharp melting peaks of 284 °C and 258 °C respectively (Figure 3-3). We note that the melting point of the polymer appears to decrease when the length of the alkyl substituent increases; this could be because the bulkier alkyl chains caused a reduction in the main-chain interactions of the polymer film.

### 3.3.3 Electrochemical characterisation

Cyclic voltammetry was carried out on the copolymers according to the procedure described in Section 2.5.3. The polymers had very similar oxidation onsets of around 0.35-0.45 V vs Fc/Fc⁺ (see Figure 3-4) which translates to HOMO levels of between -5.15 eV and -5.25 eV. The polymer with the deepest HOMO level was **Copolymer 1** (m:n = 1:1) at -5.25 eV; increasing the DTT content caused the HOMO level to increase marginally to -5.24 eV for **Copolymer 2** (m:n = 1:2) and -5.19 eV for **Copolymer 3** (m:n = 1:3). **Copolymers 4** to **6** had HOMO levels of between -5.15 to -5.18 eV, which was slightly higher than that of **Copolymer 2**.
Figure 3-4: Cyclic voltammograms of thin films of Copolymers 1 to 6. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocenium couple was used as an internal reference and the oxidation onsets were used to calculate the HOMO values of the polymers.

3.4 OPV Characterisation

3.4.1 Comparing the performances of copolymers with different m:n ratios

The OPV characterisation work described in this section was performed by Dr. Ging-Meng Ng and Dr. Siew-Lay Lim. Solar cells with the structure of
ITO/PEDOT:PSS/Polymer:PCBM blend/Ca/Ag were fabricated from blends of Copolymers 1, 2 and 3 and PC$_{61}$BM according to the procedure described in Section 2.5.4 (page 48). Polymer:PCBM weight ratios ranging from 1:1 to 1:5 were used. The spin rate used was 1000 rpm, which resulted in active layer thicknesses of around 150 nm. The devices were not annealed. The results are shown in Figure 3-5 and Tables 3-2, 3-3 and 3-4.

Figure 3-5: Current-voltage characteristics of PDPP-T-DTT:PC$_{61}$BM solar cells. Polymer:PCBM ratios of 1:1, 1:2, 1:4 and 1:5 were tested. The device structure was ITO/PEDOT:PSS/Polymer:PCBM blend/Ca/Ag and the device active area was 0.09 cm$^2$.

<table>
<thead>
<tr>
<th>Copolymer 1:PC$_{61}$BM</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>5.54</td>
<td>0.52</td>
<td>48.93</td>
<td>1.40</td>
</tr>
<tr>
<td>1:2</td>
<td>8.10</td>
<td>0.49</td>
<td>39.83</td>
<td>1.59</td>
</tr>
<tr>
<td>1:4</td>
<td>8.71</td>
<td>0.48</td>
<td>49.33</td>
<td>2.06</td>
</tr>
<tr>
<td>1:5</td>
<td>7.35</td>
<td>0.50</td>
<td>47.58</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 3-2: Device parameters of Copolymer 1:PC$_{61}$BM solar cells
Table 3-3: Device parameters of Copolymer 2:PC$_{61}$BM solar cells

<table>
<thead>
<tr>
<th>Copolymer 2:PC$_{61}$BM</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>9.55</td>
<td>0.55</td>
<td>60.55</td>
<td>3.20</td>
</tr>
<tr>
<td>1:2</td>
<td>10.93</td>
<td>0.54</td>
<td>61.00</td>
<td>3.58</td>
</tr>
<tr>
<td>1:4</td>
<td>9.90</td>
<td>0.52</td>
<td>63.22</td>
<td>3.24</td>
</tr>
<tr>
<td>1:5</td>
<td>11.28</td>
<td>0.51</td>
<td>59.25</td>
<td>3.44</td>
</tr>
</tbody>
</table>

Table 3-4: Device parameters of Copolymer 3:PC$_{61}$BM solar cells

<table>
<thead>
<tr>
<th>Copolymer 3:PC$_{61}$BM</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>10.17</td>
<td>0.54</td>
<td>56.21</td>
<td>3.06</td>
</tr>
<tr>
<td>1:2</td>
<td>8.67</td>
<td>0.52</td>
<td>60.96</td>
<td>2.77</td>
</tr>
<tr>
<td>1:4</td>
<td>11.24</td>
<td>0.53</td>
<td>46.52</td>
<td>2.75</td>
</tr>
<tr>
<td>1:5</td>
<td>11.69</td>
<td>0.52</td>
<td>41.81</td>
<td>2.54</td>
</tr>
</tbody>
</table>

From the results, it can be seen that the highest PCE for **Copolymer 1** was 2.06 %, that of **Copolymer 2** was 3.58 %, and that of **Copolymer 3** was 3.06 %. The best ratio of polymer to PCBM varied between the polymers, with **Copolymer 1** requiring a 1:4 ratio, **Copolymer 2** a 1:2 ratio and **Copolymer 3** a 1:1 ratio.

The open circuit voltages for these cells ranged between 0.48 to 0.55 V, which is lower than that of P3HT-PC$_{61}$BM cells. For all 3 polymers, it was observed that an increase in the PC$_{61}$BM content resulted in a slight decrease in the V$_{oc}$. This has previously been observed for other donor polymers, such as MDMO-PPV, AFPO3$^{111}$, P3HTV$^{112}$ and PF10TBT$^{113}$. For the PF10TBT and PCBM blends, it was shown that the reduction in the V$_{oc}$ correlated with the decrease in the energy of the charge transfer (CT) states with increasing PCBM concentrations. Both of these phenomena were attributed to the higher relative permittivity of PCBM compared to that of PF10TBT.$^{113}$
For **Copolymer 2**, substituting PC$_{71}$BM for PC$_{61}$BM resulted in a device with $J_{sc}$ of 12.91 mA/cm$^2$, $V_{oc}$ of 0.50 V, FF of 58.41% and PCE of 3.81%. The increase in PCE was due to an increase in the $J_{sc}$ (12.91 mA/cm$^2$ vs 10.93 mA/cm$^2$), which can be attributed to the better absorption properties of PC$_{71}$BM compared to PC$_{61}$BM.$^{114}$

### 3.4.2 Comparing the performances of copolymers with different alkyl substituents

In the previous section, we observed that **Copolymer 2** (m:n = 1:2) gave the best results among the three copolymers. **Copolymers 4, 5 and 6** were synthesised with different N-alkyl substituents (2-ethylhexyl, 2-butyloctyl and 2-octyldodecyl respectively) with the same 1:2 ratio in order to improve the processability of the polymer. It was observed that the solubility of **Copolymer 4** was poorer than that of **Copolymer 2**. However, the solubility of **Copolymers 5 and 6** were improved compared with **Copolymer 2**.

**Copolymers 4, 5 and 6** were tested in solar cells utilising a 1:2 weight ratio blend of polymer to PC$_{71}$BM, and the results are shown in Figure 3-6 and Table 3-5 below.

**Figure 3-6**: Current-Voltage characteristics of solar cells made from 1:2 blends of Copolymers 2 (R = dodecyl), 4 (R = 2-ethylhexyl), 5 (R = 2-butyloctyl) and 6 (R = 2-octyldodecyl) and PC$_{71}$BM.
Comparing the performances of all the polymers in combination with PC$_{61}$BM, it is observed that cells with Copolymer 4 had a lower PCE (3.07 %) than those with Copolymer 2 (3.58 %). This could be attributed largely to a drop in the fill factor of these devices, which we believe is due to reduced film quality stemming from its poorer solubility. Cells utilising Copolymer 5 had a slightly higher $J_{sc}$, $V_{oc}$ and FF than those of the Copolymer 2, resulting in an improved PCE of 4.39 %. As with Copolymer 2, the substitution of PC$_{71}$BM for PC$_{61}$BM resulted in higher $J_{sc}$ values and improved PCEs of 3.79 % and 4.85 % for Copolymers 4 and 5 respectively.

Although Copolymer 6 was much more soluble than their counterparts with shorter alkyl chains, the performance of this polymer in OPVs was much poorer.

AFM studies of the Copolymer 5:PC$_{71}$BM and Copolymer 6:PC$_{71}$BM devices (Figure 3-7) revealed the cause of the poor performance for Copolymer 6. It was observed that the domains of the Copolymer 6:PC$_{71}$BM film were at least 50 nm in size. Such large domain sizes are detrimental for charge separation as there is a greater likelihood of excitons recombining before they reach an interface where charge separation can take place. The domains for the Copolymer 5:PC$_{71}$BM film

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer 4:PC$_{61}$BM</td>
<td>10.82</td>
<td>0.55</td>
<td>51.61</td>
<td>3.07</td>
</tr>
<tr>
<td>Copolymer 4:PC$_{71}$BM</td>
<td>13.75</td>
<td>0.55</td>
<td>50.33</td>
<td>3.79</td>
</tr>
<tr>
<td>Copolymer 5:PC$_{61}$BM</td>
<td>11.55</td>
<td>0.57</td>
<td>67.21</td>
<td>4.39</td>
</tr>
<tr>
<td>Copolymer 5:PC$_{71}$BM</td>
<td>12.90</td>
<td>0.56</td>
<td>67.07</td>
<td>4.85</td>
</tr>
<tr>
<td>Copolymer 6:PC$_{71}$BM</td>
<td>3.30</td>
<td>0.59</td>
<td>62.07</td>
<td>1.21</td>
</tr>
</tbody>
</table>

Table 3-5: Device parameters of 1:2 blends of Copolymers 4 and 5 with PC$_{61}$BM and PC$_{71}$BM.
were much smaller at around 20 nm, leading to much better charge separation and a higher short circuit current.

Figure 3-7: a) Height and phase AFM images of Copolymer 5:PC71BM film b) Height and phase AFM images of Copolymer 6:PC71BM film
3.5 **TFT characterisation**

The TFT characterisation work described here was performed by Dr. Huei-Shuan Tan. Top-contact TFT devices were fabricated from **Copolymer 5** in order to investigate its charge transport properties. Each device consisted of a polymer semiconductor layer that was spin-coated onto a heavily n-doped silicon wafer substrate with 220 nm of surface oxide as the gate dielectric. Gold was used as the top electrode. The devices had a 120 µm channel length (L) and a 4 mm channel width (W). The TFT, which was annealed at 160 °C for 30 min, showed p-type transport, with saturation hole mobility of about $8.7 \times 10^{-3}$ cm$^2$/Vs and an on/off ratio of $1.7 \times 10^5$. The hole mobility is about an order of magnitude lower than that of PBTDTT-15 ($0.05 - 0.06$ cm$^2$/Vs),$^{107}$ which is likely to be due to the reduced ordering of the random **Copolymer 5** compared to the alternating copolymer PBTDTT-15.

![Figure 3-8](image.png)

**Figure 3-8:** Output (a) and transfer characteristics (b) of a top contact TFT made from Copolymer 5. This device had a width of 4 mm and a length of 120 µm.

3.6 **Conclusion**

A series of low band-gap random copolymers incorporating the diketopyrrolopyrole and dithienothiophene units with the thiophene unit as a bridge was synthesised with good yields of above 75 %. Copolymers with DPP:DTT ratios of 1:1, 1:2 and 1:3
were investigated. These polymers had absorption onsets that were 215 to 270 nm higher than that of non-DPP polymer PBDTTT-15 (640 nm), which translates to optical band-gaps that were 0.48 to 0.56 eV lower than of PBDTTT-15 (1.93 eV).\(^{107}\)

It was found that polymers with a 1:2 ratio of DPP to DTT gave the best solar cell performance, with **Copolymer 2:**PC\(_{71}\)BM cells achieving a PCE of 3.81 %. By using 2-butyloctyl chains instead of n-dodecyl chains on the DPP moiety, the solubility and processability of the polymer could be improved, leading to better solar cell performances of up to 4.85 % for **Copolymer 5:**PC\(_{71}\)BM blends. Although the use of the bulkier 2-octyldecyl chains resulted in even better polymer solubility, it also resulted in larger domain sizes when the polymer was blended with PCBM, thus leading to a decrease in solar cell PCE.

The improvement of the polymers’ absorption characteristics has helped to raise the maximum efficiency of solar cells utilising donor polymers based on DTT from 3.2 %\(^{107}\) to 4.85 %. We note that the open circuit voltages of these cells were below 0.6 V, which could be a limitation on the performance of these cells. Thus, increasing the \(V_{oc}\) of these cells could be the key to achieving increased power conversion efficiencies. To increase the \(V_{oc}\), it may be necessary to decrease the HOMO level of the polymers. In the following chapter, we describe the synthesis and characterisation of a series of copolymers based on fluorene and DPP that have been designed to achieve higher open circuit voltages.

3.7 Experimental Section

3,6-Bis(5-bromothien-2-yl)-2,5-di-\(N\)-alkylpyrrolo[3,4-\(c\)]pyrrole-1,4-dione (M1) was synthesised as purple solids using a literature method\(^{108}\) with four different alkyl substituents – n-dodecyl, 2-ethylhexyl, 2-butyloctyl and 2-octyldecyl – with an overall yield of 35 - 40 %.

3,6-Bis(5-bromothien-2-yl)-2,5-di-N-dodecylpyrrolo[3,4-\(c\)]pyrrole-1,4-dione (M1a)

\(^1\)H NMR (CDCl₃, 400 MHz, ppm) δ 8.61 (d, 2H, \(J = 4.4\) Hz), 7.23 (d, 2H, \(J = 4.4\) Hz), 3.93 (t, 4H, \(J = 7.6\) Hz), 1.71 (s, 4H), 1.29-1.22 (m, 36H), 0.85 (t, 6H).
3,6-Bis(5-bromothien-2-yl)-2,5-di-N-(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (M1b)

$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 8.62 (d, 2H, $J = 4.0$ Hz), 7.22 (d, 2H, $J = 4.4$ Hz), 3.93 (d, 4H, $J = 8.0$ Hz), 1.88 (s, 2H), 1.29-1.22 (m, 16H), 0.89 (m, 12H).

3,6-Bis(5-bromothien-2-yl)-2,5-di-N-(2-butyloctyl)pyrrolo[3,4-c]pyrrole-1,4-dione (M1c)

$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 8.61 (d, 2H, $J = 4.4$ Hz), 7.23 (d, 2H, $J = 4.4$ Hz), 3.93 (d, 4H, $J = 7.6$ Hz), 1.88 (s, 2H), 1.29-1.22 (m, 32H), 0.85 (m, 12H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 161.4, 139.4, 135.2, 131.4, 131.2, 118.9, 108.1, 46.4, 37.8, 31.7, 31.2, 30.9, 29.6, 28.4, 26.2, 23.0, 22.6, 14.0, 13.9.

3,6-Bis(5-bromothien-2-yl)-2,5-di-N-(2-octydodecyl)pyrrolo[3,4-c]pyrrole-1,4-dione (M1d)

$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 8.62 (d, 2H, $J = 4.0$ Hz), 7.22 (d, 2H, $J = 4.4$ Hz), 3.93 (d, 4H, $J = 8.0$ Hz), 1.88 (s, 2H), 1.29-1.22 (m, 64H), 0.89 (m, 12H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 161.4, 139.4, 135.2, 131.4, 131.2, 118.9, 108.1, 46.4, 37.8, 31.9, 31.9, 31.3, 30.0, 29.6, 29.5, 29.5, 29.3, 29.2, 26.2, 22.7, 22.6, 14.0.

3-Bromo-6-pentadecyl-thieno[3,2-b]thiophene (1) was prepared according to a literature procedure.$^{110}$

1-(3-Bromo-6-pentadecyl-thieno[3,2-b]thiophen-2-yl)-pentadecan-1-ol (2): Lithium diisopropylamide solution (15 mL, 0.03 mol, 2 M in tetrahydrofuran) was added dropwise to a solution of 6-bromo-3-pentadecylthieno[3,2-b]thiophene (10.8 g, 0.025 mol) in THF (150 mL) in an ice bath and stirred for 2 h, then the reaction was quenched by hexadecyl aldehyde (6 g, 0.025 mol). The mixture was stirred overnight and quenched with water. After evaporating most of the THF, 150 mL methylene chloride was added and the mixture was washed with brine (2 x 100 mL), water (100 mL) and dried over anhydrous magnesium sulphate. The product was obtained by column chromatography on silica gel, eluting with 2% ethyl acetate in hexane (14.5 g, 86 % yield).
1H NMR (CDCl₃, 400 MHz, ppm) δ 6.99 (s, 1H), 5.11 (m, 1H), 2.68 (t, 2H, $J = 7.6$ Hz), 1.88 (m, 2H), 1.72 (m, 2H), 1.26 (m, 50H), 0.88 (t, 6H, $J = 6.8$ Hz).

1-(3-Bromo-6pentadecyl-thieno[3,2-b]thiophen-2-yl)-pentadecan-1-one (3): 4.5 g of sodium dichromate dihydrate (0.015 mol) was dissolved in a mixture of 6 g concentrated sulfuric acid and 60 mL water. This chromic acid solution was then added dropwise at room temperature into a solution of compound 2 (13.2 g, 0.02 mol) in acetone (300 mL) and stirred overnight. After evaporating off most of the acetone, 200 mL water was added, and the solid was collected by filtration. The product was obtained by column chromatography on silica gel, eluting with 12% dichloromethane in hexane (8.4 g, 63 % yield).

1H NMR (CDCl₃, 400 MHz, ppm) δ 7.23 (s, 1H), 3.06 (t, 2H, $J = 7.6$ Hz), 2.7 (t, 2H, $J = 7.6$ Hz), 1.75 (m, 4H), 1.26 (m, 48H), 0.88 (t, 6H, $J = 6.8$ Hz).

3,5-Dipentadecyl-dithieno[3,2-b;2’,3’-d]thiophene-2-carboxylic acid ethyl ester (4): Ethyl thioglycolate (0.85 g, 0.77 mL, 7 mmol) was added to a mixture of 3 (4.5 g, 6.74 mmol), potassium carbonate (K₂CO₃) (1.86 g, 13.5 mmol), and N,N-dimethylformamide (DMF) (70 mL) at room temperature. The resulting mixture was stirred for 12 h at room temperature and another 12 h at 50 °C. The mixture was then poured into an aqueous sodium chloride solution (100 mL) and extracted with ethyl acetate (150 mL). The organic layer was separated, washed with saturated aqueous sodium chloride solution (4 × 150 mL), and dried over MgSO₄. The crude product was obtained after evaporating off the solvent and used in the next step without further purification (4.2 g, 91 % yield).

1H NMR (CDCl₃, 400 MHz, ppm) δ 7.07 (s, 1H), 4.35 (q, 2H, $J = 7.2$ Hz), 3.16 (t, 2H, $J = 7.6$ Hz), 2.72 (t, 2H, $J = 7.6$), 1.75 (m, 4H), 1.40 (t, 3H, $J = 7.2$ Hz), 1.26 (m, 48H), 0.88 (t, 6H, $J = 6.8$ Hz).

3,5-Dipentadecyl-dithieno[3,2-b;2’,3’-d]thiophene-2-carboxylic acid (5): A mixture of 4 (4.2 g, 6.1 mmol) and sodium hydroxide (0.49 g, 12.2 mmol) in ethanol (80 mL) was refluxed for 6 h. The mixture was poured into water (400 mL). The pH was adjusted to 1 with aqueous 10 M HCl solution. The precipitated solid was collected by filtration and dried under vacuum. The crude product was used for the next step without any purification (3.9 g, 98% yield).
$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.10 (s, 1H), 3.18 (t, 2H, $J = 7.6$ Hz), 2.72 (t, 4H, $J = 7.6$ Hz), 1.77 (m, 4H), 1.26 (m, 48H), 0.88 (t, 6H, $J = 6.8$ Hz).

3,5-Dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene (6): Compound 5 (3.9 g, 6 mmol), copper powder (0.24 g, 3.6 mmol) and quinoline (50 mL) were heated at 250-260 °C. When no further bubbles of carbon dioxide gas could be detected (about 20 mins), the mixture was cooled to room temperature and hexane (200 mL) was added to the quinoline mixture. This mixture was washed repeatedly with dilute hydrochloric acid (1 M). The organic layer was dried over anhydrous MgSO$_4$ and the solvent was removed. Compound 6 was obtained after silica gel chromatography with hexanes as the eluent (2.37 g, 64 % yield).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 6.94 (s, 2H), 2.73 (t, 4H, $J = 7.6$ Hz), 1.77 (m, 4H), 1.26 (m, 48H), 0.88 (t, 6H, $J = 6.8$ Hz).

2,6-Dibromo-3,5-dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene (M2): A solution of N-bromosuccinimide (1.43 g, 8 mmol) in DMF (10 mL) was added dropwise into a well-stirred solution of 6 (2.35 g, 3.8 mmol) in dichloromethane (40 mL) at room temperature. The mixture was stirred for 5 h and poured into 80 mL of water, then extracted with dichloromethane (3 x 60 mL). The organic solution was combined and evaporated. The solid was dissolved in hexane and passed through a short silica gel column using hexane as an eluent. The product was obtained as white solids after recrystallisation in ethanol. (2.8 g, 95 % yield).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 2.73 (t, 4H, $J = 7.6$ Hz), 1.71 (m, 4H), 1.31 (m, 48H), 0.88 (t, 6H, $J = 6.8$ Hz).

$^{13}$C NMR (CDCl$_3$, 100 MHz, ppm) $\delta$ 138.9, 135.3, 129.1, 108.7, 31.9, 29.7, 29.7, 29.7, 29.6, 29.5, 29.3, 29.3, 29.3, 29.0, 28.1, 22.7, 22.6, 14.1.

MALDI-TOF-MS: $m/z$ calc. 774.24, obtained 773.94
Anal. calcd. for C$_{38}$H$_{62}$Br$_2$S$_3$: C, 58.90; H, 8.06; S, 12.41. Found C, 59.53; H, 8.19; S, 12.61.

2,5-Bis(trimethylstannyl)thiophene (M3) was synthesised according to a literature method with a yield of 60 %.$^{109}$

$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.38 (s, 2H), 0.37 (s, 18H).
General synthetic procedure for Copolymers 1-6: The monomers were weighed and added to a reaction vial equipped with a magnetic stirrer. The vial was then transferred to a glovebox where tris(dibenzylideneacetone)dipalladium(0) (2 mol%), tri(o-tolyl)phosphine (8 mol%) and anhydrous chlorobenzene (20 mL) were added. The vial was then stirred at 120 °C for 36 h using an oil bath. The reaction mixture was poured into 200 mL of methanol and 10mL of concentrated hydrochloric acid and stirred overnight to remove the stannylated end-groups. The subsequent purification processes depended on the solubility of the polymer. The DPP-C12 polymers, being less soluble, were washed with hexane in a soxhlet extractor overnight, following which the remaining polymer was dissolved in hot chlorobenzene and precipitated into methanol to obtain the final polymer. The polymers were subjected to soxhlet extraction with ethanol and hexanes for 24 h each. The polymers with R = C_{12}H_{25}, which had poor solubility, were then dissolved in hot chlorobenzene, precipitated into methanol and filtered to obtain the final product. All other polymers were subject to soxhlet extraction with chloroform and chlorobenzene (if necessary), precipitated into methanol and filtered to obtained the final product.

Copolymer 1: The title compound (80 mg, 75 % yield)was obtained as black solids. 
\(^1^H\) NMR (1,1,2,2-tetrachloroethane-d4, 400 MHz, 120 °C) δ 8.85 (s, 2H), 7.43-7.25 (m, 6H), 4.17 (s, 4H), 3.08 (s, 4H), 1.95-1.93 (m, 8H), 1.58-1.38 (m, 84H), 0.98-0.96 (m, 12H) 
M_n: 15.7 kg/mol, PDI: 3.44 
Anal. calcd. for C_{84}H_{122}N_2O_2S_7: C, 71.23; H, 8.68; N, 1.98. Found C, 71.20; H, 8.57; N, 1.90.
Figure 3-9: $^1$H NMR spectrum of Copolymer 1 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.
Copolymer 2: The title compound (128 mg, 96 % yield) was obtained in as black solids.

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 120 °C) $\delta$ 8.87 (s, 2H), 7.44-7.17 (m, 10H), 4.18 (s, 4H), 3.08 (s, 8H), 1.94 (m, 12H), 1.57-1.38 (m, 132H), 0.98-0.96 (m, 18H)

$M_n$: 26.7 kg/mol, PDI: 2.65

Anal. calcd. for C$_{126}$H$_{186}$N$_2$O$_2$S$_{11}$: C, 71.60; H, 8.87; N, 1.33. Found C, 71.83; H, 8.81; N, 1.37.

Figure 3-10: $^1$H NMR Spectrum of Copolymer 2 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.
**Copolymer 3:** The title compound (170 mg, 96 % yield) was obtained as black solids. 

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 120 °C) δ 8.87 (s, 2H), 7.43-7.25 (m, 14H), 4.18 (s, 4H), 3.08 (s, 12H), 1.95 (m, 16H), 1.57-1.38 (m, 180H), 0.97 (m, 24H)

$M_n$: 55.4 kg/mol, PDI: 1.40

Anal. calcd. for $C_{168}H_{250}N_2O_2S_{15}$: C, 71.79; H, 8.96; N, 1.00. Found C, 71.41; H, 8.96; N, 1.02.

**Figure 3-11:** $^1$H NMR Spectrum of Copolymer 3 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.

**Copolymer 4:** The title compound (199 mg, 82 % yield) was obtained from the chlorobenzene fraction as black solids.

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 120 °C) δ 8.87 (s, 2H), 7.43-7.25 (m, 10H), 4.12 (s, 4H), 3.07 (s, 8H), 2.03-1.94 (m, 12H), 1.56-1.32 (m, 48H), 1.02-0.97 (m, 24H)

$M_n$: 17.7 kg/mol, PDI: 10.3
Anal. calcd. for C\textsubscript{118}H\textsubscript{170}N\textsubscript{2}O\textsubscript{2}S\textsubscript{11}: C, 70.82; H, 8.56; N, 1.40. Found C, 70.32; H, 8.40; N, 1.38.

Figure 3-12: \textsuperscript{1}H NMR Spectrum of Copolymer 4 in 1,1,2,2-tetrachloroethane-d2. The asterisk denotes the solvent peak.

Copolymer 5: The title compound was obtained in two fractions as black solids. Chloroform fraction: 87 mg (29 % yield); chlorobenzene fraction: 194 mg (65 % yield); total yield 94 %.

\textsuperscript{1}H NMR (1,1,2,2-tetrachloroethane-d4, 400 MHz, 120 °C) \(\delta\) 8.85 (s, 2H), 7.42-7.26 (m, 10H), 4.11 (s, 4H), 3.06 (s, 8H), 2.08-1.94 (m, 12H), 1.56-1.26 (m, 64H), 0.97-0.95 (m, 24H)

M\textsubscript{n}: 52.4 kg/mol, PDI: 1.44

Anal. calcd. for C\textsubscript{126}H\textsubscript{186}N\textsubscript{2}O\textsubscript{2}S\textsubscript{11}: C, 71.60; H, 8.87; N, 1.33. Found C, 71.95; H, 8.89; N, 1.37.
Figure 3-13: $^1$H NMR Spectrum of Copolymer 5 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.

**Copolymer 6**: The title compound (310 mg, 93%) was obtained from the chloroform fraction as black solids.

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 120°C) δ 8.86 (s, 2H), 7.42-7.25 (m, 10H), 4.12 (s, 4H), 3.07 (s, 8H), 2.08-1.94 (m, 12H), 1.56-1.32 (m, 96H), 0.95 (m, 24H)

$M_n$: 77.8 kg/mol, PDI: 4.71

Anal. calcd. for $C_{142}H_{218}N_2O_2S_{11}$: C, 72.95; H, 9.40; N, 1.20. Found C, 72.65; H, 9.35; N, 1.20.
Figure 3-14: $^1$H NMR Spectrum of Copolymer 6 in 1,1,2,2-tetrachloroethane-$d_2$. The asterisk denotes the solvent peak.
Chapter 4: Energy Level Tuning For DPP-based polymers

4.1 Introduction

In the previous chapter, we described the synthesis and characterisation of a series of diketopyrrolopyrrole-dithienothiophene polymers and their application in solar cells. One of the limitations of the cells was the low open circuit voltages achieved. It has been established that the $V_{oc}$ is related to the difference between the HOMO level of the donor material and the LUMO level of the acceptor material. Thus, the lowering of the HOMO level of the donor material can be an effective way to increase the $V_{oc}$ of the solar cells. In this chapter, we describe the synthesis and characterisation of a series of polymers that have been designed with the aim of achieving lower HOMO levels and thus higher solar cell $V_{oc}$.

4.2 Polymer Design and Synthesis

Fluorene-based polymers generally have lower HOMO energy levels than thiophene-based polymers. Thus, replacing the dithienothiophene moiety with the fluorene moiety is expected to lead to lowered HOMO levels.

Three polymers incorporating the dialkylfluorene, dithienylketopyrrole and oligothiophene units were designed. The polymers were random copolymers similar to those described in Chapter 3. The oligothiophene bridging segment ranged in length from one to three thiophene units, and this allowed us to study the effects of the chemical structure on the material properties and device performance.

2,7-Dibromo-9,9-didecylfluorene (M4) was synthesised by alkylating 2,7-dibromofluorene according to a literature method. The bis-stannylated oligothiophenes M5 and M6 were synthesised from 2,2-bithiophene and 2,2':5',2"-terthiophene, respectively, by lithiation with n-butyllithium and subsequent quenching with trimethyltin chloride according to the same procedure used to synthesise M3.
The polymers were synthesised via Stille coupling (Scheme 4-1) and purified by soxhlet extraction with hexane, chloroform and chlorobenzene where necessary. Moderate number-averaged molecular weights of between 15 and 25 kg/mol were obtained, and the yields of the polymers were between 68 % and 82 %.

Scheme 4-1: Synthetic route of PF-mT-DPP polymers
4.3 Polymer Characterisation

4.3.1 Optical Characterisation

The UV-Visible spectra for the polymers in chlorobenzene solution and in thin film are shown in Figure 4-1.

The absorbances in the solution and film samples were very similar, though the peaks at longer wavelengths were broader in the film than in solution. Also, as was the case with Copolymers 1-3, the absorption peaks at shorter wavelengths were enhanced (relative to the longer wavelength peaks) in the film.

From the absorption onsets of the polymers, the optical band-gaps of PF-T-DPP, PF-2T-DPP and PF-3T-DPP were determined to be 1.40 eV, 1.47 eV and 1.50 eV respectively. The optical band-gap increased slightly as the number of bridging thiophene units increased. This can be attributed to the reduced ratio of the electron-accepting (DPP) units to the electron donating (fluorene and thiophene) units, leading to reduced band-gap lowering from the donor-acceptor effect. The absorbance in the low wavelength region (400 to 500 nm) also increased with an increase in the number of thiophene units.

![Figure 4-1](image-url): (a) Solution and (b) Film absorption spectra for the PF-mT-DPP polymers. The spectra were normalised to the absorption peak around 680 nm.
4.3.2 Thermal Characterisation

![TGA scans of PF-mT-DPP polymers](image)

Figure 4-2: TGA scans of PF-mT-DPP polymers. The samples were heated at 10 °C/min from room temperature to 800 °C and the weight losses were recorded. The 5% weight loss temperature was taken to be the sample’s decomposition temperature.

All three polymers exhibited excellent thermal stability, with PF-T-DPP, PF-2T-DPP and PF-3T-DPP having 5% weight loss temperatures of 395 °C, 391 °C and 385 °C respectively (Figure 4-3). DSC scans on these polymers did not reveal any clear thermal transitions even upon heating to 350 °C.

4.3.3 Electrochemical Characterisation

Cyclic voltammery was carried out on the copolymers according to the procedure described in Section 2.5.3. The oxidation onsets for PF-T-DPP, PF-2T-DPP and PF-3T-DPP vs. Fc/Fc+ were 0.46 V, 0.57 V and 0.48 V respectively, which corresponded to HOMO levels of -5.26 eV, -5.37 eV and -5.28 eV for these polymers. These HOMO levels were lower than those of Copolymers 1 to 6 (see section 3.3.3 on page 60). In particular, the HOMO levels were 0.11 eV to 0.22 eV lower than that of the best performing polymer, Copolymer 5. The introduction of the fluorene unit into the polymer structure thus successfully lowered the HOMO levels of the copolymers.
Figure 4-3: Cyclic voltammetry measurements for thin-films of PF-mT-DPP polymers. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocenium couple was used as an internal reference and the oxidation onsets were used to calculate the HOMO values of the polymers.

4.4 **OPV Characterisation**

The OPV characterisation work in this section was performed by Ms. Hoi-Ka Wong. 1:1 blends of the **PF-mT-DPP** polymers and PC$_{71}$BM were tested in solar cell devices with the structure ITO/PEDOT:PSS/PC$_{71}$BM/PC$_{71}$BM/Ca/Ag. The concentration of the polymers in the blend solutions was 8 mg/ml and the spin rate used was 500 rpm. Due to the poor solubility of **PF-3T-DPP**, the solution had to be heated to 80 °C compared with 40 °C for the other solutions prior to spin-coating to prevent gelation.

The devices showed very poor performance compared with the copolymers in the previous chapter. J$_{sc}$ values of below 4 mA/cm$^2$ were obtained for all the cells, which
is less than a third of the 12.90 mA/cm$^2$ obtained for Copolymer 5. The fill factors of these cells were also low at around 44 % for PF-T-DPP and PF-2T-DPP. The PF-3T-DPP cells had an even lower FF of around 22 %, due to the large thickness of the film (235 nm), which led to poor charge extraction. Under the same spin-coating conditions, the PF-3T-DPP:PC$_{71}$BM films were about twice as thick as the films fabricated from the other two blends; this was due to the higher viscosity of the PF-3T-DPP:PC$_{71}$BM solution compared to the others.

![Figure 4-4: Current-Voltage characteristics of solar cells made from 1:1 blends of PF-mT-DPP polymers and PC$_{71}$BM. The device structure was ITO/PEDOT:PSS/PF-mT-DPP:PCBM/Ca/Ag.](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-T-DPP</td>
<td>3.12</td>
<td>0.70</td>
<td>43.5</td>
<td>0.94</td>
<td>90</td>
</tr>
<tr>
<td>PF-2T-DPP</td>
<td>3.88</td>
<td>0.67</td>
<td>44.2</td>
<td>1.15</td>
<td>100</td>
</tr>
<tr>
<td>PF-3T-DPP</td>
<td>2.29</td>
<td>0.58</td>
<td>22.3</td>
<td>0.30</td>
<td>235</td>
</tr>
</tbody>
</table>

Table 4-1: Device parameters for solar cells made from 1:1 blends of PF-mT-DPP and PC$_{71}$BM.
We compared the solar cell performances of our polymers with alternating fluorene-DPP copolymers that have recently been reported in the literature. These polymers, PDPP-F, PF-DTDPP and PFDPP2T, also yielded relatively low $J_{sc}$ (below 3 mA/cm$^2$) and PCE (below 1 %) values when applied in solar cells. Zoombelt et. al carried out AFM studies on the active layers of the solar cells, and concluded that the morphologies of the blend films were not optimal. Large scale phase separation on the order of hundreds of nanometers were observed for the PFDPP2T-a and PFDPP2T-b blends, which was attributed to the different solubilities between the polymers and PC$_{61}$BM in the solvent which is used for processing the blends.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Blend ratio</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDPP-F: PC$_{71}$BM</td>
<td>1:2</td>
<td>2.0</td>
<td>0.78</td>
<td>49.9</td>
<td>0.78</td>
<td>74</td>
</tr>
<tr>
<td>PF-DTDPP: PC$_{61}$BM</td>
<td>1:2</td>
<td>2.51</td>
<td>0.74</td>
<td>47</td>
<td>0.88</td>
<td>72</td>
</tr>
<tr>
<td>PFDPP2T-a: PC$_{61}$BM</td>
<td>1:3</td>
<td>1.84</td>
<td>0.75</td>
<td>42</td>
<td>0.6</td>
<td>117</td>
</tr>
<tr>
<td>PFDPP2T-b: PC$_{61}$BM</td>
<td>1:3</td>
<td>1.56</td>
<td>0.89</td>
<td>55</td>
<td>0.8</td>
<td>117</td>
</tr>
<tr>
<td>PFDPP2T-c: PC$_{61}$BM</td>
<td>1:4</td>
<td>2.41</td>
<td>0.91</td>
<td>41</td>
<td>0.9</td>
<td>117</td>
</tr>
</tbody>
</table>

Table 4-2: Device characteristics of fluorene-DPP polymers in the literature
Figure 4-6: AFM height and phase images of a) PF-T-DPP:PC$_{71}$BM film, b) PF-2T-DPP:PC$_{71}$BM film and c) PF-3T-DPP:PC$_{71}$BM film.
AFM studies were carried out on the PF-mT-DPP:PC_{71}BM blend films to determine if similar characteristics could be observed. The AFM images are shown in Figure 4-6 on the previous page. We observed that the roughness of our films (< 3 nm) were much less than the values reported by Zoombelt et. al (up to 30 nm). From the phase images, it was also observed that the domains were at least 40 to 50 nm in size, which likely led to inefficient charge separation and contributed to the low J_{sc}.

Finally, we observed that all the cells reported in the literature utilised blends with PCBM loadings of between 67 % and 80 %, which is higher than what we have used. Therefore, an increase in the PCBM loading could be explored during future device optimisation work.

### 4.5 TFT Characterisation

TFT characterisation was carried out by Dr. Huei-Shuan Tan and Mr. Lionel Moh. Bottom-gate, top contact TFT devices were fabricated using the three polymers according to the procedure in Section 2.5. Each device consisted of a polymer semiconductor layer that was spin-coated onto a heavily n-doped silicon wafer substrate with 220 nm of surface oxide as the gate dielectric. Gold was used as the top electrode. All the polymers exhibited only p-type behaviour and had hole mobilities on the order of 10^{-4} cm^2/Vs. The mobilities were two orders of magnitude lower than the dithienothiophene-based Copolymer 3 from the previous chapter. The on/off ratios of the devices were also relatively low, in the order of 10^3. The I_D/V_G transfer curves for each of the devices (Figure 4-7 on the following page) showed significant hysteresis, which can be attributed to charge-trapping at/near the polymer-dielectric interface.\(^\text{118}\)

The hole mobilities of the polymers were similar to, or higher than the mobilities reported by Zoombelt et. al for the PF-DPP2T series of polymers, which had hole mobilities on the order of 10^{-4} to 10^{-6} cm^2/Vs.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mobility (cm²/Vs)</th>
<th>On/Off ratio</th>
<th>Threshold voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-T-DPP</td>
<td>6.2 x 10⁻⁴</td>
<td>9 x 10⁷</td>
<td>-2.80</td>
</tr>
<tr>
<td>PF-2T-DPP</td>
<td>4.4 x 10⁻³</td>
<td>5 x 10⁷</td>
<td>-2.27</td>
</tr>
<tr>
<td>PF-3T-DPP</td>
<td>8.2 x 10⁻⁴</td>
<td>3 x 10⁷</td>
<td>-14.88</td>
</tr>
</tbody>
</table>

Table 4-3: Summary of TFT device characteristics for PF-mT-DPP polymers

Figure 4-7: Transfer curves at saturation regime for a) PF-T-DPP, b) PF-2T-DPP and c) PF-3T-DPP TFT devices
4.6 Conclusion

Three fluorene-oligothiophene-DPP polymers were designed and synthesised. The substitution of the fluorene moiety for the dithienothiophene moiety resulted in a reduction in HOMO levels, which allowed the $V_{oc}$ of the solar cells to be increased. The solubility of the polymers decreased as the number of unsubstituted bridging thiophene units were increased. This led to poor processability for PF-3T-DPP, resulting in poor solar cell performances for this polymer.

Despite achieving increased $V_{oc}$ for the PF-T-DPP and PF-2T-DPP solar cells, the performances of the cells were much lower than those of Copolymers 1 to 6 in the previous chapter. This is due to a significant reduction in the $J_{sc}$ and fill factor for these cells. One possible reason for the huge drop in performance could be the much lower hole carrier mobilities (around two orders of magnitude lower) of the fluorene-containing polymers. Another factor impacting the solar cell performance was the non-optimal morphology of the polymer:PCBM blends films. The domains were found to be over 40 nm in size, thus leading to inefficient charge separation.

4.7 Experimental Section

2,7-Dibromo-9,9-didecylfluorene (M4) was synthesised from 2,7-dibromofluorene using a literature procedure in 93% yield.\textsuperscript{116}

$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.53 (d, 2H, $J = 8.0$ Hz), 7.46-7.44 (m, 4H), 1.93-1.88 (m, 4H), 1.26-1.05 (m, 28H), 0.86 (t, 6H, $J = 6.8$ Hz), 0.58 (t, 4H).

5,5'-bis(trimethylstannyl)-2,2'-bithiophene (M5) and 5,5''-bis(trimethylstannyl)-2,2':5',2''-terthiophene (M6) were synthesized from 2,2-bithiophene and 2,2':5',2''-terthiophene, respectively, using a literature method.\textsuperscript{109}

5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (M5): Yield = 60%.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz, ppm) $\delta$ 7.29 (d, 2H, $J = 3.6$ Hz), 7.12 (d, 2H, $J = 3.6$ Hz), 0.40 (s, 18H).
5,5''-Bis(trimethylstannyl)- 2,2':5',2''-terthiophene (M6): Yield = 63 %

\(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz, ppm) \(\delta\) 7.31 (d, 2H, \(J = 3.2\) Hz), 7.13 (d, 2H, \(J = 3.6\) Hz), 7.10 (s, 2H), 0.40 (s, 18H).

**General synthetic route for PF-mT-DPP polymers:** 3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-di-(2-butyloctyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (1 equiv.), 2,7-dibromo-9,9-diocetylfluorene (1 equiv.) and the bis-stannylated thiophene compound (2 equiv.) were added to a 100 mL reaction vial. The vial was then transferred to a glovebox where tris(dibenzylideneacetone)dipalladium(0) (4 mol%), tri(o-tolyl)phosphine (16 mol%) and anhydrous chlorobenzene (15 mL) were added. The vial was then heated at 120°C for 36 hours using an oil bath. The reaction mixture was poured into 200mL of methanol and 10mL of concentrated hydrochloric acid and stirred overnight to remove the stannylated end-groups. The polymer was filtered and subjected to soxhlet extraction with methanol (12h), hexanes (12h), and chloroform (12h). Extraction with chlorobenzene (12h) was also carried out if there was any polymer left in the extraction thimble. The chloroform and chlorobenzene fractions were then concentrated, precipitated into 200mL of methanol, filtered and dried to obtain the final product.

**PF-T-DPP:** The title compound was obtained as dark green solids in 68 % yield.

\(^1\)H NMR (1,1,2,2-tetrachloroethane-d4, 400 MHz, 100 °C) \(\delta\) 8.88 (s, 2H), 7.79-7.66 (m, 6H), 7.45-7.36 (m, 6H), 4.12 (s, 4H), 2.13-2.07 (m, 6H), 1.44-1.19 (m, 64H), 0.97-0.90 (m, 18H)

HT-GPC (1,2,4-trichlorobenzene) \(M_n:\) 15.7 kg/mol, \(M_w:\) 36.0 kg/mol, PDI: 1.73
Calc for C\(_{79}\)H\(_{108}\)N\(_2\)O\(_2\)S\(_4\): C, 76.15; H, 8.74; N, 2.25. Found C, 76.31; H, 8.66; N, 2.64.
Figure 4-8: $^1$H NMR spectrum of PF-T-DPP
**PF-2T-DPP:** The title compound was obtained as dark green solids in 82 % yield.

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 100 ºC) $\delta$ 8.88 (s, 2H), 7.76-7.65 (m, 6H), 7.39-7.26 (m, 10H), 4.11 (s, 4H), 2.11-2.07 (m, 6H), 1.44-1.19 (m, 64H), 0.93-0.91 (m, 18H)

HT-GPC (1,2,4-trichlorobenzene) $M_n$: 14.8 kg/mol, $M_w$: 37.1 kg/mol, PDI: 2.51

Calc for C$_{87}$H$_{112}$N$_2$O$_2$S$_6$: C, 74.10; H, 8.01; N, 1.99. Found C, 74.30; H, 8.01; N, 2.17.

Figure 4-9: $^1$H NMR spectrum of PF-2T-DPP
**PF-3T-DPP:** The title compound was obtained as dark green solids in 78 % yield.

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 100 °C) $\delta$ 8.89 (s, 2H), 7.75-7.64 (m, 6H), 7.43-7.23 (m, 14H), 4.10 (s, 4H), 2.11-2.06 (m, 6H), 1.43-1.18 (m, 64H), 0.92-0.91 (m, 18H)

HT-GPC (1,2,4-trichlorobenzene) $M_n$: 24.7 kg/mol, $M_w$: 65.7 kg/mol, PDI: 2.66

Calc for C$_{95}$H$_{116}$N$_2$O$_2$S$_8$: C, 72.47; H, 7.43; N, 1.78. Found C, 71.18; H, 7.23; N, 1.99.

Figure 4-10: $^1$H NMR spectrum of PF-3T-DPP
Chapter 5: High Mobility, Low Band-gap Polythiophene Polymers

5.1 Introduction

In Section 2.4.3 on page 38, we reviewed the use of polythiophenes in organic solar cell applications. Polythiophene derivatives with higher TFT mobilities than P3HT, such as poly(3,3-didodecyl quaterthiophene) (PQT-12) and poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) (Figure 2-15 on page 38), have been developed in the past few years, demonstrating that the oligothiophene unit is a strong candidate as a building block for polymers with high hole mobilities. However, these polymers have not performed well when used as donor polymers in organic solar cells. We note that the incorporation of acceptor moieties such as 2,1,3-benzothiadiazole into the polythiophene backbone has resulted in polymers with lower band-gap and improved absorption properties. The solubility and molecular weight of these polymers have also been improved by increasing the number of solubilising alkyl groups in the polymer’s repeat unit. However, solar cells associated with these polymers have yet to deliver high power conversion efficiencies.

In this chapter, we discuss the synthesis and characterisation of a new series of low band-gap polymers based on benzothiadiazole and oligothiophene that have been designed with the aims of achieving high hole mobility and good solar cell performance.
5.2 Polymer Design and Synthesis

5.2.1 Polymer Design

Our first design in this series, P2T-DDTBT, incorporated benzothiadiazole with four thiophene rings, two of which were substituted with n-dodecyl chains like PQT-12. Three synthetic routes were considered for this polymer. First, nickel catalysed Yamamoto coupling was considered. However, this was rejected as the polymer would have been a random copolymer, and the different reactivities of the monomers (electron-rich vs electron-poor) could mean that the desired polymer could not be obtained. We then considered the palladium-catalysed Suzuki and Stille copolymerization methods. We chose the Stille route as it has proven to be an effective method to achieve high molecular weight polythiophenes.

The monomers, 4,7-bis(5-bromo-4-dodecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (M7a) and 5,5’-bis(trimethylstannyl)-2,2’-bithiophene were co-polymerized via Stille cross-coupling. The P2T-DDTBT obtained had very poor solubility even in hot dichlorobenzene. This observation was also reported recently by a group which attempted the synthesis of this polymer. Thus, this polymer was deemed to be unsuitable for solution-processed solar cells.
To improve the solubility of our polymer, we redesigned the polymers to have long, branched alkyl chains in place of the n-dodecyl chains. The backbone of **POD2T-DTBT** has previously been reported (P22 in Figure 2-16 on page 4082-84). This polymer was able to achieve 1% PCE despite its relatively low molecular weight ($M_n = 7400$). The synthesis of this polymer was carried out via Stille co-polymerisation between 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole and the bis-stannyalted monomer, 5,5'-bis(trimethylstanny)-4,4'-di(3,7,11-trimethyldodecyl)-2,2'-bithiophene (Scheme 5-3). The latter compound was purified by Kugelrohr distillation. The 2-octylldodecyl...
analogue of the bis-stannylated dialkylbithiophene would be difficult to distill due to its expected high boiling point. Thus, we used the dibromo monomer 5,5’-dibromo-4,4’-di(2-octyldodecyl)-2,2’-bithiophene (M4) which could be obtained in sufficient purity through column chromatography. This was then copolymerised with 4,7-bis(2-trimethylstannylthien-5-yl)-2,1,3-benzothiadiazole (M3) using Stille copolymerisation to yield the polymer POD2T-DTBT which we found to be soluble in hot chlorobenzene and dichlorobenzene.

Scheme 5-3: Synthetic route of P22. This polymer was synthesised via Stille co-polymerisation between 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole and 5,5’-bis(trimethylstannyl)-4,4’-di(3,7,11-trimethyldodecyl)-2,2’-bithiophene. From ref. 82.

To investigate the effect of the positioning of the alkyl chains in the polymer on solar cell performance, we designed P2T-ODDTBT. The monomers for this polymer, M7b and 5,5’-bis(trimethylstannyl)-2,2’-bithiophene M2, were also easier to purify than M9 which required repeated purification using long silica gel columns. M7b and M2 were both solids which could be easily recrystallised to ensure high purity – which is a necessary criteria for obtaining high polymer molecular weights.

Next, to investigate the effects of the rigidification of the polymer on its properties, we replaced the bithiophene moiety with a bridged dithienothiophene moiety. This resulted in polymer PDTT-ODDTBT.

Finally, we designed POD4T-DTBT to investigate the effect of the number of thiophene rings in the polymer structure on its properties and solar cell performance.

The full synthetic details and characterisation data of the monomers and polymers are given in Section 5.7 at the end of this chapter. A brief summary is given in the next two sections.
5.2.2 Monomer Synthesis

5,5’-Bis(trimethylstannyl)-2,2’-bithiophene\(^{109}\) (M2), 2,6-bis-trimethylstannanyl-dithieno[3,2-b;2′,3′-d]thiophene\(^{119}\) (M5) and 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole\(^{120}\) were synthesised using literature methods. The synthetic routes of the other monomers used in this chapter are shown in Schemes 3 and 4.

3-Alkylthiophenes 7a and 7b were synthesised using a Grignard coupling procedure\(^{121}\). Lithiation with lithium diisopropylamide (LDA) and quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave the corresponding 4-alkyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-thiophenes 8a and 8b. Reactions with 4,7-dibromo-2,1,3-benzothiadiazole followed by bromination with NBS gave monomers M7a and M7b with good yields.

M8 was synthesised using a procedure adapted from literature.\(^{122}\) 4,7-Bis(2-thienyl)-2,1,3-benzothiadiazole was dissolved in THF and lithiated with lithium 2,2,6,6-tetramethylpiperidide (LTMP) followed by quenching with trimethyltin chloride. Following removal of the solvent and excess TMP, M8 was obtained in 85 % yield after recrystallisation.
Scheme 5-4: Synthesis of 4,7-bis(thien-2-yl)benzothiazole monomers M7 and M8.

Monomer M9 was synthesised by the palladium-catalyzed homocoupling of the corresponding 2-bromo-3-alkylthiophene in 54 % yield. M10 was obtained by the Stille coupling of M9 with 2-(tributylstannyl)thiophene in 75 % yield, followed by bromination with NBS in near quantitative yield.
5.2.3 Polymer Synthesis

The polymers were synthesised using a Stille copolymerisation procedure similar to the one described in Section 3.2.3 on page 56. The polymers were obtained in good yields of between 72 and 84%, with high number-averaged molecular weights ($M_n$) of between 17 and 56 kg/mol. The detailed synthetic procedures, NMR spectra, elemental analysis and molecular weight information can be found in Section 5.7 at the end of this chapter. A summary of the $M_n$ and other physical properties of the polymers are shown in Table 5-2 on page 102.
5.3 Polymer Characterisation

5.3.1 Optical Characterisation

Figure 5-1: Solution and film UV-Vis spectra (solid lines) of the polymers, and photoluminescence spectra (dashed lines) of the pristine polymer films and 1:1 polymer-PCBM blends. The photoluminescence spectra were normalised for the absorbance of the films.

UV-Visible spectra of the polymers were recorded in dichlorobenzene solution and in thin films which were drop cast from dichlorobenzene solution. POD2T-DTBT and POD4T-DTBT exhibited strong aggregation peaks in solution at around 700-710 nm, which disappeared upon heating. The absorption peaks of these two polymers shifted to around 560-575 nm upon heating. For all the polymers, the peaks of the thin film spectra were red-shifted by over 50 nm and showed significant broadening compared to the solution spectra, indicating strong inter-chain interactions in the solid state. Compared to the solution spectra, the thin film spectra also had red-shifted absorption onsets of up to 100 nm. The absorption of all the polymers extended to 750 nm or more, which allows them to absorb light across the entire visible spectrum.
From the absorption onsets of the polymer thin films, their optical band-gaps were calculated. **POD2T-DTBT** had the lowest optical band-gap of 1.59 eV; the other polymers had slightly higher band-gaps of 1.63-1.66 eV.

Photoluminescence (PL) spectroscopy was carried out on the polymer films and on 1:1 polymer:PC$_{61}$BM blend films. These films were spin-coated onto quartz slides from chlorobenzene solution. An excitation wavelength of 600 nm was used. All of the pristine polymer films exhibited emission peaks between 716 nm and 745 nm. The emission peaks were partially quenched in the blend films, indicating the presence of charge transfer from the excited states of the polymers to PC$_{61}$BM.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (kg/mol)/PDI</th>
<th>$\lambda_{\text{max}}$ solution/film (nm)</th>
<th>PL peak (nm)</th>
<th>$E_{\text{g, opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POD2T-DTBT</td>
<td>28.6/1.73</td>
<td>562/646</td>
<td>745</td>
<td>1.59</td>
</tr>
<tr>
<td>P2T-ODDTBT</td>
<td>17.3/2.18</td>
<td>573/638</td>
<td>729</td>
<td>1.63</td>
</tr>
<tr>
<td>PDTT-ODDTBT</td>
<td>36.3/1.67</td>
<td>565/623</td>
<td>716</td>
<td>1.66</td>
</tr>
<tr>
<td>POD4T-DTBT</td>
<td>56.6/2.58</td>
<td>571/624</td>
<td>725</td>
<td>1.66</td>
</tr>
</tbody>
</table>

**Table 5-1**: Summary of the number-averaged molecular weights, absorbance maxima for solution and film and optical band-gaps of the polymers.

### 5.3.2 Electrochemical characterisation

Cyclic voltammetry was carried out as described in Section 2.5.3, and the results are shown in Figure 5-2. Clear oxidation peaks were observed for all of the polymers and the HOMO levels of the polymers were determined from the onsets of these peaks. The calculated values of the HOMO levels were between -5.11 eV and -5.27 eV. Under the same conditions, the HOMO level of P3HT was determined to be -5.00 eV. Our polymers thus have lower lying HOMOs than P3HT, which implies better air stability and potentially higher $V_{oc}$ in solar cell applications. Interestingly, the HOMO levels of **POD2T-DTBT** and **P2T-ODDTBT** differed by almost 0.1 eV despite their structures differing only by the position of the alkyl chains. This difference is also
reflected in the $V_{oc}$ of their associated solar cells (see Section 5.5), with the P2T-ODDTBT cells having a $V_{oc}$ around 0.1 V higher than those of POD2T-DTBT.

The LUMO levels of the polymers were determined from the HOMO levels and the optical band-gap, and ranged from -3.45 eV to -3.64 eV. The offset between the LUMO levels of the polymers and PCBM are more than sufficient to provide a driving force for charge separation. The energy levels of the polymers are summarised in Table 5-2 on page 105.

Figure 5-2: Cyclic voltammograms of thin-films of the polymers. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocnium couple was used as an internal reference and the oxidation onsets were used to calculate the HOMO values of the polymers.
5.3.3 Thermal Characterisation

Figure 5-3: Weight loss data obtained from thermogravimetric analysis. The samples were heated to 900 °C at 10 °C/min and the decomposition temperature determined from the temperature at which the weight loss reached 5%.

Figure 5-4: DSC curves showing the second heating/cooling cycle for each polymer.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on the four polymers. The polymers exhibited excellent thermal stability, with all the polymers having 5% weight loss temperatures ($T_d$) of above 300°C.
POD2T-DTBT and P2T-ODTBT had the best thermal stability, with their 5 % weight loss temperatures being over 400 °C.

The DSC scans of the polymers are shown in Figure 5-4. Glass transition temperatures were not detected for all of the polymers. Each polymer exhibited an endothermic peak upon heating and an exothermic peak upon cooling, which can be attributed to the melting and crystallisation of the polymer backbone respectively. POD2T-DTBT and POD4T-DTBT, which differ in their structures by two thiophene rings, had similar transition temperatures. P2T-ODDDTB had a lower melting transition than POD2T-DTBT, which could be due to its lower molecular weight. (We note that the melting point of P3HT with M\(_n\) of 27 kg/mol was more than 50 °C higher than that of the same polymer with M\(_n\) of 7.2 kg/mol.\(^{124}\) PDTT-ODDDTB had the highest melting point of 279 °C.

Unlike PQT, POD2T-DTBT and P2T-ODTBT did not exhibit any liquid crystalline behaviour.\(^{75}\) This could be because the branched alkyl chains used in POD2T-DTBT and P2T-ODTBT do not facilitate the side-chain interdigitation which is seen in PQT\(^{125}\) and hence do not self-organise as readily as PQT.

<table>
<thead>
<tr>
<th></th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>(T_d) (°C)</th>
<th>(T_m) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POD2T-DTBT</td>
<td>-5.18</td>
<td>-3.57</td>
<td>406</td>
<td>213</td>
</tr>
<tr>
<td>P2T-ODDDTB</td>
<td>-5.27</td>
<td>-3.64</td>
<td>412</td>
<td>191</td>
</tr>
<tr>
<td>PDTT-ODDDTB</td>
<td>-5.13</td>
<td>-3.47</td>
<td>310</td>
<td>279</td>
</tr>
<tr>
<td>POD4T-DTBT</td>
<td>-5.11</td>
<td>-3.45</td>
<td>352</td>
<td>218</td>
</tr>
</tbody>
</table>

Table 5-2: Summary of the HOMO and LUMO energy levels, decomposition temperatures and melting points of the four polymers in this series. The HOMO levels were determined by cyclic voltammetry and the LUMO levels were obtained using the HOMO levels and the optical band-gap.
5.4 TFT Characterisation

In order to understand the charge transport properties of our polymers, top-contact TFT devices were fabricated according to the procedures detailed in Section 2.5.4. The device fabrication and characterisation work was carried out by Dr. Huei-Shuan Tan and Mr. Lionel Moh. Each device consisted of a polymer semiconductor layer that was spin-coated onto a heavily n-doped silicon wafer substrate with 210 nm of surface oxide as the gate dielectric. Gold was used as the top electrode. The results of the characterisation are shown in Figures 5-5 to 5-8 below.

Figure 5-5: a) Output curves and b) transfer curves of a POD2T-DTBT TFT. The hole carrier mobility was 0.13 cm$^2$/Vs, the on/off ratio was $7 \times 10^6$ and the threshold voltage was -3.91 V.

Figure 5-6: a) Output curves and b) transfer curves of a P2T-ODDTBT TFT. The hole carrier mobility was 0.01 cm$^2$/Vs, the on/off ratio was $1 \times 10^7$ and the threshold voltage was -1.73 V.
Figure 5-7: a) Output curves and b) transfer curves of a PDTT-ODDTBT TFT. The hole carrier mobility was 0.184 cm$^2$/Vs, the on/off ratio was 2x10$^6$ and the threshold voltage was -2.83 V.

Figure 5-8: a) Output curves and b) transfer curves of a POD4T-DTBT TFT. The hole carrier mobility was 0.022 cm$^2$/Vs, the on/off ratio was 8x10$^5$ and the threshold voltage was 3.70 V.

The **POD2T-DTBT** TFT devices which were annealed at 200°C exhibited hole mobilities of between 0.13 to 0.20 cm$^2$/Vs as well as on/off ratios in the order of 10$^6$ to 10$^7$. To the best of our knowledge, this is one of the highest values reported for low band-gap polymers. By comparison, the unannealed devices exhibited lower hole mobilities of 0.05 to 0.13 cm$^2$/Vs.

X-ray diffraction studies of films of this polymer indicated that the polymer exhibited some degree of ordering even without annealing. Annealing at 200°C greatly increased the ordering, as seen by the six-fold increase in the intensity of the peak at a
$2\theta = 4.5^\circ$, which corresponds to an inter-chain d-spacing of 19.5 Å. A second-order peak at $9.0^\circ$ also appears upon annealing. Clearly, this increased ordering is reflected in the improved TFT mobility of annealed devices.

![XRD spectra of non-annealed and annealed POD2T-DTBT films](image)

**Figure 5-9: XRD spectra of non-annealed and annealed POD2T-DTBT films**

Annealed PDTT-ODDTBT TFT devices also exhibited good hole mobilities of around $0.18 \text{ cm}^2/\text{Vs}$ and an on/off ratio on the order of $10^6$, however the TFT hole mobilities and on/off ratios of P2T-ODDTBT and POD4T-DTBT were substantially lower than for the other two polymers.

The POD2T-DTBT and PDTT-ODDTBT devices were stored inside a dry box (relative humidity of around 56%) and re-tested after one month. It was found that the PDTT-ODDTBT devices had deteriorated, with a large drop in the on/off ratio. The POD2T-DTBT devices, on the other hand, exhibited no deterioration in either the hole carrier mobility or the on/off ratio. No significant deterioration in either of these characteristics was observed even after five months (see Figure 5-10 on following page).
Figure 5-10: Transfer curves for an POD2T-DTBT TFT comparing the as-prepared device and aged device (43 days, 58 days and 150 days aged). No significant deterioration in the mobility and on/off ratios were observed even after 150 days.

To investigate the stability of the POD2T-DTBT devices under repeated switching between the on and off states, we subjected a device to cyclic stressing. A gate voltage of -60 V was applied to turn the device “on” and ensure that the device was in saturation mode, and a gate voltage of 0 V was applied to turn the device “off”. This was repeated for 100 times over an hour. The resulting current-voltage characteristics of the device is shown in Figure 5-11.

Figure 5-11: Current-voltage characteristics of POD2T-DTBT transistors under cyclic stressing. Top: Drain-source current of devices. Bottom: Applied gate voltage. a) overview of 100 cycles, b) magnified view
It can be observed that the current-voltage characteristics remained consistent during repeated stressing. The TFT hole mobility of the device dropped marginally to 0.170 cm$^2$/Vs after the stressing compared to 0.184 cm$^2$/Vs prior to the stress-testing. The threshold voltage also shifted from -0.93 V to -8.46 V after the stress-testing. The change in threshold voltage due to applied bias has been observed in TFTs made from other organic materials such as pentacene$^{126}$ and P3HT.$^{127}$ This phenomenon has been attributed to trapped charges in the semiconductor close to the interface with the dielectric.$^{128}$ In the case of our devices, this threshold voltage shift was reversible.$^{128,129}$

5.5 OPV Characterisation

5.5.1 General device characterisation

To evaluate the performance of the polymers as donor materials, solar cells with the structure of ITO/PEDOT:PSS/polymer:PC$_{71}$BM/Ca/Ag were fabricated according to the procedure detailed in Section 2.5.4 (page 48). This work was carried out by Dr. Siew-Lay Lim and Ms. Hoi-Ka Wong. The current-voltage characteristics of these cells are shown in Figures 5-12 to 5-15 in the following pages. The device parameters for each series of cells are also summarised in Tables 5-3 to 5-6.

For each polymer, blended films with polymer:PC$_{71}$BM weight ratios of 1:1, 1:2 and 1:4 were fabricated. Films with a 1:1 weight ratio of polymer to PC$_{71}$BM were found to deliver the best performances for POD2T-DTBT, P2T-ODDTBT and PDTT-ODDTBT cells, while a 1:2 weight ratio was required for POD4T-DTBT.

Cells prepared using POD2T-DTBT gave the best performances of up to 5.27 %. The active layer of the best cell was 75 nm thick. A reduction in the thickness of the cells to 60 nm resulted in a decrease in $J_{sc}$ from 11.97 mA/cm$^2$ to 9.48 mA/cm$^2$ and consequently a decrease in PCE to 4.49 %.

P2T-ODDTBT cells had lower short circuit currents than POD2T-DTBT cells. However, they also had higher open circuit voltages of between 0.72 to 0.78 V (compared with 0.63 to 0.68 for POD2T-DTBT cells). This can be attributed to the difference in HOMO energy levels of these polymers. P2T-ODDTBT had a HOMO
level that was 0.09 eV lower than that of POD2T-DTBT as measured by cyclic voltammetry (see Section 5.3.2 and Table 5-2).

![Figure 5-12: Current-voltage characteristics of POD2T-DTBT:PC_{71}BM cells.](image)

<table>
<thead>
<tr>
<th>POD2T-DTBT: PC_{71}BM (8mg/ml)</th>
<th>Spin rate (rpm)</th>
<th>J_{sc} (mA/cm(^2))</th>
<th>V_{oc} (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>500</td>
<td>11.97</td>
<td>0.659</td>
<td>66.9</td>
<td>5.27</td>
<td>75</td>
</tr>
<tr>
<td>1:1</td>
<td>1000</td>
<td>9.48</td>
<td>0.681</td>
<td>69.6</td>
<td>4.49</td>
<td>60</td>
</tr>
<tr>
<td>1:2</td>
<td>500</td>
<td>10.70</td>
<td>0.642</td>
<td>69.6</td>
<td>4.78</td>
<td>100</td>
</tr>
<tr>
<td>1:2</td>
<td>1000</td>
<td>10.80</td>
<td>0.666</td>
<td>71.3</td>
<td>5.13</td>
<td>75</td>
</tr>
<tr>
<td>1:4</td>
<td>500</td>
<td>8.96</td>
<td>0.632</td>
<td>68.9</td>
<td>3.90</td>
<td>170</td>
</tr>
<tr>
<td>1:4</td>
<td>1000</td>
<td>7.82</td>
<td>0.649</td>
<td>69.9</td>
<td>3.54</td>
<td>115</td>
</tr>
</tbody>
</table>

Table 5-3: Summary of the device parameters for POD2T-DTBT:PC_{71}BM cells.
Table 5-4: Summary of the device parameters for P2T-ODDTBT:PC_{71}BM cells.

<table>
<thead>
<tr>
<th>P2T-ODDTBT:PC_{71}BM (10mg/ml)</th>
<th>Spin rate (rpm)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>(V_{oc}) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>500</td>
<td>8.23</td>
<td>0.78</td>
<td>60.5</td>
<td>3.87</td>
<td>155</td>
</tr>
<tr>
<td>1:1</td>
<td>1000</td>
<td>5.37</td>
<td>0.75</td>
<td>62.6</td>
<td>2.54</td>
<td>-</td>
</tr>
<tr>
<td>1:2</td>
<td>500</td>
<td>3.59</td>
<td>0.75</td>
<td>60.5</td>
<td>1.62</td>
<td>180</td>
</tr>
<tr>
<td>1:2</td>
<td>1000</td>
<td>4.14</td>
<td>0.74</td>
<td>64.6</td>
<td>1.99</td>
<td>-</td>
</tr>
<tr>
<td>1:4</td>
<td>500</td>
<td>4.13</td>
<td>0.76</td>
<td>61.0</td>
<td>1.92</td>
<td>205</td>
</tr>
<tr>
<td>1:4</td>
<td>1000</td>
<td>2.42</td>
<td>0.72</td>
<td>65.4</td>
<td>1.15</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5-13: Current-voltage characteristics of P2T-ODDTBT:PC_{71}BM cells.
Figure 5-14: Current-voltage characteristics of PDTT-ODDTBT:PC$_{71}$BM cells

<table>
<thead>
<tr>
<th>PDTT-ODDTBT: PC$_{71}$BM (5mg/ml)</th>
<th>Spin rate (rpm)</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>500</td>
<td>6.83</td>
<td>0.552</td>
<td>57.1</td>
<td>2.15</td>
<td>55</td>
</tr>
<tr>
<td>1:1</td>
<td>1000</td>
<td>4.10</td>
<td>0.513</td>
<td>61.6</td>
<td>1.29</td>
<td>-</td>
</tr>
<tr>
<td>1:2</td>
<td>500</td>
<td>6.65</td>
<td>0.540</td>
<td>51.1</td>
<td>1.84</td>
<td>80</td>
</tr>
<tr>
<td>1:2</td>
<td>1000</td>
<td>5.00</td>
<td>0.518</td>
<td>59.9</td>
<td>1.55</td>
<td>-</td>
</tr>
<tr>
<td>1:4</td>
<td>500</td>
<td>5.67</td>
<td>0.526</td>
<td>49.8</td>
<td>1.48</td>
<td>95</td>
</tr>
<tr>
<td>1:4</td>
<td>1000</td>
<td>5.06</td>
<td>0.517</td>
<td>57.7</td>
<td>1.51</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5-5: Summary of the device parameters for PDTT-ODDTBT:PC$_{71}$BM cells
Figure 5-15: Current-voltage characteristics of POD4T-DTBT:PC$_{71}$BM cells

<table>
<thead>
<tr>
<th>POD4T-DTBT: PC$_{71}$BM (8 mg/ml)</th>
<th>Spin rate (rpm)</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>500</td>
<td>4.77</td>
<td>0.57</td>
<td>49.9</td>
<td>1.37</td>
<td>240</td>
</tr>
<tr>
<td>1:1</td>
<td>1000</td>
<td>7.47</td>
<td>0.57</td>
<td>56.0</td>
<td>2.40</td>
<td>120</td>
</tr>
<tr>
<td>1:2</td>
<td>500</td>
<td>7.74</td>
<td>0.56</td>
<td>50.9</td>
<td>2.19</td>
<td>260</td>
</tr>
<tr>
<td>1:2</td>
<td>1000</td>
<td>8.48</td>
<td>0.56</td>
<td>59.8</td>
<td>2.84</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 5-6: Summary of the device parameters for POD4T-DTBT:PC$_{71}$BM cells

The performances of PDTT-ODDTBT and POD4T-DTBT cells were relatively poor, with the highest PCEs obtained being 2.15 % (for 1:1 blend) and 2.84 % (for 1:2 blend) respectively. We note that both of these polymers had poor solubility in dichlorobenzene due to their higher molecular weights, which led to poor film quality with features observable even with the naked eye. Due to the high viscosity of the POD4T-DTBT:PC$_{71}$BM blends, the films which were spin-coated at 500 rpm were much thicker than films spin-coated from the other polymer blends, which led to lower fill factors. A higher spin rate of 1000 rpm reduced the thickness to 120 to 130 nm, resulting in improved fill factors and solar cell performances.
5.5.2 Solvent Annealing and Solvent Vapour Annealing for POD2T-DTBT:PC$_{71}$BM Cells

Solvent annealing (SA)$^{130}$ and solvent vapour annealing (SVA)$^{131}$ have previously been used to improve the performance of P3HT:PCBM cells. The improvement in device performance has been attributed to improved ordering of P3HT,$^{132}$ which led to better charge transport in the blend film.

We investigated the use of solvent annealing and solvent vapour annealing in POD2T-DTBT:PC$_{71}$BM (1:1 wt. ratio) solar cells. To enable thicker films to be obtained using the same spin rate of 500 rpm, a polymer concentration of 10 mg/ml was used instead of the 8 mg/ml used previously. A slower spin rate of 350 rpm was also used for one set of devices to enable even thicker films to be obtained.

For the preparation of the solvent annealed films, the spin-coating time was reduced to 40 s as compared to 140 s for cells prepared by the general method so that the films were removed from the spin coater while still wet. The wet films were then left to dry for around 3 hours in a covered Petri dish before the Ca/Ag electrodes were deposited.

Solvent vapour annealing was carried out by placing freshly spin-coated films in a covered Petri dish together with 5 drops of dichlorobenzene for 6 hours prior to electrode deposition.
Figure 5-16: Current-voltage characteristics of solvent-annealed and solvent-vapour annealed POD2T-DTBT:PC$_{71}$BM cells

<table>
<thead>
<tr>
<th>POD2T-DTBT: PC$_{71}$BM (10mg/ml)</th>
<th>Spin rate (rpm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>500</td>
<td>12.28</td>
<td>0.660</td>
<td>65.4</td>
<td>5.30</td>
<td>106</td>
</tr>
<tr>
<td>SVA only</td>
<td>500</td>
<td>12.30</td>
<td>0.661</td>
<td>66.8</td>
<td>5.43</td>
<td>109</td>
</tr>
<tr>
<td>SA only</td>
<td>500</td>
<td>12.34</td>
<td>0.655</td>
<td>66.0</td>
<td>5.36</td>
<td>118</td>
</tr>
<tr>
<td>SA + SVA</td>
<td>500</td>
<td>12.33</td>
<td>0.674</td>
<td>63.2</td>
<td>5.25</td>
<td>116</td>
</tr>
<tr>
<td>SA + thick film</td>
<td>350</td>
<td>11.74</td>
<td>0.661</td>
<td>60.1</td>
<td>4.72</td>
<td>154</td>
</tr>
</tbody>
</table>

Table 5-7: Summary of the device characteristics of solvent annealed and solvent vapour annealed cells, showing a marginal improvement in device performance for solvent annealed and solvent vapour annealed cells.
From the results (Figure 5-16 and Table 5-7), we observed that the use of a more concentrated solution resulted in thicker films being obtained as expected (106 nm vs 75 nm for a similar cell obtained using a 8 mg/ml concentration (Table 5-3)). However, no significant improvement in the power conversion efficiency (5.30 % vs 5.27 %) was achieved. A further increase in the thickness of the active layer resulted in a decrease in the PCE due to falls in the current density as well as fill-factor.

Although the power conversion efficiency was improved slightly by solvent annealing and solvent vapour annealing, the increases were considered to be relatively insignificant. To determine the effects of these processes on the morphology of the devices, AFM images of the active layers of the devices were taken. The surface morphology of the solvent annealed (Figure 5-17b) and solvent vapour annealed film (not shown) were similar to each other, and distinctly different from that of the non-solvent annealed film (Figure 5-17a). A network of fibre-like structures, which we believe to be polymer fibres, could be clearly seen in the SA film. These fibres were approximately 20 nm wide. Upon close inspection, these fibres could also be seen in the non-SA film; however they were less distinct and fewer in numbers. We believe, therefore, that the solvent annealing process helped to increase the ordering of the polymer within the blend film. The increase in texturing of the film was also reflected by an increase in the root mean square roughness of the films from 1.80 nm to 2.69 nm.

Previous reports on P3HT:PCBM cells have shown a significant increase in the solar cell PCE upon solvent annealing, which were attributed to better charge transport in the blend films. However in our case, the increase in PCE is relatively small at less than 0.2 %. One reason for this could be the large size of the fibres (~20 nm) which may not be optimum for effective charge separation as it is larger than the typical exciton diffusion length for polymers.
a) Non-solvent annealed

Figure 5-17: AFM height and phase images of a) the control sample and b) the solvent annealed sample

5.5.3 Effect of cathode material on POD2T-DTBT:PC₇₁BM cells

Further optimisation of the POD2T-DTBT:PC₇₁BM cells were carried out. In this experiment, the Ca (10 nm)/Ag (100 nm) electrode was replaced by Al (100 nm) electrode. Solvent annealing was carried out on these devices as per the previous section. The devices with an Al electrode were subjected to annealing at 100 °C for 10 min after the deposition of the electrode. The current-voltage characteristics and the incident photon to current efficiency (IPCE) of the cells are shown in Figure 5-18. It can be observed that the device with an Al electrode had a higher $V_{oc}$ (0.722 V)
than the device with a Ca/Ag electrode (0.655 V) – a difference of 0.067 V – which resulted in an increase in the device’s power conversion efficiency to 6.26 %. Although the $V_{oc}$ is reported to be governed by the energy difference between the HOMO of the donor and the LUMO of the acceptor material,\textsuperscript{41} it is not unusual to see differences in $V_{oc}$ when using different cathode materials.\textsuperscript{133,134} In our case, it is clear that the increase in $V_{oc}$ for the cell with an Al electrode is due to a decrease in dark current density of this cell compared with the one with a Ca/Ag electrode.

![Figure 5-18: a) Current-voltage characteristics of POD2T-DTBT:PC$_{71}$BM (1:1) cells illustrating the effect of different cathode materials. The device with an Al cathode had a larger $V_{oc}$ than the device with the Ca/Ag electrode as a result of a decrease in the dark current. b) The IPCE spectra of the two devices, shown together with the absorbance of the blend film.

### 5.6 Conclusions

A series of low band-gap donor polymers based on thiophene and benzothiadiazole has been synthesised and characterised. The combination of the benzothiadiazole moiety and the high mobility oligothiophene unit resulted in reduced band-gaps compared with typical polythiophenes. The use of long, branched alkyl chains ensured that the polymers could be solution-processed.

All the polymers exhibited hole mobilities of at least $10^{-2}$ cm$^2$/Vs, and up to 0.20 cm$^2$/Vs, when applied in TFT devices. Devices based on POD2T-DTBT exhibited both excellent hole mobilities and remarkable stability upon prolonged storage.
When applied in organic solar cell devices, POD2T-DTBT again exhibited the best performance. Optimisation of the cells using solvent annealing and different electrode materials resulted in cells with 6.2 % efficiency being obtained. To our knowledge, this is the highest value obtained for benzothiadiazole-thiophene polymers to date.

5.7 Experimental Section

3-Dodecylthiophene (7a) and 3-(2-ocytldodecyl)thiophene (7b) were synthesised according to a literature procedure.121

3-Dodecylthiophene (7a): Yield = 53 %. 1H NMR (CDCl₃, 400 MHz) δ 7.24-7.22 (m, 1H), 6.94-6.92 (m, 2H), 2.64-2.60 (m, 2H), 1.62-1.60 (m, 2H), 1.31-1.26 (m, 18H), 0.90-0.87 (t, 3H)

3-(2-Octyldodecyl)thiophene (7b): Yield = 49 %. 1H NMR (CDCl₃, 400 MHz) δ 7.23-7.21 (m, 1H), 6.90-6.88 (m, 2H), 2.56-2.55 (d, 2H, J=6.8 Hz), 1.61-1.59 (m, 1H), 1.25 (br, 32H), 0.90-0.87 (t, 6H).

4-Dodecyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-thiophene (8a): 3-dodecylthiophene (7a) (2.0 g, 8 mmol) was dissolved in anhydrous tetrahydrofuran (THF) (50 mL) in a 250 mL round-bottom flask and the solution was cooled to 0 °C. Lithium diisopropylamide (2.0 M in THF/heptane/ethylbenzene) (4.4 mL, 8.8 mmol) was added dropwise and the mixture was stirred for 1 hour at that temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.0 mL, 9.6 mmol) was then added, following which the mixture was allowed to warm up to room temperature and was stirred overnight. The THF was then evaporated and the mixture was redissolved in ethyl acetate and washed with water. The organic layer was concentrated and subject to column chromatography (5 % ethyl acetate in hexanes) to obtain the title compound as a colourless liquid (1.38 g, 46 %)

1H NMR (CDCl₃, 400MHz) δ 7.47 (s, 1H), 7.21 (s, 1H), 2.64-2.60 (t, 2H), 1.61-1.59 (m, 2H), 1.43-1.34 (m, 30H), 0.89-0.86 (t, 3H).
4-(2-Octyldodecyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-thiophene (8b):
This compound was synthesised from 7b in 83 % yield using the same method as above.
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ 7.40 (s, 1H), 7.20 (s, 1H), 2.58-2.56 (d, 2H, $J = 6.8$Hz), 1.61 (s, 1H), 1.33-1.27 (m, 44H), 0.91-0.87 (t, 6H).

4,7-Bis(4-dodecylthiophen-2-yl)-2,1,3-benzothiadiazole (9a): Compound 8a (1.42 g, 3.75 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (0.5 g, 1.7 mmol) and tetrakis(triphenylphosphine)palladium(0) (82 mg, 2 mol%) were added to a 50 mL round-bottom flask. The flask was purged with argon and toluene (12 mL), ethanol (4 mL) and 2M sodium carbonate solution (4 mL) were added. The mixture was then heated at 85 °C overnight. The solution was then poured into water and extracted with dichloromethane. The title compound was obtained as orange solids after column chromatography on silica (5% dichloromethane in hexanes) (0.81 g, 60 %).
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.98 (s, 2H), 7.83 (s, 2H), 7.04 (s, 2H), 2.71-2.69 (t, 4H), 1.72-1.69 (m, 4H), 1.36-1.26 (m, 36H), 0.89-0.86 (t, 6H).
MALDI-TOF-MS: m/z calc. 636.36, obtained 636.31.

4,7-Bis(4-(2-octyldodecyl)thiophen-2-yl)-2,1,3-benzothiadiazole (9b):
A 20 mL microwave glass vial was charged with a stirrer bar, 4,7-dibromo-2,1,3-benzothiadiazole (0.3 g, 1.0 mmol), compound 8a (1.2 g, 2.4 mmol) and bis(triphenylphosphine)palladium(II) chloride (29 mg, 4 mol%). The vial was then purged with nitrogen and sealed. 2M sodium carbonate (2 mL), 1,2-dimethoxyethane (5 mL), water (2.2 mL) and ethanol (1.2 mL) were then added through a septum. The vial was then heated at 120 °C for 2 min and then 160 °C for 20 min in a microwave reactor. After cooling, the contents of the vial were poured into water and extracted with dichloromethane. The title compound was obtained in 86.4 % yield after flash column chromatography on silica, with hexanes as the eluent.
$^1$H NMR (CDCl$_3$, 400 MHz): 7.95 (s, 2H), 7.83 (s, 2H), 7.01 (d, 2H), 2.64 (d, 2H, $J=6.4$Hz), 1.69 (s, 2H), 1.31-1.25 (m, 64H), 0.88-0.85 (t, 12H)
4,7-Bis(5-bromo-4-dodecyl-thien-2-yl)-2,1,3-benzothiadiazole (M7a):
Compound 9a (1.54 g, 2.4 mmol) was dissolved in chloroform (50 mL) and glacial acetic acid (50 mL) and the solution was cooled with an ice bath. N-bromosuccinimide (0.94 g) was slowly added over 20 minutes, following which the reaction mixture was stirred for a further 4 hours and slowly allowed to warm to room temperature. After that time, the mixture was washed with water (2 x 150 mL), 5% sodium hydrogen carbonate solution (150 mL) and brine (150 mL). Column chromatography on silica (5 % dichloromethane in hexanes) followed by recrystallisation in ethanol/dichloromethane afforded the title compound as orange solids (1.79 g, 93 %).

$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.78 (s, 2H), 7.76 (s, 2H), 2.66-2.62 (t, 4H), 1.67-1.66 (m, 4H), 1.37-1.26 (m, 36H), 0.88-0.86 (t, 6H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) δ 152.7, 143.5, 138.9, 128.5, 125.8, 125.3, 112.0, 32.3, 30.1, 29.8, 29.7, 23.1, 14.5.

MALDI-TOF-MS: m/z calc. 794.18, obtained 794.20

4,7-Bis(2-trimethylstannythien-5-yl)-2,1,3-benzothiadiazole (M8):
This compound was synthesised using a method adapted from literature. A mechanically stirred solution of 2,2,6,6-tetramethylpiperidine (TMP) (1.24 g, 8.8 mmol) in dry THF (100 mL) under argon was cooled to -78 °C and n-butyllithium (8.6 mmol) was added rapidly. The resulting solution was allowed to warm to room temperature. It was kept at room temperature for 10 min and subsequently cooled to -78 °C. A solution of 4,7-
bis(2-thienyl)-2,1,3-benzothiadiazole (1.0 g, 3.3 mmol) in 10 mL of dry THF was then added dropwise. The deep purple solution was stirred at -78 °C for 30 min, following which a 1 M solution of trimethyltin chloride in hexanes (8.8 mL, 8.8 mmol) was added. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Water was added to quench the reaction. Diethyl ether was added, and the mixture was washed 3 times with 0.1 M HCl to remove the TMP. The solution was then dried with MgSO₄. The solvent was removed, and the title compound (1.78 g, 85 %) was obtained as orange needles after recrystallisation in ethanol.

¹H NMR (CDCl₃, 400 MHz) δ 8.19 (d, 2H), 7.88 (s, 2H), 7.30 (d, 2H), 0.44 (s, 18H).

¹³C NMR (CDCl₃, 400 MHz) δ 152.7, 145.1, 140.2, 136.1, 128.4, 125.9, 125.8, -8.2.

MALDI-TOF-MS: m/z calc. 625.91, obtained 625.64


**2-Bromo-3-(2-octyldodecyl)thiophene (10):** Compound 7b (7.24 g, 19.9 mmol) was dissolved in 300 mL of dimethylformamide (DMF) and the mixture was cooled to -10 °C. N-bromosuccinimide (3.71 g, 20.8 mmol) in 30 mL of DMF was then added dropwise over 30 min. The solution was then allowed to warm up slowly to room temperature and stirred overnight. The DMF was then removed and the remaining liquid was poured into water and extracted with ethyl acetate. Column chromatography with hexanes afforded the title compound as a colourless oil (8.35 g, 98 %).

¹H NMR (CDCl₃, 400 MHz) δ 7.18 (d, 1H, J=5.6 Hz), 6.76 (d, 1H, J=5.6 Hz), 2.50 (d, 2H, J=7.2 Hz), 1.64 (m, 1H), 1.30-1.25 (br, 32H), 0.90-0.87 (t, 6H).

**5,5'-Dibromo-4,4'-bis(2-octyldodecyl)-2,2'-bithiophene (M9):** This compound was synthesised using a palladium-catalysed homocoupling reaction adapted from literature.²³ Compound 10 (4.5 g, 10 mmol) was weighed into a Schlenk flask and the flask was purged with nitrogen. Anhydrous dimethylsulfoxide (DMSO) (45 mL) was added to the flask and the mixture was heated to 70 °C. Silver nitrate (3.4 g, 20 mmol), potassium fluoride (1.16 g, 20 mmol) and bis(benzonitrile)palladium (II) chloride (77.8 mg, 2 mol%) were added in one portion, and the resulting mixture was
stirred at 70 °C. Two additional portions of AgNO₃ and KF (same quantities as above) were added after 3 hours and 6 hours and the mixture was stirred overnight at the same temperature. The mixture was then cooled, filtered through a short silica column, and washed 3 times with water. The title compound (2.42 g, 54 %) was obtained as a yellow oil after column chromatography on silica with hexanes as the eluent.

**1H NMR (CD₂Cl₂, 400 MHz)** δ 6.80 (s, 2H), 2.49 (d, 4H, J=7.2 Hz), 1.67 (m, 2H), 1.27 (m, 64H), 0.91-0.87 (t, 12H).

**13C NMR (CDCl₃, 100 MHz)** δ 142.2, 136.0, 124.9, 108.5, 38.5, 34.3, 33.4, 31.9, 31.9, 30.0, 29.7, 29.6, 29.6, 29.3, 29.3, 26.5, 22.7, 14.1.

MALDI-TOF-MS: m/z calc. 884.44, obtained 884.28


**3',4''-Bis(2-octyldodecyl)-2,2':5',2'''-quaterthiophene (11):** A 20mL microwave glass vial was charged with 2-(tributylstannyl)thiophene (1.03 g, 2.77 mmol), M₉ (1.11 g, 1.26 mmol) and tetrakis(triphenylphosphine) palladium(0) (160 mg, 0.14 mmol). The vial was then purged and sealed, and DMF (15 mL) was added. The vial was then heated at 180 °C for 20 min in a microwave reactor. The mixture was then poured into water and extracted 3 times with hexane. The combined organic layers were washed with water, brine, and dried over sodium sulfate. After the solvent was removed, the residue was purified by silica gel chromatography with hexane as an eluent to give the title compound (0.84 g, 75 %) as a yellow oil.

**5,5'''-Dibromo-3',4''-Bis(2-octyldodecyl)-2,2':5',2'''-quaterthiophene (M10):** Compound 11 (840 mg, 0.94 mmol) was dissolved in DMF (150 mL) and chloroform (20 mL) and the solution was cooled to -20 °C. A solution of N-bromosuccinimide (351 mg, 1.97 mmol) in 30 mL of DMF was then added dropwise. The mixture was allowed to stir overnight at room temperature. The DMF was removed under reduced pressure and 100 mL water was added. The suspension was
extracted with hexane and the organic layers were collected and dried. The crude product was purified by column chromatography on silica with hexanes as the eluent to afford the title compound (0.98 g, 98%) as a yellow oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.01-7.00 (d, 2H, $J$=3.6 Hz), 6.93 (s, 2H), 6.86-(d, 2H, $J$=3.6 Hz), 2.62 (d, 4H, $J$=7.2 Hz), 1.66 (br, 2H), 1.24 (br, 64H), 0.88-0.86 (t, 12H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 140.6, 137.4, 135.1, 130.3, 129.1, 127.0, 126.6, 111.9, 38.8, 38.8, 33.4, 31.9, 29.9, 29.9, 29.6, 29.6, 29.6, 29.3, 29.3, 26.4, 22.7, 22.7, 13.8.

2,6-Bis(trimethylstannyl)dithieno[3,2-b;2',3'-d]thiophene (M11) was synthesised according to a literature procedure.$^{119}$

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ 7.32 (s, 2H), 0.42 (s, 18H).

**General procedure for Stille-copolymerisation:** The dibromo and bis-stannylated monomers (1 equivalent each) were added to a reaction vial equipped with a magnetic stirrer. The vial was then transferred to a glovebox where tris(dibenzylideneacetone)dipalladium(0) (4 mol%), tri(o-tolyl)phosphine (16 mol%) and anhydrous chlorobenzene (20 mL) were added. The vial was then stirred at 120 °C for 36 hours using an oil bath. The reaction mixture was poured into 200 mL of methanol and 10 mL of concentrated hydrochloric acid and stirred overnight to remove the stannylated end-groups. The polymer was filtered and subjected to soxhlet extraction with methanol (12 h), hexanes (12 h), and chloroform (12 h). Extraction with chlorobenzene (12 h) was also carried out if there was any polymer left in the extraction thimble. The chloroform and chlorobenzene fractions were then concentrated, precipitated into 200 mL of methanol, filtered and dried to obtain the final product.

**POD2T-DTBT:** The title compound (165 mg, 72 %) was obtained as black solids from the chlorobenzene fraction.

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 70 °C) $\delta$ 8.20 (s, 2H), 7.95 (s, 2H), 7.34 (s, 2H), 7.15 (s, 2H), 2.91 (s, 4H), 1.92 (s, 2H), 1.47-1.25 (m, 32H), 0.97 (s, 6H)

HT-GPC (1,2,4-trichlorobenzene) $M_n$: 28.6 kg/mol, $M_w$: 49.3 kg/mol, PDI: 1.73

Anal. calcd. for C$_{62}$H$_{92}$N$_2$S$_5$: C, 72.60; H, 9.04; N, 2.73; S, 15.63. Found C, 72.52; H, 8.79; N, 2.71; S, 15.34.
Figure 5-19: $^1$H NMR spectrum with peak assignments for POD2T-DTBT in 1,1,2,2-tetrachloroethane-d$_2$ at 70 °C. The asterisk represents the solvent peak.

**P2T-ODDTBT:** The title compound (212 mg, 84 %) was obtained as black solids from the chloroform fraction.

$^1$H NMR (1,1,2,2-tetrachloroethane-d4, 400 MHz, 70 °C) δ 8.07 (s, 2H), 7.92 (s, 2H), 7.26 (s, 4H), 2.92 (s, 4H), 1.94 (s, 2H), 1.50-1.33 (m, 32H), 0.94 (s, 6H)

HT-GPC (1,2,4-trichlorobenzene) $M_n$: 17.3 kg/mol, $M_w$: 37.7 kg/mol, PDI: 2.18

Anal. calcd. for C$_{62}$H$_{92}$N$_2$S$_5$: C, 72.60; H, 9.04; N, 2.73; S, 15.63. Found C, 72.54; H, 8.86; N, 2.69; S, 15.97.
Figure 5-20: $^1$H NMR Spectrum with peak assignments for P2T-ODDTBT in 1,1,2,2-tetrachloroethane-$d_2$ at 70 °C. The asterisk represents the solvent peak.

**PDTT-DTBT:** The title compound (178 mg, 83 %) was obtained as black solids from the chlorobenzene fraction.

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 70 °C) $\delta$ 8.09 (s, 2H), 7.94 (s, 2H), 7.52 (s, 2H), 2.95 (s, 4H), 1.95 (s, 2H), 1.51-1.32 (m, 32H), 0.94 (s, 6H)

HT-GPC (1,2,4-trichlorobenzene) $M_n$: 36.3 kg/mol, $M_w$: 60.6 kg/mol, PDI: 1.67

Anal. calcd. for C$_{62}$H$_{90}$N$_2$S$_6$: C, 70.53; H, 8.59; N, 2.65; S, 18.22. Found C, 70.21; H, 8.42; N, 2.63; S, 18.31.
Figure 5-21: $^1$H NMR spectrum with peak assignments for PDTT-ODDTBT in 1,1,2,2-tetrachloroethane-$d_2$ at 70 ºC. The asterisk represents the solvent peak.

**Pod4T-DTBT**: The title compound (178 mg, 83 %) was obtained as black solids from the chlorobenzene fraction.

$^1$H NMR (1,1,2,2-tetrachloroethane-$d_4$, 400 MHz, 120 ºC) $\delta$ 8.15 (s, 2H), 7.94 (s, 2H), 7.37 (s, 2H), 7.33 (s, 2H), 7.18 (s, 2H), 7.10 (s, 2H) 2.85 (s, 4H), 1.87 (s, 2H), 1.42-1.39 (m, 32H), 0.97 (s, 6H)

HT-GPC (1,2,4-trichlorobenzene) $M_n$: 56.6 kg/mol, $M_w$: 146.2 kg/mol, PDI: 2.58

Anal. calcd. for C$_{70}$H$_{96}$N$_2$S$_7$: C, 70.65; H, 8.13; N, 2.35; S, 18.86. Found C, 72.54; H, 8.86; N, 2.69; S, 15.97.
Figure 5-22: $^1$H NMR Spectrum with peak assignments for POD4T-DTBT in 1,1,2,2-tetrachloroethane-$d_2$ at 120 °C. The asterisk represents the solvent peak.
Chapter 6: Conclusions and Future Work

6.1 Conclusions

The work in this thesis has focussed on the design, synthesis and characterisation of low band-gap polymers as donors in organic solar cells. The combination of donor and acceptor moieties, which has previously been used effectively in the design and synthesis of low band-gap polymers, was used. Two acceptor moieties, dithienyl-diketopyrrolopyrrole and 2,1,3-benzothiadiazole, were chosen and used in combination with dithienylthiophene, fluorene and oligothiophene moieties to create three series of low band-gap polymers.

The first series of polymers were random copolymers of diketopyrrolopyrrole (DPP) and dialkyldithienothiophene (DTT) that were bridged with a thiophene unit. It was found that varying the feed ratio of the monomers was an effective method of tuning the absorption properties and solar cell performance of the polymers. The polymer with a DPP:DTT ratio of 1:2 was found to give the best results when the polymers were used as donors in bulk heterojunctions solar cells. Increasing the length of the alkyl chains on the DPP moiety was found to be effective in increasing the solubility of the polymers. However, the use of overly long alkyl chains was detrimental to the solar cell device performance as the average domain size in the polymer:PCBM blend became too large for effective charge separation. The best performing cells for this series were based on blends of Copolymer 5 and PC$_{71}$BM, which gave power conversion efficiencies of up to 4.85%.

The cells based on Copolymers 1 to 6 had relatively low open circuit voltages, which placed a limit on the achievable efficiency. In order to overcome this, a series of polymers containing the fluorene moiety was synthesised. By replacing the dithienothiophene moiety with fluorene, the HOMO levels of the polymers were successfully lowered, leading to improved open-circuit voltages when these polymers were applied in solar cells. However, the reduced low hole carrier mobility of the polymers (as measured in field-effect transistors) and non-optimal morphology of the polymer:PC$_{71}$BM blend films affected the short-circuit currents and fill factors of the
cells, leading to much lower power conversion efficiencies than the polymers containing dithienothiophene.

Finally, a series of low band-gap polymers based on 2,1,3-benzothiadiazole and oligothiophene was designed, synthesised and characterised. These polymers were designed for good hole transport and the ability to harvest photons across the entire visible spectrum. The incorporation of the 2,1,3-benzothiadiazole unit into the oligothiophene backbone allowed us to achieve band-gaps of between 1.59 eV to 1.67 eV, which was lower than the 1.9 to 2.0 eV seen in thiophene-based polymers. When applied in thin-film transistors, the polymers achieved promising hole carrier mobilities on the order of $10^{-2}$ to $10^{-1}$ cm$^2$/Vs. OTFTs based on POD2T-DTBT exhibited excellent stability, with no deterioration in device performance even after five months of storage. Solar cells based on polymer:PC$_{71}$BM blends were also fabricated and characterised. Cells utilising POD2T-DTBT were found to have power conversion efficiencies of over 5 %. Upon further optimisation, efficiencies of up to 6.26 % were achieved for POD2T-DTBT:PC$_{71}$BM cells.

6.2 Future Work

6.2.1 OPV Device Optimisation

Although some optimisation work has been done on the solar cells based on the polymers in this thesis, further optimisation may result in even better device performances. Some examples of optimisation techniques which can be applied include the use of mixed solvents, the use of additives, thermal annealing and improved device architectures. For the polymers in Chapter 4, further optimisation of the active layer thickness and blend composition are also possible routes to better device performance.

6.2.2 Polymer Molecular Weight Optimisation

During the course of this work, we found that there were significant batch-to-batch differences in the molecular weight of the best-performing polymer, POD2T-DTBT. Moving forward, a systematic study of the effect of the polymer molecular weight on device performance could be carried out to identify the “ideal” molecular weight
range for optimum device performance. The synthesis conditions can then be tuned in order to achieve this “ideal” molecular weight range consistently.

For the polymers with limited solubility, such as PDTT-DTBT and POD4T-DTBT, the synthesis conditions can be tuned in order to achieve lower molecular weight polymers, which would improve solubility. Possible changes to the synthesis conditions include lowering the reaction temperature and using a less-active catalyst system.

6.2.3 Polymer Design

Although our polymers have achieved promising PCEs when applied in solar cells, further improvements in polymer design are still necessary in order to achieve cells with efficiencies of over 10 %. The $V_{\text{oc}}$ of the cells need to be improved, and to do that, polymers with lower HOMO energy levels need to be developed.
References


Appendix

Monomers from Chapter 3

Figure A1: $^1$H NMR spectrum of 2,6-dibromo-3,5-dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene illustrating the absence of peaks in the aromatic region as expected.
Figure A2: $^{13}$C NMR spectrum of 2,6-dibromo-3,5-dipentadecyl-dithieno[3,2-$b$;2',3'-$d$]thiophene in CDCl$_3$. The peaks at around 77 ppm are from the solvent.
Monomers from Chapter 5

Figure A3: $^1$H NMR spectrum with peak assignments for 4,7-bis(5-bromo-4-(2-octyldodecyl)-thien-2-yl)-2,1,3-benzothiadiazole in CDCl$_3$. The asterisks represent the CDCl$_3$ and water peaks.
Figure A4: $^1$H NMR spectrum with peak assignments for 4,7-bis(2-trimethylstannythien-5-yl)-2,1,3-benzothiadiazole in CDCl$_3$. The region between 7.2 and 8.2 ppm has been magnified for better clarity. The asterisks represent the CDCl$_3$ and water peaks.
Figure A5: $^1$H NMR spectrum with peak assignments for 5,5'-Dibromo-4,4'-bis(2-octyldecyl)-2,2'-bithiophene in CD$_2$Cl$_2$. The asterisks represent the CD$_2$Cl$_2$ and water peaks.
Figure A6: $^1$H NMR spectrum with peak assignments for 5,5'-Dibromo-3',4'-Bis(2-octyldodecyl)-2,2':5',2''-5'',2'''-quaterthiophene in CDCl$_3$. The asterisks represent the CDCl$_3$ and water peaks. The region between 6.8 and 7.1 ppm has been magnified for greater clarity.